To the Graduate Council:

I am submitting herewith a dissertation written by Richard J. Zdrahala entitled "Block Copolymers Based on Wholly Aromatic Polyamide and Poly(ethylene oxide) or Poly(dimethyl siloxane) Segments." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.

John F. Fellers

John F. Fellers, Major Professor

We have read this dissertation and recommend its acceptance:

Edward S. Clark

James L. White

J. E. Spruiell

James F. Kinstle

Accepted for the Council:

Vice Chancellor
Graduate Studies and Research

BLOCK COPOLYMERS BASED ON WHOLLY AROMATIC POLYAMIDE AND POLY(ETHYLENE OXIDE) OR POLY(DIMETHYL SILOXANE) SEGMENTS

A Dissertation

Presented for the

Doctor of Philosophy

Degree

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Richard J. Zdrahala

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1269183

PREFACE

"Science is not a system of a certain, or well-established statements; nor is it a system which steadily advances towards a state of finality. . . . We do not know; we can only guess. And our guesses are guided by the unscientific, the metaphysical (though biologically explicable) faith in laws, in regularities which we can uncover-discover. Like Bacon, we might describe our own contemporary science 'the method of reasoning which men now ordinarily apply to nature'--as consisting of 'anticipations, rash and premature' and as 'prejudices.'"

Karl Raimund Popper (1959)

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ABSTRACT

The excellent properties of wholly aromatic polyamides are a well-recognized fact. These high-temperature use, high-modulus materials cannot be processed in their molten state because they decompose at a lower temperature than they melt. Therefore processing of these materials from solution in a suitable solvent remains as the only possibility. In general, there are a limited number of solvents available. In the case of poly(p-phenylene terephthalamide), concentrated sulphuric acid represents the only available solvent, introducing considerable difficulties into the processing technology.

The purpose of this research was to investigate the synthesis and certain physical-mechanical properties of block copolymers containing aromatic polyamide segments. In addition to the influence of cosegments on tensile properties, their effect on both solubility characteristics and morphology were studied. Poly(m-phenylene isophthalamide) prepolymers were used in combination with poly(ethylene oxide) or poly(dimethyl siloxane) homopolymers for the formation of these block copolymers. For these investigations, a series of 18 poly(m-phenylene isophthalamide) homopolymers, 30 poly(m-phenylene isophthalamide-b-ethylene oxide) block copolymers and 22 poly(m-phenylene isophthalamide-b-dimethyl siloxane) block copolymers were synthesized.

A low-temperature, self-regulating copolycondensation technique was designed and modified for formation of these interesting polymeric

materials. Although precise control of sequence placement within the block copolymer backbone is not always possible by this synthetic route, it is a promising method for obtaining polymers with controlled properties for a particular application.

Molecular-level properties, (e.g., viscosity-molecular weight, solubility and composition) were determined for all the above mentioned polymers. The improved solubility of block copolymers containing poly(ethylene oxide) segments in comparison with poly(m-phenylene isophthalamide) homopolymer was clearly determined.

Physical and mechanical properties, including thermal stability, tensile strength, Young's modulus, elongation and thermomechanical behavior, were measured for all synthesized materials. The influence of block composition and sequence of cosegments was clearly manifested. The presence of poly(dimethyl siloxane) segments generally improves the elongation-to-break up to 5-fold increase while lowering the tensile strength and Young's modulus to approximately one-half to one-third of the values associated with poly(m-phenylene isophthalamide). The effect of poly(ethylene oxide) segments is more complex due to the very interesting morphologies developed within these blocks.

Polarized-light microscopy was used to determine the morphological features of all synthesized homo- and block copolymers. In general, block copolymers with a certain degree of incompatibility between the different chain segments yield unique morphologies and microphase separation. The most distinctive morphological feature in poly(m-phenylene isophthalamide-b-dimethyl siloxane) block copolymers

is the presence of small spheres rich in polysiloxane embedded in poly(m-phenylene isophthalamide) matrix. The morphology of poly(m-phenylene isophthalamide-b-ethylene oxide) block copolymers is quite striking. Perfectly developed maltese crosses are observable even at 100x magnification. At this point no clear understanding of morphology of poly(m-phenylene isophthalamide-b-ethylene oxide) is available. It is, however, important to point out that the intensive investigation of that problem is being carried out in our research team by Mr. Yu-der Lee and will be published in his dissertation.

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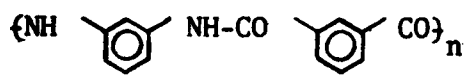
LIST OF SYMBOLS

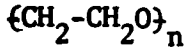
In order to simplify chemical formulae, reaction schemes and structure-oriented sketches, the following symbols and abbreviations will be used throughout this dissertation:

Poly(m-phenylene isophthalamide) homopolymer



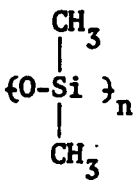
will be abbreviated hereafter by symbol: PmPIA "A"

Poly(ethylene oxide) homopolymer



will be abbreviated throughout the text as: PEO "E"

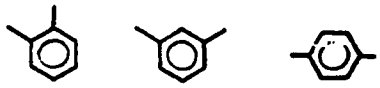
Poly(dimethyl siloxane) homopolymer



will be abbreviated by: PSX "S"

N,N-dimethyl acetamide

used very often as solvent for reactions will be represented by: DMAc

Disubstituted benzene nuclei 

are often abbreviated by: -Ø-

Molecular weight and molecular weight distribution

are abbreviated by: MW MWD

Weight percent

is expressed in tables as: Wt.%

Block copolymer structures

For different block copolymer segment sequences, $((AB)_n$, ABA or BAB), the letter "A" always represents poly(m-phenylene isophthalamide) while the letter "B" stands for either poly(ethylene oxide) or poly(dimethyl siloxane).

Block copolymer codes

The following abbreviations are used for specific cases to describe various synthesized block copolymers:

A_x - represents a poly(m-phenylene isophthalamide). The index "x" is the sample number; e.g., A_{11} represents the 11th homopolymer synthesized.

E4, E10, E40, E60 - represent poly(ethylene oxide) segments with specific molecular weight. Here the last two digits in molecular weight are always omitted; e.g., E40 stands for molecular weight of 4000 g/mole.

S15, S50, S90, S140 - represent poly(dimethyl siloxane) segments of various molecular weight; e.g., S140 stands for poly(dimethyl siloxane) segment having molecular weight of 14,000 g/mole. Here again the last two digits are omitted.

The combination of these abbreviations used in code names of block copolymers represents the actual sequence placement for each material.

CHAPTER I

INTRODUCTION

The science and art of block copolymers is one of the most interesting breakthroughs in modern polymer science. A whole treasury of phenomena guiding the behavior of macromolecular system has been discovered during the pursuit of research in this field. Hundreds of very interesting materials have been "created" in order to achieve the realization of some important needs of mankind.

This dissertation introduces a contribution to the field of block copolymer science involving a new class of block copolymers containing wholly aromatic polyamide and either polyether or polysiloxane cosegments. A relatively broad range of topics is covered within this work. The design and realization of different synthetic routes to achieve variation in the structure of block copolymers is followed by the determination of basic molecular-level properties. Thermal stability, mechanical and thermomechanical behavior of these block copolymer systems represents another integral part of this dissertation. To demonstrate the importance of molecular architecture in block copolymer systems, the basic morphology of these block copolymers was examined. The phenomena discovered and described in the chapter dealing with morphology of these synthesized block copolymers are closely linked to the previous chapters of this dissertation.

Three individual chapters were written to deal with synthesis, characterization and morphology so that an orderly presentation of rather broad ranging information could be made. No single part is emphasized more than the other ones. This is because all data available at this stage of research in this field are considered to be very important for a thorough description of these block copolymers.

CHAPTER II

HISTORICAL BACKGROUND

II.1. THE IDEA OF BLOCK COPOLYMERS

"Novel polymers" and materials "tailored" for a special application have concerned polymer researchers since the advent of polymer science.

It has been obvious that formerly known homopolymers (e.g., thermosettings, thermoplastics, rubbers, etc.) cannot satisfy all new materials needs. The desirability of having a combination of different properties in one polymeric material prompted the formation of a new branch of polymer science, namely that involving block copolymers. For example, the unfavorable brittleness of regular polystyrene has been substantially reduced by a simple operation during which "rubbery" material is "mixed-in." By application of this technique a most interesting material, ABS, was developed. This simple mechanical mixing often ends in a mixture of graft copolymers, homopolymers and degradation products. It is obvious that this method leads to poor control of desired products. Even an application of the best synthetic procedures known to polymer chemists in the early fifties often yielded random mixtures of copolymers, usually high branched.

H. Mark (1) first pointed out the probable properties of block copolymers. It was postulated that if the block copolymer consisted of

a few very large blocks, then its properties would be quite similar to those of mechanical mixtures of the respective homopolymers. Furthermore, certain responses of a block copolymer should be a superposition of the properties of the respective homopolymers. On the other hand, random or alternating copolymers are expected to have properties which in general are some sort of average of the properties of the respective homopolymers.

Older synthetic methods for producing block copolymers consisted of direct coupling of preformed homopolymers with functional groups. Ester interchange reactions, free-radical polymerization and photochemical reactions were among the most frequently used synthetic approaches (2,3,4). These methods did not provide structural control either as to the length of individual blocks or even to the number of blocks per copolymer chain. In general, the blocks formed were in reality mixtures of several polymeric species, including homopolymers. This entailed the additional task of separating and isolating various species (3,4) and correlating compositions with properties or of obtaining successive batches of block copolymers having consistent properties.

M. Szwarc (5) revealed the nonterminating character of homogeneous anionic polymerization. He and his associates (6,7) were able to demonstrate the feasibility of producing block copolymers via anionic synthesis. For example, by using sodium-naphthalene initiator and sequential polymerization of styrene and isoprene monomers in tetrahydrofuran they synthesized isoprene-styrene-isoprene triblock copolymers. Furthermore, they conclusively proved the absence of any homopolymer.

S. Schlick and associates (7), using the above initiator and monomers, synthesized copolymers consisting of alternating blocks of polyisoprene and polystyrene. In essence, these authors were able to demonstrate the advantages of anionically produced blocks with desirable and predictable lengths.

A. V. Tobolsky and coworkers (8) did not employ anionic synthesis for triblocks with thermoplastic end blocks and rubbery center block. Essentially, a preformed rubbery polymer was capped at each end with peroxide groups. The thermoplastic end blocks were then formed via free-radical polymerization of certain vinyl monomers. They postulated that for such a triblock copolymer, the rubbery component should impart impact resistance, while the thermoplastic glassy ends should give the copolymer a high modulus over a wide temperature range. Although the authors were able to demonstrate unique mechanical properties, their triblocks were not "pure" due to the synthetic complications.

At about the same time, a patent was issued to R. Milkovich (9) describing the formation of such triblock copolymers by anionic polymerization. The ABA triblock, where A stands for polystyrene and B either for polyisoprene or polybutadiene, was synthesized.

Since then a great deal of attention has been focused upon these ABA type block copolymers. Interest has been generated because their behavior is found to be similar to that of rubbery vulcanizates without the necessity of chemical crosslinks. Furthermore, at elevated temperatures they could be molded or extruded as typical thermoplastic polymer (10,11,12). This group of materials is often called

"thermoplastic elastomers." It was shown that the special character of these block copolymers could be explained by considering the morphology of the system.

A new morphology was expected. Phase separation was believed to be the most important phenomenon controlling those "novel properties." As progress continued in this field, very interesting polymer chains of block nature were synthesized. Subchains containing aromatic rings, imparting toughness and thermal, oxidative and dimensional stability, were often combined with flexible aliphatic subchains possessing a certain degree of crystallinity.

The science and "art" of complicated polymer synthesis grew up hand-in-hand with each new discovery in morphology of previously prepared materials. Since the anionic technique is limited by the nature of the monomers, procedures for block copolymer preparation are often combined to produce suitable blocks. For example, an anionically prepared prepolymer may be incorporated into a block copolymer by polycondensation or free-radical polymerization.

II.2. STRUCTURAL ORDER IN BLOCK COPOLYMER SYSTEMS

One can name several block copolymer structures of varying order. Basically there are these types: $(AB)_n$, where n = 1,2,3, ..., ABA, and the reversed sequence BAB. Within this framework one other controllable feature exists, i.e., molecular weight. The highest degree of order exists when cosegment placement is controlled along with MW and MWD. The degree of order then is lowered as one loses control of these features.

Structural order is important in block copolymers because it strongly relates to the morphology and mechanical properties of these systems. As previously alluded to, the properties of the homopolymer segments are brought together in unusual ways in block copolymers. Block copolymers possessing high molecular weight homopolymer segments manifest interactive properties as opposed to ordinary copolymers that show additive or averaged properties.

The choice of various cosegments for a block copolymer then is guided by several basic considerations. First, the available synthetic reactions to control sequence placement are determined. Next, the cosegments are usually thought of in terms of opposites or extremes in values for characteristic properties. Finally, multiphase behavior and morphology are considered. Each of these considerations is important but not independent; that is, they are interactive and strongly relate to the order criteria discussed in the first paragraph of this subsection.

II.3. VARIETIES OF COSEGMENTS USED IN BLOCK COPOLYMERS

Block copolymers involving (styrene)-(diene) type of di- and triblocks are among the most thoroughly investigated block structures. The vast majority of research work published has been for those systems. On the other hand, the synthesis of block copolymers especially "tailored" for a particular application involves a rather broad variety of polymeric segments. The following group of polymers are among the

most commonly exploited in block structures: vinyl polymers, polyolefins, polyethers, polyesters, polysiloxanes, polyurethanes, poly(phenylene oxides), polycarbonates, polysulfones and polyamides.

II.4. THE BASIC ASPECTS OF THE MORPHOLOGY OF BLOCK COPOLYMERS: BASIC THERMODYNAMIC JUSTIFICATION

When two or more polymers are mixed together, either mechanically or in solution, certain properties of such mixtures are intimately associated with a resultant morphology of the system (13,14). Morphology might be considered as a supramolecular structure (15) resulting from the interactions of like and unlike polymeric species. These are distinct from configurational and conformational structures of an individual chain molecule.

Chemically bonded block copolymers permit not only interactions between different homopolymeric subchains, polymeric chains and the environment, but also the interactions of these chains with themselves. These interactions give block copolymers colloidal properties. The interactions among different polymeric subchains could result in complete compatibility, giving ideally a uniform homogeneous system. On the other hand, essentially incompatible polymeric subchains yield a mixture or system consisting of two or more separate phases. Each phase should be rich in one particular polymeric segment.

In solution, interactions between polymer subchains and solvent stabilize organic sols lattices (16,17,18) and the interactions between different homopolymer chains and block subchains stabilize

polymeric "oil-in-oil" emulsions. If the above mentioned systems are in the solid state, those interactions lead to new morphologies and novel mechanical properties (11,21,22).

II.4.1. Colloidal Properties Based on Polymer-Solvent Interactions

The nature of the structure of block copolymers causes unusual dual solubility in solvents and their mixtures. These solutions possess a special set of colloidal properties first observed by Merrett (16,17,18). He found that when a block copolymer is dissolved in a "good" solvent for all involved segments, a stable organic sol is formed. The name "organic lattice" appears here for the first time to characterize this phenomenon. The formation of these colloidal sols was subsequently proved by other researchers (17,23-28). Sols formed during this dissolution become selective for one of the parent homopolymers. The stability of those nonaqueous colloids is very high. This stability can be understood as a result of interactions between polymer and solvent (17,18,27,28). Sols are generally composed from micelles. In analogy with soap micelles, the polymer micelles are aggregates of a number of block copolymer molecules. Homopolymeric species are occluded in the micelle quite analogously to the solubilization of an oil in soap micelle in water. The micelle nature of those sols results in the formation of "organic latex" particles.

The architecture of micelles can be determined in a solvent/nonsolvent system. Chains or subchains precipitated first form the "micelle-core." The "micelle-core" is surrounded by a shell of still

soluble subchains. Bressler and coworkers (27) have studied different micelle structures of various types of block copolymers. They have verified the presence of a "core-shell" architecture in the solid state in polymers which were prepared either by solvent evaporation or floculation of block copolymer solutions. Two modifications appear in those structures: microprecipitated cosegment A surrounded by still soluble cosegment B and vice versa. The formation of these modifications was based on partial collapsing of block molecules at a certain solvent/nonsolvent composition. This partial collapsing of block chains can be demonstrated with measurements of intrinsic viscosities as a function of solvent composition (17,27-29).

The morphology of "hard" and "soft" modifications, determined usually by electron microscopy (30), revealed that at a very low concentration of block copolymer chains, micelles are apparently monomolecular. Light-scattering (28) indicated no increase of molecular weight of copolymers due to micelle formation. At higher concentrations the number of molecules in the micelle depends generally on the temperature and kind of solvent, as indicated by Gallott et al. (28,29).

The solution behavior of polystyrene/poly(ethylene oxide) block copolymers studied by Skoulios and coworkers (31-34) has shown the formation of liquid crystals. In dilute solutions, these block copolymers formed monomolecular micelles. At higher concentrations, aggregation into polymolecular micelles was observed. A further concentration increase led to highly organized, mesomorphic structures, as determined by x-ray analysis or polarized-light microscopy. It was

observed that, depending on the nature of the solvent, the copolymer concentration in solution and the temperature, the macromolecules are in cylindrical or lamellar mesomorphic forms. At the same concentration of the block copolymer in solution, both leaflets and cylinders could coexist. Mechanical agitation or thermal shocks destroy the structure described above.

In order to study those structures, fixation of the system by using a vinyl monomer as a selective solvent, and solidification of the entire system by subsequent polymerization of the solvent, is possible. These techniques studied also by Sadron and coworkers (35-37), led to the formation of the "organized polymers."

II.4.2. Colloidal Properties Based on Polymer-Polymer Interactions

In order to determine the architecture and properties of block copolymers, the nature of polymer-polymer interactions within block chains and homopolymer subchains is important. Stockmayer (38) postulated that interactions between chains are repulsive between different units of a random block copolymer. Subsequently, Molau (39) stated that the interactions are strong enough to cause a phase separation in random copolymers of identical monomers having different compositions.

It is useful to investigate phase separation more generally, starting with solutions of homopolymers and their mixtures. From the work of Dobry et al. (40), Scott (41), Flory (42), Kern (43,44) and Slocombe (44) involving theoretical aspects of phase separation within

polymeric solutions, it is clear that incompatibility of different polymers is expected.

Experimentally it has been shown that pairs of different polymers in common solvents usually exhibited incompatibility. A system separates into two or more phases, each being rich in solvent and one polymer. Dobry (40) tested 35 polymeric pairs of which only 4 showed compatibility. Kern and Slocombe (43,44) extended that study for an additional 24 polymeric pairs for which the rule of incompatibility prevailed. Although these studies indicated that incompatibility of different polymers is a general rule, the limit of phase separation was found to be dependent upon the nature of the solvent, polydispersity among the polymer chains, and temperature (40,43,44).

Even in dilute block copolymer solutions, intermolecular phase separation should occur; the solvent dilutes incompatibility but does not eliminate it (40). If phase separation within the molecule is considered, the concentration of various polymer subchains must be taken into account with respect to the volume occupied by this molecule. If phase separation occurs within a polymer mixture dissolved in a mutual solvent, it can be expected also within different subchains in graft copolymers, but more probably in block copolymers. The repulsive nature of polymer-polymer interactions causing intramolecular phase separation has been observed and studied by a number of researchers (7,19,23,38,45-52).

Quite generally, polymer-polymer interactions are believed to have a significant influence on the morphology of block copolymers.

These polymer-polymer interactions manifest colloidal behavior of block copolymer solutions. The model of a dissolved block copolymer involves the hypothesis that chemically different subchains occupy different domains of space filled by the entire molecule and the attached solvent molecules. Considering the established incompatibility, space occupied by the block molecule in solution could have a shape of a "dumbbell" or spherical micelle (19). Similar spatial arrangement could be visualized for multi-block copolymers with many side chains.

A significant colloidal property of block copolymers in nonselective solvents is the emulsifying effect leading to polymeric "oil-in-oil" emulsions (19,53,54). Polymeric "oil-in-oil" emulsions are parepared by dissolving two different homopolymers, and a corresponding block copolymer in a mutual solvent. These emulsions are of interest because the mechanism of their stabilization is a good example of polymer-polymer interactions (19). In order to stabilize an emulsion from coalescence of its droplets, the emulsifier must accumulate at the emulsion interface. In these emulsions, dual solubility in the conventional sense with respect to the solvent cannot exist. The solvent is the same for both phases. Two phases are incompatible not because solvents are immiscible, but because polymeric solutes are incompatible. In the ideal case where the solvent is nonselective, different subchains of block copolymer emulsify alike. Phases have about the same polarity and the same solubility parameters.

The polymer-polymer interactions are responsible for accumulation of an "emulsifier" at the interface. Stability of those emulsions

depends on total molecular weight of block copolymer and the length of individual subchains. As molecular weight increases, emulsifying power does as well. It is also important to have fairly long homopolymeric segments within each block molecule to insure maximum emulsifications.

Wallach et al. (55,56) have studied dilute solution properties of (polystyrene)-(polydiene) block copolymers by IR, NMR, viscometry, osmometry, U-centrifugation, and light-scattering techniques. They have verified the importance of molecular weight distribution on morphology of films cast from these solutions. When a narrow distribution of molecular weight among subchains and chains is attained, domains with sharp boundaries are formed having generally a two phase nature. Furthermore, DSC investigation of multiple Tg's was performed and two distinctive Tg's were found, both clearly associated with the individual segments of block structure.

II.4.3. Basic Thermodynamic Interpretation of Domain Formation

The degree to which two different polymeric species will be mutually miscible is governed among others by thermodynamic considerations. From a thermodynamic standpoint (57), the Gibbs Free Energy of mixing is defined as:

$$\Delta G_M = \Delta H_M - T\Delta S_M \, . \qquad (1)$$

In order for a pair of polymers to be mutually soluble the Gibbs Free Energy of mixing, ΔG_M, should be negative (41,58). In comparison

with the mixing of ordinary monomeric species which involves a large number of molecules, the mixing of high polymers involves a relatively small number of molecules. Hence, the Entropy contribution, ΔS_M, is quite small (15,42,59). The Enthalpy of mixing, ΔH_M, has in general a positive value for most hydrocarbon polymeric pairs causing a positive value of ΔG_M and therefore polymer incompatibility.

The problems associated with polymer mixing are far more complex than the relatively simple approach taken above. In essence, what one would desire is to be able to predict the behavior of a polymer mixture without recourse to any laborious experimentation.

The calculation of the Enthalpy of mixing, ΔH_M, under constant volume conditions, based upon the solubility parameter theory of mixing (60,61), is given by Scatchard-Hildebrand equation (62):

$$\Delta H_M = V_M(\delta_A - \delta_B)^2 \cdot \phi_A \cdot \phi_B \qquad (2)$$

where: V_M = total volume,

δ_A, δ_B = solubility parameters

ϕ_A, ϕ_B = volume fractions of respective liquids.

Delta (δ), the solubility parameter, is a measure of attractive forces (cohesive energy) between molecules themselves.

Small (63) has extended the concept of solubility parameters to polymers, which permits a calculation of their solubility parameters:

$$\delta = \frac{\Sigma F}{V} \qquad (3)$$

where ΣF is a sum of all molar attraction contributions of each chemical group within a polymer repeat unit and V is a molar volume of the repeat unit.

Hoy (64) recently has refined Small's scheme, so that not only are group contributions considered, but also structural feature contributions are included in ΣF. Unfortunately, the above scheme has been restricted to nonpolar polymers. Furthermore, equation (2) does not indicate any temperature dependence of polymer compatibility.

The combination obtained from the solubility parameter theory (54,55) and a liquid lattice model theory (50,51,65,66) has been used as a better approximation of the mixing of polymer pairs (57,67). The relationship between the Flory-Huggins interaction parameters χ_{AB} for a pair of polymers and their respective solubility parameters is given by Krause (67) as:

$$\chi_{AB} = \frac{V_r}{RT} \cdot (\delta_A - \delta_B)^2 \qquad (4)$$

where: V_r = reference volume taken as close to the molar volume of the smallest possible repeat unit,

R = gas law constant,

T = absolute temperature (Kelvin).

Scott (50) has derived an expression for the critical values of χ_{AB}; in other words, above this value, phase separation will most likely occur. The equation is:

$$(\chi_{AB})_{crit.} = \frac{1}{2}(1/x_A^{1/2} + 1/x_B^{1/2})^2 \qquad (5)$$

where x_A, x_B are the degrees of polymerization of polymers A and B respectively, but are given in terms of reference volume V_r.

Krause (67), in a recent paper, has outlined a number of steps to be employed to determine the degree of compatibility for a particular nonpolar polymer pair. Essentially, one obtains values for χ_{AB} and $(\chi_{AB})_{crit.}$. If χ_{AB} is larger than $(\chi_{AB})_{crit.}$, the polymers should be incompatible. Furthermore, the greater the difference between those values, the smaller will be the range of compositions for which polymer miscibility will occur. In principle, one can also determine the degree of compatibility at a particular composition.

A serious interpretation of domain formation by the use of thermodynamics in solvent-cast films was done by Inoue et al. (68). In their work, a rather complicated treatment reveals that in solvent-cast films of AB diblock of polystyrene/polydiene block copolymers, a microheterogeneous structure is formed as a result of microphase separation of the block subchains. The structure thus formed must be stable and quite different from the structure of solvent-cast films of incompatible homopolymers. The latter situation must represent a state frozen during the course of complete separation into two macroscopic domains in order to make a total Gibbs Free Energy of mixing, ΔG_M, equal to zero.

The Free Energy minimum for micelle formation may be a characteristic feature of AB di-blocks and it is treated as an Entropic contribution to the Free Energy of domain formation. This minimum opposes the phase separation due to the incompatibility of the two

components. Blocks are expected to orient to a considerable extent along the direction perpendicular to the interface between the two domains. This particular orientation/aggregation of blocks at the interface must be reflected in the small ratio of a dimension of the effectively occupied area per block chain at the interface to that of the element for each domain structure. This particular arrangement must result in rather localized internal stress within the element. This must further cause block properties to differ from those of mechanical mixtures of corresponding homopolymers.

Summarizing, one can account for fundamental domain structure with different size of domains obtained in solvent-cast films. The combination of thermodynamic and molecular parameters such as incompatibility between two block segments, the relative solvation power of a solvent for each segment, the local chain length, and the weight fraction of block segments within block polymer molecule, all influence the domain structure.

II.4.4. Methods Used in the Structural Characterization of Block Copolymers

Basically, one has three types of characterization methods to determine the structure and properties of block copolymers:

1. Dilute-solution properties. In this category, well-known methods including all kinds of viscosity measurements, IR, NMR, and light-scattering are found to be useful for the characterization of dilute-solution properties of block copolymers. These solutions are very often used for casting films.

2. Structural architecture determination. On the above mentioned films, all kinds of optical and electron microscopy, wide- and low-angle x-ray analysis are performed (often in combination with specially selected "staining" procedures for better determination of one phase).

3. Mechanical and thermal properties measurements. Finally, dynamic mechanical measurements, all kinds of tensile testing and measurements of birefringence under stress together with DSC and DTA applications are useful for verifying the structure of block copolymers.

II.5. WHOLLY AROMATIC POLYAMIDES

The space age has brought the demand for devices operating at the high rates of speed, are light in weight and withstand heat better than conventional ones. However, past technology of most man-made resins has been based on polymers that can be fabricated from their molten state. These materials lose their useful properties far short of their melting points. It was obvious that a new technology must be developed to meet some of these needs of our times.

Quoting one of the leading scientists engaged in research of these new polymers, Dr. Jack Preston of Monsanto Company's Triangle Research Park, Durham, North Carolina: "It is one of the marvels of our age that the polymer chemists were able, when it was needed most, to bring forth a whole new technology that can be used for thermally resistant polymers for films, fibers and molded parts."

Some significant applications of these new polymers include:

1. Films for electrical applications (e.g., polyimide films) which allow construction of electrical motors that are as much as 25 percent more powerful at the same weight than conventional motors.
2. Low-friction bearings that withstand higher heat loads than Nylon or Teflon.
3. Fibers for use in: industrial processes (e.g., filtration of hot gases); hazardous environments, especially when conventional fibers melt (e.g., during deceleration of military jets and space crafts after reentry into the earth's atmosphere); reinforcing applications where low creep of fibers is essential, together with high strength and thermal stability (e.g., V-belts, tires, etc.).
4. Paper from thermally stable fibers for use in electrical insulations and reinforcement.

The subject of thermally stable polymers is quite broad. Due to the fact that high-temperature use fibers are among the most important applications of the above mentioned polymers, it would be useful to limit the discussion here to fiber-forming polymers.

Why have organic fibers for high-temperature application received so much attention, when glass, carbon, ceramic and metal fibers have been available? The answer is straightforward. The organic fibers have a lower density, better ductility, greater abrasion resistance

and can be made more readily available in a wide range of diameters than the other mentioned fibers. Unlike some metallic fibers and possibly carbon fibers too, organic fibers are not conductors for electricity. In addition, some metals and glass will not withstand certain corrosive environments, e.g., acids or bases.

II.5.1. General Principles of the Thermal Stability of Polymers

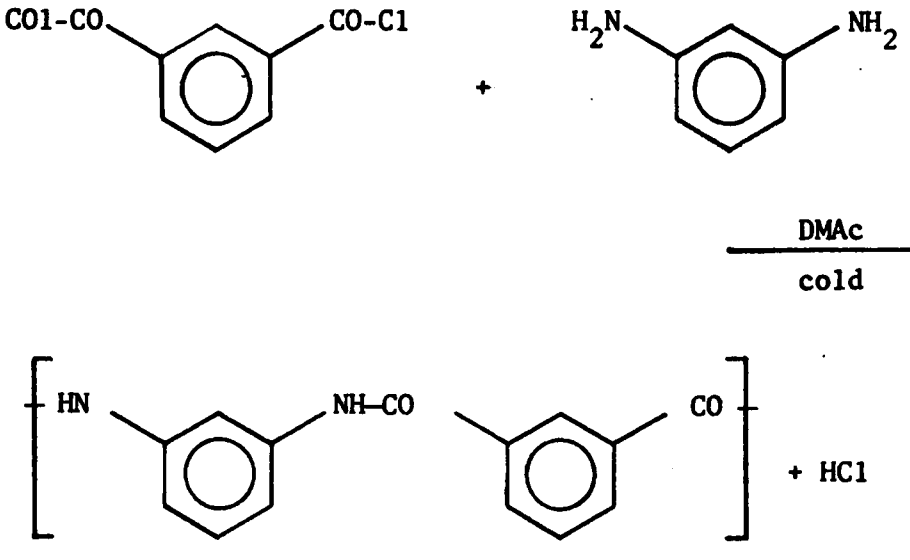
There is a very important question: What type of polymer structure should be chosen for thermally stable fibers? It has been known for many years that the maximum melting temperature for any member of a given class of organic polymers may be reached by substituting ring structures for flexible aliphatic chains. This substitution brings not only thermal stability but also increases the rigidity and dimensional stability.

Thus, polyester fibers became practical only after terephthalic acid was substituted for aliphatic diacids. In the case of polyester, a dramatic increase in thermal stability can be achieved by using a wholly aromatic system.

The real problem was not to obtain high melting polymers, but how to obtain thermally stable polymers that could be processed to films, fibers or other usefully shaped articles. Black (69) has presented a very comprehensive review of the relationship between the chemical structure of a polymer, its fabricability and final properties, particularly the tensile properties.

It is probably not surprising that the first commercial product should be a wholly aromatic polyamide. There are two important facts to be considered. The ester-linkage in polyester is less stable to attack of corrosive media than the peptide linkage in polyamides. The enhanced possibility to form H-bonds within polymers containing the peptide linkage increases the level of intermolecular forces causing in general a higher stability of the respective polymers.

DuPont Company's wholly aromatic Nylon NOMEX ^{R} represents the first available polymer (70). This material can be produced in a controlled straightforward manner by means of solution poly-condensation of two monomers, meta-phenylene diamine and isophthaloyl acid dichloride (equation 6).

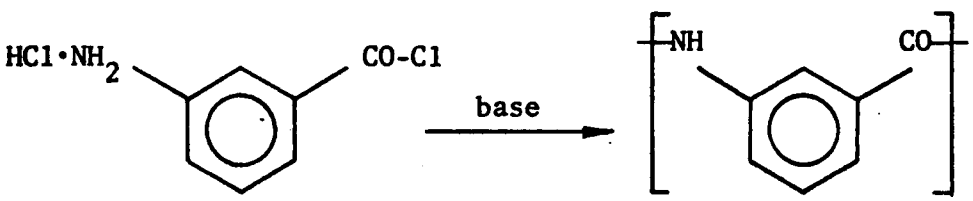


(6)

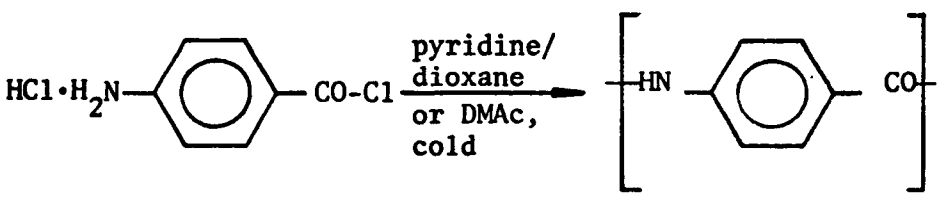
"NOMEX," Soluble in Dimethyl Acetamide,
5% Lithium Chloride

Similar polymer was prepared also by other research groups by the same or slightly modified synthetic procedures (71-82). However, NOMEX ^{R} has a softening point that is relatively low and its oxidative stability is not superior, or as good as that of some other aromatic polyamides, that have been known for quite a time (e.g., poly-terephthalamide of benzidine (83)).

The latter type of polymers are generally less soluble, are more difficult to prepare, and are considerably more difficult to spin into fibers. This is particularly true for the polybenzamides, which are made from monomers containing both an acid chloride group and an amine function (84-93). A typical reaction scheme for their preparation can be outlined as follows (equations 7 and 8):



Soluble in DMAc + 5% LiCl (7)



Soluble in conc. H_2SO_4 (8)

It can be seen that the variation in structure is limited in the case of polyamides derived from AB type monomers based on benzene rings, to all meta- or para-oriented.

Some additional latitude is gained by recourse to the polymerization of AA and BB type of monomers. In this case, basically three polymers are available: all meta-, all para-oriented and a mixed meta- and para-oriented one. While the mixed type of copolymer mentioned above was not extensively studied due to a lack of structural regularity, the all meta-oriented poly-(m-phenylene isophthalamides) (see above), and all para-oriented poly(p-phenylene terephthalamides) (70,94-106), have received extensive attention. It is quite possible that this type of wholly aromatic polyamide is the basis for additional commercially available DuPont Company's polymers, FIBER "B" or KEVLAR ^{R}. The introduction of a single para-phenylene unit into the repeat unit of simple polyamides renders the products intractable and substantially complicates the technology for the fiber spinning operation.

II.5.2. Trends to Increase Solubility of All Para-Oriented Aromatic Polyamides

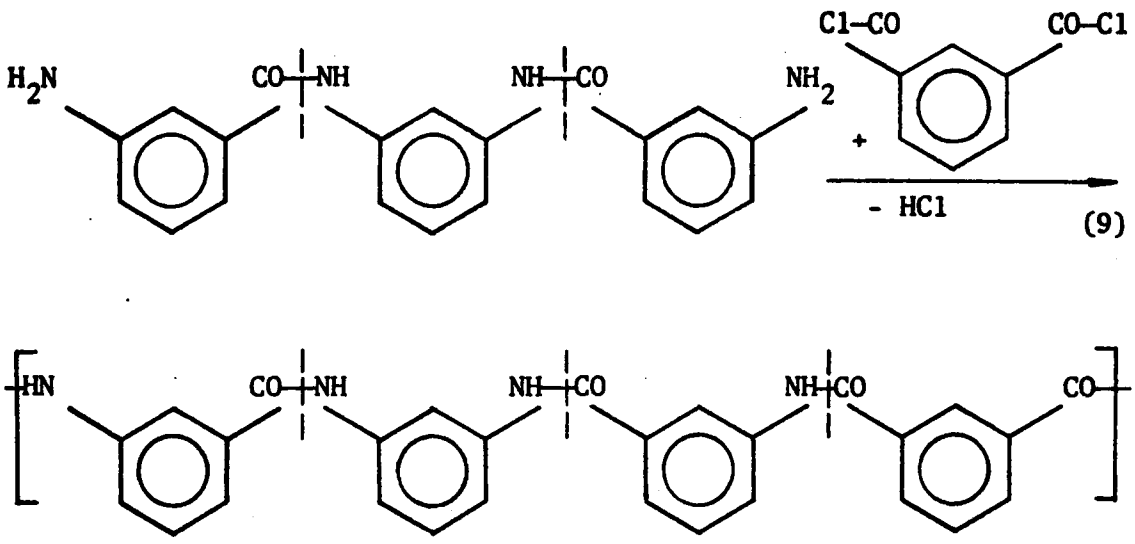
As mentioned above, the introduction of a para-phenylene unit into a wholly aromatic polyamide substantially decreases the solubility of the polymer in an already very narrow range of available organic solvents. This dilemma has existed since the first application of aromatic polyamides as thermally stable materials. The main problem consisted of improvement in solubility without a sacrifice of other, very important properties (e.g., thermal stability, high elastic modulus, etc.).

The idea of "ordered copolymers," the copolymers of so-called "limited order," and amide-heterocycle copolymers together with substitution on aromatic rings and/or amine function of meta- and para-oriented monomers previously mentioned, play a dominant role in the search for improved solubility of wholly aromatic polyamides.

Another possible approach to this problem is a subject of this proposed research. This approach will be discussed later and is based on an idea of block copolymers of aromatic polyamides with suitable linear aliphatic polymers, and possibly polysiloxanes (e.g., poly(dimethyl siloxane)).

II.5.2.1. "Ordered" and "Limited Order" Copolymers, Random Copolymers of Aromatic Polyamides

The idea of "ordered" copolymers was adopted mainly by Monsanto Company's research team (107-123) as a means of "tailoring" balanced properties of wholly aromatic polyamides. Such an effort is conducted first by preparing a difunctional unit possessing structural symmetry and then condensing it with another monomer under such conditions that no rearrangement of bonds occurs. Furthermore, the effect of structural units on the characteristic properties of the polymer can be studied in a highly systematic manner. The ordered copolymer synthesis can be illustrated by the following example (equation 9):



The component parts are arranged in a completely regular manner; there are no polymeric blocks and none of the structural units of the original species involved are touching each other. As a consequence of high chemical order that exists within these polymers, they behave like homopolymers. It should be pointed out here, that a more complex nature of repeat unit retards crystallization of these polymers from solution (when compared with all para-oriented polymers which are readily crystallizable). However, once these polymers are fabricated into films or fibers and oriented or otherwise induced to crystallize, the crystallinity that can be developed is quite high. The ability to delay crystallization until it is desired (e.g., after spinning), is a definite asset.

Some generalizations regarding structure of ordered copolymers of aromatic polyamide may be made. When increasing para-phenylene

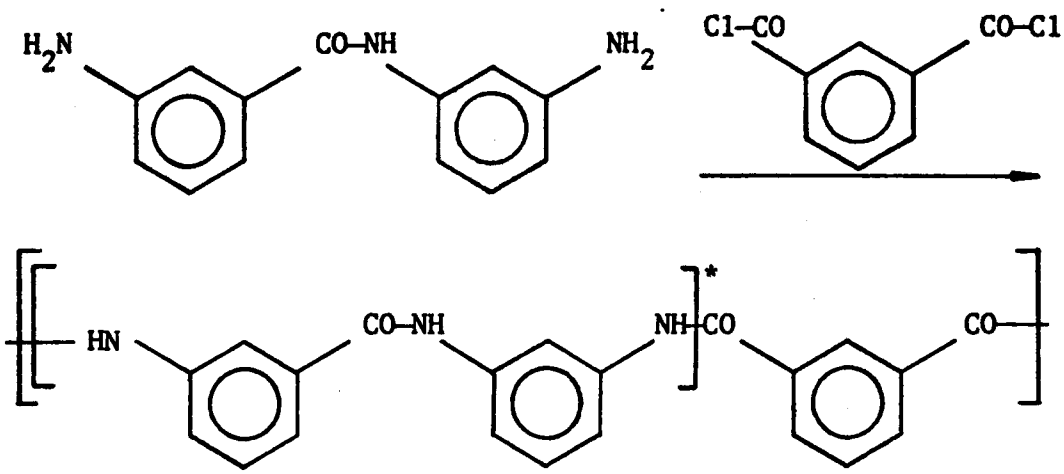
content (in both simple and ordered types) in aromatic polyamides, one can expect:

1. Solubility in organic solvents decreases.
2. Thermal and oxidative stability increases.
3. Ease of inducing crystallinity and orientation increases.
4. Tensile strength and elastic modulus of films and fibers increases (elongation-to-break decreases).

There is also a possibility of making copolymers from preformed unsymmetrical intermediates, that yield copolymers of so-called "limited order" (124). These have certain properties in common with random copolymers (although the composition is constant). For example, the melting point of all meta-oriented copolymers of "limited order" is about 290°C, whereas ordered meta-polymers melt around 400°C. The melting point of random copolymers is close to 300°C (see below).

On the other hand, all para-oriented copolymers of "limited order" have in agreement with other all para-oriented aromatic polyamides melting points as high as about 550°C. This is probably because the stiffness of such "limited order" copolymer is so great that the melting point is not much affected by irregularity in the structure (126).

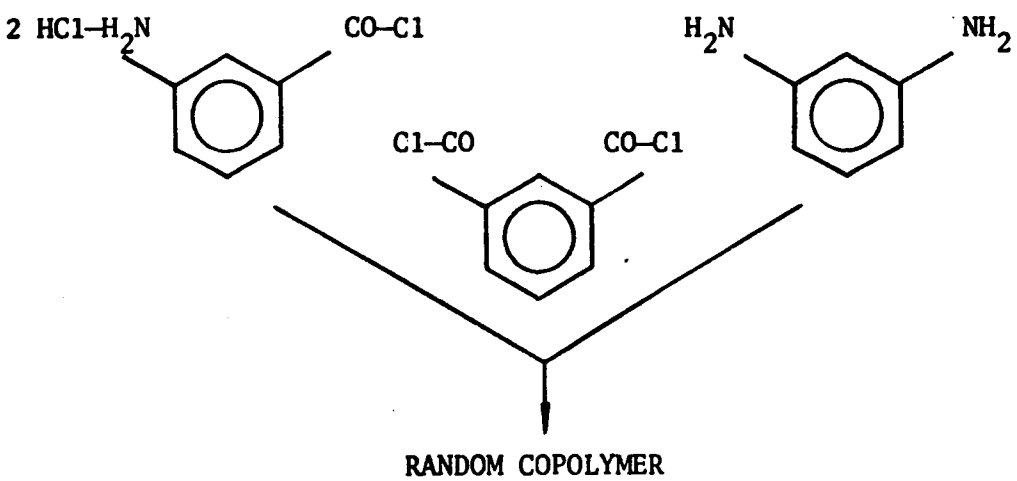
A typical synthesis of the so-called "limited order" aromatic polyamide copolymers can be outlined as follows (equation 10).



(10)

*This unit may appear in the polymer repeat unit as shown or in the reverse order because of dissymetry of the diamine used.

It might be well at this point to discuss briefly the consequence of not structuring copolymers in an ordered manner, i.e., making random copolymers. Thus, if the moieties used to make all meta-oriented ordered copolyamides are combined in random fashion from the requisite monomers and in the same ratio as they are used in the following scheme (equation 11),



(11)

a random copolymer, having a melting point temperature lower by approximately 100°C, is formed (melting point temperature compared to that of all meta-oriented, ordered copolymer).

II.5.2.2. Substituted Aromatic Rings or Amines for the Synthesis of Wholly Aromatic Polyamides

To improve the solubility of aromatic polyamides, a limited "destruction" of the close-packed, stiff, rod-like polymer chain structure can be used. To accomplish this, a substitution on the aromatic rings can be performed. Substituting "bulky" side groups (e.g., alkyls, halogens, nitro groups or even carboxy groups) on the ring structure of aromatic diacid chlorides and diamines (127-146) creates a steric hindrance effect prohibiting the closest possible packing of the aromatic polyamide chains. These substitutions, often combined with methylene bridges and/or ether linkages between aromatic rings are claimed to improve the solubility of these polymers, while characteristic properties (e.g., thermal stability, tensile strength, etc.) remain virtually unchanged.

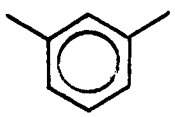
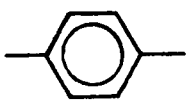
In addition to the highly regular ring structure of aromatic polyamides, H-bonding also contributes to the excellent thermal stability and resistance to organic solvents. To reduce the effect of an extensive H-bonding (between a hydrogen of an amine function and an oxygen of a carbonyl group), substitution for one hydrogen atom of an amine function is effective. Alkyl or aryl groups (147-155) are often used for this purpose. It is important to point out here that the above mentioned substitutions on an amine function not only improve

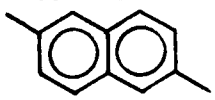
solubility, but also permanently decrease the melting point. Because the polymerization kinetic aspects are not favorable, these modifications are among the least feasible structural variations for aromatic polyamides.

II.5.2.3. Aromatic Polyamide-Heterocycle Copolymers

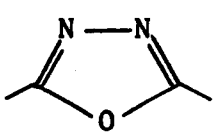
Another way to improve the solubility of aromatic polyamides is to form aromatic amide/heterocycle copolymers. A typical synthesis employed for the formation of these ordered copolymers may be illustrated by the following example (equation 12):

$$H_2N{-}R{-}H_C{-}R{-}NH_2 + Cl{-}CO{-}R'{-}CO{-}Cl \longrightarrow -(-HN{-}R{-}H_C{-}R{-}NH{-}CO{-}R'{-}CO-)- \quad (12)$$

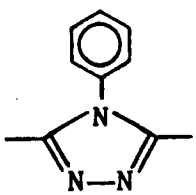
where: R - aromatic rings as  or 

R'- aromatic rings similar to R or 

$-H_C-$ - heterocyclic rings, such as:



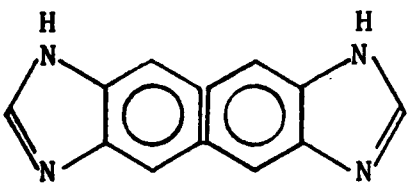
1,3,4-Oxadiaxole



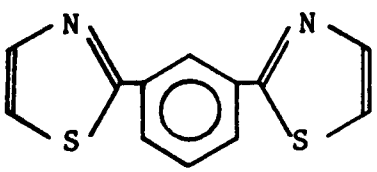
4-phenyl-1,2,4-triazole



Thiazolo 4,5-d/thiazole



2,2'-5,5'-Bibenzimidazole



m-bis-Thiazol-2-yl-benzene

The ordered amide-heterocycle copolymers, with a few notable exceptions, show higher tensile strengths at room temperature, better retention of tenacity with increase in temperature and with long-term heat-aging in air, than do wholly aromatic polyamides. This is true in the case of tensile strength at elevated temperature and on long-term heat-aging because of the lower dependence on amide bonds that are susceptible to the loss of H-bonding with an increase in temperature. The amide bonds are also sites for thermal oxidative attack on polymer chains. For long-term exposure to elevated temperature, heterocycles containing sulphur are not feasible due to rapid degradation (115,156).

The ordered aromatic amide-heterocycle copolymers are under very extensive research at the present time (109,114,115,157-172). It is believed that this approach will successfully balance the excellent stability with reasonable processability for these polymers.

II.5.2.4. Copolymers of the Aromatic Polyamide with Polyesters or Aliphatic Polyamides

The influence of aromatic rings on a predominantly aliphatic structure was studied for aliphatic polyamides as long ago as 1948 by Hill and Walker (173). Random or even ordered aliphatic-aromatic polyamide copolymers do not exhibit the properties of highly thermally stable polymers and even fractions of aliphatic polyamide within an aromatic system decrease the melting point to below or close to 300°C (174-176).

A similar situation is observed when random copolymers of an aromatic polyamide, and an aliphatic or aromatic polyester are considered (177-182). Melting points generally fall below the decomposition temperature and these materials are processable in their molten states.

II.5.3. Chemical Properties of Aromatic Polyamides

Aromatic polyamides have considerable thermal stability as shown by various researchers studying thermal degradation of aromatic polyamides (183-187). Also the role of oxygen during thermal degradation (188), and the kinetics and mechanism of thermal-oxidative stability (189) were studied.

Remarkable inertness to chemicals (i.e., common organic solvents, acids and bases) (112,190) is a definite asset; indeed, some of these polymers are spun into fibers from solution in concentrated sulphuric acid. Radiation from a gamma-source actually increases their tensile strength while slightly decreasing elongation-to-break (113).

Relatively poor behavior of thermally stable polymers is to be found in their resistance to light. Wholly aromatic polyamides are comparable in this respect to unstabilized nylons (e.g., Nylon 66) (113). It is interesting to note here that similar behavior was found also for heterocycle polymers and the development of polyoxadiazoles was terminated chiefly for this reason (191).

Although thermally stable polymers are assumed to be flame resistant, no such conclusion should be reached in the absence of experimental facts. The phenomenon of burning is not well understood, and many apparent contradictions exist. But in general, it is true that wholly aromatic polyamides resist burning much better than do aliphatic polyamides and polyesters. In any event it can be said that aromatic polyamides do not melt, run or drip and consequently are more suitable for clothing where fire is a potential hazard (192). Even in the most severe case where wholly aromatic polyamide is ignited, a protective fabric char is formed. It is quite important not to overlook the lack of dimensional stability of these polymers after being ignited. NOMEX ^{R} like polymers undergo appreciable shrinkage.

II.5.4. Methods for Characterization of Aromatic Polyamides

There is a real lack of information available in the literature describing methods used for characterization and studying the nature of aromatic polyamides. This is probably due to the confidentiality of all this information which is vitally important to the commercial production of these polymers. The most extensive source for that following information are papers published by Russian researchers.

The nature of conjugation in aromatic polyamides was studied by Belyakov et al. (193). The EPR and UV spectra and quantum-chemical calculations confirmed that poly(p-phenylene terephthalamide), poly(m-phenylene isophthalamide), and their low molecular weight

analogs, formed conjugated molecular systems. The conjugation-transmitting amide groups were tautomeric rather than present as isoamide isomers.

Broad line NMR spectra of some aromatic polyamides were taken by Wandward and Landis (194).

H-bonding effects in the glassy state of random copolyamides studied by Hatekeyama et al. (195), and the nature of thermal transitions in poly(m-phenylene isophthalamide) performed by Kuznetsov et al. (196) showed two thermomechanical transitions. The glass transition temperature, T_g, at about 280°C and crystallization temperature, T_{cryst}, at approximately 320-340°C were determined by DTA. The above determined values were confirmed by x-ray and NMR measurements. The decomposition temperature for this kind of polymer is at about 400°C. Melting of partially degraded polymer starts at 430°C. Comparing this value with a prediction of T_m from the known value of T_g as discussed by Lee and Knight (209), T_m for poly(m-phenylene isophthalamide) as reported above seems to be too low. According to the above cited work (209), the T_g/T_m ratio should be 0.63 for symmetrical polymers.

The evaluation of relative roles of the chemical kinetics and diffusion factors on polycondensation used for the preparation of aromatic polyamides, and the relation between polymer yields and intrinsic viscosities were studied by Sokolov et al. (197). Twenty-nine reactions were investigated and plots were made to describe the relation between the above mentioned phenomena.

The determination of MW of the aromatic polyamides is very important. Morozov et al. (198) have designed a method for determination of MWD of aromatic polyamides by turbidimetric titration. Khreshkov et al. (199) used automatic potentiometric titration for the determination of end groups for both amino and acid chloride functions. This end group analysis was used to determine the $\overline{M}_n$. They have checked their results by osmometry. Both obtained results are claimed to be in good agreement.

The intrinsic viscosities and Huggins constants for aromatic polyamides in different solvents were studied by Nikonov et al. (200). In pure solvents (without LiCl, which is essential for good solubility), viscosity numbers increased with decreasing concentrations, indicating the polyelectrolytic effect caused by the protonization of amide bonds. Addition of LiCl negates this phenomenon. Zakharov et al. (201) have studied the stability of concentrated solutions of poly(m-phenylene isophthalamide) in saline solvents. The viscosity of the above polymer was determined in solutions containing DMAc, LiCl and H_2O. These solvent systems formed so-called "stabilized solutions." Below 3 percent LiCl and 2 percent H_2O this stabilization was practically unnoticeable. Above 7 percent of LiCl and 5 percent H_2O, LiCl may crystallize from solution. A very effective range for stabilization is therefore between the above mentioned limits. The authors have postulated that the concentration range of the above mentioned polymer in DMAc or DMF solvents can be increased from 19 percent to 25 percent by weight when

the concentration of LiCl is increased from 3 percent to 7 percent. This increase in the solution concentration caused only a 15 percent increase in the values of intrinsic viscosities. This seems to be an important point especially for preparation of so-called spinning solutions, where the concentration dependence of viscosity plays a significant role.

CHAPTER III

SYNTHETIC PROCEDURES

This chapter covers all synthetic experimental work done to achieve the stated goals (cf. Abstract). In general, three different block copolymer structures might be obtained by utilizing an aromatic polyamide and another block cosegment: alternating $(AB)_n$ structure and ABA or BAB structures. Bearing this in mind, several synthetic routes were designed to synthesize these block configurations.

The equivalence in reactivity of the functional end groups of different species involved in these reactions was assumed in agreement with Flory's basic treatment of polycondensation reactions.

Self-regulating (slightly basic amide solvent is used as an acid scavenger) low-temperature (below 20°C) polycondensation and copolycondensation reactions were generally used in all cases. This type of polycondensation reaction seems to be the best available synthetic method at the present time.

III.1. SPECIFICATION OF CHEMICALS AND THEIR PURIFICATION

The following reactants were used for the synthesis of aromatic polyamide homopolymers and block copolymers utilizing both poly(ethylene oxide) and poly(dimethyl siloxane) cosegments:

Meta-phenylene diamine (Mol. weight 103.14 g/mole, mp 62-64°C), Aldrich Chemical Company brand, 97 percent purity was twice distilled by utilization of "molecular distillation." White, needle-like crystals were kept in a brown glass jar in a dessicator after distillation.

Isophthaloyl chloride (Mol. weight 203.03 g/mole, mp 79-81°C), Aldrich Chemical Company brand, 97 percent purity was distilled twice under vacuum at 65-70°C. White, powder-like product was then recrystallized from dry n-hexane and put into dried brown glass jars and stored in a desiccator.

Hexamethylene diisocyanate (Mol. weight 168.2 g/mole), Aldrich Chemical Company brand was used as is. Material was transferred into a dry bottle equipped with a serum-cap seal and stored in the freezer.

Poly(ethylene oxide) prepolymers (Mol. weight of 400, 1000, 4000 and 6000 g/mole), Union Carbide Corporation CARBOWAX ^{R} series of di-hydroxy terminated poly(ethylene oxides) were purified as follows: In order to remove low-molecular weight impurities the saturated solutions of each prepolymer in dry benzene were azeotropically distilled. The ternary mixture of benzene/ethanol/water (23.3 percent/ 22.8 percent/53.9 percent) boils at 64.9°C/760 mm Hg. This azetropic distillation was followed by removal of all remaining low-molecular weight components by applying vacuum to the molten polymers for 24 hours. Poly(ethylene oxides) were used in the solid state or as 25 percent solutions in DMAc.

Mono-hydroxy terminated poly(dimethyl siloxanes) ($\overline{M}_n$ = 5000, 8800 and 14200 g/mole) were prepared by anionic polymerization of dimethyl

siloxane cyclic trimer initiated by sec-BuLi within our research group by Dr. E. Firer. These all-liquid polymers were then kept over molecular sieves in bottles equipped with serum-cap seals.

Di-hydroxy terminated poly(dimethyl siloxanes) ($\overline{M}_w$ = 1480 and 5770 g/mole) were obtained as research samples from Dr. D. L. Bailey, Union Carbide Corporation Silicone Plant, Sistersville, West Virginia. These liquid polymers were purified by removal of low-molecular weight impurities utilizing vacuum for 48 hours. Then these polymers were stored over molecular sieves in sealed flasks.

N,N-dimethyl acetamide (Mol. weight 87.12 g/mole, bp 164-166°C), Aldrich Chemical Company brand, 99 percent + purity was first stirred for 6 hours with a few crystals of isophthaloyl chloride to remove any N,N-dimethyl formamide present. This chemical is believed to be a chief impurity causing complications during the synthesis. Then dry BaO was added to the solvent and stirred for 24 hours. This procedure should remove any labile-hydrogen containing impurities. Finally, the solvent was distilled under dry N_2 gas and the fraction boiling at 164-166°C was collected.

Dichloromethane (Mol. weight 85.04 g/mole, bp 39-41°C), Aldrich Chemical Company brand, was rinsed several times with water, then distilled at 39.5°C/760 mm Hg and finally stored over molecular sieves.

Triethyl amine (Mol. weight 101.04 g/mole, bp 85-91°C), Aldrich Chemical Company brand, was distilled under dry N_2 gas and the fraction boiling at 88°C/760 mm Hg was collected.

Molecular sieves, Linde's A-5 grade were used as a water scavenger.

Dry inert gas blanket was provided by dry N_2 gas. To achieve purity and dryness, N_2 gas was bubbled through concentrated H_2SO_4 and then passed through a drying column filled with layers of anhydrous $CaSO_4$ and molecular sieves.

Other chemicals mentioned in the text were used as received.

III.2. THE SYNTHESIS OF POLY(m-PHENYLENE ISOPHTHALAMIDE) HOMOPOLYMERS

As a starting point in the synthesis of the proposed block copolymers, the preparation of aromatic polyamide homopolymer was investigated. It will be shown below that these homopolymers were often used as "mother" polymers for the synthesis of a series of block copolymers.

The reaction scheme was outlined in Chapter II, equation (6). To overcome the formation of low-molecular weight polymers, approximately -40°C cooling is required at the start of the reaction. This cooling must be provided to "freeze-out" some or all of the following side reactions (203):

Transamidation by solvent (amide type):

(polyamide chain)-NH-CO-(polyamide chain) + $CH_3CO-N(CH_3)_2$

(polyamide chain)-NH-CO-CH_3 + $(CH_3)_2N$-CO-(polyamide chain)

Acylation of monomers by amide solvent:

$$H_2N\text{-}\emptyset\text{-}NH_2 + CH_3CO\text{-}N(CH_3)_2 \longrightarrow H_2N\text{-}\emptyset\text{-}NH\text{-}COCH_3 + NH(CH_3)_2$$

$$(CH_3)_2NH + ClCO\text{-}\emptyset\text{-}COCl \longrightarrow (CH_3)_2N\text{-}CO\text{-}\emptyset\text{-}COCl + HCl$$

The above mentioned side reactions can cause chain scission on part of the already formed poly(m-phenylene isophthalamide). The acylation reactions cause unbalancing of the stoichiometry of the reaction and prevent the formation of high-molecular weight polymer. The following example outlines the typical synthetic route used for preparation of poly(m-phenylene isophthalamide) based on 0.030 mole stoichiometry:

1. Into a three-neck reactor, equipped with a rapid stirring device, dry N_2 gas inlet and dry-seal tube, 3.24g of m-phenylene diamine was charged.
2. Then 20ml of DMAc was added into reactor to effect solution.
3. The solution of diamine in DMAc was cooled to approximately -45°C by the isopropanol/dry ice bath, until "slush" was formed.
4. Then 6.09g of isophthaloyl chloride was added at once to the cooled diamine solution and rinsed down by 10ml of precooled DMAc.
5. The formed "slush" was rapidly stirred for 20 minutes in the above mentioned cooling bath. Then, this cooling bath was replaced by an ice/salt bath and the reaction mixture was

moderately stirred for an additional 20 minutes. A white, thick paste was formed during that period of time indicating the formation of high-molecular weight polymer.

6. The ice/salt bath was then replaced with an ice bath only and stirring continued for an additional 10 minutes. Then, the cooling bath was removed, the reaction solution was brought to room temperature and stirred for 20 more minutes.
7. A calculated amount of LiOH dissolved in 30ml of DMAc was added to the reaction solution to neutralize the in-situ formed HCl. During this operation, a thick, clear solution forms in the reactor.
8. The reaction solution was then diluted by the addition of 30ml of DMAc and precipitated into a water/methanol bath. The polymer was filtered with a Buchner funnel, rinsed several times with coagulant and dried in vacuo. The reaction yield is approximately 95 percent.

III.3. THE "BALANCED STOICHIOMETRY APPROACH" FOR THE SYNTHESIS OF ALTERNATING $(AB)_n$ BLOCK COPOLYMERS

By using balanced stoichiometry among the three coreactants involved, a series of alternating $(AB)_n$ type of block copolymers was synthesized. The main objective was to synthesize block copolymers having high molecular weight. This restriction is essential for good spinnability, film casting and mechanical properties of these copolymers.

III.3.1. $(AB)_n$ Type of Block Copolymers of Aromatic Poly(m-Phenylene Isophthalamide) and Poly(Ethylene Oxide)

A simplified reaction scheme can be outlined as follows:

$$HO\text{-}\{\text{-PEO-}\}\text{-}OH + \underset{\text{excess}}{\text{calculated}}\ ClCO\text{-}\emptyset\text{-}COCl \xrightarrow[\text{DMAc, cold}]{\text{-HCl}}$$

$$ClCO\text{-}\emptyset\text{-}CO\text{-}O\text{-}\{\text{-PEO-}\}\text{-}O\text{-}CO\text{-}\emptyset\text{-}COCl + ClCO\text{-}\emptyset\text{-}COCl$$

$$+ \underset{\text{balance}}{\text{calculated amount for stoichiometric}}\ H_2N\text{-}\emptyset\text{-}NH_2 \xrightarrow{\text{-HCl}}$$

$$Cl\text{-}\left[\left[\text{-CO-}\emptyset\text{-O-}\{PEO\}\text{-O-CO-}\emptyset\text{-CO-}\right]\left[\text{-NH-}\emptyset\text{-NH-CO-}\emptyset\text{-CO-HN-}\emptyset\text{-NH-}\right]_x\right]_n\text{-H}$$

A typical synthetic route is outlined by the following procedure:

1. Into the reactor (set up similarly to the homopolyamide synthesis), 10ml of DMAc was charged, cooled on the isopropanol/dry ice bath to approximately -40°C.
2. Then 6.09g (0.030 mole) of isophthaloyl chloride was added into the reactor at once and rinsed down with 10ml of pre-cooled DMAc. Stirring was maintained.
3. Upon dissolution, 1.20g (0.0030 mole) of PEO 400 dissolved in 5ml of DMAc was added drop-wise to the reaction solution and rapidly stirred for 20 minutes. "Slush" formed in the reactor.
4. Then 2.92g (0.027 mole) of m-phenylene diamine was added at once and residue on funnel rinsed down with 10ml of DMAc. Temperature of cooling bath was increased to -25°C and "slush" in the reactor was rapidly stirred for an additional 15 minutes.

5. A cooling bath was then replaced with an ice/salt bath and the reaction solution was stirred for 20 more minutes.
6. After removal of the ice/salt bath, the reaction solution was brought to room temperature and moderately stirred for two hours.
7. Finally, 1.40g of $LiOH \cdot H_2O$ dissolved in 30ml of DMAc was added into reactor to neutralize the reaction solution. Polymer was precipitated into CH_3OH bath, collected on filter, rinsed many times with H_2O and CH_3OH and dried in vacuo.

Although the variation in ratio of cosegments involved was investigated, this synthetic procedure yielded copolymers having low molecular weight. As can be seen from Table I, the increase in mole-ratio of poly(ethylene oxide) lowers molecular weight of copolymer in the manner of added impurity unbalancing the stoichiometry for homo-polyamide formation.

III.3.2. $(AB)_n$ Type of Block Copolymers of Poly(m-Phenylene Isophthalamide) and Poly(Dimethyl Siloxane)

By using the following reaction scheme, several block copolymers were synthesized:

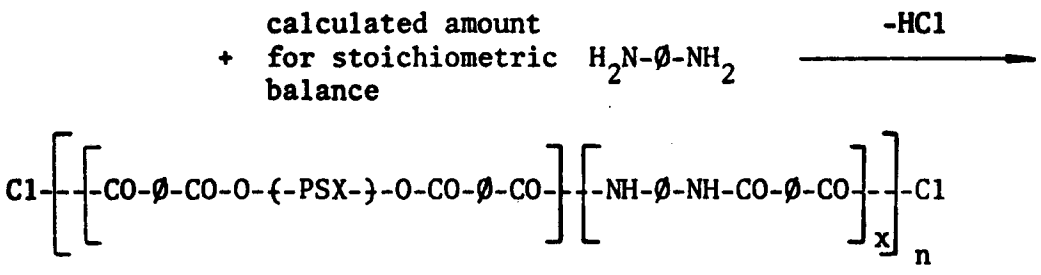
$$HO\text{-}\{\text{-}PSX\text{-}\}\text{-}OH + \underset{\text{excess}}{\text{calculated}}\ ClCO\text{-}\emptyset\text{-}COCl \xrightarrow[DMAc/CH_2Cl_2,\ cold]{-HCl}$$

$$ClCO\text{-}\emptyset\text{-}COCl + ClCO\text{-}\emptyset\text{-}CO\text{-}O\text{-}\{\text{-}PSX\text{-}\}\text{-}O\text{-}CO\text{-}\emptyset\text{-}COCl$$

TABLE I

ALTERNATING BLOCK COPOLYMERS OF POLY(m-PHENYLENE ISOPHTHALAMIDE) AND POLY(ETHYLENE OXIDE) OR POLY(DIMETHYL SILOXANE) SEGMENTS

Copolymer Code	Poly(Ethylene Oxide) or Poly(Dimethyl Siloxane) Molecular Wt. (g/mole)	Ratio of Coreactants $\phi(COCl)_2$:$\phi(NH_2)_2$:$PEO(OH)_2$:$PSX(OH)_2$ (mole)	$[\eta]$ (dl/g)
$(AE4)_n$-1	400	1.000 : 0.900 : 0.100 : ---	0.36
$(AE4)_n$-2	400	1.000 : 0.900 : 0.100 : ---	0.32
$(AE4)_n$-3	400	1.000 : 0.830 : 0.170 : ---	0.21
$(AE40)_n$-1	4000	1.000 : 0.900 : 0.100 : ---	0.28
$(AS15)_n$-1	1500	1.000 : 0.950 : --- : 0.050	0.30
$(AS50)_n$-1	5000	1.000 : 0.950 : --- : 0.050	0.32



According to the above reaction scheme, a typical synthesis is described as follows:

1. In the reactor, set up similarly to the homopolyamide synthesis, 2.217g (0.0015 mole) of poly(dimethyl siloxane) having molecular weight of 1500 g/mole (UCC's Y-7005 material) was placed and topped with 30ml of CH_2Cl_2 to affect solution.
2. Upon dissolution, 3.079g (0.0285 mole) of m-phenylene diamine was then added and rinsed down with 20ml of DMAc. The solution was cooled with an ice/salt bath.
3. Then 6.09g (0.030 mole) of isophthaloyl chloride was added to the reactants and rinsed down with 10ml of precooled DMAc and rapidly stirred for 20 minutes.
4. Then 0.20g of isophthaloyl chloride (less than $1x10^{-3}$ mole) was added to the reaction solution with rapid stirring. This step was followed by an addition of 5ml of Et_3N, and reaction solution, kept at approximately -3°C, was stirred for an additional hour.
5. Finally, 1.40g of $LiOH \cdot H_2O$ dissolved in 15ml of DMAc was added to neutralize the reaction solution. Upon addition of this reactant, a clear, oily solution was formed in the reactor.

6. Polymer was precipitated into an acetone/water bath and white, powdery precipitate was collected on filter.
7. The polymer was rinsed many times with water, acetone and chloroform and then extracted by $CHCl_3$ for 24 hours in a Soxhlet extractor.

Table I summarizes the obtained results.

In close similarity with the synthesis of $(AB)_n$ block copolymers of aromatic polyamide and poly(ethylene oxide), only low molecular weight materials were synthesized. It has been concluded that here again the added poly(dimethyl siloxane) actually unbalances the stoichiometry needed for the formation of homopolyamide, while the actual incorporation of polysiloxane remains well below the theoretically calculated amount.

The decision was then made that for the successful formation of high molecular weight block copolymers, the aromatic polyamide cosegment must be synthesized in-situ first, and then subsequent block structure formation should follow. This of course will put some restrictions on the variation in block sequence placement, and it will be discussed in the following sections.

III.4. THE "ACID CHLORIDE TERMINATION APPROACH" FOR THE SYNTHESIS OF BAB TRIBLOCK STRUCTURES

The idea to synthesize poly(m-phenylene isophthalamide) homopolymer first in a reasonable range of molecular weight, then to terminate it with isophthaloyl chloride and subsequently react with hydroxy-terminated

poly(ethylene oxide) or poly(dimethyl siloxane) was used to synthesize BAB block copolymers. It was expected that these block copolymers should possess the highest possible molecular weight. To accomplish this, a three-step synthetic route was designed and used for the entire series of block copolymers.

III.4.1. Poly(m-Phenylene Isophthalamide) and Poly(Ethylene Oxide) Triblock Copolymers Featuring "Hard" Polyamide Center Block

Using the following reaction scheme, a series of 13 different block copolymers was synthesized. CARBOWAX ^{R} poly(ethylene oxides) with molecular weights of 400, 1000, 4000 and 6000 g/mole were used in order to investigate the influence of differently-sized end blocks on the morphology and properties of these block structures.

First step:

$$n\ H_2N\text{-}\emptyset\text{-}NH_2 + n\ ClCO\text{-}\emptyset\text{-}COCl \xrightarrow[DMAc,cold]{-(2n-1)\ HCl} ClCO\text{-}\{\text{-}A\text{-}\}\text{-}NH_2$$

Second step:

$$ClCO\text{-}\{\text{-}Ar\text{-}\}\text{-}NH_2 + ClCO\text{-}\emptyset\text{-}COCl \xrightarrow[DMAc,cold]{-HCl} ClCO\text{-}\{\text{-}A\text{-}\}\text{-}COCl$$

Third step:

$$ClCO\text{-}\{\text{-}A\text{-}\}\text{-}COCl + \underset{\text{excess}}{\text{large}}\ HO\text{-}\{\text{-}PEO\text{-}\}\text{-}OH \xrightarrow[DMAc,cold]{-HCl}$$

$$H\text{-}\left[\text{--}O\text{-}\{\text{-}PEO\text{-}\}\text{-}O\text{-}\right]\left[\text{-}CO\text{-}\{\text{-}A\text{-}\}\text{-}CO\text{-}\right]\left[\text{-}O\text{-}\{\text{-}PEO\text{-}\}\text{-}O\text{--}\right]\text{-}H$$

the triblock structure

A typical reaction procedure is:

1. Approximately 20ml of aromatic homopolyamide reaction solution containing approximately 10 percent by weight of polymer was charged by syringe under dry N_2 gas into a dry 100ml reactor equipped with a stirring device. The solution was cooled to -30°C by an isopropanol/dry ice bath.
2. Then 0.50g of isophthaloyl chloride was added at once to the almost frozen reaction solution with highest possible stirring rate. During this addition the most intensive dry N_2 blanket possible was maintained over the solution of polyamide.
3. The reaction mixture was rapidly stirred for 30 minutes in the cooling bath, then brought to room temperature.
4. The excess solution of PEO in DMAc was then added and the reaction mixture was stirred overnight at room temperature. After this, 20ml of DMAc was then added to dilute the reaction solution and the copolymer was then precipitated into a warm CH_3OH bath. The reaction product was collected on a filter, rinsed many times with CH_3OH and H_2O, extracted with CH_3OH for 24 hours in a Soxhlet extractor and dried in vacuo.

This more or less "trial-and-error" synthetic route had to be used due to the lack of a reliable method for end-group analysis needed for balanced stoichiometry. It is a well-known fact that with increased polymer molecular weight, end-group analysis becomes very unreliable. In this particular case, another factor also plays an important role.

The acid chloride terminal groups are very susceptible to hydrolysis. Thus results which might be obtained from end-group analysis of carboxyl groups do not necessarily represent the number of acid chloride terminal groups available for the reaction.

Working with a large excess of some coreactants can of course cause extension of the PEO chains. The probability of a "successful collision" of hydroxy-terminated PEO with molecules of isophthaloyl chloride is considerably higher than with aromatic polyamide chains terminated with acid chloride function. This statement is based on the relative concentration of these species.

Another problem introduced by this synthetic route might be the possible chain sission via transamidation with DMAc. This might be particularly important at the increased reaction temperature maintained during this synthesis. During the final reaction stage, room temperature might enable the above mentioned transamidation. The cooling to subzero temperature of course introduces difficulties with the stirring and its retarding effect on the reaction kinetics is obvious. Table II summarizes obtained results.

III.4.2. Poly(m-Phenylene Isophthalamide) and Poly(Dimethyl Siloxane) Block Polymers with "Hard" Polyamide Center Block

The total incompatibility of the aromatic polyamide and poly(dimethyl siloxane) segments and complete insolubility of polysiloxane in DMAc or other amide solvents dictated some modifications of

TABLE II

TRIBLOCK COPOLYMERS OF POLY(m-PHENYLENE ISOPHTHALAMIDE) AND POLY(ETHYLENE OXIDE) FEATURING AROMATIC POLYAMIDE CENTER BLOCKS PREPARED BY "ACID CHLORIDE TERMINATION APPROACH"

Copolymer Code	PmPIA Reaction Solution Used	Molecular Weight of PEO Used (g/mole)	Type of Block A=PmPIA	Inherent Viscosity PmPIA Homo-polymer	Inherent Viscosity Block Copolymer
A.E4	formed in-situ	400	AB	--	0.45
E4.A_7.E4	A-7	400	BAB	0.97	0.81
E4.A_{12}-E4	A-12	400	BAB	1.10	1.15
E10.A_8.E10	A-8	1000	BAB	1.05	1.02
E10.A_9.E10	A-9	1000	BAB	1.03	0.92
E10.A_{11}.E10	A-11	1000	BAB	1.64	1.53
E10.A_{12}.E10	A-12	1000	BAB	1.10	1.04
E40.A_9.E40	A-9	4000	BAB	1.03	0.87
E40.A_{10}.E40	A-10	4000	BAB	1.31	1.05
E40.A_{11}.E40	A-11	4000	BAB	1.64	1.61
E40.A_{12}.E40	A-12	4000	BAB	1.10	1.09
E60.A_{11}.E60	A-11	6000	BAB	1.64	1.63
E60.A_{12}.E60	A-12	6000	BAB	1.10	1.08

reaction procedures for these block copolymers. A "mixed-solvent" system composed of DMAc and CH_2Cl_2 had to be used to accomplish the synthesis of 8 block copolymers by using the following reaction scheme:

First step:

Here, basically two different synthetic routes were used to synthesize poly(m-phenylene isophthalamide). The first, already described in Section III.2., utilizes amide solvent (DMAc) as the reaction medium. The second method uses a chlorohydrocarbon solvent in combination with an acid scavenger ($Et_3N/Et_3N{\cdot}HCl$ system):

$$n\ H_2N\text{-}\phi\text{-}NH_2 + n\ ClCO\text{-}\phi\text{-}COCl \xrightarrow[\text{cold}]{CH_2Cl_2,\ Et_3N\ /\ Et_3N{\cdot}HCl} ClCO\text{-}\{\text{-}A\text{-}\}\text{-}NH_2 + 2n\text{-}1\ HCl$$

Second step:

$$H_2N\text{-}\{\text{-}A\text{-}\}\text{-}COCl + \underset{\text{excess}}{\text{slight}}\ ClCO\text{-}\phi\text{-}COCl \longrightarrow ClCO\text{-}\phi\text{-}CONH\text{-}\{\text{-}A\text{-}\}\text{-}NHCO\text{-}\phi\text{-}COCl + HCl$$

Third step:

Both mono- and di-hydroxy terminated poly(dimethyl siloxanes) were used for the block copolymer formations:

$$ClCO\text{-}\{\text{-}A\text{-}\}\text{-}COCl + \underset{\text{excess}}{\text{large}}\ HO\text{-}\{\text{-}PSX\text{-}\}\text{-}OH \xrightarrow[\text{cold}]{DMAc/CH_2Cl_2}$$

$$H\text{--}\left[\text{--}O\text{-}\{\text{-}PSX\text{-}\}\text{-}O\text{--}\right]\left[\text{--}CO\text{-}\{\text{-}A\text{-}\}\text{-}CO\text{--}\right]\left[\text{--}O\text{-}\{\text{-}PSX\text{-}\}\text{-}O\text{--}\right]\text{--}H$$

The triblock structure

Focusing attention on the first step of the reaction scheme outlined above, one might use both described methods to synthesize the aromatic polyamide homopolymer. The latter mentioned route provides for a solution of the aromatic homopolyamide in CH_2Cl_2 solvent. This offers the advantage of having an aromatic polyamide in a solvent which is also a "good solvent" for poly(dimethyl siloxane). However, the dissolution power of CH_2Cl_2 for poly(m-phenylene isophthalamide) is much lower than that of DMAc. This often causes the precipitation of homopolyamide from the reaction solution and complicates the formation of block copolymer. The following procedure was used for the aromatic homopolyamide synthesis:

1. A three-neck reactor, equipped with a stirring device, dry N_2 gas inlet, a dropping funnel and dry $CaSO_4$ seal was flamed several times with a gas burner and swept with dry N_2 gas.
2. Then 9.15g of Et_3N, 5.50g $Et_3N{\cdot}HCl$ and 3.24 (0.030 mole) of m-phenylene diamine were charged into reactor and topped with 55ml of CH_2Cl_2 to affect solution. The solution was then cooled with an isopropanol/dry ice bath.
3. To the solution, 6.09g (0.030 mole) of isophthaloyl chloride was dissolved in 20ml of CH_2Cl_2 and the solution was added dropwise to the chilled solution in the reactor. Rapid stirring was provided during this addition which lasted approximately 20 minutes. White, gel-like chunks were formed in the reactor.

4. The reaction mixture was then stirred and cooled in an isopropanol/dry ice bath for 10 minutes and after this time the cooling bath was replaced with an ice/salt bath.
5. Then 20ml of DMAc was added at this point and the reaction solution was rapidly stirred for 10 additional minutes. The white chunks of precipitated polymer dissolved upon addition of the DMAc.
6. The cooling bath was replaced then with an isopropanol/dry ice bath and the reaction mixture cooled to -30°C.
7. Finally, 0.60g (less than 0.0030 mole) of isophthaloyl chloride was then dissolved in 5ml of CH_2Cl_2 and added dropwise to the reaction solution. This should provide all chain ends of the aromatic homopolyamide with acid chloride functions.
8. The reaction solution was then stirred on an ice/H_2O bath for approximately 2 hours and then 50ml of DMAc was added to it. At this stage, the reaction solution was ready for synthesis of block copolymers.

Block copolymers with aromatic homopolyamide center blocks and poly(dimethyl siloxane) end blocks were synthesized by using the following procedure:

1. A 100ml reactor equipped with a rapid stirring device was flamed with a gas burner to remove all traces of moisture and swept with dry N_2 gas. The reactor was then cooled with an ice/salt bath.

2. Then 40ml of acid chloride terminated aromatic homopolyamide solution was placed into the reactor and cooled with the ice/salt bath. At this point an estimated excess of mono- or di-hydroxy terminated poly(dimethyl siloxane) dissolved in CH_2Cl_2 was added dropwise over an extended period of time. During this addition rapid stirring was maintained.
3. A cloudy solution formed during the addition of poly(dimethyl siloxane). It was rapidly stirred for approximately 4 hours in an ice/H_2O bath.
4. The polymer was then precipitated in an acetone/water bath, collected on a filter, rinsed many times with $(CH_3)_2CO$ and extracted for 24 hours with $CHCl_3$ in a Soxhlet extractor.
5. The polymer was then dried <u>in vacuo</u> until a constant weight was reached.

The introduction of an additional solvent (CH_2Cl_2) into this reaction procedure required for the dissolution of poly(dimethyl siloxane) might have an adverse effect on copolycondensation. The presence of CH_2Cl_2 lowers the dissolution power of the solvent required for maintaining a homogeneous solution of aromatic homopolyamide. Its frequent precipitation from the "mixed-solvent" system must be "balanced-off" by the addition of DMAc. This addition then dilutes the concentration of reactants and in fact lowers the probability of successful incorporation of poly(dimethyl siloxane) in the block copolymer. Table III reports the experimental results.

TABLE III

TRIBLOCK COPOLYMERS OF POLY(m-PHENYLENE ISOPHTHALAMIDE) AND POLY(DIMETHYL SILOXANE) FEATURING AROMATIC POLYAMIDE CENTER BLOCKS PREPARED BY "ACID CHLORIDE TERMINATION APPROACH"

Copolymer Code	PmPIA Reaction Solution Used	Molecular Weight of PSX Used (g/mole)	Terminal Functionality of Polysiloxane	Inherent Viscosity PmPIA Homo-polymer	Inherent Viscosity Block-Copolymer
S15.A_{18}.S15	A-18	1500	di-hydroxy	0.85	0.87
S50.A_{13}.S50	A-13	5000	mono-hydroxy	0.96	0.86
S50.A_{18}.S50	A-18	5000	mono-hydroxy	0.85	0.86
S90.A_{13}.S90	A-13	9000	mono-hydroxy	0.96	0.95
S90.A_{18}.S90	A-18	9000	mono-hydroxy	0.85	0.85
S140-A_{13}.S140	A-13	14000	mono-hydroxy	0.96	1.04
S140.A_{14}.S140	A-14	14000	mono-hydroxy	1.10	0.69
S140.A_{15}.S140	A-15	14000	mono-hydroxy	1.58	1.05

III.5. THE SYNTHESIS OF TRIBLOCK COPOLYMERS FEATURING A "SOFT" CENTER BLOCK AND AROMATIC POLYAMIDE END BLOCKS

After developing the synthetic procedures for the triblock structures as described above, the next step was to investigate the possibility of preparing the triblock with the "soft" center block. "Soft" center blocks of poly(ethylene oxide) and poly(dimethyl siloxane) were used in a range of molecular weights. The "hard" end segments used was poly(m-phenylene isophthalamide) homopolymer. Two distinctly different synthetic routes were designed, one for each type of "soft" center block. The main problem faced was to overcome the formation of low molecular weight compounds. Both these synthetic routes were in fact the modifications of the above described "acid chloride termination approach."

III.5.1. Triblock Structures of Poly(m-Phenylene Isophthalamide) and Poly(Ethylene Oxide) Center Blocks

Isophthaloyl chloride can be used to place an acid chloride function on each end of the hydroxy-terminated poly(ethylene oxide) chains. If aromatic polyamide chains grow at each end of the acid chloride terminated poly(ethylene oxide), then a successful synthesis of herein considered block copolymer will be accomplished.

A series of 6 block copolymers was prepared according to the reaction scheme outlined below. Poly(ethylene oxides) with molecular weights of 1000, 4000 and 6000 g/mole were the "soft" center blocks.

The three-step synthesis was adapted in order to place poly(ethylene oxide) in between two homopolyamide end blocks.

First step:

Acid chloride termination of poly(ethylene oxide) chains

$$n\ HO\text{-}\{\text{-PEO-}\}\text{-}OH + 2n\ ClCO\text{-}\phi\text{-}COCl \xrightarrow[\text{cold}]{\text{DMAc}}$$

$$2n\text{-}2\ HCl + ClCO\text{-}\phi\text{-}CO\text{-}O\text{-}\{\text{-PEO-}\}\text{-}O\text{-}CO\text{-}\phi\text{-}COCl$$

Second step:

Diamine retermination of poly(ethylene oxide) chains

$$n\ ClCO\text{-}\phi\text{-}CO\text{-}O\text{-}\{\text{-PEO-}\}\text{-}O\text{-}CO\text{-}\phi\text{-}COCl + \text{calculated stoichimotric amount } H_2N\text{-}\phi\text{-}NH_2 \xrightarrow[\text{cold}]{\text{DMAc}}$$

$$HCl + H_2N\text{-}\phi\text{-}NH_2 + H_2N\text{-}\phi\text{-}NHCO\text{-}\phi\text{-}CO\text{-}O\text{-}\{\text{-PEO-}\}\text{-}O\text{-}CO\text{-}\phi\text{-}CONH\text{-}\phi\text{-}NH_2$$

Third step:

Block copolymer formation

$$H_2N\text{-}\phi\text{-}NHCO\text{-}\phi\text{-}CO\text{-}O\text{-}\{\text{-PEO-}\}\text{-}O\text{-}CO\text{-}\phi\text{-}CONH\text{-}\phi\text{-}NH_2 + H_2N\text{-}\phi\text{-}NH_2 +$$

$$\text{calculated stoichiometric amount } ClCO\text{-}\phi\text{-}COCl \xrightarrow[\text{DMAc, cold}]{\text{-HCl}}$$

$$H\text{--}\left[\text{-NH-}\{\text{-A-}\}\text{-CO-}\right]\left[\text{-O-}\{\text{-PEO-}\}\text{-O-}\right]\left[\text{-CO-}\{\text{-A-}\}\text{-NH-}\right]\text{--}H$$

The triblock structure

The -40°C dry ice/isopropanol cooling procedure could not be used in this case due to freezing of the reaction mixture in the reactor. For this reason, only an ice/salt cooling bath was used. Variation in the mole-ratio of coreactants was used to accomplish different amounts of poly(ethylene oxide) incorporated into the block copolymer system. In all cases, perfectly balanced stoichiometry among the involved reactive groups was maintained within the scope of available methods. The following step-by-step procedure describes a typical synthesis.

1. A three-neck reactor, at this point equipped with a connection to vacuum source, was heated with a gas burner and swept with dry N_2 gas.
2. Then 6.75g (1.0×10^{-3} mole) of CARBOWAX 6000 ($\overline{M}_w$ = 6750 g/mole) was charged into the reactor, melted by a 50°C warm water bath and all possibly present low molecular weight impurities were removed under vacuum for 24 hours. Then the polymer solidified on removal of warm bath.
3. A dry N_2 gas blanket was introduced into the reactor and the reactor set up was modified for a typical polycondensation reaction, as described previously.
4. For the dissolution of PEO, 60ml of DMAc was added into the reactor, providing approximately 10 percent solution by weight, and the solution was cooled in an ice/salt bath.
5. Then 0.407g (2.0×10^{-3} mole) of isophthaloyl chloride was added at once to the rapidly stirred reaction solution, rinsed down by 5ml of precooled DMAc, and then stirred for 30 minutes in the ice/salt bath.

6. Then 4.32g (0.04 mole) of m-phenylene diamine was added to the reaction mixture and rinsed down with 5ml of precooled DMAc. The mixture was intensively stirred for 10 minutes in the ice/salt bath.
7. Finally, 7.92g (0.039 mole) of isophthaloyl chloride was added at once and rinsed down by 10ml of precooled DMAc, and then the reaction mixture was rapidly stirred in the ice/salt bath for 3-1/2 hours.
8. The polymer was precipitated into a methanol/water bath, collected on a filter, rinsed many times with methanol and dried in vacuo to constant weight.

The obtained results are summarized in Table IV. As can be seen from this table, a broad variety of theoretically expected incorporation of poly(ethylene oxide) was considered. However, it would be misleading to believe that these expectations would be really accomplished. A lack of maintaining at least -30°C reaction temperature will most probably introduce the occurrence of the previously discussed side reactions, which in fact can substantially unbalance the entire stoichiometry of the reaction. In addition to that, a possible reaction between DMAc and poly(ethylene oxide) might occur causing some chain scission of polyether (204).

The determination of the exact hydroxyl content of poly(ethylene oxide) by end-group analysis according to (202) does not show consistent results (204) and therefore an additional factor unbalancing the

TABLE IV

TRIBLOCK COPOLYMERS OF POLY(m-PHENYLENE ISOPHTHALAMIDE) AND POLY(ETHYLENE OXIDE) CENTER BLOCKS

Copolymer Code	Inherent Viscosity 0.5% Solution	Molecular Weight of PEO Used (g/mole)	Mole Ratio of Coreactants $\emptyset(HN_2)$: $\emptyset(COCl)_2$: ClCO-PEO--COCl	Wt.% of $\{CH_2CH_2O\}$ Theoretical	Found
A.E10.A-1	1.03	1000	0.040 : 0.039 : 0.001	9.0	6.0
A.E10.A-2	0.70	1000	0.030 : 0.029 : 0.001	12.0	7.0
A.E40.A-1	0.91	4000	0.040 : 0.039 : 0.001	28.0	12.0
A.E40.A-2	1.02	4000	0.030 : 0.029 : 0.001	32.0	13.0
A.E60.A-1	0.76	6000	0.040 : 0.040 : 0.001	41.0	15.0
A.E60.A-2	0.77	6000	0.030 : 0.029 : 0.001	49.0	26.0

stoichiometry might be introduced here. And of course in-situ "purification" of poly(ethylene oxide) by vacuum stripping without the chance for correct reweighing of the charged polymer might introduce an additional source of error with respect to the stoichiometry of the reaction.

III.5.2. Triblock Copolymers of Poly(m-Phenylene Isophthalamide) and Poly(Dimethyl Siloxane) Center Blocks

A similar approach as described in Section III.5.1 was used to synthesize poly(dimethyl siloxane) center block copolymers. The only difference was to modify the synthetic procedure to a "mixed-solvent" system to overcome the insolubility of poly(dimethyl siloxane) in amide solvents. In order to accomplish that, the mixture of DMAc and CH_2Cl_2 solvents was used. A typical reaction procedure of 0.03 mole overall stoichiometry with $1.0x10^{-3}$ mole of poly(dimethyl siloxane) coreactant is outlined as follows:

1. A reactor set up for synthesis as previously described was used.
2. Then 5.768g ($1.0x10^{-3}$ mole) of poly(dimethyl siloxane (UCC sample Y-5900) was charged into the reactor and topped with 20ml of CH_2Cl_2 to affect solution. This approximately 20 percent solution was chilled to -30°C.
3. Upon dissolution, 0.814g ($2.0x10^{-3}$ mole) of isophthaloyl chloride was added to the reaction solution and rinsed down with 10ml of precooled DMAc. The reaction solution was then

cooled by an isopropanol/dry ice bath. Vigorous stirring was maintained for 15 minutes.

4. Then 3.24g (0.03 mole) of m-phenylene diamine was added to the reaction solution and rinsed down by 10ml of precooled DMAc. The reaction mixture was rapidly stirred for 15 minutes in the above mentioned cooling bath.
5. Finally, 5.89g (0.029 mole) of isophthaloyl chloride was then added to the reaction solution and rinsed down by 10ml of precooled CH_2Cl_2. Very intensive stirring was provided for an additional 30 minutes while the reaction solution was kept at approximately -25°C.
6. The isopropanol/dry ice bath was then replaced with an ice bath, and the reaction mixture was moderately stirred for 2 more hours.
7. A slightly yellow reaction solution was precipitated into an acetone/water bath (4:1 composition), the polymer collected on a filter, rinsed many times with $(CH_3)_2CO$ and CH_2Cl_2, extracted with $CHCl_3$ in a Soxhlet extractor for 24 hours and dried <u>in vacuo</u> to constant weight.

Table V reports the experimental results.

The formation of relatively low molecular weight copolymers resulted from this synthesis. Therefore it was necessary to look for another synthetic route to prepare block copolymers having poly(dimethyl siloxane) center blocks. In order to fulfill this, the "split-synthesis approach" was designed and will be described in Section III.7.

TABLE V

TRIBLOCK COPOLYMERS OF POLY(m-PHENYLENE ISOPHTHALAMIDE) AND POLY(DIMETHYL SILOXANE) CENTER BLOCKS

Copolymer Code	Inherent Viscosity 0.5% Solution	Molecular Wt. of Poly-siloxane Used (g/mole)	Mole Ratio of Coreactants $\emptyset(NH_2)_2$: $\emptyset(COCl)_2$: $PSX(COCl)_2$	Wt.% of Siloxane Incorporated Theoretical	Found
A.S15.A-1	0.60	1500	0.030 : 0.029 : 0.001	15.0	13.8
A.S15.A-2	0.43	1500	0.030 : 0.028 : 0.002	30.0	13.3
A.S60.A-1	0.57	6000	0.030 : 0.029 : 0.001	41.0	12.3
A.S60.A-2	0.59	6000	0.030 : 0.030 : 0.0285	55.0	14.1

III.6. THE "DIISOCYANATE COUPLING APPROACH" FOR THE SYNTHESIS OF BLOCK COPOLYMERS OF POLY(m-PHENYLENE ISOPHTHALAMIDE) AND POLY(ETHYLENE OXIDE)

The high reactivity of an isocyanate group toward any compound possessing a "labile" hydrogen was the basis for investigating the possibility to employ this approach for the synthesis of block copolymers. A series of copolymers were synthesized and believed to be of any type of block copolymer structure, e.g., $(AB)_n$, ABA or BAB.

A multi-step synthetic route was used to prepare these block copolymers. The difference in the sequence placement within these block copolymers has imposed several variations on synthetic procedures as can be seen from the following reaction schemes:

For randomly alternating or diblock structures

$$HO\text{-}\{\text{-PEO-}\}\text{-}OH + \underset{\text{excess}}{\text{8-10 fold}} OCN\text{-}\{\text{-}CH_2\text{-}\}_6NCO \longrightarrow$$

$$OCN\text{-}(CH_2)_6\text{-NH-CO-O-}\{\text{-PEO-}\}\text{-O-CO-NH-}(CH_2)_6\text{-NCO}$$

$$+ \; H_2N\text{-}\{\text{-A-}\}\text{-COOH} \longrightarrow$$

$$H\text{-}\left[\left[\text{-NH-}\{\text{-A-}\}\text{-CO-O-}\right]\left[\text{-CO-NH-(R)-NH-CO-O-}\{\text{-PEO-}\}\text{-O-CO-NH-(R)-NH-CO-}\right]\right]_x\text{-OH}$$

where: x = n for randomly alternating block structure

x = 1 for diblock structure

For triblock structure having aromatic polyamide center block

Diamine termination of polyamide chains

$$ClCO\text{-}\{\text{-A-}\}\text{-}NH_2 + H_2N\text{-}\emptyset\text{-}NH_2 \xrightarrow[\text{DMAc, cold}]{\text{-HCl}} H_2N\text{-}\{\text{-A-}\}\text{-}NH_2$$

Block copolymer formation

$$H_2N\text{-}\{\text{-A-}\}\text{-}NH_2 \;+\; \underset{\text{excess}}{\overset{\text{large}}{}}\; OCN\text{-}\{\text{-PEO-}\}\text{-}NCO \xrightarrow[\text{cold}]{\text{DMAc/Et}_3\text{N}}$$

$$H\text{--}\left[\text{--O-CO-NH-}\{\text{-PEO-}\}\text{-NH-CO-O-}\right]\left[\text{-NH-}\{\text{-A-}\}\text{-NH-}\right]\left[\text{-O-CO-NH-}\{\text{-PEO-}\}\text{-NHCO}\right]OH$$

Due to the specific requirements for preparation of each block structure and due to the lack of expected results, no typical synthetic procedure will be mentioned here. However, it should be pointed out that the excess of hexamethylene diisocyanate was distilled off from the reaction mixture by the use of vacuum distillation. Extremely anhydrous conditions were imposed during the handling of either diisocyanate or diisocyanate-capped poly(ethylene oxide). Finally, the latter mentioned material was added in proportionally large amounts to the polyamide solution.

These synthetic routes introduced undesirable species to the block copolymer structure. First, the hexamethylene diisocyanate moieties might have introduced an additional source of chain flexibility. Although it is recognized that this might be overcome by the use of toluene diisocyanate, the fact of inequality of the isocyanate groups (one being already reacted) partially restricts its use. Second, from the thermal stability point of view, the carbamate linkage is essentially stable only to 220-240°C, which in general lowers the thermal stability of these block copolymers. Table VI reports the experimental results.

TABLE VI

BLOCK COPOLYMERS OF POLY(m-PHENYLENE ISOPHTHALAMIDE) AND POLY(ETHYLENE OXIDE) PREPARED BY "DIISOCYANATE COUPLING APPROACH"

Copolymer Code	Molecular Weight of PEO Used (g/mole)	PmPIA Homo-polymer Used	Type of Block Expected A=PmPIA	Inherent Viscosity PmPIA Homo-polymer	Inherent Viscosity Block Copolymer
$(E4.A_4)_n$-Is.*)	PEO 400 HDI-capped**)	A-4	$(AB)_n$	0.64	0.36
$(E4.A_{1,2.})_n$-Is.	PEO 400 HDI-capped	A-2 A-1	$(AB)_n$	0.19 0.14	0.24
$E4.A_{1,2}.E4$-Is.	HDI-capped	A-1	BAB	0.14	0.26
$E4.A_{1,2}$-Is	HDI-capped	A-1	AB	0.14	0.30
$E4.A_7.E4$-Is.	HDI-capped	A-7	BAB	0.97	0.84
$E10.A_8.E10$-Is.	PEO 1000 HDI-capped	A-8	BAB	1.23	1.15

*-Is. represents the above mentioned synthetic approach.

**HDI-capped stands for poly(ethylene oxide) with both terminal groups converted into -NCO functions.

III.7. THE "SPLIT-SYNTHESIS" FOR THE FORMATION OF BLOCK COPOLYMERS OF POLY(m-PHENYLENE ISOPHTHALAMIDE) AND POLY(DIMETHYL SILOXANE)

It was recognized that to obtain fairly high molecular weight block copolymers of aromatic polyamide with poly(dimethyl siloxane), one must first prepare high MW poly(m-pheylene isophthalamide). Then copolymer formation could be attained by condensing properly terminated poly(dimethyl siloxane) with poly(m-phenylene isophthalamide). The "acid chloride termination approach" yields copolymers having either aromatic polyamide center blocks or possibly the diblock structure. Therefore, additional synthetic routes had to be designed to explore the synthesis of block copolymers with poly(dimethyl siloxane) center blocks.

Basically, one is limited to the principles already stated. There is no room for any "exotic" speculation due to the nature of aromatic homopolyamide synthesis. Additional restrictions with respect to the suitable solvents for both homopolymers even further limits the scale of possible combinations which might lead to successful block copolymer formation. As mentioned previously, poly(dimethyl siloxanes) are not soluble in the solvents required for successful polycondensation yielding high molecular weight aromatic polyamides. This suggests possible recourse to a modified interfacial copolycondensation. Modified in the sense of having two homopolymeric solutions, each containing appropriate functions for reaction. Vigorous stirring must then be provided in order to increase the probability of "successful collisions" of moieties bearing opposite functions.

"Split-synthesis" was designed as the best possible method to solve the above introduced problems. The preparation of amine-terminated homopolyamide chains, acid chloride capped poly(dimethyl siloxane), and the elimination of any prolonged storage of any pre-polymer are the main highlights of this synthetic route. This synthetic approach requires two separate reactors, each used for preparation of one prepolymer. The reaction design theoretically provides for synthesis of two types of block copolymers having poly(dimethyl siloxane) center or end blocks.

A series of 8 block copolymers was prepared by the following reaction scheme:

Acid chloride termination of poly(dimethyl siloxane)

$$HO\text{-}\{\text{-}PSX\text{-}\}\text{-}OH + 2\ ClCO\text{-}\phi\text{-}COCl \xrightarrow[\text{cold}]{CH_2Cl_2\ /\ Et_3N} 2\ HCl +$$

$$ClCO\text{-}\phi\text{-}CO\text{--}O\text{-}\{\text{-}PSX\text{-}\}\text{-}O\text{-}CO\text{-}\phi\text{-}COCl$$

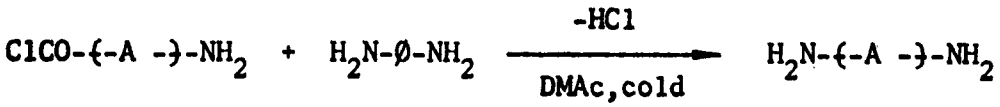
There is room for a variation of the stoichiometry in order to extend poly(dimethyl siloxane) chains. For example:

$$3\ ClCO\text{-}\phi\text{-}COCl + 2\ HO\text{-}\{\text{-}PSX\text{-}\}\text{-}OH \xrightarrow[\text{cold}]{CH_2Cl_2\ /\ Et_3N} 4\ HCl +$$

$$ClCO\text{-}\phi\text{-}CO\text{--}O\text{-}\{\text{-}PSX\text{-}\}\text{-}O\text{--}CO\text{-}\phi\text{-}CO\text{--}O\text{-}\{\text{-}PSX\text{-}\}\text{-}O\text{--}CO\text{-}\phi\text{-}COCl$$

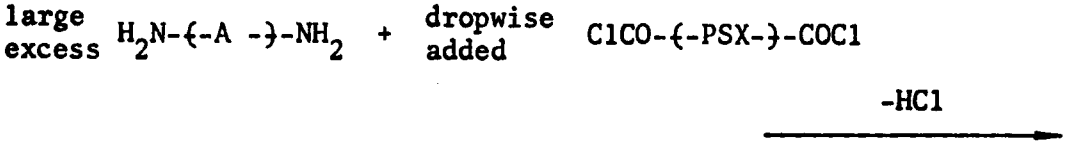
Diamine capped aromatic polyamide homopolymer

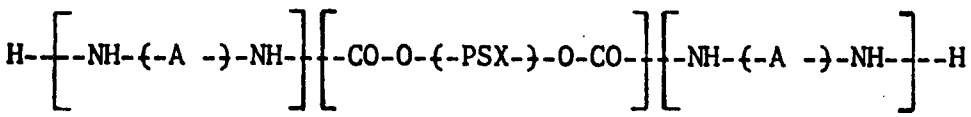
$$n\ ClCO\text{-}\phi\text{-}COCl + n\ H_2N\text{-}\phi\text{-}NH_2 \xrightarrow[DMAc,\text{cold}]{-(2n-1)HCl} ClCO\text{-}\{\text{-}A\ \text{-}\}\text{-}NH_2$$



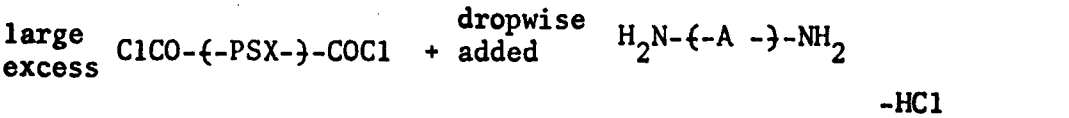
Block structure formation

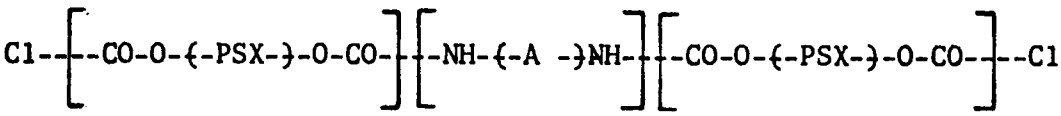
For ABA triblock structure (A=aromatic polyamide, B=polysiloxane)





For BAB triblock structure





The typical reaction procedure in a step-by-step manner can be outlined as follows:

Reactor "A"--aromatic homopolyamide preparation

1. By the use of 0.040 mole stoichiometry, the poly(m-phenylene isophthalamide) homopolyamide was prepared. Previously described reaction conditions produced approximately 120ml of the reaction solution containing 8 percent polymer by weight. The solution was cooled to -30°C and under a blanket of dry N_2 gas.

2. Then 0.50g of m-phenylene diamine was added to the reaction solution and the content of the reactor was rapidly stirred for 20 minutes in an ice/salt cooling bath. This step provides for amine capped polyamide chains.
3. Upon this termination, 40ml of the reaction solution was taken from the reactor by a syringe under a dry N_2 gas blanket, precipitated into H_2O bath, collected on a filter, and dried in vacuo. The polymer was then used for characterization of homopolyamide which was used for block copolymer formation.
4. At this point approximately 75-80ml of homopolyamide reaction solution remained in the reactor.

Reactor "B"--the formation of acid chloride capped poly(dimethyl siloxane) chains

1. Into the reactor which was assembled for polycondensation, 2.44g (0.012 mole) of isophthaloyl chloride (calculated two-fold excess) was charged and placed in an isopropanol/dry ice bath. Then 15ml of DMAc was added to effect solution.
2. After -30°C was reached, approximately 1ml of Et_3N was added to the reactor and the solution was moderately stirred.
3. Then 17.304g (0.0030 mole) of poly(dimethyl siloxane) (UCC's sample Y-5900) dissolved in 25ml of CH_2Cl_2 (approximately 43ml of solution) was added dropwise into the reactor, and vigorous stirring was maintained. The reaction mixture was rapidly stirred for 30 minutes in the isopropanol/dry ice bath. Due to the presence of poly(dimethyl siloxane), the contents of the reactor did not freeze.

4. At this time, 60ml of the polymer in the DMAc/CH_2Cl_2 solvent system was available for synthesis of block copolymers.

Block copolymer formation

Prior to any attempt in block copolymer synthesis, several "preliminary steps" had to be done. From the reactor "A," 30ml of the homopolyamide reaction solution was taken by a syringe and placed into a polyethylene bag simulating a "dry box." Reactor "A" then contained approximately 50ml of homopolymer solution. At the same time, 25ml of the solution of acid chloride capped poly(dimethyl siloxane) from reactor "B" was put aside in a syringe under a dry N_2 gas blanket.

The formation of ABA triblock structure in the reactor "A"

1. 25ml of acid chloride capped poly(dimethyl siloxane) solution was added dropwise to the 50ml of aromatic homopolyamide reaction solution, which was maintained at -39°C and vigorously stirred.
2. The isopropanol/dry ice bath was replaced by an ice bath and the reaction mixture was moderately stirred for 5 hours.
3. The polymer was precipitated into a $(CH_3)_2CO/H_2O$ bath, collected on a filter, rinsed many times with $(CH_3)_2CO$, extracted for 24 hours with hot $CHCl_3$, and dried in vacuo.

The formation of BAB block copolymer structure in the reactor "B"

The aromatic homopolyamide center block copolymers were prepared under the same conditions as the ABA triblocks. The only difference was in a reversed addition of one prepolymer solution into the other according to the reaction scheme outlined above. Table VII summarizes obtained experimental results.

TABLE VII

BLOCK COPOLYMERS OF POLY(m-PHENYLENE ISOPHTHALAMIDE) AND POLY(DIMETHYL SILOXANE) PREPARED BY "SPLIT-SYNTHESIS APPROACH"

Copolymer Code	Molecular Weight of Polysiloxane Used (g/mole)*	PmPIA Homopolymer Used	Type of Block A-PmPIA	Inherent Viscosity PmPIA Homopolymer	Inherent Viscosity Block Copolymer
S15.A_{18}.S15	1500	A-18	BAB	0.85	0.71
S60.A_{16}.S60	6000	A-16	BAB	1.79	1.68
S60.A_{17}.S60	6000	A-17	BAB	0.73	0.70
S60.A_{18}.S60	6000	A-18	BAB	0.85	0.73
A_{18}.S15.A_{18}	1500	A-18	ABA	0.85	0.77
A_{16}.S60.A_{16}	6000	A-16	ABA	1.79	1.68
A_{17}.S60.A_{17}	6000	A-17	ABA	0.73	0.78
A_{18}.S60.A_{18}	6000	A-18	ABA	0.85	0.80

*All poly(dimethyl siloxanes) used were di-hydroxy terminated materials.

CHAPTER IV

CHARACTERIZATION OF THE SYNTHESIZED MATERIALS AND OBTAINED RESULTS

IV.1. MOLECULAR-LEVEL PROPERTIES

IV.1.1. The Determination of Viscosity and Molecular Weight

The Mark-Houwink relationship $\eta = KM^a$ (if K and a are known for particular polymer/solvent pairs) is frequently used for the determination of viscosity-average molecular weight ($\bar{M}_v$) of polymers. A much more complicated case exists, however, for the determination of molecular weight of block copolymers. Although there are several methods generally used for this determination (e.g., light-scattering, U-centrifugation, etc.), none of these techniques were available for general use. Therefore, measurements of the inherent viscosity and in some cases also intrinsic viscosities were the only methods used for the determination of the size of synthesized macromolecules.

The inherent viscosity of 0.5 percent solution of polymer in DMAc • 5 percent LiCl was measured by a Ubelohde viscometer at 25°C. This viscosity was measured for all synthesized materials.

Intrinsic viscosities of aromatic homopolyamides were determined by extrapolation of different readings of inherent viscosity (each for a different concentration of measured solution) to the "zero" concentration. These data were then used for calculation of $\bar{M}_v$ of synthesized

aromatic homopolyamides. The Mark-Houwink equation with K and a determined by Burke (205) for (MMM)-P type of homopolyamide structure (M-meta, P-para linkages) in the form

$$[\eta] = 2.6 \times 10^{-4} \bar{M}_v \, 0.77$$

was used for calculation of $\bar{M}_v$ and the data obtained are collected in Table VIII.

After enough data regarding inherent viscosity, intrinsic viscosity, and $\bar{M}_v$ were collected for the first 10 poly(m-phenylene isophthalamides), a graph expressing the relationship among them was drawn (see Figure 1). That step eliminated laborious determination of intrinsic viscosity for each following aromatic homopolyamide and was used for the estimation of $\bar{M}_v$ of these polymers. The "eyeball" technique was used for the drawing of those lines.

As pointed out previously, the inherent viscosity was measured for each block copolymer reported here. Due to the fact that data were reported for each type of block copolymer structure (Tables I through VII, pages 45, 51, 56, 61, 64, 67, and 73, respectively), no summary review is presented here.

IV.1.2. Solubility Studies

One of the goals of this research was to improve the solubility of aromatic homopolyamide via the formation of its block copolymers with another polymeric segment. It has been observed (200), that upon dissolution of aromatic homopolyamides, the inherent viscosity increased

TABLE VIII

VISCOSITY-AVERAGE MOLECULAR WEIGHT DETERMINATION FOR POLY(m-PHENYLENE ISOPHTHALAMIDE) HOMOPOLYMERS

Polymer	Inherent Viscosity 0.5% Solution	Intrinsic Viscosity	$\bar{M}_v$ *
A_1	0.14	0.25	7,300
A_2	0.19	0.26	7,600
A_3	0.60	0.69	45,600
A_4	0.63	0.70	46,000
A_5	0.80	1.07	49,100
A_6	1.05	1.15	54,300
A_7	0.97	1.17	55,600
A_8	1.05	1.24	59,600
A_8 -(NH_2) capped	1.23	1.35	66,900
A_9	1.03	1.25	60,500
A_9 -(COCl) capped	1.03	1.25	60,500
A_{10}	1.32	1.49	75,300
A_{11}	1.64		93,000
A_{12}	1.10		62,000
A_{13}	0.96		52,500
A_{14}	1.10		62,000
A_{15}	1.58		90,000
A_{16}	1.79		102,000
A_{17}	0.73		45,000
A_{18}	0.71		44,000

*Calculated from equation due to Burke (205).

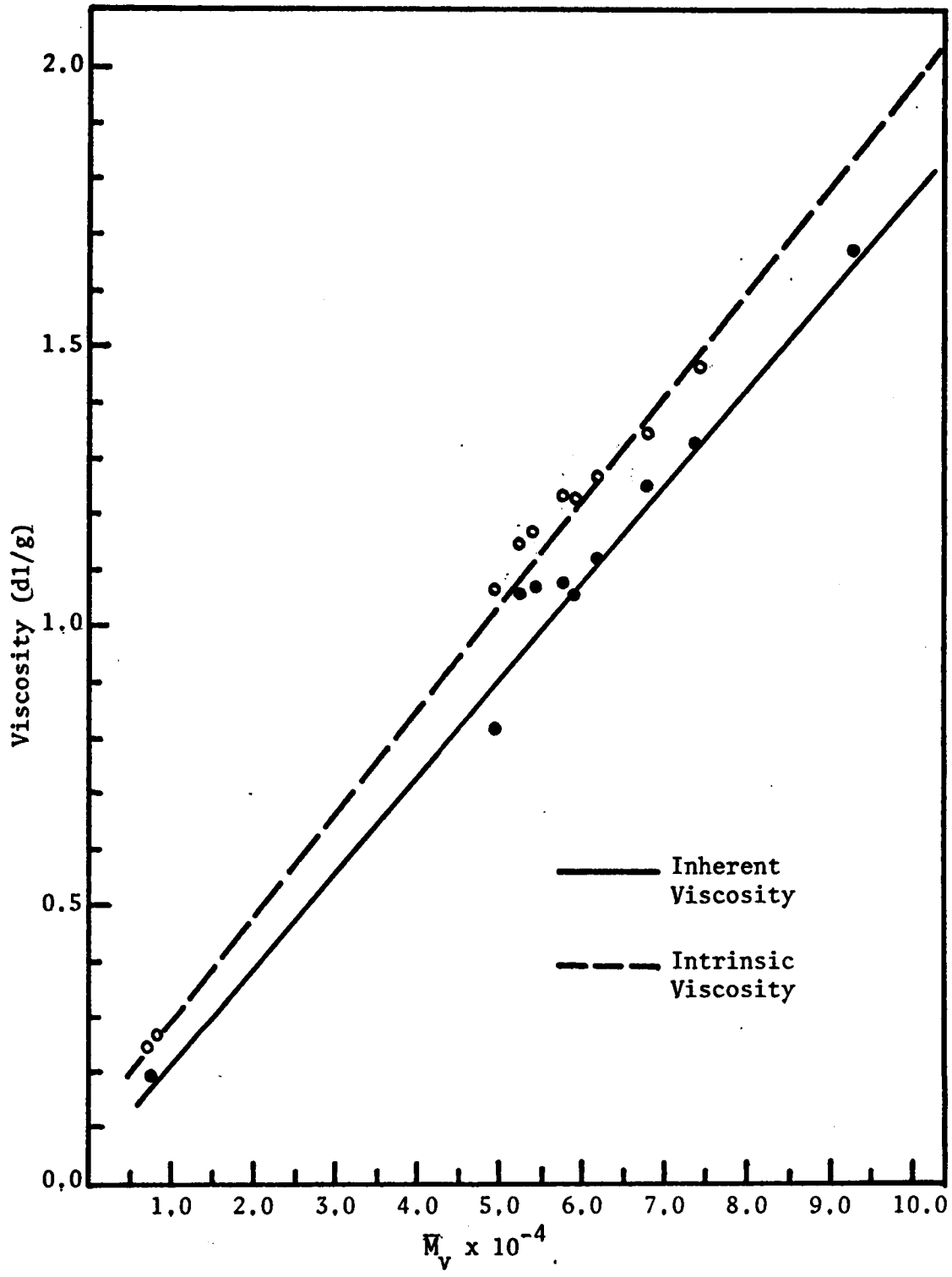


Figure 1. Calibration curve for the estimation of $\overline{M}_v$ of poly(m-phenylene isophthalamide) directly from the values of inherent viscosity.

with decreasing concentrations of solutions. This phenomenon, most probably caused by the polyelectrolytic effect resulting from the protonization of amide bonds, substantially complicates wet processing techniques mostly used for fabrications of these polymers. It is a well-known fact that so-called "saline" solvents are needed to assure good solubility of homopolyamides. Therefore, DMAc/LiCl or DMF/LiCl systems are most widely used here.

Two basic studies were conducted on block copolymers containing aromatic polyamide and poly(ethylene oxide) blocks: First, the time required for dissolution of different block copolymers (temperature and pressure being held constant), was measured; and second, concentration ranges for dissolution for a series of four selected copolymers was studied. Generally it was found that the presence of poly(ethylene oxide) in the copolymer backbone substantially improved solubility.

Block copolymers containing aromatic polyamide and poly(dimethyl siloxane) segments, even at very low concentrations, usually formed slightly opalescent solutions in DMAc·5 percent LiCl solvent. For this reason solubility in the "mixed-solvent" system, DMAc and CH_2Cl_2, was investigated for some selected copolymers.

All observations were carried out in a constant temperature bath at 25°C and at atmospheric pressure. A set of volumetric flasks was immersed into the bath and occasionally shaken. The formation of clear solutions was considered as the final stage of these observations.

The results of these observations for block copolymers containing poly(m-phenylene isophthalamide) and poly(ethylene oxide) segments are

collected in Tablex IX and X. It can be clearly seen that the presence of poly(ethylene oxide) substantially enhances the solubility of these polymers. This solubility enhancement is clearly shown in systems having poly(ethylene oxide) end blocks.

The dissolution power of "mixed-solvent" systems, composed from a mixture of DMAc and CH_2Cl_2 for some of the block copolymers containing poly(dimethyl siloaxane) end blocks, was investigated. Approximately 10 percent solutions were prepared in solvents composed of 1:9 to 9:1 parts of DMAc:CH_2Cl_2. It has been found that solvent combinations of 9:1 and 8:2 (DMAc:CH_2Cl_2) possess the highest dissolution power. Both these solvents have rather close agreement in their solubility parameters δ, ($\delta_{CH_2Cl_2}$ = 9.7 $[cal/cc]^{1/2}$, δ_{DMAc} = 10.8 $[cal/cc]^{1/2}$), thus indicating unlimited compatibility.

IV.1.3. Block Copolymer Composition

Infrared spectroscopy and nuclear magnetic resonance measurements were used to verify the formation of the block copolymers and for the determination of their composition. Both methods were used for aromatic polyamide/poly(ethylene oxide) block copolymers. Unfortunately, the complete overlap of the characteristic peaks for aromatic polyamide/poly(dimethyl siloxane) block copolymer systems in the infrared spectrum disqualified the use of this analytical tool for compositional analysis of those blocks.

IV.1.3.1. The Infrared Analysis of Poly(m-Phenylene Isophthalamide-b-Ethylene Oxide) Block Copolymers

At least two distinctive absorption bands for each homopolymer involved in these block structures are clearly defined. A strong

TABLE IX

TIME-DEPENDENT DISSOLUTION OF POLY(m-PHENYLENE ISOPHTHALAMIDE-b-ETHYLENE OXIDE) BLOCK COPOLYMERS

Copolymer	Type of Structure A=PmPIA	[η] 0.5% Solution	Approximate Time in Hours Needed for 0.5% Solutions	Approximate Time in Hours Needed for 5.0% Solutions	Presence of LiCl Required in DMAc for 0.5% Solutions	Presence of LiCl Required in DMAc for 5.0% Solutions
A_{11}	---	1.64	16	24	yes	yes
E10.A_{11}.E10	BAB	1.53	10	12	yes	yes
E40.A_{11}.E40	BAB	1.61	2	4	no	yes
E60.A_{11}.E60	BAB	1.63	1	2	no	no
A.E10.A-2	ABA	0.70	16	20	yes	yes
A.E40.A-2	ABA	1.02	9	10	no	yes
A.E60.A-2	ABA	0.77	2	4	no	no

TABLE X

CONCENTRATION-DEPENDENT DISSOLUTION OF POLY(m-PHENYLENE ISOPHTHALAMIDE-b-DIMETHYL SILOXANE) BLOCK COPOLYMERS

Copolymer	Type of Structure A=PmPIA	[η] 0.5% Solution	Approximate Concentration of Block Solutions* 1%	5%	10%	15%	20%	25%	Over
E4.A_{12}.E4	BAB	1.10	x	x	x				
E60.A_{12}.E60	BAB	1.10	x	x	x	x	x	x	x
A.E10.A-2	ABA	0.70	x	x	x	x	x		
A.E60.A-2	ABA	0.77	x	x	x	x	x	x	

*Time of 15 hours period was held constant in each case.

carbonyl stretch at 1600-1680 cm^{-1} and very distinctive -NH- stretch at 3200-3250 cm^{-1} wavenumbers are suitable for use in the characterization of the aromatic homopolyamide. The ether linkage (-C-O-C-) stretch and vibrations occurring at frequency of 1100 cm^{-1} together with ($-CH_2-$) absorption at 2950 cm^{-1} wavenumbers clearly characterize poly(ethylene oxide) macromolecules. All these absorption bands are present for each synthesized copolymer and are in fact a qualitative proof of block copolymer structure formation.

For the quantitative determination of weight percent incorporation of poly(ethylene oxide) within these block copolymers, the above mentioned carbonyl stretch (1600-1680 cm^{-1}) representing this aromatic polyamide was considered. Peaks representing the absorption due to the ether linkage vibrations (1100 cm^{-1} wavenumber) indicating poly(ethylene oxide) presence were then compared with those for aromatic polyamide in order to establish the composition of these block copolymers.

Measurements were performed on two different instruments: Perkin-Elmer Model 727, and Beckman Model IR-4. Two different techniques of sample preparation utilizing KBr pellets and NaCl salt plates were used for analysis. The KBr pellets contained 3 percent by weight polymer were pressed into 1mm uniform thickness. Standard techniques were used for their preparation. One and one-half percent solutions of polymers in pure DMAc were used for sample preparation on the NaCl salt plates. Approximately 3 drops of solution were transferred onto the salt plate

surface. The salt plates were then dried in a hot vacuum oven (65-70°C) for at least 72 hours.

Calibration curves for each instrument were determined from physical mixtures ranging from 20:80 to 80:20 weight percent of both homopolymers. The standard technique: drawing the base-line; comparing the peak heights (I_1 and I_2); obtaining their ratio (I_1/I_2); and finally plotting log I_1/I_2 versus weight percent of poly(ethylene oxide) in a mixture of homopolymers was used. The same method of spectra evaluation was used for quantitative analysis of each block copolymer composition.

In order to achieve the most precise evaluation of the composition of analyzed copolymers, several independent measurements were performed on each material. Although there was a slight variation in data obtained for some copolymers, fair agreement among collected results can be observed. Figure 2 illustrates a typical spectrum for both aromatic polyamide and its block copolymer with poly(ethylene oxide). Obtained results are then summarized in Tables XI and XII.

IV.1.3.2. The Nuclear Magnetic Resonance Analysis (NMR) of Poly(m-Phenylene Isophthalamide-b-Ethylene Oxide) and Poly(m-Phenylene Isophthalamide-b-Dimethyl Siloxane) Block Copolymers

The varying environments of the different groups of protons substantially alters their spinning characteristics in an imposed magnetic field and also their response to varying radio signals. This, one of the most basic principles of nuclear magnetic resonance spectroscopy, can be used for compositional studies on block copolymers. In many cases, this is the only precise tool available to the polymer researcher giving him a first level understanding of the formed structure.

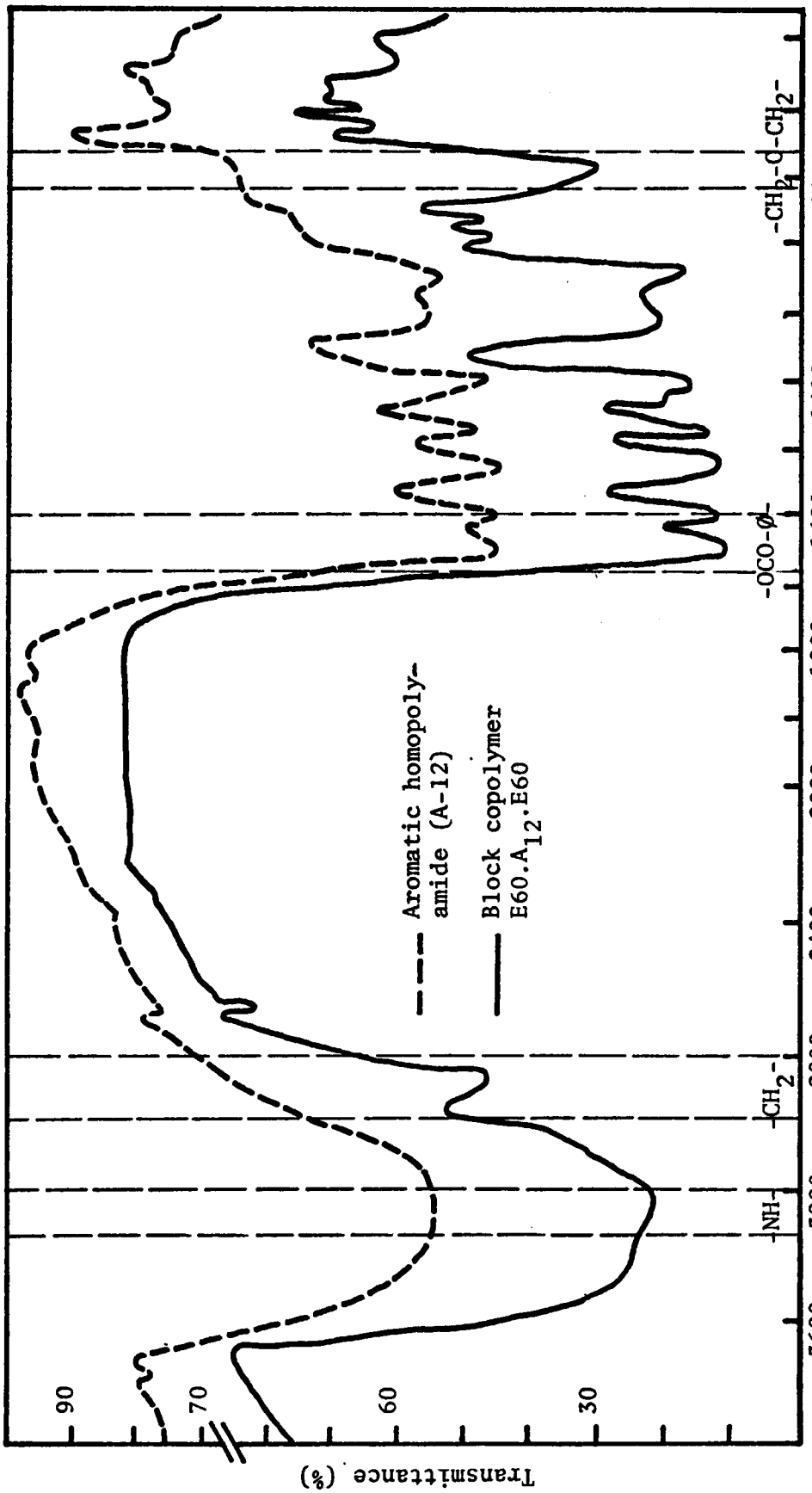


Figure 2. Schematics of typical IR spectra of poly(m-phenylene isophthalamide) and its block copolymer with poly(ethylene oxide). Spectra taken on Perkin-Elmer Spectrophotometer, Model 727.

TABLE XI

DETERMINATION OF WEIGHT PERCENT INCORPORATION OF $\{CH_2CH_2O\}$ UNITS IN POLY(m-PHENYLENE ISOPHTHALAMIDE-b-ETHYLENE OXIDE) BLOCK COPOLYMERS BY IR SPECTROPHOTOMETRY-- $(AB)_n$ AND BAB BLOCK STRUCTURES

Copolymer	Type of Block A=PmPIA	Wt.% of PEO Determined by: P.E.727(1) KBr Pellet	P.E.727(2) Salt Plate	IR-4 Salt Plate	Average Wt.% Incorporation
$(A.E4)_n$-1	$(AB)_n$	13.0	14.0		13.5
$(A.E4)_n$-2	$(AB)_n$	6.0	13.0	--	9.5
$(A.E4)_n$-3	$(AB)_n$	13.0	24.0	--	18.5
$(A_4.E4)$-Is	AB	8.5	5.0	--	6.8
$E4.A_{1,2}.E4$-Is	$(AB)_n$	14.0	17.0	--	15.5
$E4.A_{1,2}.E4$-Is	BAB	15.0	16.0	--	15.5
$(E4.A)_n$-4	$(AB)_n$	27.0	19.0	--	23.0
$(A.E4)_n$-4-Is	$(AB)_n$	25.0	20.0	--	22.5
$E4.A_7.E4$	BAB	25.0	19.0	21.0	21.7
$E4.A_7.E4$-Is	BAB	11.0	15.0	10.0	12.0
$E4.A_{12}.E4$	BAB	15.0	17.0	6.0	12.3
$E10.A_8.E10$	BAB	20.0	13.0	13.0	15.3
$E10.A_8.E10$-Is	BAB	15.0	17.0	11.0	14.3
$E10.A_9.E10$	BAB	20.0	18.0	22.5	20.2
$E10.A_{11}.E10$	BAB	23.0	20.0	22.5	21.8
$E10.A_{12}.E10$	BAB	18.0	20.0	21.0	20.0
$(A.E40)_n$-1	$(AB)_n$	10.0	13.0	10.0	11.0
$E40.A_9.E40$	BAB	22.0	22.0	21.0	22.0
$E40.A_{10}.E40$	BAB	23.0	24.0	21.0	22.6
$E40.A_{11}.E40$	BAB	40.0	23.0	31.5	31.5
$E40.A_{12}.E40$	BAB	26.0	22.0	35.0	27.7
$E60.A_{11}.E60$	BAB	45.0	39.0	40.0	41.3
$E60.A_{12}.E60$	BAB	30.0	32.0	34.0	32.0

TABLE XII

DETERMINATION OF WEIGHT PERCENT INCORPORATION OF $\{CH_2CH_2O\}$ UNITS IN POLY(m-PHENYLENE ISOPHTHALAMIDE-b-ETHYLENE OXIDE) BLOCK COPOLYMERS BY IR SPECTROPHOTOMETRY--ABA BLOCK STRUCTURES

Copolymer	Type of Block A=PmPIA	Wt.% of PEO Determined by Beckman IR-4 First Run	Second Run	Average Weight % Incorporation
A.E10.A-1	ABA	5.0	8.0	6.5
A.E10.A-2	ABA	6.0	8.0	7.0
A.E40.A-1	ABA	10.0	11.0	10.5
A.E40.A-2	ABA	10.0	13.0	11.5
A.E60.A-1	ABA	18.0	15.0	16.5
A.E60.A-2	ABA	25.0	29.5	27.3

IV.1.3.2.1. The NMR analysis of poly(m-phenylene isophthalamide-b-ethylene oxide) block copolymers. NMR spectra were taken for all the synthesized copolymers. The area under the peaks due to the absorption of radiation by 8 protons in the aromatic polyamide repeat unit (δ range 5.84-8.00 ppm), was compared to the area under the characteristic peaks for 4 protons of the poly(ethylene oxide) repeat unit (δ range 3.4-3.6 ppm). Two distinctive peaks for DMAc (singlet at 1.98 ppm and doublet at 2.96-3.02 ppm delta), were used as an internal standard.

Two instruments, both manufactured by Varian, Inc., Models A-6040 (60 MHz) and HA-100 (100 MHz) were used for these measurements. Approximately 15 percent by weight solutions of copolymers in DMAc·5 percent LiCl provided sample media. It is a well-recognized fact that a higher probe temperature results in better definition of characteristic peaks. Unfortunately, there was no way to achieve this and therefore the probe temperature was held constant at 40°C.

The following set of calculations were performed in order to determine block composition. Index "1" was assigned to the aromatic polyamide and index "2" to the polyether.

$$\text{Ratio of repeating units} = \frac{A_1/8}{A_2/4} = \frac{1}{2}\frac{A_1}{A_2} = \frac{\text{repeat units of "1"}}{\text{repeat units of "2"}}$$

$$\text{\% of PEO repeat units in copolymer} = \frac{A_2}{\frac{1}{2}A_1 + A_2} \times 100$$

$$\text{Weight \% of PEO repeat units in copolymer} = \frac{A_2 \quad M_2}{\frac{1}{2} A_1 \cdot M_1 + A_2 \cdot M_2} \times 100$$

where: M_1 = 238 g/mole

M_2 = 44 g/mole

molecular weight of the repeat units

The area under each characteristic peak was carefully retraced on a graph paper, cut out and weighed. Table XIII summarizes obtained results for the entire series of block copolymers utilizing the above mentioned cosegments, while Figure 3 illustrates the copolymer spectrum in general.

IV.1.3.2.2. The NMR analysis of poly(m-phenylene isophthalamide-b-dimethyl siloxane) block copolymers. The protons associated with methyl groups attached to silicone atoms absorb radio frequency signals during performed frequency sweeps at exactly δ = 0.0 ppm. In fact this δ value widely used as an internal standard during NMR analysis, is assigned to tetramethyl silane. In the case of more precise instruments, this internal standard is required to "lock" the frequency sweep during the measurement. If the spectrum is originally locked to that standard, performance of "up-field" frequency sweeps are a routine matter. This requirement eliminated the use of a 100 MHz instrument and, therefore, Varian's A-6040 NMR spectrophotometer remained as the only analytical tool available for compositional analysis of these block copolymers.

The area under peaks assigned to both segments (δ range 5.84-8.00 ppm for aromatic polyamide and δ = 0.0-0.6 ppm indicating poly(dimethyl

TABLE XIII

DETERMINATION OF WEIGHT PERCENT INCORPORATION OF $\{CH_2CH_2O\}$ UNITS IN POLY(m-PHENYLENE ISOPHTHALAMIDE-b-ETHYLENE OXIDE) BLOCK COPOLYMERS BY NMR SPECTROMETRY

Copolymer	Type of Block A=PmPIA	Wt.% PEO by IR	Wt.% of PEO by A-6040	Wt.% of PEO by HA-100	Average Wt.% PEO NMR+IR
$(A.E4)_n$-4	$(AB)_n$	23.0	15.0	16.0	18.1
$(A.E4)_n$-4-Is	$(AB)_n$	23.0	15.0	18.0	18.7
$E4.A_7.E4$	BAB	22.0	17.0	19.0	19.2
$E4.A_7.E4$-Is	BAB	12.0	13.0	11.0	12.0
$E4.A_{12}.E4$	BAB	12.0	13.0	14.0	13.3
$E10.A_8.E10$	BAB	15.0	11.0	13.0	13.2
$E10.A_8.E10$-Is	BAB	13.0	11.0	11.0	11.7
$E10.A_9.E10$	BAB	20.0	18.0	16.0	18.2
$E10.A_{11}.E10$	BAB	22.0	17.0	20.0	19.6
$E10.A_{12}.E10$	BAB	20.0	21.0	18.0	19.6
$(A.E40)_n$-1	$(AB)_n$	11.0	6.0	4.0	7.1
$E40.A_9.E40$	BAB	22.0	19.0	18.0	19.5
$E40.A_{10}.E40$	BAB	23.0	16.0	12.0	16.8
$E40.A_{11}.E40$	BAB	32.0	20.0	24.0	25.0
$E40.A_{12}.E40$	BAB	28.0	27.0	27.0	27.2
$E60.A_{11}.E60$	BAB	41.0	22.0	16.0	26.2
$E60.A_{12}.E60$	BAB	32.0	32.0	30.0	31.3
A.E10.A-1	ABA	6.0	7.0	6.0	6.3
A.E10.A-2	ABA	7.0	8.0	7.0	7.2
A.E40.A-1	ABA	10.0	13.0	14.0	12.3
A.E40.A-2	ABA	11.0	16.0	13.0	13.5
A.E60.A-1	ABA	15.0	16.0	14.0	15.2
A.E60.A-2	ABA	27.0	25.0	27.0	26.3

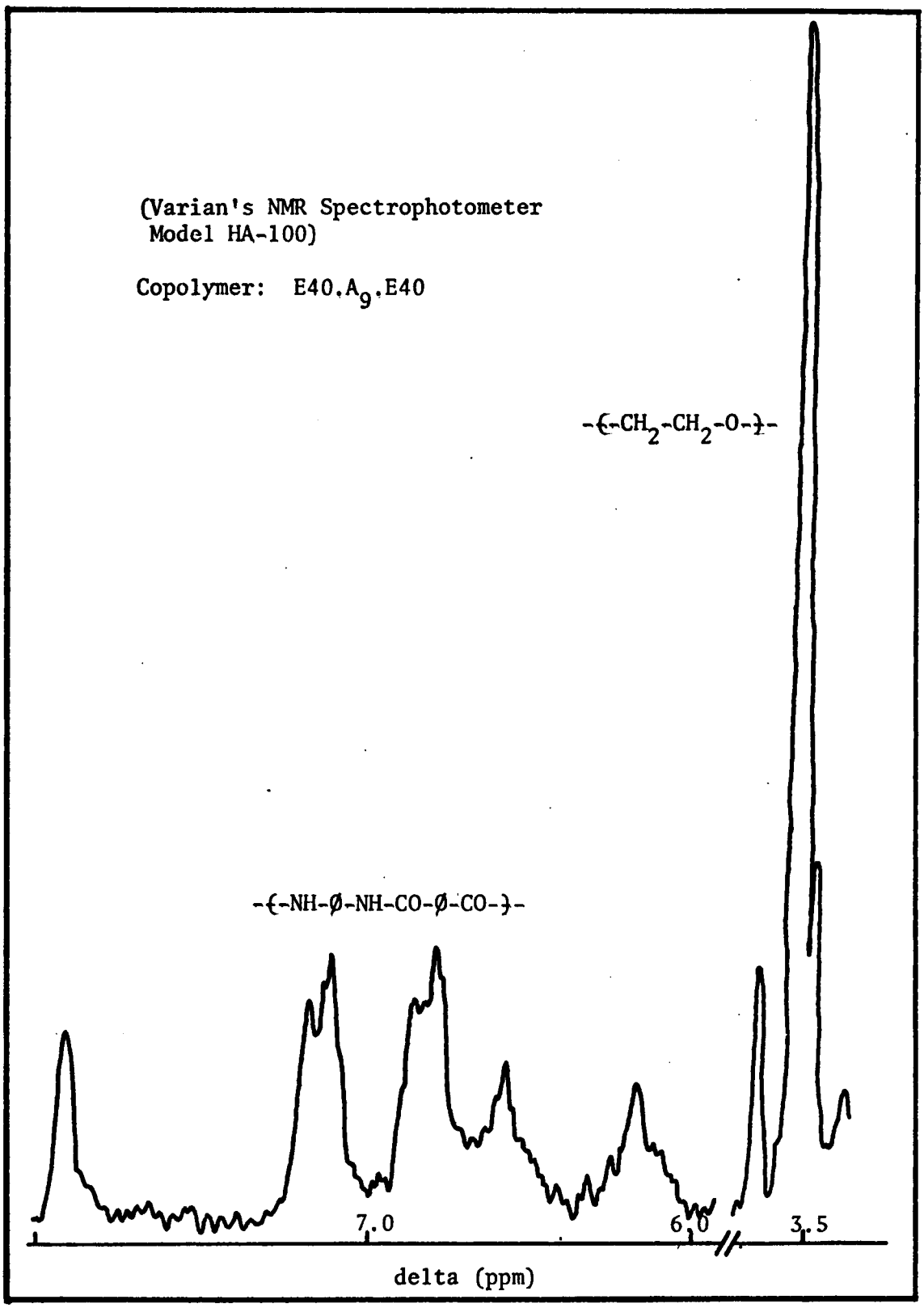


Figure 3. A schematic of typical peaks used for compositional analysis of poly(m-phenylene isophthalamide-b-ethylene oxide) block copolymers by NMR.

siloxane) presence) was carefully cut out and weighed. The following set of calculations was performed to evaluate the weight percent incorporation of poly(dimethyl siloxane) in the block copolymer systems:

$$\text{Ratio of repeating units} = \frac{A_1/8}{A_2/6} = \frac{\text{repeat units of "1"}}{\text{repeat units of "2"}}$$

$$\text{\% of PSX repeat units in copolymer} = \frac{A_2/6}{A_1/8 + A_2/6} \times 100$$

$$\text{Weight \% of PSX repeat units in copolymer} = \frac{A_2/6 \cdot M_2}{A_2/6 \cdot M_2 + A_1/8 \cdot M_1} \times 100$$

where: A_1 = the area under aromatic polyamide peaks

A_2 = the area under poly(dimethyl siloxane) peaks

M_1 = molecular weight of "1" repeat unit - 238 g/mole

M_2 = molecular weight of "2" repeat unit - 74 g/mole

Three separate measurements, each one for different concentrations of polymer solution (10.0 percent, 12.5 percent, 15.0 percent) were performed. The temperature of the probe was held constant at 40°C. Figure 4 illustrates a typical spectrum. The results obtained during the compositional analysis of these block copolymers are summarized in Table XIV.

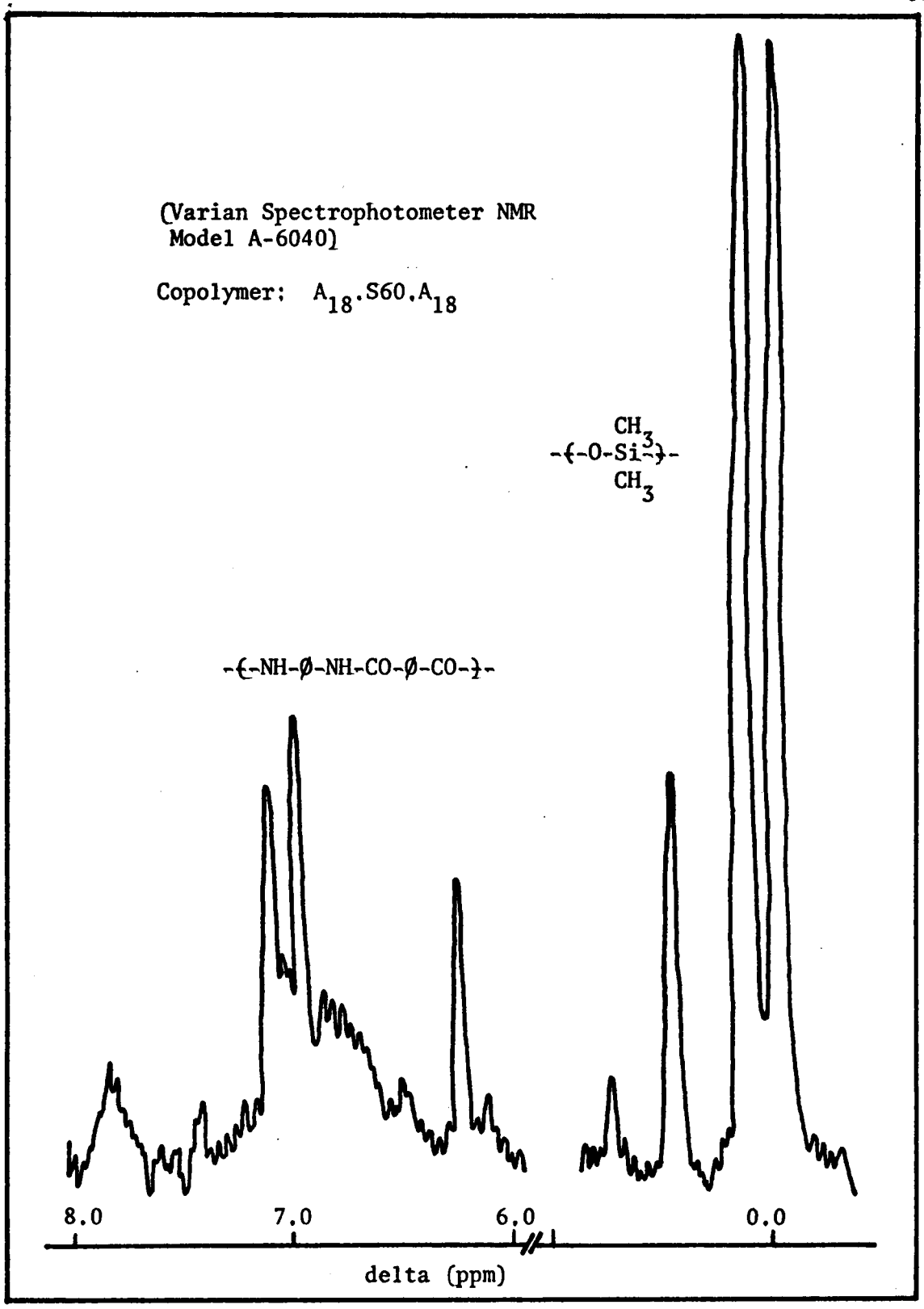


Figure 4. A schematic of typical peaks used for compositional analysis of poly(m-phenylene isophthalamide-b-dimethyl siloxane) block copolymers by NMR.

TABLE XIV

DETERMINATION OF WEIGHT PERCENT INCORPORATION OF $\{Si-(CH_3)_2-O\}$ UNITS IN POLY(m-PHENYLENE ISOPHTHALAMIDE-b-DIMETHYL SILOXANE) BLOCK COPOLYMERS BY NMR SPECTROMETRY

Copolymer	Type of Block A=PmPIA	Separate Measurements for Wt. % Incorporation on 10.0%	12.5%	15.0%	Average Wt. % Incorporation
$(A.S15)_n$-1	$(AB)_n$	13.0	13.0	13.0	13.0
$(A.S60)_n$-1	$(AB)_n$	18.0	19.0	19.0	18.7
S15.A_{18}-S15-1	BAB	12.0	14.0	10.0	12.0
S15.A_{18}.S15-2	BAB	9.0	10.0	9.0	9.3
S50.A_{13}.S50	BAB	12.0	10.0	16.0	13.0
S50.A_{18}.S50	BAB	22.0	22.0	23.0	22.7
S60.A_{16}.S60	BAB	15.0	33.0	33.0	28.0
S60.A_{17}.S60	BAB	12.0	12.0	13.0	12.3
S60.A_{18}.S60	BAB	14.0	14.0	13.0	13.7
S90.A_{13}.S90	BAB	11.0	13.0	14.0	12.0
S90.A_{18}.S90	BAB	13.0	13.0	13.0	13.0
S140.A_{13}.S140	BAB	9.0	13.0	15.0	12.3
S140.A_{14}.S140	BAB	14.0	13.0	15.0	14.0
S140.A_{15}.S140	BAB	16.0	16.0	16.0	16.0
A.S15.A-1	ABA	15.0	13.0	13.0	13.8
A.S15.A-2	ABA	12.0	14.0	13.0	13.0
A_{18}.S15.A_{18}	ABA	12.0	12.0	12.0	12.0
A.S60.A-1	ABA	12.0	12.0	13.0	12.7
A.S60.A-2	ABA	10.0	13.0	15.0	13.7
A_{16}.S60.A_{16}	ABA	19.0	28.0	25.0	24.0
A_{17}.S60.A_{17}	ABA	12.0	15.0	15.0	14.0
A_{18}.S60.A_{18}	ABA	31.0	31.0	29.0	30.3

IV.2. THERMAL STABILITY OF POLY(m-PHENYLENE ISOPHTHALAMIDE) HOMOPOLYMER AND ITS BLOCK COPOLYMERS WITH POLY(ETHYLENE OXIDE) OR POLY(DIMETHYL SILOXANE)

In order to investigate the resistance of an aromatic homopolyamide and its block copolymers to high temperature, differential scanning calorimetry (DSC) was performed on all synthesized polymers. A Perkin-Elmer DSC, Model DSC-1B, allowing analysis up to 500°C, and variable heating rates was used. An inert gas blanket was provided by N_2 gas. Unfortunately, low temperature measurements from -100°C to room temperature could not be utilized due to technical difficulties with the instrument available.

The instrument was calibrated with a lead standard (Tm = 327.4°C) and then with HDPE (Tm = 127-132°C). A sample of approximately 5mg was analyzed for each material. It was found that poly(m-phenylene isophthalamide) is essentially stable up to 350°C, while its block copolymer showed two distinctive decomposition temperatures. The following observations were made:

Poly(m-phenylene isophthalamide)

T_g = 280-290°C, not always clearly detected

T_{cryst} = 305-335°C, very strong, single exothermic peak

T_{dec} = over 385°C, progresses gradually up to 500°C

T_m = over 425°C, not always detected

Block copolymers of aromatic polyamide and poly(ethylene oxide)

a) aromatic polyamide center block

T_g = not clearly detected

T_{cryst} = 310-340°C, strong exothermic peak

$T_{dec(1)}$ = 190-265°C, decomposition of poly(ethylene oxide)

$T_{dec(2)}$ = over 365°C, decomposition of aromatic polyamide

T_m = not detected for any segment

b) poly(ethylene oxide) center block

T_g = 275-290°C, clearly detected

T_{cryst} = 305-340°C, usually strong exothermic peak

$T_{dec(1)}$ = not detected for poly(ethylene oxide)

$T_{dec(2)}$ = over 365°C for aromatic homopolyamide segments

$T_{m(1)}$ = 55-70°C, clearly detected for poly(ethylene oxide)

$T_{m(2)}$ = not detected for aromatic polyamide

Block copolymers of aromatic polyamide and poly(dimethyl siloxane)

No considerable difference was observed for different sequence placement within these block copolymers.

T_g = 260-285°C, very clearly detected

T_{cryst} = 300-330°C, not very often detected

$T_{dec(1)}$ = no decomposition observed for poly(dimethyl siloxane)

$T_{dec(2)}$ = over 350°C

T_m = over 430°C, scarcely detected for aromatic homopolyamide due to the preceding decomposition

Typical DSC curves for each particular type of polymer and copolymer are presented in Figure 5.

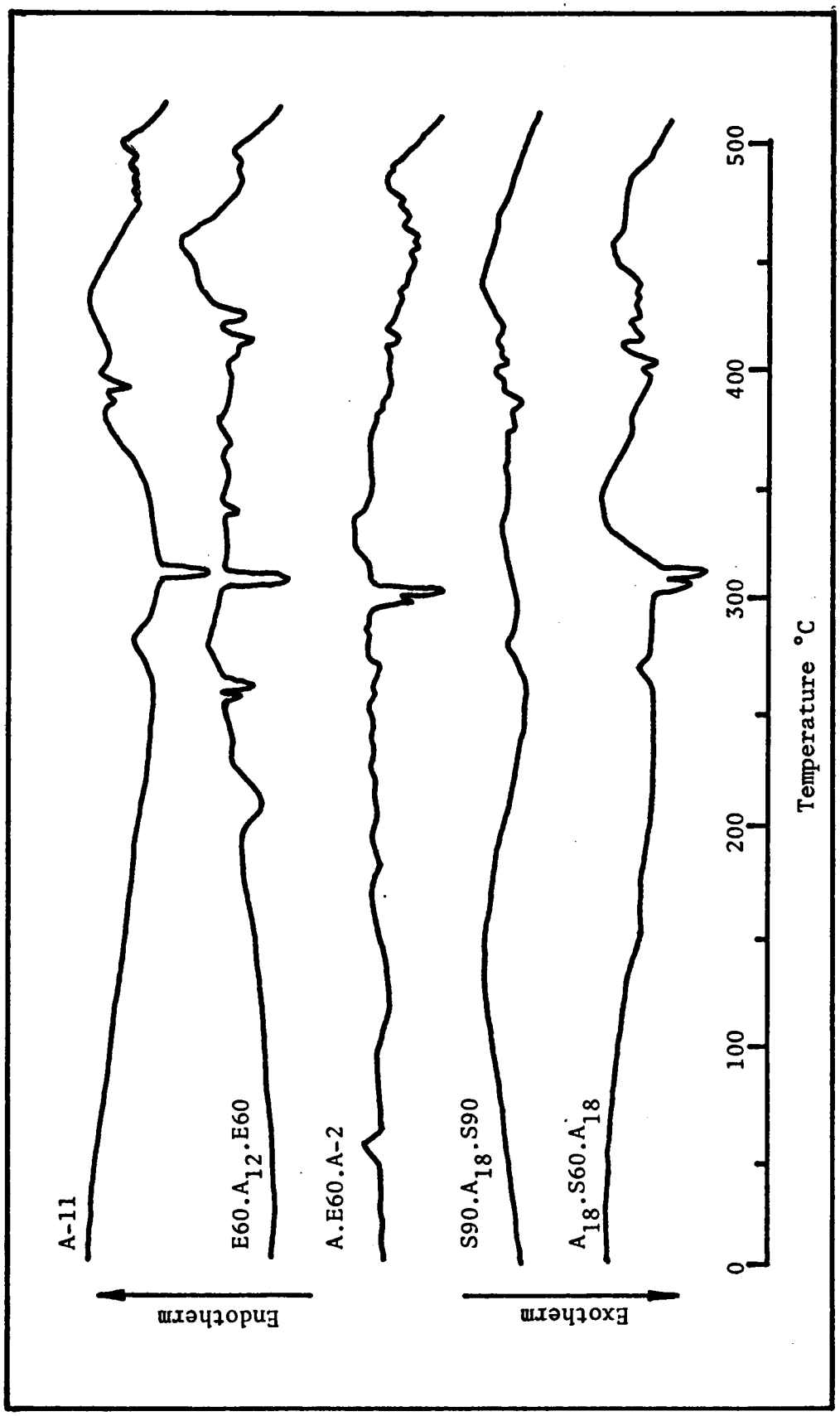


Figure 5. Typical DSC curves for poly(m-phenylene isophthalamide) homopolymer and its block copolymers with poly(ethylene oxide) or poly(dimethyl siloxane).

IV.3. MECHANICAL AND THERMOMECHANICAL PROPERTIES

IV.3.1. Tensile Properties

This chapter describes the tensile properties of poly(m-phenylene isophthalamide) homopolymer and its block copolymers. The excellent mechanical properties of aromatic polyamides are well recognized. How much modification this system will accept without the sacrifice of its main features is the question to be answered within the course of this section.

The maximum engineering strength, Young's modulus, and elongation-to-break were determined for these materials on cast films. These polymers are amorphous polymeric glasses when synthesized. Therefore, an additional treatment was undertaken to develop the crystallinity of these systems.

IV.3.1.1. Sample Preparation via Film Casting

Although it was originally intended to use wet-spun fibers as a main specimen source for tensile tests, the technique for their preparation was not yet in standard use. Therefore, film casting remained as the best option for sample preparation.

Several different techniques were investigated to prepare good, uniform films. As a conclusion of the search for a method having the highest reproducibility, two casting methods were used for preparing the entire series of samples. The basic difference between them was in the rate of solvent evaporation and in the surrounding temperature.

Films were cast from 15 percent by weight solutions of polymer in DMAc/5 percent LiCl. The evaporation of solvent was performed either in a hot oven (100-130°C) or in warm vacuo (55-65°C). The latter mentioned method introduced occasional difficulties due to formation of bubbles on the film surface. While films cast in the hot oven were essentially dry after 18-24 hours, a time period of at least 72 hours was required for drying films in warm vacuo. This "drying" operation was followed by leaching of cast films in H_2O for at least 72 hours at room temperature and then at 90°C for 1 hour. When the leaching procedure was finished, the films were mounted on glass plates and dried in vacuo for 4 days. This procedure provides for uniform films with average thicknesses of 0.005-0.01 cm. Upon drying, 1.0cm wide strips were cut from the films and used as tensile test specimens.

Generally, amorphous glassy films were obtained by these casting procedures. It might be pointed out here that only materials having an inherent viscosity greater than 0.55 are suitable for casting of films possessing good physical integrity.

IV.3.1.2. Stress-Strain Measurements on "As-Cast" Films

The stress-strain measurement is probably the most widely used mechanical test for determining engineering properties of materials. These tests are generally done by elongating the specimen at a uniform rate and simultaneously measuring the force on the specimen. This test is continued until the specimen breaks. Although it is recognized that the results of these tests depend on the temperature and on occasion

the humidity of surrounding media, and of course on the rate of jaw separation, these factors were held sensibly constant.

An Instron tensile tester, Model TTD, was used for the determination of maximum engineering strength, Young's modulus, and elongation-to-break. Conditions generally maintained during the tests were a constant rate of jaw separation (0.2 in/minute), and room temperature (20-24°C). To determine any possible jaw slippage, the specimens were marked at the end of each jaw, and any resulting change in position was carefully checked. A "DR" type load cell, having load capacity of 20-1,000 lb, was used in all cases.

IV.3.1.2.1. Poly(m-phenylene isophthalamide). In order to compare the tensile properties of block copolymers based on poly(m-phenylene isophthalamide), stress-strain measurements were performed on a series of 16 homopolyamides. In their glassy state, these polymers have the characteristics of hard, semi-brittle polymers. The data collected on water-clear to slightly yellow transparent films averaged 0.8×10^5 pascals (11,000 psi approximately), for maximum engineering strength and from 3-6 percent elongation-to-break. The Young's modulus ranged from $2.9\text{-}3.3 \times 10^7$ pascals ($4.3\text{-}4.8 \times 10^5$ psi). These values are in good agreement with data published elsewhere for commercially available duPont's NOMEX ^{R} (0.83×10^5 Pa, 3-6 percent, 3.45×10^7 Pa respectively).

It is a well-recognized fact that the physical-mechanical properties of polymers depend substantially on their molecular weight. It has been observed that the threshold values of inherent viscosities

of 0.5-0.6 dl/g (0.5 percent solution in DMAc·5 percent LiCl, 25°C) are required for development of physical strength of poly(m-phenylene isophthalamide). Table XV summarizes the obtained results.

IV.3.1.2.2. Block copolymers of poly(m-phenylene isophthalamide) and poly(ethylene oxide). Both types of block copolymers utilizing poly(ethylene oxide) end or center blocks were tested. A considerable difference in tensile properties was found between these two groups. The copolymers having poly(ethylene oxide) end blocks showed a substantial decrease in maximum engineering strength and Young's modulus while only a small gain was recorded for elongation-to-break. On the other hand, block copolymers with poly(ethylene oxide) center blocks still retained moduli and strengths typical of poly(m-phenylene isophthalamide), while the ductility of these materials improved two- or three-fold.

Data collected on semi-transparent or opaque films are summarized in Table XVI.

IV.3.1.2.3. Block copolymers of poly(m-phenylene isophthalamide) and poly(dimethyl siloxane). Although it was intended to synthesize block copolymers featuring both sequence placements (ABA and BAB triblocks), the results of stress-strain measurements did not show any considerable difference. The presence of poly(dimethyl siloxane) generally lowers the maximum apparent engineering strength and Young's modulus compared to poly(m-phenylene isophthalamide). Ductility

TABLE XV

TENSILE PROPERTIES OF POLY(m-PHENYLENE ISOPHTHALAMIDE) HOMOPOLYMERS COLLECTED ON "AS-CAST" FILMS

Polymer	Inherent Viscosity (0.5% Solution, 25°C)	Maximum Engineering Strength (Pa)x10^{-5}	Young's Modulus (Pa)x10^{-7}	Elongation-to-Break (%)
A-3	0.60	0.25	3.14	1.5
A-4	0.63	0.28	3.04	1.6
A-5	0.80	0.72	2.26	6.0
A-6	1.05	0.53	1.91	4.0
A-7	0.97	0.86	2.65	6.5
A-8	1.05	0.82	2.85	6.0
A-9	1.04	0.82	2.70	5.5
A-10	1.32	0.51	1.77	6.0
A-11	1.64	0.83	3.43	5.5
A-12	1.10	0.72	2.16	5.5
A-13	0.96	0.76	2.75	10.0
A-14	1.10	0.78	2.85	8.0
A-15	1.58	0.78	3.34	4.0
A-16	1.79	1.17	3.63	4.5
A-17	0.73	0.37	1.57	3.3
A-18	0.71	0.51	2.45	3.0
Dupont's NOMEX	over 1.65	0.83	3.43	6.0

TABLE XVI

TENSILE PROPERTIES OF BLOCK COPOLYMERS OF POLY(m-PHENYLENE ISOPHTHALAMIDE-b-ETHYLENE OXIDE) COLLECTED ON "AS-CAST" FILMS

Copolymer	Type of Block Structure A=PmPIA	Wt.% of PEO	Maximum Engineering Strength (Pa)x10^{-5}	Young's Modulus (Pa)x10^{-7}	Elongation-to-Break (%)
E4.A_7.E4	BAB	19.0	0.42	1.62	3.0
E4.A_7.E4-Is	BAB	12.0	0.26	1.03	3.0
E4.A_{12}.E4	BAB	13.0	0.75	2.69	6.0
E10.A_8.E10	BAB	13.0	0.47	1.24	3.0
E10.A_8.E10-Is	BAB	12.0	0.65	2.45	4.5
E10.A_9.E10	BAB	18.0	0.28	1.30	3.0
E10.A_{11}.E10	BAB	20.0	0.33	1.16	8.0
E10.A_{12}.E10	BAB	20.0	0.50	1.89	4.0
E40.A_9.E10	BAB	20.0	0.19	0.81	4.0
E40.A_{10}.E40	BAB	17.0	0.30	0.93	6.0
E40.A_{11}.E40	BAB	25.0	0.30	1.20	7.5
E40.A_{12}.E40	BAB	27.0	0.20	1.24	5.0
E60.A_{11}.E60	BAB	26.0	0.20	0.51	9.5
E60.A_{12}.E60	BAB	31.0	0.20	0.85	7.0
A.E10.A-;	ABA	6.0	1.00	3.43	15.0
A.E10.A-2	ABA	7.0	1.16	4.02	6.5
A.E40.A-1	ABA	12.0	0.81	2.65	6.0
A.E40.A-2	ABA	13.0	1.00	2.50	7.0
A.E60.A-1	ABA	15.0	0.86	2.45	6.0
A.E60.A-2	ABA	26.0	0.58	2.06	11.5

increases up to three- or four-fold. The data collected on semi-transparent or opaque films are summarized in Table XVII.

IV.3.1.3. Stress-Strain Measurements of Poly(m-Phenylene Isophthalamide) and its Block Copolymers with Poly(Ethylene Oxide) or Poly(Dimethyl Siloxane) on Films Treated to Develop Crystallinity

The poly(m-phenylene isophthalamide) homopolymer may exist in either an amorphous or crystalline condition. The immediately previous sections have of course just dealt with the tensile properties in the amorphous state. Consideration of crystalline PmPIA homopolymer and block copolymers was also an objective of this work.

Since PmPIA homopolymer was invariably obtained in the amorphous state, methods to promote crystallization were sought. Generally speaking, polymers that possess the potential to crystallize may be induced to do so when one or more of several techniques is employed, e.g., drawing, drawing in combination with thermal treatment, or solvent treatments. The literature (89,99,136,141) regarding these polyamides names all three of those techniques. However, treatment with concentrated formic acid is one of the most attractive methods.

The relatively high glass transition temperature (T_g = 280-290°C) of poly(m-phenylene isophthalamide) indicates the presence of strong binding forces which prevent the movement of polymeric chains and subchains. Among other factors, H-bonding significantly contributes to the retention of polymer glassy states. Therefore, the interruption of H-bonding is an important factor in phase transition from glassy to crystalline states.

TABLE XVII

TENSILE PROPERTIES OF POLY(m-PHENYLENE ISOPHTHALAMIDE-b-DIMETHYL SILOXANE) BLOCK COPOLYMERS COLLECTED ON "AS-CAST" FILMS

Copolymer	Type of Block Structure A=PmPIA	Wt.% Poly-siloxane	Maximum Engineering Strength (Pa)x10^{-5}	Young's Modulus (Pa)x10^{-7}	Elongation-to-Break (%)
S15.A_{18}.S15-1	BAB	9.0	0.60	2.06	6.0
S15.A_{18}.S15-2	BAB	12.0	0.50	1.96	7.0
S50.A_{13}.S50	BAB	13.0	1.08	3.33	11.0
S50.A_{18}.S50	BAB	23.0	0.23	0.69	25.5
S60.A_{16}.S60	BAB	28.0	0.85	2.26	10.0
S60.A_{17}.S60	BAB	13.0	0.34	1.28	5.0
S60.A_{18}.S60	BAB	14.0	0.28	1.08	17.0
S90.A_{13}.S90	BAB	13.0	0.56	2.35	7.0
S90.A_{18}.S90	BAB	13.0	0.57	1.57	16.0
S140.A_{13}.S140	BAB	12.0	0.91	3.04	7.0
S140.A_{14}.S140	BAB	14.0	0.50	2.06	6.5
S140.A_{15}.S140	BAB	16.0	0.76	2.45	11.5
A.S15.A-1	ABA	14.0	0.27	1.28	2.0
A_{18}.S15.A_{18}	ABA	12.0	0.70	3.34	3.0
A.S60.A-1	ABA	13.0	0.28	1.08	3.0
A.S60-A-2	ABA	14.0	0.25	1.32	4.0
A_{16}.S60.A_{16}	ABA	24.0	0.90	1.37	10.0
A_{17}.S60.A_{17}	ABA	14.0	0.34	1.28	5.0
A_{18}.S60.A_{18}	ABA	30.0	0.18	0.50	21.0

Two kinds of H-bonding (intra- and intermolecular) between the oxygen of carbonyl group and slightly acidic hydrogen of -NH- group can occur. H-bonding must be interrupted to accomplish any phase transition. In general, the extent of H-bonding can be influenced by high temperature, plasticizer or swelling in polar solvent. Since concentrated formic acid is polar, it is a rational and effective choice for promoting crystallization.

To investigate the crystallizability of PmPIA, precut 1.0cm wide strips of films of poly(m-phenylene isophthalamide) and its herein investigated block copolymers were immersed into concentrated formic acid for 24 hours. After washing with water, specimens were mounted on a plate glass and dried in warm vacuo for at least 72 hours. A new set of dimensions was then taken on the treated specimen. Generally, up to 15 percent concentration of the width and up to 10 percent gain in the thickness of specimen was observed.

The stress-strain measurements were performed under the same conditions as mentioned for "as-cast" films. An increase of the tensile properties of poly(m-phenylene isophthalamide) was detected.

For block copolymers of poly(m-phenylene isophthalamide) and poly(ethylene oxide) end blocks similar results were observed, but the general increase in the tensile properties was not as clearly pronounced. On the other hand, quite a different situation was observed for block copolymers of the same segments but reversed sequence placement. While the increase in ductility (up to 10-fold) was always detected for block copolymers having poly(ethylene oxide) center blocks, often there was a

considerable decrease in maximum engineering strength. The three following tables (Tables XVIII, XIX, and XX) give a summary of data collected from the testing described in this section.

IV.3.2. Dynamic Mechanical Studies

Dynamic mechanical tests measure the response of a material to periodically applied force. These tests have one considerable advantage over most mechanical tests. The wide temperature range can be used for measurements within considerably short times. From such measurements the complex modulus E* can be obtained. This modulus is given by the ratio of maximum stress to the maximum strain. For the case of tensile deformation, the complex modulus E* is defined as:

$$E^* = \sqrt{E'^2 + E''^2} = \frac{\text{stress}_{max}}{\text{strain}_{max}}$$

where: E' = represents the real part of the complex modulus, often called the tensile storage modulus being defined as:

$$E' = /E^*/ \cdot \cos\delta$$

E'' = represents an imaginary part of complex modulus, a damping term also known as a loss modulus, defined as:

$$E'' = /E^*/ \cdot \sin\delta$$

δ = represents a phase angle between stress and strain with its tangent value defined as:

$$\tan\delta = \frac{E''}{E'}$$

TABLE XVIII

TENSILE PROPERTIES OF POLY(m-PHENYLENE ISOPHTHALAMIDE) HOMOPOLYMERS MEASURED ON FILMS TREATED WITH CONCENTRATED FORMIC ACID FOR POSSIBLE DEVELOPMENT OF CRYSTALLINITY

Polymer	Maximum Engineering Strength (Pa)x10^{-5}	Young's Modulus (Pa)x10^{-7}	Elongation-to-Break (%)
A-3	0.28	0.98	2.0
A-4	0.28	0.98	2.0
A-5	0.80	2.26	8.0
A-6	0.70	2.45	3.5
A-7	0.93	2.16	13.0
A-8	1.01	2.16	14.0
A-9	0.70	2.37	4.0
A-10	0.54	2.37	4.0
A-11	0.77	2.85	15.0
A-12	1.13	2.85	13.0
A-13	0.75	2.35	11.0
A-14	0.78	2.06	6.0
A-15	0.65	2.84	7.0
A-16	0.70	2.16	7.0
A-17	0.42	2.26	8.0
A-18	0.41	2.16	3.0

TABLE XIX

TENSILE PROPERTIES OF POLY(m-PHENYLENE ISOPHTHALAMIDE-b-ETHYLENE OXIDE) BLOCK COPOLYMERS MEASURED ON FILMS TREATED WITH CONCENTRATED FORMIC ACID FOR POSSIBLE DEVELOPMENT OF CRYSTALLINITY

Copolymer	Type of Block Structure A=PmPIA	Wt.% PEO	Maximum Engineering Strength (Pa)x10^{-5}	Young's Modulus (Pa)x10^{-7}	Elongation to-Break (%)
E4.A_7.E4	BAB	19.0	0.27	1.60	2.0
E4.A_7.E4-Is	BAB	12.0	0.43	2.06	3.0
E4.A_{12}.E4	BAB	13.0	0.80	2.23	25.0
E10.A_8.E10	BAB	13.0	0.37	1.72	4.0
E10.A_8.E10-Is	BAB	12.0	0.40	1.83	4.0
E10.A_9.E10	BAB	18.0	0.16	1.22	2.0
E10.A_{11}.E10	BAB	20.0	0.41	1.42	5.0
E10.A_{12}.E10	BAB	20.0	0.72	2.83	5.0
E40.A_9.E40	BAB	20.0	0.27	1.10	3.0
E40.A_{10}.E40	BAB	17.0	0.30	1.51	3.0
E40.A_{11}.E40	BAB	25.0	0.44	1.72	10.0
E40.A_{12}.E40	BAB	27.0	0.36	1.96	4.0
E60.A_{11}.E60	BAB	26.0	0.27	1.25	9.0
E60.A_{12}.E60	BAB	31.0	0.22	0.67	13.0
A.E10.A-1	ABA	6.0	0.65	1.43	30.0
A.E10.A-2	ABA	7.0	0.36	1.32	25.0
A.E40.A-1	ABA	12.0	0.27	0.85	27.0
A.E40.A-2	ABA	13.0	0.37	1.25	27.0
A.E60.A-1	ABA	15.0	0.43	0.87	36.0
A.E60.A-2	ABA	26.0	0.14	0.93	38.0

TABLE XX

TENSILE PROPERTIES OF POLY(m-PHENYLENE ISOPHTHALAMIDE-b-DIMETHYL SILOXANE) BLOCK COPOLYMERS MEASURED ON FILMS TREATED WITH CONCENTRATED FORMIC ACID FOR POSSIBLE DEVELOPMENT OF CRYSTALLINITY

Copolymer	Type of Block Structure A=PmPIA	Wt.% of Poly-siloxane	Maximum Engineering Strength (Pa)x10^{-5}	Young's Modulus (Pa)x10^{-7}	Elongation-to-Break (%)
S15.A_{18}.S15-1	BAB	12.0	0.80	2.06	24.0
S15.A_{18}.S15-2	BAB	9.0	0.90	1.96	22.0
S50.A_{13}.S50	BAB	13.0	0.91	2.35	31.0
S50.A_{18}.S50	BAB	23.0	0.18	0.75	15.0
S60.A_{16}.S60	BAB	28.0	0.97	2.40	12.0
S60.A_{17}.S60	BAB	13.0	0.39	1.67	14.0
S60.A_{18}.S60	BAB	14.0	0.31	1.28	15.0
S90.A_{13}.S90	BAB	13.0	0.69	1.94	18.0
S90.A_{18}.S90	BAB	13.0	0.55	1.37	21.0
S140.A_{13}.S140	BAB	12.0	0.82	1.77	13.0
S140.A_{14}.S140	BAB	14.0	0.59	1.76	15.0
S140.A_{15}.S140	BAB	16.0	0.72	2.35	32.0
A.S15.A-1	ABA	14.0	0.25	1.71	3.0
A_{18}.S15.A_{18}	ABA	12.0	0.68	2.06	4.0
A.S60.A-1	ABA	13.0	0.39	1.82	3.0
A.S60.A-2	ABA	14.0	0.33	1.82	4.0
A_{16}.S60.A_{16}	ABA	24.0	1.02	1.57	19.0
A_{17}.S60.A_{17}	ABA	14.0	0.39	1.08	4.0
A_{18}.S60.A_{18}	ABA	30.0	0.14	0.44	12.0

The phase angle delta (δ) is strongly temperature dependent. Mechanical damping of low frequency oscillation depends basically on the state of the polymer during the measurement. In general, if polymers undergo certain types of phase or state transitions, the damping of low frequency oscillation goes through a sharp peak in a temperature range associated with the transition. For this reason, dynamic mechanical tests are a useful tool to study the structure of polymers.

Dynamic mechanical tests were performed on the entire series of aromatic homopolyamides and their block copolymers with poly(ethylene oxide). Takayanagi's direct reading Rheovibron, Model DDV-II, manufactured by Toyo Measuring Instruments Company, Japan, was used as an analytical tool. The great disadvantage of the available instrument was its temperature range of operation. Steady, reproducible results were obtained within the temperature range from room temperature to only 200°C. This, of course, eliminated the search for a double glass transition temperature (T_g = -67°C for PEO and T_g = 280-290°C for aromatic polyamide), a phenomenon characteristic to block copolymer structures. On the other hand, some changes in damping properties of block copolymers with respect to poly(m-phenylene isophthalamide) were expected. Also some transitions associated with melting of poly(ethylene oxide) (temperature range from 55-70°C), and its subsequent decomposition (around 190-265°C) were expected.

Table XXI summarizes the results obtained from these measurements. It can be seen that poly(m-phenylene isophthalamide) homopolymer did not

TABLE XXI

TEMPERATURE-DEPENDENT DYNAMIC TENSILE MODULI OF POLY(m-PHENYLENE ISOPHTHALAMIDE) AND ITS BLOCK COPOLYMERS WITH POLY(ETHYLENE OXIDE)

Polymer or Copolymer	Type of Block A=PmPIA	Wt.% PEO (%)	Temperature Range °C	Melting of PEO °C	Decomposition of PEO °C	$E^* = E''$ (for Low tanδ) $\times 10^{-10}$ dyne/cm^2	E' $\times 10^{-9}$ dyne/cm^2
A-3	---	---	34-58	---	---	2.13-2.16	0.68
A-4	---	---	34-82	---	---	2.04-2.16	0.70
A-5	---	---	34-280	---	---	3.52-5.01	0.88-1.23
A-6	---	---	44-280	---	---	3.70-5.00	0.90-1.20
A-7	---	---	24-272	---	---	3.40-4.00	0.70-1.60
A-8	---	---	26-270	---	---	3.53-4.70	0.80-1.30
A-9	---	---	24-260	---	---	2.20-2.50	0.60-0.90
A-10	---	---	24-264	---	---	2.25-2.65	0.67-0.95
A-11	---	---	30-282	---	---	5.00-5.70	1.45-3.35
A-12	---	---	22-284	---	---	4.60-4.95	1.30-2.35
E4.A_7.E4	BAB	19.2	26-252	44-74	170-up	2.80-1.10	1.00-1.90
E4.A_7.E4-Is	BAB	12.0	40-223	n.d.*	185-up	2.00-1.00	0.80-1.20
E4.A_{12}.E4	BAB	13.3	32-210	n.d.	n.d.	3.70-4.25	1.60-1.98
E10.A_8.E10	BAB	13.2	23-268	50-77	200-260	3.00-1.80	1.00-4.00
E10.A_8.E10-Is	BAB	11.7	24-251	n.d.	210-up	7.00-4.00	1.00-15.0
E10.A_9.E10	BAB	18.2	24-260	52-68	200-235	4.00-2.20	0.70-2.30
E10.A_{11}.E10	BAB	19.6	26-280	47-65	190-up	3.50-2.40	0.60-2.90

TABLE XXI (continued)

Polymer or Copolymer	Type of Block A=PmPIA	Wt.% PEO (%)	Temperature Range °C	Melting of PEO °C	Decomposition of PEO °C	E* = E'' (for Low tanδ) $x10^{-10}$ dyne/cm^2	E' $x10^{-9}$ dyne/cm^2
E10.A_{12}.E10	BAB	19.6	25-203	40-67	160-up	3.29-2.27	0.56-0.85
E40.A_{9}.E40	BAB	19.5	30-275	n.d.	210-245	1.10-0.70	0.30-1.10
E40.A_{10}.E40	BAB	16.8	22-282	50-86	195-up	1.60-1.00	0.40-1.50
E40.A_{11}.E40	BAB	25.0	37-280	n.d.	190-up	1.60-1.10	0.30-3.00
E40.A_{12}.E40	BAB	27.2	29-242	44-71	170-up	1.10-0.90	0.30-1.30
E60.A_{11}.E60	BAB	26.2	24-224	50-72	180-up	1.70-1.60	0.60-1.10
E60.A_{12}.E60	BAB	31.3	36-87	42-72	n.d.	1.33-122	0.19-0.65
A.E10.A-1	ABA	6.3	22-205	55-74	n.d.	4.44-4.20	0.78-0.97
A.E10.A-2	ABA	7.2	24-180	48-87	160-up	3.46-2.93	0.71-1.86
A.E40-A-1	ABA	12.3	20-203	53-83	170-up	3.01-1.82	0.72-1.42
A.E40.A-2	ABA	13.5	21-90	54-78	n.d.	2.71-2.56	0.70-0.88
A.E60.A-1	ABA	15.2	20-203	50-77	n.d.	2.86-1.42	0.73-1.39
A.E60.A-2	ABA	26.3	23-182	56-77	160-up	2.69-1.53	0.88-1.36

n.d.*--value not detected.

go through any transition. Values of the complex modulus E* and the real and imaginary parts remained essentially constant within the applied temperature range. On the other hand, the melting region of poly(ethylene oxide) was detected in many cases by the increase in tanδ value in the appropriate temperature range. The decomposition of poly(ethylene oxide) was clearly detected for block copolymers with poly(ethylene oxide) end blocks. These copolymers underwent a color change (discoloration) during their testing while samples of poly(m-phenylene isophthalamide) remained essentially unchanged.

Due to the narrow working limits of the above mentioned instrument with respect to the temperature range, it was decided not to investigate possible transitions or dynamic mechanical behavior of block copolymers of poly(m-phenylene isophthalamide) with poly(dimethyl siloxane).

CHAPTER V

BASIC MORPHOLOGICAL STUDIES

The molecular architecture of a polymeric system is primarily responsible for its microscopic structure which in turn strongly influences its mechanical properties. This basic statement is especially true for block copolymers. The different phases separated into "homopolymeric" domains of different sizes and shapes are closely interrelated to the overall material character and performance.

In the previous chapters of this dissertation, the variations among physical-mechanical properties of different block copolymers were clearly established. Only one important question remains: What caused those significant differences and after all, what is the morphology of these block copolymers? To answer these questions, transmission optical microscopy was performed on all homopolymers and block copolymers. Some very interesting observations were disclosed by this analytical tool. An extensive number of optical micrographs were taken on a LEITZ optical microscope with a NIKON camera in the magnification range of 100-500x using polarized light. "As cast" and "concentrated HCOOH treated" films were used as specimens. The translucent character of several samples was an unpleasant fact one had to deal with. To overcome this disadvantage, attempts were made to recast some of those specimens as very thin films, expectedly transparent. Unfortunately, some previously observed features were lost on these very thin films.

The close relation of the morphology to the thickness of specimen was thus established. No significant difference between "as cast" and "concentrated HCOOH treated" films was observed. Possibly the resolution/magnification was not great enough to reveal the expected changes.

V.1. THE MORPHOLOGY OF POLY(m-PHENYLENE ISOPHTHALAMIDE-b-ETHYLENE OXIDE) BLOCK COPOLYMERS

As pointed out several times already, three basically different block copolymers were synthesized. The difference in sequence placement (ABA versus BAB), generally affecting the nature of continuous and dispersed phases, could introduce different morphological features.

Starting with the aromatic homopolyamide, no spectacular observations were made. Regardless of the nature of prepared films ("as cast" versus "concentrated HCOOH treated"), the polymers showed typical characteristics of the glassy, amorphous state. No indication of any highly ordered structure was detected. A typical micrograph of glassy poly(m-phenylene isophthalamide) is presented as Figure 6a. Block copolymers having poly(ethylene oxide) center block are similar as a single phase glassy amorphous state dominates the morphology of these materials (see Figure 6b). Only in the case of one material with 27 percent by weight of ethylene oxide units incorporated within copolymer backbone, some indication of phase separation was detected.

Very interesting observations were also made for block copolymers of poly(m-phenylene isophthalamide) with poly(ethylene oxide) end

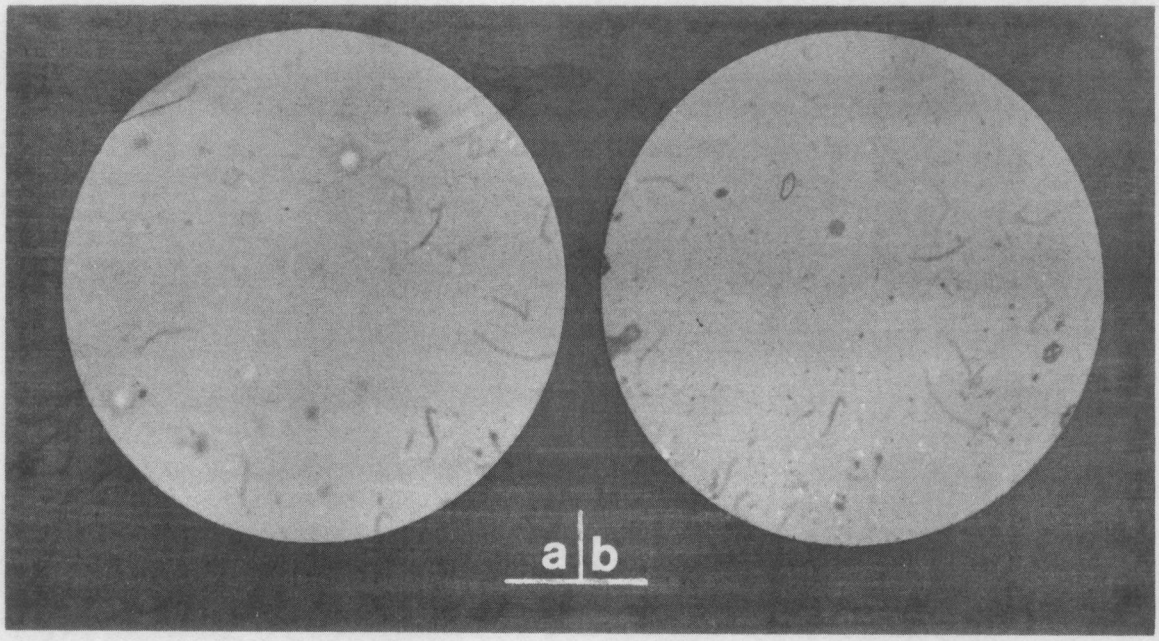


Figure 6. Optical micrographs representing the glassy amorphous state of poly(m-phenylene isophthalamide) and its block copolymer with poly(ethylene oxide) center block. Magnification 550x.

(a) Poly(m-phenylene isophthalamide) - (A_{11})

(b) Block copolymer of PmPIA with PEO center block - (A.E40.A-2)

blocks. Basically, the development of highly organized structures represented by the appearance of maltese crosses was observed for both "as cast" and "concentrated HCOOH treated" films. As can be seen from Figure 7, illustrating structure development with increasing molecular weight of end blocks, these maltese crosses appeared for the first time for poly(ethylene oxide) end blocks with molecular weight of 4000 g/mole. Note however that phase separation within these systems was clearly detected for the entire range of molecular weight of mentioned end blocks (400, 1000, 4000, and 6000 g/mole).

A search for the nature of these maltese crosses followed immediately after those observations. It was thought originally that the maltese cross was formed from poly(ethylene oxide). To prove or disprove that speculation several experiments were done. Swelling of a specimen in water, "hot stage" microscopy and differential scanning calorimetry were performed on specimens where significant maltese cross development was detected.

Prolonged "swelling" of films in water (for 45 minutes at 55°C) did not affect the appearance of maltese crosses although water is a good solvent for poly(ethylene oxide). This was the first indication that the maltese crosses were not poly(ethylene oxide).

"Hot stage" microscopy was performed in the following manner. A sample with maltese crosses was mounted between two microscope glasses. The sample was then placed on the microscope stage and hot air was blown on it from a hot-air gun. Unfortunately, no device for temperature measurement was attached to the sample. In order to overcome this

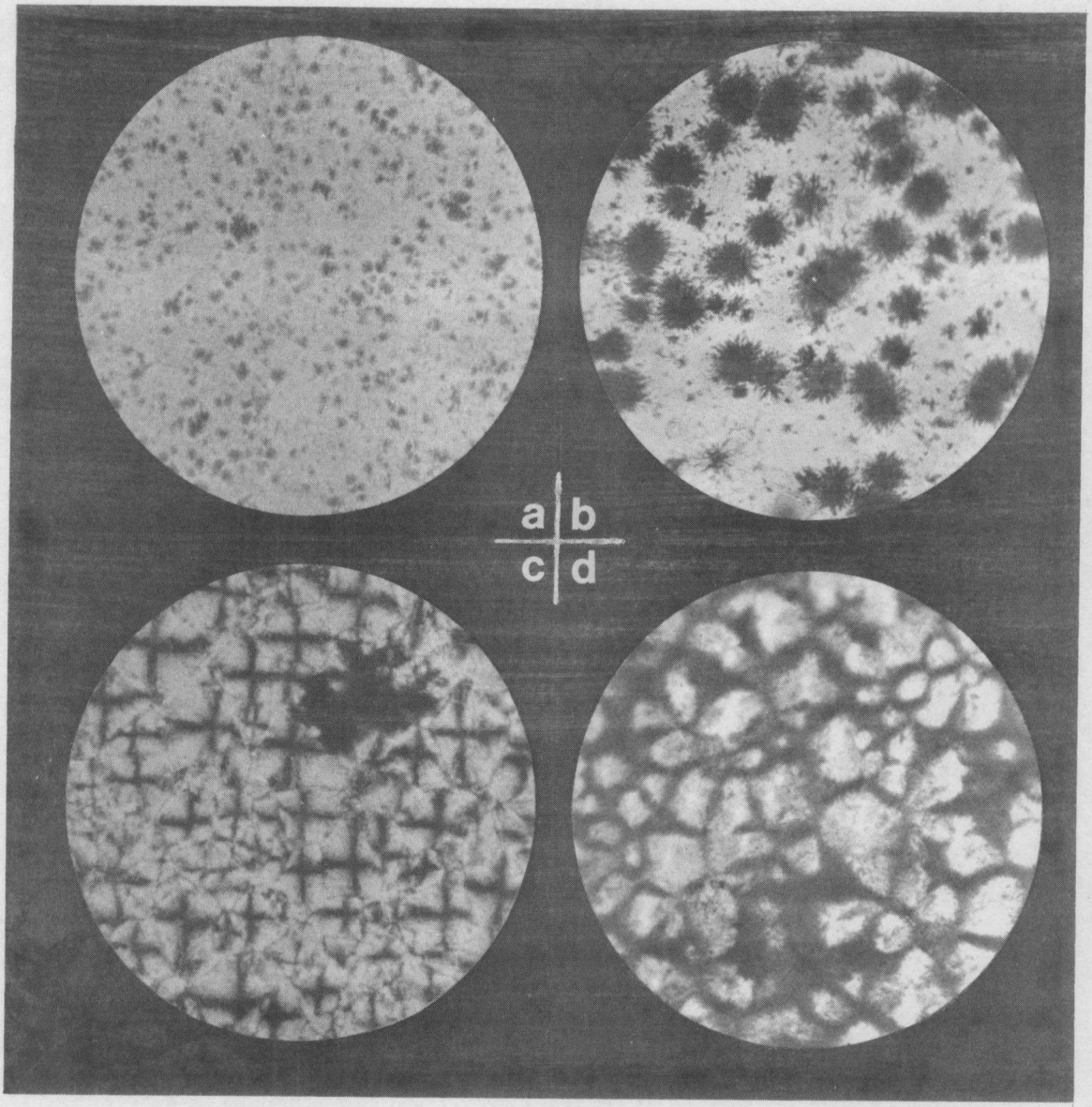


Figure 7. Optical micrographs representing the development of maltese crosses in block copolymers of poly(m-phenylene isophthalamide) and poly(ethylene oxide) end blocks. Magnification 550x.

(a) E4.A_{12}.E4

(b) E10.A_{12}.E10

(c) E40.A_{12}.E40

(d) E60.A_{12}.E60

disadvantage, this procedure was "calibrated" with a sample of polyethylene with clearly developed spherullitic structure. Those spherullites melted in a stream of hot air within approximately 30 seconds, and appeared back upon the removal of the heat source. The above described procedure was then used for all samples showing the development of maltese crosses. The heating time period was prolonged to the point where discoloration of the sample was observed. Optical micrographs were taken at 10 minute intervals. No melting of the crosses was ever detected. Quite to the contrary, a sharpening of maltese cross boundaries occurred indicating the general effect of annealing on the structure development.

Thermal investigation into the nature of the observed structures involved DSC scans. Generally, no melting endotherm was ever recorded in the temperature range characteristic for melting of poly(ethylene oxide) (45-80°C). In general, the materials were stable up to approximately 400°C before melting accompanied by a decomposition was detected. No T_g or T_{cryst} transition for poly(m-phenylene isophthalamide) was observed. There is another important observation. No decomposition of poly(ethylene oxide) (180-265°C) was detected. All those observations clearly proved that observed maltese crosses were not poly(ethylene oxide) segments. An intensive investigation of the nature of the above described observation (via electron microscopy and x-ray analysis) is being conducted by Mr. Yu-der Lee of our research team and will be presented within his dissertation (206).

V.2. THE MORPHOLOGY OF POLY(m-PHENYLENE ISOPHTHALAMIDE-b-DIMETHYL SILOXANE) BLOCK COPOLYMERS

The presence of two highly incompatible segments within the block copolymer backbone generally causes pronounced phase separation. Judging from the value of solubility parameter δ ($\delta_{\text{poly(m-phenylene isophthalamide)}} = 10.0\ [\text{cal/cc}]^{1/2}$ (207) and $\delta_{\text{poly(dimethyl siloxane)}} = 7.3\text{-}7.5\ [\text{cal/cc}]^{1/2}$ (208)), these polymers should be incompatible. This fact was clearly established within the course of the synthetic work. Thus phase separation within the system containing both of the above mentioned segments was expected and observed. Optical microscopy as previously described was used to investigate the morphology of these block copolymers. Both "as cast" and "concentrated HCOOH treated" film specimens, previously used for the determination of tensile properties, were used for morphology investigations. In general, no considerable difference was observed for "as cast" and "concentrated HCOOH treated" films.

Sphere-shaped particles dispersed in some kind of continuous phase were detected. These spheres might be "macro domains" of poly(dimethyl siloxane). The size and area density distribution of these spheres slightly varied with changes in molecular weight of poly(dimethyl siloxane). It must be pointed out here that no difference was observed for different sequence placement (ASA versus SAS) within the block copolymer backbone. This might be caused by the closeness in weight percent incorporation of poly(dimethyl siloxane)

for almost all of these synthesized copolymers. As can be seen from Figure 8, spheres of poly(dimethyl siloxane) are embedded in continuous phase of poly(m-phenylene isophthalamide). The series of those micrographs was taken on block copolymers having poly(m-phenylene isophthalamide) center blocks. This typical situation was also observed for blocks having a reversed sequence placement.

In conclusion, one can point out, that the "two-phase" nature of block copolymers made from poly(m-phenylene isophthalamide) and poly(dimethyl siloxane) was clearly established. The observed poly(dimethyl siloxane) spheres could act as kind of "energy sinks" during the application of the force on the copolymer. It is a matter of fact this could cause the increase in elongation-to-break generally measured for those block copolymers (see Section IV.3.1).

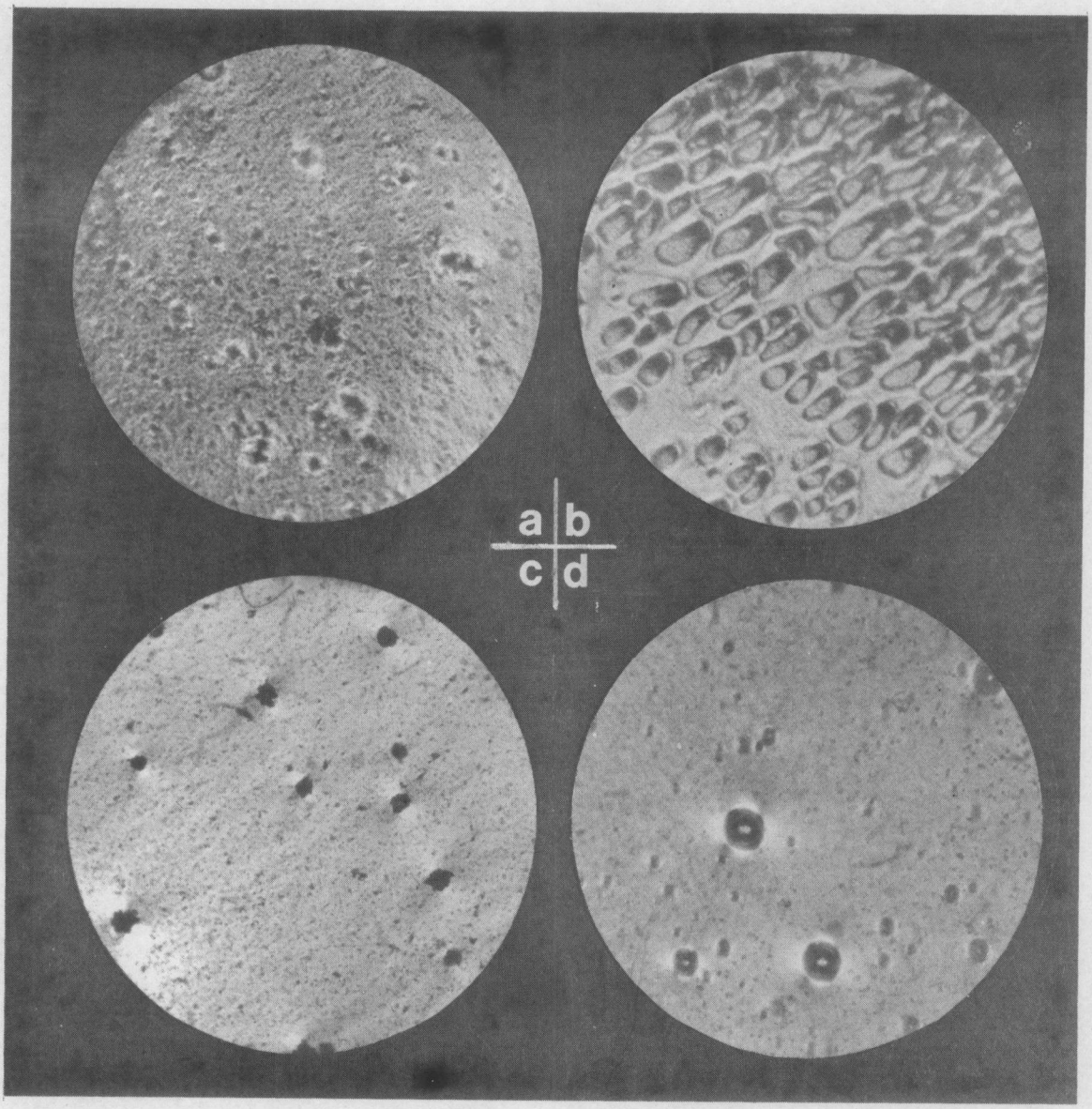


Figure 8. Optical micrographs representing the development of phase separation within poly(m-phenylene isophthalamide-b-dimethyl siloxane) block copolymers with increasing molecular weight of polysiloxane. Magnification 550x.

(a) S15.A_{18}.S15

(b) S50.A_{13}.S50

(c) S90.A_{18}.S90

(d) S140.A_{13}.S140

CHAPTER VI

DISCUSSION

Three principal accomplishments were achieved within the scope of this research. The synthesis of block copolymers with varying chemical structure based on poly(m-phenylene isophthalamide) with poly(ethylene oxide) and poly(dimethyl siloxane) cosegments gave rise to interesting molecular architectures for these systems. The differences in morphology among these synthesized block copolymers were manifested in modified physical-mechanical properties for each identifiable structural type. More specifically, different sequence placement (ABA versus BAB) together with the variation in the nature of the cosegment and its molecular weight influenced phase relationships, morphologies, and tensile behavior.

Block copolymer modification of poly(m-phenylene isophthalamide) homopolymer has not been previously investigated. Yet one can easily be impressed with its properties (strength, toughness, excellent thermal and chemical stabilities), and also by the potential for interesting properties arising from the combination of this homopolymer with certain other homopolymer cosegments.

Poly(m-phenylene isophthalamide) is a highly crystallizable polymer. This suggests the possibility to synthesize block copolymers having both segments crystallizable. Among the limited number of cosegments available for this purpose, polyethers are suitable. These

materials are highly crystallizable, fairly compatible with poly(m-phenylene isophthalamide) and are soluble in solvents required for the preparation of PmPIA. Therefore poly(ethylene oxide), the material possessing the highest thermal stability among the polyethers, was chosen for the synthesis of poly(m-phenylene isophthalamide)-polyether block copolymers.

On the other hand, the interaction of the properties of PmPIA with properties of highly flexible, noncrystallizable polymers might create a material which will not only possess high strength and stability, but also fairly high ductility. There are many polymers having the character of elastomers. Unfortunately, only a few of them retain their chemical stability at elevated temperatures. Polysiloxanes are in general a group of elastomers having excellent elasticity and good thermal stability. Therefore poly(dimethyl siloxane) was selected to form block copolymers based on poly(m-phenylene isophthalamide) and polysiloxanes.

Recalling that in general for block copolymers, the nature of the continuous and dispersed phases depends on the composition of the block copolymer and in fact determines the morphology and mechanical behavior of the material. In accord with this general statement, large variations in mechanical properties and an unusual change in morphology of block copolymers based on poly(m-phenylene isophthalamide) and poly(ethylene oxide) or poly(dimethyl siloxane) were recorded. Therefore, the intercomparison of block copolymers with varying chemical structure and sequence placement is possible.

On the other hand, changes within a given type of block copolymer have their data too scattered to be useful for a reasonable intra-comparison. There are too many uncontrolled variables involved. The dependence of mechanical properties of PmPIA on its molecular weight, the variation of molecular-level properties (MWD, solubility) of the cosegment with its molecular weight, the difference within sequence placement together with the variations in the chemical nature of cosegments considered, dictates the preparation of an extremely large number of samples to investigate all the features of a particular type of block copolymer.

VI.1. THE SYNTHESIS

Different synthetic routes were designed and used for the synthesis of $(AB)_n$, ABA and BAB block copolymer structures. The application of modified, self-regulating, low-temperature copolycondensation seems to be the only approach leading to the formation of block copolymers based on the above mentioned segments. It is recognized, however, that polycondensation in general is not the best way for synthesizing block copolymers possessing a high level of structural order. On the other hand, this is the only known method for the preparation of poly(m-phenylene isophthalamide).

The formation of alternating polyblock structures $(AB)_n$ seems to be limited to low-molecular weight compounds. There is substantial difference between the reactivity of species involved.

Several synthetic methods were used for the triblock structures. Although the highest effort was put forth to achieve balanced stoichiometry during these syntheses to control sequence placement, the formation of a mixture of the desired block copolymer together with other types of block structures and PmPIA homopolymer is possible.

IR together with NMR was used for the verification of block copolymer structure and conclusively showed block formation. There is of course no absolute way to determine the actual sequence placement within these block copolymers by those techniques. The extensive extraction of each sample prior to these analyses should eliminate the presence of any unreacted cosegments. Unfortunately the lack of proper instrumentation prohibited verification that the fractionation technique eliminated any possible PmPIA and low molecular weight "tails."

Further research in this field should be oriented toward still additional synthetic modifications of herein considered block copolymers. Poly(m-phenylene isophthalamide) homopolymer modification via ring substituted monomers influences its T_g, T_m and solubility. Another cosegment (namely, polycaprolactone possessing higher thermal stability while still fairly compatible with poly(m-phenylene isophthalamide)), might be employed for the synthesis of still other types of block copolymers.

VI.2. BASIC MORPHOLOGY

The basic morphology of these block copolymers responds to the cosegment nature and its placement within the block copolymer backbone.

Single versus two-phase behavior, microphase geometry and sequence placement are strongly interrelated while they also interact with the general performance characteristics of these block copolymer systems.

The basic morphology of poly(m-phenylene isophthalamide)/ poly(dimethyl siloxane) block copolymers, regardless of the attempted sequence placement, follows the general trends observed for most block copolymers. The continuous phase is believed to be mainly PmPIA which contains embedded spheres rich in poly(dimethyl siloxane). The size of these spheres and their area density vary with molecular weight of poly(dimethyl siloxane). Furthermore, the size distribution of those spheres appears to be quite broad. Due to the nature of both cosegments and the synthetic problems reported in Sections III.3.2, III.4.2, III.5.2, and III.7, one could speculate that only mixtures of alternating polyblocks with PmPIA homopolymer were formed and thus one would expect similar morphologies.

On the other hand, block copolymers composed from poly(m-phenylene isophthalamide) and poly(ethylene oxide) did not follow the usual behavior of most block copolymers. Block copolymers having poly(ethylene oxide) center blocks showed typical characteristics of single-phase glassy polymers. In general, no detectable phase separation was observed for these materials. This is in fact a significant observation because single phase block copolymers have not been previously reported. Although there is a lack of information about PmPIA for a serious thermodynamic treatment of phase separation, a brief look at the values of the solubility parameter δ suggests that both homopolymers are fairly

miscible. The set of δ values for PmPIA/PEO/DMAc (10.0/9.2-9.8/10.8 [cal/cc$^{1/2}$]) represent rather close agreement. One additional fact must now be highlighted. It is well known that polymer phase separation is a molecular weight dependent phenomenon. In this regard when PEO of 6000 g/mole MW and more than 20 percent center block incorporation was examined, the solubility limit was exceeded and phase separation began to become apparent.

The development of phase separation was clearly detected for block copolymers of PmPIA having PEO end blocks. The observation of maltese crosses within these block copolymers indicated the formation of some organized structure. A structural development characterized by the appearance of maltese crosses is in general associated with crystalline spherullites. However, in this case the lack of supporting evidence of crystallinity from x-ray analysis (206) rules out this characterization.

It is a known fact that strong H-bonding exists in PmPIA homopolymer systems. This secondary binding force between oxygen of the carbonyl group and hydrogen of the amide function is important to the formation of ordered structure. In the case of block copolymers of poly(m-phenylene isophthalamide) with poly(ethylene oxide) end blocks both segments can participate in H-bonding. In addition to the above mentioned source for H-bonds, the oxygen of the ether linkage of PEO introduces an additional site for H-bond formation.

Chemically-bonded poly(ethylene oxide) chain end blocks have more degrees of freedom than poly(m-phenylene isophthalamide) center

blocks. Therefore, the participation of PEO end blocks in ordered structure development can be expected. Although the synthetic routes used for the preparation of these block copolymers were designed for a particular type of block copolymer structure, the extension of PEO chains still might occur. Therefore, a simple "plasticizing effect" of these subchains can increase the free motion of copolymer macromolecules causing the possible rearrangement within the system.

In conclusion one might speculate, that the interaction of both above mentioned features can lead to the formation of organized "micelle-type" structure, probably composed of poly(m-phenylene isophthalamide) "core" surrounded by the "shell" of poly(ethylene oxide) segments. These micelles will have at least two refractive indexes (one for a "core" and other for a "shell") together with the variation in densities of inner and outer portions. The appearance of maltese crosses thus could be accounted for by the formation of the above described structural order in these block copolymers.

VI.3. MODIFIED MECHANICAL PROPERTIES

From the engineering point of view, the influence of cosegment (poly(ethylene oxide) or poly(dimethyl siloxane)) on the tensile properties of poly(m-phenylene isophthalamide) block copolymers is very important. The tensile properties respond to the nature of the cosegment and its placement within the block copolymer backbone. The variation in observed morphologies is closely tied to the differences

in maximum engineering strength, Young's modulus and ductility of these block copolymers.

The influence of cosegment molecular weight on the maximum engineering strength of block copolymers of poly(m-phenylene isophthalamide) and poly(ethylene oxide) end or center blocks was clearly determined. Generally, a decreasing trend in maximum engineering strength with increasing MW of poly(ethylene oxide) was observed for both sequence placements (ABA vs BAB), as can be seen from Figure 9.

Unfortunately, this observation was not clearly detected for block copolymers containing poly(m-phenylene isophthalamide) and poly(dimethyl siloxane) segments. Thus another variable must be used to investigate the influence of poly(dimethyl siloxane) on tensile behavior of these block copolymers. Therefore, it is more instructional to investigate the influence of weight percent incorporation of poly(dimethyl siloxane) on the maximum engineering strength of these block copolymers regardless of molecular weight of polysiloxane cosegment. In general, the maximum engineering strength decreases with the increase in the incorporation of that segment, as can be seen from Figure 10. For comparison, data representing the same phenomena for PmPIA/PEO block copolymers are also included in Figure 10.

In a similar manner Young's modulus decreases with an increasing incorporation of cosegment within a particular block copolymer system. Figure 11 illustrates this trend for "as-cast" film specimens. Similar observations were made also for specimens treated with concentrated formic acid for possible development of crystallinity, as illustrated on Figure 12.

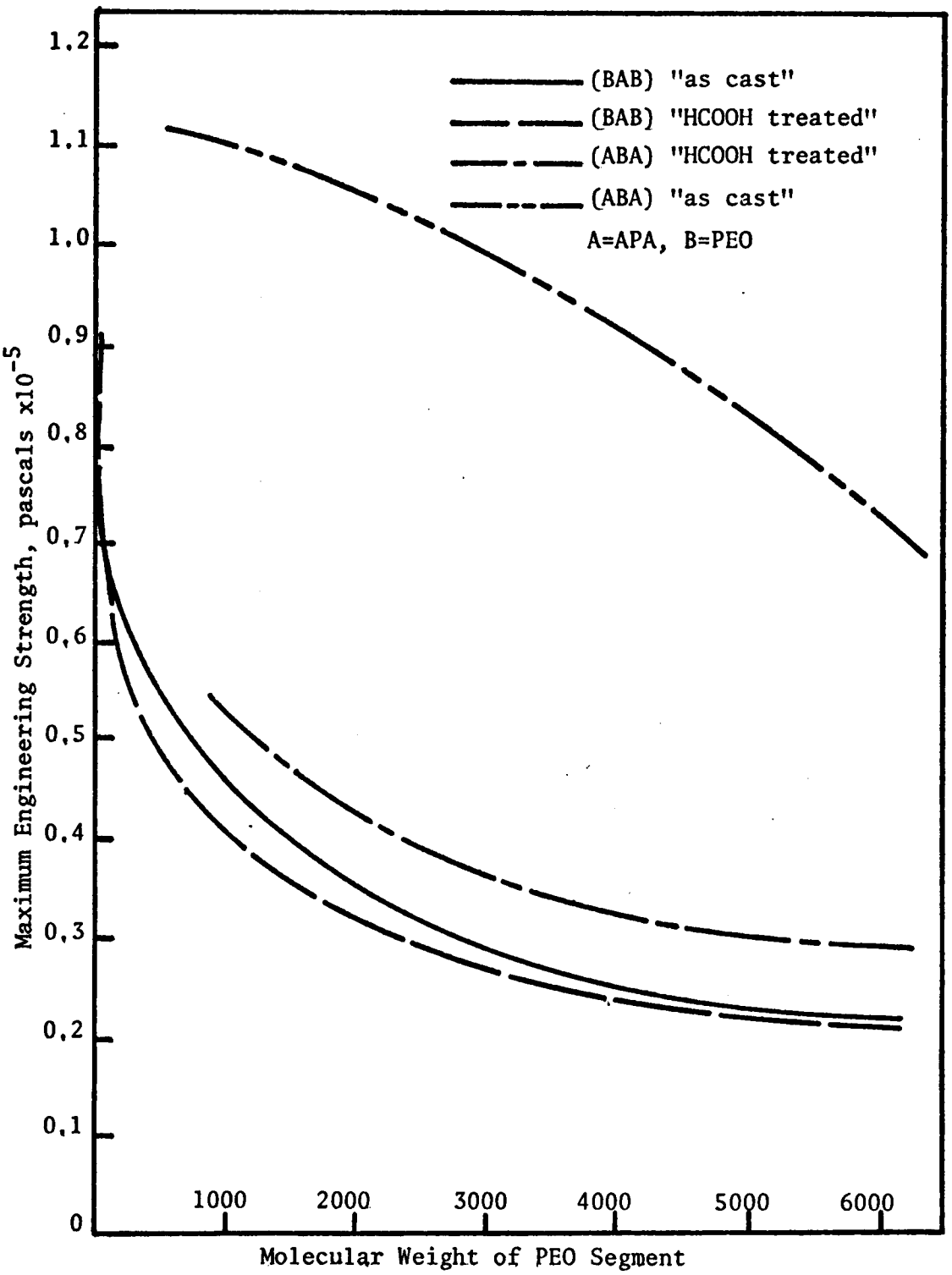


Figure 9. The influence of molecular weight of poly(ethylene oxide) segment on maximum apparent engineering strength of poly(m-phenylene isophthalamide-b-ethylene oxide) block copolymers.

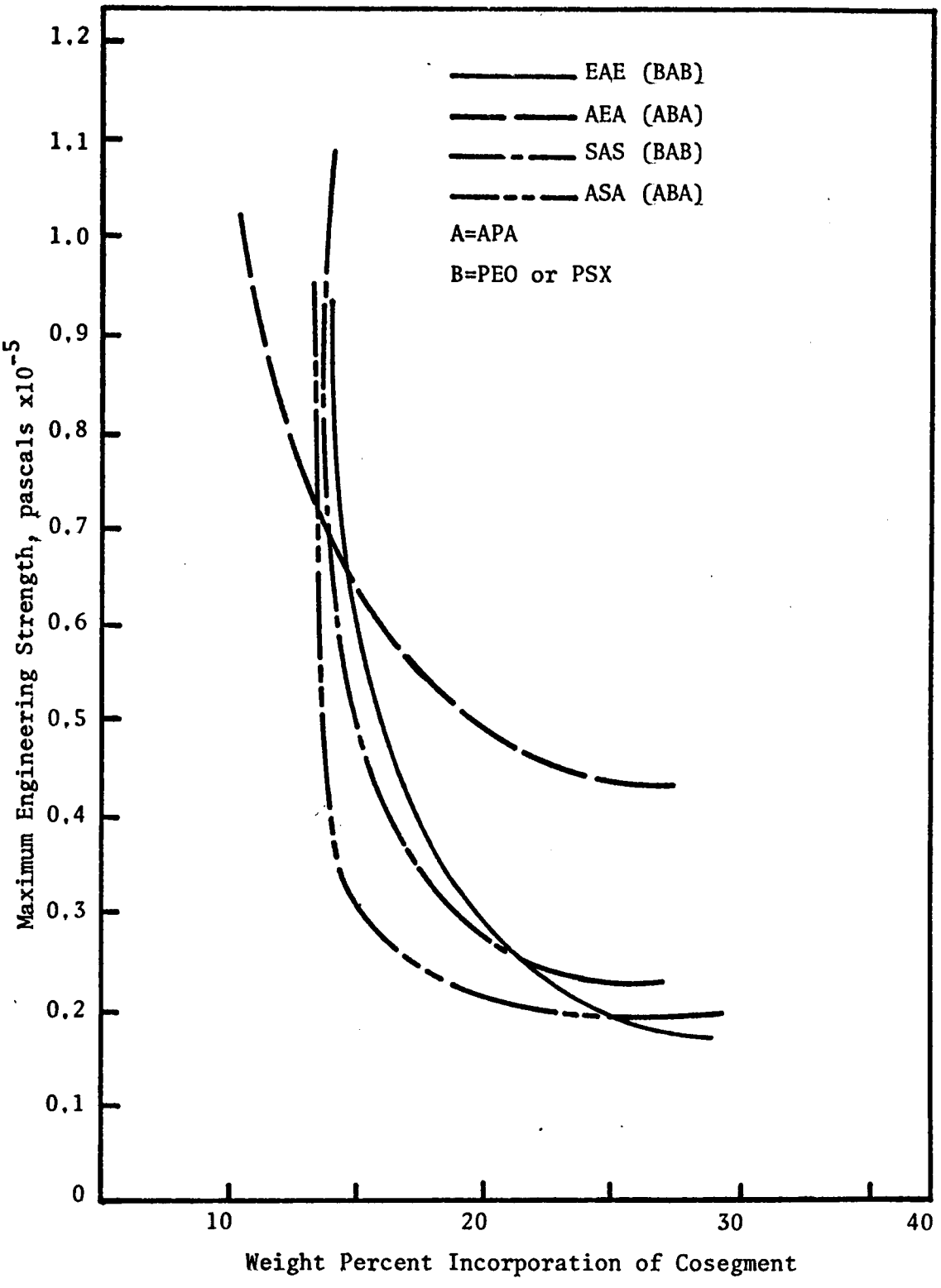


Figure 10. The influence of weight percent incorporation of cosegment on maximum apparent engineering strength of block copolymers of poly(m-phenylene isophthalamide) and copoly(ethylene oxide) or copoly(dimethyl siloxane).

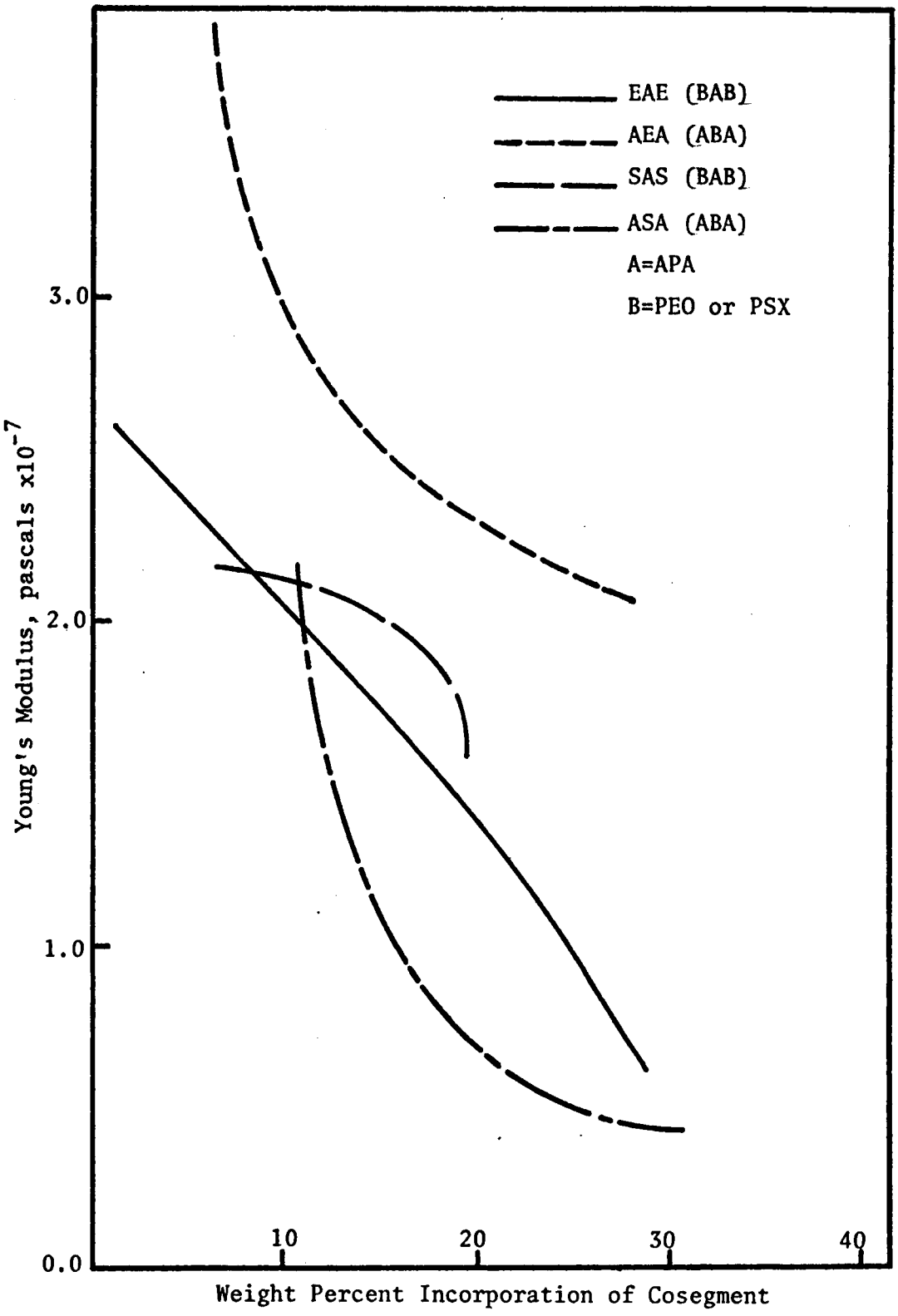


Figure 11. The variation of Young's modulus with weight percent incorporation of cosegment for block copolymers of poly(m-phenylene isophthalamide) and copoly(ethylene oxide) or copoly(dimethyl siloxane). Data collected on "as-cast" films.

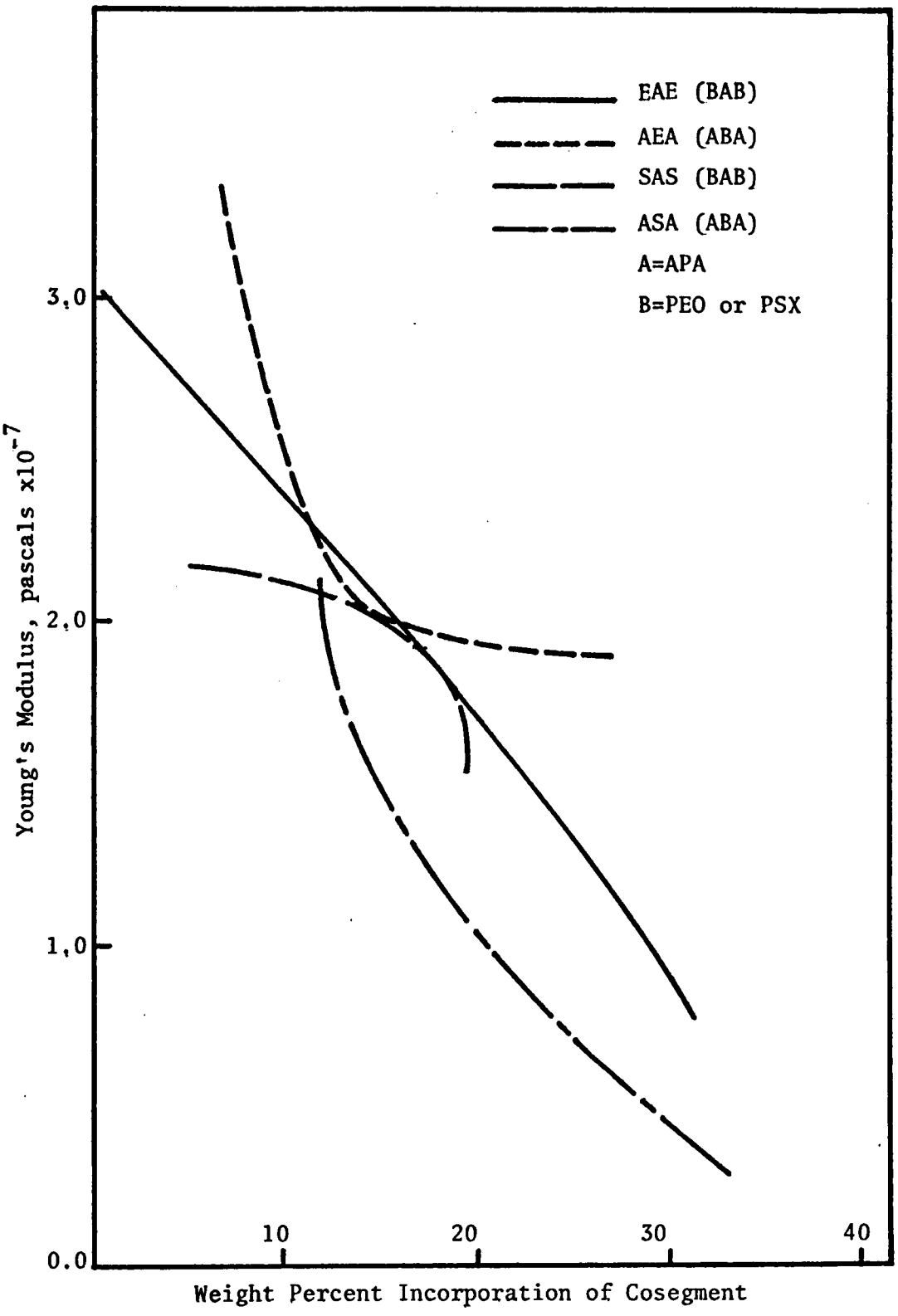


Figure 12. The variation of Young's modulus with weight percent incorporation of cosegment for block copolymers of poly(m-phenylene isophthalamide) and copoly(ethylene oxide) or copoly(dimethyl siloxane). Data collected on films treated with concentrated formic acid for possible development of crystallinity.

The interaction between the flexible cosegments and poly(m-phenylene isophthalamide) segments should yield an increase in the elongation-to-break for these block copolymers. Therefore, better ductility on the part of the block copolymers compared to PmPIA homopolymer was expected. In general, the increase in elongation-to-break with an increasing incorporation of cosegment was detected for most of these block copolymers. Figure 13 illustrates this behavior for "as-cast" films while Figure 14 represents the basic trend observed for films treated with concentrated formic acid for crystallinity development.

As can be seen from the preceding paragraphs, no quantitative relationships were drawn for the variations of the tensile properties of block copolymers with different cosegments. Only general trends illustrating the dependence of mechanical properties on the chemical nature of cosegment for block copolymers composed of PmPIA and PEO or PSX are presented. Although the best known techniques were used for the preparation of each identifiable block copolymer structure, the tensile test sample preparation and conducting of these tests, there were several variables more or less outside the control of the experimenter at the present time. The chemical composition, cosegment molecular weight and the choice of the aromatic polyamide were in fact the only controllable variables one had to deal with. Several assumptions had to be made in order to investigate the variation of the tensile properties of these block copolymers with the difference in the cosegment character. The tensile properties of PmPIA homopolymer

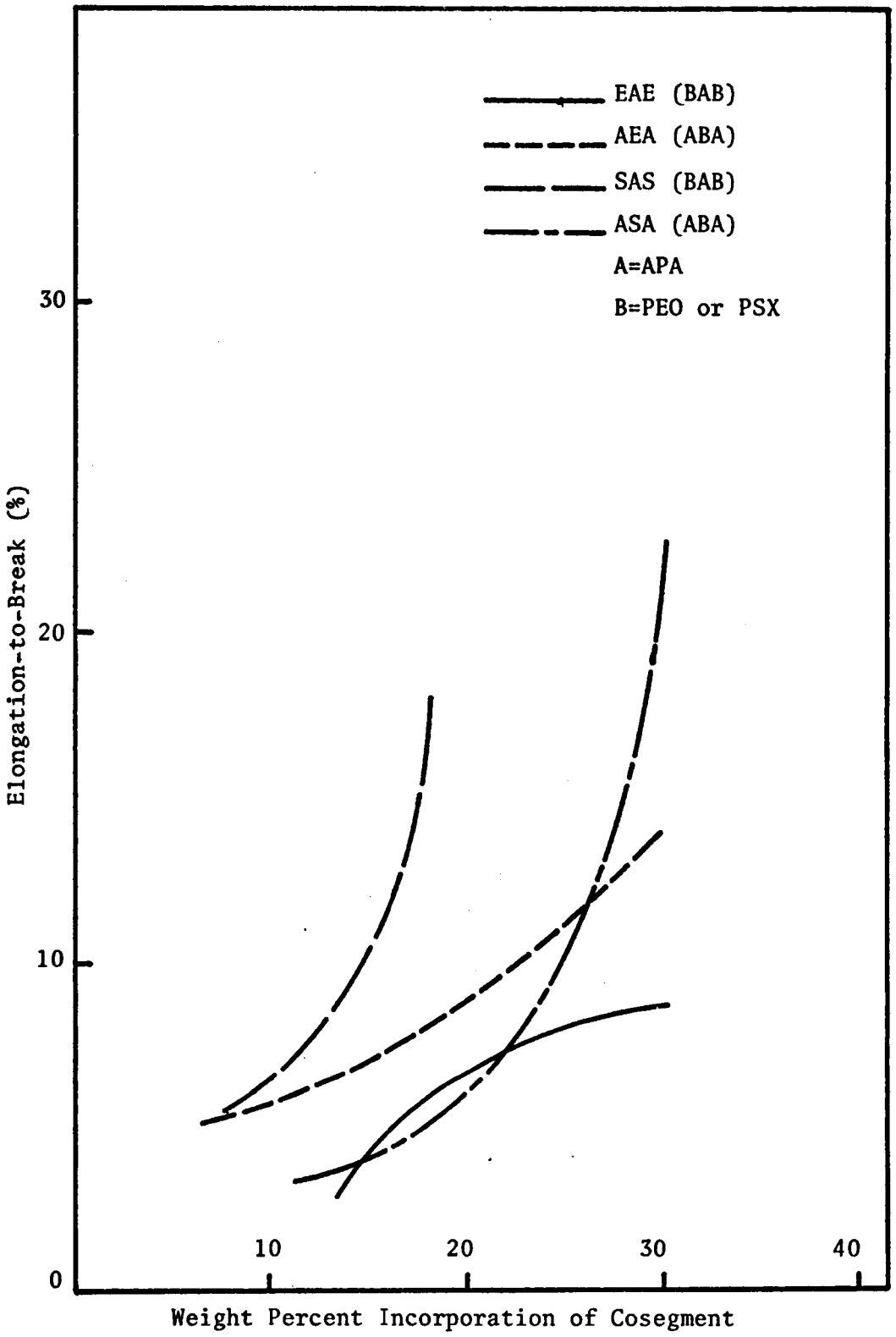


Figure 13. The variation of ductility with weight percent incorporation of cosegment for block copolymers of poly(m-phenylene isophthalamide) and copoly(ethylene oxide) or copoly(dimethyl siloxane). Data collected on "as-cast" films.

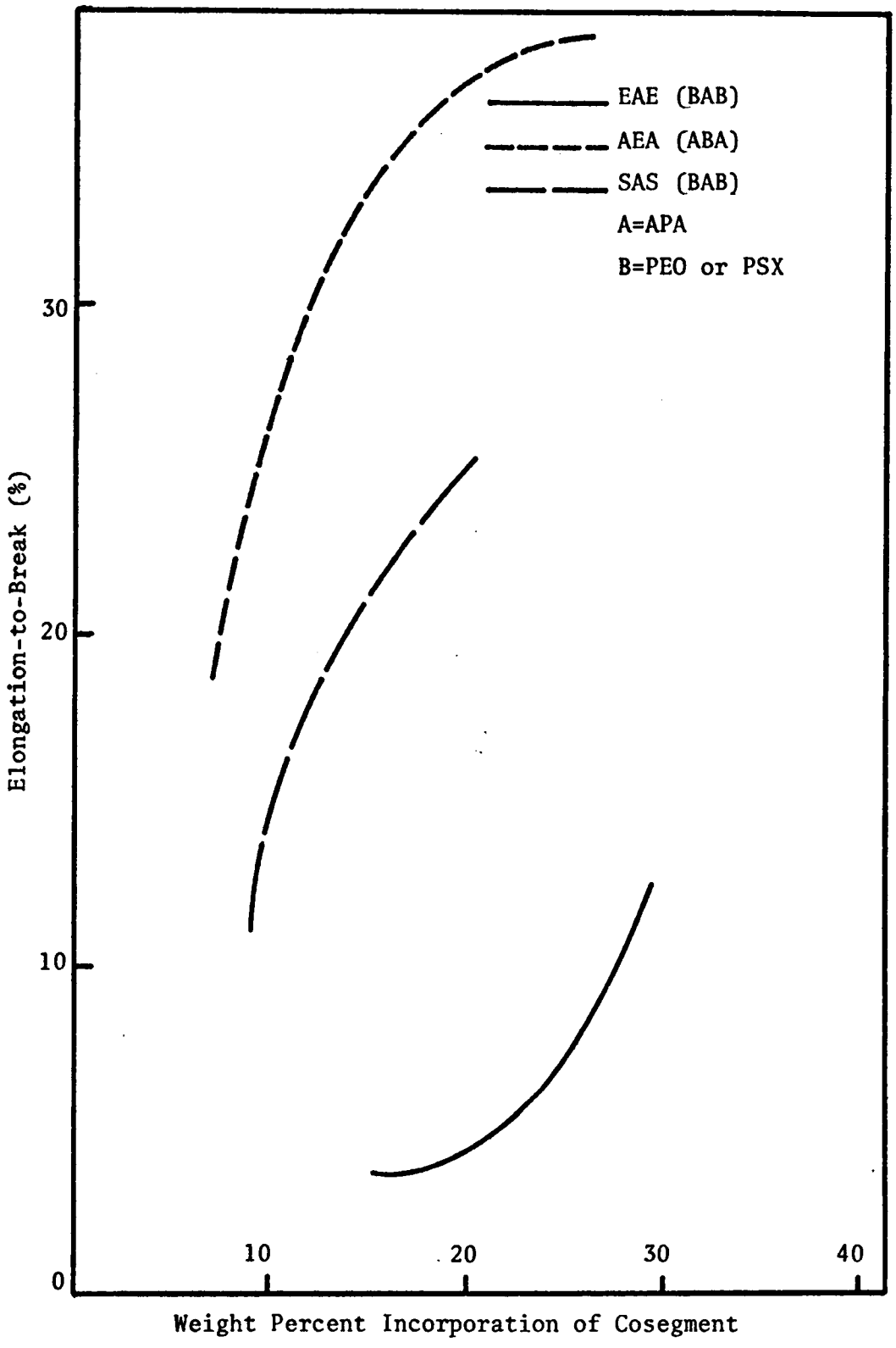


Figure 14. The variation of ductility with weight percent incorporation of cosegment for block copolymers of poly(m-phenylene isophthalamide) and copoly(ethylene oxide) or copoly(dimethyl siloxane). Data collected on films treated with concentrated formic acid for possible development of crystallinity.

were considered as the invariable property, thus independent of its molecular weight. Tensile data were collected on film specimens having different thickness (0.01-0.1 cm), possibly blemished edges, and variable degree of the surface precipitation. These, together with the already described problems during the synthesis of each type of block copolymer structure, caused scattering of the tensile testing data and thus ruled out the possibility of serious quantitative analysis of obtained results.

Recalling the earlier discussion (Chapter IV.3.1.3) dealing with the transition from amorphous to the crystalline states of poly(m-phenylene isophthalamide) and its block copolymers with poly(ethylene oxide) or poly(dimethyl siloxane), one now starts to appreciate still another influence of the morphology on mechanical properties of these systems. Starting with PmPIA homopolymer, the treatment with concentrated formic acid increased the tensile properties of this material. The increase in maximum engineering strength was often accompanied with the improvement in ductility, while Young's modulus was slightly lowered. Considerable necking was frequently noted during these tests. Table XVIII (Chapter IV.3.1.3, page 107) reported obtained results.

Turning now to the PmPIA block copolymers, the above mentioned trends were observed in some cases. A general increase in maximum engineering strength and elongation-to-break was observed for block copolymers having PmPIA center blocks with PEO or PSX end blocks. Already presented Tables XIX and XX (Chapter IV.3.1.3, pages 108 and 109) report obtained results.

While block copolymers of poly(m-phenylene isophthalamide) with poly(dimethyl siloxane) center blocks showed no considerable difference with trends described above, quite a different result was found for block copolymers of PmPIA with PEO center blocks. Although the elongation-to-break increased upon the above mentioned treatment, substantial degradation in maximum engineering strength and Young's modulus was always observed. There might be chain destruction of poly(ethylene oxide) caused by formic acid. If this destruction occurs within PEO center blocks, its influence on the size of macromolecule and subsequently on the tensile strength is self-evident.

The measurement of $T_{cryst.}$ of treated film specimens [$T_{cryst.}$ was not detected either for poly(m-phenylene isophthalamide) or its block copolymers with poly(ethylene oxide) and poly(dimethyl siloxane)], represents an additional proof of the phase transition within these materials.

VI.4. FINAL REMARKS

The research described in this dissertation should not be taken as the last stage in this field. Quite to the contrary, it is felt that the "cornerstone" was laid for additional investigations. If additional research will continue (and its continuation is strongly encouraged here), one might generate materials with even more valuable properties. Also a further understanding of some observed phenomena will reveal important information regarding the creative principle of polymer science. This is to say, for example, attaining a full

understanding of the unusual morphologies associated with EAE triblocks, its sequence dependence and development of structural order will represent a major accomplishment in polymer science.

REFERENCES

REFERENCES

1. H. Mark, Text. Res. J., 23, 294 (1953).

2. S. Prabhakas, M. Santappa, J. Sci. Ind. Res., 26 (2), 76 (1967).

3. R. J. Ceresa, Block and Graft Copolymers, Butterworth, London (1962).

4. W. J. Burlant, A. S. Hoffman, Block and Graft Copolymers, Reinhold, New York (1960).

5. M. Szwarc, Nature (London(, 178, 1168 (1956).

6. M. Szwarc, M. Levy, R. Milkovich, J. Am. Chem. Soc., 78, 2656 (1956).

7. S. Schlick, M. Levy, J. Phys. Chem., 64, 883 (1960).

8. A. V. Tobolsky, A. Rembaum, J. Appl. Polym. Sci., 8 (1), 307 (1964).

9. R. Milkovich, So. African Patent 642,271 (1964).

10. M. Morton, Encyclopedia of Polymer Science and Technology, J. Wiley & Sons, New York, 15, 508 (1971).

11. J. T. Baily, E. T. Bishop, W. R. Hendricks, G. Golden, N. R. Legge, Rubber Age, 98, 69 (1966).

12. A. W. van Breen, M. Vlig, Rubber and Plastics Age, 47, 1070 (1966).

13. G. M. Estes, S. L. Cooper, A. V. Tobolsky, J. Macromol. Sci., Rev. Macromol. Chem., C,4 (2), 313 (1970).

14. S. L. Rosen, Polym. Sci. Eng., 7, 115 (1967).

15. M. L. Miller, The Structure of Polymers, Reinhold, New York, 167, 256 (1968).

16. F. M. Merrett, Trans. Far. Soc., 50, 759 (1954).

17. F. M. Merrett, Ric. a. Sci., 25, 279 (1955).

18. F. M. Merrett, British Patent 797,346 (1958).

19. G. E. Molau, J. Polym. Sci., A-3, 1267 (1965).

20. G. E. Molau, J. Polym. Sci., A-3 , 4235 (1965).

21. G. Holden, R. Milkovich, U. S. Patent 3,265,765 (1966).

22. R. D. Deanin, JSPE, 23, 45 (1967).

23. J. Dancon, M. Jobard, M. Lautant, M. Michel, M. Riou, C. Wipper, J. Polym. Sci., 34, 948 (1957).

24. W. H. Jones, Can. J. Chem., 34, 517 (1956).

25. F. D. Hartley, J. Polym. Sci., 34, 397 (1959).

26. J. E. Climie, E. F. T. White, J. Polym. Sci., 47, 149 (1960).

27. S. Ye. Bresslov et al., Vysokomol. Soedin., 4, 250 (1962).

28. G. Gallott, M. Leng, H. Benoit, P. Rempp, J. Chim. Phys., 59, 1093 (1962).

29. G. Gallott, E. Franta, P. Rempp, H. Benoit, J. Polym. Sci., C-4, 472 (1963).

30. G. E. Molau, Macromolecules, 1, 260 (1968).

31. A. Skoulios, G. Finaz, J. Parrott, Comp. Rend., 251, 739 (1960).

32. A. Skoulios, G. Finaz, J. Parrott, Comp. Rend., 252, 3467 (1961).

33. G. Finaz, A. Skoulios, C. Sadron, Comp. Rend., 253, 265 (1961).

34. A. Skoulios, G. Finaz, J. Chim. Phus., 59, 473 (1962).

35. C. Sadron, Chim. Pure et Appl., 4, 347 (1962).

36. C. Sadron, Angew. Chem., 75, 472 (1963).

37. C. Sadron, Chim. Ind., 96, 507 (1966).

38. W. H. Stockmayer, L. D. Moore, M. Firman, P. M. Epstein, J. Polym. Sci., 16, 517 (1955).

39. G. E. Molau, J. Polym. Sci., B-3, 1007 (1965).

40. A. Dobry, F. Boyer-Kawenoki, J. Polym. Sci., 2, 90 (1947)

41. R. L. Scott, J. Chem. Phys., 17, 279 (1947).

42. J. P. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 555 (1967).

43. R. J. Kern, J. Polym. Sci., 21, 19 (1956).

44. R. J. Kern, R. J. Slocombe, J. Polym. Sci., 15, 183 (1955).

45. A. Dondos, P. Rempp, H. Benoit, J. Polym. Sci., B-4, 293 (1966).

46. M. Lautant, M. Magat, Z. Phys. Chemie, 16, 292 (1958).

47. G. M. Burnett, P. Meares, C. Paton, Trans. Far. Sco., 58, 737 (1962).

48. J. R. Urwin, J. M. Stearne, Die Makromol. Chemie, 78, 194, 204 (1964).

49. S. Krause, J. Phys. Chem., 68, 1948 (1964).

50. J. R. Urwin, J. M. Stearne, Eur. Polym. J., 1, 227 (1965).

51. H. Inagaki, Die Makromol. Chemie, 87, 166 (1965).

52. H. Inagaki, T. Miyamoto, Die Makromol. Chemie, 86, 189 (1965).

53. G. E. Molau, J. Polym. Sci., A-1, 4, 1595 (1966).

54. G. E. Molau, H. Kesskkula, Canadian Patent 754,636 (1967).

55. R. J. Angelo, R. M. Ikeda, M. L. Wallach, Polymer, 6, 141 (1965).

56. R. M. Ikeda, M. L. Wallach, R. J. Angelo, Block Polymers, Plenum Press, London-New York, A. S. Aggarwal, editor (1970).

57. A. R. Shultz, ACS, Polym. Prepr., 9 (2), 1455 (1967).

58. H. Tompa, Trans. Far. Soc., 45, 1142 (1949).

59. G. Cee, Quart. Rev., 1, 265 (1947).

60. J. H. Hildebrand, R. L. Scott, The Solubility of Nonelectrolytes, 3rd edition, Dover Publishers, New York (1964).

61. J. H. Hildebrand, R. L. Scott, Regular Solutions, Prentice-Hall, Englewood Cliffs, New Jersey (1962).

62. C. Yu, R. F. Gould, editors, Multicomponent Polymer Systems, Adv. in Chem., Series 99, ACS, Washington, D.C. (1971).

63. P. A. Small, J. Appl. Chem., 3, 71 (1953).

64. K. H. Hoy, J. Paint Technol., 42 (541), 76 (1970).

65. J. P. Flory, J. Chem. Phys., 9, 660 (1951); 10, 51 (1942).

66. M. L. Huggins, J. Chem. Phys., 9, 440 (1941).

67. S. Krause, J. Macromol. Sci., Rev. Macromol. Chem., C-7 (2), 251 (1972).

68. T. Inoue, T. Soen, T. Hashimoto, K. Kawai, J. Polym. Sci., A-2 (7), 1283 (1969).

69. W. B. Black, Trans. Acad. Sci. N. Y., 32 (7), 765 (1970).

70. S. L. Kwolek, P. W. Morgan, W. R. Sorenson, U. S. Patent 3,063,966 (1962).

71. F. L. Beste, C. W. Stephens, German Patent 1,107,399 (1958).

72. British Patent 871,581 (1961), to DuPont Company.

73. L. B. Sokolov, T. V. Kudim, DAN(USSR), 158 (5), 1139 (1964).

74. V. N. Savinov, L. B. Sokolov, Khim. Volokna, No. 4, 22-5 (1965).

75. R. Caldwell, R. Gilkey, French Patent 1,474,508 (1967).

76. R. Caldwell, R. Gilkey, French Patent 1,474,509 (1967).

77. V. S. Naumov et al., Vysokomol. Soedin., A-11 (10), 2141 (1969).

78. M. Eguchi, H. Maekawa, Japan Patent 71 41,387 (1971).

79. E. Hoeroldt, German Patent 2,037,254 (1972).

80. I. K. Nekrasov et al., Vysokomol. Soedin., A-14, 789 (1972).

81. S. Ozawa, H. Fujie, Japan Patent 72 10,863 (1972).

82. N. Ogata, K. Sanui, K. Iyjima, Kogyo Kagaku Zasshi, 73 (11), 2381 (1970).

83. E. E. Magat, U. S. Patent 2,831,834 (1958).

84. R. W. Smith, W. A. H. Huffman, W. T. Dye, Jr., U. S. Patents 3,203,933 (1965) and 3,240,758 (1966).

85. C. W. Stephens, U. S. Patent 3,472,819 (1969).

86. J. Preston, R. W. Smith, U. S. Patent 3,225,011 (1965).

87. H. Hasegawa, Bull. Chem. Soc. Japan, 27, 327 (1965).

88. J. Cologne, E. Fichet, Bull. Soc. Chim. France, 412 (1955).

89. British Patent 901,159 (1962), to DuPont Company.

90. S. L. Kwolek, French Patent 1,526,745 (1968).

91. P. S. Antal, A. J. DeDomonicis, D. L. Szucs, German Patent 1,924,736 (1969).

92. C. R. Campbell, M. J. Matthews, R. W. Smith, French Patent 1,577,262 (1969).

93. M. I. Shilhan, T. A. Lukianovich, V. V. Korshak, Vysokomol. Soedin., A-15 (3), 549 (1973).

94. L. B. Sokolov, et al., Vysokomol. Soedin., 2, 698, 710 (1960).

95. C. W. Stephens, L. F. Beste, U. S. Patent 3,068,188 (1962).

96. P. W. Morgan, S. L. Kwolek, J. Polym. Sci., A-2, 181 (1962).

97. S. L. Kwolek, French Patent 1,526,746 (1968).

98. N. K. Moshchinskaya et al., USSR Patent 209,736 (1968).

99. P. W. Morgan, S. Bair, Belgian Patent 726,050 (1969).

100. A. A. Fedorov, L. B. Sokolov, Vysokomol. Soedin., B-12 (3), 205 (1970).

101. S. L. Kwolek, German Patent 1,929,713 (1970).

102. S. L. Kwolek, German Patent 1,929,694 (1970).

103. H. Blades, German Patent 2,219,703 (1971).

104. E. Chodkowski et al., Polimery (Polish), 16, 514 (1971).

105. H. S. Morgan, Jr., German Patent 2,113,450 (1971).

106. H. Blades, German Patent 2,219,646 (1971).

107. M. A. Dahlen, U. S. Patent 2,001,526 (1935).

108. H. Preston, W. B. Black, J. Polym. Sci., B-3, 845 (1965).

109. J. Preston, W. B. Black, J. Polym. Sci., B-4, 267 (1966).

110. J. Preston, F. Dobinson, J. Polym. Sci., B-2, 1171 (1964).

111. J. Preston, J. Polym. Sci., A-1, 529 (1966).

112. F. Bodinson, J. Preston, J. Polym. Sci., A-1 (4), 2093 (1966).

113. J. Preston, W. R. Smith, C. J. Stephens, J. Polym. Sci., C-19, 7 (1967).

114. J. Preston, W. B. Black, J. Polymer. Sci., C-19, 17 (1967).

115. J. Preston, W. B. Black, J. Polym. Sci., C-23 , 441 (1968).

116. J. Preston, W. B. Black, J. Polym. Sci., A-1 (5), 2429 (1976).

117. J. Preston, W. F. DeWinter, W. B. Black, J. Polym. Sci., A-1 (7), 283 (1969).

118. J. R. Holsten, J. Preston, M. R. Lilyquist, Appl. Polym. Symp., 9, 63 (1969).

119. J. Preston, Appl. Polym. Symp., 9, 75 (1969).

120. J. Preston, W. B. Black, Appl. Polym. Symp., 9, 107 (1969).

121. J. Preston, W. B. Black, W. F. DeWinter, Appl. Polym. Symp., 9, 145 (1969).

122. French Patent 1,583,315 (1969), to Monsanto Company.

123. H. S. Morgan, Jr., U. S. Patent 3,642,706 (1972).

124. J. Preston, R. W. Smith, J. Polym. Sci., B-4 (12), 1033 (1966).

125. J. Preston, R. W. Smith, W. B. Black, T. L. Tolbert, J. Polym. Sci., C-22, 855 (1969).

126. J. Preston, R. W. Smith, S. M. Sun, J. Appl. Polym. Sci., 16 (2), 3237 (1972).

127. H. W. Hill, S. L. Kwolek, U. S. Patent 3,006,899 (1961).

128. D. C. Pease, U. S. Patent 3,197,443 (1965).

129. Netherlands Patent 6,607,006 (1966), to ICI Company.

130. N. Yoda et al., French Patent 1,448,897 (1965).

131. S. N. Krasnov et al., Vysokomol. Soedin., 7, 813 (1965).

132. S. R. Rafikov et al., Izv. Akad. Nauk Kaz. USSR, Ser. Khim., 17, 75 (1967).

133. S. V. Vinogradova, V. V. Korshak, Ya. S. Vygodskii, USSR Patent 195,100 (1967).

134. G. Roques, J. Neel, C. R. Acad. Sci. (Paris), Ser. C, 264 (1), 63 (1967).

135. S. L. Kwolek, U. S. Patent 3,328,352 (1967).

136. H. W. Hill, S. L. Kwolek, W. Sweeny, U. S. Patent 3,349,062 (1967).

137. L. Bonnard, F. Buisson, French Patent 1,466,568 (1967).

138. S. L. Kwolek, H. E. Hill, W. Sweeny, U. S. Patent 3,380,969 (1968).

139. N. K. Moshchinskaya et al., USSR Patent 249,623 (1969).

140. P. W. Morgan, German Patent 1,816,106 (1969).

141. P. W. Morgan, T. I. Bair, U. S. Patent 3,673,143 (1972).

142. M. Keichi, Japan Patent 72 35,093 (1972).

143. V. Guryaniova et al., Vysokomol. Soedin., A-14 (9), 1964 (1972).

144. B. F. Malichenko et al., Vysokomol. Soedin., A-14 (10), 2079 (1972).

145. H. E. Kuenzel, G. Blankenstein, F. Bentz, G. Nischk, German Patent 2,144,126 (1973).

146. B. F. Malichenko et al., Vysokomol. Soedin., A-15 (5), 1073 (1973).

147. Netherlands Patent 6,610,158 (1967), to Monsanto Company.

148. F. F. Holub, French Patent 1,471,563 (1967).

149. N. M. Bogdanov et al., USSR Patent 197,161 (1967).

150. J. R. Caldwell, U. S. Patent 3,297,656 (1967).

151. C. W. Stephens, U. S. Patent 3,418,275 (1968).

152. French Patent 1,526,594 (1968), to Toyo Royo Company.

153. N. M. Kozyreva et al., Vysokomol. Soedin., B-13 (3), 230 (1970).

154. E. Reske, L. Brikman, H. Cherdron, German Patent 2,118,510 (1971).

155. N. D. Malegina et al., Vysokomol. Soedin., B-14 (6), 476 (1972).

156. H. C. Bach, W. B. Black, J. B. Clements, Appl. Polym. Symp., 9, 167 (1969).

157. J. Sauer, R. Huisgen, H. J. Sturm, Tetrahedron, 11, 214 (1960).

158. J. R. Holsten, R. Lilyquist, J. Polym. Sci., A-3, 3905 (1965).

159. J. R. Holston, R. Lilyquist, J. Polym. Sci., C-19, 77 (1967).

160. C. F. Berr, U. S. Patent 3,316,213 (1967).

161. B. M. Culbertson, R. Murphy, J. Polym. Sci., B-5, 807 (1967).

162. K. Saotomo, K. Sato, Die Makromol. Chemie, 100, 91 (1967).

163. H. E. Kuenzel, F. Bentz, L. Guenter, G. Nischk, British Patent 1,238,571.

164. H. E. Kuenzel et al., Die Makromol. Chemie, 130, 103 (1969).

165. J. Preston, W. F. DeWinter, W. B. Black, W. L. Hofferbert, J. Polym. Sci., A-1 (7), 3027 (1969).

166. J. Preston, French Patent 1,566,254 (1969).

167. N. Ida, M. Kurihara, K. Ikeda, S. Yatoyama, Japan Patent 70 32,629 (1970).

168. H. E, Kuenzel et al., Die Makromol. Chemie, 138, 133 (1970).

169. H. C. Bach, U. S. Patents 3,660,361 and 3,644, 283 (1972).

170. J. Preston, U. S. Patent 3,632,548 (1972).

171. A. I. Chechik et al., Plast. Massy (Russian), No. 2, 39 (1973).

172. J. Preston, W. B. Black, W. L. Hofferbert, J. Macromol. Sci., Rev. Macromol. Chem., 7 (1), 45-98 and 325-346 (1973).

173. R. Hill, E. E. Walker, J. Polym. Sci., 3, 609 (1948).

174. G. Yoshihiro, E. Seiji, Kobunshi Kagaku, 23, 259 (1966).

175. W. Foldi, J. C. Shiwers, U. S. Patent 3,622,545 (1969).

176. V. L. Logrinodov, L. B. Sokolov, Vysokomol. Soedin., B-14 (10), 722 (1972).

177. V. P. Sarzhevskaya et al., Kkr. Khim. Zhur., 30, 83 (1964).

178. J. R. Caldwell, U. S. Patent 3,272,776 (1966).

179. R. J. Angelo, U. S. Patent 3,316,211 (1967).

180. S. Tocker, U. S. Patent 3,326,851 (1967).

181. K. Saotome, Japan Patent 69 16,023 (1969).

182. J. Preston, J. Polym. Sci., A-1 (8), 1841 (1970).

183. E. P. Krasnov et al., Vysokomol. Soedin., 8 (3), 380 (1966).

184. E. N. Javich et al., Plast. Massy (Russian), No. 11, 27 (1972).

185. G. F. Nikolskaya et al., Plast. Massy (Russian), No. 9, 32 (1972).

186. V. K. Belyakov et al., Vysokomol. Soedin., B-15 (12), 99 (1973).

187. V. K. Belyakov et al., Vysokomol. Soedin., A-15 (7), 1483 (1973).

188. A. B. Blyumenfeld et al., Vysokomol. Soedin., B-14 (6), 403 (1972).

189. A. T. Kalaschnik et al., Vysokomol. Soedin., A-14 (6), 1396 (1972).

190. J. O. Weiss, H. S. Morgan, Jr., R. Lilyquist, J. Polym. Sci., A-1, (6), 1777 (1968).

191. J. H. Ross, P. C. Opt, Appl. Polym. Symp., 9, 49 (1969).

192. W. P. Behnke, R. A. Seaman, Appl. Polym. Symp., 9, 23 (1969).

193. V. K. Belyakov et al., Vysokomol. Soedin., B-14 (9), 657 (1972).

194. A. E. Wandward, J. Landis, J. Polym. Sci., A-2 (10), 2051 (1972).

195. T. Hatakeyama, H. Kanetsuma, J. Polym. Sci., B-11 (5), 815 (1973).

196. G. A. Luznetsov et al., Vysokomol. Soedin., 7 (9), 1592 (1965).

197. L. B. Sokolov et al., Vysokomol. Soedin., A-12 (5), 971 (1970).

198. A. G. Morozov et al., Plast. Massy (Russian), No. 8, 72 (1972).

199. A. P. Kreshkov et al., Plast. Massy (Russian), No. 10, 52 (1968).

200. V. Z. Nikonov et al., Bysokomol. Soedin., 8 (9), 1529 (1966).

201. V. S. Zakharov et al., Khim. Volokna, 1, 41 (1969).

202. "Carbowax Polyols," Technical Brochure of Union Carbide Corporation, New York, New York.

203. N. Nn. Voznesevskaya et al., Vysokomol. Soedin., A-14 (8), 1822 (1972).

204. Personal communication with Dr. F. E. Critchfield, Union Carbide's Technical Center, South Charleston, West Virginia.

205. J. J. Burke, J. Macromol. Sci., Rev. Macromol. Chem., A-7 (1), 187 (1973).

206. Personal communication with Mr. Yu-der Lee. (It will be published in his Ph.D. dissertation, Department of Chemical and Metallurgical Engineering, The University of Tennessee, Fall 1975.)

207. Personal communication with Dr. Marcus Matzner, Union Carbide's Technical Center, Bound Brook, New Jersey.

208. J. Brandrup, E. H. Immergut, editors. Polymer Handbook, Wiley Interscience, New York (1965).

209. W. E. Lee, G. J. Knight, Brit. Polym. J., 2, 73 (1970).

VITA

Richard J. Zdrahala was born in Krive, Czechoslovakia, on March 3, 1943. After graduation from high school in 1960, he entered The Institute of Chemical Technology, Faculty of Organic Technology in Prague, Czechoslovakia. In May 1965 he received his Master of Science degree in Chemical Engineering with specialization in Polymer Science and Technology. After graduation he joined the research staff in PAL, National Corporation, Prague, Czechoslovakia (leading eastern European manufacturer of motor car equipment). In his position as a research engineer he was involved in applications of polymeric materials in the above mentioned field.

In May 1968 he joined the scientific staff of The Research Institute for Distilled and Canned Food Products, Prague, Czechoslovakia, as manager of the Polymer Packaging section. At the same time, he enrolled as a part-time student in The Czech Institute of Technology, Faculty of Material Science, Prague, Czechoslovakia, as a candidate for the Doctor's degree in Polymer Engineering.

Russian occupation of Czechoslovakia in August 1968 forced him to emigrate from his native country in July 1969. After immigration into the U.S.A. he joined PLAXICRETE, Inc. in Atlanta, Georgia, as a technical manager responsible for production of specialty chemical coatings.

In June 1972 he accepted a graduate assistantship in the Department of Chemical and Metallurgical Engineering, The University

of Tennessee, and received the Doctor of Philosophy degree with a major in Chemical Engineering in August 1975.

By the process of naturalization, he became a U. S. citizen in December 1974. He is a member of the American Chemical Society and its Polymer Division as well.

He is married to the former Ivanka Jirasek of Prague, Czechoslovakia.