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Understanding the Thermodynamic Behavior of Nanoparticles to Tailor Polymer Nanocomposite Structure

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To the Graduate Council:

I am submitting herewith a dissertation written by Mary Catherine Mutz entitled "Understanding the Thermodynamic Behavior of Nanoparticles to Tailor Polymer Nanocomposite Structure." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Mark Dadmun, Major Professor

We have read this dissertation and recommend its acceptance:

Charles Feigerle, Jimmy Mays, Thomas Zawodzinski

Accepted for the Council:

Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)
Understanding the Thermodynamic Behavior of Nanoparticles to Tailor Polymer Nanocomposite Structure

A Dissertation

Presented for the

Doctor of Philosophy Degree

University of Tennessee, Knoxville

Mary Catherine Mutz

August 2012
Acknowledgments

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Finally, this work is dedicated to my best friend, my husband Mark, without his support I would not have been able to complete this task, and to my former co-workers at the U.S. EPA in Gulf Breeze, Florida. Thank you for believing in me.

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Abstract

The work presented in this dissertation is an attempt to understand the entropic and enthalpic forces that govern the dispersion and dissolution of nanoparticles in solutions and in thin polymer films with the end-goal of producing highly tailored products.

In the first part, neutron reflectivity was used to study the impact of nanoparticle presence on the surface segregation of deuterated polystyrene (dPS) in a polystyrene matrix. The impact of the presence of cylinders (carbon nanotubes), sheets (graphene), and spheres (polystyrene soft nanoparticles) on the surface segregation process and ultimate structure were examined. Experimental data indicate that the presence of the nanoparticles slows the dPS diffusion in all cases, and the soft nanoparticles, which contained branching and more chain ends than the dPS linear polymer matrix, are entropically driven to the air surface, resulting in a decreases of excess dPS at the surface and a decrease in free energy of the system. Graphene had the opposite effect, segregating to the silicon surface due to a higher surface energy and enhancing the dPS segregation to the air surface.

The next part focuses on developing a protocol using static light scattering and refractometry to quantitatively determine the solubility behavior of boron containing nanoparticles. With scattering, the second virial coefficient is obtained and used to calculate the solute-solvent interaction parameter, $\chi$ [chi], which quantifies the mixing behavior. UV-Vis spectroscopy and physical observations were also used to describe the systems. The solubility behavior of polyhedral boranes, boron nitride nanotubes and sheets, and single walled carbon nanotubes (SWNTs) were quantified. In all cases there is good agreement between the measured data and $\chi$ [chi]. Suitable solvents were also predicted based on the calculation of the Hildebrand solubility parameter, $\delta$ [delta]. Use of $\delta$ [delta] to predict solubility shows good agreement for
the smaller particles, but is more suspect for the nanotubes and sheets due to additional entropic factors.

Finally, two purification techniques for SWNTs, acid purification and purification via centrifugation in surfactant, were examined. Experimental evidence indicates that centrifugation leads to the isolation of more pristine tubes, appropriate for applications that require increased electrical conductivity.
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Chapter 1

Introduction
1.1 Background

Nanotechnology is defined as the study of manipulating matter on the nanometer length scale with the goal of developing new materials, initially inspired by the invention of the scanning tunneling microscope and the discovery of fullerenes in the 1980s (1,2). The Nobel Prize in Physics was awarded to the developers of the scanning tunneling microscope, Gerd Binnig and Heinrich Rohrer, making it possible to image surfaces at the atomic level, while Harry Kroto, Richard Smalley, and Robert Curl won the Nobel Prize in Chemistry for their discovery of fullerenes in 1985, paving the way for the future discoveries of carbon nanotubes and graphene (1, 2). Applications of nanotechnology are diverse and interdisciplinary, and the development of new materials for applications in medicine, electronics, biomaterials, and functional devices are active areas of research. With the dawn on the 21st century, the first commercial nanotechnology based products became available in the market place, such as silver nanoparticles as antibacterial agents and carbon nanotubes for stain resistant textiles (3).

The production of stronger, lightweight and more cost-effective products is a particular area of interest for polymer science and is a predominant driving force for nanotechnology research (4). Polymers are especially important to the field of nanotechnology, since their blends and composites with nanoparticles offer a range of materials with tailored properties (4). For instance, polymer nanocomposites are a specific class of materials comprised of polymers and nanoparticles, which have at least one dimension in the range of 1 to 100 nm. The resulting properties of the composite are a combination of both the nanoparticles and polymer matrix (5). Purely plastic-based materials usually have low strength and elastic modulus when compared to metals or ceramic materials. The incorporation of nanoparticles into a polymer matrix has been
shown to improve the mechanical, electrical and thermal properties of the material, while maintaining the flexibility and light weight inherent to the plastic (1,2,6). The wide commercial availability of plastics also makes them inexpensive, making it highly desirable to develop nanocomposite materials with reinforced properties for tailored end uses (6).

An important attribute of nano-sized fillers is their exceptionally high surface to volume ratio, which provides a high amount of surface area for interaction with polymer chains (5-9). With traditional fillers, there is less surface area per unit volume for interactions, and a significant amount of filler is required to improve the mechanical properties of the polymer (7). For instance, the ratio of interfacial area per particle volume for nano-sized fillers is up to 4 orders of magnitude more than that of conventional filler materials such as glass fiber (8-10). The increased surface area allows more interactions between nanoparticle and polymer, reinforcing the mechanical properties of polymer materials with low loadings, affecting glass transition temperature, degree of thermoset cure, tensile strength, polymer chain mobility and conformation (9-10). For example, in nylon-6 filled with 5 wt% 50 nm silica nanoparticles, improvements of tensile strength by 15%, strain to failure by 150%, Young’s modulus by 23%, and impact strength of 78% can be attained (11). Similarly, the Toyota Motor Company incorporated 4.2 wt% nanoclay into nylon-6 and doubled both elastic modulus and tensile strength, allowing them to be used under the hood of a car (4). The small amount of nanoparticles necessary to achieve desirable properties is also environmentally friendly with less waste and material consumption. In order to improve the electrical conductivity using traditional fillers, 15 wt% Cu-powder or 35 wt% Al-powder must be added to epoxy (12). In contrast, based on predicted percolation limits of single walled carbon nanotubes (SWNTs), only 0.1-0.2
wt% loadings should be required. Due to the minimal filler loadings, the final product is also much more lightweight than traditionally filled composites (12).

In recent years, carbon and boron containing nanoparticles, such as SWNTs and boron nitride nanotubes (BNNTs), have garnered attention since these particles have unique properties, including electrical conductivity and neutron capture, which can be imparted to the polymer based product (13-15). These particles have also been shown to improve the mechanical properties of polymeric materials by as much as 10% with very low loadings, < 1.0 wt% (13, 16). Manchado and coworkers blended 0.75 wt% SWNTs into isotactic polypropylene and observed the modulus increase from 0.85 GPa to 1.19 GPa (17). The strength of the material also increased 5 MPa. Similarly, with the addition of only 1 wt% boron nitride nanotubes (BNNT) to poly methyl methacrylate (PMMA), a 19% increase in elastic modulus is observed (18). A dramatic increase in thermal conductivity was also observed for PMMA composites containing 10 wt% BNNT, with a nearly 3-fold increase (18). Potential applications include solar panels and lightweight materials with improved mechanical strength for military equipment. The ability of boron to shield neutrons is also of interest for nuclear and medicinal applications (14, 15, 19, 20). Ultra lightweight and reinforced bikes have already been developed using carbon nanotubes as nanofillers and are currently available in the market place (21). In fact, the 2006 Tour de France was won riding a bike with a frame that weighed only 2.2 pounds, because it was fabricated from a composite reinforced with carbon nanotubes (21).

However, a few key issues remain to be resolved when rationally designing and expanding the technological applications of new nanocomposite materials. Unfortunately, the solubility behavior of nanoparticles is not well understood, and optimizing processing protocols requires an understanding of the solubility behavior of a variety of nanoparticles. (4, 5, 14). If the particles
are not finely dispersed during processing, aggregates of the nanoparticles will form in the composites and adequate stress transfer will not be realized in the final product. Similarly, the percolation threshold of the composite will increase, limiting the improvement of electrical conductivity, since well dispersed particles are necessary in order to create 3-D networks that provide conductive pathways throughout the composite (4-5, 14).

Poorly dispersed nanoparticles may even degrade the properties of the composite. For example, PS nanocomposites prepared with the incorporation of BNNTs showed a decrease in elastic modulus when chloroform was used as the dispersant (19). However, improvements in elastic modulus were achieved when DMF was used instead, since the solvent was better able to disperse the nanotubes (19). In addition, only modest improvements in elastic modulus and tensile strength of PMMA nanocomposites containing <0.5 wt% multi-walled carbon nanotubes (MWNTs) were observed (22). The lack of improvement was attributed to poor adhesion between the PMMA and MWNTs and the formation of MWNT bundles. Such examples are numerous, exemplifying the fact that improving dispersion greatly affects product availability (22).

In the past, several methods were developed to improve the interactions between the polymer matrix and nanoparticles. These efforts include coating carbon nanotubes and fullerenes with a dispersant or grafting polymers to the sidewalls through chemical functionalization to improve dispersions (10, 23-27). Taking advantage of \( \pi-\pi \) interactions between polymer chains and nanoparticles has also been attempted. For example, poly(vinyl pyrrolidone), poly(styrene sulfonate) and their derivates have been shown to wrap SWNTs, rendering the tubes soluble in organic solvents (28-31). Success in dispersing nanoparticles has been obtained with these techniques; yet, several drawbacks to these methods exist. Processing is time consuming,
expensive to realize on an industrial scale, and the added materials are difficult to remove once the nanoparticles are embedded inside the polymer matrix. Also, the introduction of a third component and the modification of sidewalls affect the properties of the pristine nanoparticles, such as their electrical and thermal conductive properties and should be avoided (23).

A more straightforward method is to identify the fundamental characteristics of the nanoparticle and solvent that controls the solubility of the nanoparticle. The identification of a range of good solvents for a nanoparticle provides guidelines for future scientists to effectively disperse them. Therefore, using static light scattering to determine the second virial coefficient of a nanoparticle in a range of solvents, which can then provide a measure of $\chi$, the solute solvent interaction parameter, is a potential solution, since $\chi$ quantifies the thermodynamic behavior of the nanoparticle in solution and determines whether or not a solvent is thermodynamically favorable. The interaction parameter of the nanoparticle with a range of solvents also provides a route to determine the Hildebrand solubility parameter, $\delta$, of the nanoparticle, which can then be used to predict other good solvents (32-33). Once the solubility behavior of nanoparticles in solution is defined, suitable solvents can readily be selected that lead to improved dispersion in spin casting and solution casting, lower production costs, and increased product quality.

Solubility behavior is also important for production and purification. In the case of SWNTs, a complex mixture of impurities and nanotubes of various lengths and diameters results from their synthesis. Understanding the solubility of various constituents of the complex soot will aide in their purification by centrifugation and chromatography, without the need for additional chemical functionalization or chain wrapping.

A problem arises with the use of light scattering to extract thermodynamic information. Several parameters regarding nanoparticles and their solutions must be collected to fully analyze
the data, including particle density and refractive index increment (dn/dc), which are needed to perform the quantitative analysis that leads to $\chi$ (34-36). The determination of these parameters, dn/dc in particular, is nontrivial, and thus there exist published protocols that have attempted to circumvent the need for these parameters, but these methods appear to contradict established scattering theory (32-33). In order to develop a more robust method to quantitatively characterize the solubility of nanoparticle solutions, these protocols must be reexamined and a clear protocol that addresses the collection of dn/dc, density, and light scattering data must be defined.

While an understanding of methods to control the structure of a polymer nanocomposite is important, the impact of the presence of a nanoparticle on the dynamics of the surrounding polymer chains is equally important in defining the impact of the nanoparticle on the properties of the resultant nanocomposite. Once a nanocomposite material is formed, its resulting properties are dependent on the structure and dynamics of the polymer. Additionally, the composition of the resulting structure of the polymer mixture near the air surface often differs from the bulk composition, which has important implications for the product end use and may significantly affect surface sensitive properties such as biocompatibility, friction, lubrication, flammability, and adhesion (37-38).

Previous research has indicated that the size of a nanoparticle affects the segregation and diffusion behavior of polymer chains in the melt, offering a route to manipulate dispersion based on introduced particle size. Polystyrene-$b$-ethylene propylene (PS-PEP) diblock copolymers were prepared with 3.5 nm gold nanoparticles and 21.5 silica nanoparticles (39). Upon annealing, the large silica particles were found embedded at the center of the PEP domains, while the small gold nanoparticles went to the interface of the PEP-PS. Presently, however, the
effect of chain branching and particle shape, such as SWNT cylinders or boron nitride sheets, on the resulting segregation and diffusion behavior of polymer chains remains unclear.

This knowledge is relevant for designing materials with controlled dispersions. By understanding the entropic and enthalpic forces that guide the structural development in the melt, products with particles at specified interfaces or dispersed throughout the matrix can be realized. For example, a balance of these forces will maintain a homogenous dispersion of nanoparticles for use as electrically conductive plastics, or embedded porphyrin with lower surface energy than the polymer matrix may segregate to the air interface to kill bacteria and sterilize equipment. Tailored dispersions also have applications as block copolymer nanocomposites for nonlinear optics, sensors, or separation purposes (40).

In summary, the controlled dispersion and dissolution of nanoparticles is important for producing functional products with tailored properties. Currently, there is limited knowledge regarding the thermodynamic behavior of nanoparticles in solution or the affect of the presence of nanoparticles on polymer chains in the melt state. With an improved knowledge base, nanocomposites can be fabricated to realize targeted properties that are required for specific end uses.
1.2 Nanoparticles

There are many different types of nanoparticles. Carbon based nanoparticles have received much attention with the discovery of fullerenes and single walled carbon nanotubes in the latter part of the 20th century (41). More recently, graphene has become a popular topic among researchers, having been shown to improve the electrical and thermal properties of polymer nanocomposites with the lowest reported loadings for any carbon based particle, < 0.1% (42). Polymer-nanoparticles have also received much attention as nanofillers, since they are cost effective, synthesized from monomers, and their synthesis leads to tailored particles with a wide range of sizes (43-45). There is also interest in boron containing nanoparticles due to their ability to mechanically reinforce materials and improve the thermal properties of a polymer matrix. Incorporation of these particles into a polymer matrix extends the utility of plastics.

A. Carbon Based Nanoparticles

1) Carbon Nanotubes

Carbon exists as three allotropes in nature; graphite, diamond, and buckminsterfullerenes (41). Buckminsterfullerenes include carbon nanotubes and Buckyballs. In 1985, Rick Smalley and coworkers at Rice University in Houston, Texas discovered the first Bucky ball, C\textsubscript{60}, which led the team to be the recipients of the Nobel Prize in 1996 (1,2,16). C\textsubscript{60} is a spherical shaped molecule with 60 carbon atoms bonded together in pentagons and hexagons. All of the carbon atoms are sp\textsuperscript{2} hybridized, but they are not arranged on a plane, as in graphite sheets. They are rolled into a structure resembling a soccer ball.

This discovery sparked interest in other carbon-based nanoparticles. Following in 1991, the first experimental evidence that carbon nanotubes existed was provided by transmission
electron microscopy (TEM) studies conducted by Sumio Iijima that allowed multiwalled carbon nanotubes to be viewed for the first time (41). Carbon nanotubes are graphene sheets, single layers of graphite, rolled up into a cylinder, much like a scroll. Both multi-walled carbon tubes, containing as many as 20 layers of graphene and single walled carbon nanotubes, with only one “linked” layer, were discovered (10, 24-27).

The linked sp$^2$ carbon bonds in SWNTs impart mechanical strength to a composite material (41). The tensile strength and Young’s modulus of an individual SWNT has been measured as high as 1TPa with a surface area of 1180 m$^2$/g (46). The incorporation of 1 wt% MWNTs into PMMA can result in an increase in modulus from 0.71 GPa to 2.34 GPa (13).

Buckyballs and carbon nanotubes are also electrically and thermally conductive. For SWNTs, the precise nature of these properties depends on the way in which the graphene sheet is rolled along a plane, which imposes a distinct direction with respect to the hexagonal lattice, the axial direction. The relationship between the axial direction and the unit vectors that describe the hexagonal lattice determines whether the SWNT is conductive or semi-conductive.

Additionally, carbon nanotubes possess a very large length to diameter ratio, also known as its aspect ratio. For instance, a typical diameter for carbon nanotubes is 1 nm; however, the tube is many millions of times longer. In fact, 1.0 cm long nanotubes have been produced (13).

Since the discovery of carbon nanotubes and Buckyballs, the scientific and industrial community has raced to study these tiny structures. The incorporation of carbon nanotubes and fullerenes as fillers in polymer systems imparts electrical conductivity and mechanical strength to the material (41). Applications for carbon nanotube polymer nanocomposites include nano-sized semiconductor devices, nano-probes, sensors, and field emission displays (41). The medical industry is also interested in nanotubes, since ultra-purified SWNTs were found to
produce no cytotoxic effects in vivo (47-54). Recent work has also shown that carbon nanotubes promote cell attachment, growth, differentiation and long term survival of neurons in vitro. This is especially of interest since neurons have also been shown to preferentially attach and use nanofibers as “guidance channels” for their re-growth, and cells that promote scar tissue formation are actually hindered by the presence of carbon nanofibers (47-54). Applications for medicine also include the development of load bearing scaffolds for tissue regeneration and targeting cancer cells by delivering drugs to specific cells in the human body via chemical functionalization with protein markers (47-54).

The development of fine dispersions of carbon nanotubes in solutions and polymer matrices remains a challenge for material design. Carbon nanotubes are difficult to dissolve in common solvents due to their high molecular weight and high aspect ratio (2). The surface electrons are also highly polarizable due to the extended π electron system, and carbon nanotubes are subject to large attractive intertubular van der Waals forces. Because of this, carbon nanotubes tend to aggregate and clump together in solution (2). Over the years, efforts have focused on finding appropriate media to solubilize particles. For SWNTs, non-hydrogen bonding Lewis bases with high electron pair donicity and low hydrogen-bonding parameters, such as dimethylformamide (DMF), N-methylpyrrolidone (NMP), and hexamethylphosphoramide (HMPA), have been identified as successful at producing stable carbon nanotube dispersions through sonication (55-56). Success was also achieved with aromatic solvents, such as ortho-dichlorobenzene, which interact with the nanotube sidewalls via π-π stacking (55-56). These findings are not sufficiently quantitative to predict other good solvents, however. For instance, toluene, which also contains a phenyl ring, is a poor solvent for SWNTs, and dimethylsulfoxide (DMSO), which has high electron pair donicity, also does not
readily disperse SWNTs (55-56). Currently there is a lack of understanding of the specific structural characteristics that govern the dissolution of carbon nanotubes, such as its large surface area, particle bundling, chain connectivity, and bond length and angle, and there is no universal solubility parameter that predicts the successful dissolution of SWNTs in a range of solvents. (55-56)

Developing cost effective nanotube based products also requires the purification of the as-produced carbon nanotubes. The synthesis of carbon nanotubes results in a complex mixture of carbon and metal impurities, as well as, a range of nanotubes of varying lengths and diameters (13, 41, 57). Current purification techniques are expensive, involving large amounts of solvents and thermal annealing at temperatures in excess of 500 °C. A more cost effective bulk purification method that results in purified nanotubes for tailored end-uses that are finely dispersed in solvents is much needed.

2) Graphene

Graphene was discovered in 2004 by Geim and coworkers by the micromechanical cleavage of graphite into single layers (58-60). It is composed of a one-atom-thick planar sheet of sp² bonded carbon atoms and is considered to be an indefinitely large aromatic molecule. It is also the basic structural element of fullerenes and carbon nanotubes, and the crystalline form of graphene is graphite, which consists of many graphene sheets stacked together (58).

Graphene has many unique properties that make it important for material development including its semiconductor properties, high electron transport at room temperature, and the ability to absorb white light (58, 61). Most notably, graphene lacks a band gap, making it a perfect candidate for the development of photovoltaic cells since it absorbs energy at every
frequency (61). Graphene is also one of the strongest materials ever tested with its bulk strength reported as high as 130 GPa (61). The reinforcement of the mechanical and electrical properties of its use in polymer nanocomposites was observed with the lowest reported loadings, <0.1% (42). The glass transition temperature (Tg) increased over 40 °C with the introduction of 1 wt% graphene sheets into poly (acrylonitrile). With only 0.05 wt% graphene in PMMA, an improvement of the Tg by 30 °C was observed (62). Potential applications for graphene based polymer nanocomposites range from nanoelectronic devices, conductive thin films, and nanosensors (58-60, 62).

More recently, graphene has become a candidate for nanomedicine research. In vitro studies reveal that graphene has anti-bacterial properties, and the effect is concentration dependent (63). As the amount of graphene present increases, there is an increase in the amount of bacteria that is killed, reaching a maximum, where 76.8% of *Escherichia coli* are killed with the introduction of 80 µg/mL graphene in saline solution (63).

Research involving graphene is still in its early stages, where research involving its solubility has received increased attention due to the dramatic improvements in mechanical and electrical properties achieved in its nanocomposites. In 2010, Hernandez, et al, studied the dispersability of graphene in 40 solvents using UV-Vis-NIR spectroscopy (64). Good solvents for graphene were found to contain polar aprotic rings, including cyclopentanone and N-ethyl-2-pyrrolidone.

It is also important to define the composition of the bulk and surface of an equilibrium polymer-graphene nanocomposite, since the functional properties of the composite ultimately depend on this final structure (37-38). Understanding the thermodynamic factors that govern the evolution of this ultimate structure is crucial, and directly applicable to medicinal applications.
that could take advantage of an enriched layer of graphene on the surface for use as anti-bacterial coatings (63).

3) Polystyrene Nanoparticles

Polymeric nanoparticles have received increasing attention in the past decade because of their low cost and controlled size distributions (42-44). Polystyrene nanoparticles can be prepared using microemulsion polymerization, which typically use sodium dodecyl sulfate (SDS) as a surfactant and ammonium persulfate or azobisisobutyronitrile (AIBN) as a radical initiator (43-44). Divinyl benzene is typically added to promote cross-linking during polymerization. The reaction conditions, such as temperature, mole % reaction components, and reaction time can be varied in order to produce a range of particle sizes. For instance, ~20 nm highly branched, spherical nanoparticles were produced with the polymerization of styrene and methyl methacrylate (MMA) in SDS with a weight ratio of SDS/(styrene+MMA) of 0.043 at 80 °C (44). The authors note that by increasing the amount of surfactant present in the reaction vessel, the size of the nanoparticles decreased, making their synthesis highly tailorable. Emulsion copolymerization can also be carried out to incorporate functional groups of interest, such as carboxyl, amino, hydroxyl, or acetal groups, which have known affinity for specific proteins or biomolecules.

Applications of these nanoparticles include their use in medical sciences, which can use them in drug delivery and immunodiagnostics, and as potential high performance coatings, support catalysts, and in fuel cells (43-44). As in the case of graphene, there is a need to characterize the resulting surface and bulk composition of polymer nanoparticle-composites. The effect of the presence of highly branched particles on the surface segregation behavior of
polymer chains, and the need to prepare scaffolds for tissue regeneration with nanoparticles enriched at the surface for drug delivery makes the surface segregation of these unique nanoparticles of particular interest (43-49, 65-66).

B. Boron Containing Nanoparticles

1) Boron Nitride Sheets

Boron containing nanoparticles are of special interest because of their ability to capture neutrons, which makes their incorporation into polymer matrices especially useful for nuclear applications (14-15). Boron nitride (BN) is a chemical compound that consists of equal numbers of boron and nitrogen atoms with a similar structure to the carbon lattice that comprises graphene, and exists in various crystalline forms (7). It is produced synthetically from the reaction of boric acid and boron trioxide. The initial amorphous powder is then converted to the crystalline form by heating in nitrogen gas flow at temperatures above 1500 °C and at high pressures (7). Graphitic BN is the hexagonal form, and it is the most stable and softest. In industry, this form has found use as a lubricant and as an additive in cosmetic products. It is also electrically insulating and thermally conductive (7). The cubic structure of BN is analogous to diamond, and is called c-BN. This allotrope is not as hard as its carbon counterpart; however, its thermal and chemical stability is superior, and it is used as an additive in ceramics and intermetallic composites that are used in equipment requiring thermal and chemically stability (7). BN can potentially be used as protective shielding and insulators for low and high frequency equipment. Interestingly, both the cubic and hexagonal forms emit UV light when a voltage is applied, and potential applications include light emitting diodes and lasers (67-68).
2) Boron Nitride Nanotubes

Boron nitride nanotubes are rolled up sheets of boron nitride, experimentally discovered in arc-discharged debris in 1995 by Chopra, et al (69). There are several synthesis techniques used today including laser ablation of hexagonal or cubic BN targets or chemical vapor deposition on nickel boride catalyst using borazine as a precursor (14-16). Structurally, this material is similar to carbon nanotubes, a cylinder with diameter ~ 0.5 to 5 nm and length of up to several micrometers, though, the properties of the boron nitride tubes are very different (41). Carbon nanotubes are either metallic or semiconducting, depending upon the rolling direction and radius of the nanotube, but BNNT are electrical insulators, independent of tube chirality, with a wide band gap, around 5.2-5.8 eV (14-15). The BN structure is also more thermally and chemically stable than the carbon nanotubes, and BNNT are transparent to visible light (8,14-15).

BNNTs are also difficult to disperse due to their aggregation behavior in solution. Since BNNTs possess a well-developed $\pi$ electronic structure, some success dispersing the tubes in organic solvents with polymer chain wrapping has been achieved. Poly[$m$-phenylene vinylene-co-(2,5-dioctoxy-p-phenylene vinylene)] (PmPV) wraps BNNT and renders the tubes soluble in chloroform (70). However, chain wrapping with polyaniline (PANI) did not improve dispersion, and the strong $\pi$ stacking interactions leads to a self-organized PANI-BNNT film following sonication (71).

Dispersing BNNT without chain wrapping is highly desirable, since the added processing time and materials are not cost effective and can impact the final properties of the nanocomposite (23). Improvements in BNNT nanocomposite properties have been achieved simply by using better solvents for BNNT during processing, which improved their dispersion (19). BNNTs are
promising nanofillers for insulating polymer composites, with the current main interest in protective shielding, since both mechanical and thermal improvements are imparted to materials containing BNNT, while the optical transparency of the composite remains intact (8).

3) Carboranes

Carboranes are polyhedral clusters composed of boron and carbon atoms, most often synthesized from the reaction of acetylene with decaborane (72-73). Carboranes are thermally and chemically stable and have low toxicity. The most widely studied is $o$-carborane ($C_2B_{10}H_{12}$) which is used in a wide range of applications including heat-resistant polymers and neutron capture devices. For therapeutic medicine, the high boron content makes carboranes especially important for the treatment of cancer cells, with targeted delivery of radiation (19). This is because when the Boron-10 isotope, which is itself non-radioactive, is radiated with low energy thermal neutrons, high energy $\alpha$ particles are generated that are capable of destroying cellular structures within a radius of 5-9 $\mu$m (74-75). Carboranes also undergo electrophilic aromatic substitution, and functional groups designed specifically for diagnostic imaging or therapy can readily be attached, such as nucleic acids, amino acids, sugars, and lipids (20). This tailoring makes carboranes a potential filler for scaffolds, which are often made from non-toxic polymers, such as polyethylene oxide, and are engineered for mechanical and biological support of tissues (ie: tissue regeneration or to restore and maintain organ function) (19, 76).
1.3 Issues facing composite development

A. Miscibility Issues

Common methods to fabricate polymer nanocomposites include spin casting or solution casting. These techniques involve mixing nanoparticles with a polymer in solution, the solvents then evaporate or the nanocomposite is precipitated out of solution using a non-solvent (77). Nanoparticles have proven difficult to disperse in solvents, due to strong intermolecular forces and a strong tendency of the particles to agglomerate. SWNTs, for example, clump together in solution due to strong Van der Waals forces. These forces must be overcome in order to thermodynamically dissolve the particles. Use of suitable solvents can dramatically improve the dispersions of the nanoparticle during processing and lead to improved dispersion and interaction in the resultant nanocomposite, which in turn provides targeted mechanical properties in the final composite material, such as increased tensile strength and elastic modulus (19). However, there is a lack of a clearly defined protocol that quantifies the solubility behavior of nanoparticles in solutions and in polymers. Such a protocol, which defines the solubility, will enable the definition of a range of solvents that are able to disperse nanoparticles during processing. This is especially important for boron-containing nanoparticles, such as BN powders, BNNTs, and polyhedral boranes, since there is currently little information available regarding the solubility parameters of these materials. Carboranes, for instance, have potential medicinal applications as cancer treatment devices, and knowledge of δ will aide in the selection of non-toxic solvents and polymer matrices capable of producing fine dispersions of the particles for nanocomposites used in vivo (1-6,19-20,78-81).

The miscibility of two components is controlled by the free energy of mixing, which is quantified in Equation 1.1, where $\Delta H_m$ is the enthalpy of mixing, $\Delta S_m$ is the entropy of mixing,
and T is the temperature in Kelvin \( (82) \). The interactions between components of a mixture are quantified with \( \Delta H_m \), while the entropy change resulting from the change in disorder upon mixing is \( \Delta S \). It is important to note that a negative free energy of mixing \( (\Delta G_m < 0) \) results in mixing of the two components, and the discussion that follows is relevant for both the dissolution of nanoparticles in a polymer matrix or in a solvent, since the underlying physics is governed by Equation 1.1.

\[
\Delta G_m = \Delta H_m - T\Delta S_m \quad (1.1)
\]

During the mixing process, a combination of entropy and enthalpy determines the structure of the final mixture, and affects the dispersion of a solute in solution \( (82) \). For the discussion of polymer chains that are long and disordered, the addition of a nanoparticle does not produce a significant increase in \( \Delta S_m \), and fine tuning the intermolecular interactions in the mixing process becomes important in order to produce a negative free energy of mixing.

Chemical functionalization and chain wrapping are two methods used in the past to render nanoparticles more thermodynamically miscible in both polymers and solutions. Problems arise with these methods, however, since the introduction of a third component and the modification of the sidewalls effects the properties of the nanoparticles \( (23) \). Instead, identifying solvents that interact favorably with nanoparticles is highly desirable, since attractive intermolecular interactions between solvent molecules and the solute creates a favorable enthalpic interaction and potentially leads to a negative free energy of mixing. Some success, for instance, has been achieved with aromatic and pyrrolidone solvents that appear to interact via \( \pi-\pi \) interactions with the sidewalls of SWNTs and fullerenes to disperse the particles \( (32-33) \).
In order to identify and expand the range of solvents capable of dispersing both carbon based and boron-containing nanoparticles, the Flory Huggins Solution Theory can be used to define the solubility behavior. With this theory, the enthalpy of mixing is calculated by accounting for the interaction energies between neighboring molecules or polymer segments in a statistical approach that also relates the enthalpy and entropy of mixing to the free energy of mixing and molecular properties (i.e.: interaction between the molecules) (82). This is accomplished with Equation 1.2, where $\phi$ is the volume fraction of the solute, $M$ is the molecular weight, and $\chi$ is the solute-solvent interaction parameter that describes the enthalpic interaction between the components (82-83).

$$
\frac{\Delta G_{\text{mix}}}{RT} = \left(\frac{\phi_A}{M_A}\ln\phi_A + \frac{\phi_B}{M_B}\ln\phi_B + \chi_{AB}\phi_A\phi_B\right)
$$

(1.2)

Immiscible systems tend to have a $\chi > 0.5$ that results from a positive $\Delta H_m$, which contributes to $\Delta G > 0$ (115,116). This is often due to repulsive interactions between components in the mixture that are significantly larger than the change in entropy for the system. Therefore, in order for miscibility to be achieved, $\chi$ must be negative or small (82-83).

In order to define $\chi$, static light scattering measurements are often carried out to determine the thermodynamics of a solution. The second virial coefficient is readily obtained from light scattering, and Equation 1.3 relates $A_2$ (the second virial coefficient) to $\chi$, where, $V_s$ is the solvent molar volume and $\rho$ is the density of the solute (32-33).

$$
\chi = \frac{1}{2} - A_2V_s\rho^2
$$

(1.3)

The interaction parameter of the nanoparticle with a range of solvents also provides a route to determine the Hildebrand solubility parameter, $\delta$, of the nanoparticle. $\delta$ provides a numerical
estimate of the degree of interaction between materials and is a good indication of solubility, since materials with similar values of $\delta$ are likely to be miscible (84). Many solvents have tabulated $\delta$ values and a range of good solvents for a particle can be predicted based on this relationship. Equation 1.4 illustrates this concept of “like dissolves like”, where $\Delta H_m$ is the enthalpy of mixing, $V$ is the solvent molar volume, $\delta$ is the solubility parameter, $\phi$ is the volume fraction of components A and B (84). In order for $\Delta G_m < 0$, the difference in the solubility parameters of the solute and solvent in Equation 1.4 must be small.

$$\Delta H_m/V = (\delta_A - \delta_B)^2 \phi_A \phi_B$$  \hspace{1cm} (1.4)

$\chi$ is also related to the difference in solubility parameters of the solvent and solute, as shown in Equation 1.5, where $V$ is solvent molar volume, $\delta_A$ is the solubility parameter of component A, and $\delta_B$ is the solubility parameter of component B.

$$\chi = V [(\delta_A - \delta_B)^2 / RT]$$  \hspace{1cm} (1.5)

Because of this relationship, the unknown solubility parameter of a nanoparticle or polymer can be determined by measuring $\chi$ in multiple solvents and using Equation 1.6, derived from a combination of the Flory theory with the Hildebrand-Scatchard solution theory. Equation 1.6 relates the $\chi$ of a solution to the solubility parameters of the solvent and solute, where $\delta_A$ is the Hildebrand solubility parameter of the solvent, and $\delta_B$ represents the Hildebrand solubility parameter of the nanoparticle or polymer under study. (13, 28-31):

$$(\delta_A^2/RT - \chi/V_A) = (2\delta_B/RT)\delta_A - (\delta_B^2/RT)$$  \hspace{1cm} (1.6)

A plot of $\delta_A^2/RT - \chi/V_A$ as a function of $\delta_A$ produces a straight line, with the slope of the line = $2\delta_B/RT$, from which the unknown solubility parameter, $\delta_B$, can be determined (85-86).

However, it is important to keep in mind that predicting solvents based on $\delta$ is made with the absence of specific interactions, especially H-bonding (84). Additionally, effects of
morphology, volume changes upon mixing, and cross-linking are not considered in this approach. Nonetheless, the solubility of small molecules and polymers is often successfully predicted with this approach. But for large particles, such as SWNTs, $\delta$ is not always an accurate predictor, since additional intermolecular forces are often at play (55-56).

UV-Vis spectroscopy is another method frequently used to establish the Hildebrand solubility parameter of a solute (87-88). The solubility limits of a solute are first established in a series of solvents, and a graph of solubility limit as a function of the solvent’s $\delta$ is plotted. The Hildebrand solubility parameter of the nanoparticle is then obtained from the maxima of the resulting graph, where the solubility limit has the highest value (87-88).

With these relationships in mind, Bergin and coworkers attempted to use static light scattering to quantify the solubility of carbon nanotubes (32-33). N-methyl pyrrolidone (NMP) and cyclohexyl pyrrolidone (CHP) are both able to disperse SWNTs with only mild sonication. DMF has been a preferred solvent to suspend carbon nanotubes, but require long sonication times that can damage and cut the nanotubes (1,2). Bergin and coworkers estimate that $\chi$ and $\Delta H$ are negative for carbon nanotubes in both CHP and NMP.

These results are suspect, however, as they avoid determining the refractive index increment (dn/dc) of nanoparticle solutions, as it is difficult to measure due to the aggregation behavior of the particles. The absence of this parameter questions the accuracy of the reported $\chi$, as dn/dc is necessary to quantitatively determine $A_2$ (Chapter 2). Previous researchers circumvented this parameter by performing additional scattering measurements, but the accuracy of this work is of concern (32-33). The density of the nanoparticles is also difficult to obtain and necessary for these measurements. Previous methods include AFM or SEM on spun-cast
solutions to estimate the number of particles and bundle sizes, methods with questionable accuracy. (32-33).
B. Segregation and Diffusion of Polymer Chains

The properties of the final nanocomposite depend on how the presence of the nanoparticles influences the dynamics of the polymer matrix. For surface sensitive properties, the structure of the surface, which often differs from the bulk composition, becomes very important (37). This knowledge has implications for the development of products as lubricants and anti-bacterial coatings (37-38).

Surface segregation occurs when polymer films are annealed above their glass transition temperature, and the polymer chains are in the melt state. The thermodynamic affinity of one component to the surfaces and the affinity of the polymer components to each other impact the segregation process and may result in the redistribution of the components near the air and substrate surfaces (89-102).

One aspect of particular importance is the migration of lower-surface energy components in a mixture to the air surface, which lowers the enthalpy and the Free energy of the system (103-106). Blends that contain strongly hydrophobic components, for instance, such as fluorinated polymers, will undergo segregation of the hydrophobic components to the air surface (106). A study by Yang demonstrates this point with miscible blends of PMMA and poly (vinylidene fluoride) (PVDF) showing significant enrichment of PVDF at the air surface upon annealing (107).

When enthalpic interactions are not very strong, however, entropic forces may dominate (103-106). Polymer chains typically take on a random coil conformation, and the presence of a surface constrains the coils, reducing the number of configurations possible for the polymer chains at the interface. Polymer chain ends will segregate to an interface to relieve this entropically unfavorable situation (89-95). This was observed by Steiner, et al, who varied the
ethylene content in random ethylene-ethyl ethylene copolymers, and found that the more branched polymers segregated to the air surface (108).

Segregation to the solid substrate in a thin film is also impacted by the interaction energy between the solid substrate and the polymer. This interaction is short-ranged, occurring within only a few Angstroms, and the mobility of the chains is affected mainly by the connectivity of the molecules and their molecular interactions with one another, rather than the interaction with the solid substrate itself (93, 109). When enthalpy dominates the selective surface segregation in a thin film, the higher surface energy components may be displaced to the solid substrate as lower energy components migrate to the air surface.

Deuterated polymers are of particular importance to this discussion, since they possess a lower surface energy than their protonated counterparts, which is the result of a smaller polarizability of the carbon-deuterium (C-D) bond relative to the carbon-hydrogen (C-H) bond (94). Many studies of polymer diffusion and segregation behavior take advantage of the lower surface energy of deuterated polymers. These studies often use deuterated polystyrene (dPS) as a tracer in order to follow the chain motion of annealed thin films, realizing that dPS will inevitably segregate to the air surface in a carefully planned experiment. Neutron reflectivity, for instance, is often used to monitor the segregation behavior by modeling scattering length density profiles (SLD profiles) and dPS concentration profiles from the collected reflectivity data. (99-102). The models allow the calculation of the excess dPS at the surface and the width of the interface upon annealing, providing insight into the thermodynamic driving force to selectively segregate dPS to the surface (99-102)

Monte Carlo simulations have shown that dPS will segregate to the air surface in dPS/protonated polystyrene (pPS) blends, as long as the pPS chains have greater chain lengths,
since a difference in surface energies at the surface of a thin film is the driving force for this segregation (103, 110). Kumar and Russell studied a series of deuterated and protonated polymers, and in all cases, as the molecular weight of the protonated species is lowered, the entropic driving force to sequester the shorter protonated chain dominates the enthalpic contribution, which results in selective segregation of the protonated polymer to the surface (104).

A study by Hong and Boerio, also illustrates this point (94). Blends of equivalent molecular weight dPS and pPS were prepared, and it was found that the deuterated polymer enriched the surface upon annealing (109). However, when the pPS molecular weight was lowered, it was found to enrich the air surface instead. Energetic and entropic effects contribute to the surface segregation in the system, and when the pPS chains were short in comparison to dPS, entropy is the driving force for the segregation of pPS to the air surface (109). The authors confirmed this phenomenon by preparing a blend of 70K pPS and 1950K dPS, which was annealed at 200 °C for 24 hours. No surface segregation occurred in this blend, signifying that the chain length effect equaled the isotopic effect, and the surface free energy difference between the polymers was zero (104-106, 109-110).

These experimental results demonstrate the utility of dPS as a tracer in equivalent molecular weight dPS/pPS blends, and also demonstrate that the morphology of a composite is controlled by manipulating the balance of enthalpic and entropic forces present in the system. In recent years, much research has focused on combining polymers with nanoparticles in order to improve the function and properties of the polymer matrix (111-114). The addition of nanoparticles to a polymer matrix provides a new challenge for understanding segregation behavior, since additional molecular interactions are introduced into the system and chain motion
becomes complex near surfaces and interfaces. Understanding the enthalpic and entropic forces governing the surface segregation of polymer chains in the presence of nanofillers is relevant for achieving finely tuned materials for specific applications that for instance, do not undergo segregation with applied heat, or have embedded components that segregate to specific interfaces upon annealing.

Work by Krishman, et al, demonstrates the complexity of nanoparticle systems. The surface segregation behavior of the components in two nanocomposite systems, a linear polystyrene matrix that contains crosslinked PS nanoparticles or cadmium nanoparticles, was studied (111). The PS nanoparticles ranged in size from 41 to 1500 kDa with Rg from 2.5 to 9.0 nm, and the cadmium particles had a radius of 2.4 nm and MW of 34.3 kDa. This publication built off the work of Barnes et al, who discovered that the introduction of fullerene nanoparticles to polymer thin films inhibited dewetting of PS on native silicon oxide substrates (103). Neutron reflectivity was used to investigate the depth profiles at different annealing times. The results indicate that the PS nanoparticles segregated to the silicon substrate upon annealing, and that higher molecular weight nanoparticles strongly enhanced the wetting behavior of the polystyrene thin films. The authors interpret this response as the result of an entropic gain by the linear PS chains when they moved from the solid substrate and pushed the nanoparticles down (111). However, the cadmium particles had an opposite effect, minimizing the dewetting behavior and segregating to the air interface. In this system, the authors attributed this response to an entropically driven surface segregation process. (111).

In another study, blends of PMMA and a branched random copolymer of PMMA and methoxy poly (ethylene glycol) monomethacrylate were prepared on silicon, annealed above the glass transition temperature, and the depth profiles were investigated using neutron reflectivity
The branched copolymer in this work has a higher surface energy, and is expected to segregate to the silicon substrate upon annealing; instead, however, it segregated to the air surface. The entropic effect of chain branching dominates the surface segregation process in this system, where the chain ends localized at the air surface with annealing, which reduces the overall free energy of the system (43-49, 65-66). Clearly, a more complete understanding of the impact of nanoparticle size, shape, and composition on the surface segregation in polymer nanocomposites is needed.

The reptation model, first proposed by de Gennes and Edwards, describes the diffusion of polymer chains between miscible entangled linear polymers and can also be used to describe the process of interdiffusion (115-120). For polymer bilayers annealed above their glass transition temperature, polymer-polymer interdiffusion is predicted to proceed in two stages. The first stage occurs during the period that is less than the time it takes for a polymer to diffuse a distance equal to its radius of gyration (Rg), the reptation time. This stage is dominated by segmental motion. However, at longer annealing times (i.e.: longer than the reptation time), center of mass diffusion prevails, and the polymer chains cross the interface (115-120). The addition of nanoparticles affects this reptation behavior, and in some cases, slows the diffusion of the polymer chains across the interface (121-122). For instance, Mu and coworkers report that the diffusion of the dPS chains is slowed with the introduction of SWNTs when compared to an unmodified bilayer system (121-122). Elastic recoil detection (ERD) was used to study the interdiffusion of dPS/pPS bilayers with annealing at 150 °C. Fick’s second law describes how diffusion causes the concentration profile to change with time, and was used to fit the data and calculate diffusion coefficients for each of the bilayers studied. (115-120).
Mu also reported that a minimum in diffusion coefficient occurred as the SWNT concentration was increased, and with the addition of a high enough SWNT concentration, the diffusion coefficient recovered to the pure polystyrene value. Shorter dPS chains resulted in a deeper minimum in diffusion coefficient. The lowest $M_w$ dPS studied was 75,000 g/mol, and the minimum in diffusion coefficient occurred at 0.4 vol% SWNT loading. The diffusion coefficient recovered to the pure polystyrene value with the addition of 4.0 wt% SWNTs (121-122).

The team modeled this behavior by simulating center-of-mass diffusion of the polymer chain about a 3-dimensional cylinder. Anisotropic diffusion occurs near the SWNT surface, in which polystyrene diffuses more slowly in the direction perpendicular to a SWNT relative to that which occurs in the parallel direction. The dPS diffusion decreased at low concentrations due to the anisotropy surrounding the SWNTs, while at higher SWNT concentrations, the nanotubes form a percolating network, which allows the dPS tracer to diffuse parallel to the tube and recover the pure polystyrene diffusion coefficient (121-122). The 3-dimensional cylinder model used to fit the data and describe the dynamics of dPS in this work suggests that the cylinder shape of the introduced particles affects the diffusion of the surrounding polymer chains, with a minimum in diffusion coefficient observed at low loadings.

Since segregation, diffusion, and mixing in thin polymer films are more complex with the introduction of nanoparticles, it is important to understand polymer dynamics for the development of new materials. The interdiffusion and segregation of polymer thin films in the presence of nanoparticles of various size and shapes has many practical applications, such as improving dewetting or as end uses as packaging and barriers. Improving dewetting behavior is important for producing stable polymer films that do not rupture (123). Work by Sharma, et al, for instance, has shown the arrestment of dewetting when the interactions between the polymer
matrix and particle filler is strong, as is the case of PS/PMMA bilayers prepared on silicon with introduced Si nanoparticles (123). The authors conclude that the Si nanoparticles “pin” the polymer chains at the interface, since AFM images show the distribution of the nanoparticles at the boundary. In contrast, carbon black introduced into PS/PMMA thin films increased the rate of dewetting because unfavorable interactions between the polymer and particles led to phase separation and the repulsive interactions further destabilized the thin film (123).

Thin films for uses as barriers are another potential application (124-125). Nanoparticle fillers are desirable for this purpose, since low loadings lead to the reinforcement of the material while maintaining the optical transparency, and this is especially desirable for the beverage-liquor industry for producing clear plastic bottles to replace conventional glass that are capable of protecting against oxidation, reduce breakage, and decrease the weight of the material (i.e.: reduce shipping costs) (126). The resulting diffusive properties of the material strongly depend on the morphology. For instance, nanoparticles segregated at the interface decrease permeability of the plastic, and developing PS and polyolefin bottles that can extend the shelf life of beer for upwards of 6 months by preventing its oxidation is an important area of material design (126).

1.4 Objectives and Proposed Experiments

This dissertation will describe results that study the effect of nanoparticles on the segregation and diffusion behavior of polymers in thin polymer films and experiments that define the solubility of nanoparticles in solution, with the end goal of providing fundamental information to achieve novel nanocomposites with controlled dispersions.

Thin film dPS/pPS bilayers are prepared in order to study the diffusion and segregation behavior of polymer chains in the presence of nanoparticles of varying size and shapes.
Cylinders (SWNTs), sheets (graphene), and highly branched spheres (polystyrene soft nanoparticles) are introduced into the bilayers at 1.0 wt%. Neutron reflectivity measurements are collected for a series of annealing times. Evolution of the thin film depth profile, interfacial structure and surface segregation behavior of the components are monitored. This work is presented in Chapter 3, along with a detailed discussion.

There is need for a clearly defined protocol that leads to the accurate description of the solubility behavior of nanoparticles in solution. Previous work used static light scattering to quantify such solutions, but circumvented the collection of the refractive index increment, dn/dc (32-33). Little information regarding the dn/dc of nanoparticle-solvent systems has been obtained to date, due to the difficulties of the nanoparticles clumping in solution. Unfortunately, this is a necessary parameter to quantify the particle’s behavior in solution. Here, a previous method developed by Bergin, et al, is re-tested (32-33). Several polymer-solvent systems with known second virial coefficients, $A_2$, and known molecular weights are subjected to static light scattering in the hopes of calculating the light scattering instrument constants. If the constants are determined successfully, dn/dc is not required. However, to determine dn/dc for the first time and to develop an exacting protocol, the Brice Phoenix differential refractometer is used to collect dn/dc of the nanoparticle solutions. Moreover, accurate density measurements are also collected using a gas pycnometer for all of the nanoparticle powders.

Twenty-one different nanoparticle solvent systems are monitored using static light scattering, pycnometry, and refractometry, and $\chi$ is calculated from the data for all of the systems.

UV-Vis spectroscopy is also performed to determine the solubility limits of the particle systems to serve as a self-consistent check for the data obtained with the light scattering and
refractometry. Physical observations and a solvent screen is also performed as supporting information. For each system, the Hildebrand solubility parameter of the nanoparticle is determined, and a list of predicted good solvents is put forth based on $\delta$.

In Chapter 4, an attempt to calculate the instrument constants is presented, along with the detailed calculations of $\chi$ and $\delta$. The results of four boron cage compounds (carboranes and polyhedral borane compounds) studied in toluene, THF, and methyl ethyl ketone (MEK), are presented. In Chapter 5, the solution behavior of BNNT, boron nitride sheets, and functionalized BNNT in THF and toluene are studied. SWNTs and two pre-polymers, used to form polyurethanes, are also examined in Chapter 5, since information regarding their solubility behavior was already known, and served as a self-consistent check. Additionally, in Chapter 6 the effectiveness of two purification techniques, the purification of as-prepared SWNTs (AP-SWNTs) in nitric acid reflux and the purification with centrifugation in surfactant, are evaluated. This study is important for material development because different quality nanotubes are collected with these techniques, which are desired for different end uses.

The purification of SWNTs by centrifugation in DMF is also studied as a coinciding project, since the purification of SWNTs in common solvents offers a route to reducing processing costs while collecting the final product in a medium ready for use (127). The need to define the solubility behavior for SWNTs is highlighted here, since isolating SWNTs in good solvents will improve this technique, and the final product will be a fine dispersion of pristine nanotubes.
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Chapter 2

Experimental Techniques
2.1 Commercially Purchased Materials

A. Chemicals

Acetone (99.9% Fisher Scientific), chloroform (99.9% Fisher Scientific), 1-cyclohexyl-2-pyrrolidone (99% Sigma Aldrich), dimethyl formamide (DMF) (99.9% Fisher Scientific), methyl ethyl ketone (99% Sigma Aldrich), N-methylpyrrolidone (99% Sigma Aldrich), tetrahydrofuran (THF) (HPLC grade, Sigma Aldrich), and toluene (HPLC grade, Fisher Scientific) were used in this research project. Prior to their use in preparing the samples for the light scattering and neutron reflectivity experiments, the solvents were filtered through 0.45 μm Teflon syringe filters to remove dust particles.

Nanopure water was obtained using a Millipore filtration system, Milli-Q 18 mega ohm water polisher. Deuterated water (D₂O) was purchased from Sigma Aldrich (100%) and used as received.

A mixture of sulfuric acid and 30% w/w hydrogen peroxide was used to clean wafers, using certified ACS grade (Fisher Scientific). Hydrofluoric acid (HF) (50%, Sigma Aldrich) was diluted using nanopure water to make 5% solutions and was also used during the wafer cleaning process.

Finally, nitric acid (ACS grade, Fisher Scientific) and 1% sodium dodecyl sulfate (SDS) were used during purification of carbon nanotube soot to obtain purified single-walled carbon nanotubes (SWNTs).

B. Polymers

Narrow molecular weight distribution deuterated polystyrene (dPS), protonated polystyrene (PS), and poly (methyl methacrylate) (PMMA) standards were purchased from
Scientific Polymers Products Inc and used as received. The molecular weights of the polymers used to prepare thin films for neutron reflectivity studies were verified using gel permeation chromatography (GPC). The molecular weight ($M_w$ and $M_n$) and polydispersity index properties of all of the polymers used in this dissertation are listed in Table 2.1.

Conathane EN-4 part A urethane pre-polymer (EN4) and conathane EN-8 part B curative (EN8), were purchased from Cytec Industries, Inc, West Patterson New Jersey. EN4 is composed of 10-12% free toluene diisocyanate (TDI) and 88-90% TDI end-capped polybutadiene (PBD). EN8 contains 50% bis-(2-hydroxypropyl) aniline (BHPA) and 50% 2-ethyl-1,3-hexane diol (EHD). EN4 and EN8 were stored in a desiccator to prevent the introduction of moisture and used as received.

**Table 2.1:** Molecular weight characteristics of the polymers used in the experiments reported in this thesis.

<table>
<thead>
<tr>
<th>Bottle Information</th>
<th>GPC measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>$M_n$ (g/mol)</td>
</tr>
<tr>
<td>dPS 50K</td>
<td>50,000</td>
</tr>
<tr>
<td>PS 8K</td>
<td>8,000</td>
</tr>
<tr>
<td>PS 30K</td>
<td>29,100</td>
</tr>
<tr>
<td>PS 50K</td>
<td>50,700</td>
</tr>
<tr>
<td>PMMA 177K</td>
<td>164,700</td>
</tr>
</tbody>
</table>
C. Nanoparticles

Single walled carbon nanotubes (95 wt %, 0.7-2.5 nm tube diameter, 0.5-5 μm length) were purchased from Bucky USA and used as received. Graphene was synthesized and provided by Humberto Terrones, Advanced Materials Department, Potosi Institute of Scientific and Technological Research, San Luis Potosi, Mexico (1,2).

Two PS soft nanoparticles, soft nanoparticle #1 (NP1) and soft nanoparticle #2 (NP2), were synthesized and characterized by Dr. Wade Holley at Oak Ridge National Laboratory. The soft nanoparticles were formed by reacting styrene and divinyl benzene (DVB) in micro emulsions with azobisisobutyronitrile (AIBN) as the initiator at 60 °C (Figure 2.1).

The two soft nanoparticles differed in the amount of DVB in the reaction vessel, and therefore in the extent of crosslinking. NP1 was synthesized with 2.0% DVB in the reaction vessel, while NP2 was synthesized with 8.20% DVB. Since NP2 had more DVB than NP1, it also had more cross-linking. Size exclusion chromatography multi-angled laser light scattering (SEC-MALLS) and dynamic light scattering (DLS) were used to characterize the soft nanoparticles. The ratio of the radius of gyration to hydrodynamic radius (R_g/R_h) was smaller for NP2 than NP1, 0.67 vs. 0.88, indicating NP2 is a more compact sphere with more branching than NP1 (3-8). A summary of the characteristics of the soft nanoparticles used in this work is presented in Table 2.2.
Table 2.2: Soft Nanoparticle Properties

<table>
<thead>
<tr>
<th>Particle</th>
<th>Mol% DVB</th>
<th>Radius (Å)</th>
<th>MW (g/mol)</th>
<th>$R_g/R_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP1</td>
<td>2.00%</td>
<td>158 ($R_h$)</td>
<td>3.28E+06</td>
<td>0.88</td>
</tr>
<tr>
<td>NP2</td>
<td>8.20%</td>
<td>120 ($R_h$)</td>
<td>2.19E+06</td>
<td>0.67</td>
</tr>
</tbody>
</table>
Figure 2.1. An illustration of the synthesis procedure for the PS soft nanoparticles.
Dr. Eric Eastwood from the Kansas City Plant (Honeywell Federal Manufacturing and Technologies, Kansas City, Missouri) provided a range of boron containing nanoparticles, which were synthesized in the labs of Dr. Mark Lee and Dr. Fred Hawthorne from the University of Missouri-Columbia. These nanoparticles include two polyhedral boranes, dodecahydrododecaborate dilithium salt (Li$_2$[B$_{12}$H$_{12}$]) and dodecahydrododecaborate dipotassium salt (K$_2$[B$_{12}$H$_{12}$]), and two carboranes, 1,3-di-o-carboranylpropane (tethered carborane, C$_7$H$_{28}$B$_{20}$) and 1,2-bis-(hydroxymethyl)-o-carborane (diol carborane, C$_4$H$_{16}$O$_2$B$_{10}$).

Boron nitride powder (BN-ZG Powder) was manufactured by ZYP Coatings, Inc, Oak Ridge Tennessee and used as received. Boron nitride nanotubes (BNNT) were purchased from Deakin University (30 – 100 nm tube diameter) and used as received. Functionalized boron nitride nanotubes (FBNNT) were functionalized with stearoyl chloride and provided by Dr. Eric Eastwood, as well (9-11).

Carbon nanotube soot was obtained from Oak Ridge National Lab, and used as received to evaluate carbon nanotube purification methods. The material was synthesized using laser ablation from a Ni/Co catalyst. The soot contained single-walled carbon nanotubes combined with other impurities as a result of this synthetic procedure. For easy reference, the abbreviations used in this thesis for the nanoparticles are listed in Table 2.3.
Table 2.3: The abbreviated names of the nanoparticles used in this thesis.

<table>
<thead>
<tr>
<th>Particle Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron Nitride Powder</td>
<td>BN-ZG</td>
</tr>
<tr>
<td>1,2-bis-(hydroxymethyl)-o-carborane (dial carborane, C$<em>{4}$H$</em>{16}$O$<em>{2}$B$</em>{10}$)</td>
<td>DCB</td>
</tr>
<tr>
<td>dodecahydrododecaborate dipotassium salt (K$<em>{2}$[B$</em>{12}$H$_{12}$])</td>
<td>KBH</td>
</tr>
<tr>
<td>dodecahydrododecaborate dilithium salt (Li$<em>{2}$[B$</em>{12}$H$_{12}$])</td>
<td>LBH</td>
</tr>
<tr>
<td>1,3-di-o-carboranylpropane (tethered carborane, C$<em>{7}$H$</em>{28}$B$_{20}$)</td>
<td>TCB</td>
</tr>
<tr>
<td>Functionalized Boron Nitride Nanotubes</td>
<td>BNNT</td>
</tr>
<tr>
<td>Boron Nitride Nanotubes</td>
<td>FBNNT</td>
</tr>
<tr>
<td>Single Walled Carbon Nanotubes</td>
<td>SWNT</td>
</tr>
</tbody>
</table>
D. Silicon, Glass, and NaCl Substrates

Silicon wafers were purchased from Wafer World, Inc (West Palm Beach, Fl). The silicon substrates are 2” diameter, 300-350 micron thick, single side polished, <100> crystal orientation, and N-doped. The wafers were cleaned in a boiling chloroform bath, placed into a UV/ozone cleaner to remove organic contaminants, and immersed in a hot piranha solution (sulfuric acid and hydrogen peroxide 3:1 solution) for 30 minutes (24). Upon removal, the wafers were rinsed with nanopure water and dried with nitrogen. The wafers were then placed in a 5% solution of hydrofluoric acid for 5 minutes, in order to remove the native oxide layer on the silicon wafer. The wafers were again dried with nitrogen and then immediately spun-cast with the polymer and polymer-nanoparticle solutions.

Glass slides (extra large glass microscope slides, 75x50mm, pre-cleaned) were purchased from Fisher Scientific and used as received as the substrate from which to float coat polymer thin films to fabricate bilayers on the cleaned silicon wafers. Salt plates (25x50x6mm NaCl polished rectangular salt plates, International Crystal Laboratories) were also used as substrates for the float coating process and used as received. Once the salt plates were exposed to the water bath, it was necessary to lightly sand the plates with a fine sand paper in order to maintain a smooth, even surface for subsequent reuse.

2.2 Sample Preparation Techniques

The experiments described in Chapter 3, require thin polymer films on silicon wafers to use neutron reflectivity to investigate the impact of a variety of nanoparticles on the surface
segregation behavior of dPS in thin films. Sample preparation consisted of spin coating and float-coating techniques, the details of which are described below.

The experiments described in Chapters 4 and 5 are designed to quantify the solubility of various nanoparticle-solvent and polymer-solvent solutions. To that end, solutions were prepared by dissolving nanoparticles and polymers in solvents with the aide of sonication and vortexing, and then collecting fractions with centrifugation or particle settling. The purification of SWNTs (Chapter 6) also involved the centrifugation of nanoparticle solutions in 1% SDS. The technique of centrifugation is also presented.

A. Gel Permeation Chromatography

Gel Permeation Chromatography (GPC), also known as Size Exclusion Chromatography, is used to verify the molecular weights and polydispersity indices (PDI) of the polymers used in this work. GPC is a liquid column chromatographic technique, which separates molecules based upon their size (12-14). Polymer molecules dissolved in solvent are passed through a densely packed column of porous material (typically PS beads). Separation of the molecules in the column occurs because smaller molecules are able to explore pores, thus residing in the column for longer periods of time. Larger molecules, which cannot explore the pores, elute earlier, where the elution time is related to the hydrodynamic volume of the molecules under investigation (12-14).

For linear polymers, the relationship between hydrodynamic radius and molecular weight is straightforward. GPC can therefore, separate polymers on the basis of their molecular weight using simple detection methods, including refractive index. With proper calibration using monodisperse reference samples, the correlation of elution time to molecular weight is readily
achieved. Difficulties with this technique arise when polymers are branched or have connectivities that differ from a linear homopolymer chain. (12-14).

The GPC instrument used in this work is a Polymer Labs GPC equipped with 2 Polymer Labs PLgel 5 micrometer mixed-C columns with HPLC grade tetrahydrofuran (THF) as the eluant. The instrument is equipped with a refractive index detector. Samples were prepared at a concentration of 2 mg/ml in THF. One drop of toluene was added to each sample as a marker. The results were analyzed using Polymer Labs Cirrus software, which was calibrated with narrow molecular weight polystyrene standards.

B. Spin Coating

Spin coating is a technique used to fabricate thin uniform polymer films. A fixed amount of solution containing the polymer and solvent is pipetted onto a silicon substrate, and the substrate is spun at high speeds to generate the thin film. Centrifugal force throws excess solution towards the outer edges, while the solvent evaporates. While this is occurring, the polymer forms a uniform layer on the silicon surface.

The resulting polymer film thickness depends on the spin speed, solution viscosity, and the solvent evaporation rate. The film thickness, H, is related to the angular momentum of the spinning process, ω, as (15-16):

\[ H \sim \omega^{-N} \]

In the above equation, N is a factor dependant on the evaporation rate of the solvent. If the evaporation is slow, then N is closer to unity, and if solvent evaporation is fast and unimpeded, N is closer to 0.5. Typically, a higher angular speed of spinning results in a thinner film.
Spin coating was carried out onto silicon wafers that were cleaned with HF and spun for 30 seconds at 2500 rpm using a Headway Research Inc. Model PWM32 spin coater. More details regarding the sample preparation, including concentrations, is presented in section 2.6.

C. Float Coating

The film floating technique enables well-defined multilayered samples to be produced on silicon substrates. In this procedure, layers are spun cast onto a smooth surface, such as mica or a glass slide, and the resulting thin films are floated off onto a liquid. Liquids for this technique must be a non-solvent for the thin film material. A silicon substrate then captures the floating thin film (17-21).

This technique was used to create the dPS/PS bilayers used in the neutron reflectivity work in Chapter 3. The floating process requires practice and a steady hand to remove the polymer film from the substrate. It is also necessary to first remove any excess polymer left over from the spin coating process by gently scraping the sides of the substrate using the edge of a razor blade. Slow speed while lowering the slide into the bath is necessary to prevent any tears or breaks from forming in the thin film. Tweezers were found to be much steadier than one’s hand for holding the edge of the silicon substrate to retrieve the floating layers. Nanopure water was selected as the non-solvent for the floating process, and salt plates were used as the smooth substrates from which the films were floated.

D. Centrifugation

Centrifugation exploits the centrifugal force created when spinning a sample at high speeds to compel the sedimentation of mixtures. The less dense components of the mixture
migrate towards the axis of the centrifuge, while the more dense components migrate away from it. This results in the insoluble, denser components forming a solid at the bottom of the centrifuge tube, while the remaining solution is termed the “supernatant.” The supernatant is typically withdrawn using a pipette (22). It is important to note that the settling velocity of a particle is a function of its size and shape, centrifugal acceleration, density, and viscosity of the liquid (22).

Centrifugation was used in both the preparation of samples for light scattering (Chapters 4-5) and for the purification of SWNTs (Chapter 6). In both instances, centrifugation was used to remove insoluble or clumping particles from solution using an Eppendorf 5702 centrifuge at a rate of 4400 rpm.

For the light scattering experiments, some of the nanoparticle-solvent solutions were centrifuged for 90 minutes to remove aggregates and to determine the solubility limits of the nanoparticles in the solvents. The solutions that contained SWNTs and boron nitride powder (BN-ZG) were prepared in this manner. The remaining nanoparticle-solvent and polymer-solvent systems studied in this section were simply allowed to settle for 48 hours in order to reach equilibrium.

Samples were centrifuged for up to 9 hours to purify the SWNTs. In this procedure, the supernatant was collected in scintillation vials for analysis once clumping was no longer observed.
2.3 Techniques to Monitor Chain Segregation in Nanocomposite Thin Films

A. Ellipsometry

Ellipsometry is an optical technique that characterizes thin films, including the thickness of single layers or complex multilayers, providing an excellent level of accuracy. In addition, since the technique is optically based, it is contactless and non-destructive (23-25).

Some background information on the wave nature of light is necessary in order to understand ellipsometry. To begin, as light passes through a medium it slows down, the extent of which is defined as the medium’s complex refractive index, N. N is defined in equation 2.1 as the index of refraction less its extinction coefficient. It is the value of the extinction coefficient that determines how fast the amplitude of the wave decreases in a medium. In the following equations, n is the index of refraction, c is the speed of light in a vacuum, v is the speed of light in the medium of interest, a is the absorption coefficient, and k is the extinction coefficient (23-24).

\[
N = n - ik \quad (2.1)
\]
\[
n = \frac{c}{v} \quad (2.2)
\]
\[
k = \frac{\lambda}{4 \pi} a \quad (2.3)
\]

Two perpendicular components make up light waves: the p-wave and the s-wave. The p-wave is in the plane of incidence, normal to the sample’s surface. The s-wave lies perpendicular to the plane of incidence. Light is linearly polarized when the two components are in phase, circularly polarized when the components are 90° out of phase, and elliptically polarized when the components lie out of phase between 0° and 90° (23-25).
During an ellipsometry measurement, a linearly polarized beam of light, typically from a laser source, strikes the sample’s surface. Upon reflection, there is a shift of the phases and the amplitudes of the p and s waves.

In the case of the reflection of light from a single interface, the Fresnel reflection coefficients, \( r \), which are the ratios of the amplitude of the reflected and incident waves, are determined for both the p and s portions of the wave by equations 2.4 and 2.5 (23-25):

\[
r_{12}^p = \frac{(N_2 \cos \phi_1 - N_1 \cos \phi_2)}{(N_2 \cos \phi_1 + N_1 \cos \phi_2)} \quad (2.4)
\]

\[
r_{12}^s = \frac{(N_1 \cos \phi_1 - N_2 \cos \phi_2)}{(N_1 \cos \phi_1 + N_2 \cos \phi_2)} \quad (2.5)
\]

In the above equations, \( \phi_1 \) is the angle of incidence and \( \phi_2 \) is the angle of refraction. When light is reflected from multiple layers and interfaces, the total reflection coefficients are then defined as (23-25):

\[
R^p = \frac{[r_{12}^p + r_{23}^p \exp(i2\beta)]}{[1 + r_{12}^p r_{23}^p \exp(i2\beta)]} \quad (2.6)
\]

\[
R^s = \frac{[r_{12}^s + r_{23}^s \exp(i2\beta)]}{[1 + r_{12}^s r_{23}^s \exp(i2\beta)]} \quad (2.7)
\]

In these equations, \( \beta \) is defined as:

\[
\beta = 2\pi(d/\lambda)N_2\cos \phi_2 \quad (2.8)
\]

Ellipsometry measures the phase difference between the p and s portions of the reflected light, \( \Delta \), and the angle whose tangent is the ratio of the total reflection coefficients, \( \psi \). A relationship between these measured quantities and the total reflection coefficients was discovered and defined by Paul Drude (26-27), where the following equations illustrate this point, and equation 2.11 is the Drude equation, the fundamental equation of ellipsometry.

\[
\Delta = \delta_1 - \delta_2 \quad (2.9)
\]

\[
tan \psi = \left| \frac{R^p}{R^s} \right| \quad (2.10)
\]

\[
tan \psi \exp(i\Delta) = R^p / R^s \quad (2.11)
\]
The Drude equation relates $\Delta$ and $\psi$ to the thicknesses and complex refractive indices of the layers within a sample. By fitting the collected data to a model layer profile, information regarding the layer thicknesses can then be obtained (26-27).

Both liquid and solid samples can be measured using this technique. In addition, no reference or standard is required, and no special sample preparation is needed. Only a clean surface is necessary to collect the measurements. One drawback is that only one layer can be fit at a time, making it necessary to know all of the relevant information for the other layers in the sample to analyze multilayers. (23-25).

For the experiments in Chapter 3, bilayers were prepared on silicon by spin coating and floating as described above. The same solutions that were used to prepare the bilayers were spun cast directly onto 1 inch square silicon wafer pieces, and characterized by Ellipsometry within approximately 24 hours of deposition. Film thicknesses were determined using a DRE-Dr. Riss Ellipsometerbau GmbH (Ratzeburg, Germany) ELX-02C rotating analyzer nulling ellipsometer at a 70° angle of incidence. At least 5 measurements were taken at different areas on the substrate surface, with the reported values are the average of the observed thicknesses.

The thin films measured in this work were polystyrene films that contained 1.0 wt% SWNTs, graphene, or PS soft nanoparticles. In the models used to fit the collected data, the index of refraction of the silicon is 3.88, the index of refraction of polystyrene is 1.59 (28), and the index of refraction of the polystyrene-nanoparticle layer varies between 1.57 – 1.73, depending on the sample. A summary of the data used in the ellipsometry models is in Table 2.4.
Table 2.4  Refractive Indices Used in the Ellipsometry Models

<table>
<thead>
<tr>
<th>Polymer Layer</th>
<th>Index of Refraction Used in Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>1.57</td>
</tr>
<tr>
<td>PS - 1.0% Graphene</td>
<td>1.61</td>
</tr>
<tr>
<td>PS - 1.0% SWNTs</td>
<td>1.73</td>
</tr>
<tr>
<td>PS - 1.0% NP1</td>
<td>1.59</td>
</tr>
</tbody>
</table>

B.  Depth Profile Determination Using Specular Neutron Reflectivity

1) Neutron Reflectivity

Many times it is necessary to use depth-profiling techniques to determine the interfacial morphology or diffusion profiles of polymer samples. Such experimental techniques, which have been used in the past to study diffusion and segregation processes of polymers, include attenuated total reflection infrared spectroscopy, elastic recoil detection, forward recoil spectroscopy, neutron reflectivity, and nuclear reaction analysis. Neutron reflectivity has several advantages over other depth profiling techniques, including its non-destructive behavior, increased resolution and the ability to accurately construct interfacial profiles (18, 29-30). Radiation damage is negligible to the samples since the neutrons interact with the nuclei of the atoms and not the electrons. Most noteworthy is the high contrast between the neutron scattering lengths of hydrogen and deuterium: -0.374e-12 cm verses 0.6674e-12 cm for hydrogen and deuterium, respectively. Due to the small wavelength and the high contrast between deuterium and hydrogen, NR is capable of sub-nanometer resolution (18, 29-30). Specific regions and interfaces can also be labeled with deuterium, and buried polymer interfaces can be explored. The accurate modeling of the width of the interface and the interfacial profile of the interdiffusing polymers is thus possible.
In Chapter 3, the segregation behavior of dPS chains in dPS/PS bilayers is explored in this manner. Complementary techniques can also be used to investigate the samples further (31).

2) Specular Neutron Reflectivity Theory

In a neutron reflectivity experiment, an incident beam of neutrons is focused onto the sample, and the reflected neutrons from the surfaces and buried interfaces are measured using a two-dimensional array detector. Specular conditions are met when the angle of incidence and the angle of reflected neutrons are the same. The ratio of the measured beam intensity to that of the intensity of the incident beam is the specular reflectivity, \( R(Q_z) \) (17, 31-36).

Specular reflectivity is measured as a function of the momentum transfer vector, \( Q \), in the \( z \) direction, normal to the sample surface. Equation 2.12 shows the relationship between \( Q \), the \( z \) component of the momentum vector, the grazing angle of incidence, \( \theta \), and the wavelength of the neutrons, \( \lambda \) (17, 31-36).

\[
Q_z = \frac{4\pi \sin \theta}{\lambda} \quad (2.12)
\]

\( \rho(Q_z) \) is the one-dimensional Fourier transform of \( \rho(z) \), the average scattering length density profile of the sample in the \( z \) direction. In the equations below, \( N_i(z) \) is the number density profile of species \( i \) at sample depth \( z \), and \( b_i \) is the neutron scattering length of species \( i \) (11,25-30).

\[
R(Q_z) = \left( \frac{16\pi^2/Q_z^2}{|\rho(Q_z)|^2} \right) \quad (2.13)
\]

\[
\rho(Q_z) = \int_{-\infty}^{\infty} \rho(z) \exp(iQz) \, dz \quad (2.14)
\]

\[
\rho(z) = \sum_i N_i(z)b_i \quad (2.15)
\]
Neutrons are both reflected and refracted when they strike a surface. The refractive index, \( n \), of a material is composed of both a real, \( \delta_N \), and imaginary component, \( i\beta \), as described by equation 2.16(36):

\[
n = 1 - \delta_N + i\beta \quad (2.16)
\]

The imaginary component accounts for absorption, and in most cases involving neutrons, \( i\beta \) is negligible and assumed to be zero. The real component for neutrons is defined with equation 2.17.

\[
\delta_N = \sum_i N_i(z) b_i(\lambda^2/2\pi) \quad (2.17)
\]

For most materials, the neutron scattering length is small and positive. Therefore, the refractive index is typically less than unity, and a critical angle, \( \theta_c \), exists below which total external reflection occurs. For neutrons this angle is very small, and usually on the order of \( 10^{-6} \) degrees (76-77). For this reason, neutron reflectivity measurements are made with the incident beam at small grazing angles with a highly collimated beam of neutrons (17, 31-36). Also, for single layers prepared on a substrate, the total reflection occurs at incident angles below \( \theta_c \) and the measured reflectivity is unity.

When an interface is infinitely sharp, the measured intensity of the reflected beam decays as \( QZ^{-4} \) above the critical angle. However, a more rapid reduction of intensity as a function of \( Q_z \) will occur when the interface is not sharp, as in the case of a single polymer layer prepared on a flat silicon substrate (20). A typical reflectivity profile of a single monolayer is presented in Figure 2.2, showing the reflectivity of a monolayer of dPS containing 1.0 wt% NP1. There is a series of maxima and minima present in the profile, and the thickness, \( d \), of the sample is related to the distance between successive minima as shown in equation 2.18 (20):
**Figure 2.2:** Series of Fringes Present in dPS Monolayer Containing 1.0 wt% NP1
\[ d = 2 \pi / \Delta Qz \quad (2.18) \]

The presence of interfacial roughness also dampens the depth and height of the minima and maxima observed in the reflectivity profile. The profile becomes increasingly complex as the number of layers in the sample increases, as well, because the measured reflectivity becomes a convolution of the reflections from all of the surfaces and interfaces within the sample.

One disadvantage of NR arises from the complexity of such profiles. The extraction of unique scattering length density (SLD) profiles of the sample is not obtainable directly from analysis of the measured reflectivity. (20). This is because the intensity of the reflected radiation is actually measured in a neutron reflectivity experiment, which is a function of the square of the amplitude of the reflected beam. Since the experiment measures the square of the amplitude, a complete loss of phase information of the system results.

Once data is collected, a data fitting procedure is necessary to obtain a SLD profile of the sample from the experimentally obtained reflectivity profile. Typically, an SLD profile, which is normal to the surface and a function of the sample’s depth, is modeled for a system, and then the resulting reflectivity profile is calculated. The calculated profile is then recursively fit to the measured reflectivity data (17, 31-36).

Information about the sample is used to create the model scattering length density profile, including the individual scattering length densities of the components of the system, layer thicknesses, and interfacial roughness. For example, if the sample’s thickness was previously measured with ellipsometry, a good starting point for depth is known. The measured reflectivity is then fit to the reflectivity of the model scattering length density profile.

As discussed previously, it is possible to have more than one model SLD profile that accurately fits the data. Independent information regarding the system is often required when
fitting the data in order to choose between competing fits, which must offer a reasonable explanation and make physical sense.

Fit quality is typically quantified using a $\chi^2$ statistical comparison between the experimentally obtained and modeled reflectivities using equation 2.19 (37).

$$\chi^2 = \sum \frac{(R_{(q)\text{calc}} - R_{(q)\text{exp}})^2}{R_{(q)\text{exp}}} \quad (2.19)$$

Since fitting multilayers is often difficult, reflectivity of monolayers that make up the multilayer mitigates the uncertainty in the modeling process by providing external constraints. For instance, the sample thickness and composition of a monolayer provides accurate parameters for the initial model in the fitting (20). Mass balancing also aids in the fitting process. In each subsequent model, the scattering volume, which is the product of the volume and SLD, must remain similar to that defined by the model’s components, and it should also remain constant for all the SLD models of the same sample. For example, if a bilayer was annealed through a series of times, each model, at each subsequent time, should have a similar scattering volume. This is true for all solid, nonvolatile materials since no materials will be lost from the samples that contribute to scattering. Equations 2.20, 2.21, and 2.22 relate SLD, volume, depth, and the mass balance requirement, where $d_Z$ is the depth in the Z direction normal to the sample surface and $d_A$ and $d_B$ are the depths of layers A and B.

$$\text{Scattering volume} \equiv \text{SLD}_A \times \text{Vol}_A \quad (2.20)$$

$$\text{Vol}_A \approx d_A \quad (2.21)$$

$$\int \text{SLD}_Z(d_Z) \approx d_A \text{SLD}_A + d_B \text{SLD}_B = \text{constant} \quad (2.22)$$

The specular neutron reflectivity measurements in this work were performed at the Spallation Neutron Source in Oak Ridge National Lab. Multiple angles were measured with an
effective Q range from 0.02 to 0.18Å⁻¹. The resulting data was corrected using on-site data reduction software. The reflectivity is plotted as a function of the momentum transfer normal to the surface, Q. Reflfit (National Institute of Standards and Technology, Center for Neutron Research) was used to fit the reflectivity data and to construct scattering length density (SLD) profiles. A standard chi squared (χ²) test for statistical significance was carried out, and all of fits to the data had χ² less than 10.0. Another fitting program, Mlayer (Spallation Neutron Source, Oak Ridge National Lab), was also used to confirm the fits and χ² values. All fits were consistent in both programs. The volume fraction of dPS in each layer of the SLD profile was calculated using the Tiles Program (Spallation Neutron Source, Oak Ridge National Lab).

Subsequent graphs of volume fraction dPS as a function of depth were analyzed to determine the width of the interface and the excess dPS at the surface, Z*, by integrating under the curves using Origin 8.5 (data analysis and graphing software).

2.4 Techniques for Quantifying Solubility of Nanoparticles

A. UV-Vis Spectroscopy

UV-Vis absorption spectroscopy is used to determine the concentration and as a means to quantify the solubility of particles in solution (45-48). SWNTs, graphene, and fullerenes have been tested using this method, with solubility limits obtained in various solvents (38-44). Additionally, UV-Vis spectroscopy is used to analyze the purity of SWNTs. The percent of amorphous carbon present in a sample is determined, as well as, the extent of exfoliation using this technique (45-48).
Solubility is tested by first recording the UV-Vis absorption spectra of a series of known concentrations of nanoparticles in a solvent of interest. Since absorbance increases linearly with concentration, a solution that is in the soluble regime will obey a Beer’s Law Plot. For SWNTs and fullerenes, the absorbance in the region of 300 to 700 nm is of interest, since this region corresponds to the optical transitions of the materials (45-48). The absorbance at 500nm is commonly monitored as a function of SWNT concentration, as this region corresponds to the metallic transition of the SWNTs (41). The slope of a plot of absorbance vs SWNT concentration determines the SWNT extinction coefficient. With knowledge of the extinction coefficient, the concentration of unknown solutions can be determined by applying Beer’s Law. The solubility limits of concentrated samples, often left to settle in an inert environment or subjected to centrifugation to remove aggregates, can also be determined in this manner.

The purity of SWNTs can be monitored by the evaluation of several UV-Vis peaks in the wavelength range of 600 nm – 2,000 nm (45-48). The width and structure of the bands in this region are dependent on the diameters, chiralities, and conductive properties of the carbon nanotubes. The peaks in this region also depend on the electronic band structure of the carbon nanotubes and the optical transitions that occur between the states of the semiconducting and conducting nanotubes, which represent Van Hove Singularities (50). These optical transitions are labeled the $S_{11}$ and $S_{22}$ peaks for semiconducting nanotubes and the $M_{11}$ peak for the first metallic transition (44).

For purity analysis, these peaks are more prominent in purified carbon nanotube samples (45-48, 50). Sharper optical transitions are also present, and the $S_{11}$, $S_{22}$, and $M_{11}$ peaks are higher. The percent amorphous carbon is also quantified by comparing the areas under the curves for these characteristics peaks of the UV-Vis spectra. Nanotubes that are more exfoliated
also have sharper optical transitions in their spectra, which indicates that the nanotubes are in a
more pure form or debundled after dissolution (51).
1) **UV-Vis Spectroscopy Theory**

Ultraviolet-visible spectrophotometry (UV-Vis) refers to the absorption of light in the visible, near-ultraviolet (UV) and near-infrared (NIR) spectral regions. A UV-Vis spectrophotometer measures the intensity of light passing through a sample \( I \) relative to the intensity of light that passes through a reference \( I_0 \), typically pure solvent. The ratio of \( I / I_0 \) is the transmittance and is usually expressed as a percentage (%T). Absorbance is related to transmission by equation 2.23 (52)

\[
A = - \log \left( \frac{\%T}{100} \right) \quad (2.23)
\]

The basic spectrophotometer is made of a light source, a sample holder, and a photomultiplier tube or photodiode detector. A diffraction grating in a monochromator serves the purpose of allowing only light of a single wavelength to reach the detector at one time. Several radiation sources are used to create the wavelengths of light required. Examples include tungsten filaments (300-2500 nm), deuterium arc lamps (190-400 nm), xenon arc lamps (160-2,000 nm), and light emitting diodes (visible wavelengths) (52).

Samples for UV-Vis analysis are usually liquids, although gases and even solids are measured. The width of the sample becomes the path length, \( L \), in the Beer-Lambert law, equation 2.24, where \( A \) is the measured absorbance, \( I_0 \) is the intensity of the incident light, \( I \) is the transmitted intensity, \( L \) is the pathlength, \( c \) is the concentration of the absorbing species, and \( \varepsilon \) is the extinction coefficient (53).

\[
A = \log_{10} \left( \frac{I_0}{I} \right) = \varepsilon \cdot c \cdot L \quad (2.24)
\]
The Beer-Lambert Law is used to determine the concentrations of an absorbing species in solution. The extinction coefficient is a fundamental molecular property that is a constant for a given absorber, defining how strongly a substance absorbs light at a particular wavelength.

For the nanoparticle solubility studies in Chapter 4 and 5, UV-Vis absorption spectroscopy was completed using a Thermo Scientific Evolution 600, using deuterium and halogen lamps. UV-Vis-Nir absorption spectroscopy measurements were necessary to assess the purity of SWNTs in Chapter 6, since the metallic and semi-conducting transitions occurred in the range of 600 to 2000 nm, and these measurements were conducted at Oak Ridge National Laboratory.

B. Refractive Index Increment

The specific refractive index increment, \(dn/dc\), is the amount that the refractive index of a solution varies with a change in concentration. \(dn/dc\) is defined with equation 2.25, where \(n\) is the refractive index of the solution, \(n_0\) is the refractive index of the solvent, and \(c\) is the concentration of the solution, and is expressed in units of ml/g (54).

\[
\nu = \left. \frac{dn}{dc} \right|_{c=0} = \lim_{c \to 0} \left( \frac{n - n_0}{c} \right) \quad (2.25)
\]

\(dn/dc\) is an important material specific parameter of a polymer solution, and varies only slightly with wavelength \((\lambda)\) (54). It is typical, therefore, to measure \(dn/dc\) at two or more wavelengths at a constant temperature, in order to construct a “Cauchy plot” of \(dn/dc\) verses \(\lambda^{-2}\) (54-55). The Cauchy plot produces a straight line, from which the \(dn/dc\) at any desired wavelength can be calculated.
1) Refractometry Theory

A refractometer is a laboratory instrument used to measure refractive index (56-57). Basic instruments have a split cell with two compartments, one for the solvent and one for the solution. Light bisects the cell and deflects according to Snell’s Law, and the difference in displacement is proportional to the difference between the refractive indices of the solution and solvent (Δn).

Prior to measurements, the instrument is calibrated. The response of the instrument, S, is a voltage reading on more modern instruments or a dial reading with older equipment that often use a microscope to measure the displacement (56).

The relationship of the response of the instrument to Δn is defined by equation 2.26, where O represents an offset and V is “voltage” on more modern electronic instruments or “view” on older instruments where the displacement is viewed with an ocular eye piece (56):

\[ S = \frac{dV}{dn} \Delta n + O \]  

(2.26)

A plot of S as a function of Δn gives a straight line, which calibrates the instrument by determining dV/dn and O.

Salt solutions are used for calibration since they have well defined dn/dc. By measuring the response of several concentrations of salt solutions with known Δn, a plot of S as a function of change in refractive index is produced, and dV/dn is calculated (58).

Once dV/dn is known, solutions with unknown dn/dc values are examined. In a typical experiment, a set of five carefully prepared concentrations are tested, and the instrument response, S, is measured and plotted as a function of concentration for the set of solutions. The unknown dn/dc is calculated using equation 2.27.
\[
\frac{dn}{dc} = \frac{(dV/dc)}{(dV/dn)} = \frac{\text{slope of measurement plot}}{\text{slope of calibration plot}} \tag{2.27}
\]

For the work in this thesis, a Brice Phoenix Differential Refractometer, BP-2000V, (Phoenix Precision Instrument Company) was used. This instrument is an older design that has several advantages over the more modern instruments available (56). The more modern refractometer, Wyatt Dawn EOS system (Wyatt Technology Corporation), required a flow through, filtered injection of solutions. Since the work in Chapter 4 and Chapter 5 was with nanoparticle solutions, the filter and flow-through apparatus on the more modern instrument easily clogged, and the flow of solvent was obstructed. Filtration also removed the nanoparticles from solution. For example, the lengths of SWNTs are considerably larger than the 0.45 micrometer Teflon syringe filters that fed the injection port for the instrument. Several attempts were made with the more modern instrumentation, but were unsuccessful due to these reasons.

The Brice Phoenix refractometer has two sample compartments, one for the pure solvent and one for the sample solution. Solutions are loaded via pipette and are fully recoverable following the experiments, allowing the recovery of valuable nanoparticle solutions to be studied using static light scattering or UV-Vis spectroscopy. The sample compartment was held at constant temperature, 25 °C, by using a chiller.

Calibration was carried out using a set of carefully prepared NaCl solutions. The instrument measures the displacement with the aid of a microscope and ocular eyepiece. Dial readings are recorded for pure solvent and a series of five solutions. Calculations were carried out using an Excel Spreadsheet (Microsoft, Inc), and Cauchy Plots were made for the data obtained.
C. Static Light Scattering

Static light scattering measures the intensity of scattered light at a variety of scattering angles, which can be analyzed to determine the weight average molecular weight ($M_w$) of a scattering particle (59-61). This technique is used in polymer chemistry to determine the $M_w$ of polymers or proteins. The root mean square radius of gyration ($R_g$) of the scattering particle can also be determined (59-61), while measuring the scattering intensity for various concentrations, the second virial coefficient $A_2$, is obtained.

Light scattering is a powerful tool that is used to characterize a range of particle sizes. For example, Cabannes verified Avogadro’s number by measuring the light intensity scattered by argon gas, and the molecular weight of large complex sugar molecules was determined by Debye and co-workers using light scattering (62). It is also possible to quantify the ability of a solvent to finely disperse solutes. If the $M_w$ or radius of a particle is known, for instance, then the $M_w$ and $R_g$ obtained from light scattering will quantify the aggregation behavior of the particles in solution (63-64).

1) Light Scattering Theory

Light scattering is caused by fluctuations in the refractive index of a medium. Debye is credited with relating the fluctuations of the refractive index in liquids with the molecular weights of solutes, including polymers. Mathematical relationships were established, where the fluctuation of refractive index is ascribed to the presence of the polymer molecules themselves. Equation 2.28 describes this relationship, which relates the osmotic pressure of a polymer solution to the light scattering intensity, where $\Pi$ is the osmotic pressure, $c$ is the concentration, $R_0$ is the Rayleigh ratio and $H$ is the optical constant (59-61).
\[ \frac{Hc}{R_\theta} = \frac{1}{RT} \left( \frac{\delta \Pi}{\delta c} \right) \text{ at constant temperature} \quad (2.28) \]

H is determined experimentally, and is a constant for a particular polymer-solvent system. This constant depends on the refractive index increment of the solution and the wavelength of the laser (59-61). \( R_\theta \) is defined with equation 2.29, where \( I_\theta \) is the scattered light intensity, \( \theta \) is the angle, \( V_s \) is the scattered volume, \( w \) is the distance from the source to the detector, and \( I_0 \) is the intensity of the incident light. H is defined with equation 2.30, where \( n \) is the refractive index at wavelength \( \lambda \) and \( dn/dc \) is the refractive index increment.

\[ R_\theta = \frac{I_\theta w^2}{I_0 V_s} \quad (2.29) \]

\[ H = 2 \Pi^2 n^2 (dn/dc)^2 / N_A \lambda^4 \quad (2.30) \]

Equation 2.31 relates the scattered light intensity to the solution and solute characteristics (59-61).

\[ \frac{Hc}{R_\theta} - R_{\text{solvent}} = 1/M_w P_\theta + 2A_2 c \quad (2.31) \]

In this equation, \( c \) is solution concentration and \( A_2 \) is the second virial coefficient. \( A_2 \) is a thermodynamic property that quantifies the interaction strength between the solute and solvent. When \( A_2 > 0 \) the interactions between the solute and solvent are favorable and this system is soluble. In contrast, when \( A_2 < 0 \) aggregation or precipitation occurs.

Information regarding the shape of particles is also determined from equation 2.31, where \( P_\theta \) is the particle form factor, which is dependent on scattering angle. Therefore, the angular variation in the scattering intensity provides a measure of the size of the structures under investigation (59-61).

For this discussion, it is important to define the term “radius of gyration,” \( R_g \). \( R_g \) is the mean square average distance of the segments that make up the scattering particle from the
center of gravity, where \( N \) is the number of scattering segments and \( r_i \) is the distance of segment \( i \) from the particles center of gravity in equation 2.32. (59-61).

\[
R_g = \frac{1}{N} \sum_{i=1}^{N} r_i^2 \quad (2.32)
\]

For a random polymer coil, \( R_g \) is related to the end-to-end distance, \( r \), of a polymer chain by.

\[
R_g^2 = \frac{r^2}{6} \quad (2.33)
\]

An analytical expression of \( P_\theta \) for a polymer chain is given in equations 2.34 and 2.35, where \( r \) is the end to end distance of a polymer chain and \( k_s = \left(\frac{4\pi}{\lambda}\right)\sin(\theta/2) \) (59).

\[
P_\theta = \frac{2}{x^2} \left[ e^{-x} - (1-x) \right] \quad (2.34)
\]

\[
x = \frac{([k_s]^2 r^2)}{6} \quad (2.35)
\]

For a polymer coil, the above equations can be combined to give.

\[
P_\theta = \frac{2}{R_g^4 k_s^4} \left[ R_g^2 k_s^2 - [1 - \exp(-R_g^2 k_s^2)] \right] \quad (2.36)
\]

Analytical functions have also been derived for the form factor of rods and spheres (59-62), as given by equations 2.37 and 2.38, where \( D \) is the diameter of a sphere and \( L \) is the length of a rod.

\[
\text{Sphere} \quad P_\theta = \left[\frac{3}{x^3} (\sin x - x \cos x)\right]^2 \quad x = k_s D/2 \quad (2.37)
\]

\[
\text{Rod} \quad P_\theta = \frac{1}{x} \int_0^{2x} (\sin w/w)dw - (\sin x/x)^2 \quad x = k_s L/2 \quad (2.38)
\]

For a typical light scattering experiment, several concentrations and several scattering angles are measured in order to produce a Zimm plot, a plot that extrapolates to zero scattering angle and zero concentration, using equations 2.39 and 2.40 (59).

\[
(H c/R\theta)_{\theta=0} = 1/M_w + 2 A_2 c + \ldots \quad (2.39)
\]

\[
(H c/R\theta)_{c=0} = 1/M_w [1 + 1/3(4\pi/\lambda)^2 R_g^2 \sin^2 \theta/2 + \ldots] \quad (2.40)
\]
M\_w, R_g, and A\_2, are thus determined from the y-intercept and slopes of the lines of the resulting Zimm plot.

However, complexities arise when the particle’s size is much less than or much greater than the wavelength of the laser. In the case where the particles are very small, P\_\theta is essentially unity, and this actually simplifies the initial light scattering experiments greatly (59). R\_\theta from equation 2.31 reduces to 3\tau/16\Pi, where \tau is the turbidity, which is related to the scattered light intensity as shown in equation 2.41.

\[ I = I_0e^{-\tau x} \quad (2.41) \]

Measurement of only one scattering angle, typically 90\(^{\circ}\), is necessary to determine M\_w and the second virial coefficient for this type of sample. Equation 2.42 shows the relationship of the turbidity, molecular weight and solute concentration in these experiments. Thus, several concentrations are measured, and the concentration is extrapolated to zero to determine M\_w and A\_2. However, information regarding R\_g is not obtained, and recall that H is still a constant for a particular solvent-particle or solvent-polymer system, making it necessary to obtain dn/dc for a system.

\[ H c/ \tau = 1/M\_w + 2A\_2c \quad (2.42) \]

Cabannes also established that additional scattering occurs when small particles are also anisotropic, and due to this excess scattering the measured M\_w of anisotropic particles is often higher than that of identical isotropic particles. For this situation, a correction factor is applied to the results, as shown in equation 2.43 (59,62,66). In this equation, \rho is the fraction of depolarization, and represents the ratio of scattered light in the horizontal direction to the scattered light in the vertical direction.

\[ 6(1+\rho)/ 6-7\rho \quad (2.43) \]
Depolarization increases as anisotropy increases. For an infinitely thin rod, depolarization has been established as high as 50 percent (62). For comparison, depolarization was shown to be zero percent for argon and 12.5 percent for nitrous oxide. Aromatic compounds have also been shown to have greater depolarization than their straight chain counterparts. This information is important for work in this thesis, as highly anisotropic, aromatic particles are examined here, and the interpretation of these results must be interpreted cautiously.

Although complexities arise for large or very small particles that make it difficult to quantify their size, the Zimm plot remains a valuable tool for quantifying the behavior of particle-solvent systems. As the scattering angle approaches zero, \( P_\theta \) becomes independent of particle shape. The calculation of the second virial coefficient, which quantifies the solute-solvent interaction, is also independent of \( P_\theta \). Additionally, the \( R_g \) obtained from a Zimm plot offers a means of qualitatively discussing the size and shape of the particles and their agglomeration behavior in solution, if prior knowledge regarding the \( M_w \) and shape of an individual particle is already established. It is important to keep in mind for subsequent discussions, however, that anisotropic and large particles have additional complex scattering that affects the precise value of the measured \( M_w \) (62, 66).

Prior to a light scattering experiment, calibration is performed using a strong, known scatterer (54, 59-61). Typically toluene is used for calibration, since its Rayleigh Ratio is well established. Calibration determines the laser intensity, quantum efficiency of the detectors, and the full scattering volume and solid angles of the detectors. Additionally, if more than one angle is collected, it is important that all of the angles respond in the same way. Detectors will often have slightly different gains and are detecting different geometrical scattering volumes. Normalization is necessary to correct this. Measurement of pure solvent is established first,
followed by the addition of an isotropic scatterer, typically a dilute concentration of low $M_w$ polystyrene with known Rayleigh ratio. The detector gain is then normalized by establishing the value of the gain detected at the 90° angle detector and correcting for differences in gain at the other angles.

For this work, light scattering measurements were conducted on a Wyatt Dawn EOS system (Wyatt Technology Corporation) at 25 °C using scintillation vial mode. Scintillation vial mode does not require the use of an injection port or solvent flow through. Each sample was prepared in clean, glass scintillation vials. A special cell holder was also made in the machine shop at the University of Tennessee to allow smaller diameter scintillation vials to be measured in the instrument, which conserved solvent and lowered the path length. The wavelength of the laser was 685 nm. The instrument was calibrated with toluene and normalized for each solvent studied using a low molecular weight PS sample (8,000 Mn/8,400 Mw, 1.05 PDI). Five concentrations were prepared for each nanoparticle-solvent or polymer-solvent system. Pure solvent was studied first to record a baseline, and data was collected at multiple angles in order to produce Zimm plots.

**D. Density Measurements Using a Pycnometer**

A gas pycnometer measures the change in pressure in a sample chamber of known volume with an inert flow throw gas (69). The pressure inside the empty sample chamber is established, and then, the sample is introduced and pressure is recorded. Boyle’s Law is used to establish the volume of the sample. Density is calculated from this measured volume and the previously measured weight of the sample.
For this work, a HumiPyc Model 1 gas pycnometer (Instruquest, Inc) was used to measure the density of the nanoparticle powders. Helium was used as the flow through gas. The empty sample cell’s volume was determined by flowing helium gas through the chamber under controlled temperature and pressure. 25 ºC was selected in order to remain consistent with the light scattering data. The sample was weighed just prior to the pycnometer measurements and introduced into the chamber. The volume of the sample was measured with the flow through gas, and the density was thus calculated.

The EN4 and EN8 pre-polymers are liquids, and their density was determined by carefully pipetting 1 mL of solution onto a balance and obtaining the weight. Ten measurements were recorded and averaged to calculate the density.

2.5 Techniques to Examine SWNT Purification

A. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) determines changes in weight as a function of temperature (70). For this work, a TA Instruments TGAQ50 was used. A sample size of ~5-10 mg is loaded into an aluminum pan, and the sample is heated at a rate of 10 ºC/min from room temperature to 900 ºC, in the presence of air. A weight loss curve is generated as the temperature is increased. A derivative weight loss curve is useful for the identification of the point where the rate of weight loss is greatest.

From the weight loss, degradation temperatures, absorbed moisture content of materials, and the level of inorganic and organic components in the materials are determined. For the purification of carbon nanotubes, the presence and the amount of any metal and carbonaceous
impurities are evaluated. For example, the percent weight of the SWNTs and the percent weight of the carbon impurities are calculated from this curve.

B. Scanning Electron Microscopy

The scanning electron microscope (SEM) images a sample’s surface by scanning it with a high-energy beam of electrons (72). The signals result from the interactions of the electron beam with the atoms at or near the surface of the sample and include secondary, back scattered electrons, and transmitted electrons. The amount of electrons ejected from a sample are detected electronically and used to create pixilated images of the sample.

SEM is capable of producing very high-resolution images with magnification ranging in magnitude from 10 to more than 500,000 times (72). Also, a large depth of field, inherent due to the fact that the electron beam is narrow, results in a three-dimensional appearance of images which aides in the characterization of surfaces.

SEM images in this thesis were collected using a LEO-1525 field emission scanning electron microscope located at the University of Tennessee. Multiple images were collected with magnification ranging from 20,000 to 130,000 times magnification.

C. Raman Spectroscopy

Raman monitors the inelastic scattering of monochromatic light, termed Raman scattering, from laser light that is typically in the UV, NIR, or visible region of the spectrum. The energy of the laser’s photons is shifted up or down when they interact with the molecular vibrations of a sample.
Raman spectroscopy was used in this thesis to evaluate the purity of SWNT samples, and was performed using a JY-Horiba T64000 spectrometer equipped with a CCD detector, a 514.5 nm edge filter, 600 gr/mm grating, a laser spot size of 1.0 µm and a 514.5 nm laser excitation. Samples were mounted onto glass microscope slides, where five spectra with 20 seconds acquisition and 10 accumulations were collected for each sample.

2.6 Sample Preparation

A. Neutron Reflectivity Sample Preparation

Bilayer samples, composed of dPS in the bottom layer and pPS in the top, were prepared on clean, silicon wafers with spin coating and float coating techniques. The deuterated layer was selected to be ~100 nm thick and the protonated layer was ~60 nm based on previously reported studies (74-75).

Films formed from solutions of 2.6% dPS or 1.8% pPS in toluene as well as 1.2% dPS or 0.7% pPS in chloroform resulted in the appropriate thicknesses for the dPS/pPS bilayers. A calibration curve relating film thickness to solution concentration for toluene solutions was used to guide these experiments. A similar calibration curve for PS in chloroform was also developed for this work and is shown in Figure 2.3.

The thicknesses of the initial bilayers were verified with ellipsometry with error less than 4.0%, and all samples had a total bilayer thickness within the range of 140 nm to 190 nm thick, as summarized in Tables 2.5-2.6.
Figure 2.3. Spin coating calibration curves for PS in toluene and PS in chloroform.
### Table 2.5: Film Thickness of polystyrene thin films as measured by ellipsometry

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Ellipsometer Reading (nm)</th>
<th>Reflectivity As Cast Model Layer Thickness (nm)</th>
<th>Percent Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>dPS unmodified layer</td>
<td>115.15</td>
<td>115.9</td>
<td>0.65%</td>
</tr>
<tr>
<td>pPS unmodified layer</td>
<td>71.03</td>
<td>74.0</td>
<td>4.1%</td>
</tr>
<tr>
<td>dPS with 1.0% NP1</td>
<td>99.10</td>
<td>101.4</td>
<td>2.3%</td>
</tr>
<tr>
<td>pPS with 1.0% NP1</td>
<td>69.46</td>
<td>70.6</td>
<td>1.6%</td>
</tr>
<tr>
<td>dPS with 1.0% SWNTs</td>
<td>86.58</td>
<td>Not Modeled</td>
<td>----</td>
</tr>
<tr>
<td>pPS with 1.0% SWNT</td>
<td>53.20</td>
<td>Not Modeled</td>
<td>----</td>
</tr>
</tbody>
</table>

### Table 2.6: Samples Prepared for the Neutron Reflectivity Experiments

<table>
<thead>
<tr>
<th>Bilayer Sample</th>
<th>Total Bilayer Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified dPS/pPS Bilayer</td>
<td>190</td>
</tr>
<tr>
<td>Bilayer Containing 1.0% Nanoparticle #1 (NP1)</td>
<td>172</td>
</tr>
<tr>
<td>Bilayer Containing 1.0% Nanoparticle #2 (NP2)</td>
<td>189</td>
</tr>
<tr>
<td>Bilayer Containing 1.0% Graphene</td>
<td>141</td>
</tr>
<tr>
<td>Bilayer Containing 1.0% SWNTs</td>
<td>140</td>
</tr>
</tbody>
</table>
The soft-nanoparticles dissolved readily in toluene with the aide of a vortex. The SWNTs and graphene samples were prepared in chloroform. Although chloroform is not the best thermodynamic solvent for these particles, it readily evaporates during spin-coating, leaving behind a uniform polymer film, with uniform and distinctive colors for the 100nm and 64 nm thick layers, blue and brown, respectively (Figure 2.4). Also, the SWNTs and graphene particles dispersed after 30 minutes of sonication in chloroform, forming dark solutions with no noticeable clumping (Branson 1510 sonicating bath, frequency 42KHz, power 70 watts). Spin coating took place immediately after dispersion, in order to prevent the particles from agglomerating.

All of the solutions containing nanoparticles were prepared as stock solutions in the appropriate solvents by sonication for 30 minutes, and subsequently dPS or pPS were added to the solutions at the appropriate concentrations.

The protonated layer was spin coated directly onto the prepared silicon wafer to form the first layer, and float coating was used to create the dPS/PS bilayers as described earlier. The resulting bilayers were covered with a large Petri dish to protect from dust or contaminants and dried at room temperature while standing at a 45-degree angle. Samples were stored at room temperature in silicon wafer boxes for reflectivity measurements.

An on-site vacuum oven was used to anneal the samples at 150 °C. The bilayers containing 1.0% graphene, 1.0% NP1, and 1.0% NP2 were annealed for 0 minutes (as cast), 15 minutes, and 24 hours. Reflectivity measurements for the 1.0% SWNT bilayer were collected at 15 min and 30 min of annealing.

Two monolayers were also prepared to aide in the interpretation of the results. A monolayer composed of 1.0% graphene and pPS and a monolayer of 1.0% NP1 and dPS were
Figure 2.4: Optical images of prepared thin films, showing distinctive colors that coincide with the film thicknesses. (a) 100nm dPS thin film; (b) 64nm pPS thin film; (c) floated dPS/pPS bilayer
prepared and annealed for 24 hours prior to neutron reflectivity measurements.

B. Static Light Scattering and Refractometer Sample Preparation

1) Sample Preparation to Extract Light Scattering Instrument Constants

Several polymer solutions were prepared to determine the light scattering instrument constants. Poly(methyl methacrylate) in chloroform, PS in NMP, PS in THF, and PS in Benzene were studied. The GPC data is presented in Table 2.1 for the polymers used in this work. The $A_2$ of these polymer solutions are known taken from the 2010 Polymer Handbook (28). Five concentrations were prepared for each system, ranging from 0.75 and 3.74 mg/mL. The polymer solutions were filtered through 0.45 µm Teflon syringe filters prior to testing, and static light scattering measurements were conducted at 25 ºC using a Wyatt Dawn EOS system (Wyatt Technology Corporation) in scintillation vial mode.

2) Sample Preparation for the Nanoparticles and Pre-polymers with UV-Vis Concentration Determination

For the nanoparticle and pre-polymers tested, it was necessary to determine the concentration range that is dilute enough to acquire both UV-Vis and light scattering data, since transparent solutions are required.

The first systems studied were SWNTs in NMP and in CHP. A large concentration range from 0.01 to 5.0 mg/mL was prepared using a microbalance to weigh the appropriate amount of SWNTs. For each concentration prepared, samples were placed inside of clean 14 mL glass scintillation vial in 10 mL of filtered solvent. The glass vials were pre-rinsed three times with nanopure water to remove dust before dissolution, and the vials were sealed with tin foil to
prevent the pyrollidone solvents from dissolving the lining of the vial’s cap and introducing impurities. The samples were sonicated for 20 minutes in a Branson 1510 sonicating bath (frequency 42 KHz, power 70 watts) to disperse the nanotubes. UV-Vis measurements immediately followed sonication, while the nanotubes were well dispersed. 1 mm sample cells were used for the more concentrated samples, and on the less concentrated samples, the standard 1 cm cells were used. It was established that concentrations in the range of 0.01-0.15 mg/mL did not saturate the detector, while higher concentrations were too dark to obtain readings. The samples were also examined using static light scattering, and the results show appropriate signal to noise ratio without detector saturation for the 0.01-0.015 mg/mL SWNT samples.

Similar experiments were completed for the other nanotubes studies, which showed that the BNNT and FBNNT should be studied in the concentration range of 0.02-0.20 mg/mL, and BN-ZG samples from 0.002 to 0.46 mg/mL.

The polyhedral borane compounds (DCB, KBH, LBH, and TCB) were studied at higher concentrations, 0.2-6.0 mg/mL. Solutions in this range remained clear or were only slightly cloudy following sonication. The pre-polymers, EN4 and EN8, were also studied at higher concentrations, since their behavior indicates that they were more soluble, where concentrations from 0.30 to 6.9 mg/mL were examined.

For each nanoparticle or polymer studied, five concentrations were prepared in the appropriate concentration range. The samples were dispersed by sonication for 20 minutes. All of the boron containing nanoparticles, as well as EN4 and EN8 were examined in toluene and THF. The solubility of LBH in MEK was also studied. From the literature, SWNTs are reported to be soluble in NMP and CHP. Thus, the solubility of SWNT in CHP and NMP were examined using these methods.
Static light scattering and refractometry measurements were carried out on the SWNT centrifuged samples. For all of the other samples, measurements were collected on the freshly prepared, sonicated samples.

Once samples were prepared and initial measurements collected, the samples were stored in scintillation vials, sealed with paraffin wrap, and placed in the freezer at -21.5°C to prevent solvent evaporation.

3) Sample Preparation to test the solubility of BN-ZG

The solubility behavior of BN-ZG was studied in a range of solvents at room temperature. In these studies, solutions of 1 and 5 weight percent were prepared in each solvent. Samples were prepared in 10 mL of solvent in clean, pre-rinsed 14 mL scintillation vials. Observations of the solution characteristics were taken immediately upon mixing and 1 day later upon standing at room temperature.

C. SWNT Purification Sample Preparation

For the acid purification of the SWNT, 1 gram of as-prepared SWNTs (AP-SWNTs) was placed in a 250mL round bottom flask with 100 mL of 6M HNO₃. The mixture was refluxed at 120 °C for 16 hours. The solution was filtered with polycarbonate filter paper and washed with nanopure H₂O. The collected nanotube material was easily removed from the surface of the polycarbonate paper using a metal spatula and was dried in the vacuum oven at 100 °C for 48 hours.

Following vacuum drying, the nanotube material was loaded into a quartz oven tray for thermal annealing at 450 °C with constant airflow for 75 minutes to remove amorphous carbon.
The material was then washed with concentrated HCl to remove any residual metal catalyst, and filtered with polycarbonate filter paper. The sample was subjected to another thermal annealing at 500 °C for 30 minutes and another HCl wash. Homogenization with a mortar and pestle was necessary to break up the clumps of nanotubes formed during heating and collection.

The AP-SWNTs were also subjected to a purification procedure by centrifugation in 1% SDS “Soap.” 50 mg of starting material and 250 mL of 1% SDS aqueous solution were placed in a 500 mL round bottom flask. The flask was sealed with a glass stopper, and the mixture was sonicated for one hour using a Branson 1510 sonicating bath with 75% power and a frequency of 40 Hz. The resulting mixture was transferred into glass centrifuge tubes, and centrifuged for 6 hours at 4400 rpm.

Visual inspection indicates that the centrifugation is complete when there is clear separation of black sediment that forms a pellet at the bottom of the centrifuge tube and transparent liquid resting on top. The liquid portion remains dark grey in color. The nanotubes or nanoparticles are suspended in this top liquid portion of the SDS solution, with no visual clumping of the particles. A higher speed centrifuge was also used for this work, and centrifugation was complete in 4 hours at 9000 rpm.

Following centrifugation, the top 2/3 of the solution was pipetted off and collected as the purified material. The soap solution was filtered using nitrocellulose filter paper (0.1 micron) to collect the nanotubes.

As a coinciding project, AP-SWNTs were also purified by centrifugation in DMF, following the same procedure outlined above for the purification in 1% SDS, using DMF as the solvent instead. The only exception is that polycarbonate filter paper was used to collect the final purified material.
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Chapter 3

Impact of Nanoparticle Size and Shape on Selective Surface Segregation in Polymer Nanocomposites
3.1 Publication Statement

Chapter 3 is adapted from the manuscript entitled “Impact of Nanoparticle Size and Shape on Selective Surface Segregation in Polymer Nanocomposites” with co-authors D.W. Holley, Jimmy Mays, and Mark Dadmun (Chemical Sciences Division, Oak Ridge National Laboratory and the University of Tennessee), which is submitted for publication in Macromolecules. Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

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3.2 Abstract

A study of the impact of the size and shape of a nanoparticle on the evolution of structure and surface segregation in polymer nanocomposite thin films is presented. This is realized by monitoring the evolution of structure with thermal annealing and equilibrium depth profile of a deuterated polystyrene/protonated polystyrene bilayer in the presence and absence of various nanoparticles. For the three shapes examined, sheet-like graphene, cylindrical carbon nanotubes, and spherical soft nanoparticle, the presence of the nanoparticles slowed the inter-diffusion of the polymers in the thin film. The larger nanoparticles slowed the polymer motion the most, while the smaller spherical nanoparticles also significantly inhibited polymer chain diffusion. At equilibrium, the soft spherical nanoparticles, which are highly branched, segregate to the air surface, resulting in a decrease in the excess deuterated PS at the surface. The graphene sheets and single walled carbon nanotubes, on the other hand, enhanced the dPS segregation to the air
surface. The graphene sheets were found to segregate to the silicon surface, due to their higher surface energy. Interpretation of these results indicates that entropic factors drive the structural development in the nanocomposite thin films containing the spherical nanoparticles, while a balance of the surface energies of the various components (i.e. enthalpy) controls the thin film structure formation in the polymer-carbon nanoparticle nanocomposites.

3.3 Introduction

With the introduction of nanoparticles into a polymer matrix, chain motion becomes complex near surfaces and interfaces, and polymer chain motion deviates from classic thermodynamic models (Chapter 1). It is important to quantify this behavior and to understand how the size and shape of introduced nanoparticles affects the resulting surface structure and mixing behavior of polymer chains. This knowledge has applications in many technological areas, including the development of new nanocomposite materials for the electronics, adhesives, and air space industries.

In this work, the impact of various size and shaped nanoparticles on the surface segregation of dPS in a polystyrene matrix was investigated using neutron reflectivity. dPS and pPS of similar molecular weights were chosen as the matrix polymers in bilayers. With similar polymer molecular weights, dPS acts as a marker that is tracked during the surface segregation process.

Segregation behavior was quantified by modeling the scattering length density profiles (SLD profiles) and the dPS concentration profiles from the collected reflectivity data. The models then allow the calculation of the excess dPS at the surface, $Z^*$, and the width of the interface upon annealing in the as-cast, 15 minutes, and 24 hours annealed samples. The results
therefore provide insight into the impact of the presence of the particles on the chain diffusion and ultimate surface segregation behavior of the polymer nanocomposite.

Single-walled carbon nanotubes, graphene, and soft nanoparticles, which are composed of cross-linked polystyrene, were studied. Therefore, the change in the size and asymmetry of the nanoparticles is examined, as the nanoparticle shapes consist of cylinders (nanotubes), sheets (graphene), and highly branches spheres (soft nanoparticles) (Figure 3.1). Two different soft nanoparticles were studied, which varied in their diameters and cross-link density. The results are interpreted to provide fundamental insight into the thermodynamics driving forces that drive the structural development in these thin films, as well as reveal the interplay between polymer matrix chains and the nanoparticles during the evolution of the resultant depth profile.

As explained in more detail in chapter 2, Neutron reflectivity (NR) is ideally suited for investigating diffusion and segregation of polymers with deuterium labeling. NR is capable of sub-nanometer resolution due to the small probe wavelength and the high contrast between deuterium and hydrogen. Also with NR, accurate modeling of the width of the interface and the interfacial profile of the interdiffusing polymers is possible (Chapter 2). Ellipsometry measurements were also taken, to confirm the initial film thicknesses used in the generated reflectivity models.
Figure 3.1: a) graphene sheets; b) single-walled carbon nanotubes; c) soft nanoparticles
3.4 Materials and Sample Preparation

Chloroform (99.9% HPLC grade, Fisher Scientific) and Toluene (99.9% HPLC grade, Fisher Scientific) were used as solvents in this study. Prior to the neutron reflectivity experiments, the solvents were filtered through 0.45 micrometer Teflon syringe filters to remove dust particles. Nanopure water was obtained using a Millipore filtration system, Milli-Q 18 mega ohm water polisher, and D$_2$O was purchased from Sigma Aldrich.

Narrow molecular weight distribution polymer standards were purchased from Scientific Polymers Products Inc. and used as received. The deuterated polystyrene used in this study has a reported $M_w$ of 57,500 (PDI 1.15), and the protonated polystyrene – $M_w = 50,800$ (PDI 1.01). The polymer molecular weights were verified using gel permeation chromatography, and this information is presented in Chapter 2 (Table 2.1).

Single Walled Carbon Nanotubes (SWNTs) (95 wt %, 0.7-2.5 nm tube diameter, 0.5-5 µm length) were purchased from Bucky USA and used as received. Graphene ribbon (<20-30 µm length, width 20-300 nm) was synthesized and provided by Humberto Terrones, Advanced Materials Department, Potosi Institute of Scientific and Technological Research, San Luis Potosi, Mexico (31, 32). The two soft nanoparticles used in this study were synthesized and characterized in our lab. The synthesis procedure of the PS soft nanoparticles is outline in Chapter 2 (Figure 2.1). Size exclusion chromatography multi-angled laser light scattering and dynamic light scattering were used to characterize the soft nanoparticles. The ratio of the radius of gyration to hydrodynamic radius ($R_g/R_h$) was smaller for NP2 than NP1, 0.67 vs. 0.88, indicating NP2 is a more compact sphere with more branching than NP1 (33-38). A summary of the characteristics of the soft nanoparticles used in this work is presented in Table 3.1.
### Table 3.1: Soft Nanoparticle Properties

<table>
<thead>
<tr>
<th>Particle</th>
<th>Mol% DVB</th>
<th>Radius (Å)</th>
<th>MW (g/mol)</th>
<th>$R_g/R_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP1</td>
<td>2.00%</td>
<td>158 ($R_h$)</td>
<td>3.28E+06</td>
<td>0.88</td>
</tr>
<tr>
<td>NP2</td>
<td>8.20%</td>
<td>120 ($R_h$)</td>
<td>2.19E+06</td>
<td>0.67</td>
</tr>
</tbody>
</table>

### 3.5 Experimental

Specular neutron reflectivity measurements were performed at the Spallation Neutron Source at Oak Ridge National Laboratory as described in Chapter 2. The reflectivity of a model scattering length density (SLD) profile is fit to the measured reflectivity to extract information on the depth profile of the components in this thin film. A representative fit is shown in Figure 3.2 for the 1.0% graphene bilayer. The standard chi squared ($\chi^2$) parameter to define statistical significance of all fits were consistent, where the $\chi^2$ values of all reported models are below 10.0 (Table 3.2).

The volume fraction of dPS in each layer of the SLD profile was calculated from the scattering length density profile using the Tiles Program (Spallation Neutron Source, Oak Ridge National Lab). A mass balance was performed on all of scattering length density and concentration profiles as a self-consistent check to the fit. In each sample and fit, the mass balance of each model was consistent within a sample to ± 5% (Table 3.2).
Figure 3.2: Representative Neutron Reflectivity Data and Best Fit for the 1.0% Graphene Bilayer
- collected neutron reflectivity data
- Reflectivity of the model fit
Table 3.2: Mass Balance and $\chi^2$ Values for Each Series of Heated Bilayer Samples

<table>
<thead>
<tr>
<th>Bilayer Sample</th>
<th>$\chi^2$</th>
<th>Average SLD From Models</th>
<th>Bilayer Depths</th>
<th>Area Under SLD Profile Curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As Cast</td>
<td>4.78</td>
<td>4.46</td>
<td>1898</td>
<td>0.0084</td>
</tr>
<tr>
<td>Annealed 15 Min</td>
<td>4.30</td>
<td>4.59</td>
<td>1898</td>
<td>0.0087</td>
</tr>
<tr>
<td>Annealed 24 Hours</td>
<td>1.31</td>
<td>4.62</td>
<td>1898</td>
<td>0.0088</td>
</tr>
<tr>
<td>1.0% Graphene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As Cast</td>
<td>6.06</td>
<td>3.83</td>
<td>1404</td>
<td>0.0053</td>
</tr>
<tr>
<td>Annealed 15 Min</td>
<td>2.35</td>
<td>4.03</td>
<td>1404</td>
<td>0.0057</td>
</tr>
<tr>
<td>Annealed 24 Hours</td>
<td>2.56</td>
<td>3.83</td>
<td>1404</td>
<td>0.0054</td>
</tr>
<tr>
<td>1.0% NP1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As Cast</td>
<td>6.61</td>
<td>4.34</td>
<td>1720</td>
<td>0.0074</td>
</tr>
<tr>
<td>Annealed 15 Min</td>
<td>4.35</td>
<td>4.35</td>
<td>1720</td>
<td>0.0075</td>
</tr>
<tr>
<td>Annealed 24 Hours</td>
<td>4.45</td>
<td>4.45</td>
<td>1720</td>
<td>0.0077</td>
</tr>
<tr>
<td>1.0% NP2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As Cast</td>
<td>4.95</td>
<td>5.05</td>
<td>1882</td>
<td>0.0094</td>
</tr>
<tr>
<td>Annealed 15 Min</td>
<td>5.01</td>
<td>4.91</td>
<td>1882</td>
<td>0.0094</td>
</tr>
<tr>
<td>Annealed 24 Hours</td>
<td>3.92</td>
<td>4.86</td>
<td>1882</td>
<td>0.0092</td>
</tr>
<tr>
<td>1.0% SWNT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As Cast</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Annealed 15 Min</td>
<td>8.07</td>
<td>4.50</td>
<td>1439</td>
<td>0.0065</td>
</tr>
<tr>
<td>Annealed 30 Min</td>
<td>7.43</td>
<td>4.32</td>
<td>1439</td>
<td>0.0062</td>
</tr>
</tbody>
</table>
3.6 Experimental Results

The results of the analysis described above provide a depth profile of the deuterated polystyrene in each bilayer as a function of annealing time. The further analysis of these concentration profiles provides insight into the role of the nanoparticle presence on the interdiffusion of the protonated and deuterated polymers as the bilayers mix, as well as, its impact on the ultimate segregation of dPS to the surface. The segregation of the dPS chains to the air surface is quantified by the excess dPS at the surface, $Z^*$. $Z^*$ is determined by integrating $\Phi_{\text{dPS}}(z) - \Phi_{\text{dPS}}^{\text{bulk}}$ over the film thickness, $z$. $\Phi_{\text{dPS}}(z)$ is the experimentally determined dPS volume fraction at depth $z$, and $\Phi_{\text{dPS}}^{\text{bulk}}$ is the dPS volume fraction in the bulk, far from the air surface.

The interdiffusion of the dPS and pPS during the annealing process is correlated to the change in the interfacial width between the top and bottom layer after 15 minutes of annealing time. The interfacial width between the dPS rich top layer and pPS rich bottom layer is quantified by fitting the dPS concentration profile to a hyperbolic tangent function (41-43). A typical fit of the concentration profile to the hyperbolic tangent function is shown in Figure 3.3 for the dPS/pPS bilayer.

Assuming Fickian diffusion of the polymer chains, the time needed for a polymer chain to diffuse the thickness of the film can be readily estimated.(44) Using literature values for the diffusion coefficient of polystyrene chains with $M_w \sim 50,000$ (39,45-48) the polymer chain will traverse the film (~1600 Å) in 25 minutes. Thus, the samples measured at 15 minutes will document the transient structure of the inter-diffusion process, while the sample that is annealed 24 hours has had adequate time to reach equilibrium. Please note that in Appendix 3A, graphs of the reflectivity as a function of $Q$, SLD profiles, and $Z^*$ for each of the bilayers are presented as supplementary information, as well as a table of common SLD values.
Figure 3.3: Typical fit of the biphasic interface density profile to a hyperbolic tangent. This fit provides a measure of the width of the interface, and is presented for the unmodified dPS/pPS bilayer.
A. Unmodified dPS/pPS Bilayer

In the unmodified dPS/pPS bilayer, a three-layer model was used to fit the data, where the dPS volume fraction profile is shown in Figure 3.4. For the samples prepared in this work, the as-cast samples were not subjected to any heating or vacuum procedure to insure no chain motion occurs before the original density profile is measured, which is contrary to many previously described procedures (39,45,46) that often subject bilayers to modest heating and vacuum to remove excess water and contaminants prior to initial reflectivity measurement. Because of this, the procedure used here results in a small layer of water between the two polymer layers that remains from the floating procedure. To verify that this layer is indeed water, an additional bilayer was prepared using a mixture of nanopure water and deuterated water during float coating, at a ratio of 4 to 1. The SLD of the middle layer in this sample matched that of the D₂O/H₂O mixture, 4.35E-06Å⁻², confirming the presence of a small water layer in the as-cast bilayers. The water layer was expelled from all of the samples after heating to 150 °C for 15 minutes, as expected.

The unmodified dPS/pPS bilayer that is annealed at 150 °C for 15 minutes exhibited an increase in the SLD of the bottom layer and a decrease in the SLD of the top layer, indicating the inter-diffusion of the two polymers. A decrease in surface roughness (from ~31 Å in the as-cast to 25 Å) also occurred, and this was expected to occur with annealing above the glass transition temperature, since the polymer chains are able to relax, resulting in a closer packing of the molecules (47). At this stage, the polymer at the air surface is 87% dPS, which is related to the selective segregation of dPS to the air surface (5, 15). The interfacial width between the top and bottom layer is 10.8 nm at this stage, while Z* is 6.6 nm.
Further annealing of the sample for 24 hr at 150 °C results in a further reduction of the SLD of the top layer due to the introduction of more pPS chains into this layer. Both $Z^*$ and the interfacial width between layers were also reduced from their values at 15 minutes annealing, to 2.1 and 6.5 nm, respectively, with an excess of 12% dPS segregated to the air surface at equilibrium.

The excess dPS at the air surface at 24 hours of annealing closely reflects the results of Hong, et al. Hong studied bilayers of dPS/pPS to determine the effect of molecular weight on the segregation behavior of dPS. When a bilayer containing 1,950,000g/mol PS was annealed for 24 hours, an excess of 15% dPS remained on the surface. For a 70K PS bilayer, an excess of 10% dPS remained on the surface at 24 hours (19). Annealing for times greater than 24 hours resulted in null changes to their data, indicating that equilibrium was established for these systems.
Figure 3.4: Volume Fraction Profiles of dPS for the dPS/pPS Bilayer at various annealing times
B. Bilayers with 1% Graphene

The bilayer that contains 1.0% graphene consists of 48% dPS, based on the reflectivity determined thicknesses of the two layers in the as-cast sample. The surface roughness of this bilayer increased significantly (to ~ 672 Å) as well, due to the presence of the large graphene sheets. This is shown in Figure 3.5, which shows optical images comparing the surface roughness of the 1.0% SWNT thin film to the unmodified bilayer, and surface roughness is also shown in the as-cast SLD profile.

After 15 minutes of heating, the diffusion of the pPS chains into the dPS layer reduces the SLD of the top layer. However, this analysis indicates that the composition of this layer is still 97% dPS/3% pPS, whereas the unmodified bilayer had intermixed 13% pPS into the top layer for the same annealing procedure. The volume fraction profile of dPS in this bilayer at various annealing times is shown in Figure 3.6, which is analyzed to show that Z* is also larger (~ 204 Å) than that of the unmodified bilayer after 15 minutes of annealing at 150 °C. The increase in Z* combined with the decreased amount of pPS in the top layer clearly indicates that the diffusion of the pPS is slowed significantly by the presence of the graphene sheets. In fact, the diffusion was the slowest of all of the bilayers studied in this work, with Z* three times larger than in the unmodified system. Annealing the sample at 150 °C for 24 hours forms a single layer with an excess amount of dPS at the surface. This results in an increase in Φ_{dPS} to 63% at the surface and a surface excess, Z*, of 30 Å.

In order to better understand this behavior, the depth profile of a 1% graphene pPS nanocomposite thin film that was annealed for 24 hours at 150 °C was also determined using reflectivity. The scattering length density profile of this sample is given in Figure 3.7, which
shows that the air surface of this monolayer is pure protonated polystyrene, and that the graphene sheets are segregated to the silicon surface.
Figure 3.5: Optical images of the a) unmodified bilayer; b) 1.0% SWNT bilayer; c) 1.0% SWNT SLD Profile showing increased surface roughness
Figure 3.6: Volume Fraction Profiles of dPS for the 1.0% Graphene bilayer at various annealing times
Figure 3.7: Scattering Length Density Profile for the pPS Monolayer Containing 1.0% Graphene
C. Nancomposite Bilayers with 1% Nanoparticle #1 (NP1)

The bilayer that contains 1.0% nanoparticle #1 (NP1) is 59 vol% dPS. The composition at the air surface is 75 vol% dPS after annealing at 150 °C for 15 minutes, as seen in Figure 3.8. This, again, indicates that the diffusion of the pPS into the top layer alters the density profile of the initial bilayer in those 15 minutes. At this time, the surface excess of dPS is 125 Å, nearly twice that of the unmodified bilayer. This indicates that the interdiffusion of the dPS and pPS chains is slowed by the presence of the soft nanoparticles, but not as much as the graphene slows the mixing process.

Interestingly, the NP1 sample that has been annealed for 24 hours at 150 °C shows a much lower dPS interfacial excess, Z*, interfacial width, and excess dPS at the air surface. To quantify these values, the dPS vol% at the air surface is 63%, which correlates to a minimal excess of 4 vol% over the bulk dPS volume fraction. The interfacial width between the surface layer and bulk layer is also small, 18.5 Å, while the interfacial excess Z* is 11.19 Å. These results can be understood to indicate that the soft nanoparticle displaces the dPS at the air surface, presumably due to the entropic driving force of sequestering the many chain ends of this nanoparticle to the surface.

This interpretation is verified by monitoring the depth profile of a monolayer that is composed of dPS and 1.0% NP1 after annealing for 24 hours at 150 °C. This depth profile clearly indicates that the equilibrium structure of this sample consists of a layer of NP1 (5 Å deep) at the air interface, below which is a homogeneous layer of NP1 and dPS. Thus, the entropic driving force that pushes the branched soft nanoparticles to the surface dominates the lower surface energy of the dPS in defining the surface segregation in this thin film nanocomposite.
Figure 3.8: dPS Volume Fraction Profiles for the 1.0% NP1 bilayer at various annealing times
Dynamic light scattering and multi-angle laser light scattering characterize this soft nanoparticle, NP1 as a spherically shaped, but highly branched molecule with $M_w = 2.19 \times 10^6$ g/mol. The depth profile studies show that the spherical shape and high molecular weight slows the inter-diffusion of the polymer chains. After 15 minutes of annealing, the results indicate that chain mixing was slowed by the introduction of NP1. At 24 hours of annealing, the bilayer and monolayer results clearly show that the NP1 nanoparticles selectively segregate to the air interface, displacing dPS.

D. Bilayer containing 1% Nanoparticle #2 (NP2)

Qualitatively, the introduction of the more crosslinked nanoparticles, NP2, modifies the diffusion and surface segregation behavior of the dPS similarly to the introduction of NP1; the intermixing is slowed, and the branched nanoparticle segregates to the surface, partially displacing the dPS.

A more quantitative analysis shows that the dPS volume fraction of this bilayer is 73.0%, as shown in Figure 3.9. After 15 minutes of annealing at 150 °C, the thin film has an interfacial excess of dPS, $Z^*$, that is larger than that of the unmodified bilayer, 163 Å vs. 66 Å. The volume fraction of dPS at the air surface is 95%, which is also higher than in the unmodified system, and clearly indicates that the introduction of the branched, spherical NP2 particles also slows the polymer chain inter-diffusion. Comparison of the $Z^*$ and amount of dPS at the air interface after 15 minutes of annealing time to that of the very similar NP1 particle further indicates that the diffusion of the free polymer chains is slowed more by the NP2 nanoparticle than the NP1 nanoparticle.
At equilibrium after annealing at 150 °C for 24 hr, the interfacial width, $Z^*$, and excess dPS at the surface are all smaller than in the unmodified system. The dPS volume fraction in the top layer is 73%, which corresponds to a surface excess of dPS of only 0.4%. This clearly demonstrates that the soft nanoparticle, NP2 displaces the dPS from the surface, as the NP1 nanoparticle does. The interfacial width between the surface segregated and bulk layers is 52Å, with an interfacial excess $Z^*$ of 15Å. These values are smaller than those of the unmodified bilayer, verifying that at equilibrium there is less dPS surface excess as a result of the selective segregation of the soft nanoparticle at the air surface. When compared to NP1, there was only 0.4% dPS surface excess in the NP2 bilayer, verses 4.0% excess in the NP1 sample. This suggests that more NP2 particles were segregating to the surface than in the NP1 system.

Since NP2 is composed of more DVB (8.20% verses 2.0% in NP1) and has a smaller $R_g/R_h$ ratio, NP2 has more crosslinking and more chain ends than NP1. The effect of chain branching is even greater with this nanoparticle, which is also entropically driven to the air surface. More NP2 is present at the air surface than in the NP1 system due to increased number of chain ends, which lowers the free energy of the system.
Figure 3.9: dPS Volume Fraction Profiles for the 1.0% NP2 bilayer for various annealing times
E. Bilayers Containing 1% SWNTs

The evolution in structure of the dPS/pPS bilayers that contain single walled carbon nanotubes (SWNTs) underwent a slightly different thermal annealing procedures in that the samples were measured after 15 min and 30 min annealing time at 150 °C. Thus, the “long time” behavior of these materials is not equivalent to that of all other samples and thus cannot be directly compared. Nonetheless, the acquired data provides some insight into the impact of the presence of the SWNT on the inter-diffusion of the polymer chains during annealing.

The film thicknesses of the two layers in the original bilayer were measured with ellipsometry, indicating a top dPS layer of 866 Å and the bottom pPS layer that is 532 Å thick. This results in a bilayer that is 1398 Å and 62 vol% dPS. After annealing the sample for 15 minutes at 150 °C, the composition at the air surface is 99% dPS, with a calculated Z* of 183 Å (Figure 3.10). This Z* is almost 3 times that of the unmodified dPS/pPS bilayer, which combined with the volume fraction of dPS at the surface, indicates that the presence of the SWNTs have dramatically slowed the diffusion of the dPS and pPS chains.

The sample was then annealed for an additional 15 minutes, for an overall annealing time of 30 minutes. At 30 minutes, the SLD of the top layer was further reduced from the diffusion of pPS chains, with a measured Z* of 77Å and has a volume fraction of 92% dPS at the air surface. This data clearly shows that the SWNTs do not remain at the air surface, but remain in the bottom layer. SWNTs are essentially rolled up sheets of graphene, and this chemical similarity manifests itself in the SWNT as a high surface energy, similar to that of the graphene. This high surface energy therefore is a dominant driving force to create a thin film with a large excess of dPS at the air surface in the annealed bilayer. Presumably the SWNTs segregate to the silicon surface, displacing the PS chains there as the graphene does (49-51).
**Figure 3.10:** dPS Volume Fraction Profiles for the 1.0% SWNT Bilayer at various annealing times
3.7 Discussion

The data presented above provides an abundance of information that documents the impact of adding a nanoparticle on the diffusive properties of neighboring polymer chains as well as its role in defining the surface structure of a polymer nanocomposite. The experimental protocol used exploits the interdiffusion of polystyrene and deuterated polystyrene across a biphasic interface in the intermixing that occurs during the thermal annealing of a dPS/pPS bilayer. The amount of protonated polystyrene in the deuterated polystyrene layer after 15 minutes of annealing at 150 °C serves as a marker for the rate of diffusion of the protonated polymer chains into the deuterated layer, where the behavior of pPS in polymer nanocomposites is compared to its behavior in the absence of nanoparticles. These results are summarized in Figure 3.11, which clearly shows that the amount of dPS in the top layer is much large in the nanocomposite samples, indicating that the presence of the nanoparticles slows the diffusion of the protonated polystyrene into the dPS layer in all cases.

A more careful analysis of the data clearly shows that the graphene and SWNT slow the polymer diffusion more than the two soft nanoparticles, in that these two samples have the largest dPS Z* of the four nanocomposite samples. This is not surprising in that the graphene sheet and SWNT cylinder are much larger and anisotropic objects than the soft nanoparticles. The graphene sheet is a few nm in thickness, but extend (at least) many 100’s of nm in the other two dimensions, while the SWNT has a diameter that is ~ 1nm, but are many 100’s of nanometer long. Clearly this anisotropy impacts the diffusion of the polymer chains, significantly slowing the polymer motion. This has been observed in previous work that examined the diffusion of polystyrene in SWNT nanocomposites, where the diffusion of the polymer chain decreases with added wt% SWNT up to critical value, which is correlated to the inhibition of chain motion.
perpendicular to the randomly oriented SWNTs (55-56). The diffusion coefficient of the polymer chain then increases again with the addition of further SWNT, which is attributed to the formation of a percolated network that allows the diffusion of the chain along the length of the SWNT cylinder (55-56). A similar picture can be invoked to explain the results reported here, the presence of a single walled nanotube limits the polymer chain motion due to excluded volume effects, requiring the polymer chain to meander around the tube to diffuse past it.

Similarly, the graphene sheet provides a significant roadblock to the diffusive motion of the polymer chain, requiring the molecule to detour around the sheet in order to move forward. The two-dimensional graphene sheet creates a larger blockade area than the one-dimensional SWNT, which manifests itself as an increased slowing of the polymer chain in the graphene sheet nanocomposite when compared to its motion in a SWNT nanocomposite. In both cases, the aromatic carbon based structure of the nanoparticle also provides an opportunity to form non-covalent $\pi-\pi$ interactions with the polystyrene chain that can further slow the polymer chain diffusion.

The impact of the polymer soft nanoparticles is also interesting, in that these particles also significantly slow the diffusion of the polystyrene diffusion, though not as much as the graphene or SWNT. This result is not as obvious, in that these particles are very similar in size and structure to the polymer chains themselves, and therefore might not significantly impact the polymer diffusive motion. These nanoparticles are only about twice the radius of gyration of the linear polymer chain, and thus their presence at 1% loading does not obviously provide extensive excluded volume restrictions to the motion of the linear polymer chain.
**Figure 3.11:** Interfacial excess of dPS, $Z^*$, for all samples after annealing for 15 min at 150 °C.
The fact that the polystyrene diffusion is significantly slowed by the presence of the soft nanoparticles implies that the polystyrene chains are able to entangle with these polymer nanoparticles, slowing the diffusive motion of the linear chains. Both particles are lightly cross-linked, which evidently provides a nanoparticle structure that is sufficiently open to allow the penetration of the linear polymer chain into the “nanogel”.

The depth profiles of the samples after 24 hr annealing provides information on the impact of the presence of the nanoparticle on the selective surface segregation of dPS to the air surface. The samples that are annealed for 24 hr have reached equilibrium, where samples are deemed to have reached equilibrium when the volume fraction of dPS in the annealed bottom layer (i.e. ‘bulk’) approaches the volume fraction of dPS in the initial bilayer. For instance, in the unmodified system, the initial bilayer consists of 61% dPS, and after 24 hours of annealing, the composition of the bottom layer is ~ 60% dPS. Similar correspondence is found for all samples that have been annealed for 24 hr, indicating that they have all reached equilibrium. In these samples, the surface segregation of dPS to the air surface was also affected by the introduction of the nanoparticles, where this is quantified by both the concentration of dPS at the air surface as well as the equilibrium $Z^*$ (Figure 3.12 and Table 3.3).

The presence of the graphene sheets results in an increase in the amount of dPS at the surface and interfacial excess. This is the result of the sequestration of the graphene to the silicon surface, due to the higher surface energy of the graphene (49-51). The SWNT exhibits a similar response, showing a dramatic increase in the amount of dPS at the air surface. Clearly, the similar chemical structure of SWNT and graphene provides similar driving forces for the development of the depth profile and surface excess in these two thin films.
Table 3.3: dPS concentration at the air interface that is excess to that of the bulk at equilibrium

<table>
<thead>
<tr>
<th>Bilayer</th>
<th>Equilibrium Excess dPS at the Air Interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified dPS/pPS</td>
<td>12%</td>
</tr>
<tr>
<td>1.0% Graphene Bilayer</td>
<td>15%</td>
</tr>
<tr>
<td>1.0% NP1 Bilayer</td>
<td>4.0%</td>
</tr>
<tr>
<td>1.0% NP2 Bilayer</td>
<td>0.4%</td>
</tr>
</tbody>
</table>
Figure 3.12: $Z^*$ and dPS concentration at the air interface that is excess of the bulk concentration at equilibrium
The presence of the soft nanoparticles had the opposite effect on the composition of the near surface layer in these nanocomposite thin films. In both the NP1 and NP2 films, the amount of dPS at the surface is significantly less than in the unmodified film. For instance, the volume fraction of dPS at the air interface is 4% more than the bulk composition for the NP1 sample, down from 12% in the unmodified dPS/pPS mixture. The sample containing NP2 provides a more dramatic response, where this film has a surface at the air interface that is essentially equal to the bulk composition, thus no (~ 0.4%) excess dPS.

The neutron reflectivity of the monolayer with NP1 clearly shows that these highly branched particles selectively segregate to the surface. This selective segregation is due to the branched structure of the NP1 nanoparticle, where the chain ends of the soft nanoparticle are entropically driven to the air surface (52-54). When comparing the behavior of the two soft nanoparticles, the extent of branching within the soft nanoparticle appears to be the factor that controls the surface segregation process. The NP2 particles consist of more cross-links and therefore contains more chain ends. This excess amount of chain ends provides a stronger driving force for this segregation to the air surface relative to that of the less cross-linked NP1 nanoparticle. This manifests itself in the development of a near surface composition of the NP2 samples that is very near that of the bulk, while the thin film containing the NP1 nanoparticle retains an excess amount of dPS at the air surface. The entropic driving force to sequester the NP1 nanoparticle to the surface is not sufficient to displace all of the dPS at the surface, however this same entropic force is essentially equal to the enthalpic driving force that drives the deuterated polymer chains to the surface for the NP2 nanoparticles.

Thus, the results presented here clearly show that the change in the surface segregation behavior of the polymers in the presence of the carbon nanoparticles are enthalpically driven,
dominated by the relative surface energies of the components. However, the near surface structure in the nanocomposite that contains the soft nanoparticles is dominated by entropy and its precise structure is determined by the competition between the entropy of the branched nanoparticle and the relative surface energies of the components.

3.8 Conclusions

This work was undertaken to demonstrate that the size and shape of introduced nanoparticles impacts the segregation and diffusion behavior of dPS chains in a pPS matrix and to quantify that behavior. The results presented here provide information on the diffusion of polymer chains as well as on the equilibrium surface structure that develops in polymer nanocomposites by monitoring the excess dPS at the surface, \( Z^* \). The amount of protonated polystyrene that diffuses into a deuterated polystyrene layer in 15 minutes is also tracked to qualitatively characterize the rate of diffusion. This analysis shows that the presence of all nanoparticles slows the inter-diffusion of the polymers, regardless of size, shape, or rigidity. Among the nanoparticles tested here, the results show that the introduction of the larger, anisotropic particles, graphene and SWNTs, slowed polymer diffusion the most, which is ascribed to excluded volume effects. The bilayer, which contained 1.0% graphene, for instance, had \( Z^* \) three times that of the unmodified system at 15 minutes of annealing. The smaller, spherical nanoparticles also significantly inhibited polymer diffusion, but to a lesser extent (\( Z^* \) was 2 times larger for the 1.0% NP1 bilayer and 2.5 times larger for the 1.0% NP2 bilayer when compared to the unmodified system at 15 min annealing).

The amount of deuterated polystyrene at the air surface after annealing for 24 hours is analyzed to provide information on the impact of the nanoparticle on the equilibrium surface
structure of a polymer nanocomposite. These results show that the higher surface energy of graphene drives the equilibrium structure of the thin film, segregating it to the silicon surface and increasing the amount of dPS at the air surface. In contrast, comparison of surface energies of the components indicates that entropic forces drive the soft nanoparticles to the air surface, due to their highly branched structures. The fact that more NP2 nanoparticle segregates to the air surface is consistent with this interpretation, since NP2 has more chain ends. An increase number of chain ends correlates to a stronger entropic driving force, which results in a higher concentration of the nanoparticle at the air surface.

Therefore, these results advocate the hypothesis that the primary impact of nanoparticle size on the surface segregation in polymer nanocomposites is that smaller nanoparticles will tend to be driven to the air surface for entropic reasons, while the distribution of larger nanoparticles near the air surface is dominated by the competition of the surface energies of the various components in a polymer nanocomposite.
3.9 References


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Chapter 3 Appendix 3A: Reflectivity Data, SLD Profiles, and Z*
Supplementary Table A3.1: Scattering Length Density (SLD) of the materials used in this study

<table>
<thead>
<tr>
<th>Material</th>
<th>SLD (Å(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>pPS</td>
<td>1.41E-06</td>
</tr>
<tr>
<td>dPS</td>
<td>6.41E-06</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>-5.6E-07</td>
</tr>
<tr>
<td>D(_2)O</td>
<td>6.34E-06</td>
</tr>
<tr>
<td>Silicon</td>
<td>2.07E-06</td>
</tr>
</tbody>
</table>
Supplementary Figure A3.1: Experimental Reflectivity as a function of Q and fit for the dPS/pPS Bilayer prepared using a mixture of D₂O and H₂O.
Supplementary Figure A3.2: Log Reflectivity verses Q for the unmodified dPS/pPS Bilayer at various annealing times
Supplementary Figure A3.3: Scattering Length Density Profiles for the unmodified dPS/pPS Bilayer at various annealing times
Supplementary Figure A3.4: Z* Calculations for the unmodified dPS/pPS Bilayer at a) 15 min annealed; b) 24 hours annealed
Supplementary Figure A3.5: Log Reflectivity verses Q for the 1.0% Graphene Bilayer
Supplementary Figure A3.6: Scattering Length Density Profiles for the 1.0% Graphene Bilayer at various annealing times
**Supplementary Figure A3.7:** $Z^*$ Calculations for the 1.0% Graphene Bilayer at a) 15 min annealed; b) 24 hours annealed
**Supplementary Figure A3.8:** Log Reflectivity verses Q for the 1.0% NP1 Bilayer at various annealing times
Supplementary Figure A3.9: Scattering Length Density Profiles for the 1.0% NP1 Bilayer at various annealing times
Supplementary Figure A3.10: Z* Calculations for the 1.0% NP1 Bilayer at various annealing times
Supplementary Figure A3.11: Log Reflectivity verses Q for the 1.0% NP2 Bilayer at various annealing times
Supplementary Figure A3.12: Scattering Length Density Profiles for the 1.0% NP2 Bilayer at various annealing times
Supplementary Figure A3.13: $Z^\ast$ Calculations for the 1.0% NP2 Bilayer at various annealing times
Supplementary Figure A3.14: Log Reflectivity verses Q for the 1.0% SWNT Bilayer at various annealing times
Supplementary Figure A3.15: Scattering Length Density Profiles for the 1.0% SWNT Bilayer at various annealing times
Supplementary Figure A3.16: Z* Calculations for the 1.0% SWNT Bilayer at various annealing times
Chapter 4

Quantifying the Thermodynamic Interactions in Polyhedral Borane Solutions with Static Light Scattering and Refractometry
4.1 Abstract

A protocol is presented to quantitatively determine the solubility of boron containing nanoparticles in a variety of solvents using static light scattering in conjunction with refractometry. Four polyhedral borane compounds were tested in this work, using refractometry to obtain dn/dc, while static light scattering quantifies $A_2$. $A_2$ obtained from these measurements was then used to calculate $\chi$, the solute-solvent interaction parameter, and the Hildebrand Solubility Parameter, $\delta$, which provides a quantifiable method to identify good solvents. Of the nanoparticles studied, 1,3-di-o-carboranylpropane is thermodynamically stable in toluene, with a $\chi$ less than 0.5, a solubility limit of 2.47 mg/mL, and all solutions remaining clear with no visible particle settling. For all of the particles tested, there was good correlation between the physical observations of the solutions, $\chi$, and $\delta$. For instance, lower values of $\chi$ correspond to a smaller radius of gyration ($R_g$). A list of suitable solvents based on $\delta$ is also presented.
4.2 Introduction

In order to develop novel materials using nanoparticles, their dispersion and dissolution behavior must be understood. This is because an important goal of material design is to produce homogenous dispersions of nanoparticles embedded in polymer matrices (1-2); such dispersions are needed to take full advantage of the unique properties inherent to the nanoparticles. One issue that has prevented this goal from being accomplished is aggregation of the nanoparticles in solution prior to nanocomposite fabrication and in the ultimate nanocomposite. In the case of SWNTs, for example, the nanotubes clump together due to strong interparticle van der waals forces, making it difficult to produce homogenous dispersions (3-4). Energetically favorable solvents may overcome the forces that clump nanoparticles together and allow well-dispersed solutions of nanoparticles to be produced (5-6). Once dispersed, a common method for preparing nanocomposite materials involves mixing the nanoparticle solutions with a polymer and then evaporating the solvent or precipitating into a non-solvent. Song, et al, for instance, studied the effect of dispersion on composite properties and found that epoxy nanocomposites with homogenously embedded multi-walled carbon nanotubes (MWNTs), made by sonicating the nanotubes in ethanol to improve dispersion, had higher electrical and thermal conductivity than composites embedded with poorly dispersed nanotubes (7).

The incorporation of carboranes in polymer matrices offers a variety of new materials with novel properties. Carboranes are a class of polyhedral boranes and are polyhedra clusters composed of boron and carbon atoms. The most widely studied is o-carborane (C_{2}B_{10}H_{12}), which has been explored for a wide range of applications including heat-resistant polymers and neutron capture (8-9). Of all of the applications, therapeutic medicine has garnered the most attention. The thermal and chemical stability and low toxicity of carboranes makes them ideal
candidates for drug delivery and for the delivery of boron isotopes to target cells for the
treatment of tumors. Carboranes also readily undergo electrophilic aromatic substitution to
attach functional groups that may be designed specifically for diagnostic imaging or therapy
(10). An understanding of the solubility behavior of boron containing particles is needed to
rationally develop protocols for the fabrication of polymer-borane nanocomposites with targeted
dispersion and properties. The aim of this work, therefore, is to quantitatively determine the
solubility of boron containing nanoparticles and boron cage compounds in a variety of solvents,
and to understand the benefits and limitations of the resultant experimental protocol.

In the past UV-Vis spectroscopy has been the method of choice to measure the solubility
behavior of nanoparticle-solvent systems (11-17). With this method, it is possible to quantify the
solubility limit, i.e. the maximum concentration dissolved that is free of agglomeration. Carbon
nanotubes, graphene, and POSS (polyhedral oligomeric silsesquioxane) have all been studied in
this manner using this technique (11-17). In this experiment, nanoparticle solutions are prepared
by sonication, and the UV-Vis absorbance is plotted as a function of nanoparticle concentration.
The extinction coefficient is determined from the slope of the line and then used to calculate the
unknown concentration of saturated solutions (13). The solubility limit is then determined by
monitoring the amount of dissolved nanoparticle in centrifuged solutions as a function of
nanoparticle concentration. Similarly, high pressure liquid chromatography (HPLC) may also be
used to determine the concentrations of centrifuged samples with the establishment of a baseline
(18-19).

UV-Vis also can be analyzed to determine the Hildebrand Solubility Parameter, \( \delta \), of a
solute, which can identify potential solvents with similar \( \delta \) values (10,19-22). For instance, in a
study by Hernandez, et al, the dispersibility of graphene was measured in 40 solvents using UV-
Vis (21). Cyclopentanone, 1,3-dimethyl-2-imidazolidone, and N-ethyl-2-pyrrolidone showed the best dispersions, with 8.5, 5.2 and 4.0 µg/mL solubilities, respectively. The solubility limits are graphed as a function of the solvent’s δ, showing that good solvents for graphene have δ ~23 MPa^{1/2}. Cyclopentanone, which had the highest solubility limit, for instance, has a δ in good agreement, 21.3MPa^{1/2}. Acetylpyrrolidone, butyl alcohol, and cyclohexanol were suggested solvents based on this work. A similar study by Rouff, et al, used HPLC to study graphene in 47 different solvents, where a δ of ~20.45 MPa^{1/2} was determined for graphene, which corresponds well to the findings from Hernandez’s study (19).

Additionally, static light scattering is a valuable tool to quantify the thermodynamic behavior of particle solutions. Light scattering provides insight into the solute’s size, shape and molecular weight. The second virial coefficient, $A_2$, a thermodynamic property that quantifies the interaction strength between a solute and solvent, is also determined from light scattering (Chapter 2). $A_2$ depends on the temperature and pressure of the solution and on the molar mass of the solute. The interactions between a solute and solvent are favorable when $A_2 > 0$ and aggregation or precipitation occurs as $A_2 < 0$. Once $A_2$ is determined it can be correlated to the solute-solvent interaction parameter, $\chi$, which describes the interaction of a particle or polymer with a solvent (5-6). This approach is also valuable since $\chi$ can be used to determine δ of the particle.

From the Flory-Huggins solution theory, $\chi$ is related to the intermolecular interactions between the solute and solvent by Equation 4.1, where k is the Boltzman constant, z is the coordination number, and $\Delta w$ describes the molecular interactions between solute and solvent (22).

$$\chi = z\Delta w / kT \quad (4.1)$$
The coordination number describes the number of nearest neighbors between solute and a solvent molecule. The strength of the molecular interactions is described by $\Delta w$, which takes into account the solvent-solvent, monomer-monomer, and solvent-monomer interaction energies (19-20).

The value of $\chi$ provides a measure of the enthalpic interactions between components in a mixture. For instance, if $\chi = 0.5$ the solvent is a theta solvent, the transition between a good solvent and a bad solvent where $A_2 = 0$. In a theta solvent, there are no excluded volume effects, the molecular dimension of a polymer are unperturbed by interactions (ie: steric effects) (24). Good solvents have $\chi$ values less than 0.5, where the interactions between the particles or segments of a polymer chain with the solvent are energetically favorable. For polymer molecules, the coils will expand in a good solvent, and nanoparticles will remain dispersed. Poor solvents, however, have $\chi$ values greater than 0.5, where solute-solute interactions are preferred over solute-solvent interactions. Polymer coils will contract and nanoparticles will clump together and phase separate, since interactions between the particles and solvent molecules are not energetically favorable (22-23).

From static light scattering data, $\chi$ is determined from the experimentally measured $A_2$ using Equation 4.2. In this equation $A_2$ is the second virial coefficient, $V_s$ is the solvent molar volume, and $\rho$ is the density of the solute (i.e. nanoparticle or polymer) (22).

$$\chi = \frac{1}{2} - A_2 V_s \rho^2 \quad (4.2)$$

If $\chi$ is known for a given solute molecule in a range of solvents, the Hildebrand solubility parameter of the solute can be determined. By combining the Flory theory with the Hildebrand-Scatchard solution theory, Equation 4.3 relates the $\chi$ of a solution to the solubility parameters of the solvent and solute (25-26):
\[
\left( \delta_1^2/RT - \chi/V_1 \right) = (2\delta_2/RT)\delta_1 - (\delta_2^2/RT) \tag{4.3}
\]

In this equation, \(\delta_1\) is the Hildebrand solubility parameter of the solvent, which is tabulated for many solvents, and \(\delta_2\) represents the Hildebrand solubility parameter of the nanoparticle or polymer under study. A plot of \(\delta_1^2/RT - \chi/V_1\) as a function of \(\delta_1\) produces a straight line, with the slope of the line = \(2\delta_2/RT\). Thus, the unknown solubility parameter of the nanoparticle or polymer, \(\delta_2\), can be determined from this analysis (25-26).

Difficulties arise when using this approach to define the solubility of nanoparticles, however, since the refractive index increment, \(dn/dc\), is often not known for nanoparticle solutions. \(dn/dc\) is a necessary parameter for static light scattering measurements, since the optical constant, \(H\), is the ratio of refractive index increment to the wavelength of light (27-29). The basic light scattering equation that relates the scattered light intensity to the solution characteristics is presented in Equation 4.4, where \(R\) is the Rayleigh ratio, and is dependent on the intensity of scattered light, \(P_\theta\) is the form factor of the scattering particle, \(M_w\) is the molecular weight of the scattering particle, \(c\) is solution concentration, and \(H\) is the optical constant (Chapter 2) (30).

\[
Hc / R_\theta - R_{solvent} = 1/M_wP_\theta + 2A_2c \tag{4.4}
\]
dn/dc is often difficult to obtain since nanoparticles do not easily dissolve in common solvents, and most modern instrumentation require the injection of the sample with constant solvent flow through. SWNTs, for instance, clog the tubing due to their aggregation behavior, making measurements impossible.

In 2008, Bergin and co-workers attempted to circumvent this issue by testing several polymer solvent systems with known \(M_w\) and \(A_2\) in order to estimate the instrument constants for their scattering setup (5-6). In their experimental procedure, the instrument constant, \(H\), is
determined by rearranging Equation 4.4. In the rearranged equation, Equation 4.5, C is the concentration of the solute, S and S_0 are the scattering intensities of the solution and pure solvent measured at 90°, and H' and H'' are new instrument constants (5-6).

\[
\frac{C}{S-S_0} = \left(\frac{A_2}{H'}\right)C + \left(\frac{1}{M_w H''}\right) \quad (4.5)
\]

In this procedure, the scattering from multiple polymer solutions is measured and a graph of C/S-S_0 is plotted as a function of concentration. The instrument constants are then estimated from the slope and intercept of the resultant lines (5-6). The solubility behavior of SWNTs in pyrrolidone solvents was studied using these optical constants by measuring the scattering at 90° and using Equation 4.5 to calculate \(A_2\). For SWNTs in N-methyl pyrrolidone (NMP), a positive second virial coefficient was found, 1.78E10^{-3} m^3 · mol · kg^{-1}, and \(\chi\) was -0.074, which indicates that NMP is a thermodynamically favorable solvent (31). The authors also estimated the enthalpy of mixing, \(\Delta H_{mix}\), from their estimated \(\chi\) values using Equation 4.6 (5-6), where \(V_{mix}\) is the volume of mixing, \(R\) is the ideal gas constant, \(T\) is temperature, and \(\phi\) is the volume fraction of the nanoparticles.

\[
\frac{\Delta H_{mix}}{V_{mix}} = \chi \left(\frac{RT}{V_s}\right) \phi (1-\phi) \quad (4.6)
\]

The estimated enthalpy of mixing is -720 KJ/mol and was presented as further evidence of an energetically favorable mixing process.

This approach was promising, as boron containing particles also have unknown dn/dc and have a tendency to clump in solution. Therefore, this approach was tested by measuring the light scattering of several polymer solutions with known \(A_2\) and \(M_w\), and the instrument constants, H’ and H’’ of our lab, were estimated using Equation 4.5.

To further test the validity of this procedure, a Brice Phoenix refractometer, which does not require solvent flow, was used to measure the dn/dc of the polyhedral borane compounds.
solutions for the first time. Light scattering measurements were then carried out on diol carborane, dodecahydridodecaborate dipotassium salt, dodecahydridodecaborate dilithium salt, and tethered carborane in tetrahydrofuran (THF), toluene, and methyl ethyl ketone (MEK) (Figure 4.1). Zimm plots were produced from this data, where the optical constant, $H$, is determined \textit{a priori} and $A_2$ is determined from the slope of the line of the data where the scattering angle approaches zero using Equation 4.7.

<table>
<thead>
<tr>
<th>Diol Carborane</th>
<th>Tethered Carborane</th>
<th>Dilithium Salt</th>
</tr>
</thead>
</table>

![Figure 4.1: Structures of the Polyhedral Borane Compounds](image)
\[(H \, c/R\theta)_{\theta=0} = 1/M_w + 2 A_2 c + \ldots \quad (4.7)\]
\[(H \, c/R\theta)_{c=0} = 1/M_w [1+1/3(4\Pi/\lambda)^2 R_g^2 \sin^2\theta/2 + \ldots] \quad (4.8)\]

The radius of gyration, \(R_g\), of the scattering particle is also determined from the resulting Zimm plot using Equation 4.8 and is often used to quantify aggregation behavior of particle solutions (30).

When the solution is not dilute enough to prevent particle interactions (i.e.: not below the solubility limit of the solute in solution) or the size of a particle differs considerably from the wavelength of light, interference of wavelets may contribute to the scattering, and additional considerations are necessary to describe particle shape (Chapter 2; 32-36). These additional contributions to the scattering are difficult to quantify, due to multiple scattering effects, which may result in significant inaccuracies in the reported \(M_w\) and \(R_g\). For instance, in the case of particles that are much smaller than the wavelength of light (i.e: less than \(\sim 1/20 \lambda\)) work by Cabannes reports that the additional scattering from the particle’s surface results in experimentally determined \(M_w\) and \(R_g\) that are higher than expected (32,37). The boron cage compounds studied in this work have a diameter \(~ 1.0\) nm and differ markedly from the wavelength employed (\(\lambda = 685\) nm), which may affect \(R_g\). Also, for the case of non-dilute solutions, the presence of aggregates will dominate the scattering and also affect \(R_g\), since, according to the Rayleigh approximation, there is a strong particle size dependence on the scattering intensity, shown in Equation 4.9, where \(I\) is the scattering intensity and \(d\) is the particle diameter (38).

\[I \sim d^2 \quad (4.9)\]

In a sample with two particles sizes, for example, 1 nm and 10 nm, of equal number concentrations, the scattering intensity will be \(10^2\) times stronger for the 10 nm particle when
compared to the 1 nm particle, and the presence of even larger particles or aggregates will further increase this effect (32-33, 37-38). Light scattering of the nanoparticle-solutions in this work were carried out on the initially prepared concentrations, which were not below the determined solubility limits of the nanoparticles, increasing the risk of interference from particle aggregation and affecting the measured $R_g$.

A qualitative discussion regarding the aggregation behavior from the experimentally determined $M_w$ and $R_g$ is still possible though, when additional information regarding the samples is known (39-42). For example, the measurement of $R_g$ was important to decipher the thermodynamic behavior of PS nanocomposites prepared in toluene with 10 wt% polyhedral oligomeric silsesquioxane (POSS), that were studied by static light scattering. In this work, two POSS molecules were studied, octaisobutyl POSS (Oib-POSS) and trisilanophenyl POSS (Tsp-POSS), both with small radii $< \sim 1$nm (42). The $R_g$ reported from the light scattering measurements was larger for the Oib-POSS-PS nanocomposite relative to the unmodified PS. The authors interpreted this finding to indicate that aggregation was occurring in this system. In contrast, the $R_g$ of the Tsp-POSS blend was smaller than the unmodified PS. Supporting evidence collected with AFM and TEM indicated that Tsp-POSS had greater solubility in PS, and the smaller radius was the result of enhanced interactions of the TSP-POSS molecules with the PS chains (42).

$R_g$, therefore, offers another parameter to characterize the solubility behavior of particle solutions, and for all of the polyhedral borane solutions studied here, $R_g$ is determined. UV-Vis spectroscopy quantifies the solubility limits and physical observations provide a self-consistent check to the data obtained with light scattering. In order to calculate $\chi$ using Equation 4.2, an
accurate measure of the density of the nanoparticles is needed. Therefore, the densities of the nanoparticles were determined via gas pycnometry.

4.3 Experimental

A. Materials

The materials used in this work and detailed sample preparations are described in Chapter 2. For easy reference in this chapter, the abbreviations for the nanoparticles and pre-polymers used are listed in Table 4.1.

Table 4.1: Abbreviations for the nanoparticles examined in this chapter

<table>
<thead>
<tr>
<th>Particle Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-bis-(hydroxymethyl)-o-carborane (diol carborane, C_{16}H_{16}O_{2}B_{10})</td>
<td>DCB</td>
</tr>
<tr>
<td>dodecahydrododecaborate dipotassium salt (K_{2}[B_{12}H_{12}])</td>
<td>KBH</td>
</tr>
<tr>
<td>dodecahydrododecaborate dilithium salt (Li_{2}[B_{12}H_{12}])</td>
<td>LBH</td>
</tr>
<tr>
<td>1,3-di-o-carboranylpropane (tethered carborane, C_{28}H_{28}B_{20})</td>
<td>TCB</td>
</tr>
</tbody>
</table>
B. Statistical Analysis

The $A_2$ reported in this work is the mean value obtained with static light scattering, which has some uncertainty that is quantified by its standard deviation. It is important to propagate this standard deviation through subsequent calculations. Two data points are plotted to determine the nanoparticle’s δ from the slope of the Hildebrand-Scatchard plots, as presented in Equation 4.3. To further illustrate this relationship, this equation is again presented, showing the linear relationship, Equation 4.10 and 4.11

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1}\right) = (2\frac{\delta_2}{RT})\delta_1 - (\frac{\delta_2^2}{RT}) \quad (4.10)$$

$$Y = mX + b \quad (4.11)$$

A sample calculation illustrating the propagation of error in the determination of $\chi$ for KBH is presented in Table 4.2. $\chi$ is calculated from the $A_2$ values of KBH in THF and KBH in toluene. The absolute error in $A_2$ is propagated through these calculations, resulting in corresponding uncertainty in the determination of $\chi$.

In the Hildebrand-Scatchard linear relationship, the slope of the fitted line is utilized to determine δ and is simply $\Delta Y / \Delta X$ for the two data points, where X is the solvent’s δ, and Y = $\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1}\right)$. In this calculation, $\frac{\delta_1^2}{RT}$ is a constant as previously described in Equation 4.3. Any error in the Y value is, therefore, only propagated through the term that contains $\chi \left(-\frac{\chi}{V_1}\right)$, where $V_1$ is also a constant. It is important to note that when multiplying or dividing a value that contains error by a constant, the relative error is also simply divided or multiplied by that constant, since both the error and value are affected by the same factor (22). For KBH in THF and toluene, the resulting Y values $\left(-\frac{\chi}{V_1}\right)$ and their absolute error as determined using
Equation 4.10 are reported in Table 4.3. It is important to point out that error in the Y values is minimal; yet, the error present gives rise to uncertainty in the slope, which in turn affects the nanoparticle’s $\delta$. For example, the resulting slope for KBH is $0.0306 \pm 0.0002$ mol/(cal mL)$^{1/2}$. The slope $= 2\delta_2/RT$, where $\delta_2$ is the nanoparticles $\delta$. For KBH, $\delta = 9.059 \pm 0.0504$ (cal/cm$^3$)$^{1/2}$.

Absolute error is presented for all nanoparticle’s $\delta$ in the results section in Table 4.10, and in all cases, the error is $< 0.900$ (cal/cm$^3$)$^{1/2}$.

Table 4.2: Propagation of Error in the Calculation $\chi$ for KBH in THF and Toluene

<table>
<thead>
<tr>
<th>KBH</th>
<th>$A_2 \pm \Delta A_2$ mol mL/g$^2$</th>
<th>$V_s$ mL/mol</th>
<th>$\rho^2$ g/mL</th>
<th>$\chi \pm \Delta \chi$ mol/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>$-1.14E-04 \pm 3.97E-05$</td>
<td>81.70</td>
<td>1.06</td>
<td>$0.5099 \pm 0.0034$</td>
</tr>
<tr>
<td>Toluene</td>
<td>$-2.79E-04 \pm 6.92E-05$</td>
<td>106.80</td>
<td>1.46</td>
<td>$0.5435 \pm 0.0108$</td>
</tr>
</tbody>
</table>

Table 4.3: Propagation of Error for KBH in THF and Toluene, including error in the Y values and the Resulting Slope in the Hildebrand-Scatchard Relationship

<table>
<thead>
<tr>
<th>KBH</th>
<th>$\chi/V_1 \pm \Delta \chi/V_1$ mol/mL</th>
<th>$Y \pm \Delta Y$ mol/mL</th>
<th>Slope $\pm \Delta$ Slope mol/(cal mL)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>$0.0042 \pm 2.800E-5$</td>
<td>$0.1488 \pm 2.800E-5$</td>
<td>$0.0306 \pm 0.0002$</td>
</tr>
<tr>
<td>Toluene</td>
<td>$0.0039 \pm 7.760E-5$</td>
<td>$0.1299 \pm 7.760E-5$</td>
<td></td>
</tr>
</tbody>
</table>

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4.4 Results

A. Instrument Constants

The instrument constants for our system were determined for a series of polymer solutions with known $A_2$ and $M_w$. In this analysis $c/S-S_0$ is plotted as a function of solution concentration, which, according to Equation 4.5 and Bergin’s previous work, is linear with the slope and intercept of the lines equal to $H'$ and $H''$ respectively (5-6). The instrument constants that are determined with this procedure are presented in Table 4.2, which clearly shows that the “instrument constants” vary with sample. Thus, $H'$ and $H''$ are not constants, but depend on the exact system that is measured. This is not surprising, as discussed in the introduction, $H'$ and $H''$ depend on the $dn/dc$ of the samples. Because $dn/dc$ changes with sample, $H'$ and $H''$ must change with the sample. Therefore, in order to use small angle light scattering to determine the $A_2$ of a given nanoparticle solution, the $dn/dc$ of each solution must be determined independently.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$H'$ (mol mL/g$^2$)</th>
<th>$H''$ (mol mL/g$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>178K PMMA in Chloroform</td>
<td>0.0218</td>
<td>0.0177</td>
</tr>
<tr>
<td>50K PS in NMP</td>
<td>0.0913</td>
<td>0.0850</td>
</tr>
<tr>
<td>50K PS in THF</td>
<td>0.0427</td>
<td>0.4919</td>
</tr>
<tr>
<td>97K PS in Benzene</td>
<td>0.0318</td>
<td>0.3543</td>
</tr>
</tbody>
</table>
B. UV-Vis Results

Table 4.5 provides the conditions for the UV-Vis experiments. The initial concentrations of the samples are listed, which were used to construct Beer’s Law Plots. The concentrations of the samples after particle settling are also listed, where these values are determined from their UV-Vis absorption and the extinction coefficient. The solubility limits are also presented, where these are taken from the highest amount of dissolved particles in the settled samples.

LBH in MEK had the highest solubility limit of the systems studied, 3.31 mg/mL. LBH was also tested in THF and toluene, where lower solubility limits were found for these systems, 2.1 and 0.727 mg/mL, respectively. The second highest solubility limit was found for DCB in THF, 2.85 mg/mL. In contrast, DCB in toluene had a solubility limit of only 0.41 mg/mL.

TCB was perhaps the most noteworthy, since it exhibited no solubility in THF. After particle settling, only the solvent remained in the supernant of this solution. Conversely, the solubility limit of TCB in toluene is 2.47 mg/mL. The data is also presented as a bar graph for visual comparison of the solubilities (Figure 4.2). The UV-Vis data and Beer’s Law Plots are presented in Chapter 4 Appendix A.
### Table 4.5: UV-Vis Concentration Data and Solubility Limits

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Initial Concentrations (mg/mL)</th>
<th>Concentration of Settled Samples (mg/mL)</th>
<th>Solubility Limit (mg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCB</td>
<td>THF 0.658 – 5.10</td>
<td>THF 0.00 – 2.85</td>
<td>THF 2.85</td>
</tr>
<tr>
<td></td>
<td>Toluene 1.90 – 4.90</td>
<td>Toluene 0.052 – 0.41</td>
<td>Toluene 0.410</td>
</tr>
<tr>
<td>KBH</td>
<td>THF 0.200 – 5.02</td>
<td>THF 0.093 – 0.445</td>
<td>THF 0.445</td>
</tr>
<tr>
<td></td>
<td>Toluene 0.970 – 5.50</td>
<td>Toluene 0.156 – 0.300</td>
<td>Toluene 0.300</td>
</tr>
<tr>
<td>LBH</td>
<td>THF 0.340 – 5.64</td>
<td>THF 0.050 – 2.10</td>
<td>THF 2.10</td>
</tr>
<tr>
<td></td>
<td>Toluene 0.520 – 5.40</td>
<td>Toluene 0.352 – 0.727</td>
<td>Toluene 0.727</td>
</tr>
<tr>
<td></td>
<td>MEK 0.240 – 5.20</td>
<td>MEK 0.00 – 3.31</td>
<td>MEK 3.31</td>
</tr>
<tr>
<td>TCB</td>
<td>THF 0.330 – 4.60</td>
<td>THF 0.00 – 0.00</td>
<td>THF 0.00</td>
</tr>
<tr>
<td></td>
<td>Toluene 2.50 – 6.00</td>
<td>Toluene 1.60 – 2.47</td>
<td>Toluene 2.47</td>
</tr>
</tbody>
</table>
Figure 4.2: Solubility Limits of the nanoparticles compounds in THF, Toluene, and MEK
C. Refractometry Results

The refractive index increment, $dn/dc$, of each nanoparticle/solvent system was independently measured, where the protocol is verified using a polystyrene (PS) standard in THF. Measurements were completed at three different wavelengths, and a Cauchy Plot is constructed in order to determine the $dn/dc$ at any desired wavelength. For PS in THF, the $dn/dc$ results matches previously reported values, $0.211 \text{ mL/g } (\lambda = 436 \text{ nm}; 25 \degree C)$ and $0.198 \text{ mL/g } (\lambda = 546 \text{ nm}; 25 \degree C)$ (Figure 4.3) (43).

All of the nanoparticle solutions tested were freshly sonicated and well dispersed prior to measurement. Using this protocol, the $dn/dc$ of each nanoparticle solution was determined at $\lambda = 685 \text{ nm}$ to correlate to the conditions of the light scattering experiment. These results are summarized in Table 4.6, and the Cauchy Plots are attached in Chapter 4 Appendix B.

Table 4.6: $dn/dc$ of the solutions studied in these experiments at 6850 Angstroms (ml/g)

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>THF</th>
<th>Toluene</th>
<th>MEK</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCB</td>
<td>0.1107</td>
<td>0.0517</td>
<td></td>
</tr>
<tr>
<td>KBH</td>
<td>0.0239</td>
<td>0.0035</td>
<td></td>
</tr>
<tr>
<td>LBH</td>
<td>0.2097</td>
<td>0.0302</td>
<td>0.2785</td>
</tr>
<tr>
<td>TCB</td>
<td>0.1565</td>
<td>0.0433</td>
<td></td>
</tr>
<tr>
<td>Wavelengths (Angstroms)</td>
<td>dn/dc (mL/g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td>-------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4410</td>
<td>0.215</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5470</td>
<td>0.191</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5770</td>
<td>0.187</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.3: Cauchy Plot and Refractometry Data for Polystyrene in THF
D. Density Results

Calibration for the gas pycnometer was completed using a steel ball, 0.5 inch diameter, with known mass, volume, and density. Further calibration was completed using solid polymers with known densities. The measured densities of both high-density polyethylene (HDPE) and polystyrene (PS) matched the published values within 0.5% deviation as shown in Table 4.7.

The measured densities of the polyhedral borane compounds are summarized in Table 4.8. LBH is known to be very hygroscopic, so the impact of exposure to atmospheric humidity on the LBH density was monitored. Therefore, the density of LBH was determined after being stored in a desiccator, after heating for 24 hours in a vacuum oven at 100 °C to remove moisture, and upon air-exposure for 48 hours. There was little variation in the density after storage in the desiccator and heating in a vacuum for 24 hours. Upon air-exposure for 48 hours, the density increased 3.7%, presumably due to water uptake.

Table 4.7: Calibration

<table>
<thead>
<tr>
<th>Sample Tested</th>
<th>Measured Mass (grams)</th>
<th>Determined Volume (mL)</th>
<th>Determined Density (g/mL)</th>
<th>Actual Density (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel Calibration Ball</td>
<td>8.3477</td>
<td>1.0720</td>
<td>7.787</td>
<td>7.85</td>
</tr>
<tr>
<td>100K HDPE</td>
<td>1.0348</td>
<td>1.1053</td>
<td>0.9362</td>
<td>0.941</td>
</tr>
<tr>
<td>PS 300K</td>
<td>0.2592</td>
<td>0.2472</td>
<td>1.0485</td>
<td>1.05</td>
</tr>
</tbody>
</table>
Table 4.8: Densities of the Nanoparticle Samples

<table>
<thead>
<tr>
<th>Sample Tested</th>
<th>Mass Measured (grams)</th>
<th>Volume Determined (mL)</th>
<th>Density Determined (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCB</td>
<td>0.8014</td>
<td>0.6873</td>
<td>1.166</td>
</tr>
<tr>
<td>KBH</td>
<td>0.7949</td>
<td>0.6577</td>
<td>1.209</td>
</tr>
<tr>
<td>LBH (unheated)</td>
<td>0.3759</td>
<td>0.3183</td>
<td>1.181</td>
</tr>
<tr>
<td>LBH (heated)</td>
<td>0.7224</td>
<td>0.6105</td>
<td>1.183</td>
</tr>
<tr>
<td>LBH (exposed 48 hours to air)</td>
<td>0.2818</td>
<td>0.2302</td>
<td>1.224</td>
</tr>
<tr>
<td>TCB</td>
<td>0.4765</td>
<td>0.4900</td>
<td>0.972</td>
</tr>
</tbody>
</table>

E. Static Light Scattering Results

Static light scattering was completed to determine the radius of gyration and the second virial coefficient of each nanoparticle in the various solvents. Using the experimentally determined dn/dc values, other instrumental parameters and the measured scattering intensity, Zimm Plots were constructed and analyzed to determine the second virial coefficient and the radius of gyration of the nanoparticle (3). The Zimm Plots and data are shown in Chapter 4 Appendix C. The experimentally determined $A_2$, $\chi$, and $R_g$ are summarized in Table 4.9 for each nanoparticle-solvent system, along with physical observations.
F. Observations

Observations that describe the visual state of dispersion in the solutions were recorded 30 minutes after the samples were freshly prepared and sonicated. Many solutions were cloudy or had particle settling in the 3 highest concentrations prepared, and this is indicated on Table 4.9.

LBH in THF, LBH in MEK, and TCB in Toluene were observed to be clear at all of the concentrations prepared. In contrast, LBH in Toluene was cloudy, and DCB in toluene had particle settling in all of the concentrations prepared. The remaining solutions were cloudy or had particle settling in the three highest concentrations prepared.

Table 4.9: Sample appearances, $A_2$, $\chi$, and $R_g$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>Appearance</th>
<th>$A_2$</th>
<th>$\chi$</th>
<th>$R_g$ (nm)</th>
<th>$R_g$ % Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBH</td>
<td>THF</td>
<td>Clear</td>
<td>-9.16E-05</td>
<td>0.5104</td>
<td>47.3</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>Cloudy</td>
<td>-4.86E-04</td>
<td>0.5724</td>
<td>202</td>
<td>29</td>
</tr>
<tr>
<td>MEK</td>
<td>Clear</td>
<td></td>
<td>-7.751E-5</td>
<td>0.5097</td>
<td>354</td>
<td>94</td>
</tr>
<tr>
<td>TCB</td>
<td>Toluene</td>
<td>Clear</td>
<td>2.93E-04</td>
<td>0.4704</td>
<td>97.9</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>Settling high conc</td>
<td>-2.574E-03</td>
<td>0.6987</td>
<td>167</td>
<td>56</td>
</tr>
<tr>
<td>DCB</td>
<td>Toluene</td>
<td>Settling</td>
<td>-5.973E-04</td>
<td>0.5867</td>
<td>216</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>Cloudy high conc</td>
<td>-1.08E-04</td>
<td>0.5120</td>
<td>86.9</td>
<td>6</td>
</tr>
<tr>
<td>KBH</td>
<td>Toluene</td>
<td>Settling high conc</td>
<td>-2.79E-04</td>
<td>0.5436</td>
<td>182</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>Cloudy high conc</td>
<td>-1.140E-4</td>
<td>0.5136</td>
<td>102</td>
<td>63</td>
</tr>
</tbody>
</table>
G. Determination of Hildebrand Solubility Parameters

The Hildebrand solubility parameter of each nanoparticle was determined from the $\chi$ values of the nanoparticle in two or three solvents using Equation 4.3. These results are presented in Table 4.10. Lists of solvents that are predicted to readily solubilize each nanoparticle based on the similarity of $\delta$ are presented in Table 4.11. The plots of $(\delta_1^2/RT - \chi/V_1)$ as a function of $\delta_1$ for each polyhedral borane are shown in Chapter 4 Appendix D.

Table 4.10: Hildebrand Solubility Parameters

<table>
<thead>
<tr>
<th>Solvents and Nanoparticle</th>
<th>Hildebrand Solubility Parameter (cal/cm$^3$)$^{1/2}$</th>
<th>Hildebrand Solubility Parameter Error (cal/cm$^3$)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>9.520</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>8.900</td>
<td></td>
</tr>
<tr>
<td>MEK</td>
<td>9.270</td>
<td></td>
</tr>
<tr>
<td>LBH</td>
<td>9.177 ± 0.4245</td>
<td></td>
</tr>
<tr>
<td>TCB</td>
<td>8.378 ± 0.8293</td>
<td></td>
</tr>
<tr>
<td>DCB</td>
<td>9.207 ± 0.1330</td>
<td></td>
</tr>
<tr>
<td>KBH</td>
<td>9.059 ± 0.0504</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.11: Potential Suitable Solvents of each nanoparticle based on Similar Hildebrand Solubility Parameters

\( (\text{MPa}^{1/2}) = 2.0455 \ (\text{cal/cm}^3)^{1/2} \)

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Particle (\delta) (MPa(^{1/2}))</th>
<th>Solvent (\delta) (MPa(^{1/2}))</th>
<th>Solvents</th>
</tr>
</thead>
</table>
| DCB          | 18.83                             | 18.80                             | Ally acetate  
Benzene  
Propyl formate  
Ethyl chloride  
Diacetone alcohol  
Trichloroethylene  
Tripropylene glycol |
| KBH          | 18.53                             | 18.60                             | Diamyl phthalate  
Ethyl acetate  
Vinyl toluene  
cis-1,2-Dichloroethylene  
Isophorone |
| LBH          | 18.77                             | 18.80                             | Ally acetate  
Benzene  
Propyl formate  
Ethyl Chloride  
Diacetone alcohol  
Trichloroethylene  
Tripropylene glycol |
| TCB          | 17.14                             | 17.2                              | Amyl iodide (normal)  
Anethole (para)  
Benzonitride  
Trimethyl-3,5,5-hexanol  
Tricresyl phosphate |
4.5 Discussion

The dn/dc of nanoparticles is especially difficult to measure due to their aggregation behavior in solution that prevents flow through instrumentation to obtain readings. This has led to previous work that has tried to circumvent the need for this parameter in using light scattering to characterize the thermodynamics of nanoparticle solutions. Scattering theory (Chapter 2), however, clearly indicates that the light scattering instrument constants, $H'$ and $H''$, depend on the change of refractive index of the solution with solute concentration, and therefore must change with a variation in solvent-solute pair (27-30). This is because the instrument constants, $H'$ and $H''$, are related to the optical constant, $H$, from the basic scattering equation (Equation 4.4) (27-30). In fact, since the basic scattering equation is simply rearranged to obtain the instrument constants, $H''$ is actually equal to the optical constant, while $H'$ is one half of the optical constant, which is shown in Equations 4.12 and 4.13.

$$H' = H \quad (4.12)$$
$$H'' = H/2 \quad (4.13)$$

In this work, we tested the validity of this protocol and found it lacking. $H'$ an $H''$ were determined for a series of polymer solutions. Unfortunately, the experimentally determined instrument constants were found to vary with polymer-solvent pair. This is clearly due to the fact that the optical constants depend on dn/dc, which varies with sample. Thus, it became necessary to determine dn/dc for each nanoparticle solution independently, in order to use static light scattering to quantify the solubility of the nanoparticle-solvent systems.

The Polymer Characterization laboratory at the University of Tennessee has a Brice Phoenix Refractometer BP-2000V, (Phoenix Precision Instrument Company). This refractometer does not require solvent flow-through (44). A dual sample cell holds the pure
solvent and sample of interest for measurements, and once measurements are completed, the samples are completely recoverable. Expensive solvents, such as N-methyl pyrrolidone, are tested with little waste, and nanoparticles that clog tubing in flow-through refractometers do not pose a problem in the dual sample holder. The instrument was calibrated prior to measurements using NaCl salt solutions with known dn/dc (Chapter 2). Prior to measuring the polyhedral borane solutions, polystyrene in THF was measured and its dn/dc matched published values.

A complete workup of refractometry, static light scattering, pycnometry, UV-Vis, and physical observations was completed for the nanoparticle solutions, and of the systems tested, only TCB in toluene was found to have a χ below 0.5, which indicates thermodynamically favorable mixing (7). UV-Vis results corroborate the stability of this system, showing a high solubility limit of 2.47 mg/mL, and all of the concentrations of TCB in toluene prepared were clear, with no particle settling.

The extracted Hildebrand solubility parameter for TCB also agrees with these findings (Table 4.12). δ for TCB is reported to be 8.4 (cal/cm^3)^(1/2), while that of toluene is 8.9 (cal/cm^3)^(1/2), where the proximity of the two values is an indicator of good solubility. A list of potential good solvents based on δ indicates that the connected cage structure of TCB (Figure 4.1) interacts favorably with solvents that have conjugated ring structures, such as anthole, benzonitrile, and tricresyl phosphate, each of which have solubility parameters of 8.41 (cal/cm^3)^(1/2). These solvents are also capable of only weak hydrogen bond interactions and are nonpolar or polar aprotic. Toluene also follows this trend, since it is a nonpolar, conjugated ring.

Although THF is also a polar aprotic ring, it lacks conjugation, and solutions of TCB in THF showed settling in the higher concentrations with pure solvent remaining on top of the vial. χ is found to be much greater than 0.5 (~ 0.7), which indicates repulsive interactions between the
polyhedral borane and solvent. This, not surprisingly, manifests itself in a measured solubility limit of 0.0 mg/mL. Comparison of the solubility parameters of THF and TCB are also self-consistent. TCB has the lowest δ of the polyhedral borane compounds studied, while THF has the highest δ of the solvents studied. Thus the difference in δ_{THF} − δ_{TCB} is the largest of the systems studies, and this solution exhibits the least compatibility.

Table 4.12: The values for χ and δ for the nanoparticle solutions studied.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Solvent</th>
<th>χ</th>
<th>Solvent Solubility Parameter (cal/cm^3)^{1/2}</th>
<th>Hildebrand Solubility Parameter (cal/cm^3)^{1/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBH</td>
<td>THF</td>
<td>0.5104</td>
<td>9.52</td>
<td>9.18</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>0.5724</td>
<td>8.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MEK</td>
<td>0.5097</td>
<td>9.27</td>
<td></td>
</tr>
<tr>
<td>TCB</td>
<td>Toluene</td>
<td>0.4704</td>
<td>8.90</td>
<td>8.38</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>0.6987</td>
<td>9.52</td>
<td></td>
</tr>
<tr>
<td>DCB</td>
<td>Toluene</td>
<td>0.5867</td>
<td>8.90</td>
<td>9.21</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>0.5120</td>
<td>9.52</td>
<td></td>
</tr>
<tr>
<td>KBH</td>
<td>Toluene</td>
<td>0.5435</td>
<td>8.90</td>
<td>9.06</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>0.5136</td>
<td>9.52</td>
<td></td>
</tr>
</tbody>
</table>

The solubility of LBH was examined in toluene, THF, and MEK. THF was found to be a fair solvent for LBH with a χ of 0.5104 and a solubility limit of 2.10 mg/mL. In contrast, toluene was not a good solvent for LBH, with a χ = 0.5724, which corresponds to the physical observations of cloudy solutions, and a solubility limit of only 0.730 mg/mL.

MEK was the best solvent tested for LBH in this work. χ is very close to 0.5 for this system, and the concentrations tested were very close to being thermodynamically stable. The solubility limit was 3.31 mg/mL, and samples tested were prepared in the concentration range of
0.240 – 5.20 mg/mL. The solubility limit was just below that of the samples tested with light scattering, and gentle heating should improve the miscibility. All of the solutions prepared in MEK also appeared to be clear with no particle settling.

Inspection of the Hildebrand solubility parameter for LBH also agrees with these findings, where $\delta$ for LBH is 9.20 (cal/cm$^3$)$^{1/2}$. This value is very similar to the solubility parameter for MEK, which is 9.27 (cal/cm$^3$)$^{1/2}$. Other possible solvents for LBH based on $\delta$ are ally acetate, propyl formate, and tripropylene glycol, which have solubility parameters of 9.20 (cal/cm$^3$)$^{1/2}$. All of these solvents, including MEK, are straight chain alkanes that contain polar groups, such as carbonyls or chlorines, or conjugated double bonds. They also have weak hydrogen bonding capability, and are therefore nonpolar or polar aprotic. Benzene is also a suggested solvent and is a nonpolar, conjugated ring. The charged surface of the LBH cage appears to interact favorably with the conjugated or polar groups present in these solvents.

Similar solvents are also suggested for the other salt tested in this work, KBH, where $\delta$ for KBH is 9.06 (cal/cm$^3$)$^{1/2}$, and highly conjugated rings or straight chains that contain polar groups, such as ethyl acetate or isophorone, are suggested solvents. Neither toluene nor THF were favorable, where $\chi$ values $> 0.5$ were found.

All of the remaining particle solutions also had $\chi$ values greater than 0.5. DCB in THF and toluene both had $\chi > 0.5$. In toluene, particle settling occurred in all of the solutions prepared, and a low solubility limit with a $\chi$ value of 0.5867 was found. In THF the interactions were more favorable with a lower $\chi$, 0.5120, and a higher solubility limit of 2.85 mg/mL. $\delta$ for DCB is determined to be 9.21 (cal/cm$^3$)$^{1/2}$. This value does lie in the middle, between the solubility parameter of THF and that of toluene, which is consistent with the observations, but the $\delta$ of DCB is not sufficiently close to either of these two solvents studied to form beneficial
interactions to form a stable solution. Possible good solvents for DCB are aromatic or contain polar functional groups, such as ally acetate, benzene, and propyl formate, and have solubility parameters of 9.20 (cal/cm$^3$)$^{1/2}$.

$R_g$ values from these experiments are also compared to the reported $\chi$, and a general trend emerges. For particle systems with lower $\chi$ values, the experimentally obtained $R_g$ was lower, indicating less aggregation. For example, TCB in THF has a $\chi$ of 0.6987 and $R_g$ of 167 nm, while TCB in toluene has a $\chi$ of 0.4704 and $R_g$ of 98.0 nm. Similarly, DCB in toluene has a $\chi > 0.5$ and large $R_g$ of 216 nm, while DCB in THF was found to be a more miscible system with $\chi$ approaching 0.5 and a smaller $R_g$ of 87.0 nm. The only exception to this trend was LBH in MEK. For this system, error in the $M_w$ and $R_g$ values was much higher than the other systems (Table 4.9). Contamination due to dust particles and inaccurate concentrations from UV-Vis are reasons for the increase in error. The other LBH systems studied, however, remained consistent with the trend. LBH in THF had an $R_g$ of 47.0 nm and a $\chi$ of 0.5104. LBH in toluene had a higher $\chi$ value, 0.5724, and higher $R_g$, 202 nm.

It is important to note that the $R_g$ values are higher than expected. Work by Debye and Bender describe complexities that arise from light scattering when particles are much larger or smaller than the wavelength of light or in non-dilute solutions, resulting in multiple scattering effects, and additional calculations (ie: the Mie Calculations, which take into account differences in the refractive index of the components and scattering interference for particles $< 1/6 \lambda$, or the application of the Cabannes Factor, for particles $< 1/20 \lambda$) are necessary to quantify the size and shape of a particle (37). These calculations are increasingly difficult for particles that are not perfect spheres, and a more computational approach remains a work-in-progress (33). The boron cage compounds in this work have a diameter ~ 1.0 nm and differ markedly from the wavelength.
employed ($\lambda = 685$ nm), and static light scattering of the nanoparticle-solutions were carried out on the initially prepared concentrations, which is not below the determined solubility limits of the nanoparticles, increasing the risk of interference from particle aggregation; qualitatively, though, the lower $\chi$ is responsible for less particle aggregation and smaller $R_g$ in these systems (36, 45).

A discussion regarding error is also necessary when interpreting these results. Static light scattering for samples that are not dilute enough to prevent particle interactions result in high errors due to multiple scattering centers, and defining $R_g$ from the scattering curve becomes difficult (Chapter 2) (33-48).

However, the data collected is consistent. Particle solutions that have positive $A_2$ values also had $\chi$ values below 0.5 and were observed to be clear and free from particle settling. UV-Vis data support the light scattering data, with higher solubility limits in systems with low $\chi$ values, indicating that the nanoparticle-solutions measured with light scattering were adequately disperse to obtain accurate $A_2$ values.

The determined Hildebrand solubility parameters also contain error since only two data points were used to plot lines using the Hildebrand-Scatchard solution theory. The slope and intercepts of the lines will vary if either data point contained error. One exception was LBH, for which three solvents were studied and three data points were plotted. Statistical analysis of the data was carried out to determine the affect of uncertainty in the measured $A_2$ on the obtained $\delta$, and standard deviation was propagated through the calculation that led to $\delta$. Error in the $Y$ values was found to be minimal, and even though only a few data points were plotted, error in the obtained $\delta$ is $< \pm 0.900$ (cal/cm$^3$)$^{1/2}$ for all of the nanoparticles studied in this thesis. In fact, TCB actually had the highest error $\pm 0.8293$(cal/cm$^3$)$^{1/2}$, while all of the remaining particles had
error < ± 0.500 (cal/cm³)¹/². For instance, KBH has error ± 0.0504 (cal/cm³)¹/². Good solvents are defined as having the solute and solvent Δδ within 1.0 (cal/cm³)¹/² and as the Δδ increases, the solubility limit of the solute also decreases correspondingly (22). All of the reported error in this work is less than 1.0 (cal/cm³)¹/², and it is important to keep in mind that the error reported (δ± Δδ) arises from the highest possible deviation in the calculated Y values. If the actual δ value falls anywhere else within this range, there is also a corresponding decrease in error. This fact, and the minimal error in the Y values, slope of the resulting lines, and δ support the use of this method. Also, it is worth noting, that the δ value was determined from the slope of the line in all cases, but it is also possible to calculate δ from the intercept, as shown in Equation 4.3. Comparing the δ values determined from the intercept and slope shows very good agreement, within 2% error. The estimated δ values also showed good agreement with χ. Favorable solvents had δ in close concert with the nanoparticle’s solubility parameter and offered further support to the protocol developed for this work.

4.6 Conclusions

A protocol that has previously been presented to measure the second Virial coefficient of a solute in solution via light scattering without determining the refractive index increment, dn/dc is tested. This was completed by establishing the light scattering instrument constants of an instrument for a series of polymer-solutions with known A₂ and M_w. The previously presented protocol would be advantageous because it avoids the need to measure the refractive index increment, dn/dc, of the nanoparticle-solutions; however, the instrument constants obtained in this work are not consistent, which verifies that the instrument constants do in fact depend on the
dn/dc of the sample and that measurements of dn/dc are required to determine the solubility behavior of nanoparticle solutions.

Therefore, static light scattering and refractometry experiments were completed for nine nanoparticle-solvent systems. DCB, TCB, KBH, and LBH boron cage compounds were examined in toluene, THF, and MEK. UV-Vis spectroscopy was used to determine the concentrations and solubility limits of the systems studied. Gas pycnometry was also used to accurately determine the density of the polyhedral borane powders. The solute-solvent interaction parameter, χ, and the Hildebrand solubility parameter, δ, were determined for each nanoparticle and used to quantify the solubility behavior and to predict good solvents based on similar δ.

TCB in toluene has a favorable χ value of 0.47. UV-Vis data provides further evidence of the stability of the mixture with a high solubility limit of 2.47 mg/mL. The extracted δ for this system is also in good agreement, with a value close to that of toluene’s δ. Predicted good solvents based on δ are also aromatic and capable of only weak hydrogen bonding interactions, similar to toluene.

For all of the remaining nanoparticle solutions, the scattering data collected is consistent with the UV-Vis solubility limits and physical observations. Higher χ values result in lower solubility limits and particle settling. In addition, smaller $R_g$ values correspond to better dispersion. A list of possible good solvents for the nanoparticles tested is presented based on the determined δ values. Good agreement between δ and χ is also found for all the polyhedral borane compound systems tested. These results therefore demonstrate that the static light scattering experiments in conjunction with refractometry is a powerful technique to quantify the solubility behavior of nanoparticles in solution.
4.7 References


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Chapter 4 Appendix A.: UV-Vis Data and Beer’s Law Plots
### Supplemental Figure A4.1: UV-Vis Data and a) Beer’s Law Baseline for DCB in THF; b) the change in absorbance of initial concentrations

<table>
<thead>
<tr>
<th>Vial #</th>
<th>Initial Concentrations</th>
<th>Settled Samples</th>
<th>Concentration</th>
</tr>
</thead>
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<td></td>
<td>Vial #</td>
<td>ABS g/mL</td>
<td>g/mL</td>
</tr>
<tr>
<td>1</td>
<td>0.0023</td>
<td>0.0007</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0.0120</td>
<td>0.0010</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>0.0130</td>
<td>0.0022</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>0.0300</td>
<td>0.0038</td>
<td>4</td>
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<tr>
<td>5</td>
<td>0.0400</td>
<td>0.0051</td>
<td>5</td>
</tr>
<tr>
<td>Vial #</td>
<td>ABS</td>
<td>Concentration mg/mL</td>
<td>Vial #</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
<td>----------------------</td>
<td>-------</td>
</tr>
<tr>
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<td>1</td>
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<tr>
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<td>0.0520</td>
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<td>3</td>
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<td>3.800</td>
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<td>4.900</td>
<td>5</td>
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**Supplemental Figure A4.2:** UV-Vis Data and a) Beer’s Law Baseline for DCB in Toluene; b) the change in absorbance of initial concentrations
### Baseline Samples Settled Samples

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<th>Vial #</th>
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<th>Concentration</th>
<th>Vial #</th>
<th>ABS</th>
<th>Concentration</th>
</tr>
</thead>
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<tr>
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<td>0.0360</td>
<td>0.2000</td>
<td>1</td>
<td>0.0230</td>
<td>0.0930</td>
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<tr>
<td>2</td>
<td>0.0390</td>
<td>1.120</td>
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<td>0.0180</td>
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<td>3</td>
<td>0.6520</td>
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<td>3</td>
<td>0.0490</td>
<td>0.1980</td>
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<tr>
<td>4</td>
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<td>4.100</td>
<td>4</td>
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<tr>
<td>5</td>
<td>1.254</td>
<td>5.020</td>
<td>5</td>
<td>0.1100</td>
<td>0.4450</td>
</tr>
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</table>

**Supplemental Figure A4.3:** UV-Vis Data and a) Beer’s Law Baseline for KBH in THF; b) the change in absorbance of initial concentrations

\[ y = 0.2473x \]
\[ R^2 = 0.9458 \]
### Supplemental Figure A4.4: UV-Vis Data and a) Beer’s Law Baseline for KBH in Toluene; b) the change in absorbance of initial concentrations
Supplemental Figure A4.5: UV-Vis Data and a) Beer’s Law Baseline for LBH in THF; b) the change in absorbance of initial concentrations
<table>
<thead>
<tr>
<th>Vial #</th>
<th>ABS</th>
<th>Concentration (mg/mL)</th>
<th>Vial #</th>
<th>ABS</th>
<th>Concentration (mg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>0.5200</td>
<td>1</td>
<td>0.2060</td>
<td>0.3520</td>
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<td>2</td>
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<td>1.060</td>
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<td>0.1710</td>
<td>0.2920</td>
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<tr>
<td>3</td>
<td>2.202</td>
<td>2.740</td>
<td>3</td>
<td>0.2780</td>
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<tr>
<td>4</td>
<td>2.451</td>
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<td>4</td>
<td>0.4250</td>
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<td>5.500</td>
<td>5</td>
<td>0.3280</td>
<td>0.5610</td>
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</table>

**Supplemental Figure A4.6:** UV-Vis Data and a) Beer’s Law Baseline for LBH in Toluene; b) the change in absorbance of initial concentrations

\[ y = 0.6186x \]
\[ R^2 = 0.9168 \]
<table>
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<th>Concentration</th>
<th>Vial #</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/mL</td>
<td></td>
<td>mg/mL</td>
</tr>
<tr>
<td>1</td>
<td>0.0030</td>
<td>1</td>
<td>0.0000</td>
</tr>
<tr>
<td>2</td>
<td>0.0200</td>
<td>2</td>
<td>0.0080</td>
</tr>
<tr>
<td>3</td>
<td>0.0570</td>
<td>3</td>
<td>0.0290</td>
</tr>
<tr>
<td>4</td>
<td>0.0640</td>
<td>4</td>
<td>0.0390</td>
</tr>
<tr>
<td>5</td>
<td>0.1180</td>
<td>5</td>
<td>0.0690</td>
</tr>
</tbody>
</table>

Supplemental Figure A4.7: UV-Vis Data and a) Beer’s Law Baseline for LBH in MEK; b) the change in absorbance of initial concentrations
### Table 1: Baseline and Settled Samples

<table>
<thead>
<tr>
<th>Vial #</th>
<th>ABS</th>
<th>mg/mL</th>
<th>Vial #</th>
<th>ABS</th>
<th>mg/mL</th>
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<tbody>
<tr>
<td>1</td>
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<td>3</td>
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<td>0.000</td>
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</table>

**Supplemental Figure A4.8:** UV-Vis Data and a) Beer’s Law Baseline for TCB in THF; b) the change in absorbance of initial concentrations

\[
g = 0.0101x \\
R^2 = 0.9548
\]
### Supplemental Figure A4.9: UV-Vis Data and a) Beer’s Law Baseline for TCB in Toluene; b) the change in absorbance of initial concentrations
Chapter 4 Appendix B: Refractometer Data and Cauchy Plots
### Table: DCB in THF Cauchy Plot

<table>
<thead>
<tr>
<th>( \lambda ) (Å)</th>
<th>( 1/\lambda^2 )</th>
<th>( \text{dn/dc ml/g} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4410</td>
<td>5.14E-08</td>
<td>0.1214</td>
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<td>0.1152</td>
</tr>
<tr>
<td>5770</td>
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</table>

**DCB in THF Cauchy Plot**

\[
y = 350267x + 0.1034
\]

**Supplemental Figure B4.1:** Refractometer Data and Cauchy Plot for DCB in THF
Supplemental Figure B4.2: Refractometer Data and Cauchy Plot for DCB in Toluene
<table>
<thead>
<tr>
<th>$\lambda$ (Å)</th>
<th>$1/\lambda^2$</th>
<th>dn/dc (ml/g)</th>
</tr>
</thead>
<tbody>
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<td>5770</td>
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</table>

**KBH in THF Cauchy Plot**

$y = 2E+06x - 0.0187$  \hspace{1cm} $R^2 = 0.9478$

Supplemental Figure B4.3: Refractometer Data and Cauchy Plot for KBH in THF
<table>
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<tr>
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<th>$1/\lambda^2$</th>
<th>dn/dc (ml/g)</th>
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<td>5770</td>
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**KBH in Toluene Cauchy Plot**

$y = 71560x + 0.002$

**Supplemental Figure B4.4:** Refractometer Data and Cauchy Plot for KBH in Toluene
<table>
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**Supplemental Figure B4.5:** Refractometer Data and Cauchy Plot for LBH in THF

The Cauchy plot for LBH in THF is represented by the equation:

$$y = 520350x + 0.1986$$
Supplemental Figure B4.6: Refractometer Data and Cauchy Plot for LBH in Toluene
## Supplemental Figure B4.7: Refractometer Data and Cauchy Plot for LBH in MEK

### Table

<table>
<thead>
<tr>
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### Cauchy Plot

The Cauchy plot for LBH in MEK is shown below with the equation:

$$y = 1E+06x + 0.2227 \quad R^2 = 0.9938$$
<table>
<thead>
<tr>
<th>$\lambda$ (Å)</th>
<th>$1/\lambda^2$</th>
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</thead>
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**Supplemental Figure B4.8:** Refractometer Data and Cauchy Plot for TCB in THF
Supplemental Figure B4.9: Refractometer Data and Cauchy Plot for TCB in Toluene
Supplemental Figure C4.1: Light Scattering Data and Zimm Plot for DCB in THF
Supplemental Figure C4.2: Light Scattering Data and Zimm Plot for DCB in Toluene
Supplemental Figure C4.3: Light Scattering Data and Zimm Plot for KBH in THF
### Measured Values

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<table>
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<tbody>
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<td>$R_g$ (nm)</td>
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</tr>
<tr>
<td>$M_w$ (g/mol)</td>
<td>3.522E+5</td>
</tr>
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<td>$A_2$ (mol·cm³/g²)</td>
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**Supplemental Figure C4.4:** Light Scattering Data and Zimm Plot for KBH in Toluene
## Measured Values

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<tr>
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<td>(mol·cm³/g²)</td>
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**Supplemental Figure C4.5:** Light Scattering Data and Zimm Plot for LBH in THF
### Measured Values

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**Supplemental Figure C4.6**: Light Scattering Data and Zimm Plot for LBH in Toluene
**Supplemental Figure C4.7:** Light Scattering Data and Zimm Plot for LBH in MEK
### Measured Values

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<td>A₂ (mol·cm³/g²)</td>
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**Supplemental Figure C4.8:** Light Scattering Data and Zimm Plot for TCB in THF
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<tr>
<td>$M_w$ (g/mol)</td>
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<tr>
<td>$A_2$ (mol·cm³/g²)</td>
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**Supplemental Figure C4.9:** Light Scattering Data and Zimm Plot for TCB in Toluene
Chapter 4 Appendix D: Determination of Hildebrand Solubility Parameters
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solvent $\delta$ $(\text{cal/cm}^3)^{1/2}$</th>
<th>DCB $\delta$ $(\text{cal/cm}^3)^{1/2}$</th>
<th>$\Delta\delta$</th>
<th>$\chi$</th>
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<tbody>
<tr>
<td>THF</td>
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<td>8.900</td>
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<td>0.3070</td>
<td>0.5867</td>
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**Supplemental Figure D4.1:** Hildebrand Solubility Parameter Data and Plot of $(\delta_1^2/RT - \chi/V_1)$ as a Function of $\delta_1$ for DCB
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solvent $\delta$ (cal/cm$^3$)$^{1/2}$</th>
<th>KBH $\delta$ (cal/cm$^3$)$^{1/2}$</th>
<th>$\Delta\delta$</th>
<th>$\chi$</th>
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<tr>
<td>Toluene</td>
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<td>9.059</td>
<td>0.1590</td>
<td>0.5436</td>
</tr>
</tbody>
</table>

Supplemental Figure D4.2: Hildebrand Solubility Parameter Data and Plot of $(\delta_1^2/RT - \chi/V_1)$ as a Function of $\delta_1$ for KBH
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solvent $\delta$ (cal/cm$^3$)$^{1/2}$</th>
<th>LBH $\delta$ (cal/cm$^3$)$^{1/2}$</th>
<th>$\Delta\delta$</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>9.520</td>
<td>9.177</td>
<td>0.3426</td>
<td>0.51044</td>
</tr>
<tr>
<td>Toluene</td>
<td>8.900</td>
<td>9.177</td>
<td>0.2774</td>
<td>0.57244</td>
</tr>
<tr>
<td>MEK</td>
<td>9.270</td>
<td>9.177</td>
<td>0.0926</td>
<td>0.5097</td>
</tr>
</tbody>
</table>

**Supplemental Figure D4.3:** Hildebrand Solubility Parameter Data and Plot of $(\delta_1^2/RT - \chi/V_1)$ as a Function of $\delta_1$ for LBH

\[ y = 0.031x - 0.1466 \]
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solvent $\delta$ (cal/cm$^3$)$^{1/2}$</th>
<th>TCB $\delta$ (cal/cm$^3$)$^{1/2}$</th>
<th>$\Delta \delta$</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>9.520</td>
<td>8.378</td>
<td>1.142</td>
<td>0.6987</td>
</tr>
<tr>
<td>Toluene</td>
<td>8.900</td>
<td>8.378</td>
<td>0.5219</td>
<td>0.4704</td>
</tr>
</tbody>
</table>

**TCB Solubility Parameter**

$y = 0.0283x - 0.1206$

Supplemental Figure D4.4: Hildebrand Solubility Parameter Data and Plot of $(\delta_1^2/RT - \chi/V_1)$ as a Function of $\delta_1$ for TCB
Chapter 5

Quantifying the Solubility of Boron Nitride Nanotubes and Sheets
5.1 Abstract

The dissolution of nanoparticles, particularly those containing boron, is an important area of interest for polymer nanocomposite formation and material development (1-2). In this work, the solubility of boron nitride nanotubes (BNNT), functionalized boron nitride nanotubes (FBNNT), and boron nitride sheets (BN-ZG) is quantified in toluene and THF with static light scattering, refractometry, UV-Vis spectroscopy, and physical observations. UV-Vis spectroscopy provides a method to determine the concentration and solubility limits of the solutions tested. Using light scattering, the second virial coefficient, $A_2$, is determined and used to calculate $\chi$, the solute-solvent interaction parameter. The Hildebrand solubility parameter, $\delta$, is then extracted from this data using the Hildebrand-Scatchard solution theory (3-4). A list of potential good solvents based on the extracted $\delta$ value is provided for each nanoparticle. SWNTs and pre-polymers (EN4 and EN8) used to synthesize polyurethanes were also tested, since the published $\delta$ and molar attraction constants of these materials provided a self-consistent check. The $dn/dc$ of SWNTs and boron containing particles was measured for the first time in this work. A solvent screen for BN-ZG provides additional information that supports the obtained $\delta$ and $\chi$. Three systems were found to have $\chi$ values below 0.5 and were thermodynamically soluble, BNNT in THF, EN8 in THF, and EN8 in toluene.
5.2 Introduction

Boron containing nanoparticles are of special interest for the development of novel polymer nanocomposite materials because of their ability to capture neutrons, which makes their incorporation into polymer matrices especially useful for military and nuclear applications that require neutron shielding. Boron nitride nanotubes (BNNTs), which are structurally similar to carbon nanotubes (i.e.: a cylinder with diameter ~ 0.5 to 5 nm and length up to several microns), have very different properties than their carbon counterparts, they are electrical insulators and more thermally and chemically stable (5). However, their mechanical properties are comparable with carbon nanotubes, and the incorporation of BNNTs into poly(methyl methacrylate) (PMMA) at very low loadings (< 1.0%) has been shown to improve the elastic modulus of PMMA as much as 20% (6). The superior thermal and chemical stability and improvements in mechanical strength make BNNTs especially desirable boron-nanoparticles for nanocomposite development (5-8).

To realize the full potential of boron nanotubes as additives in polymer nanocomposites, it is important to define the solubility and dispersion behavior of BNNTs in solvents and polymers, since one of the most common methods for preparing polymer nanocomposites involves mixing nanoparticle-solutions with a polymer and evaporating the solvent (6). Homogenous dispersions of nanoparticles in solution during processing are required to realize their homogenous dispersion in a polymer matrix, where well dispersed particles lead to improvements in the electrical and mechanical properties of the resulting material (6). Finding a suitable solvent is the first step in this process, and work by Zhi, et al, has shown that better solvents for BNNT create better end products (9).
In previous work (Chapter 4), a protocol was developed to define the thermodynamic solubility behavior of boron nanoparticle-solvent systems with static light scattering in conjunction with refractometry to obtain the refractive index increment (dn/dc). Equation 5.1 presents the basic light scattering equation that relates the scattered light intensity to the solution characteristics, where \( R \) is the Rayleigh ratio, and is dependent on the intensity of scattered light, \( P_\theta \) is the form factor of the scattering particle, \( M_w \) is the molecular weight of the scattering particle, \( c \) is solution concentration, \( A_2 \) is the second virial coefficient, and \( H \) is the optical constant (10).

\[
\frac{Hc}{R_\theta - R_{\text{solvent}}} = \frac{1}{M_w P_\theta} + 2A_2c \quad (5.1)
\]

It is necessary to define \( dn/dc \) since the optical constant, \( H \), depends on the \( dn/dc \) of the solution and the wavelength of the laser light employed (10-13). Previous methods circumvented the collection of \( dn/dc \), since it was difficult to define this parameter for nanoparticle-solvent systems, due to their inherent aggregation behavior in solution, which clogs the tubing in modern flow-through instruments (Chapter 4) (10). Here, the collection of \( dn/dc \) is made possible by a refractometer equipped with a dual sample cell, to which sonicated solutions of nanoparticles are delivered via pipette.

With \( dn/dc \) defined, the intensity of light scattered by a range of nanoparticle-solution concentrations at multiple scattering angles is measured, and equations 5.2 and 5.3 are used to form a double extrapolation plot (i.e.: Zimm plot) where \( H \) is the optical constant, \( \theta \) is the scattering angle, and \( R_\theta \) is the Rayleigh ratio, the ratio of scattered intensities, and \( R_g \) is the radius of gyration of the scattering particle.

\[
\left( \frac{Hc}{R_\theta} \right)_{\theta=0} = \frac{1}{M_w} + 2A_2c + \ldots \quad (5.2)
\]

\[
\left( \frac{Hc}{R_\theta} \right)_{c=0} = \frac{1}{M_w} \left[ 1 + \frac{1}{3}(4\pi/\lambda)^2 R_g^2 \sin^2 \theta/2 + \ldots \right] \quad (5.3)
\]
The second virial coefficient is determined from the slope of the line of the data where the scattering angle approaches zero using Equation 5.2 and is a thermodynamic property that quantifies the interaction strength between a solute and solvent (10-13).

Once $A_2$ is determined it can be correlated to the solute-solvent interaction parameter, $\chi$, which describes the interaction of a particle or polymer with a solvent, using Equation 5.4, where $V_s$ is the solvent molar volume, and $\rho$ is the particle density obtained from gas pycnometry measurements (10-13).

$$\chi = \frac{1}{2} - (A_2 V_s \rho^2)$$ \hspace{0.5cm} (5.4)

From the Flory Huggins Solution Theory, the value of $\chi$ provides a measure of the enthalpic interactions between components in a mixture. For instance, if $\chi = 0.5$ the solvent is a theta solvent, the transition between a good solvent and a bad solvent where $A_2 = 0$ (14). A $\chi$ value less than 0.5 describes a good solvent for a material, with favorable interactions occurring between solvent molecules and segments of the chain or particle. A value that is greater than 0.5 describes an unfavorable mixing process and possible phase separation (15-16).

When $\chi$ is defined for a given solute molecule in a range of solvents, the Hildebrand solubility parameter of the solute, $\delta$, can be determined from the combination of the Flory Theory and the Hildebrand-Scatchard Solution Theory using Equation 5.5, where $\delta_1$ is the Hildebrand solubility parameter of the solvent, $R$ is the ideal gas constant, $T$ is temperature, and the Hildebrand solubility parameter of the polymer or nanoparticle is $\delta_2$ (3-4). A plot of $\delta_1^2/RT - \chi/V_1$ as a function of $\delta_1$ produces a straight line, and the slope = $2\delta_2/RT$ is used to determine the Hildebrand solubility parameter of the nanoparticle.

$$\delta_1^2/RT - \chi/V_1 = (2\delta_2/RT) \delta_1 - \delta_2^2/RT$$ \hspace{0.5cm} (5.5)
δ provides a numerical estimate of the degree of interaction between materials and can be a good indication of solubility, since materials with similar values of δ are likely to be miscible (i.e.: like dissolves like), and since many solvents have tabulated δ values, a range of good solvents for a particle can often be predicted based on this relationship.

UV-Vis spectroscopy offers a complimentary test to the data obtained from light scattering, since the solubility limits of the nanoparticle systems are defined with this technique (17). A Beer’s law plot of samples with known concentration is first constructed to correlate absorbance with concentrations. Unknown samples are then allowed to settle by gravity or are centrifuged to remove aggregates. The supernatant is subsequently characterized with UV-Vis to determine unknown concentrations using the established concentration-absorbance relationship (Chapter 2,4). The maximum concentration that is free of agglomeration is the solubility limit of the nanoparticle-system.

In our previous work, static light scattering, refractometry, UV-Vis, and physical observations were used to study four polyhedral borane compounds in tetrahydrofuran, toluene, and methyl ethyl ketone (Chapter 4). Good correlation was shown for these small particles, with UV-Vis spectroscopy data supporting the obtained χ. Physical observations were also consistent with the data, with particle settling occurring in samples with χ > 0.5, while concentrations that remained clear had χ < 0.5. Experimentally determined δ values for the nanoparticles were then used to define suitable solvents, where some predicted suitable solvents effectively dispersed the nanoparticles.

The consistency of the observations, UV-Vis, and scattering from this previous work was reason to move forward to test three additional boron containing particles, boron nitride nanotubes (BNNT), boron nitride nanotubes functionalized with stearoyl chloride (FBNNT), and
boron nitride sheets (BN-ZG). The solubility of these particles was tested in THF and toluene, where refractometry, light scattering, UV-Vis spectroscopy, and physical observations were used to describe and quantify the solubility of the nanoparticles. In addition, a solvent screen for BN-ZG was conducted to provide additional information regarding the solubility of these nanoparticles. Finally, suitable solvents are presented based on the experimentally determined Hildebrand solubility parameters.

As a self-consistent check, SWNTs in NMP and cyclohexyl pyrollidone (CHP) and polyurethane pre-polymers in THF and toluene were also tested, since information regarding their solubility behavior was already published, and the known molar attraction constants of these materials offered another route to determine their Hildebrand solubility parameters (18-20). Thus, the Hildebrand solubility parameters for these particles were also calculated using equation 5.6, where $\rho$ is the density, $M$ is the molecular weight or the monomer molecular weight for a polymer, and $G$ is the molar attraction constant (21).

$$\delta = \frac{\rho \Sigma G}{M} \quad (5.6)$$

The calculated solubility parameters and known, published solubility parameters are compared to the values determined in this study.

5.3 Experimental

A. Materials

The materials used in this work are described in Chapter 2. For easy reference in this report, the abbreviated names of the nanoparticles are also listed in Table 5.1.
### Table 5.1: Abbreviations for the nanoparticles examined in this chapter

<table>
<thead>
<tr>
<th>Particle Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron Nitride Sheets</td>
<td>BN-ZG</td>
</tr>
<tr>
<td>Functionalized Boron Nitride Nanotubes</td>
<td>BNNT</td>
</tr>
<tr>
<td>Boron Nitride Nanotubes</td>
<td>FBNNT</td>
</tr>
<tr>
<td>Conathane Part A Urethane Pre-polymer</td>
<td>EN4</td>
</tr>
<tr>
<td>Conathane Part B curative</td>
<td>EN8</td>
</tr>
<tr>
<td>Single Walled Carbon Nanotubes</td>
<td>SWNT</td>
</tr>
</tbody>
</table>

**B. Statistical Analysis**

The $A_2$ reported in this work is the mean value obtained from static light scattering, which has some uncertainty that is quantified by the reported standard deviation. It is important to propagate this standard deviation through further calculations. Two data points are plotted in this work to determine the $\delta$ of the nanoparticle from the slope of the Hildebrand-Scatchard plots, as presented in Equation 5.5. Error propagation was described in detail in Chapter 4. The same method was performed in the work presented here, and the absolute error in the obtained $\delta$ ($\delta \pm \Delta\delta$) values is presented in the results section in Table 5.8 for all of the nanoparticles studied. In all cases, the absolute error is $< 0.600$ (cal/cm$^3$)$^{1/2}$. 
5.4 Results

A. UV-Vis

The UV-Vis data collected is summarized in Table 5.2. The initial concentrations used to prepare Beer’s Law plots were transparent following 20 minutes of sonication, which allowed the acquisition of both UV-Vis and light scattering readings. BN-ZG was studied at concentrations ranging from 0.002 – 0.460 mg/mL, and the nanotubes (BNNT, FBNNT, and SWNT) were studied in the range of 0.010 – 0.200 mg/mL. The concentrations of nanoparticles that remained in solution after centrifugation and particle settling were determined from their measured absorbance at 500 nm using Beer’s Law and the determined extinction coefficient.

BNNT was readily soluble in THF, and higher concentrations were studied in this system. A solution of 1.0 mg/mL BNNT in THF was analyzed as described above, providing a solubility limit of 0.695 mg/mL. For convenience, the data is also presented in bar graphs. The solubility limits of the nanotubes and sheets are presented in Figure 5.2, while those of the pre-polymers are presented in Figure 5.1. The Beer’s Law plots for each nanoparticle solution are found in Appendix A.
Table 5.2: UV-Vis Concentration Data and Solubility Limits

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Initial Concentrations (mg/mL)</th>
<th>Centrifuged or Settled Concentrations (mg/mL)</th>
<th>Solubility Limit (mg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BN-ZG</strong></td>
<td>THF 0.0200 – 0.1000</td>
<td>THF 0.0003-0.0016</td>
<td>THF 0.0016</td>
</tr>
<tr>
<td></td>
<td>Toluene 0.0400 – 0.4600</td>
<td>Toluene 0.0037 – 0.1029</td>
<td>Toluene 0.1029</td>
</tr>
<tr>
<td><strong>FBNNT</strong></td>
<td>THF 0.0300 – 0.1600</td>
<td>THF 0.0022 – 0.0801</td>
<td>THF 0.0801</td>
</tr>
<tr>
<td></td>
<td>Toluene 0.0200 – 0.1600</td>
<td>Toluene 0.0042 – 0.0199</td>
<td>Toluene 0.0199</td>
</tr>
<tr>
<td><strong>BNNT</strong></td>
<td>THF 0.0200 – 1.000</td>
<td>THF 0.0178 – 0.6950</td>
<td>THF 0.6950</td>
</tr>
<tr>
<td></td>
<td>Toluene 0.0200 – 0.2000</td>
<td>Toluene 0.0064 – 0.0160</td>
<td>Toluene 0.0160</td>
</tr>
<tr>
<td><strong>EN4</strong></td>
<td>THF 0.7800 – 5.500</td>
<td>THF 0.2820 – 0.8450</td>
<td>THF 0.8450</td>
</tr>
<tr>
<td></td>
<td>Toluene 1.500 – 3.500</td>
<td>Toluene 0.5000 – 0.8500</td>
<td>Toluene 0.8500</td>
</tr>
<tr>
<td><strong>EN8</strong></td>
<td>THF 0.3000 – 6.900</td>
<td>THF 0.5800 – 2.500</td>
<td>THF 2.500</td>
</tr>
<tr>
<td></td>
<td>Toluene 0.9000 – 6.500</td>
<td>Toluene 0.4800 – 2.000</td>
<td>Toluene 2.000</td>
</tr>
<tr>
<td><strong>SWNT</strong></td>
<td>CHP 0.0120 – 0.1600</td>
<td>CHP 0.0014 – 0.0206</td>
<td>CHP 0.0206</td>
</tr>
<tr>
<td></td>
<td>NMP 0.0100 – 0.1500</td>
<td>NMP 0.0013 – 0.0068</td>
<td>NMP 0.0068</td>
</tr>
</tbody>
</table>
Figure 5.1: Solubility Limits of EN4 and EN8 in THF and toluene
**Figure 5.2:** Solubility Limits of SWNT, BN-ZG, BNNT, and FBNNT in the studied solvents
B. Refractometry

The measurement of dn/dc was verified using a known polystyrene (PS) standard in THF, as described in Chapter 4. All of the nanoparticle solutions were sonicated and well dispersed prior to measurement. Refractometry measurements were completed at three different wavelengths, and a Cauchy Plot was constructed in order to determine the dn/dc at a desired wavelength. In this case 685 nm is of interest, since the light scattering data was collected at this wavelength. The dn/dc of the solutions studied are summarized in Table 5.3, and the Cauchy Plots are attached in Appendix B.

Table 5.3: dn/dc of the solutions studied at 685 nm (ml/g)

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>THF</th>
<th>Toluene</th>
<th>MEK</th>
<th>CHP</th>
<th>NMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN-ZG</td>
<td>0.0975</td>
<td>0.0694</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FBNNT</td>
<td>0.1272</td>
<td>0.0093</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BNNT</td>
<td>0.2572</td>
<td>0.1743</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EN4</td>
<td>0.0918</td>
<td>0.0049</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EN8</td>
<td>0.0252</td>
<td>0.0037</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWNT</td>
<td></td>
<td></td>
<td></td>
<td>0.2600</td>
<td>0.1055</td>
</tr>
</tbody>
</table>
C. Density

Calibration for the gas pycnometer is described in detail in Chapter 4. All of the measurements were carried out with helium flow through gas at 25 °C, the same temperature as the light scattering and refractometry experiments. The measured densities of the boron containing nanoparticles and SWNTs are summarized in Table 5.4. The densities of the SWNT and BN-ZG compare well to literature values, keeping in mind that both BN-ZG and SWNTs may vary slightly due to diameter, length differences, etc (22-23). All other boron containing particles and the pre-polymers had unknown densities. The density of the pre-polymers was determined by careful weighing of samples with known volume, as previously described in Chapter 2, since these materials were viscous liquids (Table 5.5).
Table 5.4: Densities of the Nanoparticle Samples

<table>
<thead>
<tr>
<th>Sample Tested</th>
<th>Mass Measured (grams)</th>
<th>Volume Determined (mL)</th>
<th>Density Determined (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN-ZG</td>
<td>0.214</td>
<td>0.0697</td>
<td>3.07</td>
</tr>
<tr>
<td>BNNT</td>
<td>0.028</td>
<td>0.0175</td>
<td>1.62</td>
</tr>
<tr>
<td>FBNNT</td>
<td>0.030</td>
<td>0.0181</td>
<td>1.66</td>
</tr>
<tr>
<td>SWNT</td>
<td>0.165</td>
<td>0.1455</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Table 5.5: Densities of the Pre-Polymer Samples

<table>
<thead>
<tr>
<th>Sample Tested</th>
<th>Density (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EN4</td>
<td>0.903</td>
</tr>
<tr>
<td>EN8</td>
<td>0.894</td>
</tr>
</tbody>
</table>
D. Static Light Scattering Results

Static light scattering was then completed to determine the second virial coefficient, $A_2$ of the nanoparticle/solvent pairs. Zimm plots were used to obtain $A_2$ from the slope of the line as the scattering angle approaches zero (the green line in the attached Zimm plots, as shown in Appendix C) (24). The apparent molecular weight and $R_g$ of the nanoparticles in solution were also obtained from the Zimm Plots and are also presented Appendix C. The SWNTs in NMP and CHP were first centrifuged in order to remove large aggregates. The remaining solutions were clear after sonication, and they were measured (Table 5.6).

**Table 5.6: Concentrations Measured with Static Light Scattering (mg/mL)**

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>THF</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN-ZG</td>
<td>0.002 – 0.010</td>
<td>0.020 – 0.058</td>
</tr>
<tr>
<td>FBNNT</td>
<td>0.020 – 0.160</td>
<td>0.020 – 0.160</td>
</tr>
<tr>
<td>BNNT</td>
<td>0.020 – 0.180</td>
<td>0.020 – 0.200</td>
</tr>
<tr>
<td>EN4</td>
<td>0.780 – 5.50</td>
<td>1.50 – 3.50</td>
</tr>
<tr>
<td>EN8</td>
<td>0.300 – 6.90</td>
<td>0.900 – 6.50</td>
</tr>
<tr>
<td>CHP</td>
<td>0.0014 – 0.0206</td>
<td>0.0013 – 0.0068</td>
</tr>
<tr>
<td>SWNT</td>
<td>0.0014 – 0.0206</td>
<td>0.0013 – 0.0068</td>
</tr>
</tbody>
</table>
E. Determination of $\chi$ and Physical Observations

The solute-solvent interaction parameter of each sample was calculated using Equation 5.4. The experimentally determined $A_2$ and $\chi$ values are summarized in Table 5.7 for each system, along with a description of sample’s appearance. The state of each sample was recorded 30 minutes after the sample was freshly prepared and sonicated. Many solutions were cloudy or had particle settling in the 3 highest concentrations prepared. FBNNT in THF, EN8 in THF, and EN8 in Toluene were clear at all of the concentrations studied. The remaining solutions were cloudy or had particle settling in the three highest concentrations prepared. The SWNTs also exhibited particle settling in all of the prepared concentrations; however, this particle settling was first observed after storing the samples for 1 week in the freezer.
Table 5.7: Sample appearances, $A_2$, and $\chi$

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Solvent</th>
<th>Appearance</th>
<th>$A_2$</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT</td>
<td>NMP</td>
<td>Clear/grey with settling</td>
<td>-6.19E-05</td>
<td>0.5076</td>
</tr>
<tr>
<td></td>
<td>CHP</td>
<td>Clear/grey with settling</td>
<td>-2.37E-5</td>
<td>0.5047</td>
</tr>
<tr>
<td>BN-ZG</td>
<td>THF</td>
<td>Cloudy higher conc</td>
<td>-3.93E-5</td>
<td>0.5302</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>Cloudy higher conc</td>
<td>-2.22E-5</td>
<td>0.5223</td>
</tr>
<tr>
<td>FBNNT</td>
<td>THF</td>
<td>Clear</td>
<td>-3.19E-5</td>
<td>0.5071</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>Settling higher conc</td>
<td>-2.12E-4</td>
<td>0.5619</td>
</tr>
<tr>
<td>BNNT</td>
<td>THF</td>
<td>Clear/grey</td>
<td>6.10E-5</td>
<td>0.4869</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>Some settling higher conc</td>
<td>-1.01E-4</td>
<td>0.5282</td>
</tr>
<tr>
<td>EN4</td>
<td>THF</td>
<td>Cloudy higher conc</td>
<td>-1.54E-4</td>
<td>0.5102</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>Settling higher conc</td>
<td>-4.56E-4</td>
<td>0.5397</td>
</tr>
<tr>
<td>EN8</td>
<td>THF</td>
<td>Clear/yellow</td>
<td>8.71E-4</td>
<td>0.4431</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>Clear/yellow</td>
<td>2.61E-5</td>
<td>0.4978</td>
</tr>
</tbody>
</table>
F. Determination of Hildebrand Solubility Parameters

This analysis was completed for each nanoparticle/solvent system studied to obtain the Hildebrand solubility parameter of the nanoparticle, where these results are presented in Table 5.8 including the solubility parameters of the solvents used in this work.

The Hildebrand solubility parameter was also calculated directly for the particles and pre-polymers with known molar attraction constants. Both Small’s and Hoy’s tabulated molar attraction constants were used in this calculation (21). These results are summarized in Table 5.9. The experimentally determined and calculated Hildebrand Solubility Parameters show good agreement, with deviation of less than 8%. Published solubility parameters for structurally similar boron containing compounds are also listed in Table 5.10 (25). The solubility parameters for these compounds range between 7.98 – 14.19 (cal/cm$^3$)$^{1/2}$. The solubility parameters determined in this work fall within this range, between 8.38 – 9.21(cal/cm$^3$)$^{1/2}$.

Additionally, it is known that solutes tend to dissolve in solvents that have solubility parameters that are similar in magnitude. With this guideline, a list of likely solvents that will readily disperse and dissolve the nanoparticles and pre-polymers of interest is presented in Table 5.11.
<table>
<thead>
<tr>
<th>Solvents and Nanoparticle</th>
<th>Hildebrand Solubility Parameter (cal/cm$^3$)$^{1/2}$</th>
<th>Hildebrand Solubility Error (cal/cm$^3$)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>9.520</td>
<td>----</td>
</tr>
<tr>
<td>Toluene</td>
<td>8.900</td>
<td>----</td>
</tr>
<tr>
<td>CHP</td>
<td>10.02</td>
<td>----</td>
</tr>
<tr>
<td>NMP</td>
<td>11.24</td>
<td>----</td>
</tr>
<tr>
<td>SWNT</td>
<td>10.36</td>
<td>± 0.0157</td>
</tr>
<tr>
<td>BN-ZG</td>
<td>8.590</td>
<td>± 0.0769</td>
</tr>
<tr>
<td>BNNT</td>
<td>9.060</td>
<td>± 0.5314</td>
</tr>
<tr>
<td>FBNNT</td>
<td>9.120</td>
<td>± 0.3159</td>
</tr>
<tr>
<td>EN4</td>
<td>9.060</td>
<td>± 0.4820</td>
</tr>
<tr>
<td>EN8</td>
<td>9.180</td>
<td>± 0.0811</td>
</tr>
</tbody>
</table>
Table 5.9: Calculated Hildebrand Solubility Parameters

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Hildebrand Solubility Parameter Small (cal/cm$^3$)$^{1/2}$</th>
<th>Hildebrand Solubility Parameter Hoy (cal/cm$^3$)$^{1/2}$</th>
<th>Hildebrand Solubility Parameter Extracted (cal/cm$^3$)$^{1/2}$</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>9.050</td>
<td>9.100</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>SWNT</td>
<td>10.10</td>
<td>10.10</td>
<td>10.36</td>
<td>2.5</td>
</tr>
<tr>
<td>EN4</td>
<td>-----</td>
<td>8.570</td>
<td>9.060</td>
<td>5.5</td>
</tr>
<tr>
<td>EN8</td>
<td>-----</td>
<td>8.490</td>
<td>9.180</td>
<td>7.8</td>
</tr>
</tbody>
</table>

Table 5.10: Known Solubility Parameters for Relevant Boron Containing Compounds

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Hildebrand Solubility Parameter</th>
<th>Hildebrand Solubility Parameter Extracted Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexaborane</td>
<td>8.750</td>
<td>8.380 – 9.210</td>
</tr>
<tr>
<td>Pentaborane</td>
<td>7.980</td>
<td></td>
</tr>
<tr>
<td>Boron Trichloride</td>
<td>14.19</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.11: Potential Suitable Solvents of each nanoparticle based on Similar Hildebrand Solubility Parameters

(MPa$^{1/2}$) = 2.0455 (cal/cm$^3$)$^{1/2}$

<table>
<thead>
<tr>
<th>Nanoparticle</th>
<th>Particle $\delta$ (MPa$^{1/2}$)</th>
<th>Solvent $\delta$ (MPa$^{1/2}$)</th>
<th>Solvents</th>
</tr>
</thead>
</table>
| FBNNT        | 18.65                           | 18.60                           | Diamyl phthalate  
Ethyl acetate  
Vinyl toluene  
cis-1,2-Dichloroethylene  
Isophorone |
| BNNT         | 18.53                           | 18.60                           | Diamyl phthalate  
Ethyl acetate  
Vinyl toluene  
cis-1,2-Dichloroethylene  
Isophorone |
| EN4          | 18.53                           | 18.60                           | Diamyl phthalate  
Ethyl acetate  
Vinyl toluene  
cis-1,2-Dichloroethylene  
Isophorone |
| EN8          | 18.77                           | 18.80                           | Ally acetate  
Benzene  
Propyl formate  
Ethyl Chloride  
Diacetone alcohol  
Trichloroethylene  
Tripropylene glycol |
| SWNT         | 21.19                           | 21.10                           | Acetaldehyde  
Acetic anhydride  
Aniline  
Butyric acid (iso)  
2,5-Hexanediaol  
Octyl alchol (normal) |
|              |                                  | 21.30                           | Cyclopentanone  
1,2-Dibromoethane |
| BN-ZG        | 17.56                           | 17.60                           | Butyl idoide (normal)  
Carbon tetrachloride  
Diethyl oxalate  
Ethyl acrylate  
Pine oil  
Triphenyl phosphate |
G. Solvent Screen for Boron Nitride Sheets

The solubility behavior of BN-ZG was studied in a range of solvents at room temperature. In these studies, solutions of 1 and 5 weight percent were prepared in each solvent. Samples were prepared in 10 mL of solvent in clean, pre-rinsed 14 mL scintillation vials. Observations of the solution characteristics were taken immediately upon mixing and 1 day later upon standing at room temperature.

The results and observations are presented in Table 5.12. Water and toluene were found to disperse BN-ZG the least. Immediately following mixing, the 1% solution of BN-ZG in water is cloudy white, and there is settling of the particles on the bottom of the vial. Nanoparticles are also floating on top around the meniscus in this solution. After 24 hours, the nanoparticles have settled to the bottom of the vial. The nanoparticles clearly clumped together in these two solvents, and there was also clear separation with the nanoparticles remaining at the bottom of the scintillation vial and the solvent remaining on the top (Figure 5.3). Bromobenzene, carbon tetrachloride, and carbon disulfide are also poor solvents, with separation of the boron nitride noticeable in the vials.

In contrast, ethyl acetate, methanol, and acetone were found to be the best of the solvents tested for the boron nitride nanoparticles (Figure 5.4). Immediately after preparing the 1% solutions, the solutions were cloudy. However, there was no settling of particles at the bottom of the scintillation vials. After 24 hours, there was only a very small amount of particle settling, and the solutions were transparent. The 5% solutions were slightly cloudy in color, and after 1 day, only a small layer of nanoparticles was resting on the bottom of the vial. Dimethyl sulfoxide and dimethyl formamide are also qualitatively good solvents for BN-ZG. The 1% solution remained moderately cloudy with slight particle settling after 24 hours of standing at
room temperature. The 5% solutions were also cloudy white with only a small amount of particle settling noticeable.

Ortho-dichlorobenzene was determined to be a fair solvent for the particles. 1% solutions remained cloudy white, with noticeable particle clumping after 1 day of standing. The 5% solutions showed phase separation of the particles, with the top portion of the vial remaining cloudy and white.

THF and toluene were also fair solvents. Both the 1% and 5% solutions were cloudy, but had particle settling after 24 hours.
**Table 5.12: BN-ZG Solvent Screen: Solvents Studied and Observations Summarized**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>1 wt% Observations after mixing</th>
<th>1 wt% After 24 hours</th>
<th>5 wt% Observations after mixing</th>
<th>5 wt% After 24 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>Cloudy/ no particle settling</td>
<td>Clear/ very small amount of settling</td>
<td>Cloudy/ particles settling</td>
<td>Slightly cloudy/ small particle layer on bottom</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>Very cloudy/ settling</td>
<td>Very cloudy/ settling</td>
<td>Very white and cloudy/particles visible around meniscus</td>
<td>Cloudy white/ particle settling</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>Cloudy/ settling</td>
<td>Very cloudy/ settling</td>
<td>Cloudy white/ settling</td>
<td>Cloudy white/ particles settled</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>Translucent/ settling</td>
<td>Moderate settling/ particles floating</td>
<td>Settling/ floating around meniscus</td>
<td>Cloudy white/ settling</td>
</tr>
<tr>
<td>Ortho-dichlorobenzene</td>
<td>Cloudy/ no settling</td>
<td>Cloudy and wispy</td>
<td>Very cloudy white</td>
<td>Cloudy white/ settling</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>Cloudy/ no settling</td>
<td>Moderately cloudy/slight settling</td>
<td>Cloudy white slight settling.</td>
<td>Cloudy white/ precipitate on bottom.</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>Cloudy/ no settling</td>
<td>small amount of settling/ particles floating</td>
<td>Cloudy white with phase separation/ precipitate</td>
<td>Slightly cloudy and almost clear/precipitate on bottom</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>Cloudy/ no settling</td>
<td>One of the top three clearest solutions</td>
<td>Cloudy / phase separation -- precipitate takes up ¼ of vial.</td>
<td>Cloudy/small layer of precipitate</td>
</tr>
<tr>
<td>Methanol</td>
<td>Cloudy/ no settling</td>
<td>One of the top 3 clearest</td>
<td>Cloudy/moderate settling</td>
<td>Cloudy white/ Small layer of precipitate.</td>
</tr>
<tr>
<td>Toluene</td>
<td>Cloudy/ settling</td>
<td>Slightly cloudy/ settling</td>
<td>Cloudy / settling</td>
<td>Clear solution / particles all settling</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>Cloudy/ no settling</td>
<td>Clear/small amount of settling</td>
<td>Cloudy/ settling</td>
<td>Clear / particles settling</td>
</tr>
<tr>
<td>Water</td>
<td>Cloudy / settling and floating around meniscus</td>
<td>Clear/ settling and clumping</td>
<td>Cloudy / settling</td>
<td>Clear/ particles all settling and floating around meniscus</td>
</tr>
</tbody>
</table>
Figure 5.3: Solvent screen results for BN-ZG in water

<table>
<thead>
<tr>
<th></th>
<th>A)</th>
<th>B)</th>
<th>C)</th>
<th>D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% solution, immediately following mixing</td>
<td>1% solution, after 24 hours of standing</td>
<td>5% solution immediately following mixing</td>
<td>5% solution, after 24 hours of settling</td>
<td></td>
</tr>
</tbody>
</table>

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**Figure 5.4:** Solvent screen results for BN-ZG in methanol

<table>
<thead>
<tr>
<th></th>
<th>A)</th>
<th>B)</th>
<th>C)</th>
<th>D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% solution, immediately following mixing</td>
<td>1% solution, after 24 hours of settling</td>
<td>5% solution immediately following mixing</td>
<td>5% solution, after 24 hours of settling</td>
<td></td>
</tr>
</tbody>
</table>
5.6 Discussion

A completion of the refractometry, UV-Vis, light scattering, and physical observations of the nanoparticle and pre-polymer solutions exhibit good correlation between the obtained $A_2$, $\chi$, UV-Vis solubility limits, and physical observations for all of the systems studied.

For instance, three systems have positive $A_2$ and favorable $\chi < 0.5$, which indicates thermodynamically favorable mixing. BNNT in THF, EN8 in THF, and EN8 in toluene all have $\chi$ below 0.5, where the UV-Vis data is further evidence of the stability of the mixture, with all of these systems having high solubility limits relative to the other particle systems tested. These solutions were also observed to be clear, with no particle settling at any concentrations.

Moreover, BNNT in THF had the highest solubility of all of the nanotubes and sheets studied in the work. Additional concentrations were tested up to 1.0 mg/mL, with an experimentally determined solubility limit of 0.700 mg/mL and $\chi = 0.487$ for this system. In contrast, BNNT in toluene has a solubility limit of only 0.016 mg/mL, observed particle settling, and a $\chi > 0.5$.

Three systems have $\chi$ values close to 0.5, SWNTs in NMP, SWNTs in CHP, and FBNNT in THF. These systems were very close to being thermodynamically stable, and the solubility limit lies just below the concentrations of the sample measured by static light scattering. These samples were also observed to be clear with no particle settling. For example, with FBNNT in THF, a concentration range of 0.02 -0.16 mg/mL was studied with light scattering, and the solubility limit of this system is 0.08 mg/mL. This is a good fit with $\chi$, which was 0.507. Lower concentrations or the application of heat should render the system soluble.

It is surprising that the functionalization of the boron nitride nanotubes does not improve the dispersion when compared to the un-modified tubes. Previously, it was reported that
improved solubility in organic solvents was found for BNNT functionalized with stearoyl chloride (26-27), where Zhi et al, reported that FBNNTs were soluble in chloroform, N-N-dimethyl acetamide, THF, acetone, toluene, and ethanol, with concentrations ~ 0.5 mg/mL soluble in N-N-dimethyl acetamide (27). In this work, $\chi$ is > 0.5 for FBNNT in toluene with a low solubility limit that indicates a poor dispersion. Although $\chi$ is close to 0.5 for FBNNT in THF, the solubility limit in this system is much lower than in the un-modified BNNTs. The presence of the stearoyl side chains, which were expected to improve dispersion, actually promoted aggregation in these solutions, when compared to the un-modified BNNTs.

The remaining particle systems had $\chi$ > 0.5 and were cloudy or had particle settling at higher concentrations. The highest $\chi$ value is for FBNNT in toluene, 0.562. Settling was observed in this system at higher concentrations, with a solubility limit of 0.02 mg/mL.

The $\delta$ values that result from the analysis of the second virial coefficient of the nanoparticle in multiple solvents does not accurately predict the solubility behavior of the large nanoparticle sheets and tubes in other solvents (Table 5.13). $\delta$ for BN-ZG is 8.59 (cal/cm$^3$)$^{1/2}$, and possible good solvents based on this $\delta$ are carbon tetrachloride, diethyl oxalate, and ethyl acrylate. The solvent screen for this material, however, contradicts these predictions, indicating that carbon tetrachloride is not a good solvent, and particle settling was observed in the concentrations prepared. Good solvents from the solvent screen were ethyl acetate, methanol, and acetone, but the $\delta$ values of these solvents are dissimilar, 9.09, 14.52, and 9.92 (cal/cm$^3$)$^{1/2}$, respectively (Table 5.14).
Table 5.13: The values for $\chi$ and $\delta$ for the nanoparticle solutions studied

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Solvent</th>
<th>$\chi$</th>
<th>Solvent Solubility Parameter (cal/cm$^3$)$^{1/2}$</th>
<th>Hildebrand Solubility Parameter (cal/cm$^3$)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT</td>
<td>NMP</td>
<td>0.5076</td>
<td>11.24</td>
<td>10.36</td>
</tr>
<tr>
<td></td>
<td>CHP</td>
<td>0.5047</td>
<td>10.02</td>
<td></td>
</tr>
<tr>
<td>BN-ZG</td>
<td>THF</td>
<td>0.5302</td>
<td>9.52</td>
<td>8.59</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>0.5223</td>
<td>8.90</td>
<td></td>
</tr>
<tr>
<td>FBNNT</td>
<td>THF</td>
<td>0.5071</td>
<td>9.52</td>
<td>9.12</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>0.5619</td>
<td>8.90</td>
<td></td>
</tr>
<tr>
<td>BNNT</td>
<td>THF</td>
<td>0.4870</td>
<td>9.52</td>
<td>9.06</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>0.5283</td>
<td>8.90</td>
<td></td>
</tr>
<tr>
<td>EN4</td>
<td>THF</td>
<td>0.5102</td>
<td>9.52</td>
<td>9.06</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>0.5397</td>
<td>8.90</td>
<td></td>
</tr>
<tr>
<td>EN8</td>
<td>THF</td>
<td>0.4431</td>
<td>9.52</td>
<td>9.18</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>0.4978</td>
<td>8.90</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.13: Comparison of solubility parameters of the solvents tested in the BN-ZG Solvent Screen

<table>
<thead>
<tr>
<th>Particles and Solvents</th>
<th>Solubility Parameters (cal/cm$^3$)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN-ZG</td>
<td>8.59</td>
</tr>
<tr>
<td>Poor Solvents</td>
<td></td>
</tr>
<tr>
<td>water</td>
<td>23.4</td>
</tr>
<tr>
<td>toluene</td>
<td>8.90</td>
</tr>
<tr>
<td>bromobenzene</td>
<td>9.92</td>
</tr>
<tr>
<td>carbon</td>
<td></td>
</tr>
<tr>
<td>tetrachloride</td>
<td>8.60</td>
</tr>
<tr>
<td>carbon disulfide</td>
<td>10.02</td>
</tr>
<tr>
<td>Fair Solvents</td>
<td>THF</td>
</tr>
<tr>
<td>Good Solvents</td>
<td></td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>9.09</td>
</tr>
<tr>
<td>methanol</td>
<td>14.52</td>
</tr>
<tr>
<td>Acetone</td>
<td>9.92</td>
</tr>
<tr>
<td>dimethylformamide</td>
<td>12.14</td>
</tr>
</tbody>
</table>
The obtained $\delta$ for FBNNT, BNNT, and EN4 also do not correlate well with $\chi$. For BNNT, toluene is a poor solvent based on physical observations and $\chi > 0.5$; however, $\delta$ of the BNNT more closely matches that of toluene than THF, which is a more favorable solvent for BNNT. For the FBNNT and EN4, this was also the case, and the nanoparticle’s $\delta$ is closer in value to the $\delta$ of less favorable solvents.

$\delta$ of EN8 provides a more accurate parameter to predict good solvents. EN8 exhibits high solubility limits in both THF and toluene and $\chi$ values for both systems $< 0.5$. $\delta$ for EN8 is 9.18 (cal/cm$^3$)$^{1/2}$, and this value lies between the $\delta$ values of THF and toluene, 9.52 and 8.9 (cal/cm$^3$)$^{1/2}$. Other suitable solvents for EN8 based on $\delta$ are benzene and allyl acetate. The predicted solvent and the solvents studied in this work have many similarities. They are only capable of weak hydrogen bonding and are consequently nonpolar or polar aprotic, and they are either aromatic or contain highly polar functional groups. This is not surprising since EN8 is composed of 50% bis-(2-hydroxypropyl)aniline (BHPA) and 50% 2-ethyl-1,3-hexane diol, itself containing aromatic, hydroxyl, and amine groups.

There was also correlation between $\delta$ and $\chi$ for the SWNT systems. For both SWNTs in CHP and NMP, the concentrations of the solutions measured with static light scattering were just below the solubility limit, and results in $\chi$ values very close to 0.5. In CHP $\chi$ is 0.505, and in NMP $\chi$ is slightly higher, 0.508. The extracted $\delta$ for SWNTs is 10.36 (cal/cm$^3$)$^{1/2}$, and this value is closer to the $\delta$ value for CHP than NMP ($\Delta\delta = 0.3396$ for the CHP system; $\Delta\delta = 0.8826$ for the NMP system). A higher solubility limit, 0.0206 mg/mL, is also found in CHP, which correlates well with these results.

Work by Bergin, et al, has shown CHP can disperse nanotubes at a concentration as high as 3.5 mg/mL, while NMP disperses nanotubes up to a lower concentration of around 0.02
mg/mL (15-16). Similar results were found here, with CHP able to disperse higher concentration of SWNTs. The difference in the solubility limits from previous publications and this work is interpreted as a difference in the amount of amorphous carbon and metal content, diameter, and length of the nanotubes used in the work. These changes affect the measured solubility limits of the nanotubes (28).

Previous work has reported the Hildebrand solubility parameter of SWNTs in the range from 10.27-11.73 (cal/cm$^3$)$^{1/2}$, which also correlates well with our experimentally obtained $\delta$ (10, 15, 29). No universal solubility parameter has been determined for SWNTs though, since predicted good solvents based on $\delta$ are not always suitable. For instance, the dissolution behavior of SWNTs in a range of aromatic solvents with similar $\delta$ varies widely. SWNT solutions in ortho-dichlorobenzene shows a dispersion limit of 0.015 mg/mL, but solutions of monochlorobenzene are not as stable with a dispersion limit <0.001 mg/mL (29).

The Hildebrand-Scratchard equation, Equation 5.5, used to calculate $\delta$ assumes that all molecules are the same size and shape and that only London or dispersion interactions occur in the system. These assumptions work well for monodisperse samples and for small molecules, such as the polyhedral boranes tested in our preceding work (Chapter 4) and EN8 tested here, with good correlation between the experimentally determined $\delta$ for the particles and the ability of solvents with similar $\delta$ values to dissolve the nanoparticle.

For large particles, such SWNTs and BN-ZG, additional parameters are obviously necessary to define a range of suitable solvents that take into account specific interactions, such as hydrogen bonding, since polymers and solvents capable of $\pi-\pi$ interactions and H-bonding, such as ortho-dichlorobenzene, interact with SWNT walls via $\pi-\pi$ stacking have been shown to form stable dispersions (30-31).
Several studies have attempted to use Hansen solubility parameters, which take into account dispersive, polar, and hydrogen bonding interaction. Equation 5.7 shows the relationship of the Hansen solubility parameters to the Hildebrand solubility parameter (30-31).

\[ \delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \]  

(5.7)

However, work by Bergin and Cheng, et al, has shown that the Hanson solubility parameters also fail to provide a range of good solvents for SWNTs, (30-31). Polar solvents with high electron pair donicity, such as DMF and NMP were demonstrated to form stable dispersions with SWNTs, but dimethyl sulfoxide (DMSO) is not an effective solvent for SWNTs although it contains three lone pairs (31).

A consideration of surface energy proved to be more successful, with good solvents for SWNTs having similar surface tension, 40 mJ/m²; yet, this finding still fails to fully describe the solubility of nanotubes. CHP has the highest reported solubility in Bergin’s study, 3.5 mg/mL and similar surface tension to SWNTs, but NMP, which also has a similar surface tension, had a much lower solubility limit, indicating that although a consideration of surface energy is also important, these interactions do not completely describe the important factors that control the solubility of these systems.

Specific interactions that occur between the solvent molecules and nanotube surface may also be important; since the most successful solvents tested have amide structural units, pointing to a specific interaction (30-32). Work by Maeda, et al, studied a series of amines and found that dispersibility decreases in the order of primary, secondary, and tertiary amines (32). The authors suggest that the possible mechanism is that the amine nitrogen interacts significantly with the nanotube surface, with the estimated binding energy considerable between amines and SWNTs,
where the interaction between SWNTs and amines is sensitive to steric hindrance around the nitrogen atom (32).

Nanotubes and sheets are polydisperse in that a given sample contains a range of lengths and diameters, which also may affect $\delta$. The SWNTs studied in this work have 0.7-2.5 nm tube diameter and 0.5-5 µm length, and the BN-ZG and BNNTs samples also vary in composition with a range of $M_w$ and shapes. Work by Maiti and Usrey, et al, modeled the Hildebrand solubility parameters of SWNTs as a function of nanotube diameter. This work suggests that a wide range of $\delta$ exists in a typical nanotube sample ($\sim 8 – 31 \text{ MPa}^{1/2}$ for nanotube diameter $\sim 0.5 – 3 \text{ nm}$) and that $\delta$ scales with nanotube diameter (33-34).

A discussion regarding error is necessary when interpreting the results presented here. Static light scattering for samples that are non-dilute (i.e.: above the solubility limit of the solute), results in errors in the measured $R_g$ and $M_w$ due to the presence of aggregates, since there is a strong particle size dependence on the scattering intensity, shown in Equation 5.8, where $I$ is the scattering intensity and $d$ is the particle diameter (Chapter 4) (10-13, 35-42).

$$I \sim d^2 \quad (5.8)$$

Light scattering of the nanoparticle-solutions in this work were carried out on the initially prepared concentrations, which were not necessarily below the determined solubility limits of the nanoparticles, increasing the risk of interference from particle aggregation and affecting $R_g$. The range of sizes and shapes present in the nanotubes and sheets will also affect the measured $R_g$ and $M_w$, since the scattering intensity is sensitive to the presence of larger sized particles. Consequently, error in the measured $R_g$ and $M_w$ was high for the SWNT, BNNT, FBNNT, and BN-ZG solutions, and there is no correlation between $R_g$ and $\chi$ for this work. In Chapter 4, measured scattering errors were smaller, where lower $\chi$ values for the polyhedral borane
solutions correlate to lower $R_g$, and the lower $R_g$ in these systems indicate that there are fewer particles clumping (43-46).

However, the data collected for this work is consistent. Nanoparticle solutions that have $\chi < 0.5$ are also clear, free from particle settling. UV-Vis data supports the light scattering results, with higher solubility limits in systems with correspondingly lower $\chi$ values.

As a self-consistent check, the solubility parameters were also calculated using known molar attraction constants for SWNTs, EN4, and EN8. These calculations are all in good agreement with their experimentally determined counterparts. Additionally, the published $\delta$ values for the boron containing compounds were within the range of the determined solubility parameters for this work.

5.6 Conclusions

Static light scattering and refractometry experiments were completed on BNNTs, FBNNTs, and BN-ZG in THF and toluene. Polyurethane pre-polymers, EN4 and EN8, were also tested in THF and toluene, and SWNTs were examined in CHP and NMP, in order to serve as a self-consistent check of the data obtained, since information regarding their solubility behaviors was previously known. UV-Vis spectroscopy determines the concentrations and solubility limits of the systems studied. Gas pycnometry provides an accurate density of the polyhedral borane powders. The solute-solvent interaction parameter, $\chi$, and the Hildebrand solubility parameter, $\delta$, were determined from the data and quantify the solubility behavior and predict good solvents based on similar $\delta$.

Three systems have $\chi < 0.5$ and are thermodynamically soluble: BNNT in THF, EN8 in THF, and EN8 in toluene. It is not surprising that EN8 has good solubility in both THF and
toluene, since it is comprised of small aromatic molecules that interact favorably with solvents that are also aromatic or contain highly polar functional groups. The high solubility of BNNT in THF was less expected, and additional concentrations out to 1 mg/mL were tested in order to obtain its solubility limit, ~ 0.700 mg/mL, which is the highest value for any of the boron sheets and tubes.

The least soluble system (i.e.: highest \( \chi \) value obtained) was surprising. FBNNT, functionalized with stearoyl chloride, has a \( \chi \) value of 0.562 and a low solubility limit in toluene. Likewise, FBNNT in THF has \( \chi > 0.5 \) and a low solubility limit. The addition of the stearoyl side groups does not improve dispersion and leads to increased aggregation in these systems, when compared to the un-modified BNNT systems.

For all of the solutions, the scattering data collected is consistent with the UV-Vis solubility limits and physical observations. There is also good qualitative agreement between \( \chi \), \( A_2 \), and solution appearance, since clear solutions have favorable \( \chi \) values and positive \( A_2 \). A solvent screen was also conducted for BN-ZG and the data collected agree with \( \chi \), indicating that both THF and toluene were not suitable solvents for BN-ZG.

For the small molecular pre-polymer, EN8, the determined Hildebrand solubility parameter correlates well with \( \chi \), with the obtained \( \delta \) close to both THF and toluene, which are both good solvents with \( \chi < 0.5 \). Predicted solvents based on \( \delta \) and the solvents studied in this work also all had similar properties, such as the presence of polar functional groups, aromaticity, and weak hydrogen bonding capability. As mentioned, this is rather anticipated, since EN8 itself is composed of small aromatic molecules.

But for the remaining particles, this correlation breaks down, and the quantitative use of the solubility parameter to predict solution behavior of the nanotubes and boron nitride sheets is
more suspect. From the BN-ZG solvent screen, both good and bad solvents had a wide range of δ values. Good solvents range from 9.09-14.52 (cal/cm³)⁴/², while poor solvents also encompassed this range, from 8.6-23.4 (cal/cm³)⁴/². Based on the obtained δ, carbon tetrachloride is a suitable candidate for dissolution, but the solvent screen showed particle settling in all prepared concentrations. Similarly, THF is a favorable solvent for BNNT, but BNNT’s δ more closely matched toluene’s δ, which contradicts the findings.

For SWNTs, there is a better correlation. Based on χ and the solubility limits, CHP is found to be a more thermodynamically favorable solvent than NMP, and the extracted δ for SWNTs is also closer to the δ value for CHP (Δδ = 0.3396 for the CHP system). But predicting good solvents based on δ for SWNTs is not as consistent. Ausman, et al, performed UV-Vis solubility studies of SWNTs in organic solvents and found that cyclopentanone, a predicted good solvent in this work, was only a fair solvent for SWNTs, when compared to dispersions prepared in DMF and NMP (46). The use of a universal solubility parameter to predict solution behavior for large particles is not well established, since current theory does not account for additional non-covalent interactions, such as π-π interactions, which are known to be important factors for the dissolution of SWNTs and graphene (29, 31-32, 47).

As a self-consistent check, δ was calculated for the pre-polymer and SWNT solutions using equation 5.6. Differences between the calculated and the experimentally obtained δ in this work were minimal, with error less than 8% in all cases. Boron containing particles with published δ are also referenced, and the boron particles measured here fall within this range.

However, the close agreement of the physical observation, UV-Vis, and χ values shows that light scattering in conjunction with refractometry is a powerful method for quantifying the thermodynamic solubility behavior of nanoparticle systems, and the determination of the high
solubility limit of BNNT in THF is important for future nanocomposite development, that require fine dispersions of nanotubes in solution during processing.
5.7 References


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Chapter 5 Appendix A: UV-Vis Measurements for the nanoparticle solutions
### Supplemental Figure A4.1: UV-Vis Data and a) Beer’s Law Baseline for BN-ZG in THF; b) the change in absorbance of initial concentrations
**Baseline Samples**

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**Supplemental Figure A4.2:** UV-Vis Data and a) Beer’s Law Baseline for BN-ZG in Toluene; b) the change in absorbance of initial concentrations

\[ y = 3.2763x \]

\[ R^2 = 0.9887 \]
Supplemental Figure A4.3: UV-Vis Data and a) Beer’s Law Baseline for FBNNT in THF; b) the change in absorbance of initial concentrations
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### Settled Samples

Supplemental Figure A4.4: UV-Vis Data and a) Beer’s Law Baseline for FBNNT in Toluene; b) the change in absorbance of initial concentrations
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Supplemental Figure A4.5: UV-Vis Data and a) Beer’s Law Baseline for BNNT in THF; b) the change in absorbance of initial concentrations
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**Supplemental Figure A4.6:** UV-Vis Data and a) Beer’s Law Baseline for BNNT in Toluene; b) the change in absorbance of initial concentrations
Supplemental Figure A4.7: UV-Vis Data and a) Beer’s Law Baseline for EN4 in THF; b) the change in absorbance of initial concentrations
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**Supplemental Figure A4.8**: UV-Vis Data and a) Beer’s Law Baseline for EN4 in Toluene; b) the change in absorbance of initial concentrations
### Supplemental Figure A4.9: UV-Vis Data and a) Beer’s Law Baseline for EN8 in THF; b) the change in absorbance of initial concentrations

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### Supplemental Figure A4.10: UV-Vis Data and a) Beer’s Law Baseline for EN8 in Toluene; b) the change in absorbance of initial concentrations
### Supplemental Figure A4.11

UV-Vis Data and a) Beer’s Law Baseline for SWNTs in CHP; b) the change in absorbance of initial concentrations

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\[ y = 16.174x \]
\[ R^2 = 0.9931 \]
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### Centrifuged Samples

**Supplemental Figure A4.12:** UV-Vis Data and a) Beer’s Law Baseline for SWNTs in NMP; b) the change in absorbance of initial concentrations
Chapter 5 Appendix B: Refractometer Data and Cauchy Plots
Supplemental Figure B4.1: Refractometer Data and Cauchy Plot for BN-ZG in THF
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**BN-ZG in Toluene Cauchy Plot**

\[ y = -5E+06x + 0.1795 \]

**Supplemental Figure B4.2:** Refractometer Data and Cauchy Plot for BN-ZG in Toluene
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</table>

**FBNNT in THF Cauchy Plot**

\[ y = -1E+07x + 0.3402 \]

**Supplemental Figure B4.3:** Refractometer Data and Cauchy Plot for FBNNT in THF
### FBNNT in Toluene Cauchy Plot

\[ y = -2 \times 10^7 x + 0.4355 \quad R^2 = 0.9868 \]

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**Supplemental Figure B4.4:** Refractometer Data and Cauchy Plot for FBNNT in Toluene
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Supplemental Figure B4.5: Refractometer Data and Cauchy Plot for BNNT in THF
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Supplemental Figure B4.6: Refractometer Data and Cauchy Plot for BNNT in Toluene
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**EN4 in THF Cauchy Plot**

$y = 2E+06x + 0.0492 \quad R^2 = 0.975$

**Supplemental Figure B4.7**: Refractometer Data and Cauchy Plot for EN4 in THF
Supplemental Figure B4.8: Refractometer Data and Cauchy Plot for EN4 in Toluene
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<th>( \text{dn/dc (ml/g)} )</th>
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Supplemental Figure B4.9: Refractometer Data and Cauchy Plot for EN8 in THF
Supplemental Figure B4.10: Refractometer Data and Cauchy Plot for EN8 in Toluene
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Supplemental Figure B4.11: Refractometer Data and Cauchy Plot for SWNTs in CHP
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**Supplemental Figure B4.12:** Refractometer Data and Cauchy Plot for SWNTs in NMP
Chapter 5 Appendix C: Static Light Scattering Data
### Measured Values

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**Supplemental Figure C4.1:** Light Scattering Data and Zimm Plot for BN-ZG in THF
### Measured Values

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**Supplemental Figure C4.2**: Light Scattering Data and Zimm Plot for BN-ZG in Toluene
Supplemental Figure C4.3: Light Scattering Data and Zimm Plot for FBNNT in THF
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**Supplemental Figure C4.4:** Light Scattering Data and Zimm Plot for FBNNT in Toluene
### Measured Values

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**Supplemental Figure C4.5:** Light Scattering Data and Zimm Plot for BNNT in THF
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**Supplemental Figure C4.6:** Light Scattering Data and Zimm Plot for BNNT in Toluene
### Measured Values

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**Supplemental Figure C4.7:** Light Scattering Data and Zimm Plot for EN4 in THF
### Measured Values

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**Supplemental Figure C4.8:** Light Scattering Data and Zimm Plot EN4 in Toluene
### Measured Values

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Supplemental Figure C4.10: Light Scattering Data and Zimm Plot for EN8 in Toluene
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**Supplemental Figure C4.11:** Light Scattering Data and Zimm Plot for SWNT in NMP
### Measured Values

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**Supplemental Figure C4.12:** Light Scattering Data and Zimm Plot for SWNT in CHP
Chapter 5 Appendix D: Determination of Hildebrand Solubility Parameters
Solvent | Solvent $\delta$ (cal/cm$^3$)$^{1/2}$ | BN-ZG $\delta$ (cal/cm$^3$)$^{1/2}$ | $\Delta \delta$ | $\chi$  
--- | --- | --- | --- | ---  
THF | 9.520 | 8.585 | 0.9347 | 0.5302  
Toluene | 8.900 | 8.585 | 0.3147 | 0.5223  

**Supplemental Figure D4.1:** Hildebrand Solubility Parameter Data and Plot of $(\delta_1^2/RT - \chi/V_1)$ as a Function of $\delta_1$ for BN-ZG
<table>
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<th>$\Delta\delta$</th>
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**Supplemental Figure D4.2:** Hildebrand Solubility Parameter Data and Plot of $(\delta_1^2/RT - \chi/V_1)$ as a Function of $\delta_1$ for FBNNT

\[
y = 0.0308x - 0.1465
\]
<table>
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<th>Solvent</th>
<th>Solvent δ (cal/cm³)¹/²</th>
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<th>χ</th>
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Supplemental Figure D4.3: Hildebrand Solubility Parameter Data and Plot of \((δ_1^2/RT - χ/V_1)\) as a Function of δ₁ for BNNT
### Table

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### Equation

$$y = 0.0306x - 0.1424$$

### Graph

Supplemental Figure D4.4: Hildebrand Solubility Parameter Data and Plot of $\left(\delta_1^2/RT - \chi/V_1\right)$ as a Function of $\delta_1$ for EN4
<table>
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**Supplemental Figure D4.5:** Hildebrand Solubility Parameter Data and Plot of $(\delta_1^2/RT - \chi/V_1)$ as a Function of $\delta_1$ for EN8
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**Supplemental Figure D4.6**: Hildebrand Solubility Parameter Data and Plot of $(\delta_1^2/RT - \chi/V_1)$ as a Function of $\delta_1$ for SWNT
Chapter 6

Comparison of Purification Methods of Single Walled Carbon Nanotubes
6.1 Introduction

There are several techniques to produce sizeable quantities of single walled carbon nanotubes (SWNTs), including arc discharge, laser ablation, and chemical vapor deposition. All of these processes involve high pressure, high heat, a carbon source, and a metal catalyst (1-2). In the laser ablation process, for example, a pulsed laser vaporizes a graphite target in a high temperature reactor, and the nanotubes and by-products are collected via condensation on a cold finger downstream using helium flow-through gas (1-2). This method was developed by Richard Smalley and co-workers at Rice University and has been improved upon by using a composite of graphite and a metal catalyst, such as cobalt or nickel, to give yields as high as 70% SWNTs (1-2).

A complex mixture of SWNTs, impurities and by-products are the result of the synthesis process, including carbon nanoparticles, fullerenes, graphitic and amorphous carbon, and leftover metal catalyst, which complicates the goal of isolating pure SWNTs from the reaction product. The impurities also vary from sample to sample, since each synthesis method employs different types of metal catalysts, therefore the products may contain iron, nickel or cobalt. Also, depending on the procedure, various ratios of multi-walled carbon nanotubes and SWNTs of varying lengths and diameters are produced (1-2). Removal of these impurities and the separation of nanotubes based on size are important to the production of novel materials (1-3).

There are currently only a few established methods to remove both metal and carbon impurities from as-produced batches of SWNTs (AP-SWNTs). The AP-SWNTs are most commonly purified by refluxing in acids (4-6). A typical procedure involves the use of concentrated acids, such as nitric or hydrofluoric, refluxing for ~24 hrs, followed by filtration to
collect the purified nanotube material (4-6). A subsequent wash with piranha solution (sulfuric acid and 30% w/w hydrogen peroxide) or concentrated hydrochloric acid (HCl) removes residual metal catalyst. Specialized ovens are then used to heat samples above 350 ºC to remove the remaining amorphous carbon. The material obtained is high in SWNT content with negligible carbonaceous impurities and catalyst remaining (4-6), but the yield is often low (< 10%).

Several issues arise with this procedure though. Strong acids damage nanotubes by creating defects on the side-walls of the tubes through oxidation, including functionalizing the nanotubes with carboxylic groups, and altering the electrical and thermal properties of the collected material (5). Annealing with temperatures in excess of 350 ºC also creates problems, since Bucky paper forms, and the nanotubes must be mechanically homogenized to re-disperse in solvent (5).

Purification by centrifugation in surfactants is another common technique and is less destructive to the tips and sidewalls of SWNTs, since surfactants, such as sodium dodecyl sulfate (SDS), do not chemically react with SWNTs. The as-produced material is sonicated for upwards of 2 hrs in surfactants to disperse, and then the material is centrifuged for several hours. Both low speed and high speed centrifugation have been shown to separate amorphous carbon, carbon nanoparticles, and SWNTs, where filtration is used to collect fractions of the purified material (7).

Damage from prolonged ultrasonication is a concern, arising in the form of kinks and defects in the sidewalls of SWNTs. Raman Spectroscopy studies have shown that sonication for greater than 30 minutes results in such damage and should be avoided (8-9). Also of concern is the use of large quantities of surfactants, which is not environmentally “green” (10-11). Several rounds of sonication and centrifugation in surfactant are required to isolate purified nanotubes,
and large quantities of water are required to wash the recovered SWNTs to remove the added chemicals, since their presence may influence the physical properties of the tubes and induce unwanted chemical reactions (10-11). Selection of the filter paper with the proper pore size is also difficult and a matter of trial and error to efficiently separate the carbon nanoparticles and carbonaceous impurities from the soap solutions (10-11).

Several variants of this technique have garnered much attention in recent years, owing to the successful isolation of SWNTs based on nanotube size. In an approach adapted from biochemical techniques, Arnold, et al, used density gradient ultracentrifugation to separate SWNTs (12). The density gradient exploits the difference in the densities among SWNTs of different structures, and in solutions of sodium cholate, sodium deoxycholate, and sodium taurodeoxycholate there was a trend of increasing density with increasing diameter for SWNTs. Semi-conducting SWNTs with diameters of 7.6 and 8.3 Å were isolated with this approach (12).

Similar results have been achieved with a combination of centrifugation and chain wrapping. In a study by Witus, et al, sonication of SWNTs in surfactant and peptide sequences led to the isolation of SWNTs based on diameter, with smaller SWNTs isolated in solutions of peptides coated with cationic sequences and larger diameter tubes collected with centrifugation in sodium dodecyl benezenesulfonic acid (SDBS) (5). Also, work using column chromatography in conjunction with DNA chain wrapping and centrifugation has shown promise in separating tubes of various sizes and chirality (13). However, methods involving chain wrapping are hard to replicate on a large scale for industrial purposes because the large amounts of tailored peptide and DNA sequences are expensive, and it is difficult to completely remove the added materials following isolation of the tubes (12).
Ideally, purification will remove metal and carbonaceous impurities without damaging the sidewalls of SWNTs and result in their fine dispersion in a suitable medium, ready for their combination with polymers to form novel nanocomposite materials. This is important because well-dispersed nanotubes will result in their homogenous dispersion in a polymer matrix (i.e.: via solution casting), forming materials that take full advantage of the electrical and thermally conductive properties inherent to SWNTs (2). It is useful to have a limited number of purification steps, without expensive tailored reagents, to reduce costs and to ease replication on a large industrial scale.

A promising study by Nepal, et al, used a known good solvent for SWNTs, o-dichlorobenzene (o-DCB), to purify AP-SWNTs (11). Through several rounds of ultracentrifugation and filtration in o-DCB, purified SWNTs were isolated, free of impurities as evidenced with scanning electron microscopy images (SEM). The isolation of purified SWNTs with centrifugation in o-DCB suggests that other solvents will separate nanotubes. More commonly available solvents, such as dimethyl formamide (DMF) or acetone, are of interest for this purpose, since they are cost effective and readily available. Known thermodynamically favorable solvents for SWNTS, such as cyclohexyl pyrrolidone (CHP) or N-methyl pyrrolidone (NMP), are also attractive choices, as they form stable dispersions with high solubility limits (14-15). There will not be a need to remove chemicals if SWNTs are purified in a good solvent, since the final product will simply consist of a fine dispersion of SWNTs ready for combination with a polymer.

At present, there is little work comparing and contrasting the effectiveness and efficiency of the available purification techniques to remove carbon and metal impurities. With a wide range of applications for SWNTs, it is unclear which technique is best suited for producing
nanotubes for a given application. The purpose of this work, therefore, is to subject a sample of AP-SWNTs to the two most common purification techniques, acid purification and purification by centrifugation in surfactant (1% sodium dodecyl sulfate [SDS]), and to assess the efficiency of the two methods. Since purification by centrifugation in common solvents is of interest, an attempt to purify SWNTs in DMF was also made, since DMF has been shown to form stable dispersions with SWNTs through sonication. (16)

A protocol to assess the purity of SWNTs samples is well established, taking advantage of several analytical techniques (17-22). Thermal gravimetric analysis (TGA) is routinely used to determine the purity of SWNTs, since it documents the loss of chemical impurities with increasing temperature. As impurities are removed from the sample, there is a shift to a higher degradation temperature. In a study by Arepalli, et al, for instance, removal of contaminants in a batch of AP-SWNTs shifts the decomposition of the AP-SWNT sample from ~400 °C to ~600 °C for the purified tubes (20). Scanning electron microscopy (SEM) is used to visualize the presence of impurities. Metals appear as bright spots and spherical carbon nanoparticles are clearly distinguished (21). Electrical resistivity testing using a four point resistivity meter can measure the electrical resistance of the purified material, which is a measure of how strongly a material opposes the flow of an electric current. Equation 6.1 provides the inverse relationship between the resistivity, $\rho$, and the conductivity, $\sigma$.

$$\sigma = \frac{1}{\rho} \quad (6.1).$$

Since SWNTs are among the most electrically conductive materials known, as the purity of SWNTs increases, the electrical conductivity likewise increases and the resistance decreases (2). Raman spectroscopy is used to assess the presence of defects and to assess purity through the measurement of the D band (~1350 cm$^{-1}$), a peak that is sensitive to structural defects in the
graphitic sp² network, and the G band (~1600 cm⁻¹), which is sensitive to the electronic nature of the nanotubes. The intensity of the G band for purified samples increases relative to that of samples containing impurities. A shift in the G band to higher wavelength is also indicative of a SWNT enriched sample (25). Finally, UV-Vis-Nir spectroscopy (λ = 600 to 2000 nm) is routinely used to determine the solubility limits and to quantify the extent of exfoliation of SWNT samples. Nanotubes that are more exfoliated have sharper optical transitions in their spectra that indicate the nanotubes are debundled. A study by Itkis, et al, illustrates this point, with the optical transitions of AP-SWNTs have lower absorbance than the purified materials (22). The work by Itkis also indicates that the purified material that undergoes further annealing has the highest absorbance, since more carbonaceous impurities were oxidized (22). All of these techniques are described in more detail in Chapter 2.

Therefore SEM, UV-Vis, TGA, Raman spectroscopy, and electrical resistivity testing were completed to characterize the products of the purification procedures tested in this work. An exception was the SWNTs purified by centrifugation in DMF. Only UV-Vis-Nir and SEM data are presented for this purification method.
Experimental

The As-Produced SWNTs (AP-SWNTs) were synthesized using laser ablation with Ni/Co catalyst at Oak Ridge National and used as received. The materials used in this work and the acid and centrifugation procedures are described in detail in Chapter 2.

SEM images were collected using samples prepared on clean glass slides with double-sided tape. A low voltage was used to collect the images, 2.0 KV under vacuum. Samples prepared on glass slides were also examined with Raman spectroscopy and electrical resistivity. Ten independent resistivity measurements were collected from each sample and averaged. Raman spectroscopy was completed using a 100 watt laser ($\lambda = 633$ nm), with a spectra range between 100-3200 nm. Six measurements from different parts of the sample were collected, and the data was averaged to obtain the final Raman spectra.

Samples that were examined with UV-Vis-NIR were prepared by carefully weighing the purified material on a microbalance to achieve a concentration of 0.02 mg/mL in DMF. The DMF baseline was subtracted from each measurement, and data at 1669 nm was selected to normalize the data. Semi-conducting nanotubes give rise to characteristic transitions in the UV-Vis-NIR region from the additional absorption due to van Hove singularities as described in Chapter 2. In all of the spectra measured here, the $S_{11}$ peak is the most prominent feature and was selected for analysis and discussion.

The AP-SWNTs and purified samples were studied using TGA, ramping the temperature at a rate of 10 °C/min from room temperature to 900 °C in the presence of oxygen. The weight loss is monitored as the temperature increases, and a derivative weight loss curve is used to identify the point where the rate of weight loss is greatest. A limited amount of purified material was collected with the purification procedures in this work. Materials analyzed with TGA were
removed from the filter papers, as previously described in Chapter 2 and dried in the vacuum oven at 100 °C prior to measurements. However, when the amount of sample was limited, the filter paper with SWNT material attached were cut and analyzed with the TGA instrument. The filter papers degrade at ~200°C and did not interfere with the degradation peaks associated with the nanotubes, but the presence of the filter paper made quantifying the wt% of the nanotube material difficult to ascertain. A qualitative discussion of the TGA results is thus presented, and the degradation temperature of the nanotube material is the primary parameter presented. Lastly, the yield of each purification procedure was calculated by dividing the weight of the final “purified” product collected by the weight of the AP-SWNT starting material.
6.3 Results

A. Filtration

Several types of filter papers were tested during this project, with pore sizes ranging from 0.08 to 0.5 µm, to determine the most suitable candidate for collecting the SWNTs after each purification step. The results are summarized in Table 6.1. Ultimately, the pore size played a lesser role in the filtration process. The affinity of the components in the purified solution for the filter paper was the dominant driving force in determining whether or not the solution readily passes through the filter pores.

Polycarbonate filters (0.08 µ) were the most successful at collecting SWNTs from the acidic purification method. Dilute acid solutions pass easily through the paper with the filtration process taking ~2 hrs to filter 500 mL of solution, and the recovered SWNTs are simply scraped off of the paper with a spatula. In contrast, PTFE filters, with a larger pore size (0.5 µ) required 2 or 3 days to filter the same amount of liquid, and sonication in DMF and solvent evaporation was necessary to remove the collected nanotubes. Polycarbonate filters were also the most suitable choice for collecting SWNTs purified in DMF, since the process was straightforward and faster.

Filtering 1% SDS solutions proved to be more challenging. The PTFE filters did not filter the 1% SDS solutions, and the polycarbonate filter paper required 24 hours to filter 500 mL solution. Filtration was faster with 0.1 µ nitrocellulose membrane filters, taking ~ 4 hrs for 500 mL to filter solution and was thus chosen.

Collecting the nanotube material from the nitrocellulose paper, however, was not as direct. It was necessary to dissolve the filter paper to remove the SWNTs by washing excessively with
acetone and methanol. The sticky nature of the filter paper made this process difficult, requiring repeated washing to remove remnants.

Table 6.1: Summary of Filter Papers Tested

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<thead>
<tr>
<th></th>
<th>Polycarbonate</th>
<th>PTFE</th>
<th>Nitrocellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pore Size</strong></td>
<td>0.08 micron</td>
<td>0.5</td>
<td>0.1 micron</td>
</tr>
<tr>
<td><strong>Disadvantages</strong></td>
<td>1) Slow to filter 1% SDS solution</td>
<td>1) Difficult to remove SWNTs from the filter paper</td>
<td>1) Messy process to dissolve the filter paper and collect the SWNTs</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2) Not able to filter 1% SDS solution</td>
<td></td>
</tr>
<tr>
<td><strong>Advantages</strong></td>
<td>1) Easy to recover nanotubes</td>
<td>1) Able to filter dilute acid solutions—but slowly</td>
<td>1) Able to filter 1% SDS solutions</td>
</tr>
<tr>
<td></td>
<td>2) Filters dilute acid solutions with ease</td>
<td></td>
<td>2) Filter paper dissolves in common solvents</td>
</tr>
</tbody>
</table>

B. Scanning Electron Microscopy (SEM)

Figure 6.1 shows a typical SEM image of the AP-SWNTs. From this figure, bundled SWNTs, carbon impurities, and spherical carbon nanoparticles are clearly observed. Also, bright metal particles are embedded within the nanotubes.

For the samples purified in 1% SDS, fractions were collected and analyzed from both the supernant and the sediment. SEM images of the sediment, shown in Figure 6.2, reveal an increase in the SWNT content relative to the AP-SWNTs. However, it is clear from the
magnified image at the 400 nm scale (Figure 6.2a) that the SWNTs remain bundled with spherical carbon nanoparticles. In contrast, the supernant was devoid of SWNTs, as shown in Figure 6.3, with only spherical carbon nanoparticles present in the SEM image.

Purification by centrifugation in DMF resulted in the opposite trend, with the spherical nanoparticles collected in the sediment, and the nanotubes enriched in the supernant. This is shown in Figures 6.4 and Figure 6.5, showing SEM images of the fractions. Again, the nanotubes remained associated with spherical particles, as in the purification with 1% SDS.

Finally, analysis of the SWNTs purified with acid treatment indicates that the samples were highly enriched with SWNTs and nearly completely devoid of spherical particles. The SEM image in Figure 6.6 shows SWNTs, with only a few remaining particles of metal catalyst.
Figure 6.1: SEM Image of the AP-SWNTs
Figure 6.2: SEM image of the Sediment Collected from 1% SDS Centrifugation; a) 400 nm scale; b) 1.00µm scale
Figure 6.3: SEM Image of the Supernant Collected from 1% SDS Centrifugation; a) 200 nm scale; b) 500 nm scale
Figure 6.4: SEM Image of the Supernant Collected from Centrifugation in DMF
Figure 6.5: SEM Image of the Sediment Collected from Centrifugation in DMF
Figure 6.6: SEM Image of the SWNTs Collected from Acid Purification
C. Electrical Resistivity

The resistivity data for the material collected in 1% SDS is presented in Figure 6.7. The measured resistance of these purified SWNT exhibits a decrease from that of the AP-SWNT, from 16.9 to 14.0 $\Omega\text{m}$. In contrast, the resistance for the nanoparticles that are obtained from the supernant, which is enriched in spherical carbon nanoparticles, increased to 26.3 $\Omega\text{m}$.

Resistivity data was not collected for the acid or DMF purified nanotubes in this study.
Figure 6.7: The Measured Resistance of a) AP-SWNTs; b) the 1% SDS Supernatant; c) the 1% SDS Sediment
D. UV-Vis-NIR

The $S_{11}$ peak is the most prominent feature in the UV-Vis-NIR spectra of the SWNTs and is shown in Figure 6.8 for the AP-SWNT, the 1% SDS purified SWNT and the SWNT that are purified by centrifuging in DMF. All samples contain the same amount of nanotubes, 0.02 mg/mL in DMF, so the data can be analyzed as a measure of material quality. An increase in absorption of the $S_{11}$ peak is observed for both purified samples relative to that of the AP-SWNT spectra shown in Figure 6.8. The material purified by centrifugation in DMF has the highest absorbance, more than double that of the material purified using the 1% SDS procedure, as indicated in Table 6.2.

**Table 6.2: Absorbance of the $S_{11}$ Peak in the UV-Vis-NIR results for SWNTs Purified via Centrifugation**

<table>
<thead>
<tr>
<th></th>
<th>Amplitude of $S_{11}$ Peak (Absorbance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP-SWNTs</td>
<td>0.138</td>
</tr>
<tr>
<td>SWNTs Purified in SDS</td>
<td>0.208</td>
</tr>
<tr>
<td>SWNTs Purified in DMF</td>
<td>0.436</td>
</tr>
</tbody>
</table>
Figure 6.8: Plot of UV-Vis-NIR Absorbance as a Function of Wavelength for the $S_{11}$ Peak of the AP-SWNTs and the SWNTs that are purified by centrifuging.
E. Thermal Gravimetric Analysis (TGA)

Two peaks are observed in the TGA analysis of the AP-SWNTs, at 477°C and at 630 °C correlating to the decomposition of impurities and SWNTs, respectively (Figure 6.9). Figure 6.10, the TGA derivative curve for the 1% SDS sample after sonication, shows only one peak at 534 °C, denoting that much of the material that decomposes at 480 °C in the starting material is removed. After centrifugation in 1% SDS, a single peak is again present, with the temperature of degradation increasing slightly to 568 °C (Figure 6.10). The acid treated SWNTs, however, causes a dramatic increase in the temperature at which the sample decomposes, where weight loss is most apparent at 729 °C.

F. Raman Spectroscopy

For the material purified in acid, there is a shift in the G band relative to that of the AP-SWNT sample, from 1580.1 to 1585.8 cm\(^{-1}\), and the intensity of the G band increases significantly from 1038.6 to 2434.5 (Table 6.3 and Figure 6.11). The D band is also altered by this purification process, exhibiting an increase in the measured intensity relative to the AP-SWNT sample, from 26 to 114.

For the SDS purified material, the changes in the D and G bands are less pronounced. In fact, there is only a slight shift in the G band, as shown in Figure 6.12. Also, there is only a small change in the D band with the intensity increasing from 26.5 to 32.9.

Table 6.3 shows the intensities of the G and D bands and lists the ratio of these intensities (I\(_G\)/I\(_D\)) for the purified materials. Due to the increase in D band for the acid purified tubes, the I\(_G\)/I\(_D\) ratio is higher for the soap-purified material than is observed in the acid treated tubes.
Table 6.3: Intensities of the G Band and D Band of the Raman Spectra of Purified SWNTs

<table>
<thead>
<tr>
<th></th>
<th>G Band Intensity</th>
<th>D Band Intensity</th>
<th>Ratio of G and D Band Intensities (I_G/I_D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP-SWNTs</td>
<td>1039</td>
<td>27</td>
<td>39</td>
</tr>
<tr>
<td>SDS Purified SWNTs</td>
<td>1270</td>
<td>33</td>
<td>39</td>
</tr>
<tr>
<td>Acid Purified SWNTs</td>
<td>2435</td>
<td>114</td>
<td>21</td>
</tr>
</tbody>
</table>
Figure 6.9: TGA curves for a) AP-SWNT b) AP-SWNTs homogenized with mortar and pedestal to produce a smooth curve
Figure 6.10: TGA curves of a) AP-SWNT sample collected on nitrocellulose filter paper; b) SWNTs purified in 1% SDS; c) SWNTs purified with acid procedure
Figure 6.11: Raman spectra of a) AP-SWNTs; b) SWNTs purified with acid procedure
Figure 6.12: Raman spectroscopy of a) AP-SWNTs; b) SWNTs purified in 1% SDS
G. Yield of Purification Process

The yield of the purification processes are readily calculated from a measure of the mass of the recovered “purified” material. A starting weight of 1 gram AP-SWNT was used in the acid purification process and only 0.047 g purified product was collected, for a yield of 4.7%. With the SDS procedure 0.007 g of purified material was recovered from a starting weight of 0.05 g for a yield of 14%. It is important to keep in mind that the SDS purified nanotubes remained highly associated with spherical nanoparticles, as shown in the SEM image in Figure 6.4, and thus, the amount of recovered material contains this impurity.

6.4 Discussion

AP-SWNTs were subjected to an acid purification treatment and purification by centrifugation in 1% SDS, and the purified material was analyzed with SEM, TGA, UV-Vis-NIR, Raman, and electrical resistivity to compare and contrast the effectiveness and efficiency of the processes at removing metal and carbon impurities.

Both procedures are time consuming. Multiple acid washes and a series of thermal annealing were necessary to purify the SWNTs, while several hours of centrifugation were required to separate the impurities in the soap solution in the SDS purification process. Filtering to collect the acid purified material was easier, however. Purified SWNT in dilute acid solution passed with little trouble through polycarbonate filter paper, and once dry, the SWNTs were simply removed with a metal spatula. In contrast, removing the purified material from the 1% SDS solutions was a tedious process, requiring ~60 min to filter 100 mL of solution through nitrocellulose filter paper. Repeated acetone and methanol rinses were then necessary to remove filter paper remnants from the purified material.
SEM images reveal that spherical carbon nanoparticles were completely absent from the acid purified material, indicating that the successive rounds of thermal annealing and acid treatment were adequate to remove carbon impurities. A few metal artifacts are all that remained, where additional treatment of the SWNT with concentrated HCl is needed to remove the residual material.

Centrifugation in SDS was less successful at separating the carbon impurities and SWNTs. SEM images show that the SWNTs remained associated with spherical carbon nanoparticles, and that one round of centrifugation did not adequately separate the particles.

A similar study by Bonard, et al, also reports this outcome, and demonstrates that successive rounds of sonication and centrifugation in SDS are needed to improve the purity of the collected nanotubes (10). After only two consecutive centrifugations in SDS, Bonard obtained a product that is ~90 wt% SWNTs in the sediment, with only a few spherical particles remaining (10).

TGA analysis is further evidence that acid purification is more successful at removing particulates when compared to one round of centrifugation in 1% SDS. A higher degradation temperature is associated with a purer and less defective SWNT product (20). The removal of carbonaceous impurities, spherical carbon nanoparticles, and metal catalysts from the SDS treated tubes results in an increase in the decomposition temperature to 568 °C, however the acid treated tubes did not degrade until 729°C, indicating their improved purity.

A significant shift in the G band of the Raman spectra of SWNTs that are purified by acid treatment indicates their purity, but the increase in amplitude of the Raman D band indicates that this treatment damages the sidewalls from the oxidizing nature of the acids. The Raman D band
of the soap purified nanotubes only minimally increased relative to that of the AP-SWNTs, indicating that the nanotube side walls and tips remained relatively unaffected by this purification procedure, including the prolonged sonication.

The easier filtration process and Raman spectroscopy results suggest that purification of SWNTs with acid treatment is a good choice for bulk industrial applications that do not require pristine, defect free nanotubes. The increased defects on the tube from this purification process do not dramatically affect the structural properties of the SWNT, and thus applications that seek to increase the glass transition temperature or elastic modulus, for instance, of a material would be best served by utilizing SWNTs purified in this manner. The defects, however, impact the electrical and thermal conductivity, and thus, the use of SWNTs in applications that require these properties, such as the development of conductive polymers for solar panels, are probably best served to use nanotubes purified by centrifugation in SDS.

The spherical nanoparticles present in the AP-SWNTs are completely removed during the acid purification procedure. With the SDS procedure, these particles are also separated from the SWNTs. Given this information, it appears that a large-scale centrifugation process that uses a series of centrifuges to separate SWNTs and nanoparticles, and recycles the SDS is a viable suggestion for industry to purify SWNTs.

As a parallel study of interest, SWNTs were purified by centrifugation in DMF. The influence of a different solvent relative to the 1% SDS solution on the purification of the AP-SWNTs results in the spherical nanoparticles collecting in the sediment, while the nanotubes are collected in the supernatant. This outcome has also been reported by Yu, et al, who demonstrated that the separation of amorphous carbon, carbon nanoparticles and SWNTs is based on the different surface charges of the impurities upon application of a gravitation force (7). Yu
modified the surface charges by adjusting the pH of the solutions, and with the application of low speed centrifugation at pH 2, amorphous carbon was suspended in the supernant, while the SWNTs were left in the sediment, and at a higher pH, the opposite trend emerged (7). This work demonstrates that the properties of a SWNT solution determine the final outcome of separation with the application of centrifugation. This manifests in the different separation results observed here, with the difference in the pH of DMF and 1% SDS solutions, pH of ~9 and pH of ~ 6.5, (24). Modifying the solution properties also offers a means to tailor the collection of nanoparticles envisioned during a large-scale centrifugation process.

Anson-Casaos, et al, also studied the purification of SWNT solutions in DMF by ultrasonication and centrifugation and found the sediment enriched with SWNTs (23). The team reported a low yield of < 7 wt% SWNTs after one round of centrifugation. The SEM image shown in Figure 6.6 indicates that our nanotubes that were purified by centrifugation in DMF remain associated with carbon nanoparticles, as in the SDS purified material, and additional rounds of sonication and centrifugation are required to further isolate the SWNTs (10).

Interestingly, a comparison of the UV-Vis-NIR results indicates that the SWNTs collected in DMF are of higher purity than the nanotubes collected with centrifugation in 1% SDS. The increased absorption and higher amplitude of the $S_{11}$ peak of the DMF purified SWNTs is evidence that more amorphous carbon and metals were removed, since these impurities absorb as background noise in the UV-Vis-NIR spectra and dampen the characteristic absorbances of the SWNTs (22).

This result suggests the importance of testing more solvents, such as CHP, for their ability to remove unwanted contaminants and to render individual nanotubes finely dispersed in a suitable solvent. Increasing the % yield of SWNTs collected with sequential rounds of
sonication and centrifugation in DMF should also be tested to more thoroughly develop an efficient protocol for SWNT purification. This study also correlates well with the solubility work presented in Chapters 4 and 5, where understanding the enthalpic and entropic factors that govern the dissolution of SWNTs in a pure solvent is imperative for defining solvents that can readily disperse SWNTs, and serve as a suitable medium for centrifuge-based purification procedures.

6.5 Conclusions

The purification of AP-SWNTs by acid treatment and centrifugation in 1% SDS have been examined. Both techniques are equally time consuming, but evidence presented from SEM, TGA, and Raman spectroscopy indicates that the acid purification process results in a final product rich in SWNTs, devoid of spherical carbon nanoparticles, and nearly free of metal contaminants. However, the nanotube structure is damaged by the strong oxidizing acids as shown by an increase in intensity of the D band in the Raman spectra. Changes in the D band for the surfactant purified material were less prominent, and additional rounds of sonication and centrifugation in SDS have been shown to successfully isolate pristine nanotubes, devoid of significant damage to their tips and side walls (10).

It is apparent that purification in surfactant is a better choice for applications that require nanotubes with intact sidewalls, such as electrical conductive nanocomposites, while acid purification is a viable choice for nanotubes with end uses as structural materials. Large scale operations are envisioned to separate SWNTs and spherical carbon nanoparticles with SDS, including recycling the soap solutions using large centrifuges. The nitrocellulose filter paper
used to collect the SWNTs produced by centrifugation is problematic, as it requires the use of acetone and methanol to obtain the final product in a tedious process. There remains a need to test more filtering methods to separate the purified SWNTs after centrifugation.

As a corresponding project, the purification of SWNTs by centrifugation in DMF was also attempted. These purified tubes were analyzed by UV-Vis-NIR and SEM. The UV-Vis-NIR revealed that the material was higher in quality than the SDS purified nanotubes, based on the increased amplitude and absorbance of the characteristic $S_{11}$ peak. SEM images of the DMF purified SWNTs show that the nanotubes remain associated with spherical carbon nanoparticles present in the soot, and further sonication and centrifugation in DMF should increase the purification. Continuing this study by testing the materials with Raman spectroscopy to assess the presence of damages to the tubes and purity, and measuring the electrical resistivity of these purified tubes is important to establish the benefits of this method. Nanotubes purified by centrifugation in good solvents for SWNT may solve several processing issues. There will be no surfactant to remove, and the purified tubes will be dispersed in a solvent ready for combination with a polymer to form polymer nanocomposites. Known good solvents for SWNTs, such as CHP and NMP, should be explored for this purpose.
6.6 References

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Chapter 7

Conclusions and Future Work
7.1 Final Conclusions

This thesis presents experimental efforts to understand the entropic and enthalpic factors that govern the dissolution of nanoparticles in solutions and the segregation of polymer chains in the presence of various size and shape nanoparticles in polymer nanocomposite thin films. Defining the solubility behavior of nanoparticles is important, since they have a tendency to clump together in solution due to strong intermolecular forces, and these forces must be overcome in order to produce homogenous dispersions; otherwise, poorly dispersed nanoparticles that are used to produce polymer nanocomposites via solution casting will result in resultant nanocomposites with poor mechanical properties (1-2). For example, PS nanocomposites prepared with the incorporation of BNNTs show a decrease in elastic modulus when chloroform was used as the dispersant, but when dimethylformamide (DMF) is used as the solvent improvements in elastic modulus were achieved. This is ascribed to that fact that DMF is a better solvent for the nanoparticles, and is able to sufficiently disperse the nanotubes (2).

Understanding the segregation and diffusion behavior of polymer chains in the presence of nanoparticles also extends product utility, since the resulting properties of nanocomposite thin films are morphological dependent. Work by Lange, et al, has shown that the presence of well dispersed nanoparticles increases the permeability of nanocomposites, while nanoparticles segregated to the air interface decrease permeability (3). Understanding segregation behavior is also important for the development of plastic containers that are impermeable to gases; for instance, plastic beer bottles that protect their contents from oxidation (3).

In the first part of this thesis (Chapter 3), the affect of the presence of nanoparticles of various size and shapes on the segregation of deuterated polystyrene (dPS) chains in a protonated polystyrene (pPS) matrix was examined. In all systems studied, the presence of nanoparticles
slowed the diffusion process, as shown with dPS concentration profiles determined from neutron reflectivity. It was also demonstrated that small, highly branched polystyrene-soft-nanoparticles segregate to the air surface in the annealed polymer thin films. Subsequently, less dPS remained on the air surface in this system. The presence of chain branching is responsible for this segregation behavior, since chain ends are entropically driven to the air surface to relieve constraints placed upon the polymer coils when confined to the surface. When chain branching increased, this effect also increased, with more nanoparticles segregating to the surface and a negligible amount of dPS remaining on the air surface. The large carbon nanoparticles, graphene sheets and SWNT cylinders, had the opposite affect. Their high surface energies led to their segregation to the silicon surface, displacing dPS to the air surface. This work suggests that small, branched, nanoparticles segregate to the air surface due to entropic reasons, while large nanotubes and sheets are controlled by the surface energies of the components in the melt.

In the second part of this work, (Chapter 4 and Chapter 5) a protocol was established that defines the solubility behavior of boron containing nanoparticles in solution. Previous protocols circumvented the collection of refractive index increment (dn/dc) of nanoparticle solutions, which is a necessary parameter for subsequent light scattering experiments (4). The determination of this parameter is non-trivial, since nanoparticles clump in common solvents, and modern refractometers require the injection of samples and constant solvent flow-through to acquire data. In Chapter 4 and 5, an older refractometer (Brice Phoenix), which does not require sample injection, was used to obtain dn/dc of SWNT and boron-containing nanoparticle solutions for the first time. Static light scattering in conjunction with refractometry, to determine dn/dc, was then used to determine the second virial coefficient, $A_2$, of the nanoparticle-solutions. $A_2$ was used to calculate the solute-solvent interaction parameter, $\chi$, of nanoparticle-solvent
systems using Equation 7.1, where $V_s$ is the solvent molar volume, and $\rho$ is the density of the solute (i.e. nanoparticle or polymer) (4).

$$\chi = \frac{1}{2} - A_2 V_s \rho^2$$  \hspace{1cm} (7.1)

Nanoparticle density is also a non-trivial parameter. Previous methods have included AFM or SEM on spun-cast solutions to estimate the number of particles and bundle sizes, with questionable accuracy. (5-6). In this work, a gas pycnometer was used to accurately measure the density of the nanoparticles (Chapter 4).

Both $A_2$ and $\chi$ quantify the thermodynamic interactions occurring between the solute and solvent, and indicate the stability of the mixture; $\chi < 0.5$ (i.e.: $A_2 < 0$) indicates that the interactions between the nanoparticle and solvent are thermodynamically favorable, resulting in a well-dispersed system (4, 7). Of the systems tested, 1,3-di-o-carboranylpropane (TCB) in toluene and boron nitride nanotubes (BNNTs) in THF were found to be thermodynamically favorable.

Solubility limits, determined with UV-Vis spectroscopy, and physical observations support the information obtained with light scattering and refractometry, and for all of the particle systems studied, there was good agreement between all of the data collected; high solubility limits correspond to favorable values of $\chi$ and $A_2$, while insoluble systems had particle settling, low solubility limits and $\chi > 0.5$. TCB in THF, for example, had particle settling in all of the samples prepared and a $\chi$ value approaching 0.7.

For each nanoparticle, $\chi$ was measured in multiple solvents and Equation 7.2 (resulting from a combination of the Flory theory and the Hildebrand-Scatchard Solution theory) was used to determine the solubility parameter of the nanoparticle, where $\delta_A$ is the Hildebrand solubility
parameter of the solvent, and $\delta_B$ represents the Hildebrand solubility parameter of the nanoparticle (8-11).

$$\frac{\delta_A^2}{RT} - \frac{\chi}{V_A} = (2\delta_B/RT)\delta_A - (\delta_B^2/RT)$$  

The slope of the resulting line $(2\delta_B/RT)$ determines the nanoparticle solubility parameter, $\delta_B$ (8-11).

The Hildebrand Solubility parameter is a good indicator of solubility, since materials with similar $\delta$ are likely to be miscible, and for all of the nanoparticles studied, $\delta$ is used to predict a range of suitable solvents. For the smaller nanoparticles studied (i.e.: the carboranes and pre-polymers tested in Chapter 4) there is good correlation. Methyl ethyl ketone (MEK) is a good solvent for dodecahydrododecaborate dilithium salt (LBH) with a favorable $\chi$ value, and predicted good solvents for LBH based on $\delta$ are also straight chain alkanes that contained polar groups, similar to MEK’s structure. However, for the large nanotubes and sheets, $\delta$ does not accurately predict suitable solvents, as solvents indicated by $\delta$ do not adequately disperse the particles. For large particles, $\delta$ does not appear to be an accurate predictor of solubility, since additional intermolecular forces are often at play, and predicting solvents based on $\delta$ is made with the absence of specific interactions, such as H-bonding (12-14). This is especially important for defining the dissolution behavior of nanotubes and sheets, since polymers and solvents that are capable of $\pi$-$\pi$ interactions and H-bonding, such as ortho-dichlorobenzene, which interacts with nanotube sidewalls via $\pi$-$\pi$ stacking, have been shown to form stable dispersions (12-14). Significant improvements in the electrical conductivity of poly(vinyl alcohol) (PVA), for instance, was achieved with the introduction of graphite oxide, since PVA was able to effectively disperse the graphite through the formation of H-bonds (15).
Good agreement between $\chi$, solubility limits, and physical observations for all the examined systems, however, offers validity to the protocol developed and demonstrates that the static light scattering experiments in conjunction with refractometry are a powerful technique to quantify the solubility behavior of nanoparticles in solution, with consistency among all of the parameters.

In Chapter 6, the effectiveness and efficiency of two SWNT purification methods, purification via acid treatment and purification by centrifugation in surfactant, were compared and contrasted. The acid treatment results in the collection of highly purified nanotubes, devoid of any carbon nanoparticle contaminants, as indicated in scanning electron microscopy images (SEM) and thermal gravimetric analysis (TGA). Yet, the purified material is damaged due to the strong oxidizing nature of the acids, as evidenced with Raman spectroscopy. Purification by centrifugation in surfactant, on the other hand, results in the enrichment of SWNTs in the sediment with pristine tips and sidewalls. Different end uses for the collected materials are suggested, with surfactant purified tubes more suitable for applications that require a non-damaged $sp^2$ carbon network, such as solar panels, while acid treated tubes are suitable for mechanical reinforcement. The purification of SWNTs by centrifugation in DMF was also studied as a coinciding project. UV-Vis-NIR data indicated that the collected nanotubes were higher in purity and material quality than the surfactant treated tubes. This presents the possibility that other, better, solvents may be suitable to purify nanotubes, thereby reducing processing costs, since the final collected product will be dispersed in a solvent ready for combination with a polymer to form polymer nanocomposites, eliminating the need to remove surfactants. Previous work by Nepal, et al, has shown that a known good solvent for SWNTs, $o$-dichlorobenzene ($o$-DCB), was able to isolate SWNTs when as-prepared soot was subjected to
centrifugation (16). Once a range of good solvents for SWNTs is defined, more solvents should be tested for this purpose.

The end goal of the knowledge presented in this thesis is to provide fundamental information that can lead to highly tailored nanocomposites. A fine dispersion of nanoparticles in solvent, for instance, can lead to improved homogeneity of the dispersion of nanoparticles in a polymer matrix when the composite is prepared from solution casting. Tailored nanocomposite thin films that contain highly branched nanoparticles, which localize at the air surface when the thin film is annealed, may find end uses for sterilization purposes; the incorporation of highly branched porphyrins, which kill bacteria by damaging their cell walls, is a possible candidate for the development of nanocomposites for medical equipment (17). Other applications include electrically conductive materials for solar panels or block copolymer nanocomposites for nonlinear optics, sensors, or separation purposes (18).

7.2 Future Work

In order to more fully understand the affect of nanoparticle presence on the segregation and diffusion behavior of polymer chains, a wide range of particle shapes and sizes should be explored. It would be interesting to test small, spherical nanoparticles that do not contain chain branching, such as fullerenes (radius ~ < 1 nm) (19). Highly branched polymer chains segregate to the air surface to relieve an entropically unfavorable situation, since polymer chains typically take on a random coil conformation and the presence of a surface constrains the coils, reducing the number of configurations possible at the interface (20-26). The work in Chapter 3 also shows that small highly branched spherical particles (radius ~ 15 nm) segregate to the air interface to result in a more entropically favorable structure. Without the presence of chain
branching, it is not clear whether or not small particles will segregate to the air surface or have a sufficiently high surface energy that promotes their displacement to the silicon surface instead. Neutron reflectivity measurements of deuterated/protonated polystyrene (dPS/pPS) bilayers containing 1 wt% fullerenes and annealed for a series of times, would shed light on this behavior. Also, since the synthesis of soft polystyrene nanoparticles is highly tunable, a range of nanoparticle sizes are available for testing. As the size of the soft nanoparticles is increased, will the chain branching continue to dominate and lead to segregation to the air surface or will the particles segregate to the silicon surface due to an increase in surface energy?

Work by Hong and Boerio has shown that no segregation or diffusion occurred when a balance of entropic and enthalpic forces was achieved in a blend of 70K pPS and 1950K dPS annealed at 200 ºC for 24 hours (27-30). Typically, deuterated polymers segregated to the air interface due to a difference in polarizability of the C-D and C-H bonds. However, when the pPS molecular weight is lower than the dPS, it enriches the air surface instead. A balance of these driving forces is achieved in the blend prepared by Hong and Boerio (30). It would be interesting to homogenously disperse SWNTs, graphene, or soft nanoparticles into this composition and anneal the blend for a series of times. Neutron reflectivity measurements that determine the depth profiles of these blends would answer several interesting questions. Would the polystyrene chains be affected by the presence of nanoparticles of various sizes and shapes, and would segregation and diffusion occur? Or will the nanoparticles remain dispersed when the thin film is subjected to annealing? This information is valuable for producing novel materials, such as electrically conductive plastics, which require well-dispersed SWNTs, and are subjected to heat (i.e.: solar panels).
Further experiments would also shed light on the miscibility of nanoparticles in solutions and polymer matrices. In the work presented in Chapter 4 and 5, the solubility behavior of several boron-containing nanoparticles in solutions was determined. More solvents should be explored using the protocol established in Chapter 4, with static light scattering and refractometry to determine $\chi$. The list of suggested good solvents in Chapter 4 for the polyhedral borane compounds would be a good starting point, to determine whether or not these solvents are indeed favorable.

It would also be of interest to determine the solubility behavior of BNNTs and polyhedral boranes in solutions of various monomers and polymers. Widely available polymers, such as polystyrene or poly(methyl methacrylate) are of interest for industrial applications, since they are cost effective, and they offer a good starting point for this work. Optimizing fine dispersions in the resulting nanocomposite requires the use of a known good solvent for the nanoparticle, but also requires the use of a polymer that is known to interact well with both the solvent and the nanoparticle. Continuing the work in Chapter 4 and 5 would define $\chi$ for nanoparticle-polymer systems.

Since the solubility parameter does not accurately predict good solvents for large nanoparticles, such as nanotubes and boron nitride sheets, it would be of interest to investigate the reasons for this deviation. Non-covalent interactions and additional entropic factors are present in these systems. To achieve this, a wide range of solvents should be screened using static light scattering and refractometry to determine $\chi$ and UV-Vis spectroscopy to determine the solubility limits. Graphs of concentration as a function of the Hanson solubility parameters of the examined solvents may shed light onto the additional factors that govern dissolution of nanoparticle sheets and tubes, since the Hanson solubility parameters take into account
dispersive, polar forces, and Hydrogen bonding strength. The resulting maxima on the graphs may reveal the important forces governing dissolution.

A combination of dynamic light scattering (DLS) and static light scattering offers another route for quantifying dispersion, since this combination determines the number of aggregating particles in solution and polydispersity (31-36). Also with these measurements, the shape factor, which is the ratio of hydrodynamic radius to radius of gyration, can be established. This ratio determines the amount that the shape of a nanoparticle deviates from a homogenous sphere, and this information would be of particular value for computational work involving SWNTs or graphene sheets (37). Computation simulations, in order to determine additional forces governing dissolution of nanoparticle tubes and sheets, take into account the surface energies of large nanoparticles, binding energies, and require accurate particle shape (37). DLS measurements of the nanoparticle solutions studied in Chapter 4 and 5 would establish the number of aggregating particles in the systems and establish the shape factor of the particles tested for future computational work.

Finally, SWNTs purified in known good solvents may solve several processing issues. As discussed previously, the collected purified tubes will be dispersed in a solvent ready for combination with a polymer to form polymer nanocomposites. In Chapter 6, SWNTs purified in DMF were shown to be higher in material quality than the nanotubes purified in surfactant, based on the increased amplitudes and absorbance in the corresponding UV-Vis-NIR spectra. Work in this thesis and work by Nepal et al, offers validity to this approach, since both centrifugation of as-prepared nanotube soot in DMF and o-DCB isolates SWNTs. Continuing this work by testing the materials purified in DMF with Raman spectroscopy to assess the presence of damages to the tubes and purity, and measuring the electrical resistivity of these purified tubes is important to
establish the benefits of this method. Known good solvents for SWNTs, such as
cyclohexylpyrrolidone (CHP), should also be explored for this purpose.

A fundamental goal of this work is to determine the entropic and enthalpic factors that
impact the segregation and diffusion behavior of polymer chains in the presence of nanoparticles
and those that govern the dissolution of nanoparticles in solvents and polymers. More light
scattering and neutron reflectivity measurements are necessary to clearly define these
relationships and to build-off of the work presented in this thesis.
7.3 References


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Vita

Mary Catherine Mutz was born in Oberlin, Ohio on January 30\textsuperscript{th} 1981. Mary traveled the United States during her early life, and subsequently attended ten different elementary schools before taking up permanent residence in the Florida panhandle, where she graduated from Pace High School, in Pace, Florida, in 1999. In her early student life, she was active in many clubs and organizations, including marching band, student dance, chess club, and the student humane association, for which she was elected secretary-treasurer. She also volunteered with the American Red Cross and at several hospitals and nursing homes. She was awarded scholarships for both her volunteer efforts and work as a journalist, having written for her high school and college newspapers. In December 2002, Mary graduated from the University of West Florida with a Bachelor’s Degree in Biology and a minor in pre-medicine. Later she received her substitute-teaching license, and worked as a dance instructor at a local senior center. She also became an Anatomy and Physiology teacher and a Biology teacher at a local adult high school and massage therapy school. In 2003, she enrolled in a registered nursing program at a local junior college, pursuing a career as a nurse practitioner. In September 2004, Hurricane Ivan destroyed much of the Florida panhandle and closed the nursing school for some time. With much luck, Mary’s resume was remembered by the human resources department at the United States Environmental Protection Agency Gulf Ecology Division Laboratory, in Gulf Breeze, Florida, and she was recommended for employment. She was hired in June 2005 and began work as a personal services contractor. Duties included working as a marine aqua-culturist and serving as technical support on several scientific research projects. Experiments focused on assessing the health affects of endocrine disrupting compounds in sheepshead minnows \textit{(Cyprinodon variegatus)} and modeling coral communities with 3D imaging software to evaluate
growth. She also worked offshore helping team members to assess the hypoxic region of the Gulf of Mexico. In 2007, she made the decision to pursue a higher education and accepted a position at the University of Tennessee (UT) in Knoxville, Tennessee, where she was also able to work at Oak Ridge National Laboratory on joint projects. She studied polymer chemistry from August 2007 until April 2012 at UT with funding for scientific research from the Department of Energy and the National Nuclear Security Administration’s Kansas City Plant (managed by Honeywell Federal Manufacturing & Technologies, LLC). In October 2011, she became happily married to her college sweetheart, and then, just six months later in April 2012, she successfully defended her dissertation under the advisement of Dr. Mark Dadmun. In the future, she hopes to work for the Federal government again, enjoy time writing, and pursue family life.