

The Effect of Attractive Polymer-Nanoparticle Interactions on the Local Segmental Dynamics of Polymer Nanocomposites

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*This work is dedicated to my wonderful family and especially to my wife, Jen, whose
love and support made my dream a reality.*

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"What a fine persecution—to be kept intrigued without ever quite being enlightened."

—Guildenstern, *Rosencrantz and Guildenstern Are Dead*

Abstract

Considerable progress has been made in understanding the miscibility and morphology of polymer nanocomposites (PNCs). However, to date, there is little understood concerning the modification of segmental mobility at the polymer-nanoparticle interface, which due to prevalence of interfaces in PNCs, will predominantly control the viscoelastic and mechanical properties of these materials.

In this dissertation, static and dynamic experimental techniques are combined to identify the specific parameters controlling the modification of segmental dynamics at the polymer-nanoparticle interface in the model system of poly(2-vinyl pyridine)/silica nanocomposites. In general, the experimental results clearly demonstrate that the segmental dynamics at the polymer-nanoparticle interface are suppressed relative to the bulk-like polymer and moreover that this effect is dependent on the molecular weight (MW) of the polymer matrix. Additionally, the density of the polymer-nanoparticle interface was found to unexpectedly decrease with increasing MW. These unexpected results indicate a competition between a suppression due to adsorption and a speeding up due to the reduction in density—which suggests that the chain packing at the polymer-nanoparticle interface becomes frustrated at higher MWs. Lastly, by comparing the strength of the polymer-nanoparticle interaction and molecular weight, it is proposed that the orientational anisotropy of the chain conformations primarily controls the magnitude of the dynamic suppression at the polymer-nanoparticle interface and suggests a new way to tailor the segmental dynamics on the nanoscale.

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Chapter 1

Introduction

A brief description of the scientific motivation and organization of the dissertation are discussed. The crucial scientific concepts are given, the current problems are outlined, and the main objectives of the dissertation are presented.

1.1 Motivation

Polymers are macromolecules that consist of many repeating molecular units (monomers) and are most commonly visualized as a linear chain following the Gaussian statistics of a three-dimensional random walk. There are many examples of polymers in nature such as polysaccharides (*e.g.*, cellulose), polynucleotides (*e.g.*, DNA and RNA), or natural latex rubber produced by the Para rubber tree. The unique physical properties of polymers are largely due to the complexity of the dynamics which are occurring simultaneously at different length scales (intra- and inter- molecular motions as well as diffusive motions). One of the most important properties of polymers is vitrification which is associated with the rapid suppression of conformational motions (or collective change in the bond angles) along the polymer backbone known as segmental dynamics. The time scale of these motions occur over 12 orders of magnitudes, are highly sensitive to temperature,

and directly control many important properties such as mechanical strength, ion transport, and gas permeability or small molecule diffusion.

Polymer composites have demonstrated to be useful materials in the aeronautical, nautical, and automobile industries. In actuality, most polymers used today contain reinforcing fillers such as carbon black or silica to improve their mechanical properties. Whereas traditional reinforcing fillers materials are essentially limited to modifying mechanical and thermal properties, the use of nanotechnology grants the modification of optical, electrical, and transport properties as well.[26–28] Polymer nanocomposites (PNCs) are the result of combining polymeric materials with nanoparticles such as carbon nanotubes, montmorillonite clays, or quantum dots. For example, many organic photovoltaic solar cells are based on the conjugated polymer poly(3-hexylthiophene) and the nanoparticle known as phenyl-C61-butyric acid methyl ester (PCBM) and offer the advantages of low-cost manufacturing, large-scale feasibility, being light weight and flexible, and most importantly is the ease of solution processing provides an avenue for printable solar cells.[29–31] Another rapidly growing area of PNCs is in polymer membrane technology where many rubbery polymers are ideal for CO₂ separation but lack the mechanical strength for robust industrial applications.[32] Even more recently, it was shown that nanoparticles with plasmonic properties can be dispersed in a polymer matrix and then used to locally heat the polymer matrix *via* laser stimulation to repair strain induced damages.[33]

The large difference in the surface area-to-volume ratio (see Fig. 1) in PNCs leads to a much larger amount of interfacial interactions than in traditional composites materials. The large amount of interfaces within PNCs categorizes them among other multicomponent polymeric systems such as thin polymer films, block copolymers, ionomers, and semi crystalline polymers where the dynamics of the interfacial regions are strongly influenced by interfacial interactions and confinement effects.[1]

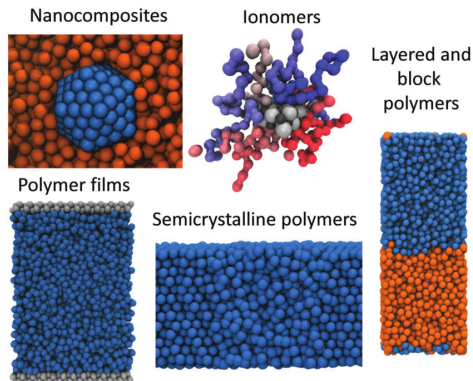


Figure 1.1: Examples of nanostructured polymeric materials that have a large amount of interfacial interactions. Image reproduced from reference [1].

Simulations have predicted that polymer-NP interactions (whether attractive or repulsive) can greatly influence the T_g of PNCs.[11, 34] Also, several experiments have demonstrated that strong, attractive polymer-NP interactions (a case in which simulations are currently limited due to significant slowing down of polymer dynamics) can significantly increase the T_g of PNCs.[13, 22] It has been postulated that the polymer near the NPs adsorbs to the surface, exhibiting a gradient of dynamics due to steric hindrance, confinement effects, and polymer-nanoparticle interactions.

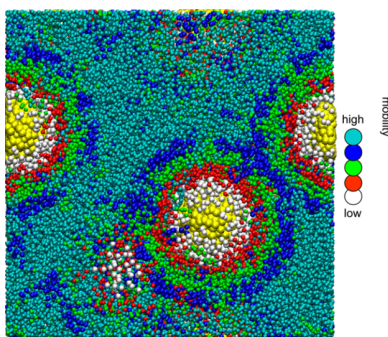


Figure 1.2: A molecular dynamic simulation of segmental mobility in the presence of nanoparticles that illustrates the modification of dynamics within the interfacial region. The interface exhibits a gradient of mobility which is slowest at the surface of the nanoparticles and quickly returns to that of the unperturbed bulk polymer. Image reproduced from reference [2].

By controlling the chemistry and the concentration of the nanoparticles it should be possible to transform the entire polymer into an interfacial material where the interfacial dynamics can be predicted and controlled. Therefore, gaining an understanding the dynamics of the interfacial region and the role of polymer-NP interactions is of great technological importance. In this work, the dynamics of the interfacial polymer layer, its influence over the macroscopic dynamic properties, and the parameters that ultimately control the interfacial dynamics are thoroughly investigated.

1.2 Thesis Outline

Chapter 2 provides a detailed overview of the polymer dynamics and discusses the current understanding of how the macroscopic dynamic properties can be modified in polymer nanocomposites.

Chapter 3 outlines the experimental methods as well as any theoretical models used in the Dissertation.

Chapter 4 investigates the influence of different oxide nanoparticles on segmental and chain dynamics of poly(2-vinylpyridine). While significant changes in rheological properties are observed with increasing nanoparticle loading, only weak effects are found in the average glass transition temperature, the segmental mobility, and fragility. These results indicate that the segmental dynamics are only locally affected in the direct vicinity of the nanoparticle's surface, *i.e.* in the adsorbed interfacial layer, and are discussed in the context of recent controversies in studies of polymer nanocomposites and polymer thin films.

Based on the findings of the previous chapter, chapter 5 investigates the static and dynamic properties of the interfacial layer in poly(2-vinylpyridine)/silica nanocomposites. Both static and dynamic techniques detect the presence of an interfacial polymer layer near the surface of the nanoparticles exhibiting a

suppressed segmental mobility (~ 2 orders slower). These findings suggest that interfacial layer is by no means a “dead” layer but is instead dynamically “alive”.

Chapter 6 studies the effect of molecular weight (MW) on the static and dynamic properties of the interfacial layer in poly(2-vinylpyridine)/silica nanocomposites. The MW of the polymer matrix is found to play a significant role in the magnitude of the effect at the interface in an unexpected way—where the influence of interfacial layer on the overall segmental dynamics decreases with increasing MW. These findings suggest that the interfacial chain conformations can influence the interfacial dynamics.

Chapter 7 attempts to understand the mechanism responsible for the suppression of interfacial dynamics in poly(2-vinylpyridine)/silica nanocomposites. In this chapter, the static and dynamic properties of the interfacial layer in polymer nanocomposites are directly compared to polymer grafted nanoparticles. The interfacial dynamics are found to be strongly suppressed in both systems. However, the magnitude of this effect is different for each system and is dependent on the MW of the polymer matrix. At intermediate MW, the interfacial dynamics are found to be more strongly influenced by the covalent bonding than by chain adsorption but it is proposed that this not due to the strength of the interaction but rather to the uniformly stretched chain conformations near the interface. These results potentially suggest that polymer chain conformations (stretching) in the interfacial region can strongly influence the segmental dynamics and suggests a new way to tailor the glassy behavior of interfacial dynamics in multi-component polymeric systems.

Chapter 8 summarizes the results of the four experimental chapters and provides a future outlook for understanding the segmental dynamics in other heterogeneous and multi-component polymeric systems.

Chapter 2

Historical Background

In this chapter, the fundamental knowledge of polymers and glass formation will be discussed in the context of experimental data and theoretical models. The concept of cooperative dynamics is introduced and discussed with regards to geometrical confinement effects.

2.1 Polymers

2.1.1 The Random Walk

A polymer is a macromolecule consisting of many repeating monomeric units, consisting of sometimes similar or different molecular moieties. While polymers are naturally found in biology such as cellulose or DNA, the synthetic type are more prevalent in daily life. Synthetic polymers, which are mainly carbon-based and created from petroleum, have many outstanding properties such as chemical resistance, high tensile strength, and high viscoelasticity.

A unique aspect of polymers when compared to traditional crystalline solid materials is the fact that the only periodicity is present along the path of a given polymer chain. Therefore, a single linear chain of sufficient chain length should follow the statistics of a three dimensional random walk. This can be more readily

seen when the polymer is diluted by solvent molecules, where the polymer-solvent and polymer-polymer interactions are balanced and the chains resemble an ideal random coil. For an ideal chain with a number of steps, n , of certain length, l , performing a 3-D random walk the probability to have an end-to-end distance of r can be shown to be:

$$P(r) = \frac{4\pi r^2}{(2/3\pi\langle r^2 \rangle)^{3/2}} e^{-\frac{3r^2}{2\langle r^2 \rangle}} \quad (2.1)$$

This approximation assumes each step has an equal statistical probability and excludes volume effects. However, real polymer chains occupy at least their van der Waals volumes which would strongly influence the possible bond angles and increase the actual end-to-end distance. Therefore, a more meaningful quantity to characterize the size of a macromolecules is the average sized defined by its center of mass. This quantity is known as the radius of gyration, R_g , and can be calculated and experimentally determined for a 3D random walk. For a polymer with an almost infinite number of conformations, the R_g is an ensemble average over all molecules in the system and time. Therefore, we can calculate R_g^2 as:

$$R_g^2 = \frac{1}{N} \left\langle \sum_{k=1}^N (\mathbf{r}_k - \mathbf{r}_{mean})^2 \right\rangle \quad (2.2)$$

Where N is the number of steps, r_k is the position vector of a given monomer, and r_{mean} is the average position of the center of mass. The R_g of many polymers can be determined by static and dynamic light scattering or small angle scattering techniques such as neutron and X-ray scattering.

For discussions within this Dissertation the radius of gyration, R_g , will be used to compare several properties. The resulting R_g can be shown to be:

$$\langle R_g^2 \rangle = C_n \frac{nl^2}{6} \quad (2.3)$$

where C_n is the characteristic ratio which is the ratio of the mean square end-to-end distance of a model chain ($\langle r^2 \rangle_0$) to the value for a freely jointed chain (nl^2).

2.2 Polymer Dynamics

The unique physical properties of polymers are largely due to the complexity of the dynamics which are occurring at different time and length scales (intra- and inter-molecular motions as well as diffusive motions). In this section, the differences between these dynamics will be clearly described as well as the specific properties related to each dynamic component.

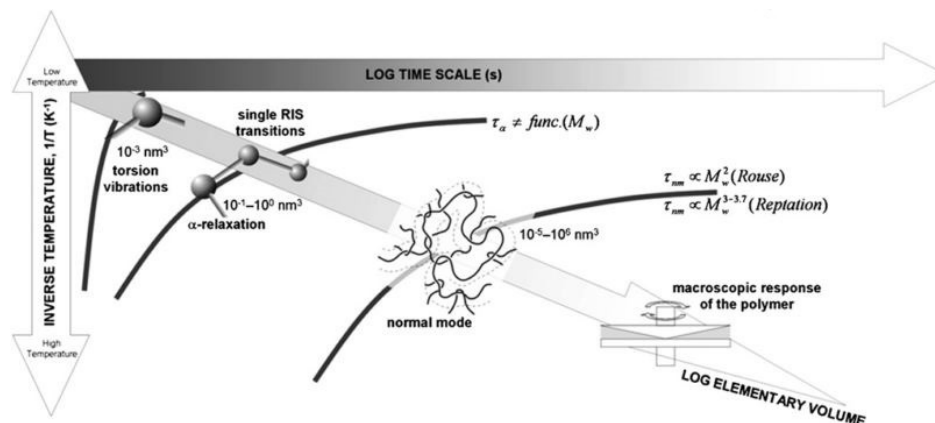


Figure 2.1: The characteristics volumes associated with molecular motions as a function of time scale and temperature. Image reproduced from reference [3].

2.2.1 Local Segmental Dynamics

The molecular motions that must first be discussed are those related to the cooperative re-arrangement of polymer segments. These motions are referred to the segmental dynamics or perhaps better known as the α -process to many experimentalist due to the fact that the time scale of all other molecular motions are ultimately controlled by these motions. A real world analogy for segmental dynamics would be the comparison to automobiles in a highly congested traffic; where the motion of a single automobile (segment) is ultimately controlled by the

cooperative effort of the surrounding automobiles (other segments). The driver of the automobile can still manipulate devices or controls within his vehicle (intramolecular or fast dynamics which are discussed below) but to travel faster or switch lanes it is limited by the local environment. Similarly, any hopes of long range travel (diffusive motion of the chain, also discussed below) is also limited by the segmental motions.

The dynamics in polymers can be measured by frequency dependent techniques including mechanical, dielectric, and light scattering spectroscopies. In these spectroscopies, a spectral response related to the out-of-phase component of the perturbation appears as peaks. These peaks are directly related to the energy dissipation of different molecular motions. The molecular motions that correspond to the largest energy dissipation are the segmental motions which are illustrated in Figure 2.4 by broadband dielectric spectroscopy (described in Chapter 3). In BDS, a small electric field is applied across a polymer film in a broad frequency range (10^{-2} to 10^7 Hz) and in-phase and out-phase components of the dielectric permittivity are measured. As shown in Figure 2.4, the segmental relaxation of poly(2-vinyl pyridine) can be observed within our accessible frequency window at several temperatures. The maximum of the peak is the average rate of segmental motions at a given temperature and very sensitive to temperature changes when approaching T_g .

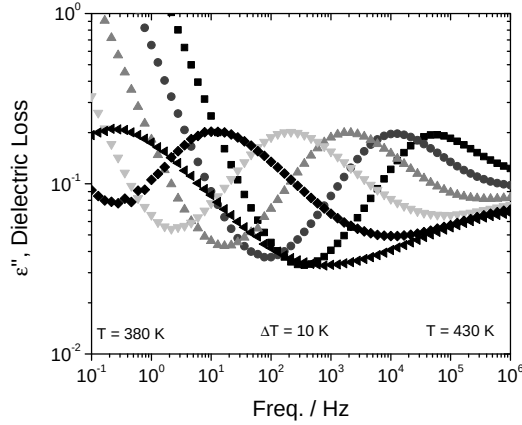


Figure 2.2: Dielectric loss spectra illustrating the dispersion of the segmental relaxation in poly(2-vinyl pyridine) at several temperatures (430 K to 380K in 10K steps).

The timescale for the cooperative motion of polymer segments, or segmental dynamics, is responsible for the vitrification of the polymer matrix. The vitrification or glass transition in polymeric materials signifies the transition between a molten, rubber-like state (melt) and a brittle state (glass), at which the internal degrees of freedom fall out of equilibrium into a metastable state. Therefore, the glass transition is not a transition between thermodynamic equilibrium states but is a thermodynamically arrested, non-equilibrated state. This transition can be observed by the rapid changes in the mechanical properties or segmental motions as it is cooled or heated about a temperature known as the glass transition temperature, T_g . Once a polymer is below its T_g , the segmental motions are essentially frozen from the human perspective where segmental motions take up to 100–1000s to occur. However, even though the inter- molecular motions are frozen, intra- molecular motions still occur and are responsible for the interesting glassy properties and will be discussed in the next subsection.

The glass transition in polymers usually appears as a sharp change in the temperature dependence of many material properties such as volume, density, sound velocity, specific heat, or the thermal expansion coefficient. Furthermore,

the glass transition can also be observed by the dramatic increase in viscosity or structural relaxation time as T_g is approached. As such, T_g is commonly defined as the temperature at which the segmental relaxation time scale, τ_α , reaches 100 seconds. The most commonly used technique to define the T_g is by differential scanning calorimetry (DSC). Typically, the sample is heated well above its T_g and then cooled/heated multiple times at a fixed rate (10 K/min). The T_g is defined as the midpoint of a nearly discontinuous change in the heat capacity of the sample which represents the change from a liquid-like (or melt-like state) to the non-equilibrium glassy-like state, as shown in Figure 2.3.

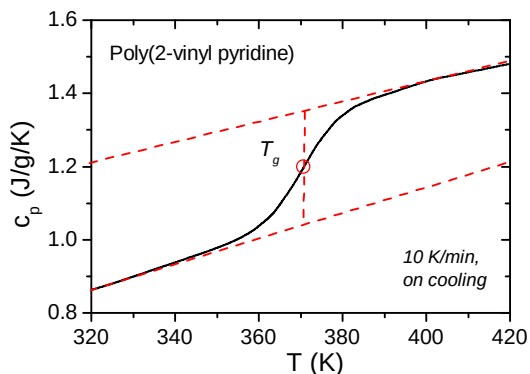


Figure 2.3: The specific heat capacity versus temperature of poly(2-vinyl pyridine) upon cooling.

As mentioned above, dramatic changes in the dynamic properties such as viscosity, d.c. conductivity, and segmental relaxation times are observed and can change up to 14 orders of magnitude as the T_g of a polymer is approached from the liquid or melt state. This dynamic behavior is commonly presented on an Angell plot where relaxation times are plotted vs. T_g/T as shown in Figure 2.4.

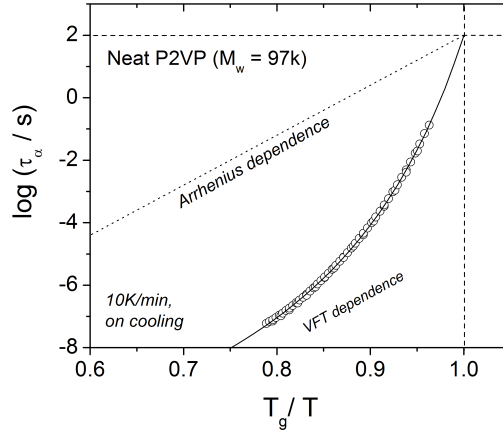


Figure 2.4: Segmental relaxation times for poly(2-vinyl pyridine) (P2VP) from broadband dielectric spectroscopy demonstrating the approach to 100 seconds where the dynamic glass transition temperature is commonly defined.

Although the temperature dependence of the segmental relaxation times allows for the dynamic definition of T_g , it also yields information about the kinetic pathway that the polymer traversed into the glassy state. The Arrhenius law, $\tau_\alpha = \tau_0 \exp(E_A/(k_B T))$, can be used to describe a kinetic process in which molecular conformational changes require a constant activation energy, E_A , to execute and are independent of temperature. However, the temperature dependence of segmental relaxation for polymeric materials are often highly non-Arrhenius (*i.e.*, non-linear on the Angell plot) and dramatic changes in relaxation times or viscosity occur near T_g . The slope of the Angell plot at T_g/T is defined as the fragility and is a useful quantity to compare the temperature dependences of relaxation times for different glass forming materials. Although there are several different definitions of fragility used to quantify this deviation from Arrhenius dependence, but the most common used is the isobaric fragility index, m .

$$m = \left(\frac{\partial \log_{10} \tau_\alpha}{\partial T_g/T} \right) \bigg|_{T=T_g} \quad (2.4)$$

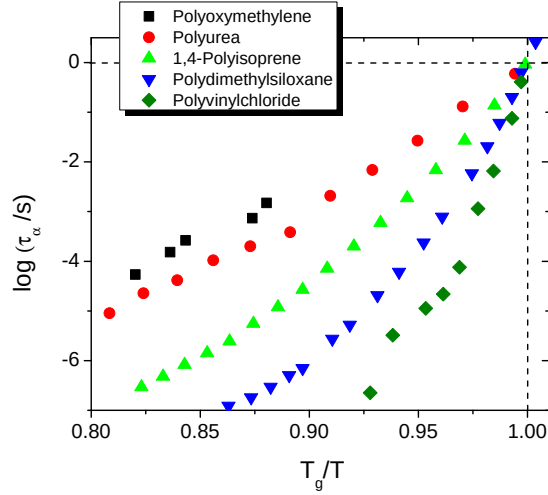


Figure 2.5: An Angell plot for polymers with different chemical structures where T_g is defined at $\tau_\alpha = 1$. Data are from reference [4]

Glass forming materials that closely follow the Arrhenius temperature dependence and exhibit less curvature are referred to as strong ($m < 60$), otherwise they are referred to as fragile ($m > 60$) and strongly deviate from the Arrhenius behavior. Relaxation times for polymers cannot be explained by the Arrhenius law and a wide array of theoretical models exist to describe the non-Arrhenius temperature dependences. For the purposes of this dissertation research, the empirical Vogel-Fulcher-Tammann (VFT) equation $\log \tau_\alpha = \log \tau_0 + B/(T - T_0)$ will be used to describe the relaxation data. It has a functional form that can be rationalized in the framework of both the Adam-Gibbs model and free volume theory.[35]

The isobaric fragility index of polymers are usually much higher than that of van der Waal molecular liquids (e.g. propylene carbonate, ortho-terphenyl, etc) or hydrogen bonding liquids (e.g. glycerol, sorbitol, etc). For example, the m of glycerol is 53 and ortho-terphenyl is 80. Many polymers have very high m indices up to 190. The fragility of the cooperative, segmental dynamics is a direct consequence of the polymer structure (*i.e.*, a consecutive set of monomers) and the inherent connectivity.[36] In other words, fragility almost always systematically

increases with increasing chain length with few exceptions. However, this does not always hold for all polymers—where the relative backbone rigidity to the sidegroup rigidity has recently been proposed to explain polymer fragility.[5]

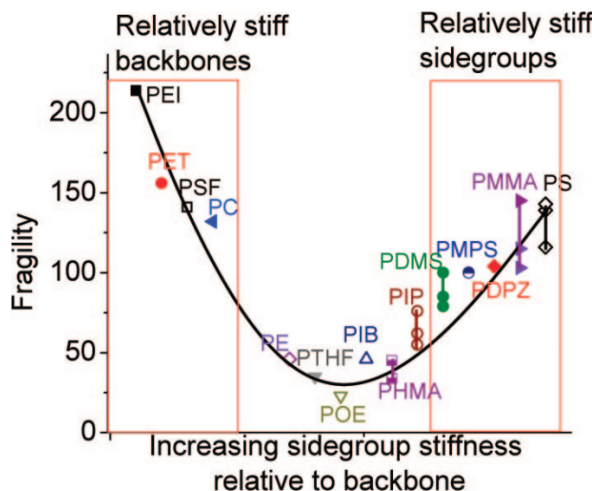


Figure 2.6: A suggested picture for the specific parameters (backbone stiffness to sidegroup stiffness) that control the fragility in polymers. Image reproduced from reference [5].

The physical meaning of fragility is not yet completely understood and has been related to conformational entropy, dynamical heterogeneity, molecular packing, and even directly to the Pössions ratio.[37] Unfortunately, the exact origin of the glass transition phenomenon still remains an open theoretical question. There are many competing theories such as the Adam-Gibbs[38], Random First-Order Transition Theory[39], and Mode-Coupling Theory[40] that attempt to describe the mechanism controlling the glass transition phenomenon. However, a single theory has yet to predict the properties of different glass forming materials such as hydrogen bonding, van der Waals, ionic, and polymeric liquids over a broad temperature range.

2.2.2 Fast Dynamics

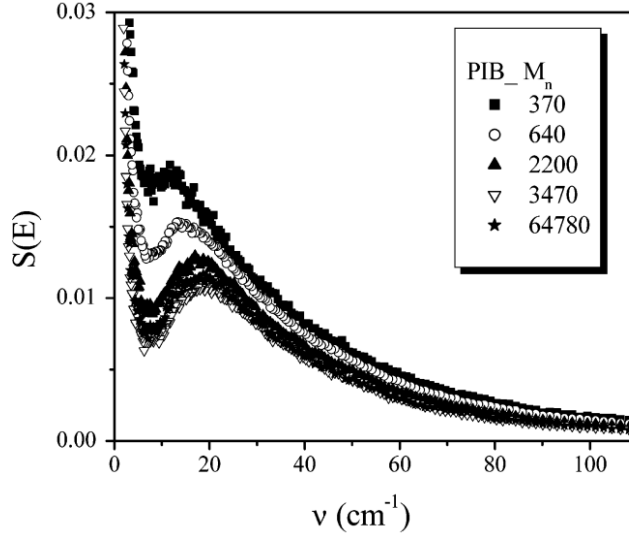


Figure 2.7: The fast dynamics of polyisobutylene for various molecular weights measured by quasielastic neutron scattering techniques at $T = 100\text{K}$. Image reproduced from reference [6]

At much higher frequencies than segmental dynamics ($\sim 1000\text{ GHz}$) and slower than characteristic vibrations of molecules or atoms, a unique dynamic feature can be observed which clearly distinguishes crystalline and amorphous materials known as the fast dynamics. These relaxations are related to the so-called “rattling in a cage” dynamics, the collective motions prior to a molecule escaping the cage. An example spectra of the fast dynamics for a polyisobutylene is presented in Figure 2.7. However, the fast dynamics are out of the scope of this Dissertation and are not discussed.

2.2.3 Secondary Relaxations

There are many other relaxation processes in polymers that occur in between the time scale of fast dynamics and segmental relaxation (α) and are hence referred to as β , γ , or δ relaxations (in increasing separation from α). For polymers, the most prevalent of these are known as β -relaxations which involve small-angle reorientation

dynamics within the monomer unit of a polymer (intra- molecular motions). The β -relaxations sometimes appear as a large, broad peak in the spectrum (Fig 2.8(a)) or as a broad shoulder to the high-frequency wing known as an excess-wing. There are different classifications of β -relaxations that are dependent on several criteria such as pressure and temperature dependences, separation of α and β relaxation times, the activation energy of the relaxation, and the dielectric strength of the β -relaxation.[41]

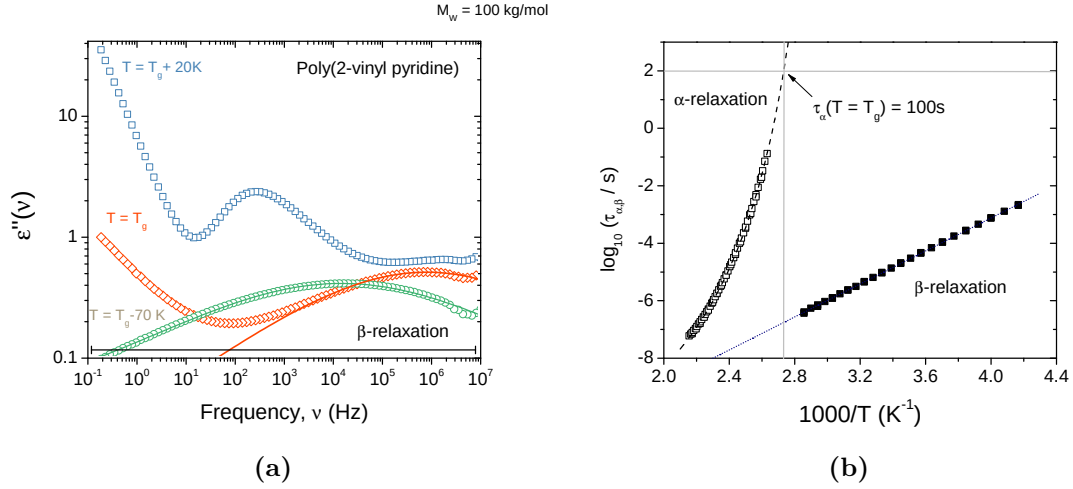


Figure 2.8: (a) Dielectric loss spectra for poly(2-vinyl pyridine) above T_g (blue), at T_g (orange), and below T_g (green) to show the emergence of the secondary β -relaxation with cooling. (b) The temperature dependence of the segmental and secondary relaxation times for poly(2-vinyl pyridine) above and below the glass transition temperature, T_g . The dotted lines are Vogel-Fulcher-Taumann fits and the grey lines denote the dynamic T_g where the segmental relaxation time exceeds 100 seconds.

Figure 2.8(a) shows an example of a secondary β -relaxation in dielectric spectra of poly(2-vinyl pyridine) above, at, and below T_g . The contributions from the β -relaxation to the spectrum are present at all shown temperatures. Figure 2.8(b) shows the temperature dependence of the relaxation times for both the segmental (α) and the β -relaxation. Notably, the β -relaxation is not nearly as sensitive to temperature as the segmental relaxation and it exhibits a completely Arrhenius

temperature dependence. If the time scale of the β -relaxation is extrapolated to high temperature (or to the left on Figure 2.8(b)) the time scale of both processes appear to merge. The activation energy of the β -process is 4.5 kcal/mol and corresponds to a similar energy as the rotational motion of pyridine (the pendent sidegroup of P2VP). In other systems, these motions are typically associated with intra- molecular motions along the polymer backbone such as double bond rotations in 1,4-polybutadiene, rotational flips of phenyl rings in polystyrene, or even more complicated systems like polycarbonate that exhibit up to three different intramolecular motions (phenylene ring flips, coupled carbonate-phenylene 90 degree rotations, and oscillatory motions). These secondary motions are believed to be directly related to the glassy mechanical properties of many polymeric materials, where the highly activate molecular motions can give rise to high impact resistance, elasticity, and mechanical strength.

2.2.4 Chain Dynamics

At low chain length, the physical properties of polymers are similar to liquids or oligomers instead of the common viscoelastic properties that are observed at high chain length. This is largely due to chain entanglements, or the topological constraint that two chains may not cross, which dramatically reduces chain diffusion and gives rise to rubbery, elastic properties and high viscosity. However, the chain dynamics are also not in the scope of this Dissertation and will not be discussed.

2.3 Confinement and Interfacial Interactions

2.3.1 Polymer Thin Films

For the past decade, there has been a significant interest in the glass forming properties of polymers when confined on the nanoscale. The simplest system is

that of polymer thin films where polymers are solvent-cast onto a substrate, or supported polymer thin films, where film thicknesses of 10 nm or below can be achieved. In 1994, Keddie and coworkers discovered that poly(styrene) (PS) films spin cast onto silicon substrates exhibited a much lower T_g (or faster segmental dynamics) than the bulk polymer with a dependence on thickness. They proposed that the free surface experiences much faster, liquid-like dynamics due to the loss of nearest neighbors at the surface and as the film thickness decreases the liquid-like dynamics dominates the material response.

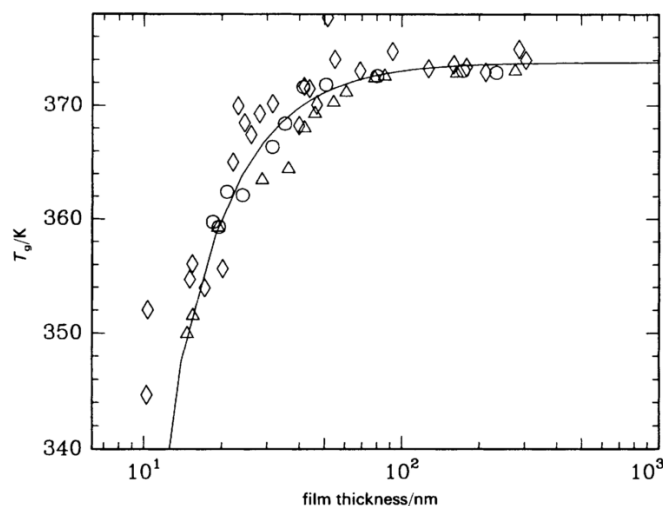


Figure 2.9: The glass transition temperature of thin films of poly(styrene) on silica substrates as a function of decreasing film thickness. [7]

However, they also found that this phenomena changes by varying the substrate material: where mutually attractive interactions cause a suppression of dynamics and passive interactions cause no change in dynamics at the surface of substrate. In fact, for polymer-substrate systems with mutually attractive interactions the suppression of dynamics at the interface was shown to counteract the effect of the liquid-like dynamics at the free surface at small film thicknesses—indicating a gradient of segmental mobility.[7–9, 42]

The dynamics of polymer thin films are often characterized by surface probing techniques (ellipsometry, dilatometry) which is why the measurements usually

reflect the contributions from the surface dynamics. These results along with others[8, 43–45] emphasize the importance of the experimental techniques that are used to characterize and measure the glass transition temperature and segmental dynamics of materials with heterogeneous dynamics, especially on the nanoscale. Another popular method used to characterize the glass transition of polymer thin films is dilatometry. Dilatometry measures the thermal expansion of a material with changing temperature where the glass transition is typically demarcated by a kink in the temperature dependence.

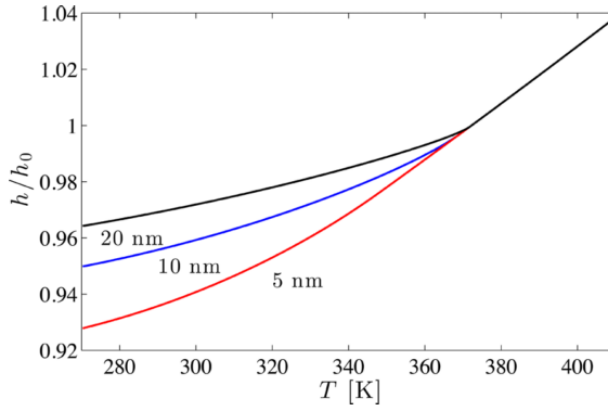


Figure 2.10: The dilatometric T_g as a function of decreasing film thickness which illustrates the significant broadening of the melt-glass transition in the thermal expansion of the material. Image reproduced from reference [8].

The major problem with these techniques, illustrated in Figure 2.10, is that the transition in the property of interest becomes extremely smeared at small film thicknesses and the question becomes how to characterize the transition between high and low temperature regions. Recently, J.A. Forrest proposed a simple method to parameterize the surface mobility in polymer thin films measured by dilatometry and to describe some characteristic length scale, $\xi(T)$, of enhanced mobility.[8] With the proposed parameterization method, the surface dynamics are equated to some temperature, T , related to the bulk at different temperature, R_s , which can be expressed by: $T_g(h) = R_s + (T_g^{bulk} - R_s)/(1 - f[h/2\xi(T_g)])$.

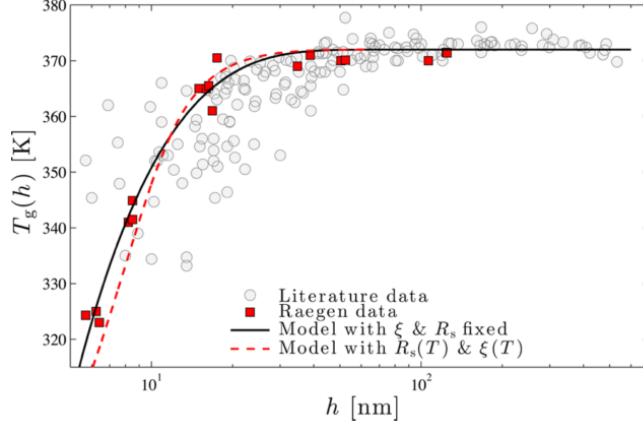


Figure 2.11: The parameterization method used to explain previous literature data. Image reproduced from reference [8].

As shown in Figure 2.11, the parameterization method, Forrest argues, can be used to explain the previously measured dilatometric T_g values for the past 20 years by accounting for the dynamics at free surface. But most importantly it emphasizes the existence of heterogeneous dynamics or a gradient of segmental mobility for supported polymer thin films—and this effect is from a single free interface.

This situation can become rather complicated with the addition of more interfaces such as free-standing polymer films which have two free interfaces or sandwiched polymer thin films with two polymer-substrate interfaces where the interfacial interactions must be considered. Therefore, it is difficult to characterize the spatial distribution of segmental dynamics via a single parameter such as T_g . To characterize the spatial distribution of relaxation dynamics is a challenging experimental task, however, in molecular dynamic simulations all of the information can be obtained. Recently, Hanakata *et al.*, performed an extensive simulation on the dynamics of supported polymer thin films where they investigated the effect of substrate roughness, polymer-substrate interaction parameter, and confinement parameter (film thickness).[9]

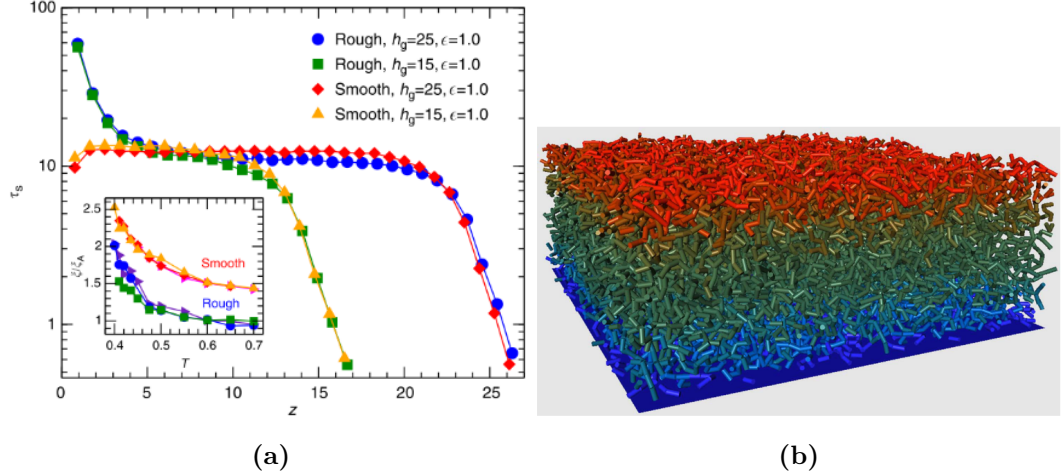


Figure 2.12: (a) The spatial distribution of relaxation times as a function of distance away from the substrate’s surface, demonstrating a gradient of molecular mobility as well as the effect of surface roughness. Increasing surface roughness enhances the suppression of mobility at the interface when compared to smooth surfaces which have little effect on the interfacial dynamics. (b) A visualization of segmental mobility for the case of a rough substrate. Images are reproduced from reference [9].

As shown in Fig 2.12, the spatial distribution of segmental dynamics at the free surface and substrate can be determined. Additionally, the effect of the surface roughness increases the accessible surface area which in turn leads to a suppression in segmental mobility at the polymer-substrate interface. Nevertheless, the dynamics at distances far away from the substrate are always enhanced. The timescale of dynamics also shows an exponential gradient in their spatial distribution where one can imagine at sufficiently low film thickness that the entire profile is continuous distribution of time scales, *i.e.* an entirely interfacial material.

With regards to polymer thin films, the above mentioned studies are important to consider for several reasons: (1) they emphasize the effect of substrate interactions on segmental dynamics or T_g , (2) they demonstrate some of the largest changes in dynamics in the past twenty years, (3) reinforces that the experimental technique in fact matters when detecting nanoscale changes in dynamics (this point will be a reoccurring theme throughout this Dissertation).

2.3.2 Polymer Nanocomposites

The previous section provided an overview key issues concerning polymer thin films and the concept of interfacial interactions and confinement effects in one-dimension. However, as described below, there are many facets yet explored when quantitatively comparing polymer thin films and polymer nanocomposites.[46, 47]

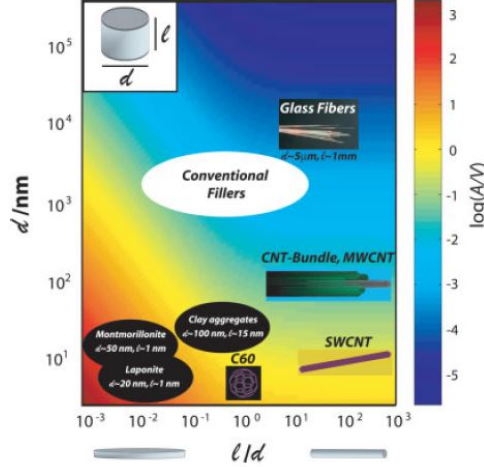


Figure 2.13: A visual representation of the different aspect ratios and surface-to-volume ratios for varying nanoparticle geometries. Image reproduced from reference [10]

A variety of nanoparticle can be used in polymer nanocomposites and somewhat differentiates polymer thin films from polymer nanocomposites. The geometry of the nanoparticle can be an extremely important parameter, especially when considering the relative aspect ratios of shapes. The most commonly used geometries are planar, cylindrical, and spherical. Depending on the specific application that is desired for the polymer nanocomposite, one may be forced to use a specific geometry for the material properties of that nanoparticle *i.e.*, spherical for quantum dots or cylindrical to increase tensile strength along one dimension.

Besides the obvious geometrical limitations mentioned above, for purposes of modifying polymer dynamics the relative surface area-to-volume ratio (SVR) is a crucial parameter. The geometry with the largest SVR is planar ($\sim 2(l + 2h)/(lh)$)

and closely followed by cylindrical ($\sim 2(d + 2l)/(ld)$) and spherical ($\sim 6/d$). However, despite the advantage of surface area, the anisotropy of the shape raises issues when uniformly dispersing anisotropic nanoparticles. The anisotropy of graphene or carbon-nanotubes, for example, will result in a dispersion with a preferred directionality that can change with stress or flow of the polymer matrix—which can be an advantage or disadvantage depending on the specific application. For the purposes of this Dissertation, only isotropic, spherical nanoparticles will be discussed in detail.

The question of how to disperse nanoparticles into a polymer matrix has stalled the progress of understanding the attainable physical properties of polymer nanocomposites as well as caused long-standing controversial results within the literature. Within the plastics and rubbery industries, traditional micron-sized fillers have long been physically mixed with the polymer matrix by batch mixers or continuous flow mixers (twin screw extruders) by shear flow mixing. However, achieving uniform dispersion becomes an extremely difficult task with nanosized fillers which readily aggregate into micron-sized agglomerates when removed from their solution state. One of the most successful methods for producing uniformly dispersed nanocomposites utilizes the stability of nanoparticles in their solution state and is known as the solvent mixing and evaporation method. In this method, a solvent is chosen that can adequately dissolve both the polymer matrix and nanoparticle, the two phases are mixed for some time duration, and the final solution is transferred to a Teflon mold for the solvent to evaporate. The solvent molecules stabilize the mixture from aggregation and facilitate the dispersion of the nanoparticles—where different solvents could influence the final dispersion state of the material.

As briefly discussed above, the interfacial interactions between the polymer and nanoparticles are expected to augment the segmental dynamics in the local vicinity of the nanoparticle surfaces. However, for the case of polymer nanocomposites this phenomenon is now in 3-dimensions, has a staggering number of interfaces, and has

no free surfaces. Despite the complexity of this problem, several simulations have investigated these systems.

Simulation Results

Simulations have several advantages over experiments—such as well-dispersed nanoparticles and spatially relevant information concerning static structure and dynamic processes. Typically, experiments can only measure an ensemble averaged value which stresses the importance of multiple techniques and will be discussed in detail hereafter. However, the accessible time scale for current simulations is limited to microsecond dynamics and adds some ambiguity to interpretation of segmental dynamics ($\tau_\alpha \gg \mu\text{s}$) near T_g .

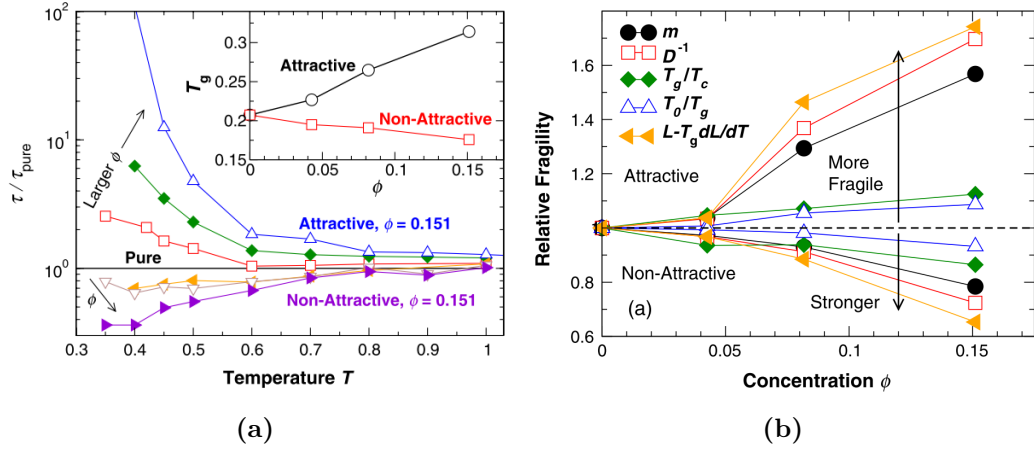


Figure 2.14: (a) Normalized relaxation times as a function of temperature at multiple NP concentrations and for attractive and non-attractive interfacial interactions. (b) The relative fragility index determined from multiple methods for different interfacial interactions. Images reproduced from reference [11].

Many simulations have attempted to probe the dynamics within polymer nanocomposites,[2, 48–50] however, Starr and Douglas recently investigated the role of interfacial interactions on cooperative dynamics in polymer nanocomposites.[11] As shown in Figure 2.14(a), these authors studied the temperature dependence of segmental relaxation times with a variety of nanoparticle concentrations and with

either non-attractive or attractive interfacial interactions. They found that as the nanoparticle concentration increased, the relaxation times increased for attractive systems and decreased for non-attractive systems. The change in relaxation times are directly related to the corresponding T_g shifts, as shown in the inset of Figure 2.14(a). The change in dynamics is also captured in the fragility index, as shown in Figure 2.14(b), otherwise known as the steepness of relaxation times at T_g which is proposed to be related to the cooperativity of the relaxation. The fragility index is found to change systematically following the trend of the relative T_g shift. The authors explain these dynamic changes in terms of an increase in cooperative string-like motions along the polymer chain, which is consistent with Adam-Gibbs theory of glass formation. However, the exact mechanism driving the increase in the cooperative string-like motion is not yet understood.

Experimental Results

It remains a challenge to experimentally investigate the interfacial dynamics in polymer nanocomposites, since many techniques probe the ensemble averaged response of the material. However, at high enough NP concentrations, the entire material is expected to be effectively an interfacial material, which is much easier to measure when compared to polymer thin films, *i.e.*, more material.

The qualitative relationship between confinement and interfacial effects polymer thin films and polymer nanocomposites has been discussed for the past twenty years. Obviously, dimensionality is different between the two systems; where polymer thin films are confined perpendicular (1-D) to the substrate regardless of the number of substrates or free surfaces and confinement in polymer nanocomposites depends on the geometry of the filler. For confinement purposes, the simplest filler to consider are spherical nanoparticles to exploit symmetry. Therefore, the confinement parameter for polymer nanocomposites with spherical nanoparticles is the surface-to-surface distance between adjacent nanoparticles—which demands the criteria for a uniformly distributed nanoparticles throughout

the polymer matrix. Previously, Bansal *et al.* made the experimental comparison between supported PS thin films on silica substrates and well-dispersed silica nanoparticles ($D = 20$ nm) in a PS matrix.[12] They found that the calorimetric T_g of the polymer nanocomposite decreased with increasing nanoparticle loading or rather decreasing surface-to-surface distance similar to supported thin films (See Figure 2.15(a)). However, this comparison was limited by the quality of nanoparticle dispersion at high nanoparticle concentrations where aggregation becomes a problem. Interestingly, the width of the calorimetric glass transition was found to broaden with decreasing interparticle spacing and film thickness which corroborates the gradient of segmental mobility being present in both systems (Figure 2.15(b)).

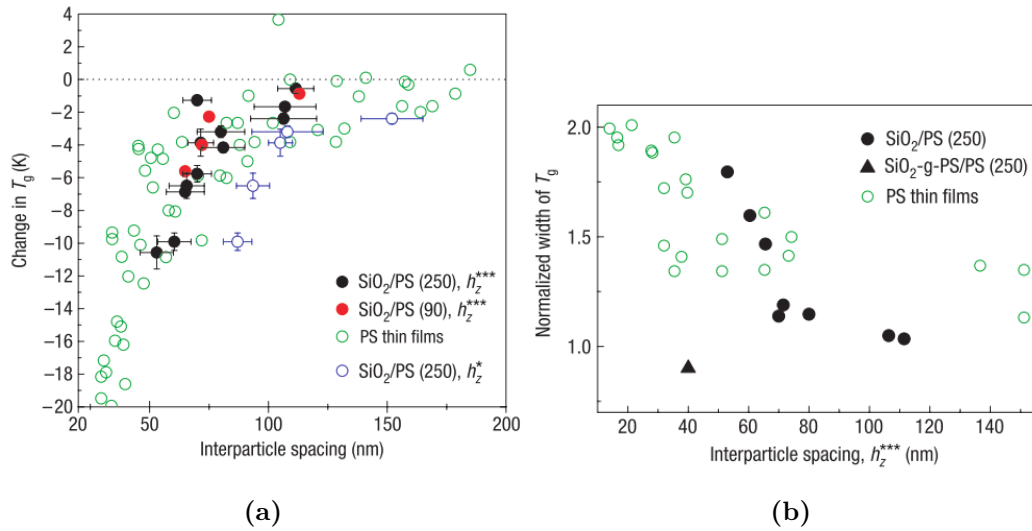


Figure 2.15: (a) The relative change in T_g as a function of interparticle spacing and film thickness for both polymer thin films and polymer nanocomposites. (b) The relative width of the calorimetric glass transition as a function of interparticle spacing and film thickness for multiple systems. Images reproduced from reference [12].

Despite this so-called quantitative equivalence between polystyrene thin films on silica substrates and polystyrene/silica nanocomposites, the mechanisms responsible for the changes in the T_g are different. This is because polymer

thin films experience a suppression of segmental mobility at the interface due to physical adsorption and an enhancement of segmental mobility at the free surface due to a loss of nearest neighboring molecules. For the case of the polymer nanocomposite the particles dewet (repulsive force) from the polymer matrix and enhance dynamics of the local surrounding segments—with no competing effects to suppress the segmental mobility which leads to overall faster dynamics. It should be noted that the use of nanoparticles that dewet from the polymer matrix will eventually diffuse and aggregate at temperatures above T_g , so the practical use of these materials is not promising. However, the calorimetric glass transition temperature used in the above mentioned study only detects the average change in segmental dynamics and cannot be used to understand the interfacial dynamics in these materials alone—opposite to the dilatometric measurements which only probe the dynamics of the free surface in polymer thin films.

Another group of authors attempted to understand the relationship between polymer thin films and polymer nanocomposites by systematically comparing the dynamics of capped polymer thin films (two opposing substrates with polymer in between) and polymer nanocomposites. In these studies, they used fluorescence spectroscopy to detect changes in the glass transition temperature in both systems. Fluorescence spectroscopy uses a very small amount of a fluorescent dye molecule to monitor the normalized changes in intensity as a function of temperature. Therefore, this technique indirectly probes the segmental dynamics by monitoring the intensity of the tracer molecule.

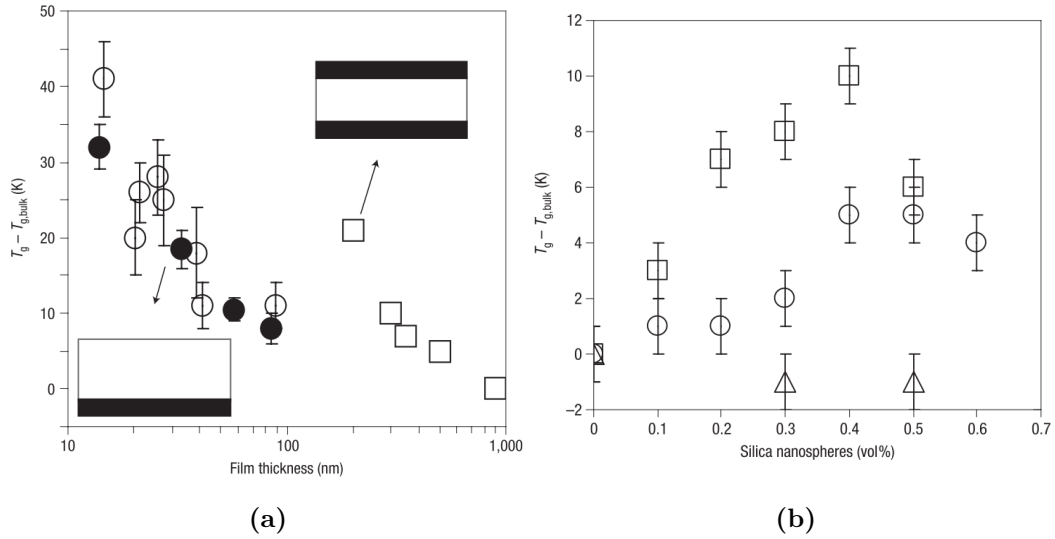


Figure 2.16: (a) The relative change in T_g of poly(2-vinyl pyridine) as a function of interparticle spacing and film thickness for both supported thin films (empty and solid circles) and capped thin films (empty squares). (b) The relative change in T_g of poly(2-vinyl pyridine)/silica (empty squares), poly(methyl methacrylate)/silica (empty circles), and polystyrene/silica (empty triangles) nanocomposites. Images reproduced from reference [13].

In their study, three different polymer chemistries were investigated: polystyrene, poly(methyl methacrylate), and poly(2-vinyl pyridine). For the capped polymer thin films, a dramatic increase in T_g was observed at much larger film thicknesses than previously reported for supported polymer thin films ($h < 30$ nm). For example, a 22 K increase in the glass transition temperature was observed at a film thickness of 200 nm for capped poly(2-vinyl pyridine) films.[13] This would imply that the change in segmental dynamics at the substrates propagate more than 100 nm in these films, *i.e.*, that interfacial interactions impose some sort of long-range effect in these amorphous materials. These results were compared to polymer nanocomposites with loadings of silica nanospheres that had approximately similar interparticle spacing (the comparable confinement parameter to thin film thickness). Intriguingly, they found that the T_g of the polymer nanocomposites had comparable values to the polymer thin films at similar interparticle spacing and

film thicknesses for poly(2-vinyl pyridine) and poly(methyl methacrylate) implying a similar relationship between interfacial interactions and confinement in both systems. However, it should be mentioned that fluorescence spectroscopy has no control where the tracer molecules are within these nanomaterials, which implies that they could be preferentially drawn to the substrate or nanoparticle surface and could only reflect the interfacial dynamics instead of the overall response of the system.

To date, several experiments have demonstrated that strong, attractive polymer–NP interactions (a case in which simulations are currently limited due to significant slowing down of polymer dynamics) can significantly increase the T_g of PNCs.[13, 22] It has been postulated that the polymer near the NPs adsorbs to the surface, essentially immobilizing the polymer at the interface and ultimately leading to formation of the so-called dead layer which is a dynamically frozen polymer layer.[51, 52] The concept of the dead layer stems from the Long–Lequeux picture of dynamics in polymer nanocomposites.[53–55] The dynamic signature of the dead layer is often attributed to the decrease in the amplitude of the glass transition step from calorimetric measurements or the dielectric strength from dielectric spectroscopy.[52, 56] However, the existence of this dead layer still lacks an explanation for significant changes in T_g at extremely low NP concentrations (0.4vol%) as the segmental dynamics of the polymer between NPs would be affected on length scales comparable to interparticle spacing (greater than 100 nm) which implies some sort of long range effect. Unfortunately, the progress in understanding how polymer-NP interactions affect the glass transition phenomenon in PNCs is rather slow due to numerous quantitative and qualitative discrepancies in the reports of T_g shifts in PNCs measured by different experimental techniques,[13, 20, 22, 56–59] as described in detail within the work of Robertson and Roland.[60]

2.4 Summary

In summary, as the length scale of nanoparticles approach that of individual polymer chains, the presence of the nanoparticle is expected to perturb and modify the polymer dynamics on several different time and length scales (fast dynamics, secondary dynamics, segmental dynamics, and chain dynamics). The most important dynamic process for many practical applications, related to the vitrification of the polymer matrix, is the segmental dynamics which has been shown to be significantly influenced by two competing effects: interfacial interactions and confinement. When considering the case of one-dimensional confinement, specifically polymer thin films, there can be a variety of effects depending on the number of interfaces (substrate or free surfaces). By applying these experimental findings to the arena of polymer nanocomposites (3-dimensional confinement with numerous interfaces), the relationships are not quite as clear although there are some clear similarities. Fundamental progress in this field has been stalled by the numerous difficulties in nanoparticle dispersion, direct and indirect experimental techniques, and many conflicting experimental reports. Thus, it still remains a relatively open question as to how the polymer-NP interactions affect the interfacial dynamics and especially the overall properties of polymer nanocomposites.

Chapter 3

Experimental Methods

This chapter will consider the theoretical and experimental details of the techniques that will be used throughout the remainder of this dissertation.

3.1 Sample Preparation Methods

3.1.1 Materials

A variety of molecular weights (M_W) of poly(2-vinyl pyridine) ($M_W = 8,700$ g/mol, $M_W/M_N = 1.07$; $M_W = 100,000$ g/mol, $M_W/M_N = 1.05$; $M_W = 400,000$ g/mol, $M_W/M_N = 1.08$) were purchased from Scientific Polymer, Inc. All other M_W 's were synthesized in our own laboratories by RAFT polymerization and will be discussed in more detail within their respective chapters.

Tetraethyl orthosilicate (TEOS, >95%), Ethanol, ammonium aqueous solution (30–33 wt %), and methyl ethyl ketone (MEK) were purchased from Sigma Aldrich and were used without further purification. From these materials, we synthesized monodisperse colloidal silica nanoparticles (D=25 nm) by the modified Stober method following previous reports.[23,24]

3.1.2 Preparation Methods

Rapid Precipitation Method

In chapter 4, the following approach was used to mix our polymer and nanoparticles. To ensure a well-dispersed polymer nanocomposite, solution mixing and rapid precipitation were employed. The polymer and NPs were separately dissolved with dimethylformide and bath-sonicated for 30 min. The two solutions were mixed and sonicated again for 30 min. Afterward, the solution was slowly precipitated at the interface of a hexane and water (50:50) mixture, recovered, and transferred to a vacuum oven where they were kept for at least 3 days at 150 centigrade to remove any residual solvents.

Solvent Evaporation Method

For chapters 5 and 6, the polymer nanocomposites were prepared by mixing different concentrations of silica nanoparticles in a water/ethanol solution (50:50) with P2VP dissolved in a MEK. The samples were then stirred for 1-2 hours, transferred to a Teflon mold, and then placed into a vacuum oven at room temperature for solvents to evaporate for 24 hours at 1 mbar. The resulting samples were then annealed under vacuum at 150 centigrade for an additional 48 hours before further measurements.

For sample characterization, independent of preparation method, the samples were hot pressed at 150 centigrade by placing samples between Mylar sheets and using a heated hydraulic press, resulting in films thicknesses of $\sim 100 \mu\text{m}$. These solid uniform films were then cut into geometries which could be used for dielectric spectroscopy, thermal analysis, and small angle X-ray scattering.

3.2 Thermodynamic Gravitational Analysis (TGA)

TGA was performed using Q50 (TA Instruments) to verify the weight percent of nanoparticles within our composites. TGA was conducted from room temperature to 1000 centigrade under a nitrogen atmosphere at a rate of 10 K/min or 20 K/min. As the organic carbon-based polymer thermally degrades, the final inorganic nanoparticles remain and the relative concentration of nanoparticles can be determined.

3.3 Transmission Electron Microscopy (TEM)

The quality of nanoparticle dispersion of polymer nanocomposites are often crucial to the desired physical properties. While not always a quantitative technique, TEM offers a visual check on nanoparticle polydispersity, nanoparticle spatial dispersion, and interparticle spacing.

For successful TEM measurements, the sample thickness were required to be ≈ 200 nm or less. To achieve such film thicknesses, the polymer nanocomposites were embedded into an epoxy resin, cured, and then microtomed with a Leica Ultra microtome EM UC7 using a diamond knife at ambient conditions with resulting specimens having thicknesses 200 nm. To accurately determine the correct thicknesses, the polymer films were cut and floated onto water which the color of the refracted light identified the appropriate sample thicknesses. The thin films cut from the microtome were then transferred to a copper TEM grid (200 or 400 grid number) and allowed to dry for 24 hours to remove any residual water. TEM measurements were performed on Zeiss Libra 200 HT FE MC with an operating voltage of 200 kV and an emission current of 230 mA. For low molecular weight samples, a low electron beam intensity had to be used to avoid heating the samples above their respective T_g 's.

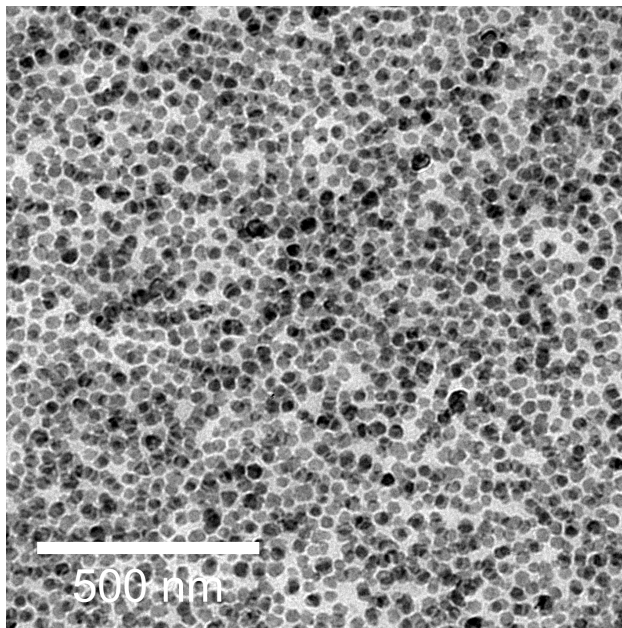


Figure 3.1: A representative TEM image of silica nanoparticles embedded in poly(2-vinyl pyridine) ($M_W = 100$ kg/mol) at 40 wt% to demonstrate that the nanoparticles are well-dispersed in the polymer.

3.4 Small Angle X-Ray Scattering (SAXS)

Small angle X-ray scattering (SAXS) is an experimental technique that uses X-ray diffraction to determine the static structure of materials. Unlike wide angle X-ray scattering, that probes the small length scales close to atom lattice spacing of crystalline materials, SAXS can detect rather large structural inhomogeneities within the 1-50 nm range. This limit can be further pushed by using ultra small angle X-ray scattering (USAXS) which can probe structures up to 1 micron. Therefore, SAXS and USAXS are particularly useful techniques for studying amorphous materials as well as inhomogeneous systems such as block copolymers and polymer nanocomposites.

Regardless of the chosen technique, X-rays are sensitive to changes in the electron densities of different materials and will be reflected in the diffraction pattern. WAXS diffraction patterns will reflect intra-molecular or inter-atomic level

correlations, SAXS will contain inter-molecular level and some macromolecular aggregate correlations, and USAXS will reveal correlations for large-scale aggregates or structures.

3.4.1 Principles of X-ray scattering

For small angle X-ray scattering in a transmission geometry, the sample is placed at some distance away from the detector (≈ 2.5 m) and exposed to a source of coherent X-rays. The X-rays reach the sample, scatter (coherently and incoherently), and cast a diffraction pattern onto the detector as shown in Figure 3.2.

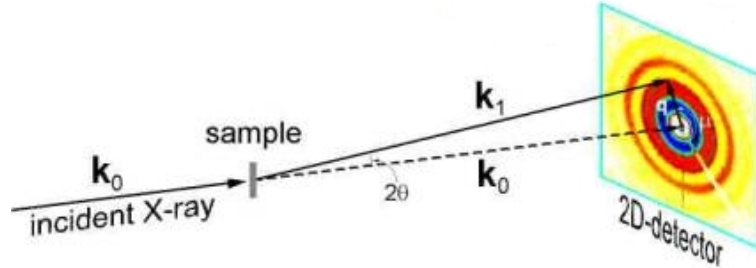


Figure 3.2: A simplified experimental schematic for a small angle X-ray scattering setup in a transmission geometry. Image reproduced from reference [14].

The q -dependence of the scattering intensity can be described by the following expression:

$$I(q) = A \int_0^\infty n(r) [f(qr)]^2 S(qr) dr \quad (3.1)$$

where A is the scaling factor, $n(r)$ is the size distribution, $f(qr)$ is the form factor, and $S(qr)$ is the structure factor. The first two terms of the scattering intensity are dependent on the contrast, experimental geometry, and the variation in the size of the scattering objects. The form factor is purely dependent on the geometry or the aspect ratio of the scattering object (disc, spherical, or oblong). The structure factor is essentially a correlation factor for the inter-particle scattering.

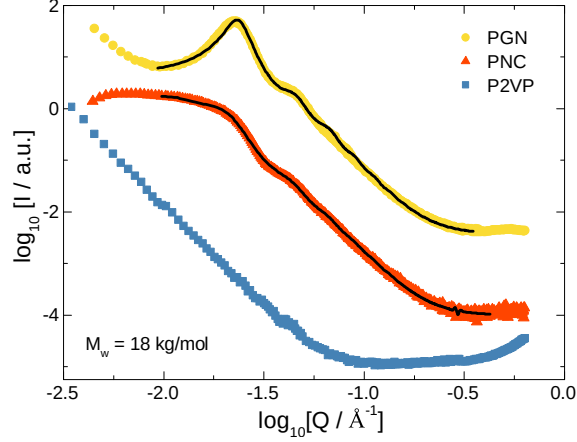


Figure 3.3: Small angle x-ray scattering profiles for the intermediate molecular weight poly(2-vinyl pyridine)-based nanocomposites and corresponding fits obtained from the polydisperse core-shell model. The curves are arbitrarily shifted for clarity. These data are explained in detail within Chapter 7.

For the work presented in this Dissertation, the scattering model used was the polydisperse core-shell model (PCSM). The PCSM assumes that the $n(r)$ follows a Schulz distribution of particle radii and calculates a form factor for polydispersed spherical particles with a core-shell structure. The form factor is normalized by the average volume of the particles, $\langle V_c \rangle = \frac{4\pi}{3} \langle r_c^3 \rangle$, and averaged over the distribution of radii. No interparticle interactions are included in this model.

The form factor for a spherical particle with a core-shell structure which is normalized by the particle volume can be expressed by the following:

$$f(q) = \frac{A}{V_s} \left[3V_c(\rho_c - \rho_s) \frac{\sin(qr_c) - qr_c \cos(qr_c)}{(qr_c)^3} + 3V_s(\rho_s - \rho_{solv}) \frac{\sin(qr_s) - qr_s \cos(qr_s)}{(qr_s)^3} \right] + C \quad (3.2)$$

where C is a constant background, V_s is the volume of the shell, V_c is the volume of the core, ρ_c is the scattering length density of the core, ρ_s is the scattering length density of the shell, ρ_{solv} is the scattering length density of the solvent/matrix, and the respective radii are r_s and r_c .

The structure factor, $S(q)$, which accounts for the particle-particle interactions is a hard sphere structure factor and accounts for the volume fraction of the cores.

3.5 Differential Scanning Calorimetry (DSC)

3.5.1 Instrumental Details

DSC measurements were performed with a Q2000 (TA Instruments). For the majority of the measurements presented within this Dissertation, the sample preparation for DSC was similar. First, standard aluminum pans purchased from TA instruments were weighed, a small sample mass was added (ranging from 5 to 20 mg), and then the pans were sealed. After determining the mass of the sample within the standard pan, the sample pans were loaded into the Q2000 autosampler, and measured. For a standard DSC measurement, a heating/cooling rate of 10K/min was used and was typically annealed at high temperature, T_{high} ($T_g + 50\text{K}$), for 10 minutes to erase any thermal history. Therefore, a typical DSC run will begin at T_{high} , ramp to T_{low} , and then ramp back to T_{high} at the same rate and repeat two more times to check for hysteresis. The Q2000 was calibrated by indium and sapphire standards and all samples were run three times.

3.5.2 Principles of Calorimetry

Calorimetry is a technique used to measure the thermodynamic properties of materials. Differential scanning calorimetry (DSC) measures how thermodynamic properties change with temperature and time by applying a constant and linear heating (or cooling) rate and measuring the resulting heat flow through the material. DSC is commonly used to determine information related to phase transitions such as crystallization, melting, and glass transition temperatures.

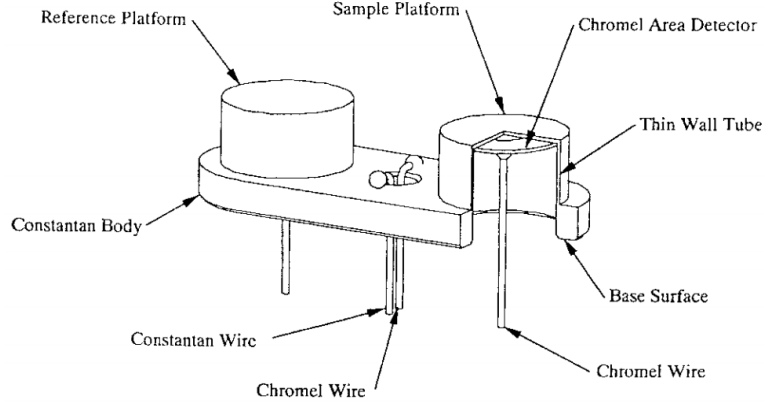


Figure 3.4: A detailed experimental schematic for a heat flux differential scanning calorimeter produced by TA Instruments. [15]

For heat flux DSCs, a sample is placed into a thermally conductive pan and placed ontop a thermocouple within an insulated furnace alongside an identical empty reference pan. The furnace is sealed and a linear heating or cooling rate is applied and the difference in the temperature between the two pans is recorded by the thermocouples. The heat flow, $\dot{q}$, through the sample is determined by using a simple expression,

$$\dot{q} = E(T)\Delta T \quad (3.3)$$

where $E(T)$ is some proportionality factor that is dependent on the geometry and thermal conductivities of the furnace construction. By performing a heat balance, we can determine the heat flow through the sample as well as the reference in terms of known parameters.

$$\dot{q}_s = \frac{T_0 - T_s}{R_s} - C_s \frac{dT_s}{dt} \quad (3.4)$$

$$\dot{q}_r = \frac{T_0 - T_r}{R_r} - C_r \frac{dT_r}{dt} \quad (3.5)$$

The sensor parameters are defined as: R_s is the thermal resistance of the sample, R_r is the thermal resistance of the reference, C_s is the heat capacity of the sample, C_r is the heat capacity of the reference, and T_s , T_r , and T_0 are the temperatures of the sample, reference, and the cell, respectively.

To calculate the heat flow through the sample of interest, the contribution from the reference pan is removed by taking the difference, $\dot{q} = \dot{q}_s - \dot{q}_r$:

$$\dot{q} = \frac{T_s - T_r}{R_r} + (T_0 - T_s) \left(\frac{1}{R_s} - \frac{1}{R_r} \right) + (C_r - C_s) \frac{dT_s}{dt} - C_r \frac{d(T_s - T_r)}{dt} \quad (3.6)$$

The main difference between the heat flux DSC and traditional DSC is that we no longer assume identical parameters for the sample and reference (eq. 3.1) and measure both sample and reference pans independently. By correct calibration methods, all the the sensor parameters can be acquired and used in equation 3.4 to accurately determine the heat flow of the sample and the sample pan.

However, to determine the heat flow of the actual sample, we need to account for the sample pan.

$$\dot{q}_{sample} = \dot{q}_s - m_{sp} c_{pan} \frac{dT_{sp}}{dt} \quad (3.7)$$

where m_{sp} is the sample pan mass, c_{pan} is the specific heat capacity of the pan (typically aluminum), and $\frac{dT_{sp}}{dt}$ is the temperature change through the sample pan. By using eq. 3.3, we can use the expression for the specific heat capacity of reference pan to solve eq. 3.5.

$$\dot{q}_r = m_{rp} c_{pan} \frac{dT_{rp}}{dt} \quad (3.8)$$

where m_{rp} is the reference pan mass, c_{pan} is the specific heat capacity of the pan (typically aluminum), and $\frac{dT_{rp}}{dt}$ is the temperature change through the reference pan.

Finally, we find a simple expression, very similar to eq. 3.5 except with a prefactor on the second term, that accounts for any differences in mass or temperature delay between the two pans.

$$\dot{q}_{sample} = \dot{q}_s - \dot{q}_s \left(\frac{m_{sp}(dT_{sp}/dt)}{m_{rp}(dT_{rp}/dt)} \right) \quad (3.9)$$

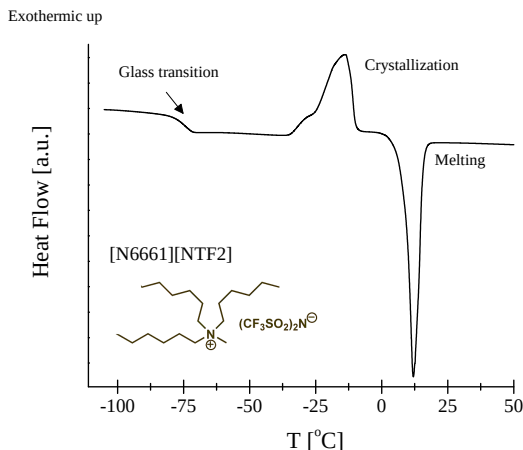


Figure 3.5: An example of differential scanning calorimetry data (Heat flux DSC, TA Instrument Q2000) for an ionic liquid that undergoes a glass transition, crystallization, and melting transitions when heated at a rate of 5 C/min.

DSC is a very useful tool when characterizing the thermodynamic properties of new materials, especially due to its relative speed and ease of operation. However, for the purposes of this Dissertation, the accurate determination of specific heat capacity values as well as the extraction of more detailed dynamical information are required. Therefore, the use of temperature modulated DSC was required. The remainder of this section will be used to explain *why* it was needed and the differences between conventional DSC and temperature modulated DSC.

3.5.3 Temperature Modulated DSC (TM-DSC)

The main advantage of TM-DSC over traditional DSC is the deconvolution of the heat flow response of the sample into reversing and non-reversing components. The

reversing component is related to reversible processes such as glass transitions, some melting, and accurate heat capacity measurements. The non-reversing component is related to kinetic processes that depend on time such as enthalpic recovery, evaporation, crystallization, thermal curing reactions, and decomposition.

Simply put, the heat flow through our system can be expressed as:

$$\dot{q} = C_p \frac{dT}{dt} + f(T, t) \quad (3.10)$$

where the first term is the reversing component and is directly proportional to the heat capacity while the non-reversing component is the second term and is not related to heat capacity.

Many processes can contribute to the overall signal of traditional DSC. This is even true in a purely amorphous polymer system, where the time spent in the glassy state causes physical aging effects which are visible in the calorimetric glass transition upon heating—manifested by an overshooting of heat capacity known as an enthalpic relaxation.

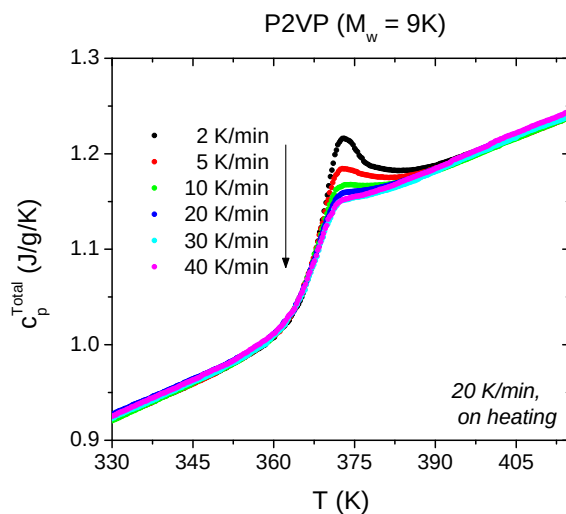


Figure 3.6: The calorimetric glass transition and enthalpic relaxation both overlapping in the heat specific heat capacity of standard DSC upon heating at constant heating rate of 20 K/min, where each color is cooled through the glass transition at different rates.

TM-DSC separates the reversing and non-reversing components in a single measurement (Fig 3.7) by creating 2 raw signals. We first apply a modulated heating rate (stimulus) and measure the modulated heat flow (response). When compared to standard DSC, we are still applying a linear average heating or cooling rate with a sinusoidal oscillating heat flow as shown in Fig. 3.6.

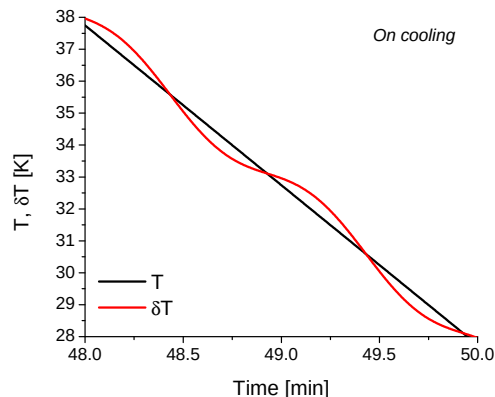


Figure 3.7: The average temperature, T , and modulated temperature, δT , versus time for a typical TM-DSC measurement at 5K/min with a modulation of 1K/min.

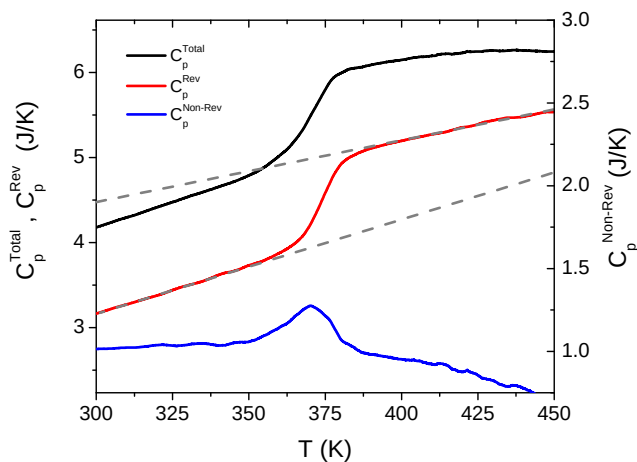


Figure 3.8: TM-DSC data for the total, reversing, and non-reversing heat capacities obtained by cooling at 5K/min and with a modulation of 1 K/min. Notice that the total heat capacity is decreasing at high temperatures due to a process in the non-reversing component, while reversing component has a constant slope above and below the glass transition.

Therefore, to accurately track changes in the glass transition (the transition step height, mid-point of transition, or absolute values of the specific heat) of polymers, we are solely interested in the reversing component from TM-DSC.

3.6 Dielectric Spectroscopy (DS)

Dielectric spectroscopy (DS) is technique that uses an external electric field to determine the dielectric response of material. This technique is particularly useful for studying the dielectric response of molecular liquids and polymers with strong dipole moments or asymmetric structures. The external electric field which will cause a rotational reorientation of the dipolar molecule (or polymer side group) in order to align with the electric field. Therefore, the reorientational dynamics of molecules can be studied by measuring the frequency dependence of the dielectric response to an oscillating electric field. This concept also applies to ionic molecules and ion transport properties can be measured but will not be covered in this Dissertation.

3.6.1 Instrumental Details

The dielectric spectroscopy measurements are recorded by a Novocontrol Concept 80 device. Figure 3.9 illustrates the electrical schematic for this device. For the purposes of this dissertation, all measurements were carried out in a parallel plate capacitor configuration.

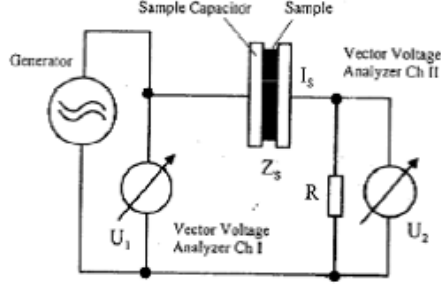


Figure 3.9: The electrical schematic for the Novocontrol Concept 80 setup in the parallel plate configuration. Image reproduced from [16].

Dielectric spectrometers measure the dielectric response of a material to an electric field as a function of frequency and is often expressed in terms of complex permittivity, $\epsilon^*(\omega)$. However, since we cannot directly measure $\epsilon^*(\omega)$ it is calculated from the complex impedance, $Z^*(\omega)$.

In the simplest configuration, the device applies a sinusoidal voltage across the capacitor and determines the current through the sample, I_S , by the voltage drop across, U_2 , a test resistor, R , and measures the $Z^*(\omega)$ of the sample as shown in Figure 3.9.

We can express $Z^*(\omega)$ in terms of all measured quantities by:

$$Z^*(\omega) = \frac{U_S^*(\omega)}{I_S^*(\omega)} = \frac{U_1^*(\omega) - U_2^*(\omega)}{U_2^*(\omega)/R} = R \left(\frac{U_1^*(\omega)}{U_2^*(\omega)} - 1 \right)$$

To obtain $\epsilon^*(\omega)$, we relate the $Z^*(\omega)$ to the complex capacitance, $C^*(\omega)$, in terms of the measurable quantities.

$$C^*(\omega) = \frac{1}{i\omega Z^*(\omega)} = \left(i\omega R \left(\frac{U_1^*(\omega)}{U_2^*(\omega)} - 1 \right) \right)^{-1} \quad (3.11)$$

The final step is relating the complex capacitance to the complex permittivity by the simple expression $\epsilon^*(\omega) = C^*(\omega)/C_0$, where C_0 is the capacitance of the empty cell.

$$\epsilon^*(\omega) = \left(i\omega RC_0 \left(\frac{U_1^*(\omega)}{U_2^*(\omega)} - 1 \right) \right)^{-1} \quad (3.12)$$

Dielectric spectroscopy provides a wealth of information like complex impedance, conductivity, electric modulus, and capacitance, however only the real and imaginary permittivity representations will be discussed for the purposes of this Dissertation.

3.6.2 Theory of Dielectric Spectroscopy

Electrostatics

In electrostatics, an electric field applied to a dielectric medium will induce a macroscopic polarization, $\mathbf{P}$, which can be directly related to the permanent microscopic dipole moments, $\boldsymbol{\mu}_i$, of a given volume by:

$$\mathbf{P} = \frac{1}{V} \sum_i \boldsymbol{\mu}_i + \mathbf{P}_\infty \quad (3.13)$$

where $\mathbf{P}_\infty$ accounts for all other processes besides orientation polarization of permanent dipole moments such as electronic and atomic polarization. Furthermore, if the system consists of only one kind of dipole moment, eq. 3.13 can be written as:

$$\mathbf{P} = \frac{N}{V} \langle \boldsymbol{\mu} \rangle + \mathbf{P}_\infty \quad (3.14)$$

where N is the total number of dipoles and $\langle \boldsymbol{\mu} \rangle$ is the average dipole moment. By assuming that dipole-dipole interactions and local electric fields do not strongly affect the macroscopic polarization we can calculate the contribution of the average dipole moment to the overall polarization. By Boltzmann statistics we can express the average dipole moment as the following:

$$\langle \boldsymbol{\mu} \rangle = \frac{\int_{4\pi} \boldsymbol{\mu} \exp\left(\frac{\boldsymbol{\mu} \cdot \mathbf{E}}{k_B T}\right) d\Omega}{\int_{4\pi} \exp\left(\frac{\boldsymbol{\mu} \cdot \mathbf{E}}{k_B T}\right) d\Omega} \quad (3.15)$$

Since the energy associated from a dipole interacting with the electric field is $U = -\boldsymbol{\mu} \cdot \mathbf{E}$, the $\exp(\frac{\boldsymbol{\mu} \cdot \mathbf{E}}{k_B T}) d\Omega$ term yields the probability of a dipole moment having an orientation from Ω to $\Omega + d\Omega$. However, only the dipole moments oriented parallel to the applied electric field will contribute to the polarization (i.e. $U = -\mu E \cos \theta$). Therefore, at sufficiently small values of U relative to the thermal energy eq. 3.15 simplifies to:

$$\langle \boldsymbol{\mu} \rangle = \frac{\mu^2}{3k_B T} \mathbf{E} \quad (3.16)$$

and we can now rewrite eq. 3.14 as:

$$\mathbf{P} = \frac{\mu^2}{3k_B T} \frac{N}{V} \mathbf{E} + \mathbf{P}_\infty \quad (3.17)$$

We can relate the polarization to the dielectric permittivity, ϵ , of an isotropic dielectric medium by $\mathbf{P} = \epsilon_0(\epsilon - 1)\mathbf{E}$ and eq. 3.17 becomes:

$$(\epsilon - 1)\epsilon_0 \mathbf{E} = \frac{\mu^2}{3k_B T} \frac{N}{V} \mathbf{E} + (\epsilon_\infty - 1)\epsilon_0 \mathbf{E} \quad (3.18)$$

or

$$\Delta\epsilon = \epsilon_s - \epsilon_\infty = \frac{1}{3\epsilon_0} \frac{n\mu^2}{k_B T} \quad (3.19)$$

where n is the number density of dipole moments and ϵ_s is the static permittivity.

Equation 3.19 gives for the difference in permittivity, or dielectric strength, of the dipolar reorientation process that is associated with the applied electric field. This relation connects the macroscopic polarization to the molecular dipole moments and their reorientation process when perturbed by an electric field. However, it is important to remember the two assumptions for this equation to be valid: (1) dipole-dipole interactions and (2) local electric fields or screening effects are negligible.

Linear Response Theory

So far we have only considered a system under a static field and need to develop our understanding for time-dependent perturbations. For a given system, an external perturbation, $x(t)$, can be applied and the system will give a response, $y(t)$. By assuming the perturbation is in the linear regime, or that the two perturbations are equal to the sum of two reactions, and time causality, that only previous perturbations contribute at some time, t , the response $y(t)$ can be described by the following:

$$y(t) = y_{\infty} + \int_{-\infty}^t J(t-t') \frac{dx(t')}{dt'} dt' \quad (3.20)$$

where $J(t)$ is the memory function of a material that can be measured by the time dependent response to an external perturbation (such as a step-like perturbation like the Dirac function). Assuming a Dirac function for the perturbation, $\frac{dx(t)}{dt} = x_0 \delta(t)$ yields:

$$J(t) = \frac{y(t) - y_{\infty}}{x_0} \quad (3.21)$$

By partial integration, it can be shown that equation 3.3 can also be expressed as:

$$y(t) = y_{\infty} + \int_0^{\infty} \frac{J(t')}{dt'} x(t-t') dt' \quad (3.22)$$

where y_{∞} is the response for very long times and is not due to relaxation processes.

Within the framework of linear response theory, $x(t)$ and $y(t)$ form a pair of conjugated variables and can be inverted if they are linear:

$$x(t) = x_{\infty} + \int_0^{\infty} \frac{G(t')}{dt'} y(t-t') dt' \quad (3.23)$$

Depending on if the response of the system, $y(t)$, is an extensive or intensive quantity, the memory function $J(t)$ is regarded as a generalized compliance and the time dependent process is called a retardation or $G(t)$ is a generalized modulus and the time dependent process is called a relaxation, respectively. These two functions are related to each other by:

$$\delta(t) = \int_{-\infty}^{\infty} J(t-t')G(t')dt' \quad (3.24)$$

In the stationary state, one can determine the generalized complex susceptibility, $J(\omega)$, from an external periodic perturbation $x = x_0 \exp(-i\omega t)$ and find that:

$$J^*(\omega) = J'(\omega) - iJ''(\omega) = J_{\infty} - \int_0^{\infty} \frac{dJ(\tau)}{d\tau} \exp^{-i\omega\tau} d\tau \quad (3.25)$$

and a corresponding expression for the generalized complex modulus,

$$G^*(\omega) = G'(\omega) - iG''(\omega) = G_{\infty} - \int_0^{\infty} \frac{dG(\tau)}{d\tau} \exp^{-i\omega\tau} d\tau \quad (3.26)$$

Furthermore, from eq. 3.24 we can show that

$$G^*(\omega)J^*(\omega) = 1 \quad (3.27)$$

is valid for both the generalized compliance and generalized modulus in the frequency domain.

For dielectric spectroscopy, where an electric field is used as a periodic perturbation ($x(t)$) and the polarization of the material is the material response ($y(t)$), the complex permittivity, $\epsilon^*(\omega)$ will be discussed at length and represents the complex compliance, $J^*(\omega)$.

Electrodynamics

As discussed above, the frequency-dependent complex permittivity of a material can be determined from dielectric spectroscopy from eq. 3.12 or more simply put as

$$\epsilon^*(\omega) = \frac{C^*(\omega)}{C_0} = \epsilon'(\omega) - i\epsilon''(\omega) \quad (3.28)$$

where C_0 is the capacitance of the empty capacitor cell.

The external perturbation used in dielectric spectroscopy is a sinusoidal electric field, $E^*(\omega) = E_0 \exp(i\omega t)$, with a sufficiently low field strength ($E_0 < 10^6$ V/cm).

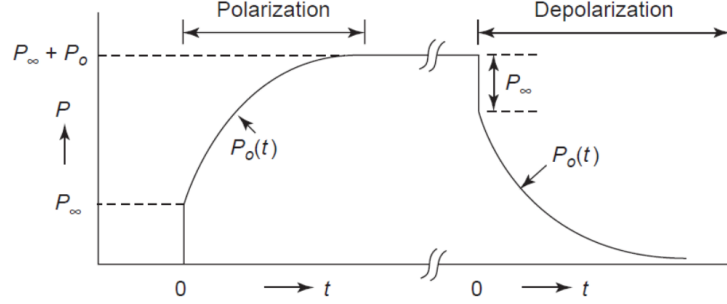


Figure 3.10: An example of a material's time-dependent polarization response to an applied electric field. Image reproduced from reference [17].

According to linear response theory, the material becomes polarized in response to the electric field. The time dependence of the polarization or *retardation* is illustrated in Figure 3.10 (in the time-domain) and can be shown to be similar to eq. 3.13.

$$P(t) = P_\infty + \frac{E(t)\epsilon_0}{\epsilon(\omega)} \quad (3.29)$$

By using the Fluctuation-Dissipation theorem, the transient polarization fluctuations in the absence of an electric field or under an applied electric field are related by the autocorrelation function,

$$\psi(t) = \frac{\langle \Delta P(0)\Delta P(t) \rangle}{\langle \Delta P(0)^2 \rangle} \quad (3.30)$$

where ΔP_0 is the value of polarization fluctuations at $t = 0$ and $\Delta P(t)$ are the fluctuations of the polarization about the average value for some time. The

autocorrelation function of polarization fluctuations can be shown to be related to the complex permittivity by a one-sided Fourier transform (eq. 3.30).[?]

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \int_0^\infty \exp^{-i\omega t} \left(-\frac{d}{dt}\psi(t) \right) dt \quad (3.31)$$

Where the derivative of the autocorrelation function, $-\frac{d}{dt}\psi(t)$, is essentially the transient current decay that occurs after the system reaches steady state and the electric field is removed (or Depolarization in Figure 3.10). Furthermore, the fluctuation of dipolar polarizations in a given material can be determined by inverting eq. 3.28 and expressing the autocorrelation function in terms of the real or imaginary parts of the complex permittivity.

The most simple relaxation processes would be a purely exponential process, otherwise known as a Debye relaxation, in which dipoles are solely independent and do not interact with neighboring dipoles. Therefore, the autocorrelation function, $\psi(t)$, for the polarization of a purely exponential processes would follow the form of $\exp(-\frac{t}{\tau_D})$, where τ_D is the Debye relaxation time. This simplifies eq. 3.31 to the following:

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty \exp^{-i\omega t} \left(\frac{1}{\tau_D} \exp^{-\frac{t}{\tau_D}} \right) dt \quad (3.32)$$

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\Delta\epsilon} = \frac{1}{1 + \omega^2\tau_D^2} - i\frac{\omega\tau_D}{1 + \omega^2\tau_D^2} = \frac{1}{1 + i\omega\tau_D} \quad (3.33)$$

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{1 + \omega^2\tau_D^2} - i\frac{\Delta\epsilon\omega\tau_D}{1 + \omega^2\tau_D^2} \quad (3.34)$$

Where the respective real and imaginary components can be expressed simply as:

$$\epsilon'(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{1 + \omega^2\tau_D^2} \quad (3.35)$$

$$\epsilon''(\omega) = \frac{\Delta\epsilon \cdot \omega\tau_D}{1 + \omega^2\tau_D^2} \quad (3.36)$$

However, this is for the ideal case of a purely exponential relaxation—which rarely occurs in nature. Molecular liquids and polymers that exhibit ideal glass forming properties are best described by several non-exponential or stretched relaxation functions such as Cole-Cole, Cole-Davidson, or Havriliak-Negami equations. These empirical equations are modified versions of the Debye equation (eq. 3.36) and utilize stretching exponents to help capture the asymmetric and symmetric broadening often observed in dielectric spectroscopy.

The most versatile of the three relations is the Havriliak-Negami (HN) equation, since it accounts for both symmetric and asymmetric spectral broadening,

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{(1 + (i\omega\tau_{HN})^\gamma)^\beta} \quad (3.37)$$

where γ and β are the symmetric and asymmetric stretching exponents, respectively.

3.6.3 Types of Relaxation Phenomena

The measured dielectric spectra of molecular liquids and polymers will show many different relaxation features. However, the physical meaning of these relaxations will depend on how the dipoles are arranged along the backbone of the polymer chain. There are three main categories for dipole distributions for polymer chains (Fig 3.10): type-A, type-B, and type-C polymers. Typically, if the dipole moment is directed along the backbone of the chain, a strong relaxation process will be observed in the dielectric spectra corresponding to the end-to-end re-orientation or relaxation of these dipoles. Therefore, the chain relaxation process of type-A polymers can be measured by dielectric spectroscopy. For type-B polymers, the dipole moment is oriented perpendicular to the backbone and therefore will

correspond to the reorientation or relaxation process of the polymer segments. In the dielectric spectra, type-B polymers will show a relaxation that corresponds to the motion of several polymer segments known as segmental relaxation. Finally, type-C polymers also have a dipole distribution like type-B polymers—except with an additional dipole on a sidegroup that also will have a much faster, secondary relaxation process.

In reality, polymers exhibit combinations of all type-A, type-B, and type-C relaxation features and can possess all three relaxation processes.

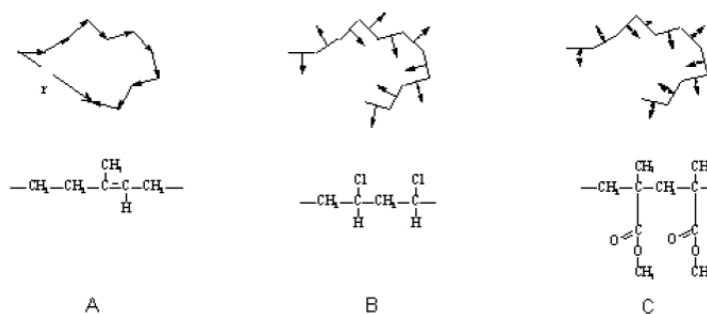


Figure 3.11: A cartoon of dipolar polymer chains and the possible distribution of dipole moments. Type-A polymers have a dipole moment in along the direction of the backbone of the chain while the moment of Type-B polymers is perpendicular to the backbone of the chain. Type-C polymers have two dipolar moments like Type-B polymers but with an additional dipole contribution on the chemical side group. In reality, some polymers exhibit properties of all types. [16]

Examples Relaxation Features

Figure 3.12 illustrates the way in which different relaxation features manifest themselves in the real and imaginary permittivity of poly(propylene glycol) (a polymer that is simultaneously both a type-A and type-B polymer). The spectra were measured at a constant temperature of 223.15K and with varying frequency of the applied external field ($V_{A.C.} = 0.5V$). There are two prominent features in the spectra of the real permittivity, $\epsilon'(\nu)$: (1) a small step at low frequencies and (2) a more dramatic step at 10^3 Hz. These features are better visualized in the imaginary permittivity, $\epsilon''(\nu)$, where they occur as peaks. These features are the relaxation

processes corresponding to the chain relaxation (*i.e.*, end-to-end dipolar relaxation) and the segmental relaxation. The much faster process is related to the cooperative motion of segments of the chain backbone since the oscillating electric field causes them to reorient more rapidly than the reorientation of the end-to-end dipole of the chain. The slower process corresponds to the chain relaxation. The feature at very low frequencies is the motion of ions near steady state and hence is related to the d.c. conductivity of the material.

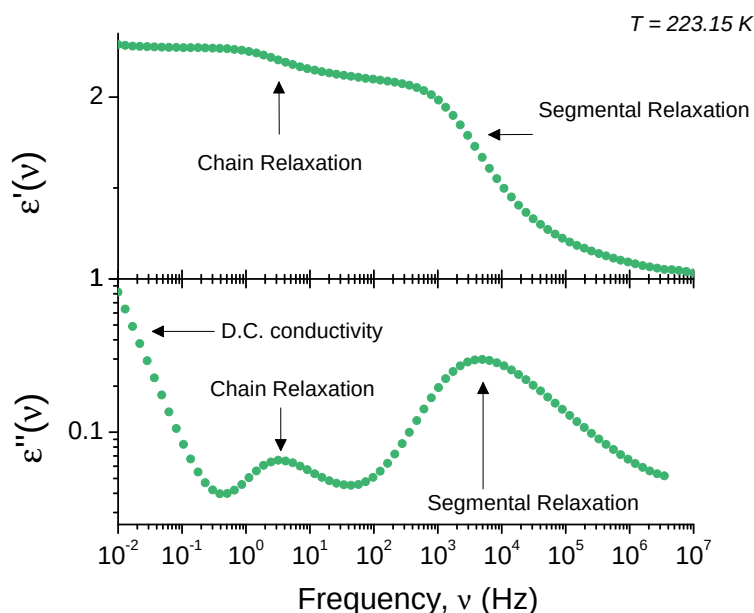


Figure 3.12: The frequency dependence for the real and imaginary parts of the complex permittivity for poly(propylene glycol) to illustrate how polymer dynamics are studied *via* dielectric spectroscopy.

The most interesting aspect of glass forming materials is the fact that these relaxation features can be studied as a function of different temperatures and times through the time-temperature superposition principle. Therefore, the frequency-dependent spectra measured in isothermal conditions will not vary as the temperature of the material is changed. This essentially allows the experimentalist, whom is limited to measure in a certain frequency range, to observe the relaxation features as a function temperature. As shown in Figure 3.13, the segmental and

chain relaxation processes can be observed and analyzed at different temperatures in both representations of permittivity.

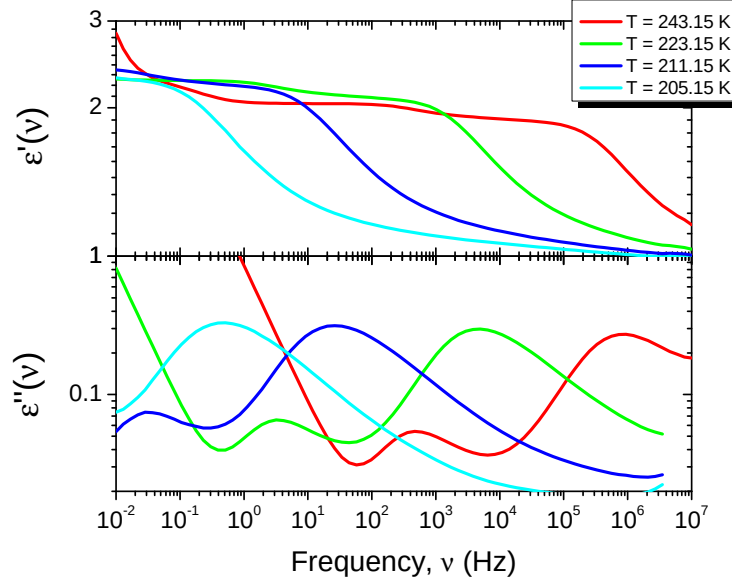


Figure 3.13: The real and imaginary parts of the complex permittivity for poly(propylene glycol) at different temperatures above the glass transition temperature.

The above mentioned relaxations are occurring in the material while the temperature is above the glass transition temperature, T_g . Many polymers with type-C properties also show faster, secondary relaxations once the polymer has become a glass (below T_g , commonly defined as when segmental motions becomes slower than 100 seconds). Figure 3.13 shows a type-C polymer that exhibits a strong secondary relaxation, referred to as a β -relaxation, below T_g . These secondary relaxations are much less sensitive to changes in temperature than segmental relaxations and consist of a broad distribution of relaxation times (~ 7 orders of magnitude in Fig. 3.13) and are discussed in more detail in Chapter 2.

3.6.4 Detailed Analysis of Relaxation Phenomena

The extraction of quantitative parameters from dielectric spectra can easily be accomplished by fitting the spectra with a linear combination of HN-functions (eq.

3.37). Typically, the easiest method is to fit the real and imaginary permittivity separately, where the latter is much easier to interpret than the former.

For the spectra shown in Figure 3.14, the data can be fit by the summation of two HN-functions and a power-law for D.C. conductivity.

$$\epsilon''(\omega) = -Im \left[\frac{\Delta\epsilon_1}{(1 + (i\omega\tau_1^{HN})^{\gamma_1})^{\beta_1}} + \frac{\Delta\epsilon_2}{(1 + (i\omega\tau_2^{HN})^{\gamma_2})^{\beta_2}} + \frac{\sigma_0}{i\omega\epsilon_0} \right] \quad (3.38)$$

The exact mathematical relations that are used to fit the data are described in detail within reference 21 on page 62.[16]

Figure 3.14 demonstrates the results from the additive fitting procedure as well as decomposes the individual contributions of each relaxation process to the overall spectra. The integrated area under each curve corresponds to the dielectric strength of the process, $\Delta\epsilon$. The α and β parameters characterize the symmetric and asymmetric broadening of the dispersion peaks. For example, the segmental relaxation in this polymer has $\gamma_1 = 0.8$ and $\beta_1 = 0.5$ while the chain relaxation is much more asymmetric with $\gamma_2 = 0.5$ and $\beta_2 = 1.0$.

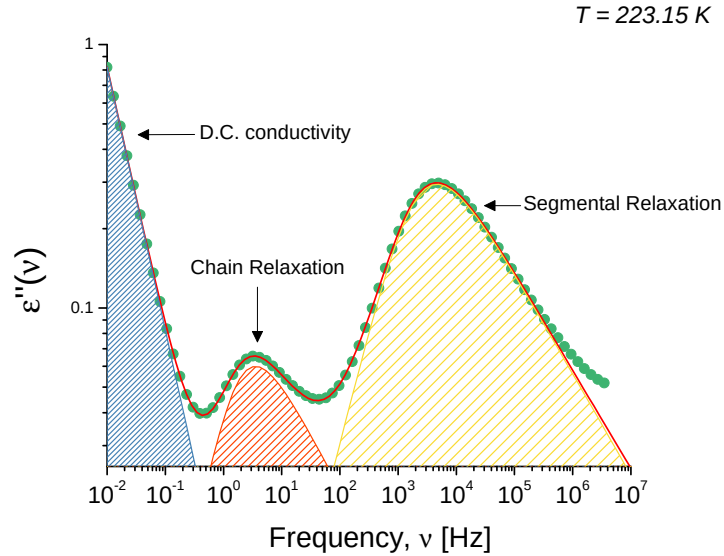


Figure 3.14: The analysis of the imaginary permittivity using a linear combination of two Havriliak-Negami functions and a power-law for the D.C. conductivity term to extract relaxation information.

Other than the dielectric strength or the dispersion of the relaxation, the average time scales of the processes are the most important parameter when considering the glass transition temperature of a material. The mean relaxation time, τ_{mean} , is related to τ_{HN} by the following relation:

$$\tau_{mean} = \tau_{HN} \left(\frac{\sin \frac{\pi\gamma\beta}{2(\beta+1)}}{\sin \frac{\pi\gamma}{2(\beta+1)}} \right)^{\gamma^{-1}} \quad (3.39)$$

The τ_{mean} is used to characterize the mean peak position for relaxation features that are fit by HN functions.

Once the spectra are analyzed by the appropriate fitting functions over all temperature values of interest, one can follow the temperature dependence of the relaxation times. Figure 3.15 plots the temperature dependence of the chain and segmental relaxation times as a function of inverse temperature. The time scale of both relaxations increase in a non-Arrhenius manner (i.e. non-linear on a semi-log scale) as the temperature is cooled towards the glass transition temperature. Since the glass transition temperature is an ill-defined quantity in general, dielectric spectroscopists define it as the temperature at which the segmental relaxation reaches 100 seconds (or $\log_{10}\tau_s = 2$).

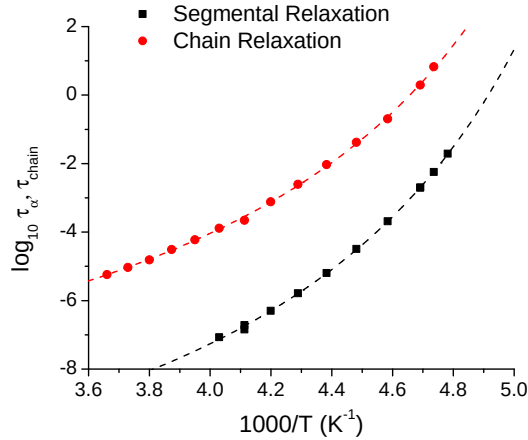


Figure 3.15: The relaxation times obtained for the chain and segmental relaxations of poly(propylene glycol) as a function of inverse temperature obtained by Havriliak-Negami analysis. The dotted lines are Vogel-Fulcher-Taumann fits.

3.6.5 Maxwell-Wagner-Sillars Polarization effects

There are other processes that appear in the dielectric spectra of soft materials related to long-lived polarization effects such as electrode polarization and Maxwell-Wagner-Sillars (MWS) polarization. The phenomena of electrode polarization is much more relevant to ionic systems and will not be discussed in any capacity. However, MWS polarization is very relevant to much of the presented work in this Dissertation and will be briefly discussed here.

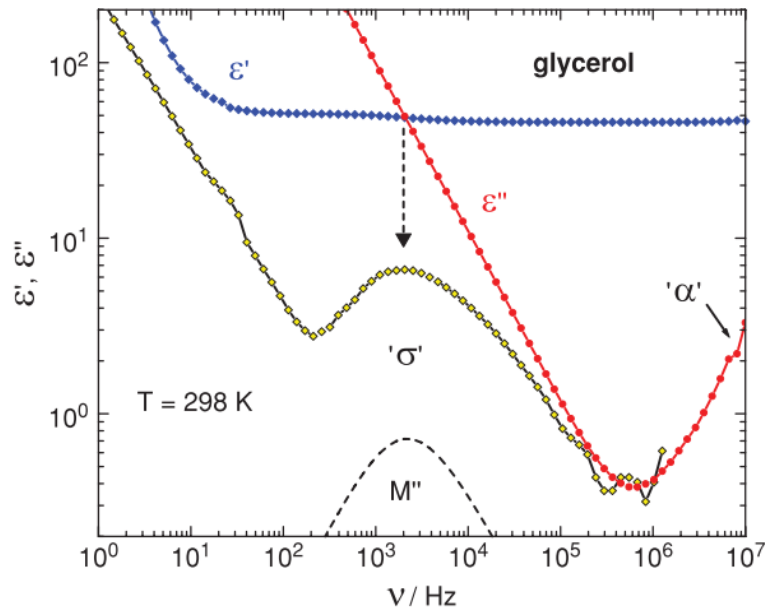


Figure 3.16: Dielectric relaxation data for glycerol at a temperature $T = 298$ K obtained with standard filling procedure. Blue solid diamonds and red dots show ϵ' and ϵ'' , respectively. Yellow open diamonds are estimated via the derivative of ϵ' and the dashed curve represents the conductivity peak of the modulus, M'' , scaled arbitrarily. Image reproduced from [18]

MWS polarization occurs due to the differences in conductivity and permittivity of a multi-component material (such as a layered structure or filled polymer). However, as shown in Fig 3.16, this phenomenon has been shown occur in simple molecular liquids where microscopic air bubbles can also cause differences in the permittivity. Typically, the MWS polarization manifests itself as a large peak in

the dielectric loss spectra, ϵ'' , and occurs near the frequency at which $\epsilon' = \epsilon''$ in magnitude. Given that the experimentalist knows the geometry in which the two-phase material (layered domains, spheres, cylinders) the time scale and magnitude of the effect for simple scenarios can be accurately estimated. More specific details about MWS effects are discussed in Chapter 5.

Chapter 4

The Influence of Interfacial Interactions on the Glass Transition Temperature of Polymer Nanocomposites

In this chapter, the influence of different oxide nanoparticles on segmental and chain dynamics of poly(2-vinylpyridine) is studied. While a significant change in rheological properties is observed with nanoparticle loading, the glass transition temperature, the segmental mobility, and fragility are only slightly affected. These results are discussed in the context of recent controversies in studies of polymer nanocomposites and polymer thin films.

4.1 Introduction

One of the key properties of amorphous polymers is the glass transition temperature, T_g , which governs almost all transport properties in polymer systems. It is expected that the interactions of polymers with NPs may lead to changes in

T_g of the polymer nanocomposites. Numerous authors have discussed the effects of nanoparticles (NPs) on the T_g which is directly related to the segmental relaxation in polymeric materials.[11, 34] In recent years, experiments have indicated that the nature of polymer-NP interactions (whether attractive or repulsive) can influence the T_g of PNCs by enhancing or hindering polymer segmental mobility.[20, 21, 56] It is expected that strong, attractive interactions between the polymer and NPs result in a so-called interfacial layer with reduced segmental mobility in the vicinity of NPs.[58, 61] In a previous study by Rittigstein and Torkelson, interfacial effects in PNCs were investigated and changes of T_g up to 10 K observed in PNCs with NP loadings of only 0.4 and 0.6 volume percent (vol%).[22] Additionally, Rittigstein *et al.*,[13] and Bansal *et al.*,[12] have qualitatively studied the equivalence between polymer thin films and PNCs, in which polymer films of different thicknesses were compared directly to PNCs with similar interparticle spacing. The authors stressed strong similarities in both situations.

However, other studies indicate that PNCs exhibit less pronounced changes in the segmental dynamics than thin films. For example, Moll and Kumar observed only slight shifts of T_g (~ 6 K) in well dispersed PNCs even at NP concentrations as high as 60 weight percent (wt%).[20] In a separate study, Harton *et al.*, also found that the T_g of P2VP increased by a mere 5 K with Silica NP loaded at 62 wt%. [21] These discrepancies are similar to those in the literature of thin polymer films, in which some authors observe similar deviations in T_g with substrate and thickness dependences,[7, 12, 62, 63] while other authors observe little or no changes.[43, 64] It has been suggested that such discrepancies have little to do with strong interfacial or confinement effects but are more likely due to preparation methods, ambient humidity, and inadequate annealing times.[43, 64] Therefore, systematic experimental studies are necessary to resolve the current controversy and unravel the role of nanoparticle interactions on the interfacial dynamics as well as the overall polymer dynamics and, ultimately, establish an efficient strategy for tuning the specific polymer dynamics for various applications.

In this chapter, broadband dielectric spectroscopy, rheology, and differential scanning calorimetry are employed to systematically investigate the influence of inorganic oxide nanoparticles (titania, alumina, magnesia, and silica) at very high NP concentrations on the dynamics of poly(2-vinyl-pyridine). A detailed analysis reveals that the average T_g increases by only 2–3 K even for NP concentrations as high as 60 wt%, indicating that the interfacial dynamics are weakly affected. Additionally, in contrast to recent theoretical predictions, the fragility of the polymer nanocomposites does not change significantly with the addition of nanoparticles.

4.2 Experimental Section

Poly(2-vinyl-pyridine) ($M_W = 97\text{K}$, $M_W/M_N = 1.07$, $T_g = 368\text{ K}$) was purchased from Polymer Source. Spherical titania (TiO_2), magnesia (MgO), silica (SiO_2), and alumina (Al_2O_3) NPs (Average particle size = 20 nm) were obtained from U.S. Research Nanomaterials and MkNano, inc. All materials were used as received. It appears that all received NPs were strongly aggregated (see characterization methods below). To ensure a well-dispersed PNC, solution mixing and rapid precipitation was employed. The polymer and NPs were separately dissolved with dimethylformide and bath-sonicated for thirty minutes. The two solutions were mixed and sonicated again for thirty minutes. Afterwards, the solution was slowly precipitated at the interface of a hexane and water (50:50) mixture, recovered and transferred to a vacuum oven where they were kept for at least 3 days at 150 C to remove the residual solvent. The samples were hot pressed at 150 C by placing PNC between Mylar sheets and using heated hydraulic press, resulting in films thicknesses of approximately 100 μm . A total of four sets of samples were prepared using this method, including four different oxide nanoparticles at four concentrations (0.1, 1, 10, 60 wt%).

Thermodynamic gravitational analysis (TGA) was performed using Q50 (TA Instruments) to verify the NP weight percent. TGA was conducted from room temperature to 550C under a nitrogen atmosphere at a rate of 10 K/min. For high loading PNCs (60 wt%), the expected weight percent was only achieved for Titania. After precipitation, the alumina and magnesia samples prepared at 60 wt% were found to be 47 wt% and 33 wt%, respectively. The silica sample prepared at 60 wt% did not result in the desired nanoparticle loading. The loss in nanoparticle loading for the samples is due to a large percentage of nanoparticles staying in the solvent phase during the precipitation. In the analyses the NP loading the measured by TGA loading is used. Moreover, hereafter the volume percentage (vol%) of NPs with respect to the polymer matrix is used instead of mass percentage, to better compare the different oxide nanoparticles with different densities.

4.3 Characterization Methods

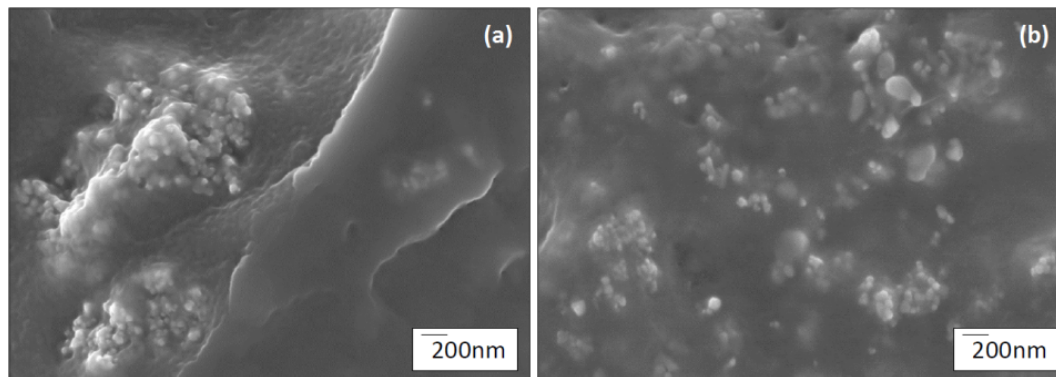


Figure 4.1: SEM images for (a) P2VP/ TiO_2 (3 vol %) and (b) P2VP/ TiO_2 (28 vol %) used to characterize the quality of TiO_2 nanoparticle dispersion. Image reproduced from reference [19].

Scanning electron microscopy (SEM) was used to assess the quality of nanoparticle dispersion from the solution mixing and precipitation method. Figure 4.1 illustrates the quality of dispersion in the Titania PNCs at 3 and 28 vol% respectively.

Analysis shows aggregates of Titania NPs. However, the dispersion of aggregates is reasonably homogenous across the sample area. From TEM we estimate the average size of these aggregates to be approximately 100-150 nm in diameter. Dynamic light scattering (DLS) was employed to estimate the initial hydrodynamic radius and polydispersity of our NPs. It appears that even after sonication of the NPs their average particle size in a solution is approximately 100 nm with a polydispersity of ± 10 nm. This analysis indicates that our dispersion method worked very well but the nanoparticles were aggregated prior to solution mixing and precipitating the PNCs.

Differential scanning calorimetry (DSC) measurements were performed with a Q1000 (TA Instruments). In all measurements the same temperature range of 300 – 430 K was probed at a rate of 5 K/min. All measurements were done under a nitrogen atmosphere. The glass transition temperature was determined from the heat capacity inflection point *via* the TA Universal Analysis 2000 software. Examples of DSC diagram for a few samples with different nanoparticle loading are presented in Figure 4.2.

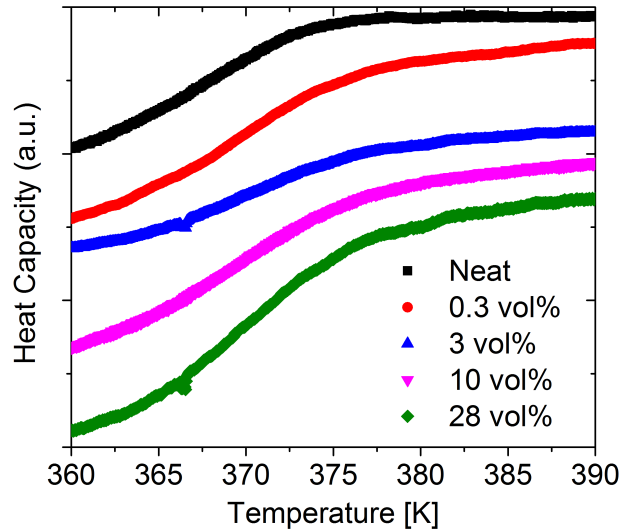


Figure 4.2: DSC thermograms for P2VP and P2VP/ TiO_2 nanocomposites illustrating the glass transition step and its dependence on the nanoparticle loading. Image reproduced from reference [19].

Small-amplitude oscillatory shear measurements of PNCs were carried out on an AR2000ex rheometer (TA Instruments). The experiments were performed in parallel plate geometry using 8 mm plates. The temperature was controlled by an environmental test chamber with nitrogen as the gas source.

Broadband dielectric spectroscopy (BDS) measurements were performed with an impedance analyzer from Novocontrol (Alpha analyzer) and the sample temperature was controlled by a Novocontrol Quatro Cryosystem with a stability of ± 0.2 K. Prior to measurements the samples were annealed at 400K under a nitrogen atmosphere to ensure thermal equilibrium was achieved. We annealed our samples in the dielectric sample chamber and measured the response as a function of time until the real and imaginary permittivity became constant for a given frequency. The measurements were performed in the temperature range from 490 – 240 K in the frequency range of 10^{-1} to 10^6 Hz. Examples of dielectric loss spectra are shown in Figure 4.3. The segmental relaxation process and the DC conductivity contribution can clearly be seen at higher temperatures with a broad secondary

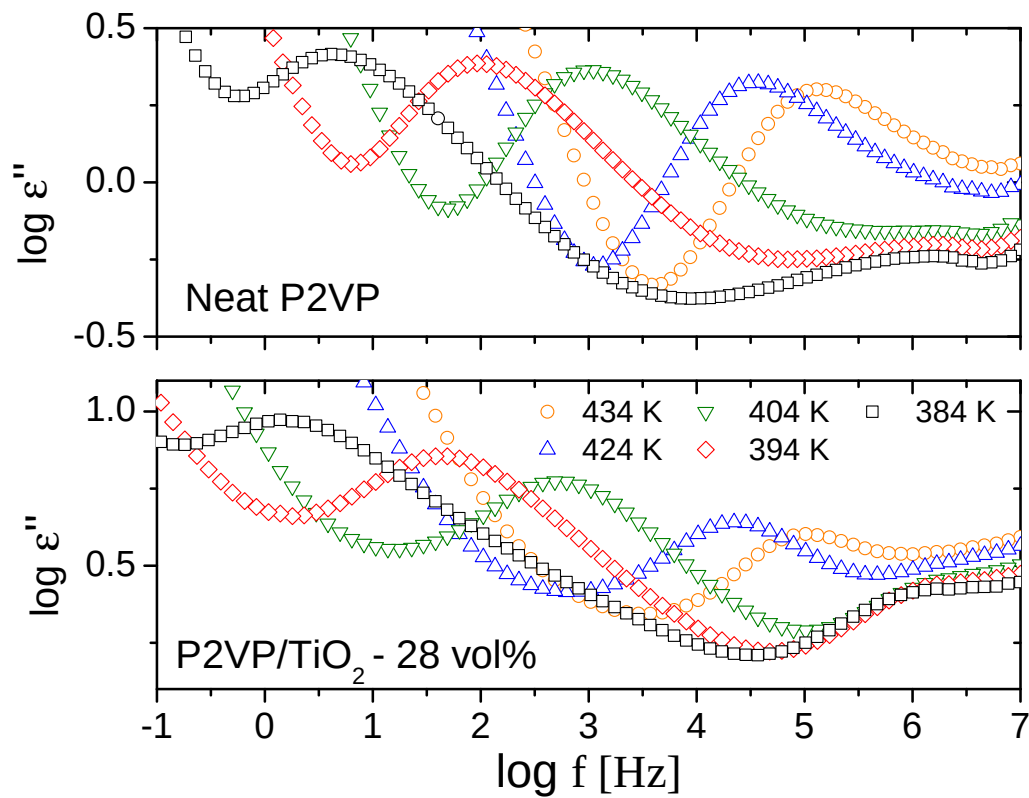


Figure 4.3: Dielectric loss spectra for neat P2VP and P2VP/*TiO*₂ nanocomposite versus frequency at different temperatures for a qualitative comparison of the effects of high loading on segmental dynamics. Image reproduced from reference [19].

relaxation process clearly resolved at lower temperatures. The secondary relaxation processes is out of the scope for the present work and will not be discussed in the current article.

4.4 Results and Discussion

Let us begin our discussion with the influence of nanoparticles on segmental dynamics. It is expected that bare oxide nanoparticles experience attractive interactions with P2VP between the nitrogen atoms of the polymer with hydroxyl groups on the surfaces of the oxides.[65, 66] The spectral shape of the segmental relaxation peak broadens with addition of nanoparticles, especially at higher loading. This might reflect broader distribution of relaxation times due to more heterogeneous environment of segments. However, further discussion of these broadening effects is not within the scope of this chapter and a detailed analysis of the spectral shapes shall be discussed in the proceeding chapters. The temperature dependence of the segmental relaxation rates estimated from the dielectric measurements is shown in Figure 4.3.

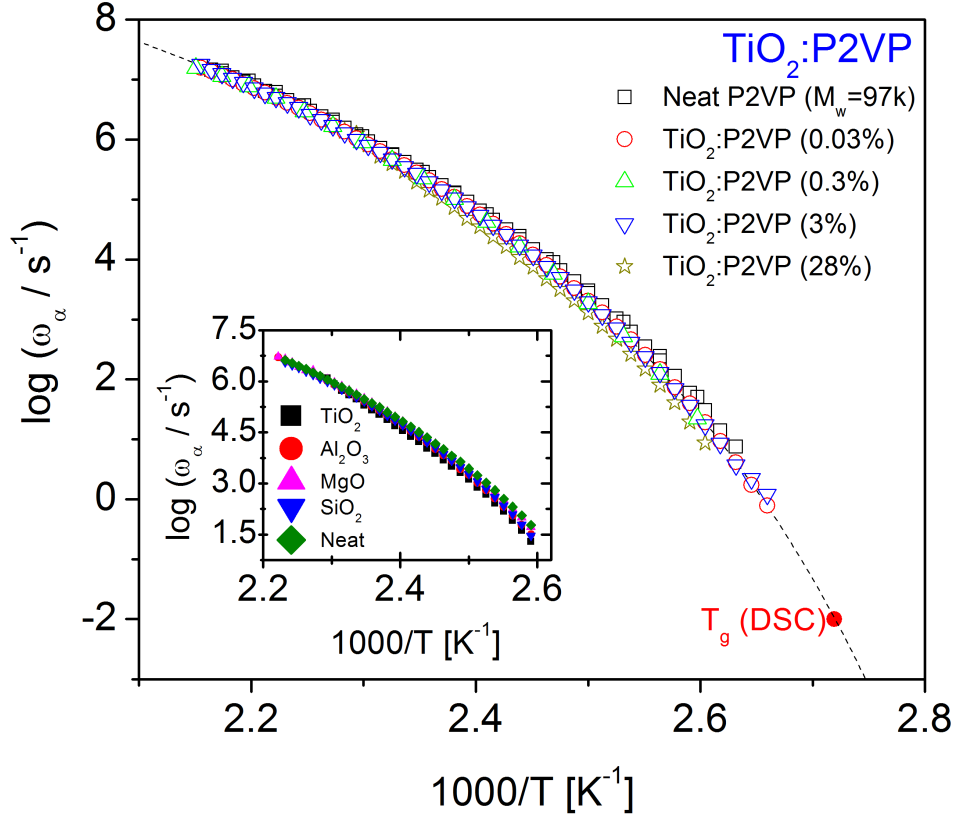


Figure 4.4: Temperature dependence of relaxation rates for the segmental relaxation for neat P2VP and P2VP/ TiO_2 nanocomposites (0.03, 0.3, 3, & 28 vol%). (As obtained from Havriliak-Negami fits). Inset: relaxation rates for Titania (28 vol%), Magnesia (14 vol%), Silica (5 vol%), and Alumina (21 vol%) nanocomposites at their highest respective loading. Image reproduced from reference [19].

The presence of TiO_2 nanoparticles has no significant effect on the segmental dynamics of P2VP even at high loadings. This result is not unique to TiO_2 -based nanocomposites. The segmental relaxation rates, ω_α , for P2VP composites with SiO_2 , MgO , and Al_2O_3 NPs at their highest loading ($\sim 15\text{-}30$ vol %) are shown in the inset of Fig 4 and reveal a similar trend. A careful analysis indicates a slight reduction (factor of 2) in the relaxation rates at lower temperatures implying a suppression of segmental mobility. This effect is expected for attractive interfacial

interactions and has been reported in the literature by many authors[20, 21, 67] and predicted by simulations.[11, 34] However, our results are in contrast to studies of the impact of silica and alumina nanoparticles on the dynamics of P2VP, which report changes in T_g by more than 10 K.[13, 22]

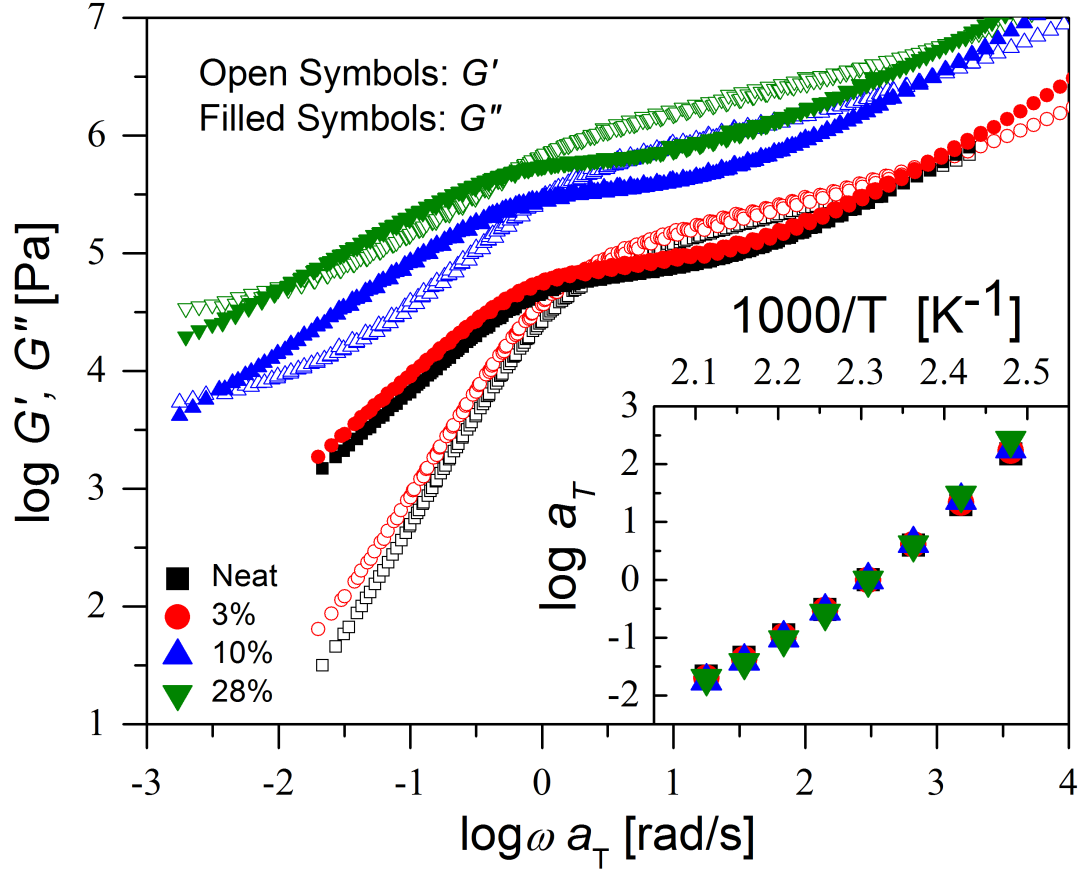


Figure 4.5: Spectra of the real and imaginary components of the shear modulus for P2VP and P2VP/ TiO_2 nanocomposites (unfilled, 3, 10, and 28 vol% TiO_2) as a function of scaled frequency (obtained using time-temperature superposition). Inset: Horizontal shift factors for each TiO_2 polymer nanocomposites. Image reproduced from reference [19].

The linear viscoelastic properties of the PNCs were determined using dynamic mechanical measurements. Unfortunately, the segmental dynamics measured by commercial rotational rheometers are often complicated by the contribution from instrument compliance and therefore are excluded from our current discussion.[68]

However, the influence of nanoparticle loading on the chain dynamics of P2VP can be studied well. The time-temperature master curves for storage and loss modulus of neat P2VP and P2VP/ TiO_2 nanocomposites are shown in Figure 5. The master curves were constructed by using the horizontal shift factor, a_T , as shown in the Figure 5 inset. Neat P2VP shows the typical response of an entangled linear polymer with the expected terminal relaxation at the low frequency end of the spectrum. Samples with NP loading of 10 and 28 vol% exhibit a lack of the flow in the low frequency region due to the formation of large-scale nanoparticle network. In the intermediate frequency region, the usual filler reinforcement takes place. The temperature dependence of the horizontal shift factor, a_T , is essentially identical for all the samples, except for the 28 vol%, where a slight difference is observed at low temperatures. The temperature dependence of a_T qualitatively agrees with the temperature dependence of segmental relaxation times. The results presented imply that NPs do not slow down significantly the overall chain and segmental dynamics, despite significant changes in the low-frequency mechanical response.

The most interesting question becomes: why do oxide NPs have rather weak effect on segmental dynamics in our case? Numerous studies of the interfacial effects on segmental mobility present a wide array of conflicting experimental results—some with large changes in T_g and others with negligible changes. A comprehensive review on the subject has been compiled by Robertson and Roland.^[60] It is not easy to identify the source of these discrepancies because the large amount of variables involved: quality of nanoparticles, samples preparation, NP dispersion and aggregations, as well as annealing procedures, among others. T_g and fragility index (m) are the two key parameters employed to characterize the polymer segmental dynamics. By convention, T_g is assigned to the temperature at which the structural (segmental) relaxation time reaches 100s. In addition to the T_g , the fragility index, as previously described in chapter 2, quantifies how strongly the temperature dependence of segmental relaxation time deviates from an Arrhenius behaviour. Recent theoretical studies predict that the fragility of a

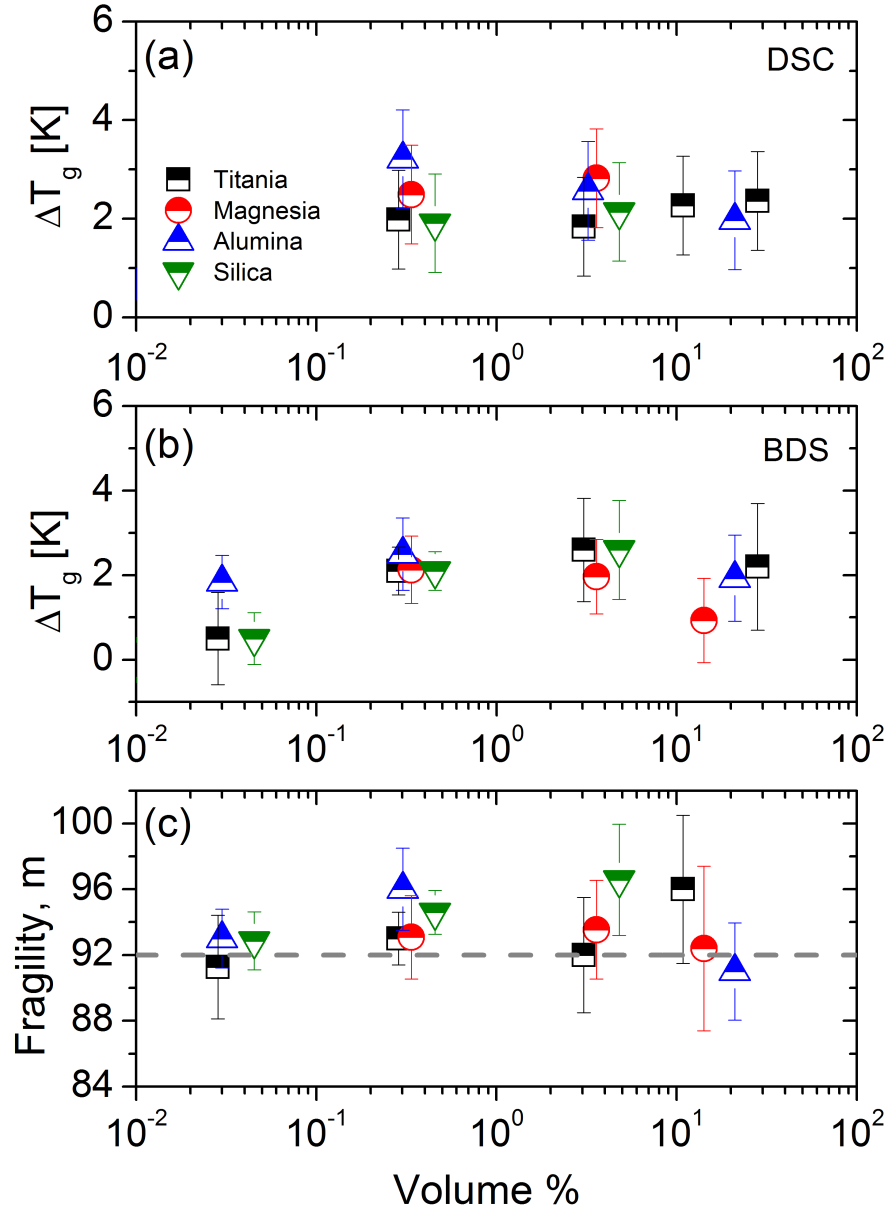


Figure 4.6: The effect of nanoparticle species and loading on the (a) change in T_g from DSC relative to neat P2VP, $T_g^{DSC} = 371$ K; (b) change in T_g from dielectric spectroscopy relative to neat P2VP, $T_g^{BDS} = 366$ K; and (c) the fragility index from BDS. Half-filled squares denote Titania NP, half-filled circles denote Magnesia NP, half-filled upright triangles denote Alumina NP, and half-filled right triangles denote Silica NP. Dashed line represents the fragility of neat P2VP. Image reproduced from reference [19].

polymer should change with the addition of nanoparticles.[11, 34] In particular, nanoparticles with attractive interactions were predicted to increase the T_g and fragility of the host polymer.

Our analysis of DSC results (Figure 4.6a) reveals the expected increase in T_g for attractive nanoparticles. However, the observed increase is rather weak even at high NP loadings (15-30 vol %) for all nanoparticles. To estimate T_g from BDS measurements, we fit the segmental relaxation rates in Figure 4.4 by the Vogel-Fulcher-Tammann (VFT) equation, $\omega_\alpha = 1/\tau_\alpha = \omega_\infty \exp[(-B)/(T - T_0)]$, where ω_∞ , T_0 , and B are fitting parameters. T_g values were estimated as the temperature at which $\omega_\alpha = 10^{-2} \text{ rad s}^{-1}$. Once again only weak increases in T_g relative to neat P2VP (Figure 4.6b) are observed, in agreement with the DSC data. Dielectric data provide also estimates of fragility and reveal no changes in m within the error-bars (Figure 4.6c) for all types of oxide nanoparticles and their respective loadings.

Observation of such small changes in T_g agrees with the recent results by Kumar and co-workers[21] that also find only $\sim 5 \text{ K}$ increase in T_g of P2VP even at 62.5 wt% silica NP with diameter of 15 nm. Significantly larger effects, ΔT_g , have been reported in ref. [13] for P2VP with $\sim 0.4 \text{ vol\%}$ ($\sim 0.9 \text{ wt\%}$) of 10-15 nm diameter silica nanoparticles; and $\Delta T_g \sim 17 \text{ K}$ has been reported by the same group [22] for P2VP with $\sim 4 \text{ vol\%}$ ($\sim 16 \text{ wt\%}$) of alumina nanoparticles (diameter of 47 nm).

The NP surface area (*i.e.*, size of NP) could play an important role in the resulting polymer dynamics by changing the area of the polymer/nanoparticle interface with NPs of different diameters; however we will not discuss the dependence of dynamics on NP diameter and consider the NPs with a fixed diameter and varying the NP concentration.

To directly compare all these results we estimate the effective confinement effect introduced by the nanoparticles. Assuming homogeneous dispersion of NP, one can estimate the distance between nanoparticle surfaces (or interparticle spacing) using the equation:

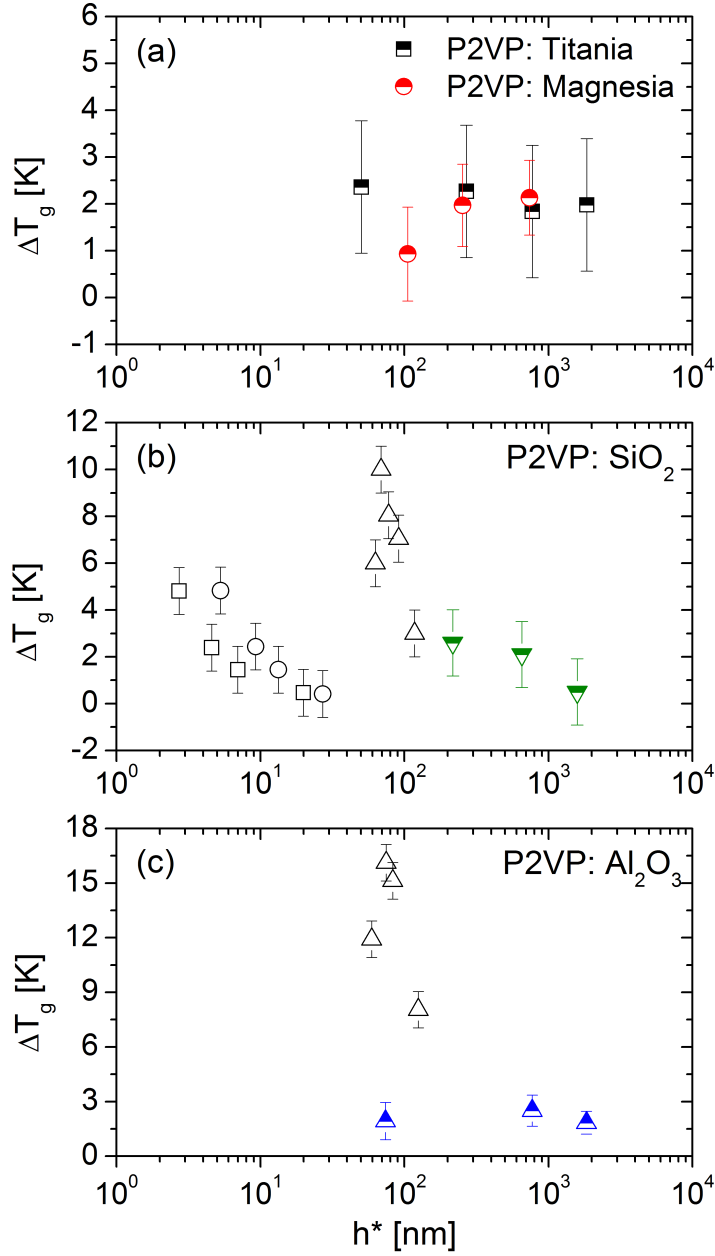


Figure 4.7: Change in T_g estimated using BDS measurements as a function of effective interparticle spacing, h^* within our polymer nanocomposites estimated by eq. 4.1. (a) T_g deviations for Titania and Magnesia PNCs as a function of interparticle spacing by assuming a diameter of 150 nm. (b) T_g deviations for Silica PNCs from literature compared to our results as a function of h^* . Empty squares, circles, and triangles are from references [20], [21], and [13], respectively. (c) T_g deviations for alumina PNCs from reference [22] directly compared to our results as a function of h^* . Image reproduced from reference [19].

$$h^* = D \left[\left(\frac{\psi_{max}}{\psi} \right)^{1/3} - 1 \right] \quad (4.1)$$

where ψ is the polymer volume fraction, ψ_m is the maximum particle packing fraction (can be assumed ~ 0.7 for hard spheres) and D is the diameter of the nanoparticle.[40] This will provide ~ 70 nm distance for P2VP with 0.4 vol% of 15 nm silica NP used in [17], ~ 75 nm for P2VP with 4 vol% of 47 nm alumina NP used in [18], and ~ 5.3 nm for P2VP with 62.5 wt% of 15 nm silica NP used in [21]. In case of our studies the particles with nominal diameter of ~ 20 nm were aggregated and according to DLS and TEM measurements had average size ~ 100 - 150 nm in diameter. Figure 4.7a presents ΔT_g as a function of h^* for P2VP with TiO_2 NPs assuming their diameter 150 nm. It is obvious, that even in this case, we reach confinement comparable to the length scale reported in [22] for P2VP with silica and alumina nanoparticles, although in our experiments the changes in segmental dynamics are significantly smaller (Figure 4.7b and 4.7c). It is possible that the aggregation of our NPs could influence our results when compared to reference [22], however, our results agree well with the changes in T_g reported in [20, 21].

To the best of our knowledge, the dramatic changes in segmental dynamics of a polymer host is not well understood and has only been qualitatively explained by the picture of a region of lower mobility, or bound layer, surrounding nanoparticles. Sargsysan *et al.*, [56] and Harton *et al.*, [21] have experimentally shown the thicknesses of such bound polymer layers are between 0.5–2 nm, which is comparable to the length scale of the segmental dynamics. Based on this explanation and estimates, it is difficult to expect the presence of nanoparticles to significantly affect the segmental dynamics when the distance between them is greater than ~ 50 nm. There might be several reasons for the differences in our and [20, 21] data from one side and data presented in [13, 22] from another side. One of them maybe the difference in experimental techniques used. In our case and in the case of [20, 21]

segmental dynamics have been directly probed by DSC and dielectric spectroscopy, while authors of [13, 22] analyzed T_g using fluorescence of probe molecules. This indirect method might have several complications and results will depend strongly on position of the dye molecule in the heterogeneous nanocomposite sample, which may be preferentially drawn to the polymer–NP interface.[69]

4.5 Summary

The influence of attractive nanoparticles on segmental and chain relaxation in poly(2-vinyl-pyridine) was studied using broadband dielectric spectroscopy, rheology, and calorimetry. Titania, alumina, silica and magnesia NP with average sizes ~ 20 nm and loadings of up to 28 vol% were used in these studies. Scanning electron microscopy (SEM) and dynamic light scattering (DLS) data reveal that NP formed aggregates with diameters ~ 100 – 150 nm. As expected, rheological measurements exhibit an increase of the shear modulus with nanoparticle loading. In particular, an enhancement of modulus in the rubbery plateau region and suppression of the terminal flow is observed. The analysis of the shift factor indicates that the overall chain dynamics does not slow down significantly in the presence of the nanoparticles. More surprisingly, the presence of nanoparticles has little effect on segmental dynamics in all prepared PNCs even with NP loadings up to 28 vol%. The segmental relaxation time decreases by a factor of two with the addition of nanoparticles, leading to an increase in T_g by only ~ 3 K. It is plausible that the large aggregates prevent the adequate confinement necessary to observe dramatic changes in the T_g , however at such large NP loadings a larger effect should be observed. The existing controversy in the known literature data is emphasized by comparing our results to the reported changes in T_g for polymer nanocomposite materials and furthermore it is proposed that the segmental dynamics in these systems are weakly affected only at the surface of the NP.

Chapter 5

The Effect of Interfacial Interactions on Segmental Dynamics in Polymer Nanocomposites

The segmental dynamics of poly(2-vinylpyridine)/silica nanocomposites are investigated by temperature modulated differential scanning calorimetry and broadband dielectric spectroscopy (BDS). The static structure and nanoparticle dispersion are characterized by small angle X-ray scattering (SAXS) and transmission electron microscopy. Both BDS and SAXS detect the existence of an interfacial polymer layer on the surface of the nanoparticles. The results show that whereas the average calorimetric glass transition temperature varies only weakly with nanoparticle loading, the segmental mobility of the polymer interfacial layer is slower than the bulk polymer by two orders of magnitude. A detailed analysis of BDS and SAXS data reveal that the interfacial layer has a thickness of 4–6 nm irrespective of the nanoparticle concentration. These results demonstrate that in contrast to the previous understanding of polymer nanocomposites, the interfacial polymer layer is

by no means a “dead layer”. However, its existence might provide some explanation for controversies surrounding the dynamics of polymer nanocomposites.

5.1 Introduction

Several simulations have predicted that polymer/NP interactions (whether attractive or repulsive) can greatly influence the glass transition temperature (T_g) of PNCs.[11, 34] However, as mentioned in the previous chapter, only a few experiments have demonstrated that attractive polymer-NP interactions can significantly increase the overall T_g of PNCs.[12, 13, 22] The mechanism responsible for these dynamic changes has been attributed to the adsorption of polymer to the NP surface, essentially immobilizing the polymer at the interface and ultimately leading to formation of a so-called dead layer.[51, 52] However, as described in Chapter 4, the formation of this dead layer still lacks an explanation for significant changes in T_g at relatively low NP loading as the dynamics of the polymer in between the NPs would have to be greatly affected on length scales comparable to interparticle spacing (greater than 100 nm).[19]

The polymer near the surface of the NP, or interfacial polymer, is expected to exhibit significantly different chain and segmental dynamics due to steric hindrance and polymer/NP interactions. Many attempts have been made to characterize the extent of the interfacial polymer layer, with estimates varying from 1–10 nm from the surface of spherical nanofillers.[20, 21, 56–59, 70] However, some of these estimates are dependent upon the assumption that the interfacial polymer is a dead layer, *i.e.*, completely immobilized with respect to the remaining polymer. Recent studies investigating the local dynamics of the polymer chains in the interfacial region *via* neutron scattering, broadband dielectric spectroscopy, and simulations have determined that the dynamics are in fact not immobilized.[60, 61, 71] Instead, these studies demonstrated that a wide distribution of segmental relaxation rates exist in these interfacial regions. By controlling the chemistry of nanoparticles

it should be possible to carefully tune the distribution of relaxation times in a polymer around the nanoparticle, and at high loading of NPs it should be possible to transform the polymer into an almost entirely interfacial material with specific properties that are different from the neat polymer. Therefore, gaining an understanding of the difference in dynamics of the bulk polymer and interfacial polymer and specifically the interplay between them could be of great technological importance.

In this chapter, temperature modulated differential scanning calorimetry (TMDSC), broadband dielectric spectroscopy (BDS), small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM) are used to investigate the effects of silica NPs on the static and dynamic properties of poly(2-vinylpyridine) (P2VP). This PNC was chosen as a model attractive polymer-NP system due to the relatively strong hydrogen bonding between the polar P2VP and hydroxyl groups on the surface of the silica NP. The presence of an interfacial polymer layer is indicated by calorimetric and dielectric techniques as a systematic broadening of the step in heat capacity at T_g and a corresponding apparent broadening of the segmental relaxation process in the BDS spectra. A detailed analysis of the dielectric spectra reveals that this apparent broadening cannot be accounted for by changes in the shape of the segmental relaxation process alone. Instead the changes of the BDS spectra can be accounted for by the emergence of a new, slower relaxation process that corresponds to the interfacial polymer layer. Furthermore, the static structure of the PNCs indicates the existence of a core-shell morphology. The average thickness of the interfacial region was estimated to be approximately 3–6 nm from both static (SAXS) and dynamic (BDS) measurements.

5.2 Experimental Details

Poly(2-vinylpyridine) ($M_W = 97$ kg/mol, $M_W/M_N = 1.07$, $T_g = 368$ K) was purchased from Polymer source, Inc. Tetraethyl orthosilicate (TEOS, >95%),

Ethanol, ammonium aqueous solution (30-33wt%), and Methyl ethyl ketone (MEK) were purchased from Sigma Aldrich and were used without further purification. Monodisperse colloidal silica nanoparticles ($D = 30$ nm) were synthesized by the modified Stober method according to the previous reports.[72, 73] Different concentrations of the nanoparticles in a water/ethanol solution were mixed with P2VP in MEK. The mixtures were stirred for 1–2 hours, transferred into Teflon mold, and then placed into a vacuum oven at room temperature and 1 mbar for 24 hours. To remove remaining solvent, temperature was raised to 80C and samples were kept in a vacuum oven for an additional 48h. The resulting samples were transparent.

Thermodynamic gravitational analysis (TGA) with a Q50 (TA Instruments) confirms the final weight percent of the nanoparticles in all polymer nanocomposites.

For TEM measurements the samples were embedded in epoxy, cured overnight, and subsequently microtomed with a Leica Ultra microtome EM UC7 using a diamond knife at ambient conditions with resulting specimens having thicknesses 200 nm. TEM measurements were performed on Zeiss Libra 200 HT FE MC with an operating voltage of 200 kV and an emission current of 230 mA.

TMDSC measurements were carried out on a Q2000 (TA Instruments), calibrated by indium and sapphire standards, using standard TZero aluminum pans. Samples were equilibrated at 473 K for 10 minutes and then cooled to 293 K at 10 K/min with a modulation of ± 1 K/min.

BDS measurements were performed using a Novocontrol Alpha analyzer and the sample temperature was controlled by a Quatro Cryosystem with a stability of ± 0.1 K. Prior to measurements the samples were annealed at 400K in the dielectric sample chamber and the response measured as a function of time until the real and imaginary permittivity became constant for any given frequency, which indicated that thermal equilibrium was achieved. The measurements were performed in the

frequency range of 10^{-1} to 10^7 Hz and all samples were measured twice to ensure data reproducibility.

SAXS was performed with a Molecular Metrology instrument equipped with a monochromatic X-ray source (Cu $K\alpha$, $\lambda=1.54$ Å), a pair of Kirkpatrick-Baez micro-focusing mirrors, and a 2-dimensional position sensitive detector. The sample-detector distance was 1.5 m with a q -range of 0.01 to 0.15 Å $^{-1}$. The x-ray operating voltage was 45 kV with a current of 0.66 mA and the exposure time was 1 hour for each sample.

5.3 Results and Discussion

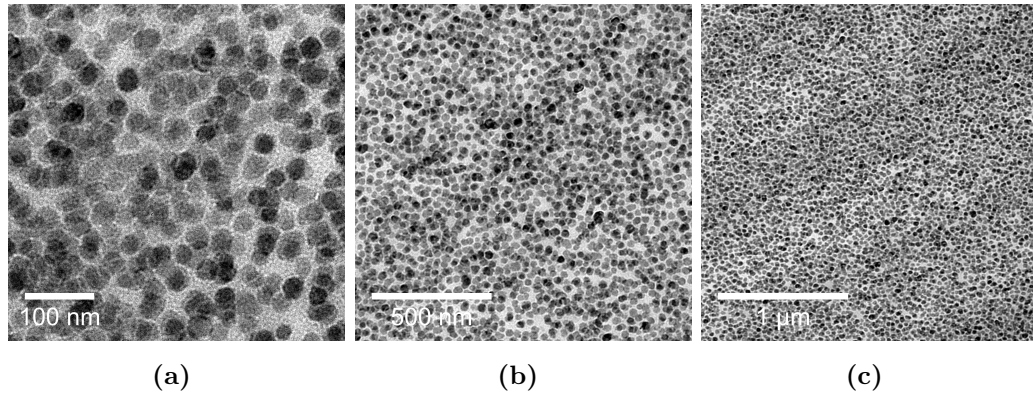


Figure 5.1: Transmission electron microscopy images of silica nanoparticles embedded in poly(2-vinyl pyridine) ($M_W = 100$ kg/mol) at 40 wt% silica to demonstrate that the nanoparticles are well-dispersed in the polymer.

We first performed transmission electron microscopy (TEM) measurements to verify the nanoparticles are (1) monodisperse and (2) uniformly distributed. In Fig. 5.1, TEM images of a highly filled polymer nanocomposite (40wt%, 23vol% silica) are shown to illustrate the well dispersed silica nanoparticles. The silica nanoparticles are uniformly distributed across the entire sample even at length scales larger than 2 microns and have an average interparticle spacing of 15 nm, which corresponds well to the estimated interparticle spacing for ideal spherical packing.^[74]

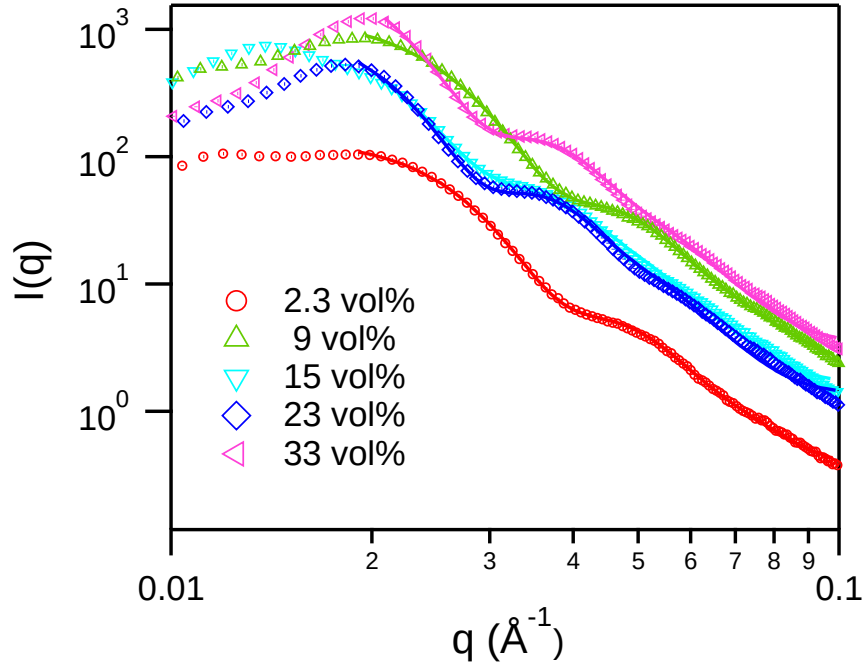


Figure 5.2: Small-angle X-ray scattering profiles of polymer nanocomposites for various silica concentrations and corresponding fits obtained with a linear combination of the Beaucage and coreshell models. For clarity, the curves are arbitrarily shifted vertically to compare the structure.

Figure 5.2 shows the X-ray scattering profiles of the PNCs. The peak position of $q = 0.02 \text{ \AA}^{-1}$ persists for all NP concentrations and corresponds to a distance of 31.5 nm, the diameter of our NPs. To quantitatively characterize the structure of these nanocomposites, the scattering curves are fit to model scattering functions. The data could not be fit to the scattering of dispersed spheres, indicating that the structure of this nanocomposite cannot be described as spherical nanoparticles homogeneously distributed in a continuous matrix. The scattering data did fit well (Fig. 5.2) to a linear combination of the Beaucage^[75, 76] and core-shell models.^[77] The core-shell model is chosen to model the silica nanoparticle (core) and the interfacial bound polymer layer (shell), where the inclusion of the Beaucage model allows us to account for any non-uniformity of the density of the shell and the fact that the interface between the shell and the matrix is not sharp. From this

analysis, the size of the interfacial polymer (*i.e.*, shell) is found to be approximately 4-5 nm for all nanocomposites. The results also show that the interface between the bound layer and matrix is fairly broad, exhibiting a Porod exponent of 3 (a sharp interface has a Porod exponent = 4). These results therefore indicate that the interfacial layer is not uniform, but exhibits a gradient in structure. This suggests that the decrease in segmental mobility near the NP surface presumably changes with the distance from the surface.

Having verified the quality of NP dispersion and structure in our PNCs, we then measured the temperature dependent heat capacity, C_p , of each PNC via TMDSC. Traditional DSC measures the heat flow from a material described by the following relation, $(dH)/(dt) = C_p(dT)/(dt) + f(T, t)$, where dH/dt is the total heat flow, C_p is the heat capacity of the sample, dT/dt is the heating rate, and $f(T, t)$ is the kinetic term. We employ TMDSC in order to separate the reversing heat flow term, $C_p(dT)/(dt)$, and the non-reversing term, $f(T, t)$ and use the reversing heat flow term to accurately determine the heat capacity of the sample while avoiding kinetic effects such as solvent evaporation, crystallization, and enthalpic recovery. From this point on any mention of heat capacity or specific heat capacity will refer to the reversing component.

The inset in Figure 5.3 illustrates the temperature dependent specific heat capacity, c_p , in the vicinity of the calorimetric glass transition temperature for the neat polymer and PNCs. The overall specific heat capacity and the magnitude of the glass transition step decreases with increasing NP loading which is due to the lower specific heat capacity of silica. To quantitatively compare the specific heat capacity of the remaining polymer fraction within the PNC, we have removed the NP contribution with the following relation:

$$c_p^{polymer} = \frac{C_{PNC} - C_{NP}}{M_{polymer}} = \frac{C_{PNC} - c_p^{NP} M_{NP}}{M_{polymer}} \quad (5.1)$$

Table 5.1: Selected fitting parameters from the linear combination of Beaucage and Core-shell models.

SiO ₂ (wt%, vol%)	5, 2.3%	18, 9%	28, 15%	40, 23%	52, 33%
R_g (Å)	125 ± 0.5	140 ± 0.3	160 ± 0.3	161 ± 0.5	182 ± 0.5
Porod exp.	3.05 ± 0.01	3.02 ± 0.07	3.32 ± 0.04	3.26 ± 0.03	3.07 ± 0.03
Shell (Å)	41.9 ± 0.2	43.2 ± 0.1	41.4 ± 0.3	46.7 ± 0.1	46.3 ± 0.1
Core Radius (Å)	89.5 ± 0.2	100.0 ± 0.1	121.9 ± 0.3	116.6 ± 0.1	125.1 ± 0.1
Core SLD (Å ⁻² / 10 ⁻⁵)	2.068 ± 0.002	2.067 ± 0.001	2.070 ± 0.002	2.011 ± 0.001	2.153 ± 0.002
Shell SLD (Å ⁻² / 10 ⁻⁵)	1.699 ± 0.001	1.383 ± 0.001	1.733 ± 0.001	1.69 ± 0.001	1.531 ± 0.001
Matrix SLD (Å ⁻² / 10 ⁻⁵)	1.415 ± 0.001	1.090 ± 0.001	1.406 ± 0.001	1.107 ± 0.005	1.109 ± 0.002

where C_{PNC} and C_{NP} are the heat capacities of the PNC and NP, c_p^{NP} is the measured specific heat capacity of silica, $M_{polymer}$ is the mass of the polymer fraction, and M_{NP} is the mass fraction of the filler. Using eq. 5.1 and subtracting the NP contributions from the heat capacity curves, the $c_p^{polymer}$ curves are then arbitrarily shifted on the y-axis to illustrate the changes in specific heat capacity at the glass transition with increasing NP loading. As is seen in Figure 5.3, a systematic broadening of the glass transition is observed with increasing NP loading, while the magnitude of the glass transition step, Δc_p , remains essentially constant and independent of NP concentration. A decrease in Δc_p with increasing NP loading has been observed for some PNCs and was attributed to the interfacial polymer being essentially immobilized relative to the bulk polymer. However, a decrease in Δc_p is not observed for the presented P2VP PNCs, and instead the glass transition step is significantly broadened. Since the calorimetric glass transition process broadens without a clear decrease in glass transition strength with increasing NP concentration, this indicates that the interfacial polymer segments are not completely immobilized relative to the bulk in our system, but they are instead slightly suppressed and likely possess a wide distribution of segmental relaxation times. Even though the presence of the interfacial polymer seems to significantly broaden the glass transition step, the T_g of the PNCs changes only slightly, as shown in Table 5.2.

We employ broadband dielectric spectroscopy (BDS) to better understand the effects of silica NPs on the polymer dynamics, specifically the changes in dielectric strength, the segmental relaxation times, and T_g . Figure 5.4 presents the imaginary part of the complex permittivity of polymer nanocomposites with increasing NP concentrations measured at 400 K. The spectra are normalized with respect to the secondary relaxation process, assuming that it is not affected significantly by NPs.[78] The spectra clearly show a decrease in amplitude and broadening on the low-frequency side of the segmental relaxation peak (Fig 5.4a). This is especially obvious in the spectrum of the derivative of the real part (Fig 5.4b) which is not

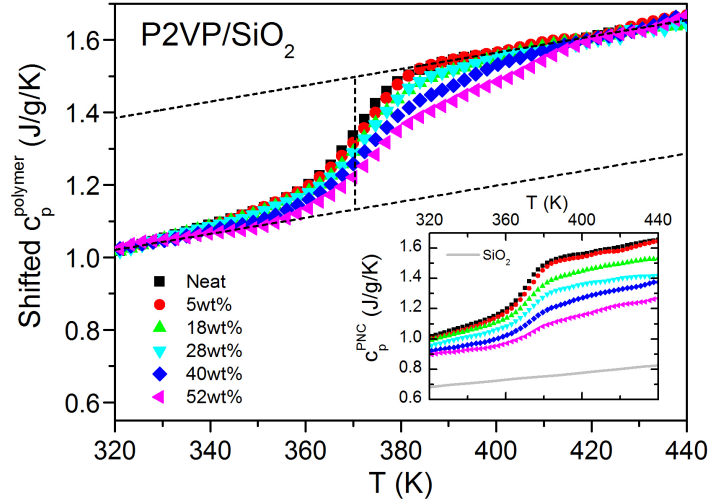


Figure 5.3: Specific heat capacity of the polymer fraction in the nanocomposites (with the silica contribution removed) with different silica loading. The curves are arbitrarily shifted to align at lower temperatures to illustrate the broadening of the glass transition step. Dotted lines are guides for the eye. Inset: The measured specific heat capacity curves for polymer nanocomposites, prior to accounting for the silica contribution.

affected by the conductivity contribution at lower frequencies. For neat P2VP, a single Havriliak–Negami (HN) function (eq. 3.37) and conductivity describes the data well (Figure 5.4c). However, a single HN function is not sufficient to fit the PNC data. So, we fit the imaginary part of the dielectric spectra by the additive approach with two HN functions and a conductivity term (see page 55 and equation 3.38 for additional details):

$$\epsilon''(\omega) = -Im \left[\frac{\Delta\epsilon_1}{(1 + (i\omega\tau_1^{HN})^{\gamma_1})^{\beta_1}} + \frac{\Delta\epsilon_2}{(1 + (i\omega\tau_2^{HN})^{\gamma_2})^{\beta_2}} + \frac{\sigma_0}{i\omega\epsilon_0} \right] \quad (5.2)$$

where $\Delta\epsilon$ is the dielectric strength of the relaxation process, τ^{HN} is the Havriliak–Negami relaxation time, and the exponents γ and β describe the width and asymmetry of the spectra, respectively. In addition, σ_0 and ϵ_0 denote the D.C. conductivity and the permittivity of free space, respectively.

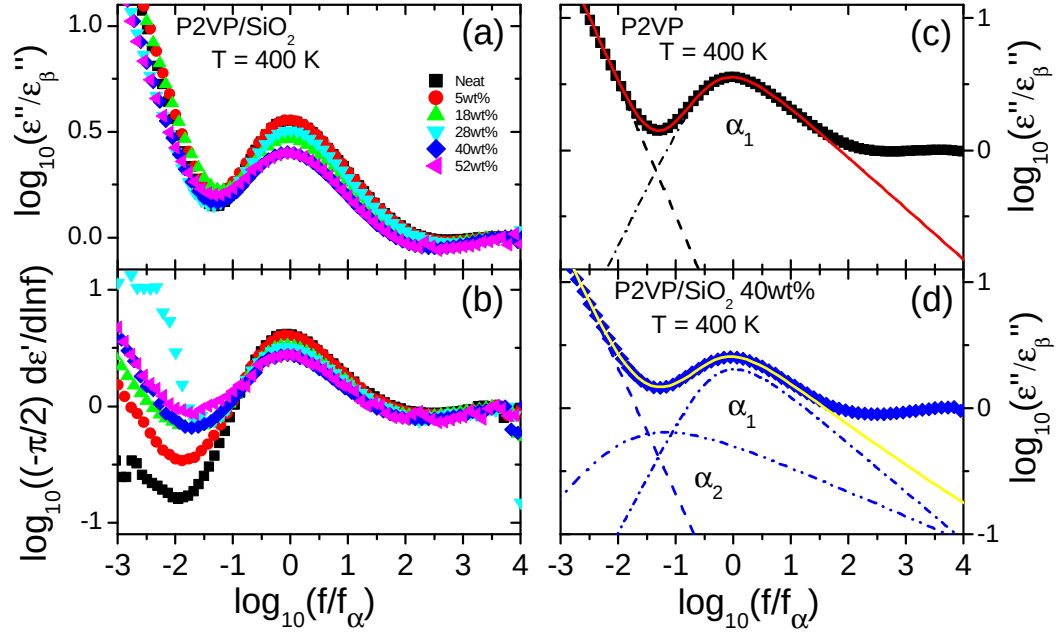


Figure 5.4: (a) Imaginary part of the complex permittivity normalized with respect to the β -process versus normalized frequency of P2VP/*SiO*₂ nanocomposites at 400 K. (b) Derivative of the real part of the complex permittivity showing the emergence of a secondary process with NP loading. (c) Normalized imaginary part of the complex permittivity of neat P2VP fit by a single Havriliak–Negami function, and (d) P2VP/*SiO*₂ (40wt%, 23 vol%) showing the individual HavriliakNegami components, α_1 , α_2 , and dc conductivity at T = 400 K.

Figure 5.4(d) shows the spectra of the 23 vol% SiO₂ PNC, where two HN functions are necessary to accurately fit the data. The fitting of the dielectric spectra of the silica composites was performed as follows. The stretching parameters γ and β for the segmental relaxation process in the composites were taken to be equal to those of neat P2VP and were kept constant during the fit procedure regardless of the NP loading. The stretching parameters for the slow interfacial relaxation process were initialized as being equal to those of the bulk-like relaxation process and were allowed to vary. The $\Delta\epsilon$'s of the segmental and slow interfacial relaxation processes were initialized according to volume fractions of silica and polymer and then allowed to vary. The characteristic HN relaxation time for the bulk-like segmental relaxation was initialized as that of the pure matrix and for the slow interfacial process as a 100 times slower than the main segmental process, both τ_{HN} 's were set as free parameters during the fit procedure. The slower relaxation, referred to as α_2 , clearly increases in amplitude with an increase in NP concentration. So, we ascribe it to the relaxation of the interfacial polymer at the nanoparticle/polymer interface. The dynamics of the interfacial polymer layer are usually thought to be highly suppressed. However, in the case of our P2VP/silica nanocomposites, we observe the neat polymer segmental dynamics bifurcate into two relaxation peaks, with one peak related to the bulk relaxation of P2VP and the other most likely due to that of the interfacial polymer. Additionally, the sum of $\Delta\epsilon_1$ and $\Delta\epsilon_2$ for PNCs of all silica concentrations is found to remain constant and equal to the dielectric strength of the alpha relaxation in pure polymer, indicating that the decrease in $\Delta\epsilon_1$ is accounted for by an increase in $\Delta\epsilon_2$. Thus, we find evidence in the dielectric spectrum for an interfacial polymer region where the segmental mobility is on average slower by ~ 2 orders of magnitude relative to that of the remaining bulk polymer. Since neither $\Delta\epsilon_{Total}$ nor $\Delta\epsilon_p$ of the polymer decrease with increasing NP concentration, we conclude that there is no dead layer of polymer in any of our PNCs but instead, a layer of reduced mobility at the polymer-NP interface.

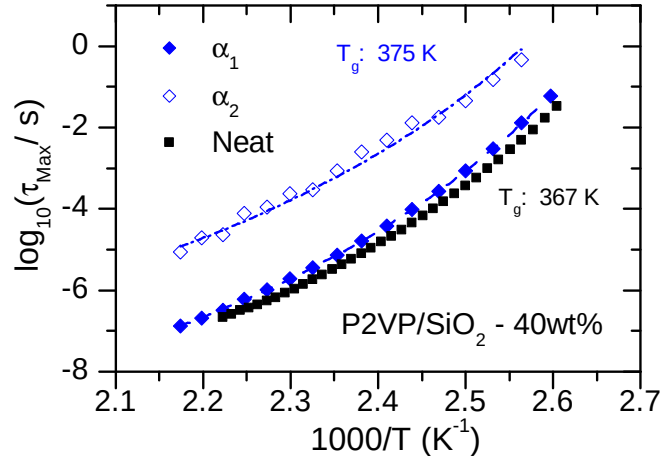


Figure 5.5: Temperature dependences of relaxation times for P2VP/ SiO_2 (40 wt%) nanocomposite and their fit by the Vogel-Fulcher-Tammann (VFT) equation with estimated values of T_g .

Figure 5.5 shows the temperature dependence of the interfacial and bulk polymer relaxation times for the 23 vol% SiO_2 PNC as well as the estimated glass transition temperatures from the Vogel-Fulcher-Tammann (VFT) equation, $\tau_\alpha = \tau_0 \exp(B/(T - T_0))$, where τ_0 , B , and T_0 are fitting parameters and T_g defined as the temperature at which $\tau_\alpha = 100$ s. The interfacial polymer exhibits a relaxation time that is approximately 2 orders of magnitude slower than that of the bulk polymer, a slightly weaker temperature dependence, and a higher estimated T_g from the VFT fit (8 K higher). It is noteworthy that the temperature dependence of the segmental relaxation times of the bulk polymer is essentially unaffected by the presence of NPs. This indicates that presence of NPs simply slows down the dynamics of polymer segments in the vicinity of the NPs surface.

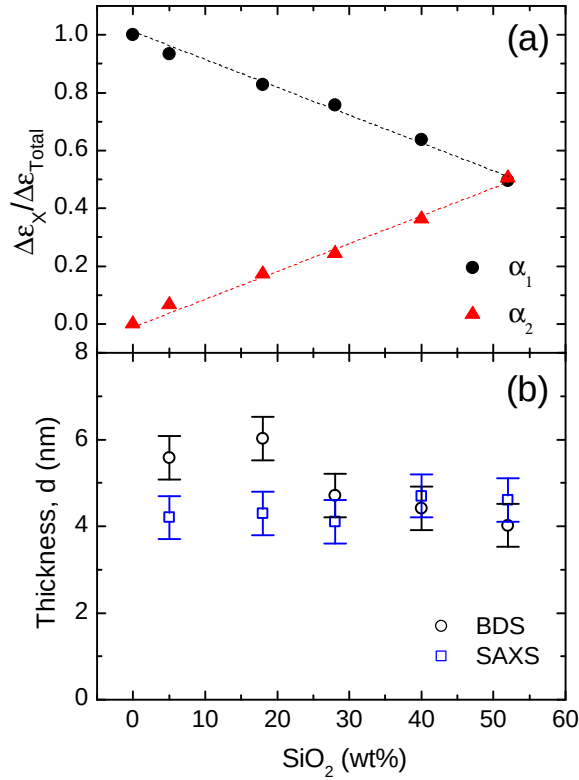


Figure 5.6: (a) Normalized values of $\Delta\epsilon$ as a function of NP loading from the additive approach. The dotted lines are a guide for the eye. (b) Calculated interfacial polymer thickness surrounding the silica nanoparticles from different experimental techniques.

The $\Delta\epsilon$ of the bulk and interfacial segmental relaxation processes are now analyzed to determine the fraction of polymer adsorbed at the interfacial region in our PNCs. The estimation of thickness of the interfacial polymer layer within PNCs from BDS is well established and can be found in references [57] and [56]. The interfacial layer thickness is computed using a simple volumetric estimate using the following relation: $d = R_{NP}[(\phi_{IP}/\phi_{NP}) + 1]^{1/3} - 1$ where, R_{NP} is the radius of the NPs, ϕ_{IP} is the volume fraction of interfacial polymer determined as $(1-\phi_{IP}) \Delta\epsilon_2/\Delta\epsilon_{Total}$ and ϕ_{NP} is the volume fraction of NPs. Figure 5.6(a) reveals the volume fraction of the interfacial polymer increases linearly with silica loading and the bulk-like volume fraction decreases accordingly. One aspect of interfacial

polymer which is particularly interesting is its dependence on interparticle spacing. As discussed previously, as the interparticle spacing approaches the length scale of the interfacial thickness, the dynamics are expected to significantly change. The volume percent of interfacial polymer should nearly reach 100 percent at 48 vol% silica (~ 68 wt%). Therefore, the PNC studied with the highest NP loading is 15 volume percent below the NP loading at which the interparticle spacing becomes comparable to a single interfacial polymer thickness, a condition where one would expect $\Delta\epsilon_1/\Delta\epsilon_{Total}$ to decrease non-linearly to zero. These calculations suggest that a future study with well dispersed NP at very high NP concentrations could provide further insight into such confinement effects.

Table 5.2: Nanoparticle Concentrations, Average Glass Transition Temperatures from TMDSC and BDS, Average Interparticle Spacing (h^*), and the Dynamic Thickness of the Interface from BDS.

SiO ₂ (wt%)	SiO ₂ (vol%)	T _g (TMDSC) (K)	T _g (BDS) (K)	h* (nm)	Interfacial Thickness BDS, (nm)
0	—	371	366.6 $\pm$ 1.1	—	—
5	2.3	371	368.0 $\pm$ 1.5	50.3	5.6 $\pm$ 0.5
18	9	372	367.5 $\pm$ 1.8	23.0	6.0 $\pm$ 0.5
28	15	373	367.6 $\pm$ 2.8	15.6	4.7 $\pm$ 0.5
40	23	373	369.3 $\pm$ 1.1	10.0	4.4 $\pm$ 0.5
52	33	373	369.9 $\pm$ 2.4	6.5	4.0 $\pm$ 0.5

The interfacial shell thickness is calculated from the dynamic data and plotted along with the SAXS measured interfacial thickness as a function of NP loading in Fig. 5.6(b). Two results are readily apparent from these data: (1) the length scales obtained from static and dynamic measurements are in good agreement—in contrast to previous studies[57], and (2) the length scale stays essentially constant with NP loading. These two observations further validate the presence of the interfacial layer, which should only depend on the number of OH- groups on the surface of

the silica NPs and the molecular weight of P2VP.[79] It has been suggested that the thickness of the interfacial layer is similar to the radius of gyration, R_g , of the polymer molecule.[80] In the case of this study, the thickness of the interfacial layer is only half of R_g (R_g of P2VP with $M_W = 100K$ is ~ 11 nm). In the future, it would be interesting to unravel the dependence of the layer thickness on molecular weight, rigidity of the polymer chain, and the strength of its interaction with the NP surface.

5.3.1 Model Free Analysis, the Relaxation Time Distribution Function

Until this point, the interfacial and bulk-like segmental relaxation processes have been treated as additive processes and explained by the summation of two Haviliak-Negami functions. While this approach appears to describe the experimental data on a phenomenological level, it cannot be accurately modeled and can only qualitatively explain our systems. Below, a model free approach is used to demonstrate that there is a real change in the dielectric permittivity of the interphase and a quantitative model is used that can account for the changes in the dielectric permittivity of the interphase. In this model free analysis, we numerically calculate the relaxation time distribution of the dielectric spectra for the polymer matrix—assuming a two-phase effective medium consisting only of a matrix and filler.

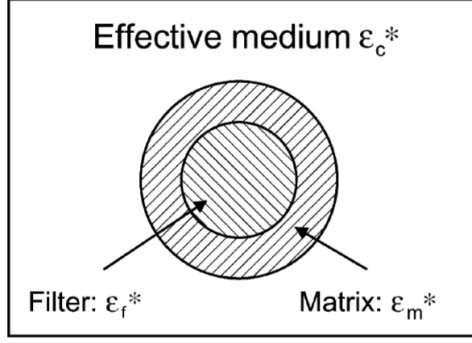


Figure 5.7: The effective medium for a heterogeneous material with an interfacial layer in between the filler and matrix.

An inhomogeneous medium consisting of two non-miscible phases leads to a complex permittivity that can be simply modeled as an effective medium as shown in Figure 5.7. By knowing the dielectric response of the filler and the measured effective medium, the dielectric response of the matrix component, ϵ_m^* , can be directly calculated by:

$$\epsilon_m^*(\omega) = \epsilon_0 \frac{(1 + 2\psi_f)\epsilon_f^*(\omega) + 2(1 - \psi_f)\epsilon_c^*(\omega)}{(1 + 2\psi_f)\epsilon_f^*(\omega) + (2 + \psi_f)\epsilon_c^*(\omega)} \quad (5.3)$$

where ϵ_0 is the permittivity of free space, ϵ_f^* is the complex permittivity of the filler, ϵ_c^* is the measured complex permittivity of the effective medium, and ψ_f is the volume fraction of the filler.

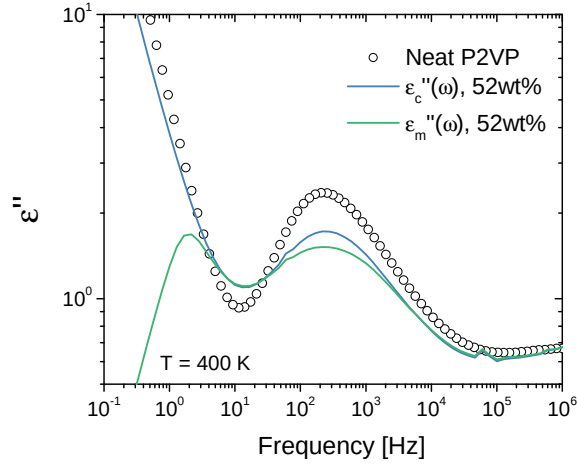


Figure 5.8: Imaginary component of the complex permittivity versus frequency for pure polymer, nanocomposite (at 33vol% silica), and the polymer matrix without the nanoparticle contribution (assuming a two-phase inhomogenous medium.)

As can be seen in Figure 5.8, the broadening of the $\epsilon_m^*(\omega)$ spectra still remains after accounting for the presence of the silica nanoparticles. To more clearly illustrate this point, we now calculate the relaxation distribution times of the pure polymer contribution, $\epsilon_m^*(\omega)$. This provides a model free analysis that will demonstrate how the segmental relaxation(s) are distributed. According the linear dielectric response theory, the overall dielectric response can be taken as a superposition of several Debye process with different relaxation times and dielectric strengths described by:

$$\epsilon^*(\omega) = \epsilon_\infty + \Delta\epsilon \int \frac{g(\ln \tau)}{1 + i\omega\tau} d\ln \tau \quad (5.4)$$

where, $g(\ln \tau)$ is the relaxation time distribution function (RTDF) and is normalized under the condition of $\int g(\ln \tau) d\ln \tau = 1$, $\Delta\epsilon$ is the dielectric strength of each process, ϵ_∞ is the constant permittivity value when approaching infinite frequency.

Since the PNCs have a large contribution from ion conductivity, we introduce an addition parameter to the imaginary permittivity component:

$$\epsilon'_{eff}(\omega) = \epsilon_{\infty} + \Delta\epsilon \int \frac{g(\ln \tau)}{1 + (\omega\tau)^2} d \ln \tau \quad (5.5)$$

$$\epsilon''_{eff}(\omega) = \frac{\sigma_0}{\epsilon_0} \omega^{-1} + \Delta\epsilon \int \frac{g(\ln \tau) \omega\tau}{1 + (\omega\tau)^2} d \ln \tau \quad (5.6)$$

where σ_0 is the d.c. conductivity or frequency independent conductivity value at a specific temperature.

The solutions to these equations for $g(\ln \tau)$ are non-linear and considered an ill-defined problem which can be numerically calculated by a regularization method. In our analysis, we use a generalized regularization method developed method by Weese.[?]

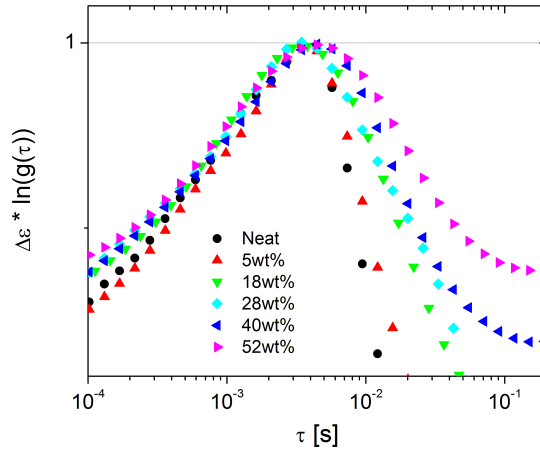


Figure 5.9: The normalized relaxation time distribution function numerically computed for each concentration of SiO_2 .

Figure 5.9 shows the computed RTDF for all the concentrations of nanoparticles and illustrates the broadening of the segmental relaxation process with an emphasis at longer time scales (*i.e.*, the low-frequency wing). Keeping in mind that the RTDF is calculated assuming only a two-phase system of polymer and nanofiller,

we observe that the segmental dynamics are indeed affected and the dispersion of the relaxation broadens with increasing nanoparticle loading or, rather, the decreasing interparticle spacing. Therefore, the assumption of a distribution of two inhomogeneous phases cannot solely account for the spectral changes obtained from dielectric spectroscopy.

5.3.2 Heterogeneous Medium, The Interfacial Model

In the previous sub-section, the dielectric permittivity of the nanocomposite material could not be modeled by a simple two-phase effective medium. It can be shown that the dielectric permittivity, which is directly measured, can be well described by the interfacial model [16]. The interfacial model describes the total complex permittivity from the three constituent phases, a nanofiller, an interfacial layer, and a polymer matrix as illustrated in Figure 5.10.

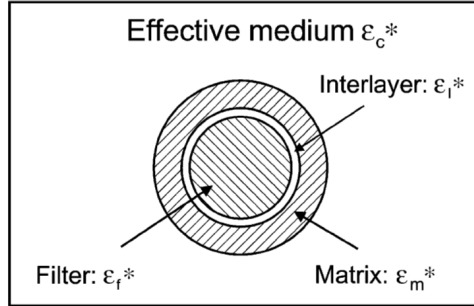


Figure 5.10: The effective medium for a heterogeneous material with an interfacial layer in between the filler and matrix. Image reproduced from reference [16]

Derived from Maxwells mean-field theory for a material filled with dielectric occlusions, it can be shown that the effective medium of a two-phase heterogeneous material can be described the by the following equations:[16]

$$\epsilon_{eff}^*(\omega) = \frac{\epsilon_f^*(\omega)\psi_f + \epsilon_{IL}^*(\omega)\psi_{IL}R^*(\omega) + \epsilon_m^*(\omega)\psi_mS^*(\omega)}{\psi_f + \psi_fR^*(\omega) + \psi_fS^*(\omega)} \quad (5.7)$$

where,

$$R^*(\omega) = \frac{(1-n)\epsilon_{IL}^*(\omega) + n\epsilon_f^*(\omega)}{\epsilon_{IL}^*(\omega)} \quad (5.8)$$

and

$$S^*(\omega) = \frac{(n\epsilon_m^*(\omega) + (1-n)\epsilon_m^*(\omega))(n\epsilon_f^*(\omega) + (1-n)\epsilon_{IL}^*(\omega))}{\epsilon_{IL}^*(\omega)\epsilon_m^*(\omega)} + \frac{dn(1-n)(\epsilon_l^*(\omega) - \epsilon_m^*(\omega))(\epsilon_f^*(\omega) - \epsilon_{IL}^*(\omega))}{\epsilon_{IL}^*(\omega)\epsilon_m^*(\omega)} \quad (5.9)$$

Where $d = \psi_f/(\psi_f + \psi_l)$, n is the shape factor of the filler ($n = 1/3$ for spheres, $0 < n < 1/3$ for rod-like, and $1/3 < n < 1$ for disc-like), $\epsilon_{eff}^*(\omega)$, $\epsilon_m^*(\omega)$, $\epsilon_f^*(\omega)$, and $\epsilon_{IL}^*(\omega)$ are the complex dielectric responses of the composite, pure matrix, filler, and interlayer, respectively and ψ_m , ψ_{IL} , ψ_f are the corresponding volume fractions for each phase and summate to 1.

The application of this model is crucial to the analysis of dielectric spectra of polymer nanocomposites or any other multi-component polymeric system. Most importantly, it explicitly demonstrates that the spectrum does not only have contributions from the two components which can be described in an additive way, but also that there is an important cross term. Secondly, it allows the calculation of the dielectric properties of the interlayer including the dielectric strength, dispersion (breadth of the relaxation), and time scale. The interfacial model will be employed to analyze the dielectric spectra for polymer nanocomposites for the remaining majority of the Dissertation.

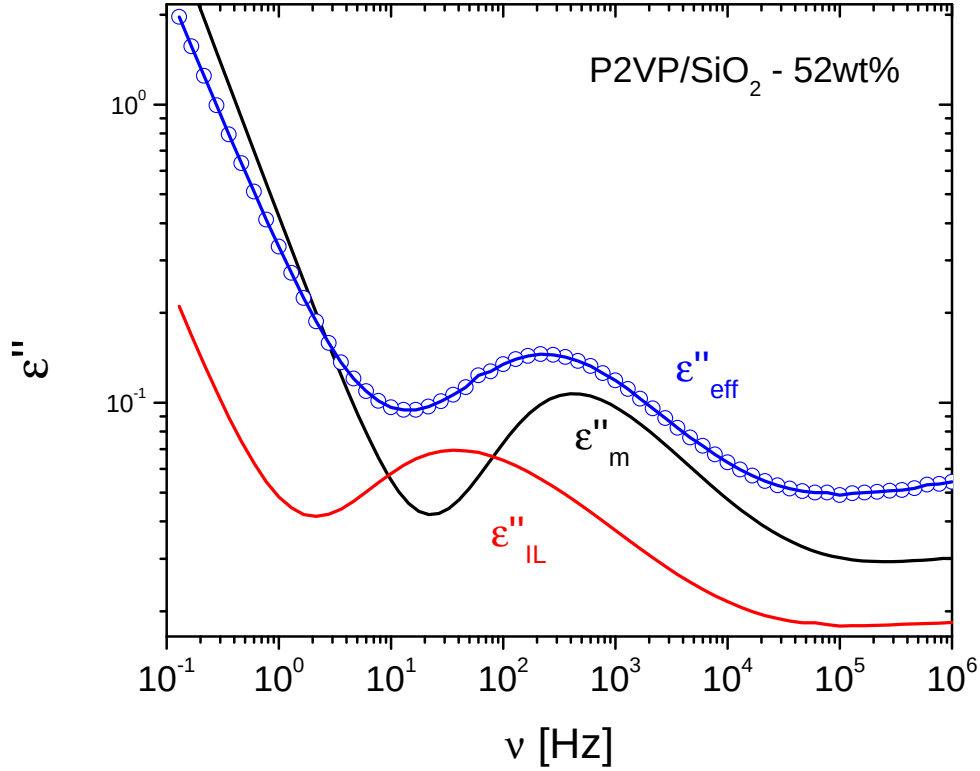


Figure 5.11: An example of the deconvolution of the dielectric loss spectra at $T = 400$ K (blue circles, $\epsilon''_{eff}(\omega)$) into the individual components by the interfacial layer model (black line, ϵ''_m and red line, ϵ''_{IL}) at the highest nanoparticle concentration of 52 wt%. Each contribution is normalized by their respective volume fractions.

The deconvolution of the dielectric loss spectrum into the respective components, ϵ''_{eff} , ϵ''_m , and ϵ''_{IL} , can be accomplished with the interlayer model. Through this analysis, the volume fraction and spectrum of the interfacial layer can be determined numerically. To determine the dielectric properties of the interfacial layer we experimentally determine ϵ''_{eff} , ϵ''_m , and ϵ''_{NP} from BDS measurements and then numerically compute and ϵ''_{IL} . Since there are two unknowns, the following analysis is performed: the volume fraction of the interfacial layer, ψ_{IL} , is initialized to zero and equation 5.7 is numerically solved for a finite number of steps and if the solution converges on a realistic solution it is then accepted. This procedure

is repeated until a realistic solution is found and the minimum value of ψ_{IL} is determined. It should be noted that after the solution for ϵ''_{IL} is determined, any additional increases in ψ_{IL} does not change the spectral shapes of the solution—or in other words the ψ_{IL} is the minimum volume fraction of interface and it could be larger than the presented values.

Figure 5.11 illustrates a representative plot of the individual contributions of each phase at a single temperature ($T = 400$ K) for the polymer nanocomposite with the highest silica concentration (52wt%). The most obvious difference between the ϵ''_{eff} and ϵ''_m components is the peak position and dispersion where the interfacial layer component is more than an order of magnitude slower than the bulk-like and effective components. First, to quantitatively understand the time scale of the interfacial process and to compare it to the effective process, the dielectric loss spectra is fit by a single HN function and power law for the d.c. conductivity term (linear line at low frequencies) for the sole purpose of extracting the mean time scale of the relaxation peak.

The temperature dependence of the interfacial segmental relaxation from the interfacial model analysis is presented in Figure 5.12. The difference in time scale between the bulk-like and effective processes is small but still noticeable, especially as the temperature approaches T_g . However, for the interfacial process there is a noticeable slowing down of dynamics for the majority of temperatures which dissipates at high temperatures and returns to bulk-like behavior. By fitting the interfacial process by the VFT equation the estimated T_g corresponding to the interfacial dynamics is found to be identical to the results of the previously mentioned additive analysis. The stark contrast between the two analysis techniques is the temperature dependences of the interfacial process. The temperature dependence determined from the additive approach is almost Arrhenius-like and suggests a different dynamic pathway into the glassy state which may be unphysical. The temperature dependence from interfacial layer model approach

reveals similar dynamics at high temperature that then decouples from the bulk-like or effective segmental dynamics when approaching T_g . These results could suggest that these two relaxations share a similar dynamic origin which would be consistent with the diminishing strength of hydrogen bonding at high temperatures (P2VP interacts with silica *via* hydrogen bonding).

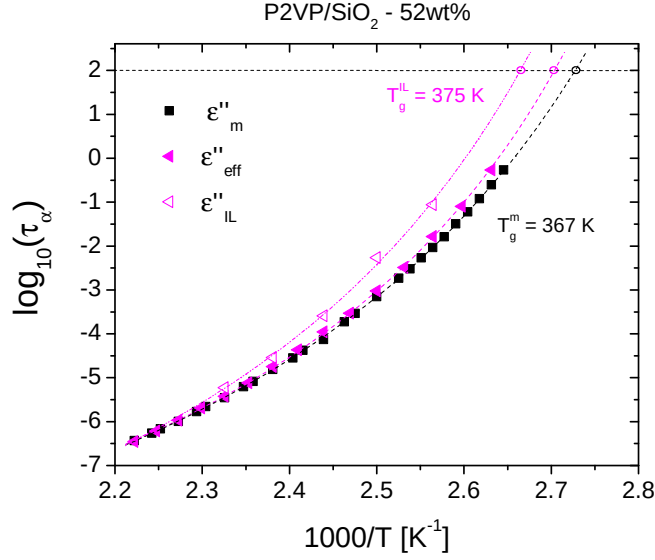


Figure 5.12: Temperature dependence of the segmental relaxations for each constituent phase (ϵ''_{eff} , ϵ''_m , and ϵ''_{IL}).

The results from the interfacial model analysis again demonstrate that the interfacial segments are affected (suppressed) by the adsorption process to a similar degree as additive approach (where the T_g of the interface ~ 375 K) while the majority of the polymer is unaffected by the presence of the polymer-NP interactions (where the overall T_g of the material has only changed slightly). Determining the amount of polymer influenced by the polymer-NP interactions, *e.g.* the volume fraction of interfacial polymer, is also accessible from the interfacial model analysis as presented in Figure 5.13. Figure 5.13 demonstrates the volume fraction of interfacial and free polymer within these polymer nanocomposites from both the additive approach (Figure 5.6(a)) and interfacial model. In contrast to the additive approach, the interfacial model systematically estimates a lower

volume fraction of interfacial polymer. This effect becomes most prominent at the highest silica volume fraction where a significant difference between the two techniques occurs. This behavior is consistent with the observation of mild overall changes in the dynamics despite the entire material being highly confined with the average interparticle spacing of ~ 6 nm and should be considered a minimum volume fraction of interfacial polymer.

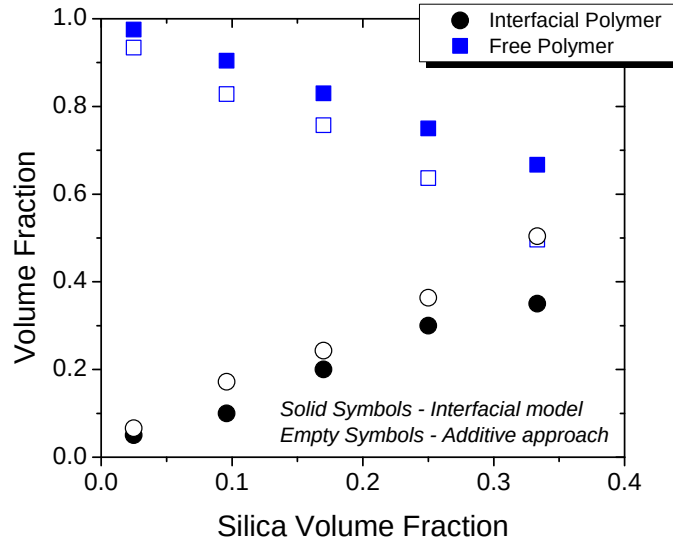


Figure 5.13: The volume fraction of the free and interfacial polymer populations as determined from BDS at $T = 400$ K. Solid symbols are determined by the interfacial model analysis and empty symbols are calculated by the additive approach.

From the dynamically affected volume fractions, the dynamic thickness of the interfacial layer can be computed by assuming a uniform density between the bulk polymer and NP interface (eq. is on page 87). The dynamic thickness of the interfacial layer is presented in Figure 5.14 for both approaches. As expected, with the smaller volume fraction of interfacial polymer, the dynamic thickness of the interface for the interfacial model analysis is lower than the additive approach (between 4–6 nm) and found to be 3–4 nm regardless of nanoparticle loading.

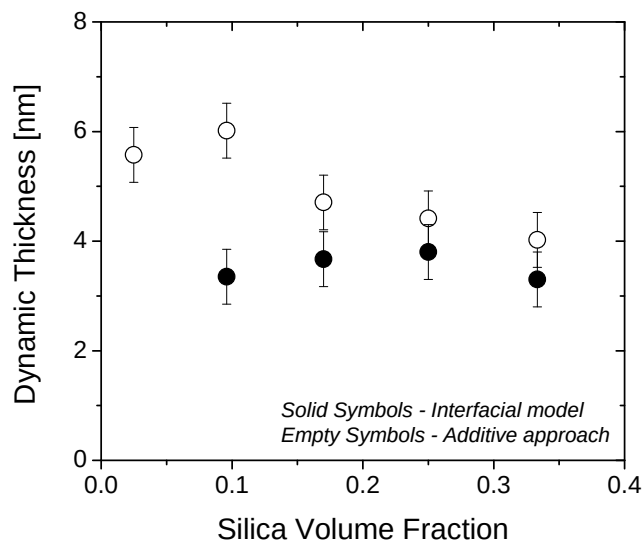


Figure 5.14: Dynamic thickness of the interfacial layer as a function of silica loading calculated by assuming volume additivity and that the density of the interface is identical to the bulk.

The observed existence of the interfacial layer with significantly slower segmental dynamics may provide an explanation to the well-known controversies in studies of PNC using different experimental techniques.[60] The group of Torkelson reported a significant change in T_g ($\Delta T_g \sim +11\text{K}$) of P2VP by adding just 0.4 vol.% of SiO_2 NPs, [22] while other studies found changes of T_g by only a few K with loadings up to ~ 30 vol.%.[19–21] Torkelson and co-workers did not measure directly segmental dynamics, but instead analyzed the fluorescence of dye molecules that are sensitive to the T_g of the polymer.[13, 22] If the dye molecules are preferentially drawn to the surface of NP instead of being homogeneously distributed in the polymer matrix, then this technique will measure T_g of the interfacial layer even at low NP loading. However, the shift in T_g then should not depend much on the NP concentration above some threshold. This is exactly what has been reported.[22] On the other hand, earlier studies using BDS data focused mostly on the main segmental relaxation times (Fig. 5.4) and thus detected only minor variations in T_g even at higher NPs loading.[19] Thus, this controversy

reflects the co-existence of bulk-like polymer and an interfacial layer in the same PNC sample, and different experimental techniques may report the T_g of different parts of the sample. Finally, it is emphasized that both BDS and DSC directly measure segmental dynamics, but their analysis should include a possibility of the existence of an interfacial layer with dynamics that differ significantly from the dynamics of a pure polymer.

5.4 Summary

The static and dynamic properties of poly(2-vinylpyridine)/silica nanocomposites are characterized by SAXS, TEM, BDS, and TMDSC. Monodisperse silica nanoparticles (25 nm in diameter) are well dispersed even up to high loadings, as verified by TEM. The static structure of the polymer nanocomposites are shown to consist of core-shell structures with a broad interface, where the core is the spherical nanoparticle and the shell is ascribed to the presence of an interfacial polymer layer. Although there is only a slight change in the calorimetric glass transition temperature, a broadening of the glass transition step from TMDSC and the apparent broadening of segmental relaxation process from BDS is observed with NP loading. Furthermore, the apparent broadening of the BDS relaxation is found to be caused by the emergence of a new, slower (~ 100 times) relaxation process corresponding to the interfacial polymer. Two models (additive and interfacial model) are used to determine the length scale of this interfacial polymer layer as estimated from BDS and SAXS is 4–6 nm. One of the most interesting results of this chapter is that the presence of the interfacial polymer, which is considerably slower than the bulk, has no significant effect on the overall segmental dynamics or the glass transition temperature of the composite sample.

Chapter 6

The Effect of Chain Length on the Interfacial Dynamics in Polymer Nanocomposites

In the previous chapter, the segmental dynamics at the attractive polymer-nanoparticle interface were shown to slow down an effect which is believed to occur due to the formation of an adsorbed interfacial layer. The general expectation is that the length scale of this layer and its influence will grow with increasing polymer molecular weight (MW). However, the results in this chapter reveal the opposite behavior where the length scale of the interfacial dynamics diminishes with increasing MW.

6.1 Introduction

Polymer nanocomposites (PNCs) are used in almost every aspect of our daily lives, yet the properties at the nanoparticle (NP) interface has just begun to be thoroughly investigated. In the previous chapter, the polymer dynamics near a mutually attractive polymer-NP interface have been shown to be suppressed—similar to polymer-substrate effects in polymer thin films. This effect was attributed to

polymer adsorption and shown to influence segmental dynamics up to $\sim 3\text{--}5$ nm from the surface of the NPs resulting in a relatively short-range, spatial gradient of mobility. [81, 82] Furthermore, this phenomenon would be reflected by a change in the local glass transition temperature (T_g) and the distribution of segmental relaxation times where the alteration of T_g with the addition of nanoparticles has long been debated in the community due to many discrepancies—which has recently been thought to arise from different experimental techniques (indirect *vs.* direct). [19, 60]

Despite recent experimental investigations of PNCs, the effect of several parameters on the properties of the interfacial layer such as molecular weight, interaction strength, nanoparticle size, and chain rigidity are still not understood.[60] The most widely neglected aspect of PNC studies is the variation of the polymers molecular weight (MW). Most relevant works typically employ high MW polymer matrices well above the entanglement MW. [13, 22] However, the length scale of the adsorbed bound layer is known to scale with the radius of gyration (R_g) of the polymer matrix. Since the R_g is dependent on the MW of the matrix then the length scale of the interfacial layer should be proportional to the MW as previously shown by Koga *et al.* for polymer thin films.[83] Therefore, it should be possible to tune the length scale of the interfacial layer, which possesses different dynamic properties, with an appropriate choice of MW and to rationally design the macroscopic properties of PNCs.

In this chapter, the static and dynamic properties of the interfacial layer in PNCs with different MWs are thoroughly investigated at similar nanoparticle concentrations. From the static measurements, a clear difference in the interfacial structure is found by varying MW: at high MW a polydisperse core-shell structure is observed while the low MW PNCs can only be described by simple hard sphere scattering structure (uniform interfacial density). Furthermore, a reduction in the overall mass density of the high MW PNCs is discovered from both SAXS and pycnometry measurements. In contrast to the static differences, the dynamic

measurements reveal negligible changes at high MW and a systematic increase in the T_g and suppression of segmental dynamics with decreasing MW. A thorough and detailed analysis of the dielectric spectra by the interfacial model reveals that the relative time scale of interfacial dynamics and the volume fraction of interfacial polymer varies with MW. These unexpected results are explained in terms of poor chain packing at the polymer-NP interface and the emphasize the complex interplay between interfacial structure and dynamics in PNCs.

6.2 Experimental Details

Three different molecular weights of poly(2-vinylpyridine) ($M_W = 8,700$ g/mol, $M_W/M_N = 1.07$; $M_W = 100,000$ g/mol, $M_W/M_N = 1.05$; $M_W = 400,000$ g/mol, $M_W/M_N = 1.08$) were purchased from Scientific Polymer, Inc. We synthesized monodisperse colloidal silica nanoparticles ($D = 25$ nm) by the modified Stober method. The polymer nanocomposites were prepared by mixing different concentrations of silica nanoparticles in a water/ethanol solution (50:50) with P2VP dissolved in a MEK. The samples were then stirred for 1-2 hours, transferred to a Teflon mold, and then placed into a vacuum oven at room temperature to dry for 24 hours at 1 mbar. The resulting samples were annealed under vacuum at 150 centigrade for an additional 48 hours before further measurements.

For TEM measurements the samples were embedded in epoxy, cured overnight, and subsequently microtomed with a Leica Ultra microtome EM UC7 using a diamond knife at ambient conditions with resulting specimens having thicknesses ≈ 200 nm. TEM measurements were performed on Zeiss Libra 200 HT FE MC with an operating voltage of 200 kV and an emission current of 230 mA. SAXS was performed with a Molecular Metrology instrument equipped with a monochromatic X-ray source (Cu $K\alpha$, $\lambda = 1.54$ Å), a pair of Kirkpatrick-Baez micro-focusing mirrors, and a 2-dimensional position sensitive detector. The sample-detector distance was 1.5 m with a Q-range of 0.01 to 0.15 Å⁻¹. The x-ray operating voltage

was 45 kV with a current of 0.66 mA and the exposure time was 1 hour for each sample.

For pycnometry measurements PNC films were prepared into small pieces and placed in a sample cell (total volume 0.1 cm^3). Two-thirds of the total sample volume was filled (around 60–100 mg of samples) to produce better volume statistics. The weight of the samples were measured five times by using a weight balance (Mettler Toledo NewClassic MF Model MS105DU) with an accuracy of 0.01 mg. The gas pycnometer (Micromeritics Accupyc II 1340) measured the volume of penetrable helium gas within the sample and sample cup until the pressure did not vary more than 0.005 psig/min during the equilibration period. The accuracy of the volume measurement is 0.0001 cm^3 . This cycle was repeated 10 times for reproducibility. The density was then determined from the mass to volume ratio and the error of this measurement is less than 0.1%. All the density data were obtained at atmospheric pressure and at $T = 293.15\text{ K}$.

Broadband dielectric spectroscopy (BDS) measurements were performed by using a Novocontrol Alpha Analyzer with a Quatro Cryosystem to control the sample temperature with a stability of $\pm 1\text{ K}$. The samples were annealed at 450 K in the dielectric sample chamber prior to measurements and the response was measured as a function of time until thermal equilibrium was achieved (*i.e.*, the real and imaginary permittivity become constant values at a given frequency.) Isothermal frequency scans were taken in the range of $10^{-1} - 10^7\text{ Hz}$ at each temperature. The temperature range used was 375–473 K with a thermal equilibration time of 10 minutes for each set point prior to measurements with a cooling/heating rate of 5 K/min. The samples were measured two separate times to ensure data reproducibility and the presented analysis was performed on cooling data runs.

The calorimetric measurements were performed on a Q2000 (TA Instruments) devices in the temperature modulated differential scanning calorimetry (TMDSC) mode, calibrated by indium and sapphire standards, and using TZero aluminum

pans. The samples were measured by equilibrating the sample at 473 K for 30 minutes and cooling at 5 K/min with a modulation of 0.5 K/min to 293 K. These measurements were repeated three times to ensure data reproducibility.

6.3 Results and Discussion

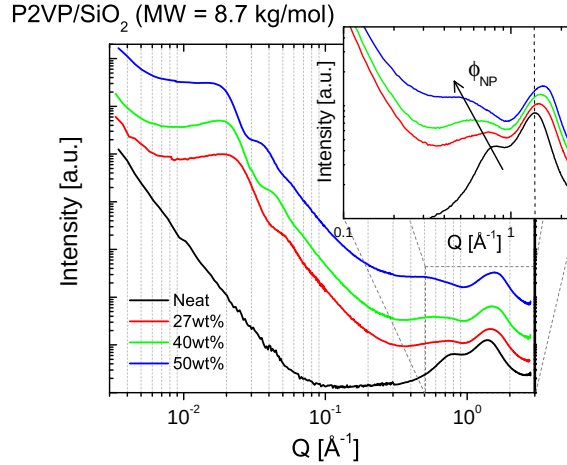


Figure 6.1: SAXS scattering profiles for low MW (8.7 kg/mol) PNCs at different nanoparticle concentrations. All curves are arbitrarily shifted for clarity. Inset: Magnification of the high Q-region

Similar to chapter 5, the static structure of the interfacial layer was characterized by SAXS. Figure 6.1 presents SAXS spectra for the low MW (8.7 kg/mol) PNC samples over a large Q-range. In this chapter, polydisperse core-shell models and hard sphere models were used to better describe these data. The polydisperse core-shell model includes three structural different regions: the core, the shell, and the matrix whereas the hard sphere model only includes two regions: the core and the matrix. For low MW, the experimental data was best described by hard sphere model as no shell could be distinguished which indicates that there is no distinct difference between the interface and the surrounding matrix—independent of NP concentration. The inset of Figure 6.1 illustrates the differences in the spectral features in high Q-region. However, the discussion of the high Q-region is out of

the scope of the current chapter. The complete set of fitting parameters for the low MW PNC set are presented in Table 6.1.

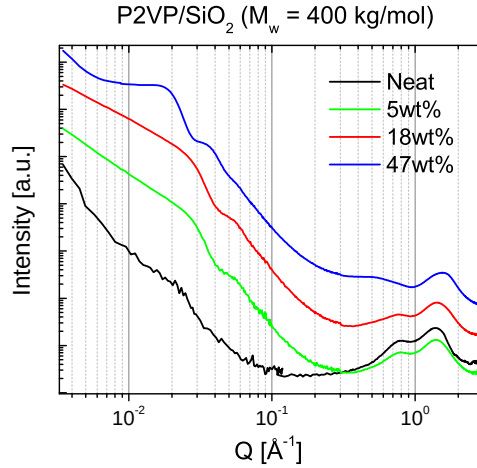


Figure 6.2: SAXS scattering profiles for high MW (400 kg/mol) PNCs at different nanoparticle concentrations. All curves are arbitrarily shifted for clarity.

Figure 6.2 presents the SAXS spectra of the high MW (400 kg/mol) PNCs. For high MW, the data were best described by the polydisperse core-shell model. The properties of the shell (interfacial layer) in this model can be best described by the scattering length density and static thickness of the shell. For the highest NP concentration of the high MW PNCs, the static length scale of the shell was found to be 5.25 nm which is larger than the 100 kg/mol thickness of 4.6 nm. Even more interesting, the scattering length density (SLD) of the shell is found to be $\sim 15\%$ lower than the surrounding matrix. A reduction in the SLD of the shell would indicate a reduction in the mass density of the interfacial layer. This is opposite to the results presented in chapter 5 for the core-shell and beaucage analysis (the linear combination) and these changes may be due to the different analysis models or perhaps the larger accessible Q -range for the data in this chapter. A complete set of the fitting parameters for the high MW PNCs can also be found in Table 6.1.

Table 6.1: Selected parameters from the hard sphere and polydisperse core-shell model form factors with a hard sphere structure factor.

Sample:	Radius (nm) Core	PDI Core	SLD ($\text{\AA}^{-2}$) Core	SLD ($\text{\AA}^{-2}$) Shell	SLD ($\text{\AA}^{-2}$) Matrix	Height Shell (nm)
8.7 kg/mol, 27wt%	10.9	0.194	1.68×10^{-5}	N/A	1.18×10^{-5}	N/A
8.7 kg/mol, 40wt%	13.1	0.200	1.82×10^{-5}	N/A	1.26×10^{-5}	N/A
8.7 kg/mol, 50wt%	15.2	0.197	1.83×10^{-5}	N/A	1.32×10^{-5}	N/A
400 kg/mol, 5wt%	10.1	0.175	2.37×10^{-5}	7.04×10^{-6}	8.0×10^{-6}	4.94
400 kg/mol, 18wt%	9.98	0.157	1.84×10^{-5}	1.05×10^{-5}	1.17×10^{-5}	5.38
400 kg/mol, 47wt%	12.28	0.159	1.94×10^{-5}	7.94×10^{-6}	9.86×10^{-6}	5.25

Table 6.2: Selected parameters from the small angle X-ray scattering models for each set of PNCs with the highest NP concentrations.

Samples:	SiO ₂ (vol%)	Core Radius (nm)	SLD, Core 10 ⁻⁵ / Å ⁻²	SLD, Shell 10 ⁻⁵ / Å ⁻²	SLD, Matrix 10 ⁻⁵ / Å ⁻²	Shell (nm)
P2VP/SiO ₂ , 400 kg/mol	34.0	12.76	2.11	0.454	0.909	5.25
P2VP/SiO ₂ , 100 kg/mol	35.5	12.51	2.153	1.531	1.109	4.6
P2VP/SiO ₂ , 8.7 kg/mol	34.0	15.20	1.83	N/A	1.32	N/A

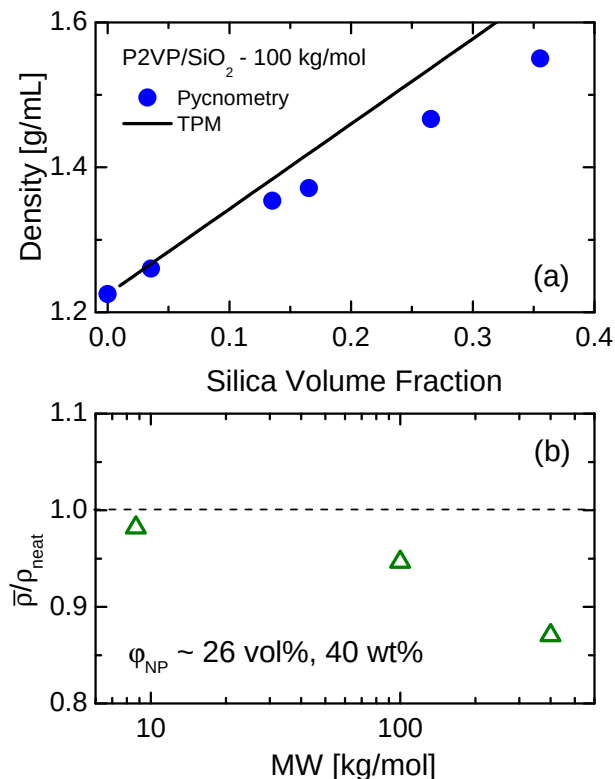


Figure 6.3: (a) The mass density of 100 kg/mol P2VP/SiO₂ nanocomposites as a function of silica concentration measured by pycnometry. Solid points are experimental data and the solid black line are the predicted values from the two phase mixing (TPM) rule assuming simple volume additivity. (b) The normalized average mass density of the matrix for each MW at identical silica concentrations (~26 vol%, 40wt%) calculated with eq. 6.1.

Following the unexpected results from SAXS, where the static structure of the interfacial layer revealed an unexpected MW dependence, pycnometry was used to directly investigate the differences in densities. Figure 6.3(a) presents the measured mass density from pycnometry for the 100 kg/mol PNCs as a function of NP concentration. By assuming the volume additivity, one can compare the measured density to the expected density by the simple two-phase mixing (TPM) rule. As Figure 6.3(a) illustrates, the density of the PNCs (blue circles) is much lower than expected from the TPM predictions (black line). However, it appears that this difference is much lower at low NP concentrations and only deviates with increasing NP concentration (~10vol%). As the interparticle spacing (IPS) becomes

very small and the material becomes predominately an "interfacial" material, a decrease in the overall density could be expected for an interfacial layer with a lower density—also consistent with the 400 kg/mol results from SAXS. For all MWs, a similar trend is observed: the density of the PNCs is lower than expected from the TPM rule. To best illustrate the reduction in the density, the average density is calculated assuming volume additivity by using the following expression:

$$\overline{\rho_m} = (\rho_{PNC} - \rho_{NP}\psi_{NP})/(1 - \psi_{NP}) \quad (6.1)$$

where ρ_{PNC} is the measured density, ρ_{NP} is the density of the NPs (found to be 2.4 g/mL), and ψ_{NP} is the volume fraction of the NPs. The $\overline{\rho_m}$ normalized by the neat density, ρ_{neat} , is presented in Figure 6.3(b) for each MW at identical NP concentrations ($\psi_{NP} \sim 26$ vol%). The MW dependence of $\overline{\rho_m}/\rho_{neat}$ reveals that the overall density of the polymer within the PNC becomes less dense with increasing MW and remains relatively constant at low MW. These unexpected results are interesting since they imply that the structure of the interfacial layer in PNCs is dependent on MW and are consistent with positron annihilation lifetime spectroscopy studies that also found an increase in free volume in high MW PNCs and supported polymer thin films.[21, 84] Similarly, a reduction in density was previously reported for PVAc/ SiO_2 nanocomposites under pressure up to 10 MPa, which implies an even larger reduction at atmospheric pressure. The increase in the free volume would typically be accompanied by a lower T_g and faster segmental dynamics; however, as shown in Chapter 5 this behavior was not observed for 100 kg/mol PNCs. As demonstrated from pycnometry, consistent with the SAXS data, these results indicate that the static length scale of the interfacial layer MW dependent and that the density of the interfacial layer unexpectedly decreases with increasing MW.

The changes in the static properties of the interfacial layer can also be observed dynamically by two different experimental techniques: temperature modulated

differential scanning calorimetry (TMDSC) and broadband dielectric spectroscopy (BDS). These techniques are used to specifically study the changes in the calorimetric glass transition strength, T_g , dielectric strength, and segmental relaxation times. The specific heat capacity of the polymer fraction within the PNC is determined by eq. 5.1 (by the procedure described in chapter 5). This allows the quantitative analysis of the magnitude of the glass transition, Δc_p as well as the glass transition temperature, T_g . As discussed in chapter 5, the magnitude of the glass transitions, Δc_p , yields information concerning the internal degrees of freedom and is directly proportional to the number density of relaxing units. In chapter 5, the concentration of NPs was demonstrated to have almost no effect on the Δc_p of the polymer within the PNCs. Figure 6.4 presents the specific heat capacity for the neat polymers and PNCs with the highest NP loading for each MW. Again, the Δc_p of the polymer within the PNCs is not affected by the presence of the nanoparticles and is not MW dependent. However, there is a difference in the midpoint of the transition and the breadth of the glass transition step as the MW decreases. It becomes clear that not only the breadth of the glass transition but also the T_g of low MW PNCs are more influenced by the addition of NPs while relatively unaffected at high MW. Most notably, the breadth of the transition extends to much higher temperature than neat polymer, consistent with recent simulations.[11]

Figure 6.5 reveals the gradual increase in the relative T_g with NP concentration for each respective MW. These results are unexpected since the amount of the adsorbed or bound polymer should be larger at higher MW and smaller at lower MW, at least when considering the total adsorbed polymer. It appears that the opposite trend is observed for the amount of polymer affected on the segmental level where an increase of MW leads to a dramatic decrease in volume fraction of dynamically affected polymer. These results appear to be consistent with the changes in the overall density of the PNCs at high NP concentrations—where a uniformly dense interface is observed for low MW as well as a large change in the

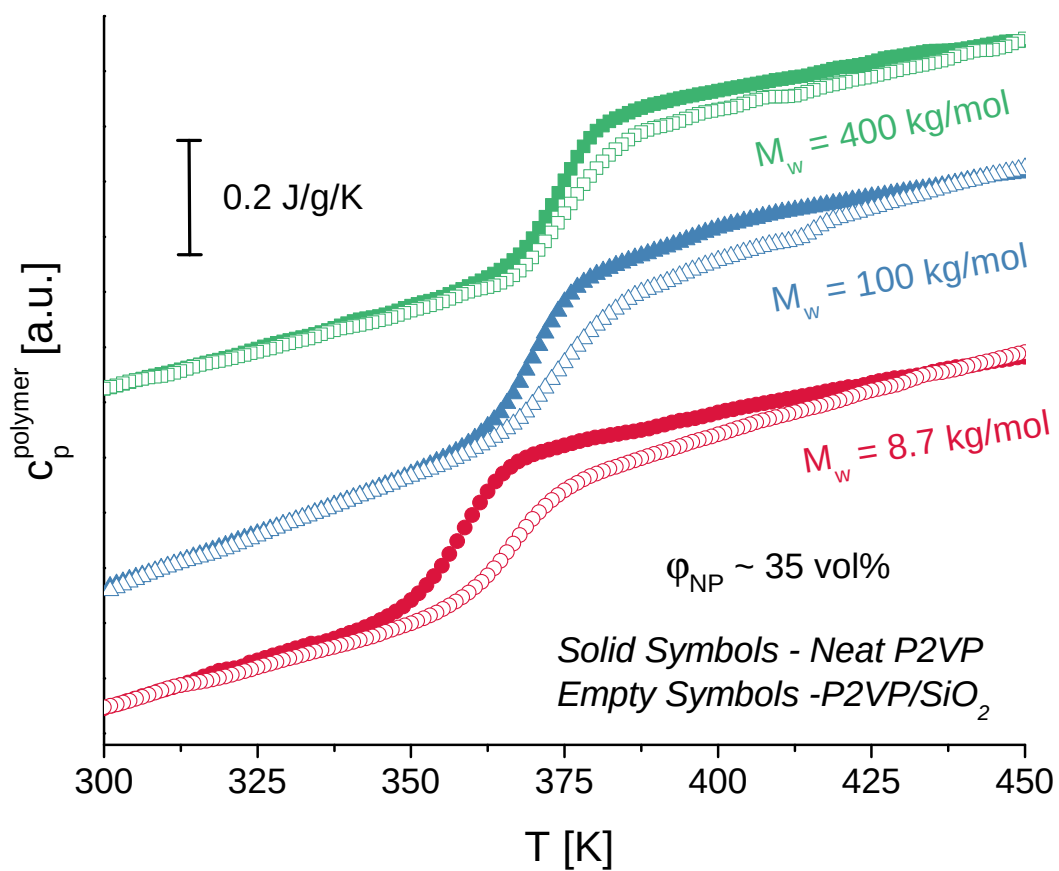


Figure 6.4: Specific heat capacity of the polymer matrix (without the contribution from the NPs) illustrating the glass transition from TMDSC for neat P2VP and PNCs with at high NP concentrations.

dynamics (increase in T_g) and an interface with low density is found for high MW accompanied by very small changes in the dynamics. This would imply that the strong polymer-NP interactions suppress the segmental dynamics of the adsorbed polymer units, however, the apparent reduction in density at the interface appears to compensate for this effect.

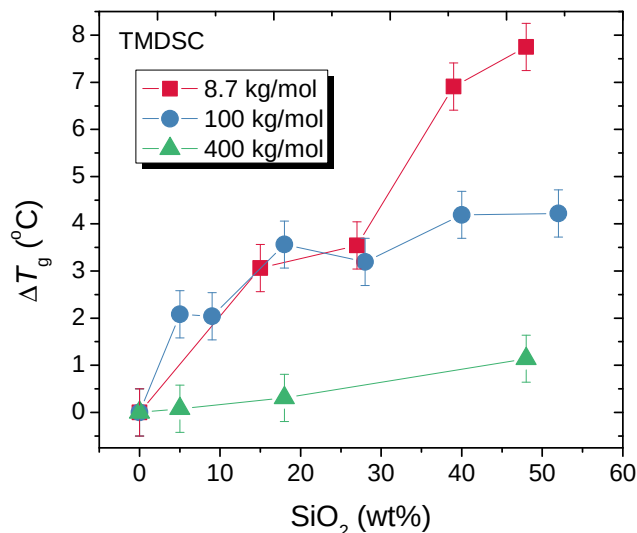


Figure 6.5: The relative change in the glass transition temperature from TMDSC for each MW as a function of NP concentration.

To provide a better understanding of the changes in dynamics within the interfacial layer, broadband dielectric spectroscopy is utilized. The complex permittivity, $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$, was obtained from BDS to understand the segmental relaxation in these PNCs. The imaginary part of the complex permittivity, $\epsilon''(\omega)$, is presented in Figure 6.6 at selected temperatures for all MW PNCs. In this representation, there are two spectral features: (1) the d.c. conductivity at low frequencies and (2) the segmental relaxation process which appears as a peak.

For the high MW (Figure 6.6(a)), there is no change in the peak position of the segmental relaxation process and a negligible change in the breadth of

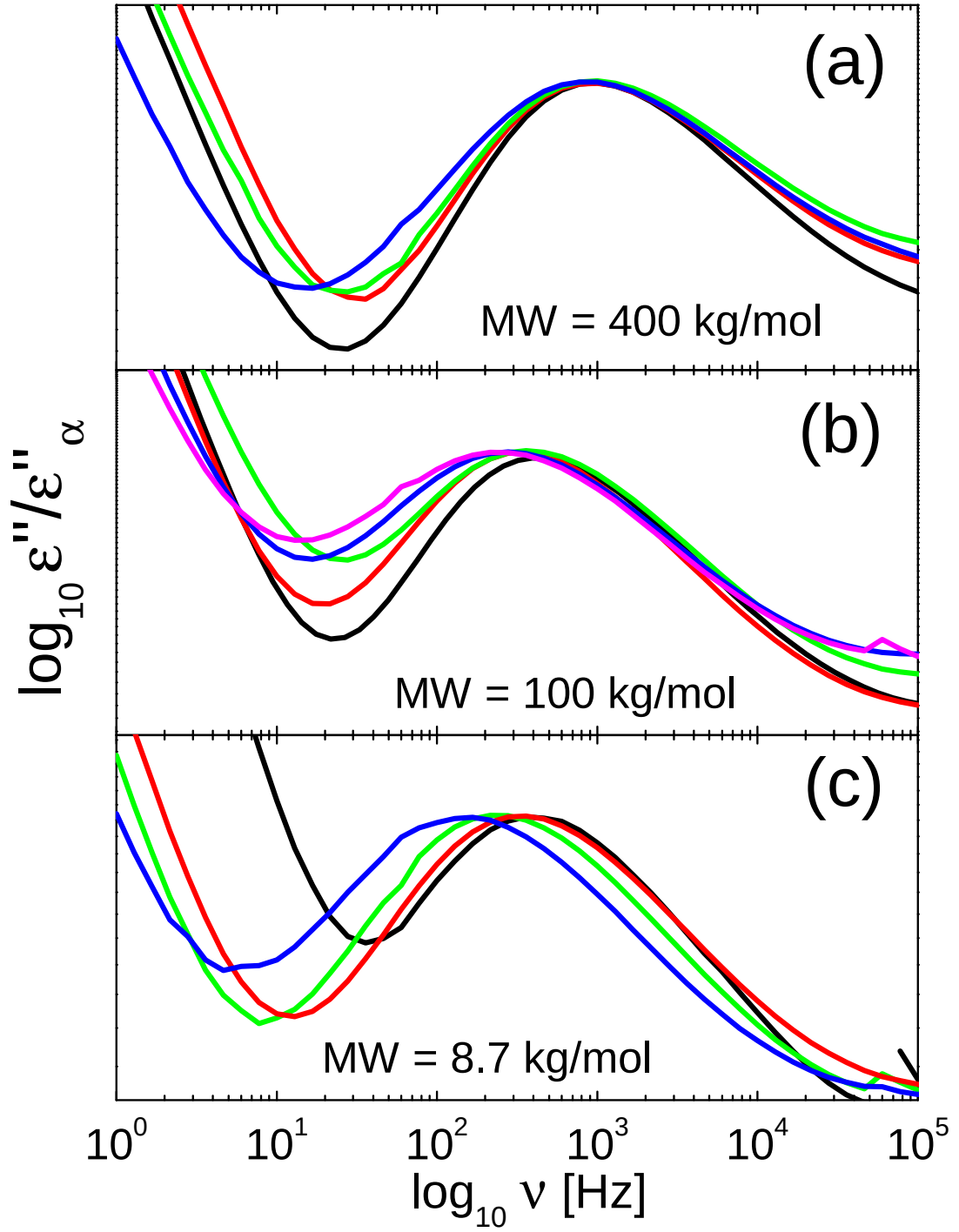


Figure 6.6: Normalized imaginary permittivity obtained from BDS demonstrating the effect of increasing silica concentration on the segmental relaxation process for each MW: (a) 400 kg/mol at $T = 405$ K, (b) 100 kg/mol at $T = 405$ K, and (c) 8.7 kg/mol at $T = 408$ K.

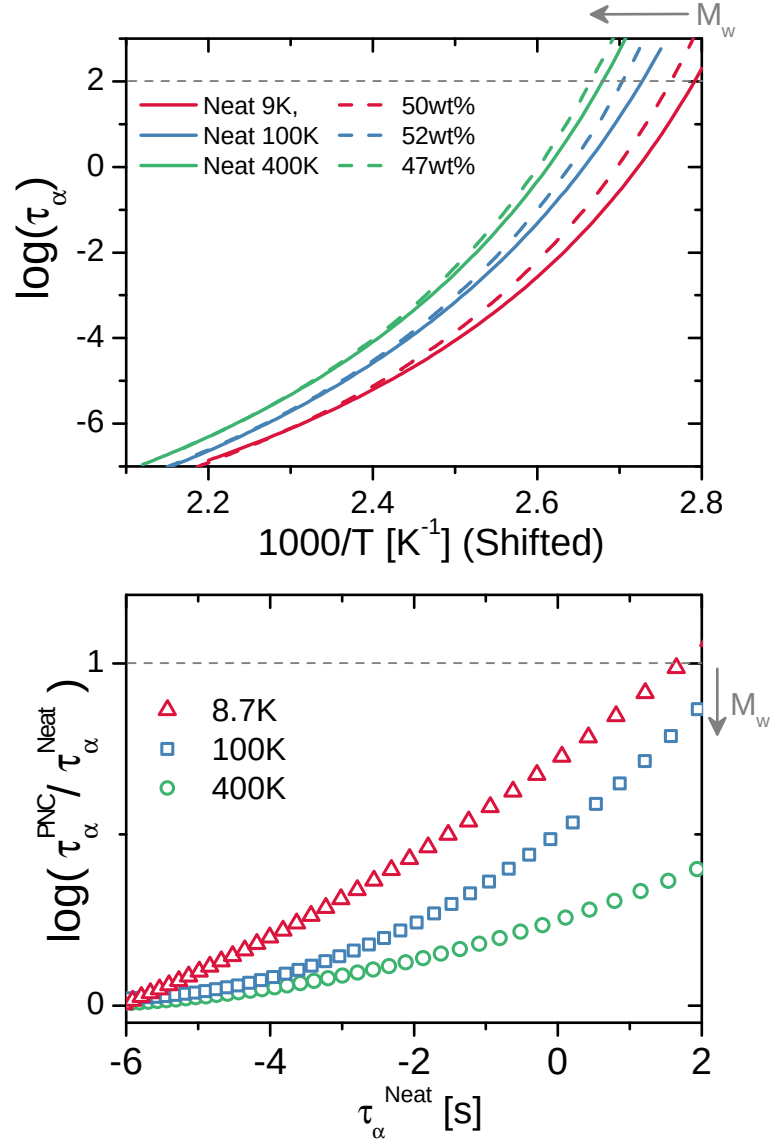


Figure 6.7: (top) The temperature dependence of average segmental relaxation times for 8.7K (black), 100K (blue), and 400K (green) molecular weight polymers (solid lines) and compared to the highest concentration PNC (dashed lines). The grey dotted line signifies $\tau_\alpha = 100s$. Note: The 400K data is shifted horizontally by 0.01. (bottom) The decoupling ratio for the segmental relaxation times from bulk-like behavior for the highest concentration PNCs (circles high MW, squares intermediate MW, and triangles low MW).

the relaxation similar to the TMDSC results. In Figure 6.6(b), the 100 kg/mol systems, as discussed in the previous chapter, reveal a systematic broadening of the segmental relaxation process as well as the gradual shift of the peak position to lower frequencies. Figure 6.6(c) shows a systematic slowing down of the segmental relaxation peak position for the low MW PNCs with increasing NP concentration with the additional broadening of the low and high frequency tails expected for multi-component systems.

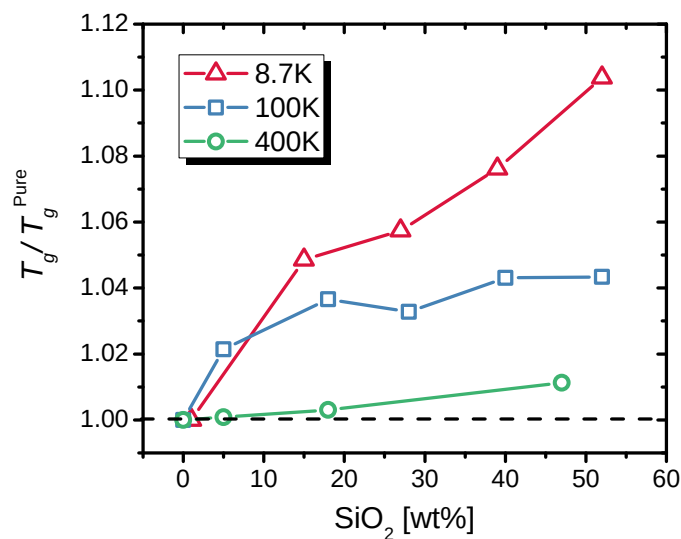


Figure 6.8: Relative change in T_g as determined by BDS for each molecular weight as a function of silica loading.

The temperature dependence of the average segmental relaxation times, τ_α , can be obtained fitting these data with a single HN function (eq. 3.37). The temperature dependence of the segmental relaxation times for the three different MW polymers and respective PNCs with the highest concentration of NPs is presented in Figure 6.7. The deviation of τ_α from bulk-like behavior and the dependence on MW can clearly be observed. At high temperatures the segmental dynamics are unaffected by the presence of NPs even at extremely high concentrations. However, the segmental relaxation times deviate from the

bulk-like values as the temperature approaches T_g and this deviation shows a relatively strong MW dependence. The ratio of the deviation or decoupling is plotted in Figure 6.7 where the lower MWs show a maximum difference of an order of magnitude.

The dynamic T_g from BDS can be determined from the temperature dependence of segmental relaxation times where it is commonly defined as the temperature at which τ_α reaches 100s. For all MWs, the PNCs exhibit longer the segmental relaxation times and corresponding larger T_g values. This also indicates that the isobaric fragility index, m , (eq. 2.4) which is defined as the slope of the relaxation times at T_g , is strongly affected. The fragility index is often related to dynamical heterogeneity or AG-cooperative dynamics. Starr and Douglas have predicted a qualitative trend for the segmental relaxation times, fragility, and T_g in low MW-based PNCs which agree well these results (Fig. 6.8 and 6.9). [11]

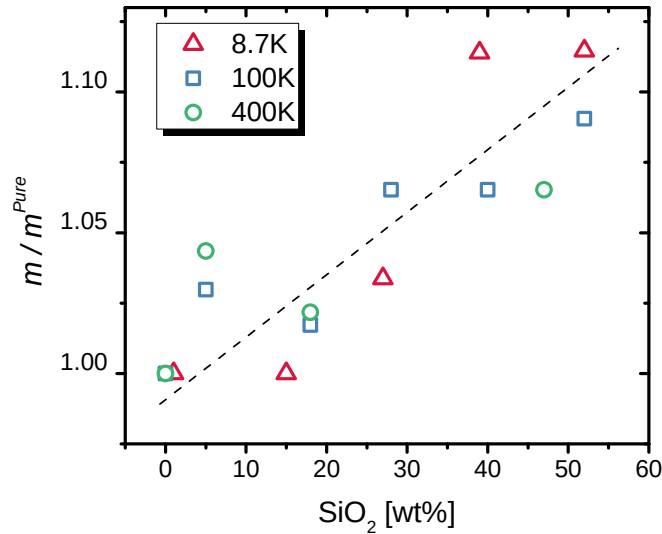


Figure 6.9: Relative change in the isobaric fragility index, m , for each molecular weight as a function of silica loading.

It is well-established that the timescale of segmental dynamics of different polymers or structural dynamics for small molecule glass formers behave in

specific ways to thermal and density changes—the so-called thermodynamic scaling. Therefore, the relaxation time can be expressed as $\tau = f(T, V^\gamma)$, where the exponent, γ , is a material constant and intrinsically linked to the intermolecular potential in many amorphous materials.[85] However, it has been shown that scaling of the segmental dynamics of poly(vinyl acetate)/silica and poly(styrene)/silica nanocomposites does not follow the expected behavior of a pure material, where the thermodynamic scaling exponent is dependent on NP loading.[86, 87] An increase in the thermodynamic scaling exponent implies that the segmental dynamics experiences a higher degree of sensitivity to volume or density changes rather than thermal changes. It should be noted that γ is MW dependent and typically becomes less sensitive to density changes with increasing MW which may also play a role.[88] Therefore, it is likely that there is a competition between the slowing down of polymer segments from the adsorption process, the reduction in density occurring at the polymer-NP interface, and the thermodynamic scaling of segmental mobility in PNCs.

To further unravel the dynamic properties of the interfacial layer and its dependence on MW, the interfacial model is employed to further analyze the BDS spectra at high and low MW (refer to chapter 5 for a detailed analysis of 100 kg/mol PNCs). Through the interfacial model analysis, the contributions of the interfacial and bulk-like segmental dynamics are separated. Furthermore, it allows an estimate of the volume fraction of affected segments and their characteristic relaxation times. For a detailed explanation of the criteria used to determine these quantities, refer to eq. 5.7 and the description of the analysis on page 95.

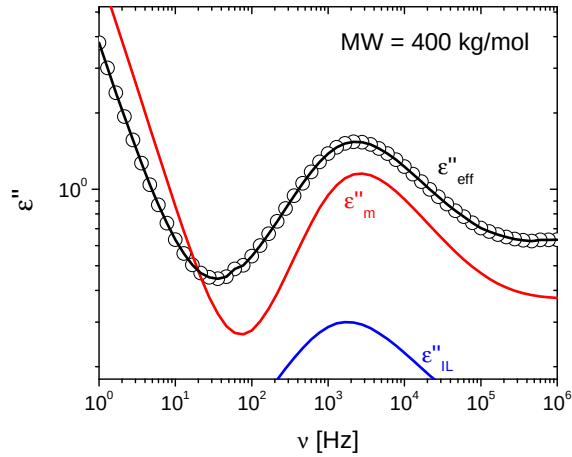


Figure 6.10: The deconvolution of the dielectric loss spectra at $T = 410$ K into the individual components by the interfacial model analysis for the high MW system at the highest NP concentration.

Figure 6.10 reveals the individual contributions of the interface (ϵ''_{IL}), matrix (ϵ''_m), and effective (ϵ''_{eff}) dielectric loss spectra at $T = 410$ K and normalized by their respective volume fractions for the high MW PNC at the highest NP loading. While there is a drastic change in the dielectric strength of the matrix relative to the interfacial layer, the time scales of each respective process are similar. These results indicate that the interfacial dynamics in high MW PNCs are negligibly affected by the presence of the nanoparticles and are similar to that of the average segmental dynamics within these systems (Fig. 6.7(a)). However, as the MW decreases, as previously shown for the 100 kg/mol PNCs in chapter 5, the time scale and the volume fraction of the interfacial dynamics begin to change (Fig. 5.12 and 5.13).

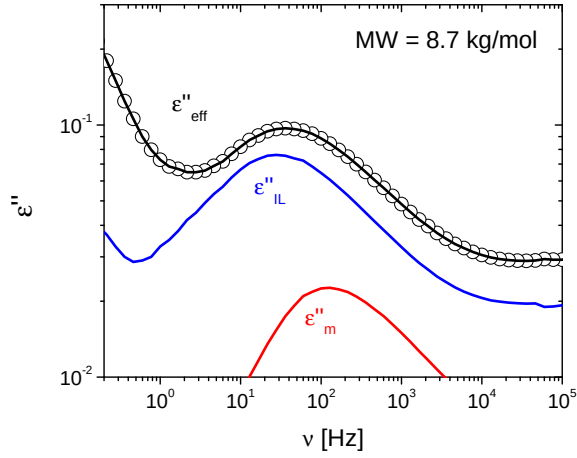


Figure 6.11: The deconvolution of the dielectric loss spectra at $T = 385$ K into the individual components by the interfacial model analysis for the low MW system at the highest NP concentration. Each spectral component is normalized by the respective volume fraction.

The dielectric loss spectra contributions for the low MW PNC at highest NP loading (35vol%) are shown in Figure 6.11. Similar to Figure 6.10, each component is normalized by their respective volume fractions. The difference in the volume fractions and time scales between the matrix and interfacial layer components is now reversed when compared to the high MW PNCs. These results clearly show that the dynamics at the interfacial layer are approximately an order of magnitude slower than the bulk-like dynamics and that the majority of the polymer is affected by the suppression of dynamics. This is consistent the majority of the polymer being an "interfacial material" and with the results from TMDSC, where a broadening of the glass transition and increase in the overall T_g is also clearly observed at low MW and at high NP loading—a result that one would expect to be independent of MW.

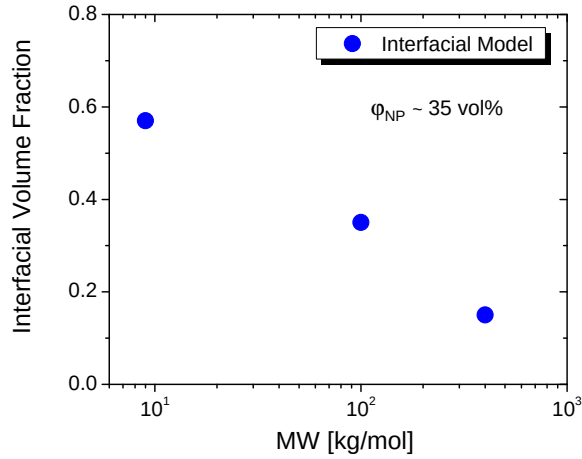


Figure 6.12: The volume fraction of the interfacial layer as a function of MW at the highest NP loading of each PNC set.

The amount of polymer affected by the presence of the NPs is also determined by the interfacial model and presented in Figure 6.12 for the PNCs with the highest NP loadings ($\sim 35\text{vol}\%$). The volume fraction of dynamically affected segments is found to be drastically different between high and low MW PNCs, $15\text{vol}\%$, $35\text{vol}\%$, and $57\text{vol}\%$ respectively. From these volume fractions, an estimated length scale of the interfacial layer thickness can be calculated with $d = R_{NP}[(\phi_{IL}/\phi_{NP})^{1/3} - 1]$ where, R_{NP} is the radius of the NPs, ϕ_{IL} is the volume fraction of interfacial polymer determined from the interfacial model and by assuming a uniform density. However, as mentioned above the density is found not to be uniform for the higher MW PNCs at high NP loadings so the actual thickness will even less than the reported values. Figure 6.13 presents the estimated thickness of interfacial layer from dynamic (BDS) and static (SAXS) techniques. Additionally, the bound layer of P2VP (the physically bound polymer but not affected on the segmental level) determined from diffusion measurements with identical NPs from reference [23] is presented in Figure 6.13. The length scale of the bound layer scales with the MW of the polymer and shows a very different MW dependence than the dynamic interfacial thickness from BDS. Although there are not enough data points

to clearly identify a trend, the static thickness of the interfacial layer appears to scale differently than the dynamic thickness. This is likely due to the static thickness scaling with poor chain packing (lower density at the interface) while the dynamic thickness scales with good chain packing (uniform or higher density at the interface).

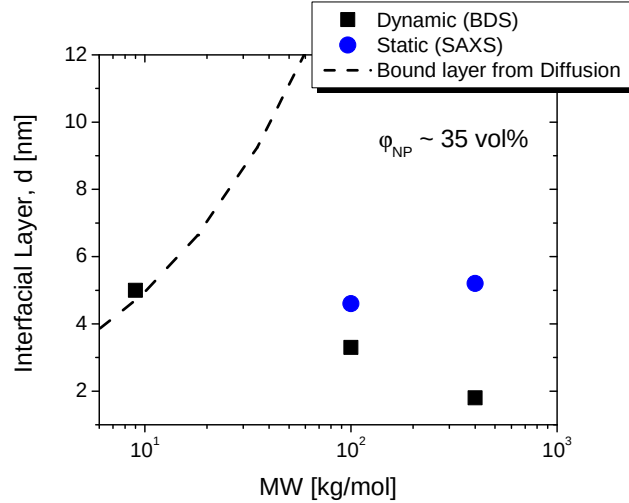


Figure 6.13: Comparison of the static and dynamic thickness of the interfacial layer from BDS (black symbols) and SAXS (blue symbols) as a function of MW. Additionally, the scaling law for length scale of the bound layer which is the total length scale of adsorbed polymer experimentally determined from diffusion experiments of P2VP/*SiO*₂ from reference [23].

The changes in the density at interfacial layer with molecular weight provides a clear explanation for the decrease in the change of dynamics with increasing MW. A more densely packed interfacial layer in low MW PNCs would lead to a significant slowing down of segmental mobility and a larger dynamic thickness. In contrast, the competition between the polymer adsorption and frustrated chain packing causes the unexpected dynamics changes within the high MW PNCs.

The peculiar interfacial structure in these materials raises the question of thermodynamic stability. It has been demonstrated that annealing effects can strongly influence the effect of the chain packing in polymer thin films—where the initial interfacial structure is stuck in a long-lived metastable state.[89] The lifetime

of these metastable states would depend on strongly on the MW which limits the rate of chain diffusion and affect the high MW systems more so than the low MW systems.

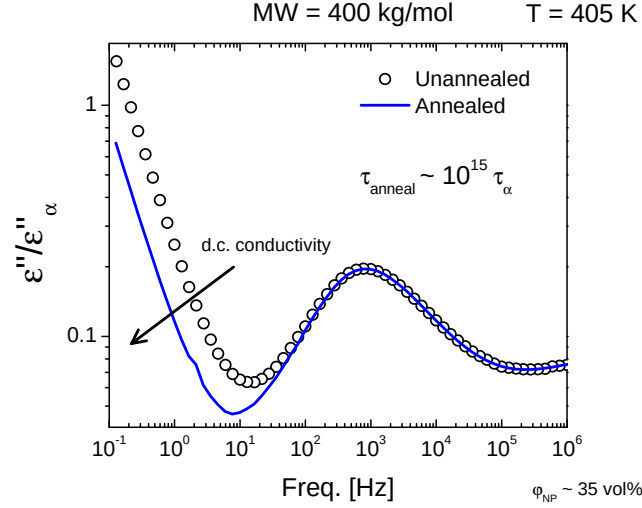


Figure 6.14: Comparison of dielectric loss spectra for the high MW PNC before and after the thermal annealing procedure under vacuum, at $T = T_g + 50$ K, and for $\sim \tau_\alpha \times 10^{15}$.

To explore this idea, the high MW PNC system was annealed at $T_g + 50K$ for up to $\tau_\alpha \times 10^{15}$. The dielectric spectra were measured before and after the annealing procedure and are presented for a single temperature in Figure 6.14. However, according to these annealing data, the time to reach equilibrium in high MW PNCs requires unrealistically long times. Therefore, high MW-based PNCs could be considered to be trapped in a deep metastable state and further understanding these non-equilibrium states could be applicable for many applications where aging effects need to be avoided.

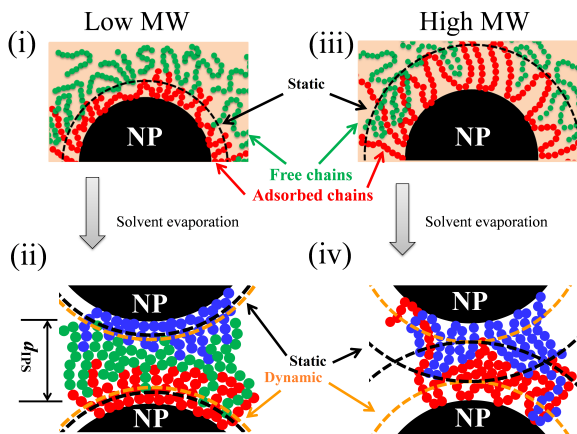


Figure 6.15: A cartoon illustrating the proposed adsorption process for low and high MW polymer during the solvent evaporation preparation process and the resulting MW dependent polymer-NP interface. Image reproduced from reference [24].

Figure 6.15 presents a cartoon illustrating the proposed MW dependence of chain packing at the polymer-NP interface. In a concentrated solution or melt, low MW chains form much shorter loops with less anchoring points per chain compared to high MW PNCs. Upon solvent evaporation, the adsorbed chains that are short can adjust their conformations much easier than longer chains, and therefore low MW polymer chains are likely to form a more uniformly packed interfacial layer when attractive polymer-NP interactions are present. However, long chains are more likely to form long loops and bridges between NPs which is suspected to create additional frustration in chain packing in high MW PNCs and a resulting low density interfacial layer.

6.4 Summary

These results provide a new perspective in understanding the complex dynamics of multi-component polymeric systems such as PNCs. The interfacial layer around silica NPs were shown in Chapter 5 to be strongly influenced by chain adsorption, *i.e.* by formation of an irreversibly bound polymer layer. In this

Chapter, the adsorption process and its influence on properties of the interfacial layer is demonstrated to be strongly dependent on the MW of the polymer but in an unexpected way.

The static structure measurements revealed a clear difference in scattering length density for the nanoparticle, interface, and matrix for high MW while the low MW only show a difference between the NP and matrix—indicating an interface with uniform density. Furthermore, the scattering length density of the interface was found to be lower than that of the bulk matrix and implies that the interfacial layer exhibits a lower density. These results are corroborated by pycnometry measurements which also revealed a reduction in the mass density with increasing MW. However, opposite to the static properties, the dynamic properties of the interfacial layer revealed that the length scale of affected segmental mobility decreases with increasing MW.

From these results, it is proposed that the changes in the interfacial layer with MW is due to a frustration in chain packing at the interface which leads to a competition of effects: (1) an initial slowing down due to physical adsorption and (2) a speeding up due to a reduction in density. The thermal stability of the interfacial layer at high M_W appears to be very stable even when annealed for $\tau_\alpha \times 10^{15}$ well above T_g . These unexpected findings have far-reaching implications since they aid in developing a predictive understanding for the interfacial properties of these materials.

Chapter 7

Comparing the Effect of Covalent Bonding versus Physical Adsorption in Polymer-Based Nanocomposites

The popularity of polymer grafted nanoparticles (PGNs) has increased significantly in the past few years due to improvements in miscibility, stability, and dispersibility of PGNs over traditional nanoparticle surface functionalities. However, despite the large interest of the miscibility and dispersibility of PGNs in polymer melts, a fundamental understanding of the polymer dynamics of PGNs has yet to be investigated. In this chapter, broadband dielectric spectroscopy, temperature modulated differential scanning calorimetry, small angle X-ray scattering techniques, and self-consistent field theory calculations are used to understand the structural and dynamical properties of PGNs and are directly compared with polymer nanocomposites (PNCs).

7.1 Introduction

For the past decade, the successful dispersion of nanoparticles (NPs) within a polymer matrix has been shown to dramatically influence the glass transition of polymers and has been attributed to the modification of segmental dynamics at the polymer-NP interface due to attractive interfacial interactions.[20, 21, 60, 61, 81, 90] For highly interacting systems, the interfacial region was previously estimated to be a few nanometers and to exhibit different dynamical[61, 81] and mechanical properties[91] when compared to the individual components. Furthermore, the properties of interfacial region have been shown to be affected by changing the size of NPs,[90] their surface chemistry,[92–94] or the molecular weight of the polymer matrix.[24]

In regards to polymer nanocomposites (PNCs), in the previous chapter, the conformations of the polymer chains at the polymer-NP interface were suggested play a preeminent role in the suppression of segmental dynamics in well-dispersed poly(2-vinyl pyridine)/silica nanocomposites. However, developing a complete understanding the interfacial segmental dynamics in regards to physical adsorption remains a challenge due to the random nature of chain packing at the interface. Theoretical models, such as Scheutjens-Fleers self-consistent field theory, have attempted to predict the resulting chain conformations (trains, tails, or loops) after physical chain adsorption to flat or curved interfaces but can only provide a distribution of probabilities.[95]

An alternative, and perhaps innovative, approach to this problem is to investigate an ideal system where the polymer conformations can be predicted more reliably or known such as polymer grafted-to-nanoparticles (PGNs). PGNs can be produced by covalently attaching polymer to the surface of a NP (or by *in situ* polymerization from the NP surface) and can be dispersed within the same or a different polymer matrix; therefore solving many of the aggregation problem associated with PNCs. Furthermore, PGNs possess the ability to self-assemble

into specific NP arrangements such as strings or fractals morphologies by tuning grafting density or grafting molecular weight.[96] In PGNs, particularly those prepared by the grafting-from approach (opposed to the grafting-to approach), the polymer conformations at the NP surface are predominately composed of tails (one chain end fixed and one free end) and can be calculated more accurately for a given specific grafting density.[97] Therefore, from an experimental standpoint, solvent-free PGNs are an ideal system in which to study how chain conformations in the interfacial region can affect the segmental dynamics relative to the case of random physical chain adsorption (PNCs). When directly comparing PNCs to PGNs the general expectation is that covalent bonding will more significantly affect the dynamics of the polymer matrix than physical adsorption, especially at the polymer-NP interface. However, despite the tremendous interest in interfacial materials, only a few attempts have been made to investigate the polymer dynamics of PGNs with a focus on the global, chain dynamics.[98–100]

In this chapter, the effect of covalent bonding and physical absorption of polymer chains on the interfacial properties of well-dispersed poly(2-vinyl pyridine)/silica nanocomposites (PNCs) and poly(2-vinyl pyridine)-grafted-from-silica (PGNs) are directly compared using broadband dielectric spectroscopy (BDS), temperature modulated differential scanning calorimetry (TMDSC), and small-angle x-ray scattering (SAXS). For PGNs, the chain grafting density is identical at 0.3 chains/ nm^2 and the relative silica-to-polymer ratio is a fixed quantity which can only be tuned by varying the molecular weight (MW). Three MW systems (6, 18, and 140 kg/mol) are investigated for both PGNs and PNCs at identical silica ($R_{NP} = 12.5$ nm) concentrations. A detailed analysis revealed only a weak change in the dynamics of PGNs and PNCs with high MW (140 kg/mol, $R_{NP}/R_g = 1.13$), most likely due to the relatively low content (~ 6 vol% silica) of NPs. However, there is a clear difference in the properties of interfacial layer at intermediate MW (18 kg/mol, $R_{NP}/R_g = 3.16$) where the interfacial dynamics are more strongly suppressed by the covalent bonding than by physical adsorption. Interestingly, the

PGNs and PNCs with low MW (6 kg/mol, $R_{NP}/R_g = 5.4$) exhibit an identical suppression of dynamics, a large gradient of segmental mobility and an interfacial region that occupies essentially the entire material despite the magnitude of the interactions. In lieu of these results, it is proposed that anisotropic chain stretching of segments at the interface, a phenomenon previously suggested by Oyerokun and Schweizer,^[101] rather than the polymer-NP interaction strength, plays a critical role in suppression of segmental dynamics, which ultimately determines the magnitude of the change in the average glass transition temperature in these heterogeneous materials. These results suggest that the interfacial dynamics in PNCs or PGNs can be tuned by controlling the degree of chain stretching at the interface, which should be an adjustable parameter *via* the MW for PNCs or the grafting density for PGNs.

7.2 Experimental Details

Materials: 2-Vinylpyridine (2-VP, 97%, Aldrich) was deinhibited via passing through activated alumina column. 4-cyano-4-(phenylcarbo-*thio*ylthio)pentanoic acid N-succinimidyl ester (RAFT agent, Aldrich), hexanes (BDH), tetrahydrofuran (THF, BDH) were used as received. 2,2-azobis(isobutyronitrile) (AIBN, 99%, Aldrich,) was purified by recrystallization prior to use.

Synthesis of Silica Nanoparticles and Attachment of RAFT Agent:

Silica nanoparticles with the diameter of 20-25 nm were synthesized following the modified Stoeber method. The details of the synthesis are described elsewhere.^[72] As prepared, silica was modified with 3-aminopropyldimethyl-ethoxysilane. For that, 100mL of silica nanoparticles (15 mg/ml) in ethanol was rotary evaporated and re-dispersed in 100 mL of dry THF, 1 mL of silane was added to the silica nanoparticles in THF, and the mixture was refluxed for 24h. The particles were centrifuged three times to remove any unreacted silane. The washed particles were then re-dispersed in 50 mL of dry THF and 0.1 g of RAFT agent was added to

the solution. The resulting mixture was stirred at room temperature for 12 h. Centrifugation was used to separate unreacted RAFT agent from RAFT agent functionalized silica particles.

Synthesis of Poly(2-vinylpyridine) on Silica Nanoparticles via RAFT Polymerization: 2-Vinylpyridine (5.31 g, 5.45 mL) and AIBN (6.64 10^{-6} mol, 1.09 mg) were put into RAFT agent functionalized silica particle THF solution (17 mL). Argon was bubbled through the solution for 10 min. The reaction proceeded for 3 h, 6h and 21 h, respectively, at 65 C (Scheme 1, (2)). The resulting poly(2-vinylpyridine) (P2VP)-attached silica NPs were precipitated into hexanes, centrifuged, washed with THF/hexanes mixture for 3 times. The supernatant was also collected, dried and the unattached P2VP was collected. The precipitated particle and isolated free P2VP were dried at 40 C in vacuum for 24 h. Molecular weight characteristics of the unattached polymers were obtained from size exclusion chromatography (SEC) equipped with both light-scattering and refractive index detectors. Our SEC system consisted of a Waters 2695 Alliance HPLC pump equipped with degasser and autosampler, 3 X Polymer Labs Mixed-C Ultrapolystryagel columns in a thermostatted compartment, a Wyatt miniDAWN 3-angle ambient light scattering detector, and a Waters 2414 refractive index detector; N,N-dimethylformamide (DMF) was used as the eluent at a 0.5 mL/min flow rate with the columns at 60 C. MW values were preferentially taken from light-scattering-based calculations, by using Wyatt Astra software. Conventional calibration MW and PDI values were also taken according to the RI detector results and Waters Empower software; 3rd-order polynomial calibrations were made by using either poly(2-vinylpyridine) standards or polystyrene standards; and these standards were also passed the same day as unknown analytes to verify calibration durability.

Preparation of polymer nanocomposites: The free (unattached) P2VP chains collected from the grafted nanoparticle synthesis were used to prepare composites with identical silica nanoparticles (with unmodified surface functionality)

with the molecular weights identical to the grafted samples. The polymer and nanoparticles were mixed in ethanol and the solvent was evaporated during stirring and samples were dried in the Teflon plates at 100 C for 48 hours. The amount of silica nanoparticles in composite materials was added at the identical weight fraction of P2VP than that of the covalently grafted systems and confirmed by thermogravimetric analysis. Thermogravimetric analysis was used to determine the weight fraction of silica and grafted P2VP. This information together with the molecular weight obtained from GPC were used to estimate grafting density of P2VP. The grafting density was found equal to 0.3 chains/ nm^2 .

Pycnometry Measurements: PNC films were prepared into small pieces and placed in a sample cell (total volume 0.1 cm^3). At least two-thirds of the total volume was filled (around 60–100 mg of samples) to produce better statistics. The weight of the samples were measured five times by using a weight balance (Mettler Toledo NewClassic MF Model MS105DU) with an accuracy of 0.01 mg. The gas pycnometer (Micromeritics Accupyc II 1340) measured the volume of penetrable helium gas within the sample and sample cup until the pressure did not vary more than 0.005 psig/min during the equilibration period. The accuracy of the volume measurement is 0.0001 cm^3 . This cycle was repeated 10 times for reproducibility. The density was then determined from the mass to volume ratio and the error of this measurement is less than 0.1%. All the density data were obtained at atmospheric pressure and at $T = 293$ K.

7.3 Results and Discussion

The excellent quality of nanoparticle dispersion in our samples is confirmed by small angle X-ray scattering (SAXS) and transmission electron microscopy images (Fig. 7.1). The changes in macroscopic properties, *e.g.*, T_g , should be directly associated with the presence of interfacial polymer in both PNCs and PGNs.[3, 102] To explore this idea, we use SAXS to determine the peculiarity of the static

structure of our materials within the glassy state. Based on the results of the previous chapters, it is known that the P2VP/silica nanocomposites exhibit a core-shell structure with a finite shell thickness.[24, 81] In this chapter, we use a polydisperse core-shell model and hard sphere models to fit our SAXS data.[103] The properties of the shell in this model are described by the scattering length density, the static shell thickness, and the polydispersity of the shell thickness. These parameters combined provide important information concerning the static length scale, relative density, and the uniformity of the density of the shell.

Figure 7.1(a) presents the SAXS spectra with the corresponding fits to the best model. The 18 kg/mol and 140 kg/mol PNC and PGN samples fit to the PCSM model, requiring three structurally different regions, core, shell, and polymer matrix. The 6 kg/mol PNC and PGN fit best to the hard sphere model, as no shell was distinguishable. The complete set of the fit parameters can be found in Table 7.1. For PGNs, the static length scale of the interfacial shell was found to stay relatively constant for the intermediate and high MW with values of 3.4 ± 0.7 nm and 3.8 ± 0.7 nm, respectively. Interestingly, the length scale of the interfacial shell was found to be systematically $\sim 20\%$ - 35% smaller in the PNCs than in the PGNs. Also, the scattering length density in the interfacial region is $\sim 20\%$ lower than scattering length density of the matrix for the 18 kg/mol and 140 kg/mol PNCs and PGNs. However, the 6 kg/mol samples are best described by a hard sphere model, which indicates that the matrix surrounding the nanoparticles is homogeneous. This is consistent with a nanocomposite where the entire surrounding matrix is interfacial polymer due to the high silica loading (~ 50 vol% silica).

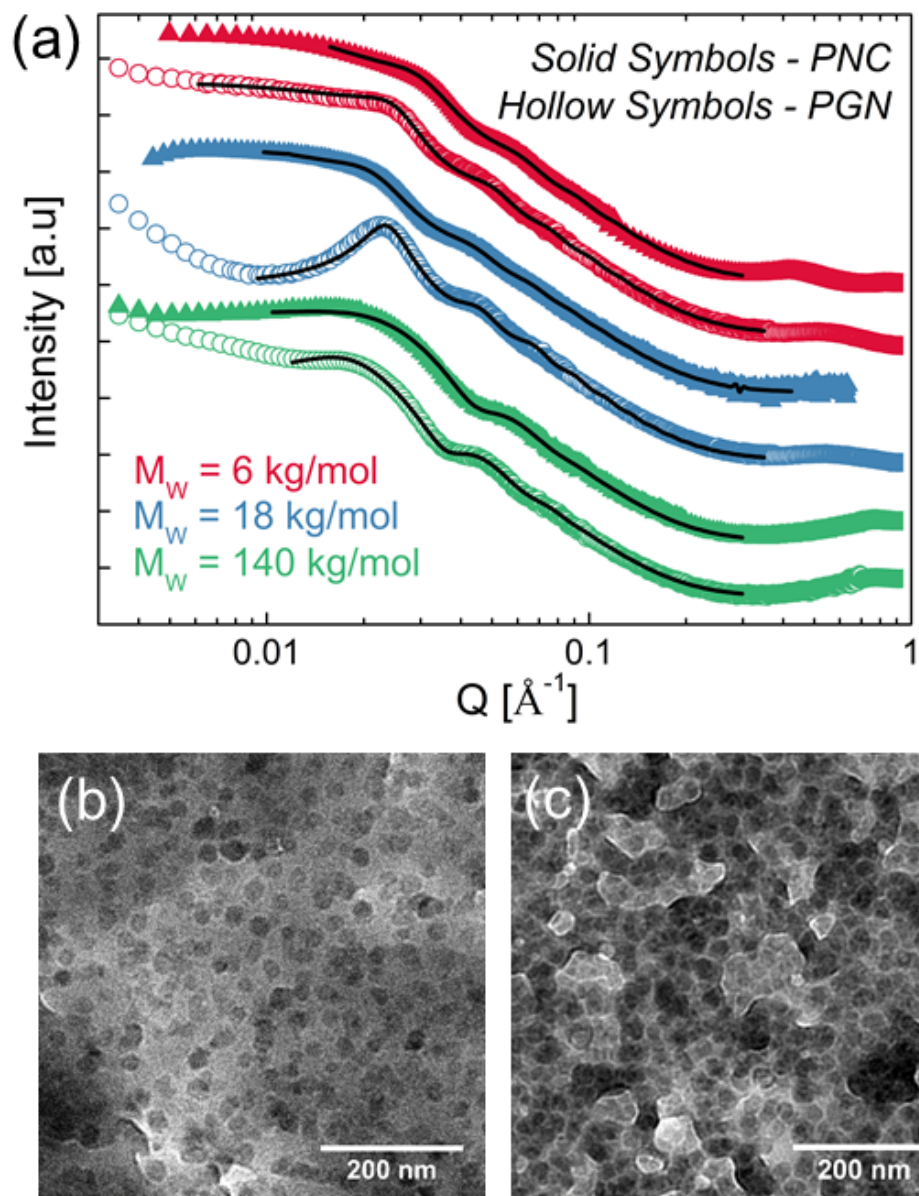


Figure 7.1: (a) Small angle X-ray scattering profiles for PGNs and PNCs at the same relative silica volume fractions and the fits obtained from a poly-disperse core-shell and hard sphere scattering models. The curves are arbitrarily shifted for clarity. Transmission electron microscopy images to illustrate the similar dispersion state of the 18 kg/mol (b) PNC and (c) PGN. Image reproduced from reference [25].

Table 7.1: Small angle X-ray scattering fitting parameters from the hard sphere and polydisperse core-shell model form factors with a hard sphere structure factor.

Sample:	Radius (nm)	PDI	SLD ($\text{\AA}^{-2}$)	SLD ($\text{\AA}^{-2}$)	SLD ($\text{\AA}^{-2}$)	Height	PDI
	Core	Core	Core	Shell	Matrix	Shell (nm)	Shell
6 kg/mol, PNC	10.9	0.3	2.11×10^{-5}	NA	1.08×10^{-5}	NA	NA
6 kg/mol, PGN	10.9	0.3	2.11×10^{-5}	NA	1.08×10^{-5}	NA	NA
18 kg/mol, PNC	11.8	0.45	2.08×10^{-5}	0.79×10^{-5}	1.10×10^{-5}	2.4 ± 0.8	0.85
18 kg/mol, PGN	10.6	0.21	2.11×10^{-5}	0.83×10^{-5}	1.09×10^{-5}	3.4 ± 0.8	0.85
140 kg/mol, PNC	10.7	0.21	2.11×10^{-5}	0.94×10^{-5}	1.11×10^{-5}	3.1 ± 0.7	0.71
140 kg/mol, PGN	10.7	0.21	2.11×10^{-5}	1.08×10^{-5}	1.11×10^{-5}	3.8 ± 0.9	0.69

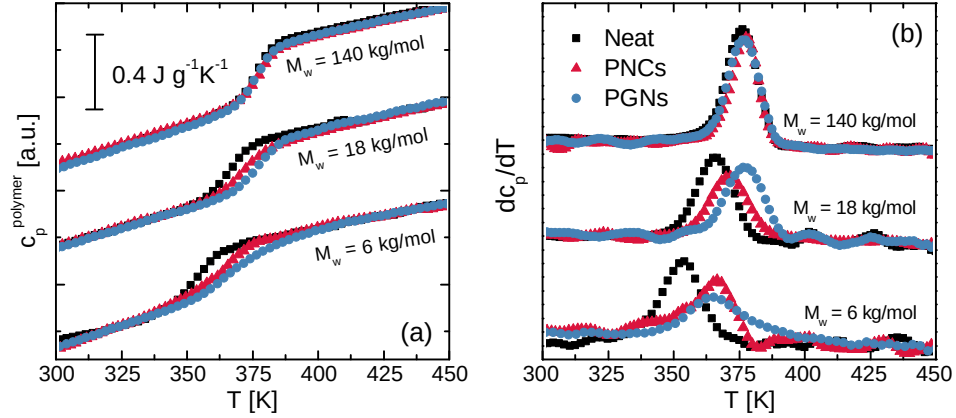


Figure 7.2: Specific heat capacity from TMDSC illustrating the glass transition of the matrix component for the PNCs and PGNs for each MW. (b) The derivative of specific heat capacity. All curves are arbitrarily vertically shifted for clarity. Image reproduced from reference [25].

The glass transition of the PGNs and PNCs were measured by temperature modulated differential scanning calorimetry (TMDSC). Figure 7.2(a) shows the specific heat data after accounting for the silica contributions as previously explained in references [56] and [81]. The thermal glass transition temperature T_g , (taken as the midpoint of the transition step) for both PNCs and PGNs (Table 7.2) are found to be dependent on MW (and relative silica concentration). Both PNC and PGN with high MW (140 kg/mol) exhibit a negligible shift in T_g , and the experimental data almost coincide with the data of the neat polymer. This result is likely due to the low silica concentration (6 vol% silica or average interparticle spacing ~ 30 nm). The intermediate MW systems show a clear change in T_g , with a larger shift for PGNs (~ 9 K) and a smaller shift for PNCs (~ 3 K). The low MW (6 kg/mol) samples show a much stronger change in the glass transition than the other MWs. Although the shift in T_g (*e.g.*, the midpoint of the transition) ~ 13 K appears to be the same for PNC and PGN, a significantly broader step is observed in the PGN system. The broadening of the glass transition of the PGN relative to the corresponding PNC can be clearly seen from the derivative analysis of the TMDSC data presented in Figure 7.2(b). The width of the glass

transition of the PGN extends to higher temperatures than for the PNC system. This increase in the breadth of the glass transition indicates two important points: (1) the segmental mobility has a large gradient and (2) a significant amount of the segmental mobility is slower than the average mobility (*i.e.*, midpoint of the transition). The results for the low MW systems, which have extremely high silica loadings and an estimated interparticle spacing of ~ 3.0 nm, are consistent with recent simulations and predictions that segmental dynamics of nanoconfined polymers exhibit a large gradient of segmental mobility.[2, 8, 9, 11, 34, 48, 49, 81]

To better understand the interfacial segmental dynamics and their effect on the overall segmental dynamics in these systems, broadband dielectric spectroscopy (BDS) is employed. The segmental relaxation process appears as a peak in the dielectric loss spectra (Fig. 7.3). The spectral shape of the segmental relaxation for poly(2-vinyl pyridine) is of specific interest at temperatures above and close to T_g . The presented dielectric loss data are normalized to the high-frequency tail of the segmental relaxation to compare the shift and overall broadening of the relaxation process at low-frequency as in Chapter 5 and 6. While the high-frequency tail of the segmental process is slightly affected in both systems, the systematic broadening of the low-frequency part is evident for both PGN and PNC systems. These results corroborate the previously presented calorimetric data (Fig. 7.2). For high MW PNC and PGNs, the width and peak position of the segmental relaxation is essentially unaffected, similar to the TMDSC data. However, at intermediate MW (Fig. 7.3(b)), the dispersion and peak position in the spectra of PNC and PGN are different at the same temperature. The corresponding intermediate MW PNC system has a peak position similar to the pure polymer and a smaller broadening than PGN. At low MW (Fig. 7.3(c)), the most significant changes in the dielectric loss spectra are observed where the entire segmental peak shifts to lower frequencies and clearly broadens for both systems. However, despite the same peak position of the segmental relaxation, there is a clear difference in the

amount of broadening (Fig. 7.3(c)): the distribution in PGN system is much wider, similar to calorimetric data in Figure 7.2(b).

An indication of the presence of the interfacial layer is the broadening of the segmental relaxation process in the dielectric spectra (Fig. 7.3) and in the calorimetric data (Fig. 7.2). Although broadening of the spectra and heterogeneous dynamics in composite materials has been reported and associated with the formation of the interface, traditional analysis is often limited to the comparison of the average values for T_g (midpoint of transition) and relaxation time (peak position) resulting in averaged information about the structure and properties of the material. However, the properties of the interfacial region itself are extremely important as they impact the macroscopic properties of PNCs that are coupled to segmental dynamics, such as ion transport or small molecule diffusion.^[104–106] To reveal the properties of the interfacial layer we utilize the interfacial model as described in chapters 5 and 6, which describes an effective medium approximation for the dielectric response ($\epsilon''_{eff}(\omega)$) of a heterogeneous system, accounting for the dielectric response of the particle ($\epsilon''_{NP}(\omega)$), interfacial layer ($\epsilon''_{IL}(\omega)$), and matrix ($\epsilon''_m(\omega)$). Using the interfacial model, two critical parameters are determined: (1) the time scale of the interfacial segmental dynamics and (2) the volume fractions of polymer populations that are bulk-like or interfacial. The latter also provides an estimate for the length scale of affected segments near the NP surface.

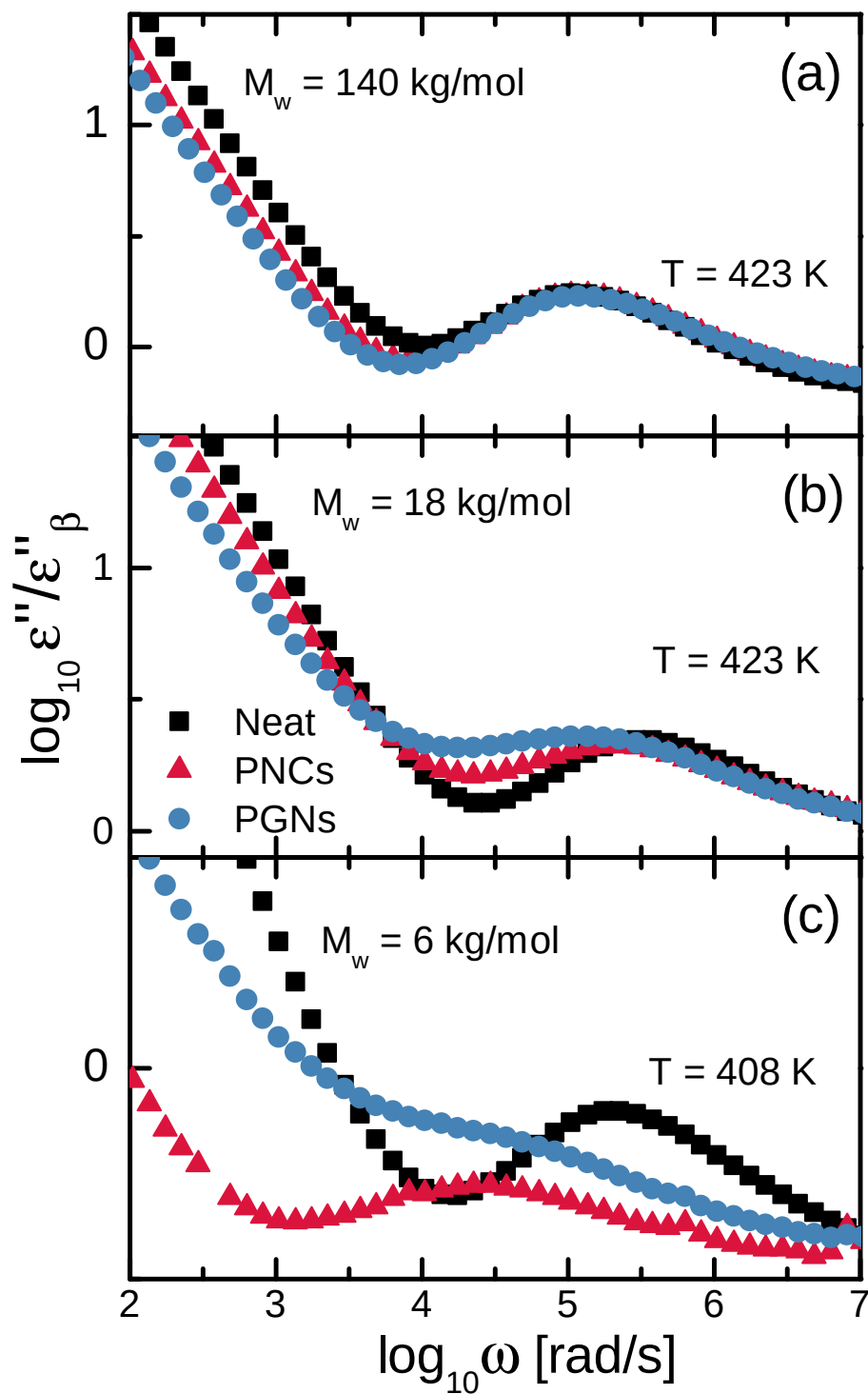


Figure 7.3: The normalized dielectric loss spectra for pure poly(2-vinyl pyridine) (black), PNCs (red), and PGNs (blue) for each molecular weight set: (a) 140 kg/mol, (b) 18 kg/mol, and (c) 6 kg/mol. Image reproduced from reference [25].

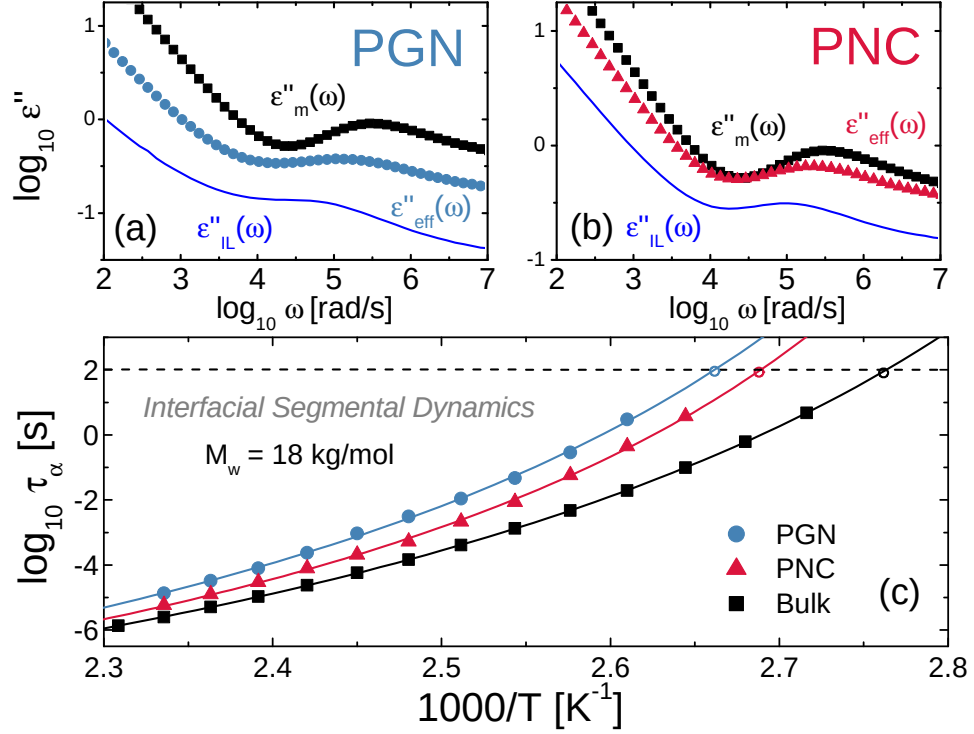


Figure 7.4: The deconvolution of effective dielectric loss spectra ($\epsilon''_{eff}(\omega)$) into individual components: the matrix response ($\epsilon''_m(\omega)$, black squares) and the interfacial layer response ($\epsilon''_{IL}(\omega)$, blue line) for the intermediate molecular weight (a) PGN and (b) PNC from the interfacial model analysis ($T = 423.15$ K). The presented $\epsilon''_{IL}(\omega)$ component is normalized by the corresponding volume fraction of interfacial polymer. (c) The temperature dependence of the interfacial segmental relaxation times for PGNs (blue), PNCs (red), and bulk-like dynamics (black) with corresponding Vogel-Fulcher-Tammann fits. Image reproduced from reference [25].

Here, we analyze the data for these PGN and PNC at the intermediate MW since they demonstrate the most pronounced change in the dispersion of the segmental relaxation. The interfacial model analysis (Fig. 7.4) separates the contributions of the interfacial and bulk-like segmental dynamics, and provides an estimate for the respective volume fractions and characteristic relaxation times. For the intermediate MW systems, the characteristic relaxation times of the interfacial layer are determined by fitting the obtained $\epsilon''_{IL}(\omega)$ with a single Havriliak-Negami function. At high temperatures, the segmental relaxation times of the interfacial and bulk-like dynamics converge (Fig. 7.4c), indicating more homogeneous

dynamics. However, even at high temperatures the segmental dynamics in the PGN remain slower than in the neat polymer. As the temperature approaches T_g ($\tau_\alpha = 100$ s, as indicated by the horizontal dotted line), the slowing down of the interfacial dynamics relative to the neat polymer increases strongly, especially for the PGN system. The dynamic glass transition temperatures, T_g , can be determined by fitting the relaxation times to the Vogel-Fulcher-Tammann (VFT) equation and extrapolating to the temperature at which $\tau_\alpha = 100$ s (Table 7.2). A different behavior is observed for PNC and PGN for the lowest MW samples (Fig. 7.5). In that case, the characteristic relaxation times are extracted by fitting the entire $\epsilon''_{eff}(\omega)$ by a single Havriliak-Negami function, because essentially the entire sample is an interfacial region at this high loading. Both PNC and PGN exhibit a similar timescale of segmental dynamics at temperatures close to T_g (consistent with calorimetric data), while the PGN shows stronger deviations from the behavior of neat polymer than PNC at higher temperatures. The observed suppression of interfacial dynamics is in line with several molecular dynamic simulations[2, 11, 34, 48] (which spatially map the distribution of relaxation times) and qualitatively agrees with the expectation that covalently bonded chains experience a larger suppression of segmental dynamics, depending also on the grafting density[2] and molecular weight.[107]

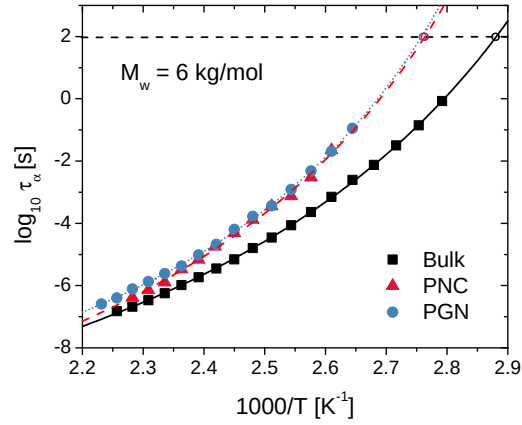


Figure 7.5: The temperature dependence of the segmental relaxation times for low MW (6 kg/mol) PGNs (blue), PNCs (red), and bulk-like dynamics (black) with the corresponding Vogel-Fulcher-Tammann fits (lines). Image reproduced from reference [25]

To rationalize these results, one must first understand how much of the polymer matrix is actually influenced by the nanoparticles (*i.e.*, the volume fraction of interfacial polymer). Figure 7.6(a) presents the normalized volume fraction of interfacial polymer (obtained from the interfacial model analysis) with respect to the total amount of polymer in our system for both PGNs and PNCs. At high MW, there is a very small amount of nanoparticles and as a result very little interfacial polymer. Therefore, it is difficult to distinguish the difference between interfacial dynamics of PGNs and PNCs for the high MW systems. However, as shown in Figure 7.3(b), the intermediate MW systems show a rather large difference in the dispersion of the segmental relaxation process and also a clear difference in the time scale of interfacial dynamics between PGNs and PNCs. The difference in relaxation dynamics can be related to the volume fraction of interfacial polymer in the PGN system which is 0.75 while and almost half of that for the PNC system (~ 0.4). Interestingly, the lowest molecular weight systems, which are almost entirely silica nanoparticles (52vol% silica), reveal an entirely interfacial material, regardless of physical adsorption or covalent bonding.

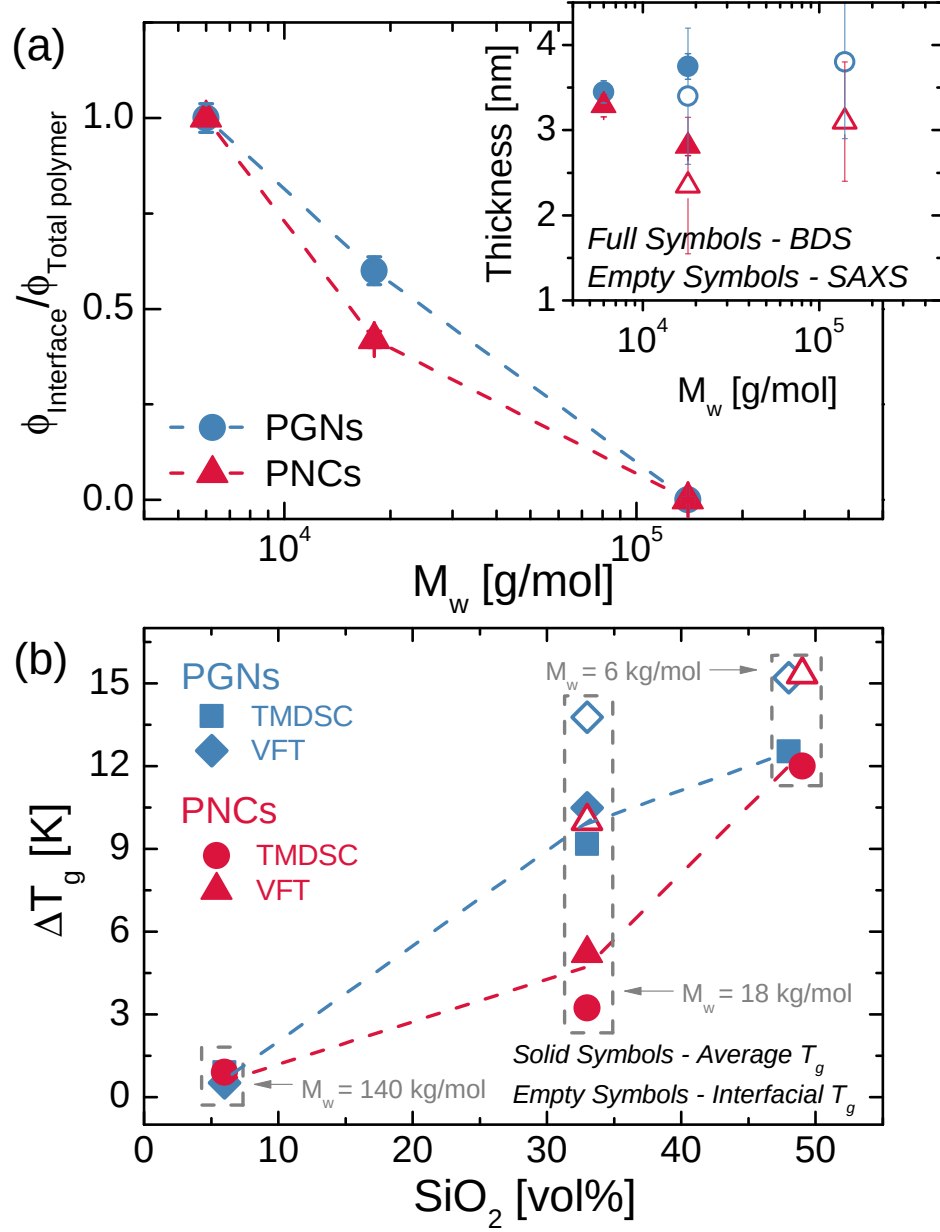


Figure 7.6: (a) The relative volume fraction of interfacial polymer with respect to the total polymer for PNCs (maroon) and PGNs (blue) as a function of molecular weight (MW). Inset: A comparison of the static and dynamic thickness of the interfacial region estimated using BDS (full symbols) and SAXS (empty symbols) as a function of MW. (b) The change in the average glass transition temperature, T_g , from calorimetry as well as the average and interfacial T_g from BDS by evaluating the Vogel-Fulcher-Tammann (VFT) function for each MW as a function of silica concentration. The boxes indicate data at the same respective MW's and the dashed lines are guides for the eye. Image reproduced from reference [25].

Additionally, the length scale of the interfacial region can be estimated from the volume fraction of the interfacial polymer by assuming a core-shell morphology, as described in [81]. The dynamic length scale of the interfacial layer estimated from the BDS measurements is also compared to the static shell thickness estimated from SAXS (inset Fig. 7.6(a)). For PGNs, the interfacial layer thickness seems to slightly decrease with decreasing MW, while no systematic changes can be found in PNCs as a function of MW. It seems that for all systems exhibiting a distinct interfacial layer, the static interfacial layer thickness is larger for PGNs than PNCs, although the difference is within the experimental error-bars (inset Fig. 7.6(a)). Earlier studies on PNCs with fixed NP loading [24] revealed a decrease in the interfacial layer thickness and significant decrease of the averaged T_g shift with increasing MW. However, it is difficult to identify a certain trend in the current data set since the static length at low MW or the dynamic length at high MW cannot be detected. The analysis also reveals that the dynamic length scale of the interfacial layer increases slightly upon cooling (Fig. 7.7), consistent with earlier observations in model glycerol/ SiO_2 nanocomposites.[108] The observed increase in the dynamic length scale of the interfacial layer upon approaching T_g might be related to an increase in cooperativity of the segmental dynamics.[11, 34]

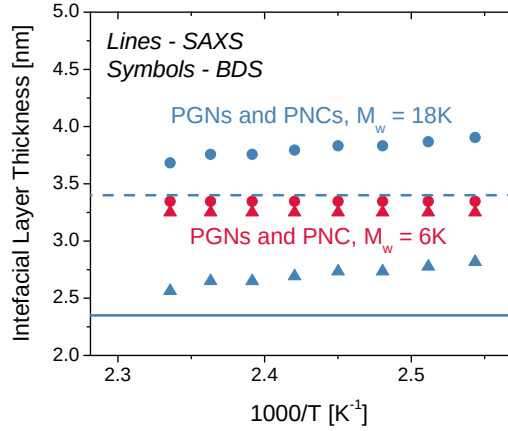


Figure 7.7: The dynamic length scale of the interfacial layer in both PGN (circles) and PNC (triangles) systems for the low (red) and intermediate MW systems (blue). For the SAXS data (at $T = 300\text{K}$), the dashed line represents the PGN system and the solid line represents the PNC system. Image reproduced from reference [25].

From Figure 7.6(b), it becomes clear that the low MW PNCs and PGNs experience the same interfacial dynamics (similar T_g of interface, same volume fraction of polymer involved in interfacial dynamics) resulting in the same average T_g from both techniques at the same silica concentration and interparticle spacing. However, the intermediate MW PNCs and PGNs show a clear difference in the average T_g from both techniques as well as a large difference in the interfacial T_g which can be accounted by the large change in interfacial volume fraction. For high molecular weight it is difficult to conclude due to sensitivity issue associated with the small content of silica nanoparticles. It is suspected that these observations are related to the differences in conformations that a chain can experience at the NP interface whether covalently attached at one end in PGN or physically adsorbed in PNCs which changes as MW increases. These results are in line with recent studies of nanocomposites of poly(vinyl acetate)/silica and poly(2-vinyl pyridine)/silica in which the MW of the polymer matrix and attractive interaction between polymer and nanoparticles were shown to strongly impact the adsorption of the polymer

chain at the nanoparticle which in turn influenced the overall segmental dynamics, or rather the glass transition of the polymer nanocomposite.[24]

Figure 7.6(b) presents the relative change in T_g (with respect to neat polymers) estimated using three techniques: (1) the average T_g from TMDSC (midpoint of transition), (2) the average T_g from BDS (using a single Havriliak-Negami relaxation process to describe the $\epsilon''_{eff}(\omega)$ spectra and VFT extrapolation), and (3) the interfacial T_g from the interfacial model analysis (using a single Havriliak-Negami relaxation process to describe the $\epsilon''_{IL}(\omega)$ spectra and VFT extrapolation). From Figure 7.6(b), it becomes clear that the low MW PNCs and PGNs experience similar interfacial dynamics resulting in the same average T_g from TMDSC and BDS. It is difficult to draw any conclusions from the high molecular weight systems due to the relatively low fraction of the interfacial region at such a small content of silica NPs. However, the intermediate MW PNC and PGN show a clear difference in the average T_g from both techniques, as well as a large difference in the interfacial T_g . Following the results from earlier chapters, these observations are likely due to the differences in chain conformations within the interfacial layer.

In general, it is difficult to directly assess the conformations of polymers in PNCs with physically adsorbed chains. However, the conformations of covalently attached chains are very well studied experimentally[97] and can be described theoretically.[109–111] Polymers attached to the surface can experience different conformations ranging from mushroom-like structure at low grafting density where neighboring sites do not overlap and to highly stretched conformation at high grafting density. In general cases, chain stretching can be described by the dimensionless parameter $\sigma_{||} = h/2R_g$ where h is the brush height for a given interparticle spacing (IPS), where the IPS corresponds to each respective silica loadings, and R_g is the unperturbed radius of gyration in the polymer melt. By this definition, the interfacial chain conformations are considered Gaussian when $\sigma_{||}$ is much less than one and stretched when $\sigma_{||}$ is one or greater. The specific values of $\sigma_{||}$ for the experimental systems studied in this work are listed in Table

Table 7.2: The summary of dynamic information from TMDSC and BDS combined with selected parameters from the interfacial model analysis.

Sample:	Silica (vol%)	Avg. T_g [K] (TMDSC)	Avg. T_g [K] (BDS, VFT)	Inter. T_g [K] (BDS, VFT)	Inter. Polymer (vol%)	Dynamic Layer [nm] (BDS)	Static Shell [nm] (SAXS)
6 kg/mol, Neat	0	353.1	347.1	NA	NA	NA	NA
6 kg/mol, PNC	49	365.2	362.4	362.4	~ 100	$3.28 \pm 0.10^*$	NA
6 kg/mol, PGN	48	365.6	362.3	362.3	~ 100	$3.45 \pm 0.10^*$	NA
18 kg/mol, Neat	0	367.9	361.9	NA	NA	NA	NA
18 kg/mol, PNC	33	371.1	367.0	371.9	28	2.85 ± 0.11	2.4 ± 0.8
18 kg/mol, PGN	33	371.1	367.0	371.9	40	3.75 ± 0.11	3.4 ± 0.8
140 kg/mol, Neat	0	375.6	370.4	NA	NA	NA	NA
140 kg/mol, PGN	6	376.5	370.9	NA	NA	NA	3.1 ± 0.7
140 kg/mol, PGN	6	376.5	370.7	NA	NA	NA	3.8 ± 0.9

7.3, which are based on the results obtained from our self-consistent field theory (SCFT) calculations in two dimensional polar coordinate system. The SCFT calculations were done for a compressible system. In addition, the attractive interactions between the polymer segments and the nanoparticle surface were included for both the PGN and PNC systems. The polymer-NP interactions were modeled *via* a step function which only acts on the exterior of the NPs. The range of the interaction potential was kept fixed at 1.7 nm, representing the rough native oxide layer present on the silica nanoparticles.[112] The strength of the interaction potential was chosen to match the line averaged density profile for PNCs (between the nanoparticles) obtained from simulations with the experimentally obtained spatially averaged density profile ($\sim 1.0 \text{ gm/cm}^3$). As shown in Table 7.3, $h/2R_g$ systematically increases from ~ 1 at low MW to nearly 1.5 at high MW. This suggests that the polymer chains exhibit highly stretched conformations at the interface and that the degree of stretching increases with MW for the PGN systems.

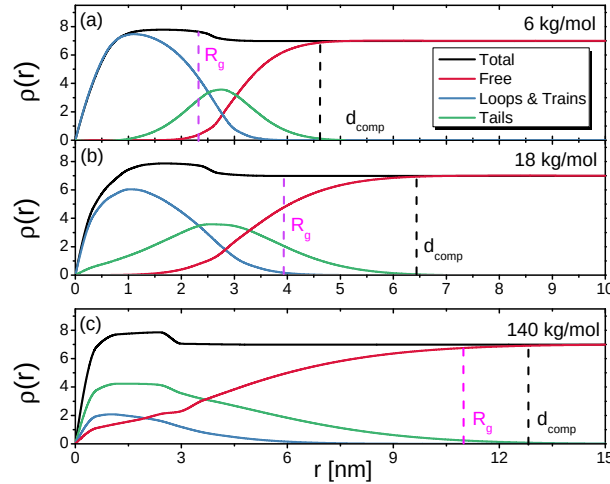


Figure 7.8: The self-consistent field theory (SCFT) calculations for all PNC systems. Here, the adsorbed chain conformations near the nanoparticles surface are illustrated by comparing the distribution of segments and the length scale that they persist into the free polymer (dashed vertical black lines, d_{comp}) relative to the matrix unperturbed radius of gyration (dashed vertical pink lines, R_g). Image reproduced from reference [25].

To understand chain stretching for the case of physical adsorption, we use SCFT to calculate the distribution of chain conformations for our PNC systems, where packing factors are excluded. As shown in Figure 7.8, the distribution of chain conformations were calculated for our exact systems and provide quantitative information concerning the spatial distribution of polymer segments near the spherical NP interfaces. To quantify the degree of chain stretching in PNCs; we analyzed the distribution of tails, loops, and trains and the length scale that they persisted into the free polymer population far away from the surface of the nanoparticles, d_{comp} . At low MW, we find that the maximum populations of tails and loops are spatially distributed further away from the NP surface than the length scale of the unperturbed R_g (Fig. 7.8(a)). For intermediate MW, fewer tail conformations are observed with a more significant population of loops and trains, especially near the NP interface (Fig. 7.8(b)). The maximum population of tail conformations are now found at distances approaching the R_g and only a small fraction of the tails propagate beyond R_g . Additionally, the interfacial region up to 2.5 nm largely consists only of segments that are in direct contact with the NP (Fig. 7.8(b)). For high MW, the majority of the chain conformations actually consist of tails that persist up to 12 nm (approximately R_g) away from the NP surface where they mix with the free polymer chains (Fig. 7.8(c)). The spatial distributions of the tails, loops and trains depend on interplay of adsorption energy and chain conformational entropy. For shorter chains, the conformational entropy is weaker compared to the interaction energy between the polymer chains and the nanoparticle surfaces. This, in turn, leads to more loops and trains in comparison with the number of tails. In contrast, the conformational entropy of the polymer chains dominates over the polymer-NP interactions for the longest chains studied in this chapter, which results in a larger number of tail conformations than loop or train conformations.

Table 7.3: The estimated stretching parameters from SCFT calculations for both polymer nanocomposites and polymer grafted nanoparticles.

MW:	$2R_g$ (nm)	h (nm)	d_{comp} (nm)	$h/2R_g$	$d_{comp}/2R_g$
6 kg/mol	4.64	4.7	4.6	1.01	0.99
18 kg/mol	7.9	9.0	6.4	1.13	0.81
140 kg/mol	22.2	32.5	12.3	1.46	0.55

To quantify the degree of chain stretching for all PNCs, we determine the ratio of the distance that the adsorbed polymer segments persist into the free polymer segments, d_{comp} , and the unperturbed R_g , a parameter that is similar to $h/2R_g$, and is presented in Table 7.3. The stretching factor, $d_{comp}/2R_g$, of the PNCs decreases with increasing MW, behavior that is opposite to that of the PGN systems. Interestingly, the stretching factor for both systems converge at low MW ($h/2R_g \approx d_{comp}/2R_g \approx 1.0$) suggesting that same degree of stretching exists in these two systems. These findings explain why the low MW PNCs and PGNs systems exhibit the largest changes in segmental dynamics. For the intermediate MW, the stretching factors also agree with the corresponding differences in the interfacial dynamics between PNC and PGN: the more strongly stretched PGN system ($h/2R_g \geq 1.0$) exhibits a larger suppression of interfacial dynamics while the less stretched PNC system ($d_{comp}/2R_g < 1.0$) exhibits a less pronounced effect. The latter statement is corroborated by direct mass density measurements by pycnometry (See Fig 7.9(a)).

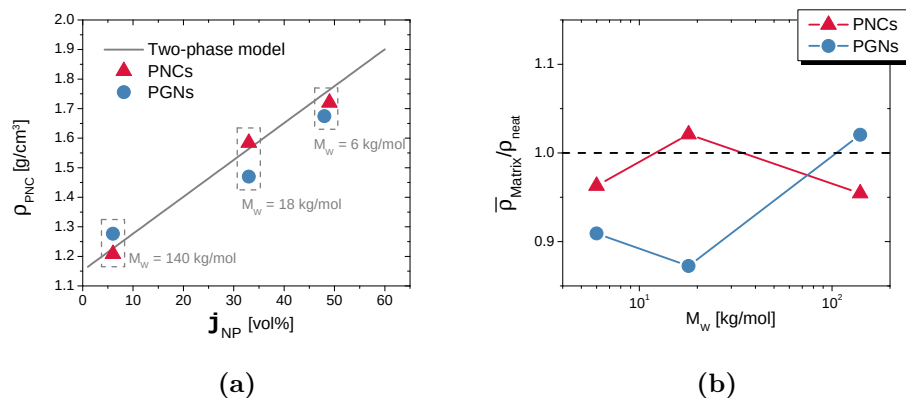


Figure 7.9: (a) The overall PNC mass density from pycnometry measurements. The grey line is the predicted density values from an effective two-phase medium (TPM). (b) The normalized average mass density of the polymer matrix after using eq. 6.2 to remove the contribution of the silica nanoparticles.

As shown previously, the segmental dynamics of the lowest MW PNCs and PGNs reflect an entirely interfacial material with the corresponding changes in the calorimetric data. These results are confirmed by SAXS measurements which is well-described by hard sphere scattering model. Additionally, the mass density was measured by pycnometry and the average matrix mass density was determined by using eq. 6.2. The $\bar{\rho}_m$ for the low MW PNCs and PGNs was found to be 1.054 g/cm^3 and 0.995 g/cm^3 , respectively and are close to that of the neat (1.095 g/cm^3). The similarity in density for the low MW PNCs and PGNs also suggests that the chain conformations are similar, where the physically adsorbed chains exhibit a similar stretched conformation as the covalently grafted chains. This hypothesis agrees with the relative change in the dielectric and calorimetric data for low MW where the average ΔT_g as well as the time scale of segmental dynamics for low MW PNCs and PGNs represent the largest changes within the current Dissertation. For the intermediate MW, the stretching factors also agree with the corresponding differences in the interfacial dynamics for both PNCs and PGNs—where the more stretched system ($d_{\text{comp}}/2R_g$ or $h/2R_g > 1.0$) show a larger suppression in interfacial dynamics. The measurements for intermediate

MW demonstrate a substantial deviation between the density of the PNCs and PGNs where the overall density was found to be 1.176 g/cm^3 and 1.005 g/cm^3 , respectively, which is a $\sim 15\%$ difference.

The densification in the composite materials likely reflects the conformational rearrangement of the chains at the interface which could be possible when the rigid chains of P2VP become less stretched and can pack much more efficiently. However, despite the densification of PNC matrix, the segmental dynamics are weakly affected in the PNC system which suggests that the segmental dynamics are more influenced by the chain stretching than density. These results would be in agreement with previous results which demonstrate the segmental dynamics of P2VP are primarily controlled by thermal effects rather than density effects.[88, 113] Interestingly, the overall density for the high MW PNC is lower than the corresponding high MW PGN which corroborates the results of Chapter 6 where the chain packing in high MW PNCs was proposed to be far worse than in low MW PNCs. However, a detailed and systematic study of grafting density and MW is needed to fully understand these effects.

Table 7.4: The average mass density of the polymer matrix when accounting for the volume fraction of silica nanoparticles from eq 6.2.

MW:	ρ_m , Neat (g/cm^3)	$\overline{\rho}_m$, PNC (g/cm^3)	$\overline{\rho}_m$, PGN (g/cm^3)
6 kg/mol	1.0951 ± 0.0116	1.05457 ± 0.0033	0.99567 ± 0.0019
18 kg/mol	1.1521 ± 0.0079	1.17636 ± 0.0047	1.00507 ± 0.0058
140 kg/mol	1.1805 ± 0.0038	1.1267 ± 0.0039	1.2046 ± 0.0039

There are two main questions to address: (1) the magnitude of the dynamic suppression and (2) how far the suppression propagates from the surface of the NPs. The combined evidence from these results indicates that on the time scale of segmental dynamics, the strength of the polymer-NP interaction, *e.g.*, physical adsorption or covalent bonding, is not the primary mechanism responsible for

the suppression of segmental dynamics at the interface. Instead, the primary mechanism is suggested to be directly correlated with the degree of stretching (anisotropy) of the polymer chains near the polymer-NP interface (Fig. 7.8). This means that the orientation of specific chain conformations at the interface would ultimately control the resulting properties of the interfacial layer. The dynamics of chain conformations with multiple adsorbed polymer segments ("train" conformations, parallel to the NP) would intuitively be influenced the most by the interfacial interactions. However, the number of segments forming these conformations is finite and furthermore limits how far the dynamic suppression persists from the surface of the NP. Thus, the orientational anisotropy of the chain conformations perpendicular to the interface, known as "tail" conformations are suspected to propagate the dynamic suppression of segmental mobility to longer length scales. From a fundamental perspective, these results qualitatively agree with predictions by Oyerokun and Schweizer for the dynamics of polymer systems with anisotropic conformations (thin films, planar grafted brushes) which predicted that segmental stretching increases the correlation between segmental motions (intra- chain) and increases the local T_g at the interface.[101] This phenomenon is likely due to the difference in the chain crowding at the interface where chain crowding imposes stronger steric hindrances at the NP surfaces and segmental motions become more correlated, an effect that should quickly dissipate with increasing distance from the NP surface (unlike planar systems). Therefore, the curvature of the NP should play a significant role in this effect, and one should expect larger changes for larger NPs or planar surfaces. This was independently reported by Gong *et al.* where the interfacial thickness was found to increase with increasing NP size—consistent with the concept of chain crowding and chain stretching.[90]

This concept is corroborated by the results from SCFT calculations which revealed that the interfacial chain conformations in the PNC systems consist of various chain conformations and that the volume fraction of each depends on the

MW. As shown in Figure 7.8(a), the low MW PNC is predominately composed of loops and train conformations with the maximum population located ≈ 1.5 nm from the NP surface and eventually extending to 3.5 nm. However, the tail conformations persist up to 5 nm, similar to the brush height of the PGNs. Thus, the tail conformations in both PGNs and PNCs at low MW persist to a similar length scale from the NP surface (and hence a similar degree of stretching) with the only difference being the number of chains, where the interfacial layer in PGNs predominately consists of tails. The difference in the uniformity of chain stretching at the interface is suspected to cause the larger gradient in segmental mobility that was observed from TMDSC (Fig. 7.2) for the low MW PGN system, despite the similarities in the average T_g . However, more systematic studies focusing on the effect of grafting density and interfacial chain conformations would be needed to verify this idea.

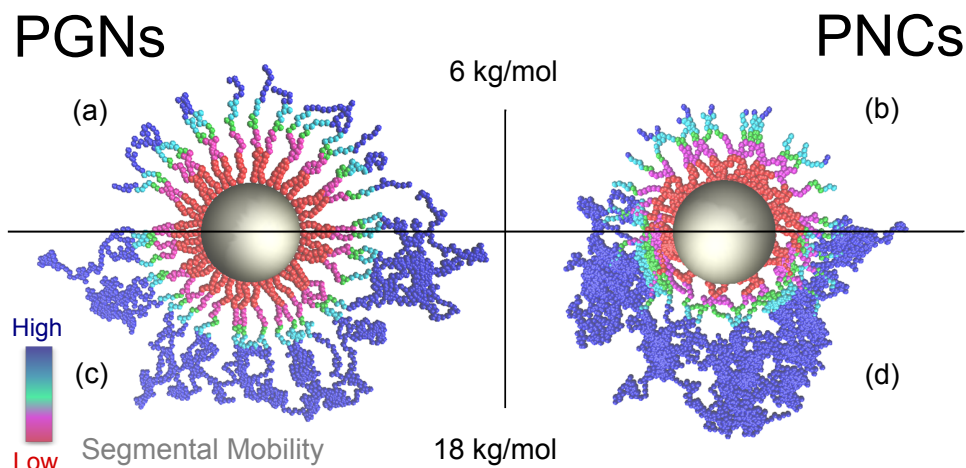


Figure 7.10: A cartoon based on the SCFT results that illustrates how chain stretching can cause the suppression of segmental mobility at the interface in polymer grafted nanoparticles, PGNs, (a, c) and polymer nanocomposites, PNCs, (b, d) at different molecular weights.

It should be noted that the results presented in this chapter are specific to polymer-NP systems with strong attractive interactions. The behavior might be different if the time scale of chain adsorption (to the nanoparticles) will be

comparable to the segmental relaxation time. In general, one would expect that PNC systems and PGNs may exhibit significant differences in the dynamics depending on NP loading, molecular weight, or grafting density, especially in the case of unfavorable (repulsive) polymer-NP interactions. That does not necessarily imply that the underlying mechanism would be different, but rather that the magnitude of the effect will be different—and that covalent bonding may provide a route to modify the segmental dynamics of polymer-NP systems with naturally weak polymer-NP interactions.

7.4 Summary

The interfacial structure and dynamics of P2VP/silica nanocomposites and matrix-free P2VP-grafted-from-silica nanoparticles are studied under identical conditions (MW and NP loading). The interfacial model is used to unravel the time scale of the interfacial segmental dynamics from the dielectric relaxation spectra. The high MW systems do not show significant variations due to relatively low volume fraction of nanoparticles and interfacial region. However, a strong gradient of segmental mobility in the interfacial region was revealed by TMDSC and BDS techniques for both low and intermediate MW PNCs and PGNs.

At intermediate MW, detailed analysis reveals a significant influence of the chain attachment mechanism, *e.g.*, physical adsorption of the chains for PNC versus covalent grafting of the chains for PGNs, on segmental dynamics and T_g of the material. Interestingly, for low MW PNCs, the dynamic properties were found to be similar to low MW PGNs, indicating that these systems experience a similar effect at the interface—independent of the method of their preparation. In lieu of these results, it is proposed that the chain stretching at the interface, rather than the polymer-nanoparticle interaction strength, plays a critical role in suppression of segmental dynamics, which ultimately determines the magnitude of the change in the average glass transition temperature in these heterogeneous materials. In other

words, the intermediate MW PGNs exhibit a higher degree of chain stretching at the interface, and therefore are accompanied by a more dramatic change in T_g when compared to their PNC counterparts whereas the low MW systems share similar degree of chain stretching and also exhibit a similar change in dynamics.

Overall, these results demonstrate that polymer chain conformations in the interfacial region can strongly influence the interfacial segmental dynamics and provide physical insight concerning dynamic interfaces in polymer nanocomposites and other nanostructured polymer systems, thereby suggesting a way to rationally tailor polymer dynamics on the nanoscale.

Chapter 8

Concluding Remarks

A brief description of the work presented in the dissertation is reviewed and an outlook on the future of polymer nanocomposites is discussed.

8.1 Conclusions

For PNCs with attractive polymer-NP interactions, it has long been thought that polymer adsorption occurs at the surface of the NPs and the dynamics are strongly suppressed due to steric hindrance and confinement effects. The immobilization of the adsorbed polymer was previously described as a "dead" layer (*i.e.*, glassy with respect to the remaining polymer), which was responsible for the major changes in the T_g of PNCs with high concentration of NPs.

In Chapter 4, the overall effect of attractive NPs on the T_g of highly filled poly(2-vinylpyridine)/silica nanocomposites was found to be surprisingly minor even at extremely high NP concentrations and suggested that the interfacial dynamics are only weakly affected.

In Chapter 5, the interfacial segmental dynamics of poly(2-vinylpyridine)/silica nanocomposites were carefully and systematically investigated over a wide range of NP concentrations. Contrary to previous expectations, the interfacial segmental dynamics are found not to be "dead" but are instead only slowed (~ 100 times)

with respect to the bulk-like segmental dynamics. The region of affected dynamics, or the interfacial layer, determined from dielectric spectroscopy and calorimetry (3–4 nm) could also be observed in small angle X-ray scattering spectra (4–5 nm). Despite the presence of interfacial polymer, which is considerably slower than the bulk, there is no significant effect on the overall glass transition temperature of the remaining polymer matrix.

In Chapter 6, following expectations that the length scale of polymer adsorption should scale with the molecular weight (MW) of the polymer matrix, three MWs were prepared with a variety of silica concentrations and under similar conditions. Using the analysis techniques described in Chapter 5, an unexpected MW dependence of the interfacial properties was found: the length scale of the interfacial layer with suppressed segmental mobility decreases with increasing MW, contrary to theoretical predictions. Further analysis revealed a reduction in mass density of the interfacial layer with increasing MW, which suggested that the chain packing at the interface is largely frustrated and while some segments are affected, this frustration leads to a competition between effects: (1) slowing down due to adsorption and (2) speeding up due the reduction in density. These surprising results indicated that the interfacial regions in high MW PNCs are trapped in a deep metastable state far away from equilibrium that could be exploited for specific industrial applications.

Lastly, the effect of interaction strength at the interface was explored. In Chapter 7, the interfacial region in PNCs (physical adsorption) was directly compared to the system of matrix-free polymer grafted nanoparticles (covalently bonded) for three different MWs. The interfacial dynamics are found to be strongly suppressed in both systems. However, the magnitude of this effect was found to be different for each system and is dependent on the MW of the polymer matrix. Based on self-consistent field theory calculations, it is proposed that these changes are not mainly due to the strength of the interaction but rather to the uniformly stretched chain conformations near the interface. This suggests

that chain stretching, *i.e.*, the anisotropy of the segmental conformations, in the interfacial region primarily influences the segmental dynamics while the interaction strength only plays a secondary role. Furthermore, these results imply that the interfacial dynamics can be effectively tuned by the degree of stretching—a parameter accessible from the MW or grafting density.

8.2 Future Outlook

The potential applications for the results presented in this Dissertation are important for several reasons. These results indicate that polymer adsorption on the nanoscale is not as simple as merely mixing two components and that proper reinforcement will not be maximized unless proper polymer adsorption occurs at the interfaces. Also, the results indicate that high MW systems have a large degree of percolating free volume near the interfacial regions which may be useful for polymer electrolyte or gas separation applications.

There is still much work to be done in this field regarding the effect of interfacial dynamics in other nanostructured polymeric systems. This dissertation only investigated the case of spherical nanoparticles in an ideal system with $R_g \approx R_{Silica}$. The logical next steps would be to investigate the dynamics when the length scale of the nanofiller is smaller than the polymer coil size ($R_g > R_{Silica}$), change the nanofiller geometry to planar to increase the accessible surface area, the polymer-NP interactions, grafting density, and the polymer backbone rigidity (semi-flexible to flexible).

Bibliography

- [1] David S Simmons. An Emerging Unified View of Dynamic Interphases in Polymers. *Macromolecular Chemistry and Physics*, 217:137–148, 2015. [xii](#), [2](#), [3](#)
- [2] Azadeh Ghanbari, Mohammad Rahimi, and Jaber Dehghany. Influence of Surface Grafted Polymers on the Polymer Dynamics in a Silica-Polystyrene Nanocomposite: A Coarse-Grained Molecular Dynamics Investigation Influence of Surface Grafted Polymers on the Polymer Dynamics in a Silica-Polystyrene Nanocomposite. *Journal of Physical Chemistry C*, 2013. [xii](#), [3](#), [24](#), [137](#), [141](#)
- [3] J. Jancar, J.F. Douglas, F.W. Starr, S.K. Kumar, P. Cassagnau, a.J. Lesser, S.S. Sternstein, and M.J. Buehler. Current issues in research on structure–property relationships in polymer nanocomposites. *Polymer*, 51(15):3321–3343, 2010. [xii](#), [8](#), [132](#)
- [4] C.M. Roland. *Viscoelastic Behavior of Rubbery Materials*. Oxford, 2011. [xii](#), [13](#)
- [5] Kumar Kunal, CG Robertson, and Sebastian Pawlus. Role of chemical structure in fragility of polymers: a qualitative picture. *Macromolecules*, pages 7232–7238, 2008. [xiii](#), [14](#)
- [6] Y. Ding, V. N. Novikov, and A. P. Sokolov. 75.Influence of Molecular Weight on Fast Dynamics and Fragility of Polymers.pdf. pages 9264–9272, 2004. [xiii](#), [15](#)

- [7] Joseph L. Keddie, Richard a. L. Jones, and Rachel a. Cory. Interface and surface effects on the glass-transition temperature in thin polymer films. *Faraday Discussions*, 98:219, 1994. [xiii](#), [18](#), [60](#)
- [8] J A Forrest and K. Dalnoki-Veress. When Does a Glass Transition Temperature Not Signify a Glass. *ACS Macro Letters*, 3:310–314, 2014. [xiii](#), [19](#), [20](#), [137](#)
- [9] Paul Z Hanakata, Jack F Douglas, and Francis W Starr. Interfacial mobility scale determines the scale of collective motion and relaxation rate in polymer films. *Nature communications*, 5(May):4163, January 2014. [xiii](#), [18](#), [20](#), [21](#), [137](#)
- [10] Michael R. Bockstaller, Rafal a. Mickiewicz, and Edwin L. Thomas. Block copolymer nanocomposites: Perspectives for tailored functional materials. *Advanced Materials*, 17(11):1331–1349, 2005. [xiv](#), [22](#)
- [11] Francis W. Starr and Jack F. Douglas. Modifying Fragility and Collective Motion in Polymer Melts with Nanoparticles. *Physical Review Letters*, 106(11):115702, March 2011. [xiv](#), [3](#), [24](#), [60](#), [68](#), [71](#), [76](#), [112](#), [118](#), [137](#), [141](#), [144](#)
- [12] Amitabh Bansal, Hoichang Yang, Chunzhao Li, Kilwon Cho, Brian C Benicewicz, Sanat K Kumar, and Linda S Schadler. Quantitative equivalence between polymer nanocomposites and thin polymer films. *Nature materials*, 4(9):693–8, September 2005. [xiv](#), [26](#), [60](#), [76](#)
- [13] Perla Rittigstein, Rodney D Priestley, Linda J Broadbelt, and John M Torkelson. Model polymer nanocomposites provide an understanding of confinement effects in real nanocomposites. *Nature materials*, 6:278–282, 2007. [xiv](#), [xviii](#), [3](#), [28](#), [29](#), [60](#), [68](#), [71](#), [72](#), [73](#), [74](#), [76](#), [100](#), [103](#)
- [14] Small angle scattering. [xiv](#), [35](#)

- [15] Robert L. Danley. New Heat Flux DSC Measurement Technique. *Thermochimica Acta*, 395:201–208, 2003. [xv](#), [38](#)
- [16] Friederich Kremer and Andreas Schönhals. *Broadband Dielectric Spectroscopy*. Springer, 2002. [xv](#), [xvi](#), [xix](#), [44](#), [52](#), [55](#), [94](#)
- [17] KC Kao. Electric polarization and relaxation. *Dielectric phenomena in solids*. Elsevier Academic Press, San Diego, 2004. [xv](#), [49](#)
- [18] Ranko Richert, Alexander Agapov, and Alexei P Sokolov. Appearance of a Debye process at the conductivity relaxation frequency of a viscous liquid. *The Journal of chemical physics*, 134(10):104508, March 2011. [xvi](#), [57](#)
- [19] Adam P. Holt, Joshua R. Sangoro, Yangyang Wang, Alexander L. Agapov, and Alexei P. Sokolov. Chain and Segmental Dynamics of Poly(2-vinylpyridine) Nanocomposites. *Macromolecules*, 46(10):4168–4173, May 2013. [xvi](#), [xvii](#), [xviii](#), [62](#), [64](#), [65](#), [67](#), [68](#), [70](#), [72](#), [76](#), [100](#), [103](#)
- [20] Joseph Moll and Sanat K. Kumar. Glass Transitions in Highly Attractive Highly Filled Polymer Nanocomposites. *Macromolecules*, 45(2):1131–1135, January 2012. [xviii](#), [29](#), [60](#), [68](#), [72](#), [73](#), [76](#), [128](#)
- [21] Shane E. Harton, Sanat K. Kumar, Hoichang Yang, Tadanori Koga, Kyle Hicks, HyungKi Lee, Jovan Mijovic, Ming Liu, Richard S. Vallery, and David W. Gidley. Immobilized Polymer Layers on Spherical Nanoparticles. *Macromolecules*, 43(7):3415–3421, April 2010. [xviii](#), [60](#), [68](#), [71](#), [72](#), [73](#), [76](#), [100](#), [111](#), [128](#)
- [22] Perla Rittigstein and John M Torkelson. Polymer Nanoparticle Interfacial Interactions in Polymer Nanocomposites : Confinement Effects on Glass Transition Temperature and Suppression of Physical Aging. pages 2935–2943, 2006. [xviii](#), [3](#), [29](#), [60](#), [68](#), [71](#), [72](#), [73](#), [74](#), [76](#), [100](#), [103](#)

- [23] Phillip Griffin. Unpublished Data. 2016. [xxii](#), [122](#), [123](#)
- [24] Shiwang Cheng, Adam P. Holt, Huiqun Wang, Fei Fan, Vera Bocharova, Halie Martin, Thusitha Etampawala, B. Tyler White, Tomonori Saito, Nam-Goo Kang, Mark D. Dadmun, Jimmy W. Mays, and Alexei P. Sokolov. Unexpected Molecular Weight Effect in Polymer Nanocomposites. *Phys. Rev. Lett.*, 116(3):038302, 2016. [xxii](#), [125](#), [128](#), [133](#), [144](#), [146](#)
- [25] Adam P Holt, Vera Bocharova, Shiwang Cheng, Alexander M Kisliuk, Benjamin Tyler White, Tomonori Saito, David Uhrig, Jyoti P Mahalik, Rajeev Kumar, Adam E Imel, et al. Controlling interfacial dynamics: Covalent bonding versus physical adsorption in polymer nanocomposites. *ACS nano*, 2016. [xxii](#), [xxiii](#), [xxiv](#), [134](#), [136](#), [139](#), [140](#), [142](#), [143](#), [145](#), [148](#)
- [26] Michael D Kelzenberg, Shannon W Boettcher, Jan a Petykiewicz, Daniel B Turner-Evans, Morgan C Putnam, Emily L Warren, Joshua M Spurgeon, Ryan M Briggs, Nathan S Lewis, and Harry a Atwater. Enhanced absorption and carrier collection in Si wire arrays for photovoltaic applications. *Nature materials*, 9(3):239–44, March 2010. [2](#)
- [27] I Honma, S Nomura, and H Nakajima. Protonic conducting organic/inorganic nanocomposites for polymer electrolyte membrane. *Journal of Membrane Science*, 185(1):83–94, April 2001.
- [28] Sunny S. Wicks, Roberto Guzman de Villoria, and Brian L. Wardle. Interlaminar and intralaminar reinforcement of composite laminates with aligned carbon nanotubes. *Composites Science and Technology*, 70(1):20–28, January 2010. [2](#)

- [29] Jose M Lobe, Trisha L Andrew, Vladimir Bulović, and Timothy M Swager. Improving the performance of P3HT-fullerene solar cells with side-chain-functionalized poly(thiophene) additives: a new paradigm for polymer design. *ACS nano*, 6(4):3044–56, April 2012. [2](#)
- [30] Yi Yang, Kamil Mielczarek, Mukti Aryal, Anvar Zakhidov, and Walter Hu. Nanoimprinted polymer solar cell. *ACS nano*, 6(4):2877–92, April 2012.
- [31] Chun-chao Chen, Letian Dou, Rui Zhu, Choong-heui Chung, Tze-bin Song, Yue Bing Zheng, and Chen E T Al. Cells Produced by Solution Processing. pages 7185–7190, 2012. [2](#)
- [32] Norman C Su, Zachary P Smith, Benny D Freeman, and Jeffrey J Urban. Size-dependent permeability deviations from maxwells model in hybrid cross-linked poly (ethylene glycol)/silica nanoparticle membranes. *Chemistry of Materials*, 27(7):2421–2429, 2015. [2](#)
- [33] David B. Abbott, Somsubhra Maity, Mary T. Burkey, Russell E. Gorga, Jason R. Bochinski, and Laura I. Clarke. Blending with Non-responsive Polymers to Incorporate Nanoparticles into Shape-Memory Materials and Enable Photothermal Heating: The Effects of Heterogeneous Temperature Distribution. *Macromolecular Chemistry and Physics*, pages n/a–n/a, September 2014. [2](#)
- [34] Beatriz a. Pazmiño Betancourt, Jack F. Douglas, and Francis W. Starr. Fragility and cooperative motion in a glass-forming polymernanoparticle composite. *Soft Matter*, 9(1):241–254, 2013. [3](#), [60](#), [68](#), [71](#), [76](#), [137](#), [141](#), [144](#)
- [35] K.L. Floudas, G. Paluch, M. Grzybowski, A. Ngai. *Molecular Dynamics of Glass-Forming Systems: Effect of Pressure*. Springer, 2011. [13](#)
- [36] A. P. Sokolov, V. N. Novikov, and Y. Ding. Why many polymers are so fragile. *Journal of Physics: Condensed Matter*, 19(20):205116, May 2007. [13](#)

- [37] V N Novikov and a P Sokolov. Poisson’s ratio and the fragility of glass-forming liquids. *Nature*, 431(7011):961–3, October 2004. [14](#)
- [38] Nicolas Giovambattista, Sergey Buldyrev, Francis Starr, and H. Stanley. Connection between Adam-Gibbs Theory and Spatially Heterogeneous Dynamics. *Physical Review Letters*, 90(8):085506, February 2003. [14](#)
- [39] Giulio Biroli and Jean-philippe Bouchaud. The Random First-Order Transition Theory of Glasses: a critical assessment. 2009. [14](#)
- [40] David R Reichman and Patrick Charbonneau. Mode-coupling theory. *Journal of Statistical Mechanics: Theory and Experiment*, 2005(05):P05013, May 2005. [14](#)
- [41] K. L. Ngai and M. Paluch. Classification of secondary relaxation in glass-formers based on dynamic properties. *Journal of Chemical Physics*, 120(2):857–873, 2004. [16](#)
- [42] Stephen Mirigian and Kenneth S Schweizer. Communication: Slow relaxation, spatial mobility gradients, and vitrification in confined films. *The Journal of chemical physics*, 141(16):161103, 2014. [18](#)
- [43] Michael Erber, Martin Tress, Emmanuel U. Mapesa, Anatoli Serghei, Klaus-Jochen Eichhorn, Brigitte Voit, and Friedrich Kremer. Glassy Dynamics and Glass Transition in Thin Polymer Layers of PMMA Deposited on Different Substrates. *Macromolecules*, 43(18):7729–7733, September 2010. [19](#), [60](#)
- [44] A. Serghei, H. Huth, C. Schick, and F. Kremer. Glassy Dynamics in Thin Polymer Layers Having a Free Upper Interface. *Macromolecules*, 41(10):3636–3639, May 2008.
- [45] A Serghei, M Tress, and F Kremer. The glass transition of thin polymer films in relation to the interfacial dynamics. *The Journal of chemical physics*, 131:154904, 2009. [19](#)

- [46] Victor Pryamitsyn and Venkat Ganesan. A Comparison of the Dynamical Relaxations in a Model for Glass Transition in Polymer Nanocomposites and Polymer Thin Films. *Macromolecules*, 43(13):5851–5862, July 2010. [22](#)
- [47] Jamie Kropka, Victor Pryamitsyn, and Venkat Ganesan. Relation between Glass Transition Temperatures in Polymer Nanocomposites and Polymer Thin Films. *Physical Review Letters*, 101(7):075702, August 2008. [22](#)
- [48] Azadeh Ghanbari, Tinashe V M Ndoro, Mohammad Rahimi, Michael C Bo, and Florian Mu. Interphase Structure in Silica - Polystyrene Nanocomposites : A Coarse-Grained Molecular Dynamics Study. 2012. [24](#), [137](#), [141](#)
- [49] Tinashe V. M. Ndoro, Evangelos Voyiatzis, Azadeh Ghanbari, Doros N. Theodorou, Michael C. Bohm, and Florian Muller-Plathe. Interface of Grafted and Ungrafted Silica Nanoparticles with a Polystyrene Matrix: Atomistic Molecular Dynamics Simulations. *Macromolecules*, 44(7):2316–2327, April 2011. [137](#)
- [50] Francis W. Starr, Thomas B. Schrø der, and Sharon C. Glotzer. Molecular Dynamics Simulation of a Polymer Melt with a Nanoscopic Particle. *Macromolecules*, 35(11):4481–4492, May 2002. [24](#)
- [51] Simone Napolitano and Michael Wübbenhorst. Dielectric signature of a dead layer in ultrathin films of a nonpolar polymer. *The journal of physical chemistry. B*, 111(31):9197–9, August 2007. [29](#), [76](#)
- [52] Cinzia Rotella, Michael Wübbenhorst, and Simone Napolitano. Probing interfacial mobility profiles via the impact of nanoscopic confinement on the strength of the dynamic glass transition. *Soft Matter*, 7(11):5260, 2011. [29](#), [76](#)
- [53] Aurelie Papon, Kay Saalwachter, Kerstin Schaler, Laurent Guy, Francois Lequeux, and Hele‘ne Montes. Low-Field NMR Investigations of

- Nanocomposites: Polymer Dynamics and Network Effects. *Macromolecules*, 44(4):913–922, February 2011. [29](#)
- [54] Julien Berriot, Hélène Montes, François Lequeux, Didier Long, and Paul Sotta. Evidence for the shift of the glass transition near the particles in silica-filled elastomers. *Macromolecules*, 35(26):9756–9762, 2002.
- [55] A Dequidt, D. R. Long, P Sotta, and O Sanséau. Mechanical properties of thin confined polymer films close to the glass transition in the linear regime of deformation: theory and simulations. *The European physical journal. E, Soft matter*, 35(7):61, July 2012. [29](#)
- [56] Albert Sargsyan, Anahit Tonoyan, Sevan Davtyan, and Christoph Schick. The amount of immobilized polymer in PMMA SiO₂ nanocomposites determined from calorimetric data. *European Polymer Journal*, 43(8):3113–3127, August 2007. [29](#), [60](#), [73](#), [76](#), [88](#), [136](#)
- [57] Panagiotis Klonos, Christos Pandis, Sotiria Kripotou, and Apostolos Kyritsis. Interfacial Effects in Polymer Nanocomposites Studied by Dielectric and Thermal Techniques. 19(4):1283–1290, 2012. [88](#), [89](#)
- [58] Daniel Fragiadakis and Polycarpos Pissis. Glass transition and segmental dynamics in poly(dimethylsiloxane)/silica nanocomposites studied by various techniques. *Journal of Non-Crystalline Solids*, 353(47-51):4344–4352, December 2007. [60](#)
- [59] Daniel Fragiadakis, Polycarpos Pissis, and Liliane Bokobza. Glass transition and molecular dynamics in poly(dimethylsiloxane)/silica nanocomposites. *Polymer*, 46(16):6001–6008, July 2005. [29](#), [76](#)
- [60] C. G. Robertson and C. M. Roland. Glass Transition and Interfacial Segmental Dynamics in Polymer-Particle Composites. *Rubber Chemistry and Technology*, 81(3):506–522, July 2008. [29](#), [69](#), [76](#), [100](#), [103](#), [128](#)

- [61] Daniel Fragiadakis, Liliane Bokobza, and Polycarpos Pissis. Dynamics near the filler surface in natural rubber-silica nanocomposites. *Polymer*, 52(14):3175–3182, June 2011. [60](#), [76](#), [128](#)
- [62] Hung K Nguyen, Daniele Prevosto, Massimiliano Labardi, Simone Capaccioli, Mauro Lucchesi, Pierangelo Rolla, Fisica Enrico, and Largo Pontecorvo. Effect of Confinement on Structural Relaxation in Ultrathin Polymer Films Investigated by Local Dielectric Spectroscopy. pages 6588–6593, 2011. [60](#)
- [63] Virginie M. Boucher, Daniele Cangialosi, Huajie Yin, Andreas Schönhals, Angel Alegría, and Juan Colmenero. Tg depression and invariant segmental dynamics in polystyrene thin films. *Soft Matter*, 8(19):5119, 2012. [60](#)
- [64] Hung K Nguyen, Massimiliano Labardi, Mauro Lucchesi, Pierangelo Rolla, Daniele Prevosto, and Simone Capaccioli. Interfacial and Annealing Effects on Primary α -Relaxation of Ultrathin Polymer Films Investigated at Nanoscale. 2012. [60](#)
- [65] Harold H. Freedman. Intramolecular H-Bonds. I. A Spectroscopic Study of the Hydrogen Bond between Hydroxyl and Nitrogen. *Journal of the American Chemical Society*, 83(13):2900–2905, jul 1961. [66](#)
- [66] S. B. Hendricks, O. R. Wulf, G. E. Hilbert, and U. Liddel. Hydrogen Bond Formation between Hydroxyl Groups and Nitrogen Atoms in Some Organic Compounds. *Journal of the American Chemical Society*, 58(10):1991–1996, oct 1936. [66](#)
- [67] Y. Ding and A. P. Sokolov. Comment on the dynamic bead size and Kuhn segment length in polymers: Example of polystyrene. *Journal of Polymer Science Part B: Polymer Physics*, 42(18):3505–3511, September 2004. [68](#)

- [68] K Schröter, S A Hutcheson, X Shi, A Mandanici, and G B McKenna.
Dynamic shear modulus of glycerol: corrections due to instrument
compliance. *The Journal of chemical physics*, 125(21):214507, dec 2006. [68](#)
- [69] Katelyn Parker, Ryan T. Schneider, Richard W. Siegel, Rahmi Ozisik,
Juan Carlos Cabanelas, Berna Serrano, Claire Antonelli, and Juan Baselga.
Molecular probe technique for determining local thermal transitions: The
glass transition at Silica/PMMA nanocomposite interfaces. *Polymer*,
51(21):4891–4898, October 2010. [74](#)
- [70] P. Klonos, a. Panagopoulou, a. Kyritsis, L. Bokobza, and P. Pissis.
Dielectric studies of segmental dynamics in poly(dimethylsiloxane)/titania
nanocomposites. *Journal of Non-Crystalline Solids*, 357(2):610–614, January
2011. [76](#)
- [71] T. Glomann, G. J. Schneider, J. Allgaier, a. Radulescu, W. Lohstroh,
B. Farago, and D. Richter. Microscopic Dynamics of Polyethylene Glycol
Chains Interacting with Silica Nanoparticles. *Physical Review Letters*,
110(17):178001, April 2013. [76](#)
- [72] Motoyuki Iijima and Hidehiro Kamiya. Layer-by-layer surface modification
of functional nanoparticles for dispersion in organic solvents. *Langmuir : the
ACS journal of surfaces and colloids*, 26(23):17943–8, December 2010. [78](#), [130](#)
- [73] Hidehiro Kamiya, Hisao Suzuki, Daisuke Kato, and Genji Jimbo.
Densification of alkoxide-derived fine silica powder compact by ultra-high-
pressure cold isostatic pressing. *Journal of the American Ceramic Society*,
76(1):54–64, 1993. [78](#)
- [74] Tian Hao and Richard E Riman. Calculation of interparticle spacing in
colloidal systems. *Journal of colloid and interface science*, 297(1):374–7, May
2006. [79](#)

- [75] G Beaucage. Approximations leading to a unified exponential/power-law approach to small-angle scattering. *Journal of Applied Crystallography*, 28(6):717–728, 1995. [80](#)
- [76] G Beaucage. Small-angle scattering from polymeric mass fractals of arbitrary mass-fractal dimension. *Journal of Applied Crystallography*, 29(2):134–146, 1996. [80](#)
- [77] A. Guimer and G. Fournet. Small angle scattering of x-rays. *J. Wiley & Sons, New York*, 1955. [80](#)
- [78] Josef Jancar, Robert S Hoy, Alan J Lesser, Ema Jancarova, and Jan Zidek. Effect of particle size, temperature, and deformation rate on the plastic flow and strain hardening response of pmma composites. *Macromolecules*, 46(23):9409–9426, 2013. [83](#)
- [79] Nicolas Jouault, Dan Zhao, and Sanat K. Kumar. Role of Casting Solvent on Nanoparticle Dispersion in Polymer Nanocomposites. *Macromolecules*, page 52465255, July 2014. [90](#)
- [80] Nicolas Jouault, Joseph F. Moll, Dong Meng, Kendra Windsor, Stacy Ramcharan, Clare Kearney, and Sanat K. Kumar. Bound Polymer Layer in Nanocomposites. *ACS Macro Letters*, 2(5):371–374, May 2013. [90](#)
- [81] Adam P Holt, Philip J Griffin, Vera Bocharova, Alexander L Agapov, Adam E Imel, Mark D Dadmun, Joshua R Sangoro, and Alexei P Sokolov. Dynamics at the polymer/nanoparticle interface in poly(2-vinylpyridine)/silica nanocomposites. *Macromolecules*, 47(5):1837–1843, 2014. [103](#), [128](#), [133](#), [136](#), [137](#), [144](#)
- [82] M Fullbrandt, PJ Purohit, and A Schonhals. Combined FTIR and Dielectric Investigation of Poly (vinyl acetate) Adsorbed on Silica Particles. *Macromolecules*, 2013. [103](#)

- [83] Tadanori Koga, N Jiang, P Gin, MK Endoh, S Narayanan, LB Lurio, and SK Sinha. Impact of an irreversibly adsorbed layer on local viscosity of nanoconfined polymer melts. *Physical review letters*, 107(22):225901, 2011. [103](#)
- [84] Hans-Jürgen Butt, Hatice Duran, W Egger, F Faupel, Vagelis Harmandaris, S Harms, Karen Johnston, Kurt Kremer, Fan-Yen Lin, L Lue, et al. Interphase of a polymer at a solid interface. *Macromolecules*, 47(23):8459–8465, 2014. [111](#)
- [85] R. Casalini and C. M. Roland. Determination of the thermodynamic scaling exponent for relaxation in liquids from static ambient-pressure quantities. *Physical review letters*, 113(8):085701, 2014. [119](#)
- [86] R. B. Bogoslovov, C. M. Roland, A. R. Ellis, A. M. Randall, and C. G. Robertson. Effect of Silica Nanoparticles on the Local Segmental Dynamics in Poly (vinyl acetate) . *Macromolecules*, pages 1289–1296, 2008. [119](#)
- [87] Ran Tao and Sindee L. Simon. Pressure-volume-temperature and glass transition behavior of silica/polystyrene nanocomposite. *Journal of Polymer Science Part B: Polymer Physics*, 2015. [119](#)
- [88] C. M. Roland. Relaxation phenomena in vitrifying polymers and molecular liquids. *Macromolecules*, 43(19):7875–7890, 2010. [119](#), [152](#)
- [89] Simone Napolitano and Michael Wübbenhorst. The lifetime of the deviations from bulk behaviour in polymers confined at the nanoscale. *Nature Communications*, 2:260, March 2011. [123](#)
- [90] Shushan Gong, Quan Chen, Joseph F Moll, Sanat K Kumar, and Ralph H Colby. Segmental Dynamics of Polymer Melts with Spherical Nanoparticles. pages 1–5, 2014. [128](#), [153](#)

- [91] Victor Pryamitsyn and Venkat Ganesan. Origins of Linear Viscoelastic Behavior of Polymer - Nanoparticle Composites. pages 844–856, 2006. [128](#)
- [92] F Chen, A Clough, B M Reinhard, M W Grinsta, N Jiang, T Koga, and O K C Tsui. Glass Transition Temperature of Polymer - Nanoparticle Composites : E ff ect of Polymer - Particle Interfacial Energy. 2013. [128](#)
- [93] Yogendra Narayan Pandey, George J. Papakonstantopoulos, and Manolis Doxastakis. Polymer/Nanoparticle Interactions: Bridging the Gap. *Macromolecules*, 46(13):5097–5106, July 2013.
- [94] Bharath Natarajan, Yang Li, Hua Deng, L Catherine Brinson, and Linda S Schadler. E ff ect of Interfacial Energetics on Dispersion and Glass Transition Temperature in Polymer Nanocomposites. [128](#)
- [95] Gerard J Fleeer. Polymers at interfaces and in colloidal dispersions. *Advances in colloid and interface science*, 159(2):99–116, September 2010. [128](#)
- [96] Nicolas Jouault, Danmi Lee, Dan Zhao, and Sanat K. Kumar. Block-Copolymer-Mediated Nanoparticle Dispersion and Assembly in Polymer Nanocomposites. *Advanced Materials*, April 2014. [129](#)
- [97] Douglas Dukes, Yu Li, Sarah Lewis, Brian Benicewicz, Linda Schadler, and Sanat K. Kumar. Conformational transitions of spherical polymer brushes: Synthesis, characterization, and theory. *Macromolecules*, 43(3):1564–1570, 2010. [129](#), [146](#)
- [98] Praveen Agarwal, Sung a. Kim, and Lynden a. Archer. Crowded, Confined, and Frustrated: Dynamics of Molecules Tethered to Nanoparticles. *Physical Review Letters*, 109(25):258301, December 2012. [129](#)
- [99] Sung a Kim, Rahul Mangal, and Lynden A. Archer. Relaxation Dynamics of Nanoparticle-Tethered Polymer Chains. *Macromolecules*, page 150817142432000, 2015.

- [100] Cornelius Friedrichs, Sebastian Emmerling, Gunnar Kircher, Robert Graf, and Hans Wolfgang Spiess. Glass transition of poly(ethylmethacrylate) admixed and bound to nanoparticles. *The Journal of chemical physics*, 138(12):12A503, March 2013. [129](#)
- [101] Folusho T. Oyerokun and Kenneth S. Schweizer. Theory of glassy dynamics in conformationally anisotropic polymer systems. *Journal of Chemical Physics*, 123(22), 2005. [130](#), [153](#)
- [102] Dan Zhao, Dirk Schneider, George Fytas, and Sanat K Kumar. Controlling the thermomechanical behavior of nanoparticle/polymer films. *ACS nano*, 8(8):8163–73, August 2014. [132](#)
- [103] P. Bartlett and R. H. Ottewill. A neutron scattering study of the structure of a bimodal colloidal crystal. *The Journal of Chemical Physics*, 96(4):3306–3318, 1992. [133](#)
- [104] Norman C. Su, Zachary P. Smith, Benny D. Freeman, and Jeffrey J. Urban. Size-dependent permeability deviations from maxwells model in hybrid cross-linked poly(ethylene glycol)/silica nanoparticle membranes. *Chemistry of Materials*, 27(7):2421–2429, 2015. [138](#)
- [105] Changyu Tang, Ken Hackenberg, Qiang Fu, Pulickel M Ajayan, and Haleh Ardebili. High ion conducting polymer nanocomposite electrolytes using hybrid nanofillers. *Nano letters*, 12(3):1152–6, March 2012.
- [106] Zhiping Song, Terrence Xu, Mikhail L. Gordin, Ying Bing Jiang, In Tae Bae, Qiangfeng Xiao, Hui Zhan, Jun Liu, and Donghai Wang. Polymer-graphene nanocomposites as ultrafast-charge and -discharge cathodes for rechargeable lithium batteries. *Nano Letters*, 12(5):2205–2211, 2012. [138](#)

- [107] Alexandros Chremos, Athanassios Z Panagiotopoulos, and Donald L Koch. Dynamics of solvent-free grafted nanoparticles. *The Journal of chemical physics*, 136(4):044902, January 2012. [141](#)
- [108] Shiwang Cheng, Stephen Mirigian, Jan-Michael Y Carrillo, Vera Bocharova, Bobby G Sumpter, Kenneth S Schweizer, and Alexei P Sokolov. Revealing spatially heterogeneous relaxation in a model nanocomposite. *The Journal of chemical physics*, 143(19):194704, November 2015. [144](#)
- [109] P. G. de Gennes. Conformations of Polymers Attached to an Interface. *Macromolecules*, 13(5):1069–1075, sep 1980. [146](#)
- [110] A.N. Semenov. Contribution to the theory of microphase layering in block-copolymer melts. *Journal of theoretical and experimental Physics*, 61(4):733–742, 1985.
- [111] M Daoud and JP Cotton. Star shaped polymers: a model for the conformation and its concentration dependence. *Journal de Physique*, 1982. [146](#)
- [112] Rajeev Kumar, Bradley S. Lokitz, Scott W. Sides, Jihua Chen, William T. Heller, John F. Ankner, James F. Browning, S. Michael Kilbey II, and Bobby G. Sumpter. Microphase separation in thin films of lamellar forming polydisperse di-block copolymers. *RSC Adv.*, 5(27):21336–21348, feb 2015. [148](#)
- [113] P. Papadopoulos, D. Peristeraki, G. Floudas, G. Koutalas, and N. Hadjichristidis. Origin of glass transition of poly(2-vinylpyridine). A temperature- and pressure-dependent dielectric spectroscopy study. *Macromolecules*, 37(21):8116–8122, 2004. [152](#)

Vita

Adam Prillaman Holt was born in Nashville, Tennessee. After graduating from Centennial High school in Franklin, Tennessee in 2006, he enrolled at Tennessee Technological University where he pursued a bachelor degree in Physics. After his sophomore year, he participated in an undergraduate research experience program at the University of Alabama, Birmingham in 2008 which fueled his interest in academic research. After receiving his B.S in Physics from Tennessee Technological University in the May of 2010, he attended the graduate School at the University of Tennessee, Knoxville to pursue his Doctorate in Physics. Adam married his wife Jennifer during his first year of graduate school in 2011. After receiving his Ph.D in the summer of 2016, he was nominated as a Karle Research Fellow in the polymer physics branch at the Naval Research Laboratory in Washington, DC, and plans to study the formation and properties of ultra-stable molecular and polymeric glasses.