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I am submitting herewith a thesis written by Shek Chee Horne entitled "Synthesis, Characterization and Morphological Studies of Poly(m-phenylene isophthalamide), Its Block Copolymers and Some Mixtures." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

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SYNTHESIS, CHARACTERIZATION AND MORPHOLOGICAL STUDIES OF POLY(M-PHENYLENE ISOPHTHALAMIDE), ITS BLOCK COPOLYMERS AND SOME MIXTURES

A Thesis

Presented for the

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ABSTRACT

The morphological interest in the BAB type triblock copolymers, in which A is poly(m-phenylene isophthalamide) and B is poly(ethylene oxide), was the major motivation for carrying out this research. In the present work, poly(m-phenylene isophthalamide) homopolymers and their various block copolymers were synthesized. The syntheses were followed by characterization and morphological studies. In addition, the morphological studies were also extended to include poly(ethylene oxide)-4000, isophthalic acid, mixtures of poly(ethylene oxide)-4000 with poly(m-phenylene isophthalamide) and mixtures of isophthalic acid with the BAB and ABA block copolymers.

The syntheses of poly(m-phenylene isophthalamide) homopolymers and their block copolymers employed the low temperature solution polymerization method developed by Kwolek and co-workers. Characterization was done by Dilute Solution Viscometry, Infrared Spectroscopy, Differential Scanning Calorimetry, X-ray Diffraction and Light Scattering. Morphological studies were mainly conducted on solution cast films by using a LEITZ polarizing optical microscope.

Results from the present work showed no spherulitic crystallization in the solution cast films of poly(m-phenylene isophthalamide) and its block copolymers. On the other hand, the mixtures of poly(m-phenylene isophthalamide) with poly(ethylene oxide)-4000 and the mixtures of isophthalic acid with block copolymers showed well-developed Maltese cross patterns. These observations were compared with those reported by

Bernauer and Keith and Padden. Detailed comparison and discussion are presented in Chapter VI.

Several factors which influence the film morphology are revealed in this research. These include: (1) the chemical nature of the material, (2) the composition of the solution, (3) the thermal history of film preparation, (4) the thickness of the film, (5) the presence of LiCl in the casting solution, and (6) the presence of a more viscous high molecular weight polymer.

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CHAPTER I

INTRODUCTION

Aromatic polyamides are a group of high temperature resistant polymers developed during the 1950's and 1960's. These polymers can also have unusually high strengths. Other properties also include excellent resistance to corrosive atmospheres and outstanding resistance to degradation by high energy particles and gamma ray radiation. They also exhibit high tenacity, good work recovery and high flex life at elevated temperature.

A limitation of these polymers is that they are difficult to process. Even for the wet spinning process, not many solvents are available. However, when aliphatic cosegments are introduced into these polymer backbones, their solubility greatly increases and mechanical properties are also modified.

Several block copolymers based upon poly(m-phenylene isophthalamide) had been synthesized in this laboratory (78). The cosegments used were poly(ethylene oxide) and poly(dimethyl siloxane). In the present work, the syntheses will mainly involve poly(m-phenylene isophthalamide) homopolymers and their block copolymers with poly(ethylene oxide)-4000. The morphological studies will be conducted on solution cast films prepared from these materials.

CHAPTER II

LITERATURE SURVEY

II.1. THE DEVELOPMENT OF WHOLLY AROMATIC POLYAMIDES

Research on an aromatic polyamide was reported as early as 1940 in a British patent (1). By 1950, an American patent devoted to polyamides containing aromatic rings appeared (2). These partially aromatic polyamides, made from alicyclic diamines and diphenyl terephthalate, were found to have much higher melting points, better stiffness and thermal stability than those in aliphatic polyamides.

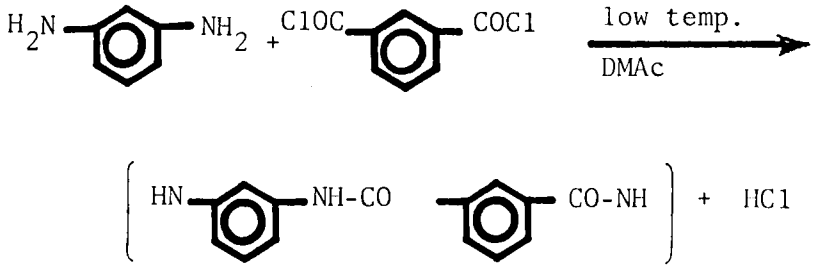
Commercially, most polyamides are prepared by melt polymerization, involving temperature up to 300°C. Only highly colored, low molecular weight or cross-linked products are obtained for wholly aromatic polyamides via these methods. In order to overcome this problem, the interfacial polymerization technique to synthesize wholly aromatic polyamides was developed by Morgan and Wittbecker (3) and others (4) at DuPont. In this method, the reaction temperature is relatively low, usually in the range of -10°C to +60°C. However, this method has the disadvantage of requiring a large amount of solvent for the production of only a small amount of polymer. It is therefore rather expensive.

The problem was eventually solved by the development of low temperature solution polymerization method (5,6). The new method was discovered independently in the laboratories of DuPont Co. and Monsanto Co. In Monsanto Co., Preston and Black made aromatic polyamides from

symmetrical and unsymmetrical diamines containing preformed amide linkage (7-13). By using these diamines and various diacid chlorides, they were able to vary the relative amount of meta and para linkage in the polymer backbone. On the other hand, Kwolek and co-workers at DuPont made aromatic polyamides directly from diamines and diacid chlorides (5,6,14-19). There were no preformed linkage. The main variables were ring structure and substitution.

The prepared meta linked aromatic polyamides were found to have a dramatic improvement over previously developed polymers in terms of strength, tenacity and heat stability. This eventually led to the commercial success of DuPont's NOMEX® fiber in 1969. This new fiber has found extensive fire-proof applications.

The synthetic scheme used by Kwolek is as follows:



II.2. CHARACTERIZATION OF POLY(M-PHENYLENE ISOPHTHALAMIDE)

Although poly(m-phenylene isophthalamide) has been commercialized since 1969 under the trade name of NOMEX, not much information about its characterization methods was revealed by the industry. Some early information was reported by Russian researchers. Among them, Kuznetsov

et al. (20) showed that two thermo-mechanical transitions occurred in poly(m-phenylene isophthalamide). The glass transition temperature, T_g, at about 280°C, and the crystallization temperature, $T_{cryst.}$, at approximately 320-340°C were determined by DTA. These values were confirmed by x-ray and NMR measurements. The decomposition temperature was reported to be around 400°C, with melting of partially degraded polymer at about 430°C.

The glass transition temperature of poly(m-phenylene isophthalamide) was also investigated by several other scientists. Black (21) reported a value of 273°C from sonic modulus measurement. Butta (22) and co-workers reported a value about 280°C by using the same method. On the other hand, DSC value of T_g reported by Gan and co-workers was 275°C (23). Preston (24) also reported T_g values in the range of 290-335°C for several ordered aromatic copolyamides from DTA and penetrometer measurements.

The IR spectrum of poly(m-phenylene isophthalamide) was studied by Gan and co-workers (23). The absorption at 1000^{-1} cm was used to identify the presence of meta monomer units and absorptions at 684 and 1080 cm^{-1} were regarded as indicative of m-substituents. Strong absorptions at 800 and 900 cm^{-1} were found to be due to aromatic rings bearing both -NH and -CO groups and absorption at 862 cm^{-1} indicated the presence of m-NHC_6H_4NH- group. It was also found that the intensity of the amide NH absorption at 3300 cm^{-1} was markedly affected by the moisture content of the sample.

Good quality IR spectra of NOMEX® fibers have also been published recently by Hummel and co-workers (25) by using both ATR and KBr pellet techniques.

Light scattering and dilute solution viscosity measurements of poly(m-phenylene isophthalamide) were made by Lee in this laboratory (43). The Mark-Houwink equation of poly(m-phenylene isophthalamide) in DMAc/5% LiCl was found to be:

$$[\eta] = 3.7 \times 10^{-4} \overline{M}_w \, 0.73 \ .$$

The development of crystallinity in poly(m-phenylene isophthalamide) films and fibers was also investigated by Lee. It was found difficult to develop any crystallinity and orientation in a poly(m-phenylene isophthalamide) sample after it was formed.

On the other hand, according to Lee, the x-ray analysis of the highly oriented NOMEX® fiber showed that the unit cell dimensions are: a = 6.8Å, b = 7.8Å, c (fiber axis) = 11.2Å and $\gamma = 99°$.

II.3. POLY(ETHYLENE OXIDE): ITS DEVELOPMENT AND PROPERTIES

The first polymer prepared from ethylene oxide was reported by Wurtz in 1859, the same year he reported the synthesis of the monomer (26). Following the contribution of Wurtz, little was added to the knowledge in this field until Staudinger began his classic publications more than sixty years later (27,28). Since then, new techniques in olefin oxide polymerization have made possible the commercial production of polymers of ethylene oxide with molecular weights ranging from a few hundred up to ten million or more (29,30).

The high molecular weight poly(ethylene oxide), PEO, has been marketed by Union Carbide since 1958 as Polyox® water soluble resins.

Lower molecular weight homologs are under the trade name of Carbowax®.

The kinematic viscosities of polyethylene oxides rise with increasing molecular weight. Melt viscosities are relatively unaffected by temperature changes, and become less sensitive to temperature as molecular weight is increased (31).

The high molecular weight polyethylene oxides of an inherent viscosity of from 2 through 16 have a melting point of 66°C (32), only about 6°C higher than the wax-like homologs with up to 8,000 molecular weight (intrinsic viscosity 0.1 to 0.5).

Molecular weight determinations on polyethylene oxides were performed cryoscopically, viscosimetrically, and by end-group analysis by Staudinger (27). Dilute solutions of polymer in benzene and dioxane were used for cryoscopic determinations. The equation used by Staudinger to describe the viscosity-molecular weight relationship is:

$$\eta_{sp/c} = K_m \cdot M$$

where M is the number average molecular weight and $\eta_{sp/c}$ is the reduced viscosity. In 4.4% solutions of polymers in dioxane the constant was found to vary widely for polymers up to a degree of polymerization of 20 where it had a value $K_m = 2.2 \times 10^{-4}$. Thereafter, up to molecular weights of 13,000 it diminished to a low of 1.5×10^{-4}.

Commercially, molecular weight determinations of conventional polyethylene oxides are performed by end-group analysis using phthalic anhydride (33).

The x-ray diffraction patterns of polyethylene oxides were studied by Sauter (27,34). Polymers with molecular weights ranging from 2400 to 100,000 were investigated, the very high molecular weight species being sufficiently rubbery to permit the preparation of fiber diagrams. Using copper radiation (λ = 1.54Å), the diagrams showed about twenty distinct halos of which four were reported as strong bands. Barnes and Ross (35) corroborated these findings in their studies of Hibbert's mono- and polydisperse polymers. The range of available molecular weights went only to 3000 and required study solely by means of powder diagrams. They found fewer bands than had been reported by Sauter but the results were generally in good agreement.

The recent introduction of very high molecular weight polymers has resulted in further studies on crystallinity. Smith and Van Cleve (36) reported crystallinities of the order of 95% for polymers with intrinsic viscosities of about 10. Maximum crystallinity, 95%, is found in samples cast from solution or carefully annealed. Quenched samples are about 40-65% crystalline.

Infrared spectra of polyethylene oxides were studied by Kuroda and Kubo (37). A fine spectrum can also be found in Hummel's book (38).

According to Todokoro (39), the poly(ethylene oxide) molecule is a loosely turned helix. It has a monoclinic crystal structure, with a = 8.16Å, b = 12.99Å, c (fiber axis) = 19.30Å, and β = 126°5'.

II.4. THE MORPHOLOGY OF CRYSTALLINE POLYMERS

Polymers which crystallize rapidly, such as polyethylene and polypropylene, always do so no matter how rapidly one attempts to cool

them; but polymers which crystallize more slowly, e.g., isotactic polystyrene, can be quenched to below T_g in the amorphous state (40). The following are the basic morphological features of a crystalline homopolymer:

II.4.1. Polymer Single Crystals

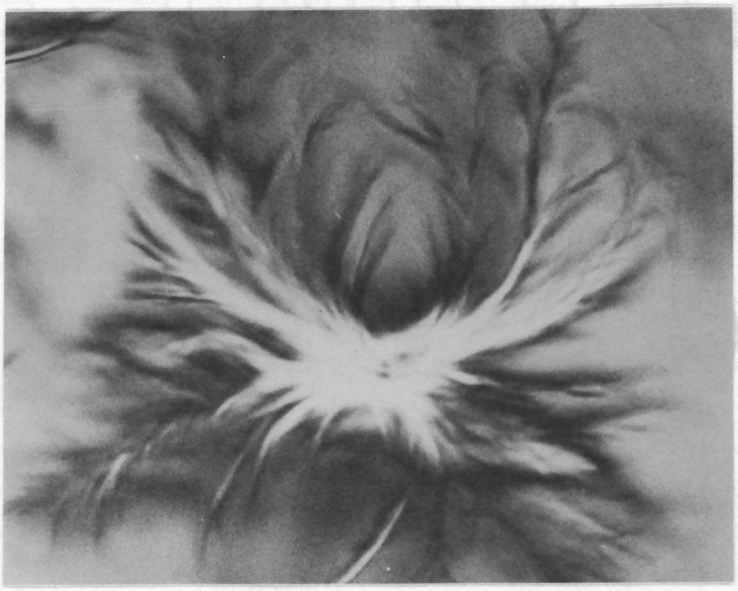
Single crystals of many polymers have been grown from dilute solutions. Most of them have the same general appearance, being thin platelets or lamellae, about 100Å thick and 1-10 mμ in lateral dimensions. Many examples are shown in Geil's book (41).

Single crystals of aromatic polyamides were reported by Livingston and Gregory (42). They have synthesized terephthalamide nylons with two to five carbon atoms in the aliphatic portion of the chain. It was found that these aromatic nylons can be recrystallized from aqueous solutions of hexafluoro-2,2-propandiol. The single crystals are in rod-like shape.

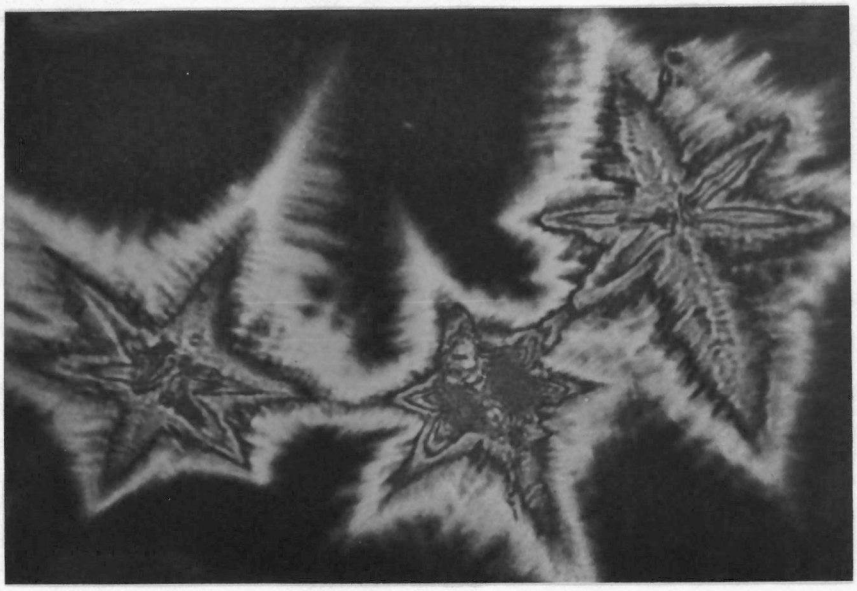
Single crystals of poly(m-phenylene isophthalamide) grown from DMAc were reported by Lee. Dendritic and granular shapes of structures were observed by using a transmission electron microscope (43).

II.4.2. Dendrites

Dendrites are branched crystals which in some cases take on a tree-like shape. Typical polyethylene dendrites grown from dilute solutions are shown in Figure 1. All branches of the dendrites are shown to have crystallographic relationships with each other. A schematic drawing of a polyethylene dendrite is presented in Figure 2. In principle, crystals



(a)



(b)

Figure 1. Interference Micrographs of Polyethylene Dendrites. (a) Grown from 0.06% solution in toluene on cooling; (b) grown from 0.05% solution in toluene at 70°C (44).

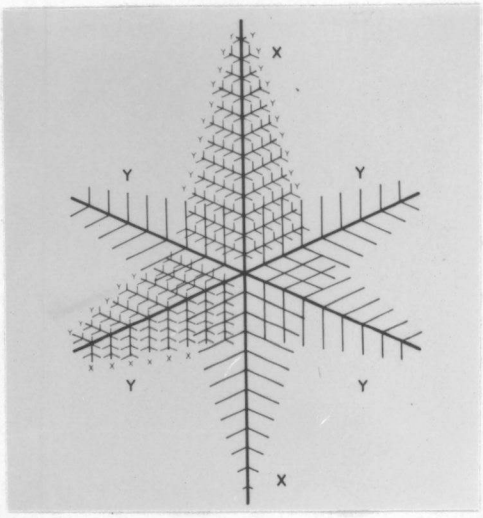


Figure 2. A Schematic Drawing of a Polyethylene Dendrite as Shown in Figure 1(b) (44).

of increasingly skeletalization grew at increasingly lower temperature, finally going over into branched dendrites. Therefore, crystallization on fast cooling is accordingly usually dendritic in nature (44).

Saratovkin (45) showed that dendrites growth is linked to a local change of crystallization conditions, which can be concentration gradients caused by rejection of noncrystallizing species or temperature gradients caused by directional dissipation of the heat of crystallization.

Besides the regular dendrites just described, most dendritic crystal preparation also showed a certain number of irregular dendrites called "hedgehog dendrites" (see Figure 3). Wunderlich and Mehta (46) showed that the introduction of heterogeneous particles increased the number of hedgehog dendrites. At the same time, they also showed that hedgehog dendrites nucleated epitaxially on crystallographically unrelated material.

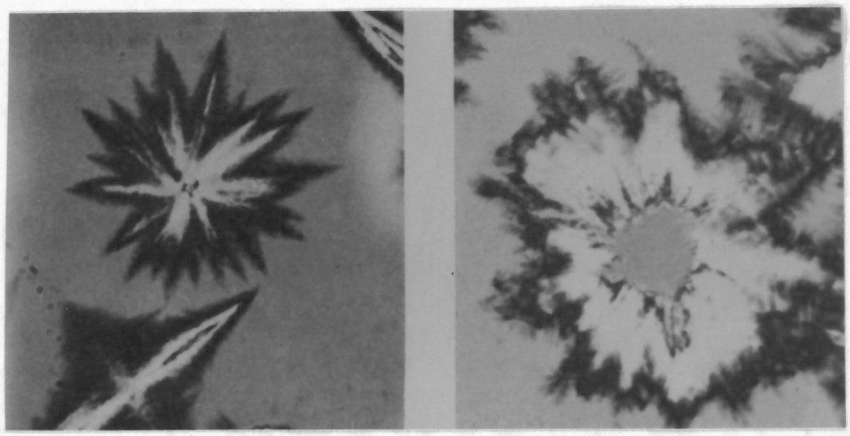


Figure 3. Interference Micrographs of Polyethylene "Hedgehog Dendrites." Left: Grown from 0.04% solution in o-xylene. Right: Grown from 0.3% solution in toluene. Both dendrites are about 100 μm in diameter. At higher concentration a thicker structure developed. The gray center area is an unresolved thick area of collapsed branches of the dendrite which were close to vertical before collapse (44).

II.4.3. Spherulites

Crystallization of crystalline polymers from the melt under a quiescent environment usually shows spherulitic morphology. The basic structure of a spherulite can occur in two ways (44). In Figure 4A, spherulitic radiation of the substructure is achieved initially by perhaps a heterogeneous nucleus. To become space filling the substructure must branch. In Figure 4B, spherulitic radiation of the substructure is achieved by branching starting from a single substructure. The central portion has an inhomogeneous structure. Fibrous or needle-like morphology is obviously most suited as substructure for spherulites; however, ribbons, lammellae, and more complicated crystal morphologies are also able to make the substructure of spherulites (44). According to Keith and Padden (47), the branching necessary for uniform space

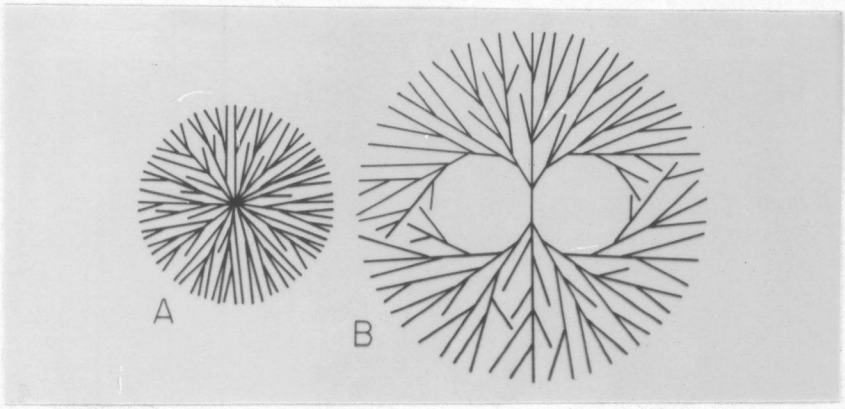


Figure 4. Schematic Drawing of the Two Basic Spherulite Types. Two-dimensional representation (44).

filling must be at a small angle and appears as a noncrystallographic branch. A good example of such an initial stage of spherulite development is shown in Figure 5 (48).

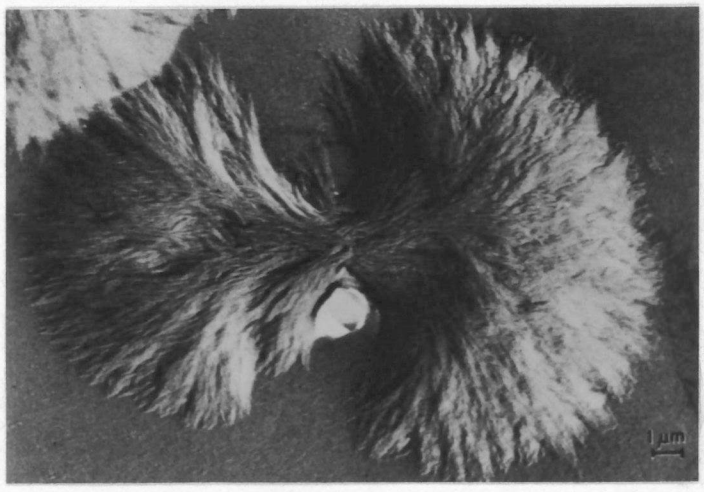


Figure 5. Electron Micrograph of the Early State of a Nylon 6 Spherulite. Note the almost parallel growth at stage A which splays apart by later branching at stage B, giving rise to an inhomogeneous central body (48).

For the polyamides, the solution cast film morphology is dependent on the polymer, temperature and solvent. Spherulites of nylon 6 develop when the glycerine solutions are cooled (49). The spherulitic material appears to consist of irregular ribbon-like lamellae, twisted together to form a sheaf-like center. Similar spherulitic structures were obtained by crystallization during cooling of a 50/50 methanol, water solution. On the other hand, crystallization of nylon 6 in formic acid solution at room temperature resulted in the development of compact, fibrillar appearing, sheaf-like spherulites (50).

Spherulites of nylon 610 formed from glycerine solutions are also composed of rolled or folded lamellae (49). Spherulites with ribbon-like lamellae are formed during crystallization by the addition of benzyl alcohol to a dilute m-cresol solution (51).

The growth of spherulites in polycarbonate above or at T_g was studied by Geil (52). He reported that, in a suitable thickness, the annealing polycarbonate at T_g can show the single crystal growth (see Figure 6). However, in the thicker films, crystallization did not occur, even for a prolonged annealing at T_g if the films were kept clean. Contact with various substrates, including the salt resulting from fingerprints, would often result in crystallization. It is apparent that thickness and salt presence are among the dominating factors which control the development of spherulites.

The spherulitically crystallizing polymers are most easily studied by the polarizing optical microscope. It is characterized by the unique appearance of Maltese cross pattern (see Figure 7).

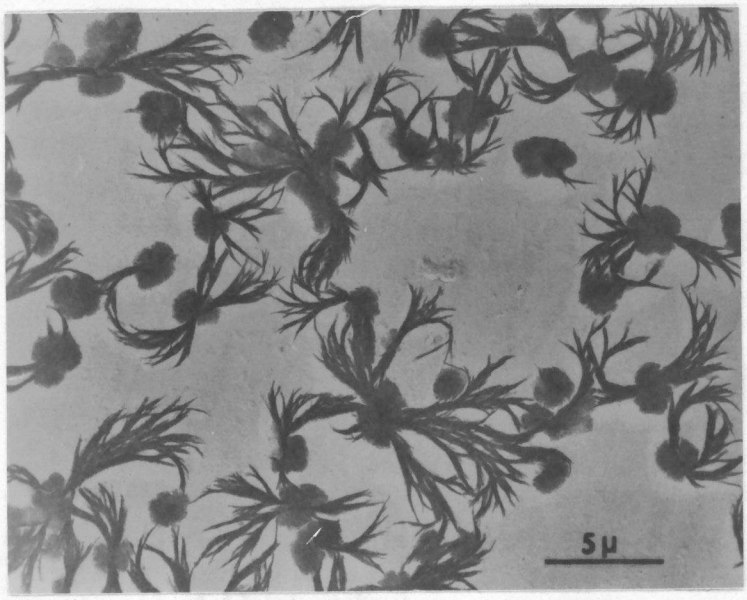


Figure 6. Single Crystals of Polycarbonate Grown in Solvent Cast Films Annealed at 145°C (40).

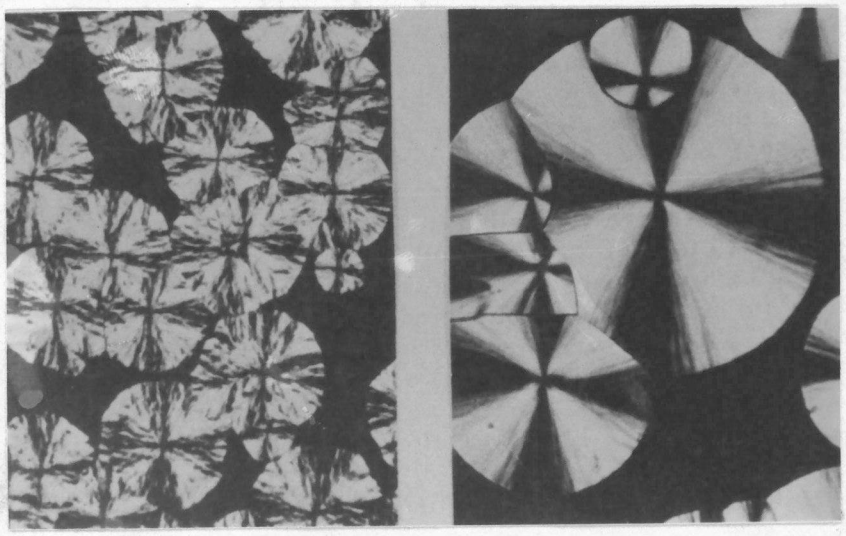


Figure 7. Polyepichlorohydrin Spherulites. Left: Spherulites developed after melting at 170°C and crystallizing at 50°C for 185 min. (128x). Right: Spherulites developed after melting at 150°C and crystallizing at 50°C for 222 min. (128x) (57).

II.4.4. Crystallization in a Dynamic Environment

The above discussed single crystals, dendritic structures and spherulites are the type of morphology formed in a quiescent environment. However, the morphology which results from a dynamic environment is different. Crystallization of polyethylene from dilute solution under stress (by rapid stirring) produces the Shish-kebab structure (54,56). A central thread of extended chain structure is formed under the dynamic stress on the supercooled solution. This nucleus initiates the formation of overgrowth of "ordinary" chain-folded lamellae. The predominant structure is a highly oriented overgrowth of lamellae, often called a row structure with the central thread being a minor component of the volume.

The crystallization of stressed melt also produces rows of chain-folded lamellae that grow perpendicularly to the stress direction (53). The degree of stress was found to have an important effect on the morphology. If the degree of stress is high, the lamellae have a planar conformation; if the degree of stress is low, the lamellae twist. The major crystalline constituent (the lamellae) is oriented with its long dimension perpendicular to the stress direction.

II.4.5. Needle-Like Crystals

Wunderlich and Sullivan (58) showed that polyethylene can also roll up in the form of needles. These needles were grown from an 0.1% solution of polyethylene in chlorobenzene at the interface of pure toluene layered on top of the chlorobenzene solution.

II.4.6. The Morphology of Amorphous Polymers

Ever since the beginning of polymer science it has been gradually assumed and accepted that amorphous polymers, both in the glassy state and above T_g, consist of randomly coiled, entangled chains with no local order being present (59). However, according to Geil (60), amorphous polymers compose of numerous small, nematic-liquid-crystal-like domains, with the majority, but not all, of the molecules running from one domain to another. In the glassy state, this structure will be frozen, whereas above T_g there will be a continual redistribution of segments among the domains, individual domains forming and disappearing. This statement is still in argument stage.

A review of the morphology of amorphous polymers has been published by Yeh (61).

II.4.7. Phase Separation in Homopolymer Systems

Complete crystallization resulting in extended chain crystals by melt crystallization is only possible by annealing a homopolymer at high temperatures under the influence of high hydrostatic pressure ($\sim$ 5000 atm) (62). The conventional processing operations for a crystallizing homopolymer give rise to a two-phase material containing crystalline and amorphous regions.

A complete mixture of one crystalline homopolymer and a second homopolymer, crystalline or amorphous, is rarely possible. Mixing in a binary system will occur when the Gibbs free energy ΔG is negative, as defined by

$$\Delta G = \Delta H - T\Delta S$$

where ΔH and ΔS are the heat and entropy of mixing respectively and T is the absolute temperature. The heat of mixing for a pair of homopolymers is generally endothermic like the mixing of two simple liquids and is defined by the Van Laar—Scatchard-Hildebrand regular solution treatment (63).

The heat term can be expressed in terms of an interaction parameter χ_{AB}. The value of $(\chi_{AB})_{Cr}$ at the critical point of phase separation corresponding to $\Delta G = 0$ is given by Scott (64) as

$$(\chi_{AB})_{Cr} = \frac{1}{2}[(\frac{1}{n_A})^{1/2} + (\frac{1}{n_B})^{1/2}]^2$$

where n_A and n_B are the degree of polymerization of homopolymer A and B. When a mixture is composed of two nonpolar homopolymers, the heat of mixing can be predicted from

$$\Delta H = V(\delta_A - \delta_B)^2 V_A V_B$$

where V is the total molar volume of the system and δ_A and δ_B are solubility parameters for A and B. The solubility parameters are related to the cohesive energy density, a concept introduced by Hildebrand (63). A comparison of δ_A and δ_B can be used as a criterion for homopolymer miscibility. For nonpolar systems, phase separation will occur when ΔH is just positive, i.e., when δ_A and δ_B are slightly different (65).

Various types of morphology are possible for the mixtures. When one homopolymer is present in large excess (> 70%), it will form a continuous phase containing dispersed discrete aggregates of the second homopolymer. The states of the two phases will be temperature dependent.

When a mixture of two homopolymers is cooled, a phase may continue to exhibit melt-like characteristics or may be transformed to a hard glass depending on the glass transition temperatures of the two components, the temperature of inspection and the composition of the mixture (65).

II.5. SPHERULITIC CRYSTALLIZATION IN NONPOLYMERIC MATERIALS WITH MODIFIERS

Besides the crystallization of high polymers from the melt or concentrated solution, the following examples are known to be capable of forming spherulites (47):

1. Minerals crystallized from viscous magmas; and devitrified glasses in general (66).
2. Organic compounds crystallized from melts to which certain modifiers (generally "thickeners" which increase melt viscosity) have been added (67,68).
3. Inorganic salts crystallized by metathesis in gelatine (69).
4. Inorganic salts crystallized from solution in the presence of trace of surface active impurity (70).
5. Organic compounds which yield associated melts (70). (In essence, these may not be much different from 2 since the purity of most organic compounds usually leaves much to be desired.)
6. Substances which, in certain ranges of temperature, exist as liquid crystals (71).

In the above examples, 1 and 2 are the types in which spherulites grow from melts of relatively high viscosity; while in 3 and 4 the surface activity is probably important.

Artificial spherulites grown from organic melts had been studied by Wallerant (67) and Bernauer (68). Bernauer, for example, studied spherulitic crystallization brought about in organic compounds by the addition of impurities and attributed the phenomena he observed to crystalline disorder introduced by foreign particles becoming trapped in growing crystals. The impurities he added were mainly resins, which acted as a thickener to increase melt viscosity. Bernauer concluded that, as the temperature is lowered, impurities separate out in the melt as fine droplets which impede growing crystals and, by causing extensive disorder, break them up into fibers.

Keith and Padden have advanced Bernauer's interpretation (47). According to Keith and Padden, Bernauer's explanation is well adapted to cases where colloidal suspensions are involved; however, since most spherulite-forming melts are almost certainly homogeneous liquids, it can scarcely be one of general validity.

Attention was drawn to organic compounds in which the property of growing spherulites is conferred upon one compound (the host) by the dissolution in its melt of small quantities—a few percent—of another (the impurity). The well-known examples were those in which the host is resorcinol or malonamide and the impurity is tartaric acid or santonic acid. The dissolved impurity caused a disproportionately large increase in melt viscosity, and rates of primary and secondary nucleation are considerably reduced. At any given temperature, the radial growth rates of spherulites decrease substantially with increasing impurity content. This situation was regarded as similar to those observed in polymers. A

typical polymer melt is a multicomponent system comprising molecules which vary widely in molecular weight. The low molecular weight components and stereo-irregular components of the polymer are rejected preferentially by growing crystals, and they may be considered as impurities (47).

Therefore, Keith and Padden analyzed the organic spherulitic crystallization phenomenon together with those observed in polymers, inorganic salts and minerals. They concluded that spherulites in all of the systems share the same general features with only minor variations and that the growth of discrete fibers which exhibit noncrystallographic "small angle branching" is common to all of them (47).

II.6. BLOCK COPOLYMERS

II.6.1. General Description

Block copolymers can be visualized as homopolymers connected by chemical bonds. Because of this, the homopolymers tend to retain their own properties. In addition, new properties may arise which result from the combination of the homopolymers.

The methods used for the preparation of block copolymers are primarily free radical, ionic and condensation polymerization (72-75). The ionic polymerization method was first reported by Szwarc in 1956 (76). However, the preparation of block copolymers by condensation method has encountered difficulty as the high temperatures needed for the coupling also lead to randomization of the polymer instead of block formation (77). This is especially true for polyesters and polyamides. Several condensation methods were developed to synthesize aromatic

polyamide block copolymers by Zdrahala in this laboratory (78). These methods primarily involved the use of low temperature solution polymerization techniques.

II.6.2. Phase Separation in Block Copolymers

The physical properties of block copolymers are related to the solid state morphology. Block copolymers frequently exhibit phase separation which typically gives rise to a dispersed phase consisting of one block type in a continuous matrix of the second block type. A thermodynamic treatment of phase separation in block copolymers has been given by Krause (79).

In block copolymers, A block and B block tend to separate because they are incompatible but are prevented from doing so by the chemical bonds linking blocks together. An important consequence of arranging the chains in this way is that the phase cannot grow indefinitely. Evidence of this is shown by Matsuo and co-workers (80). It should therefore be noted that the sizes of the domains in block copolymers are much smaller than aggregates found in a mixture of homopolymers exhibiting phase separation. In view of this domain size range morphology in block copolymers has been called microphase separation.

According to Meier (81), microphase separation is predicted to occur at higher degrees of polymerization per block than for the corresponding homopolymers at the same critical value of χ_{AB}. Therefore, two homopolymers are less miscible as separate molecules than they are when linked into a block copolymer molecule.

Fine details of the morphology formed on microphase separation can be obtained by casting thin films of block copolymers from solution. If the rate of solvent evaporation is slow, domain formation occurs under equilibrium conditions. By using a good solvent for both blocks of poly(styrene-b-diene), the electron micrographs suggest that the block copolymer forms three basic morphological units—spheres, rods (or cylinders) and lamellae, depending on the compositions of solvent cast films (82). These three types of domain structure result from the formation of micelles at a critical block copolymer concentration ($\sim$ 10%) in solution; and it is assumed that the micelle geometry persists in concentrated solution and is maintained during solvent evaporation till the solid state is reached.

In practice, complete microphase separation may not occur because of kinetic factors which intervene during sample preparation. Time dependence, block copolymer sample history, molecular weight, copolymer composition and casting solvent were found to have influence on the morphology (83-86). Those solvents which are good for one segment and poor for the other lead to the greatest phase separation. Films which are cast very quickly often have a poorly defined morphology.

Another interesting morphology was observed by Kovacs and co-workers (87,88). The $(AB)_n$ type poly(ethylene oxide-b-styrene) gives lamellar crystals when crystallized from dilute solution. The crystal lattice is from the poly(ethylene oxide) blocks and rejects the polystyrene blocks which are confined to the surface of the crystals.

II.6.3. Mixtures of Block Copolymers and Homopolymers

An extensive study of the phase separation of polymer blends has been made by Riess and co-workers (89,90). Riess suggested that a block copolymer added to a mixture of homopolymers acts as an emulsifier by preventing phase separation into macroscopic domains. Molan and Wittbrodt (91) have shown by electron micrographs that the size and number of domains are influenced by block copolymer concentration for a mixture of homopolymers and block copolymers.

On the other hand, however, Inoue and co-workers (86,92) showed in separate experiments that if the homopolymer molecular weight is much greater than that of the corresponding block, a separate homopolymer phase of large size is formed alongside the domain structure of the block copolymer. Consequently, they conclude that solubilization does not behave as an emulsifier.

II.6.4. Thermal Transition Behaviors

The melting point of one type of block is hardly affected by the presence of the other block type. However, the number of glass transition temperatures of a block copolymer will be determined by the block lengths and the interactions between monomer units. Amorphous block copolymers or a mixture of homopolymers usually show two T_g's, characteristic of long sequences of the block units. If the block length is short and microphase separation is not complete, the number and positions of the transitions are not easily predicted. Some single glass transitions were reported for both $(AB)_n$ and ABA types of block copolymers (93,94).

In some ABA cases, where only partial microphase separation occurs, three glass transition temperatures were observed (95).

II.6.5. Block Copolymers Based on Poly(m-phenylene isophthalamide)

Block copolymers based upon poly(m-phenylene isophthalamide) (A) have been synthesized in this laboratory (78). The cosegments (B) used were poly(ethylene oxide) and poly(dimethyl siloxane). The molecular weights used were 400, 1000, 4000 and 6000 g/mole for poly(ethylene oxide) and 5000, 8800 and 14200 g/mole for poly(dimethyl siloxane).

The morphology of these block copolymers was studied by using electron microscopy and optical microscopy. According to Lee (43), block copolymers with poly(ethylene oxide) segment did not show significant phase separation when the content of poly(ethylene oxide) segment is low. However, an irregular shape of second phase was observed when the composition of poly(ethylene oxide) segment is above 15%. It was also found that Maltese cross pattern developed in some BAB type triblock copolymers. The optimum conditions for the observation of this pattern were (1) when the molecular weight of poly(ethylene oxide) was 4000 or 6000 g/mole, (2) when the PEO segments were placed in the chain ends, and (3) when the composition of the casting solution was 15% polymer/5% LiCl/80% DMAc.

On the other hand, it was also found that both ABA and BAB type block copolymers showed the same crystallinity development as those observed in poly(m-phenylene isophthalamide) homopolymer, i.e., the cast films were amorphous. Even for the case where Maltese cross pattern

appeared, the x-ray diffraction studies were unable to detect crystallinity. Some explanations about this observation were made by Lee and Zdrahala (43,78).

CHAPTER III

SYNTHETIC PROCEDURES

III.1. SPECIFICATION OF CHEMICALS AND THEIR PURIFICATION

The following chemicals were used in the synthesis of aromatic polyamide homopolymers and block copolymers:

Meta-phenylene diamine (mol. wt. 103.14 g/mole, mp 62-64°C). Aldrich Chemical Company brand, 97% purity. This chemical was purified by "vacuum sublimation" for three times. White, powder-like crystals were kept in a brown glass jar blanketed with dry nitrogen. The jar was then stored in a dessicator.

Isophthaloyl chloride (mol. wt. 203.03 g/mole, mp 79-81°C). Aldrich Chemical Company brand, 97% purity. Some of them could be purified by recrystallization from dry n-hexane. Some batches had to be purified by vacuum sublimation. White, needle-like crystals were then kept in a brown glass jar blanketed with dry nitrogen. The jar was also kept in a dessicator.

Poly(ethylene oxide) prepolymer (mol. wt. 4000 g/mole). Union Carbide Corporation CARBOWAX®—4000 was purified as follows: In order to remove low-molecular weight impurities, the saturated solution of the prepolymer in dry benzene was azeotropically distilled. This distillation was followed by removal of all remaining low-molecular weight components by applying vacuum to the molten polymer for 24 hours. Poly(ethylene

oxide) was used in the solid state or as 25% solution in N,N-dimethyl acetamide.

N,N-dimethyl acetamide (mol. wt. 87.12 g/mole, bp 164-166°C). Aldrich Chemical Company brand, 99%+ purity was first stirred for six 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 nitrogen gas and the fraction boiling at 164-166°C was collected. The purified liquid was stored with dry nitrogen gas blanket over the liquid surface.

Molecular sieves. Linde's A-5 grade was used as a water scavanger.

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

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

In order to synthesize the block copolymers of interest, several syntheses were conducted to prepare the necessary poly(m-phenylene isophthalamide) homopolymers.

There are two major side reactions in the homopolymer syntheses. These side reactions cause the formation of low-molecular weight polymers, which can be seen from the following equations:

Transamidation by amide-type solvent:

$$\text{(polyamide chain)-NH-CO-(polyamide chain)} + CH_3CO\text{-}N(CH_3)_2 \longrightarrow$$

$$\text{(polyamide chain)-NH-CO-}CH_3 + (CH_3)_2N\text{-CO-(polyamide chain)}$$

Acylation of monomers by amide solvent:

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

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

As indicated in the above equations, the transamidation of the amide-type solvents can break down the already-formed poly(m-phenylene isophthalamide). On the other hand, the acylation of monomers by amide-type solvent results in nonstoichiometrical amounts of monomers. If the above two side reactions occur to some extent, the formation of high-molecular weight polymers will be prohibited.

In order to minimize the occurrence of these side reactions, approximately -40°C cooling is required at the beginning of the reaction. This cooling is supposed to be capable of "freezing-out" the above side reactions (6).

The following is a typical synthetic procedure used for the preparation of poly(m-phenylene isophthalamide) homopolymers. The amount of materials used in the description of the procedure is based upon 0.090 mole stoichiometry.

1. Into a three-neck reactor, equipped with a rapid stirring device, dry nitrogen gas inlet and dry-seal tube, 9.7326g of m-phenylene diamine was charged.
2. Then 60ml of DMAc was added into the reactor to affect solution. The solution of diamine in DMAc was cooled to approximately -40°C by the isopropanol/dry ice bath, until "slush" was formed.
3. Then 18.2718g of isophthaloyl chloride was added at once to the cooled diamine solution and rinsed down by 30ml of precooled DMAc.
4. 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.
5. The ice/salt bath was then replaced by an ice bath only and stirring continued for an additional 20 minutes. Then, the cooling bath was removed, the reaction solution was brought to room temperature and stirred for 20 more minutes.
6. The solution was diluted with 180ml of pure DMAc. This solution was then ready for copolymerization.
7. If copolymerization is not desired, the reaction is terminated by adding 7.5g of LiOH in 30ml DMAc to neutralize the in-situ formed HCl. During this operation, a thick, clear solution forms. The solution is then diluted by the addition of 90ml

of DMAc and precipitated into a water/methanol bath. The polymer was filtrated with a Buchner funnel, rinsed several times with coagulant and dried in vacuo. The reaction yield is approximately 95%.

III.3. THE SYNTHESIS OF BLOCK COPOLYMERS

By using the following reaction scheme, block copolymers of poly(m-phenylene isophthalamide) with poly(ethylene oxide) cosegments were synthesized. The poly(ethylene oxide) used was CARBOWAX®-4000 (mol. wt. 4000), prepared at 25% by weight concentration in DMAc.

First Step:

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

Second Step:

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

Third Step:

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

$$H\text{-}\{\text{-}O\text{-}\{\text{-}PEO\text{-}\}\text{-}O\text{-}\}\{\text{-}CO\text{-}\{\text{-}Ar\text{-}\}\text{-}CO\text{-}\}\{\text{-}O\text{-}\{\text{-}PEO\text{-}\}\text{-}O\text{-}\}\text{-}H \qquad (1)$$

or

$$HO\text{-}\{PEO\}_n\{\text{-}OC\text{-}(Ar)\text{-}CO\text{-}\}\{\text{-}O\text{-}(PEO)\text{-}O\text{-}\}\{\text{-}CO\text{-}(Ar)\text{-}CO\text{-}\}\text{-}(PEO)_n\text{-}OH \qquad (2)$$

where $(PEO)_n$ is the poly(ethylene oxide) extended with isophthaloyl chloride, i.e., $-\{\text{-}O\text{-}\{\text{-}PEO\text{-}\}\text{-}O\text{-}CO\text{-}\phi\text{-}CO\text{-}\}_n\text{-}$. The value of n will depend on the amount of isophthaloyl chloride added.

The reaction products will depend on the third step. If large excess of poly(ethylene oxide) is added dropwise to the solution of ClDO-(Ar)-COCl, the product will mainly be with the structure of (2). On the other hand, if ClCO-(Ar)-COCl solution is added dropwise to PEO solution, the major product should be (1).

In order to investigate the difference of the optical properties between (1) and (2), two reactors were used to prepare these block copolymers. The overall reaction scheme can be seen from Figure 8.

The following is the copolymerization procedure:

1. In reactor "A" (the same reactor used for poly(m-phenylene isophthalamide) homopolymer synthesis), the reaction solution containing about 10% by weight of polymer was first cooled down to -30°C by isopropanol/dry ice bath.
2. Isophthaloyl chloride, 1.5g, was added at once to the above almost frozen reaction solution with highest possible stirring rate. During this addition, an intensive flow of dry N_2 gas blanket was maintained over the solution. The reaction mixture was stirred for 30 minutes in the cooling bath and then brought to room temperature.
3. Into another reactor "B," similarly equipped with rapid stirring device, dry N_2 gas inlet, 50g of PEO-4000 in 160ml of DMAc was charged.
4. About half amount of the solution in reactor "A" was then withdrawn by syringe and added dropwise to the PEO solution in reactor "B." During this operation, both reactors were covered

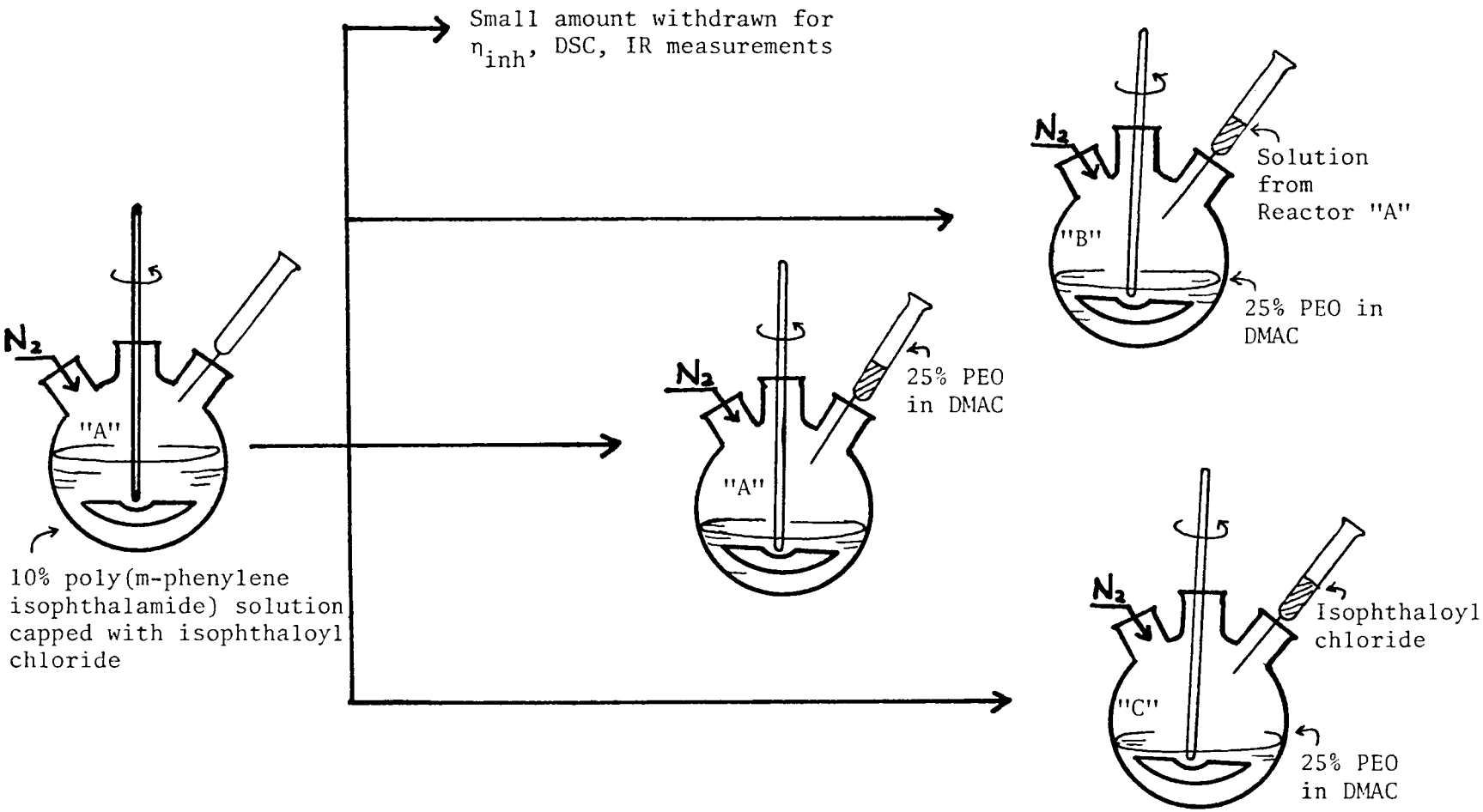


Figure 8. Flow Chart of Block Copolymer Syntheses.

by intensive dry N_2 blanket. The stirring rate of PEO solution was also maintained at its highest speed. This should give the block copolymer with structure (1).

5. At the same time, small amount of the homopolymer solution in reactor "A" was also withdrawn by syringe and precipitated into water/methanol bath. The collected polymer was rinsed several times with the coagulant, dried in vacuo and then used for the determination of inherent viscosity of the homopolymer.
6. The solution left in reactor "A" (also about half amount of the original reaction solution) was then rapidly stirred under intensive dry N_2 blanket. Another 50g of PEO-4000 in 160ml of DMAc was then added dropwise to the solution. This should result in block copolymer with structure (2).
7. The above solutions in both reactors were stirred at room temperature for 24 hours. After this, 40ml of DMAc was added to each reactor and the reaction products were precipitated into hot methanol baths. The above copolymers were kept in the baths for two days to extract any free PEO homopolymer. The copolymers were then collected on filters, rinsed several times with methanol and water, and cried in vacuo.

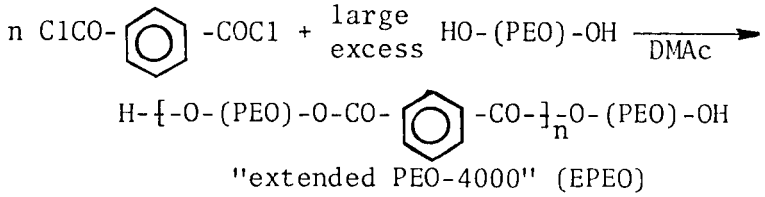
III.4. THE REACTION BETWEEN ISOPHTHALOYL CHLORIDE AND PEO-4000

It was found that Zdrahala used very large excess amounts of isophthaloyl chloride in the second step of block copolymer synthesis,

about 45 times as much as theoretically needed. The excess amount of isophthaloyl chloride will tend to react with the excess PEO added later in the third step. In order to investigate the possibility of this reaction and the nature of the reaction products, the following reaction was run for reference.

1. Into a three-neck reactor, similarly equipped as those used in block copolymer synthesis, 25g of PEO-4000 in 80ml of DMAc was charged. During this and the following operation, an intensive dry N_2 gas blanket was maintained over the solution.
2. Isophthaloyl chloride, 0.75g, was added at once to the solution. The above reactants were moderately stirred for 24 hours.
3. The reaction product was collected on a filter paper, then kept in hot methanol/water bath for two days. The final product was then collected on a filter paper again, rinsed several times with methanol and water and dried in vacuo.

The major reaction between isophthaloyl chloride and PEO-4000 is supposed to occur in the following manner:



"extended PEO-4000" (EPEO)

The final product was later found to be isophthalic acid, a hydrolyzed product from the "extended PEO" molecules due to the presence of water in the extraction process.

CHAPTER IV

CHARACTERIZATION OF THE SYNTHESIZED MATERIALS AND OBTAINED RESULTS

IV.1. THE DETERMINATION OF VISCOSITY AND MOLECULAR WEIGHT

In total, six poly(m-phenylene isophthalamide) homopolymers, two ABA and BAB type triblock copolymers, two AB type block copolymers and one isophthalic acid were synthesized during this research.

The molecular weights of the poly(m-phenylene isophthalamide) homopolymers were determined by using dilute solution viscometry. In order to insure adequate measurements, the temperature, flow time and capillary alignment were carefully controlled. The capillary viscometer was cleaned thoroughly by using concentrated H_2SO_4/Cr_2O_3 cleaning solution and DMAc/5% LiCl solution before and after each measurement.

The viscosity measurements were made in a constant-temperature bath regulated to at least ±0.02°C. The efflux time measured for the polymer solution was compared with the corresponding efflux time for the solvent. The following equations are used for the calculations:

relative viscosity $\eta_r = \eta/\eta_o = t/t_o$

specific viscosity $\eta_{sp} = \eta_r - 1 = t\text{-}t_o/t_o$

reduced viscosity $\eta_{red} = \eta_{sp/c}$

inherent viscosity $\eta_{inh} = \ln\eta_{r/c}$

intrinsic viscosity $[\eta] = (\eta_{sp/c})_{c=0} = [\ln\eta_{r/c}]_{c=0}$.

The inherent viscosity of a 0.5 g/dl solution of polymer in DMAc/5% LiCl was measured by a Ubbelohde viscometer at 25°C. The Mark-Houwink equation with K and a values determined by Lee (43) in the form of

$$[\eta] = 3.7 \times 10^{-4} \overline{M}_w^{0.73}$$

can be used to calculate the weight-average molecular weights. Since a calibration curve relating the inherent viscosities with the molecular weights of poly(m-phenylene isophthalamide) has been prepared by Zdrahala (see Figure 9), the determination of the molecular weights of the above polymers is simplified. The collected data are shown in Table I.

IV.2. BLOCK COPOLYMER COMPOSITION

Infrared spectroscopy was used to verify the formation of block copolymers and to determine their compositions. Measurements were performed on a Beckman IR-4 spectrophotometer. One and one-half percent solutions of polymers in DMAc/5% LiCl were used for the sample preparation. Approximately three drops of the solution were transferred onto a NaCl plate and then dried in a hot vacuum oven (65-70°C) for at least 72 hours. The salt plates were put into a dessicator right after being dried in the oven to prevent the absorption of moisture.

A calibration curve for the instrument was determined from physical mixtures of poly(m-phenylene isophthalamide) and poly(ethylene oxide), ranging from 20:80 to 80:20 weight percent of concentration ratio. The relative amounts of these two homopolymers can be determined by the relative intensities of their characteristic peaks in the IR spectra.

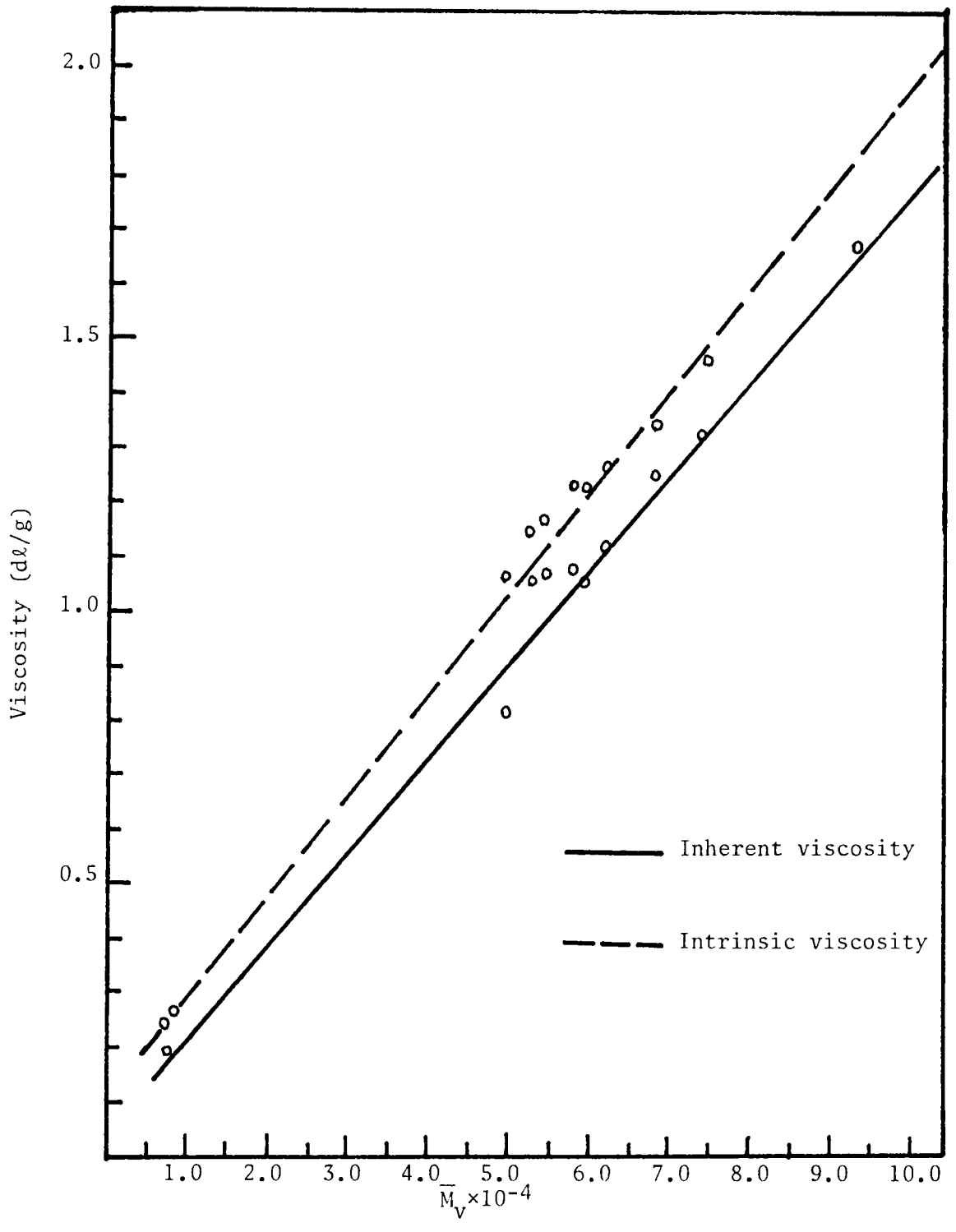


Figure 9. Calibration Curve for the Estimation of $\bar{M}_v$ of Poly(m-phenylene isophthalamide) Directly from the Values of Inherent Viscosity (61).

TABLE I

VISCOSITY-AVERAGE MOLECULAR WEIGHT DETERMINATION

Homopolymer*	Inherent Viscosity	$\overline{M}_v$	Block Copolymer*	Inherent Viscosity
A_1	0.61	3.35×10^4		
A_2	0.82	4.53×10^4		
A_3	1.61	8.95×10^4		
A_4	1.02	5.65×10^4	A_4B type	0.98
A_5	1.20	6.75×10^4	A_5B type	1.22
A_6	1.18	6.70×10^4	BA_6B type	1.26
			A_6BA_6 type	1.30

*A = poly(m-phenylene isophthalamide); B = poly(ethylene oxide)-4000.

The strong carbonyl stretch at 1600-1680 cm^{-1} and very distinctive -NH- stretch at 3200-3250 cm^{-1} wavenumbers are suitable for the characterization of aromatic polyamide. The ether linkage (-C-O-C-) stretch and vibrations occurring at 1100 cm^{-1} together with ($-CH_2-$) absorption at 2950 cm^{-1} are characteristic peaks of polyethylene oxide.

By drawing the baseline, the peak heights of carbonyl stretch (I_1) and ether linkage vibration (I_2) were measured and compared. The values of $\log(I_1/I_2)$ were then plotted versus the weight percent of PEO in the physical mixtures. This plot is the calibration curve used for the determination of block copolymer composition.

Figure 10 illustrates the typical spectra for poly(m-phenylene isophthalamide) and its block copolymers with poly(ethylene oxide). The calibration curve and the block copolymer compositions are presented in Figure 11 and Table II, respectively.

IV.3. SOLUBILITY STUDIES

During the film preparation for the optical microscopic study, it was found that phase separation occurred in some sample solutions. A solubility study was therefore conducted. The materials investigated included PEO-200, PEO-400, PEO-600, PEO-1000, PEO-4000, PEO-6000, PEO-6×10^5, PEO-4×10^6, isophthalic acid, poly(m-phenylene isophthalamide) homopolymer, its AB, ABA and BAB block copolymers, the reaction product of isophthaloyl chloride and PEO-4000, and mixtures of the above materials.

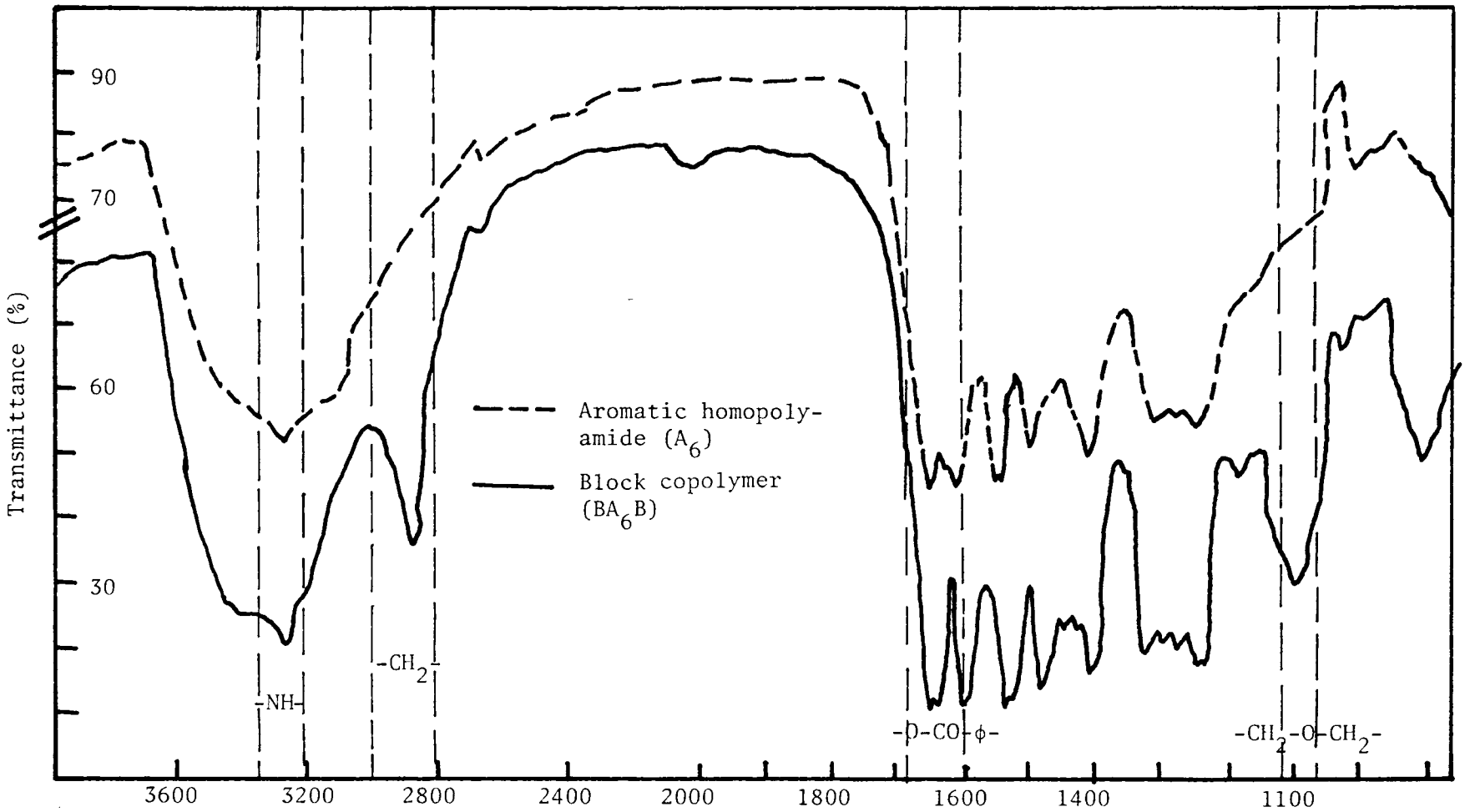


Figure 10. Schematics of typical IR Spectra of Poly(m-phenylene isophthalamide) and its Block Copolymer with Poly(ethylene oxide). Spectra taken on Perkin-Elmer Spectrophotometer, Model 727.

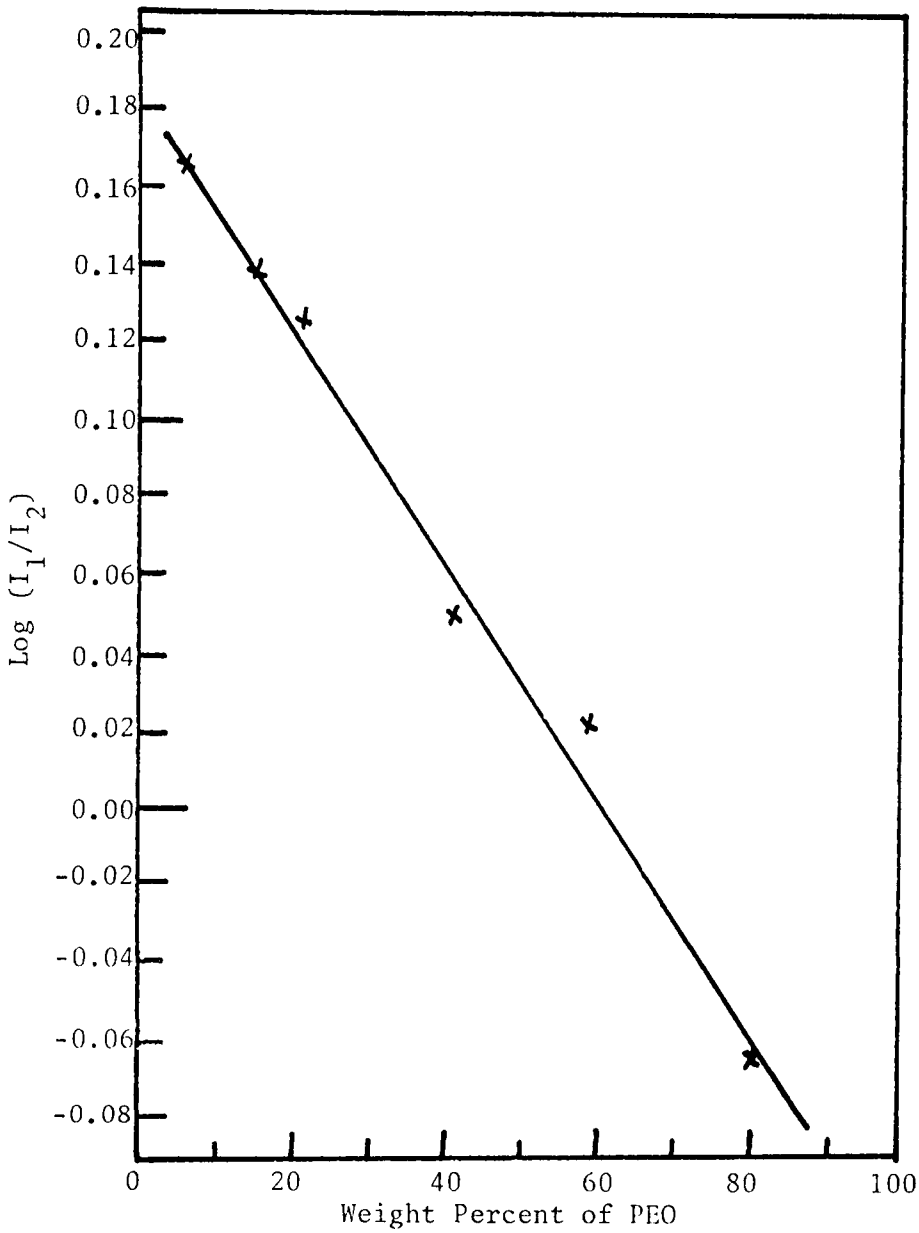


Figure 11. Calibration Curve for the Estimation of PEO Content in Block Copolymers.

TABLE II

BLOCK COPOLYMER COMPOSITION

Block Copolymer	$Log(I_1/I_2)$	Weight Percent of PEO
A_6BA_6	0.166	5.1
BA_6B	0.142	13.2

Table III shows the obtained results. According to these observations, DMAc/5% LiCl is a good solvent for both poly(m-phenylene isophthalamide) and its block copolymers, yet it is not a good solvent for PEO-4000. Therefore, phase separation occurred.

IV.4. CHARACTERIZATION OF THE REACTION PRODUCT FROM ISOPHTHALOYL CHLORIDE AND PEO-4000

Light scattering, x-ray diffraction, solubility study, infrared spectroscopy and morphological study were performed to characterize the product resulting from the reaction between isophthaloyl chloride and PEO-4000.

IV.4.1. Light Scattering

In order to measure the molecular weight, light scattering measurements were carried out with a Brice Phoenix Light Scattering Photometer, Series 2000, employing green light (wavelength 546 mμ). The solvent used was pure DMAc. Concentrations of the solutions were 0.004, 0.002, and 0.001 g/ml. These solutions were filtrated through ultrafine glass frits under pressure directly into the cell. All measurements were done at room temperature.

TABLE III

SOLUBILITY OF HOMOPOLYMERS, BLOCK COPOLYMERS AND THEIR MIXTURES IN PURE DMAc AND DMAc/5% LiCl

Material	Solubility in Pure DMAc	Solubility in DMAc/5% LiCl
PEO-200	yes	yes
PEO-400	yes	yes
PEO-600	yes	yes
PEO-1000	yes	yes
PEO-4000	partially (1)	partially (1)
PEO-6000	partially (1)	partially (1)
PEO-6×10^5	no	no
PEO-4×10^6	no	no
Poly(m-phenylene isophthalamide)	partially (2)	yes
AB copolymer	partially (2)	yes
A_6BA_6 copolymer	partially (2)	yes
BA_6B copolymer	partially (2)	yes
A_6BA_6+PEO-4000	partially (2,3)	partially (1,3)
BA_6B+PEO-4000	partially (2,3)	partially (1,3)
A + PEO-4000 (5)	partially (2,3)	partially (1,3)
EPEO	yes (4)	yes
A_6BA_6+EPEO (5)	partially (2,3)	partially (1,3)
BA_6B+EPEO	partially (2,3)	partially (1,3)
Isophthalic acid	yes	yes

Note: (1) Solution was clear when hot, but became turbid at room temperature.
(2) Small particles suspended in the solution.
(3) Phase separation occurred between two components after an extended time at room temperature.
(4) Solution was clear when hot, but became only a little bit turbid after an extended time at room temperature.
(5) A = poly(m-phenylene isophthalamide).

The basic equation describing the relation between the light scattering intensity and the molecular weight is

$$\frac{Kc}{R_\theta} = \frac{1}{\overline{M}_w} + 2A_2c + 3A_3c^2 + \ldots$$

where

$$K = \frac{2\pi^2 h^2 (\frac{dn}{dc})^2}{\lambda^4 N}$$

and the Rayleigh ratio R_θ can be calculated from the observed scattering ratio, G_θ/G_w, by means of the following equation:

$$R_\theta = \frac{TDan^2(R_w/R_c)}{1.049\ \pi h} (\frac{r}{r'}) (\frac{\sin\theta}{1+\cos^2\theta}) \left(\frac{1}{(1-K)^2(1-4R)^2}\right)$$

$$\left[\left(\left(\frac{G_\theta}{G_w} F\right)_{solution} - \left(\frac{G_\theta}{G_w} F\right)_{solvent}\right) -\right.$$

$$\left. 2R\left(\left(\frac{G_{180-\theta}}{G_w} F\right)_{solution} - \left(\frac{G_{180-\theta}}{G_w} F\right)_{solvent}\right)\right]$$

where

TD = diffuse transmittance of reference opal times diffusion correction factor = 0.316;

h = width of primary beam (cm) = 1.20;

a = working standard constant = 0.053;

F = transmittance of neutral filter, F_1=0.046, F_2=0.254, F_3=0.120, F_4=0.056;

n = refractive index of the solution;

G_w, G_θ = galvanometer readings at exit window and angle θ, respectively;

R = fraction of the primary beam reflected at the exit window = 0.039;

$R_w/R_c \approx 1$;

r/r' = calibration factor relating the narrow beam geometry and cylindrical cell to the standard beam geometry and standard cell.

The Brice Phoenix Differential Refractometer, Model BP-2000-V, was used for the measurement of the refractive index gradient (dn/dc). The refractive index difference is given by the following equation:

$$\Delta n = k\Delta d$$

where Δn is the refractive index difference between a solution and its solvent, Δd is the total slit image displacement in instrument unit and k is the calibration constant for the selected wavelength. Table IV shows the Δn and Δd values measured. Figure 12 gives the refractive index gradient a value of 0.1105.

TABLE IV

Δd AND Δn OF THE REACTION PRODUCT FROM ISOPHTHALOYL CHLORIDE AND PEO-4000

Concentration (g/ml)	Δd	Δn
0.008	0.760	6.88×10^{-4}
0.004	0.514	4.66×10^{-4}
0.002	0.251	2.28×10^{-4}
0.001	0.153	1.39×10^{-4}

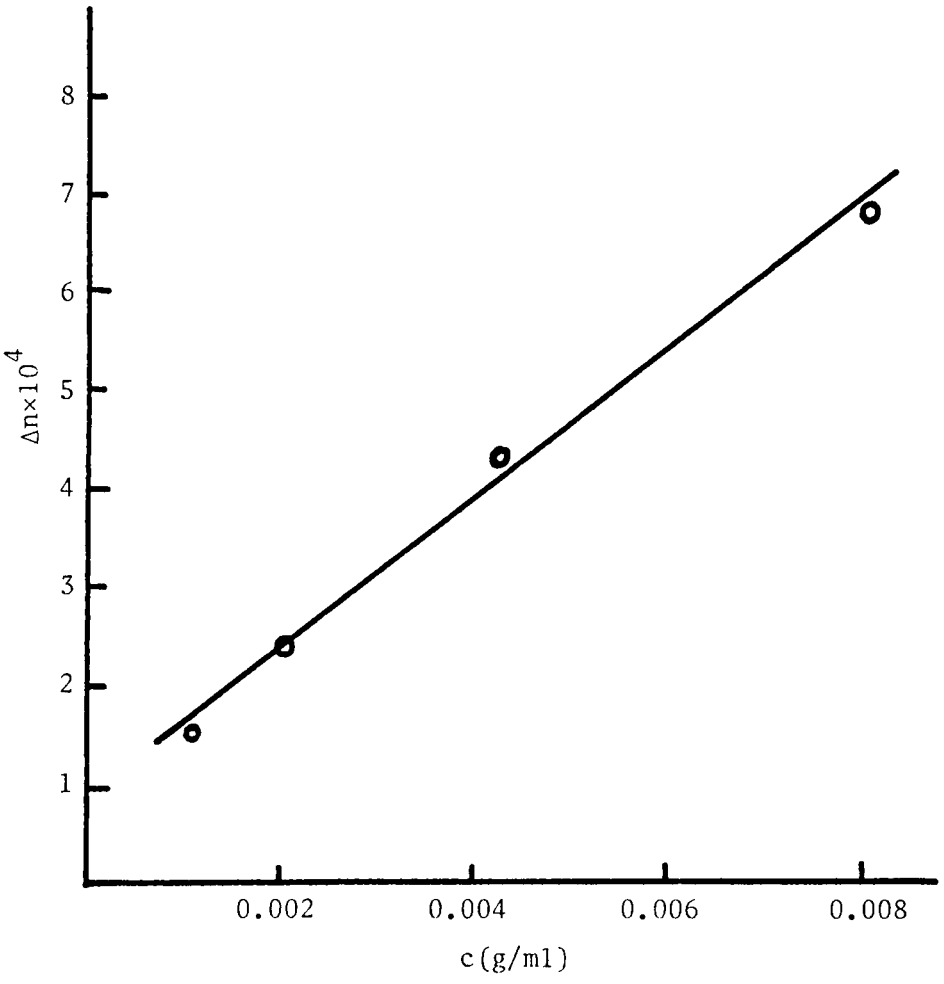


Figure 12. Refractive Index Gradient of the Reaction Product from Isophthaloyl Chloride and PEO-4000. Solvent: DMAc. $(\partial n/\partial c) = 0.1105$.

The Zimm plot was prepared with ($\sin^2 \theta/2$ + Ac) as the abscissa and Kc/R_θ as the ordinate (see Figure 13). A low value of A (=25) was chosen to separate the data points. However, the points seemed to scatter around and were found difficult to draw straight lines. As a result, the light scattering measurement was not able to give a conclusive information about the molecular weight of the material.

IV.4.2. X-Ray Diffraction Analysis

The wide angle x-ray diffraction pattern was measured by using a Philips x-ray generator. The materials investigated included PEO-4 × 10^6, isophthalic acid and the reaction product from isophthaloyl chloride and PEO-4000.

It was found that the x-ray pattern of the material resulting from reacting isophthaloyl chloride and PEO-4000 showed very sharp rings, indicating the crystalline nature of this material. However, the observed d-spacings were different from those shown by PEO-4 × 10^6.

The literature d-spacing values reported by Sauter (34) and Barnes and Ross (35) differ from each other, especially for the first four values reported by Barnes and Ross. The difference may be because Barnes and Ross investigated low molecular weight PEO (3000), while Sauter investigated high molecular weight PEO (1 × 10^5). However, the d-spacings observed by the author for PEO-4 × 10^6 are in better agreement with the values reported by Sauter (see Table V).

The d-spacing values of the reaction product from isophthaloyl chloride and PEO-4000 were compared with Sauter's values. Some of them

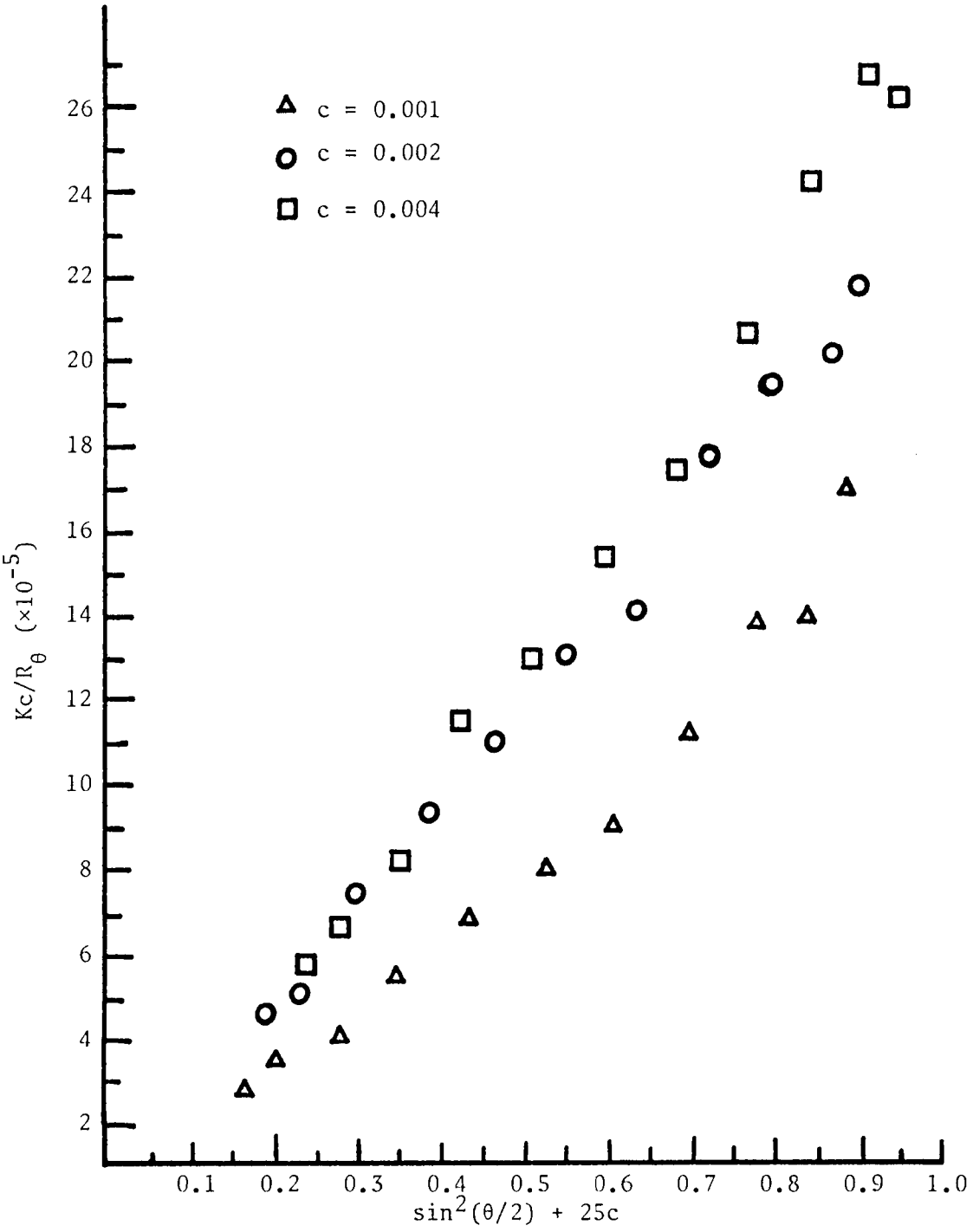


Figure 13. Zimm Plot of the Reaction Product from Isophthaloyl Chloride and PEO-4000.

TABLE V

d-SPACING VALUES OF POLY(ETHYLENE OXIDE)

No.	Sauter (1)*	Barnes and Ross (2)*	Horne (3)*	Intensities (S)	(B&R)	(H)
1	7.26			v.w.		
2	6.58			w.		
3	6.36			v.w.		
4	5.79	5.88		w.	w.	
5	5.58		5.50	v.w.		m.
6	4.72			v.w.		
7	4.56	4.64	4.57	v.s.	v.s.	v.s.
8	3.93			w.		
9	3.76	3.81	3.76	m.	v.s.	v.s.
10	3.70			v.s.		
11	3.48			w.		
12	3.36	3.33	3.33	m.	s.	m.
13	3.29			m.		
14	3.24			w.m.		
15	3.17		3.14	w.		m.
16	2.85	2.85		w.m.	w.	
17	2.72	2.71	2.67	m.	m.	v.w.
18	2.50	2.49		m.	s.	
19	2.44		2.46	m.w.		m.
20	2.24	2.25	2.24	m.	m.	m.w.
21	2.07	2.09		w.	w.	
22	1.97	1.98		w.	w.	
23	1.84	1.85		v.w.	w.	
24	1.67	1.69		v.w.	v.w.	
25	1.60	1.59		v.w.	v.v.w.	

*Molecular weights of PEO: (1) 1×10^5; (2) 3,000; (3) 4×10^6.

are very close, yet the intensities differ from each other. If compared with the values observed by the author for the PEO-4 × 10^6, more difference can be found. On the other hand, the x-ray pattern of the reaction product from isophthaloyl chloride and PEO-4000 was found almost exactly the same as that shown by isophthalic acid, including the intensities and d-spacing values (see Figure 14 and Table VI).

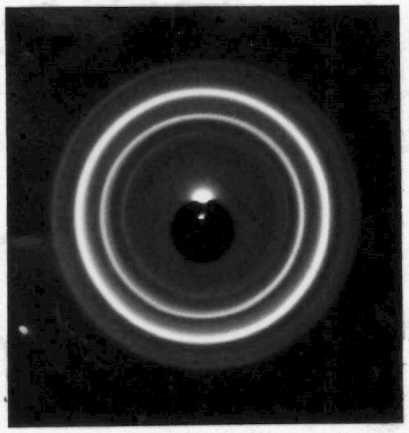
IV.4.3. The Infrared Spectra

The infrared spectra of isophthalic acid and the product from isophthaloyl chloride and PEO-4000 were taken on a Beckman IR-4 Spectrophotometer. Both spectra are similar. These spectra were then checked with the literature spectrum of isophthalic acid, and they are identical. The spectra of isophthalic acid are presented in Figure 15.

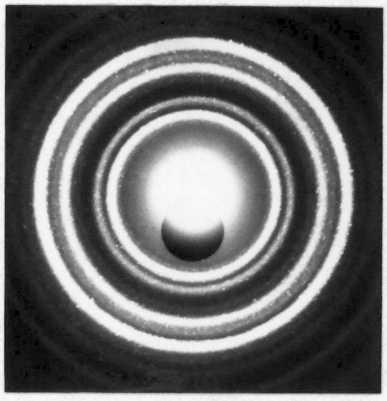
In addition to the above information, the solubility study in Section IV.3 and the morphological study in Chapter V also give favorable conclusion that the product from reacting isophthaloyl chloride with PEO-4000 was isophthalic acid. This is due to the presence of water in the extraction step. The already-formed ester linkage in the "extended PEO" chain was broken down by hydrolysis, giving isophthalic acid as the final product.

IV.5. THERMAL TRANSITION BEHAVIORS

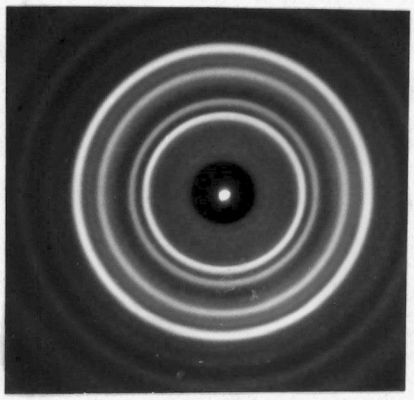
Differential Scanning Calorimetry was performed to investigate the thermal transition behaviors of the homopolymers of poly(m-phenylene isophthalamide) and poly(ethylene oxide), and their block copolymers.



(a)



(b)



(c)

Figure 14. Wide-Angle X-Ray Diffraction Patterns. (a) PEO-4×10^6; (b) isophthalic acid; (c) the reaction product from isophthaloyl chloride and PEO-4000.

TABLE VI

d-SPACINGS OF ISOPHTHALIC ACID AND THE REACTION PRODUCT FROM ISOPHTHALOYL CHLORIDE AND PEO-4000

No.	Isophthalic Acid*	Intensity	EPEO**	Intensity
1	5.55	v.s.	5.56	v.s.
2	4.84	v.s.	4.87	v.s.
3	4.02	w.	4.04	w.
4	3.70	v.s.	3.71	v.s.
5	3.46	m.w.	3.43	w.
6	3.20	v.s.	3.18	v.s.
7	2.97	m.w.	2.96	w.
8	2.78	m.	2.78	m.
9	2.51	m.	2.50	m.
10	2.25	m.	2.23	m.

*Obtained by reacting isophthaloyl chloride with distilled water.

**Obtained by reacting isophthaloyl chloride with PEO-4000.

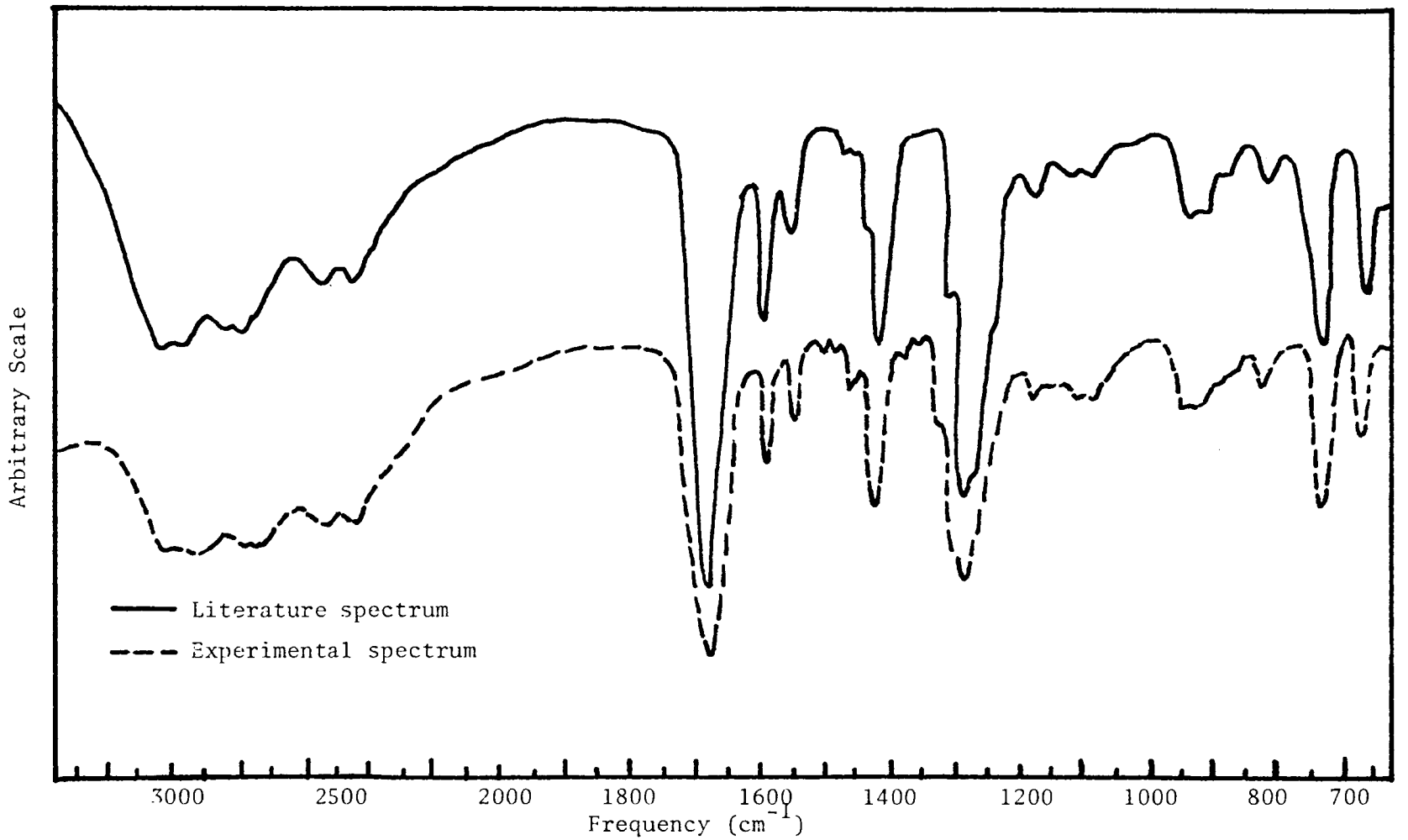


Figure 15. Infrared Spectra of Isophthalic Acid.

A Perkin-Elmer DSC, Model DSC-1B, was used in the experiments. The temperatures measured ranged from -100°C up to 500°C. The low-temperature DSC was performed by using liquid nitrogen as coolant. Calibration of the instrument was done by using Indium (T_m = 156°C), polystyrene Styron 678 (T_g = 100°C) and DMAc (T_m = -20°C) as standard materials. At least three measurements were run for each sample. In order to get reproducible results, up to seven measurements were usually done for the low temperature range. The following information was obtained based on the reproducible curves:

Poly(m-phenylene isophthalamide)

T_g = 275-285°C, clearly detected.

$T_{cryst.}$ = 303-313°C, very strong single peak.

$T_{dec.}$ = over 404°C.

T_m = around 436°C, not always detected.

Poly(ethylene oxide)-4000

T_g = around -53°C and -73°C, two values appeared, both have glass transition shapes, hard to tell which one is T_g.

T_m = 50-56°C, very sharp single peak.

BA_6B block copolymer

T_g = 280-285°C for aromatic polyamide segment, but not detected for PEO segment.

$T_{cryst.}$ = 327-337°C, peak not as strong as that in pure poly(m-phenylene isophthalamide).

$T_{dec(1)}$ = 213-226°C, decomposition of poly(ethylene oxide).

$T_{dec(2)}$ = over 400°C, decomposition of aromatic polyamide.

T_m = 50-53°C, for poly(ethylene oxide) segment, but not very strong.

T_m not identified for aromatic polyamide segment.

A_6BA_6 block copolymer

T_g = 270-280°C, for aromatic polyamide segment.

$T_{cryst.}$ = 307-327°C, strong peak.

$T_{dec(1)}$ = 203°C, for PEO segment.

$T_{dec(2)}$ = 387-392°C for aromatic polyamide segment.

T_m = around 53°C, for PEO segment.

CHAPTER V

MORPHOLOGICAL STUDIES

Morphological interest in the BAB type block copolymers was the major motivation for carrying out this research. In the present work, the morphologies of poly(m-phenylene isophthalamide) and its block copolymers were examined. In addition, many interesting morphological features in the low molecular weight homopolymer/high molecular weight homopolymer system and the organic compound/block copolymer system were also revealed in this research.

The major instrument used for the morphological studies was a LEITZ polarizing microscope equipped with a NIKON camera. Samples were prepared from solution cast films. The compositions of the solution were mainly 15% polymer/5% LiCl/80% DMAc and 15% polymer/85% DMAc. The prepared films were cast on a glass plate, dried in a hot oven (100-130°C) or in warm vacuo (55-65°C) for 24 hours, then the glass plate was immersed in a water bath for one to two days to remove LiCl. The films were then dried again in a vacuum oven for 24 hours and were ready for microscopic examination. The magnifications used were mainly 100X and 500X.

V.1. POLY(M-PHENYLENE ISOPHTHALAMIDE) AND ITS BAB AND ABA BLOCK COPOLYMERS

Films cast from the synthesized polymers exhibited no special features. However, by using the first order red wave plate, both

copolymers showed more colorful images than their parent homopolymer (see Figures 16 and 17).

V.2. POLY(ETHYLENE OXIDE)-4000

Since poly(m-phenylene isophthalamide) was featureless in the polarizing microscope and its block copolymers showed more colorful images, the morphological nature of PEO-4000 was thus investigated.

Small pellets of PEO-4000 were put on glass plates, melted and then cooled down. All gave very sharp Maltese cross patterns. These patterns differ from one another depending on the rate of cooling, their locations on the film and the thickness of the film.

When molten PEO-4000 was cooled down slowly in the air, the film showed very large and well-defined Maltese cross patterns. On the other hand, when molten PEO-4000 was quenched in dry ice bath, the Maltese cross patterns were much smaller, with much cracking in their structures (see Figures 18 and 19).

The thickness effect was verified. The most colorful and well-defined patterns always occurred in the edge regions, where the film is thinner. When the film gets thicker, the patterns became crowded, less colorful and sometimes distorted. For even thicker regions, irregular patterns with pale green color were observed.

Another effort was also tried to investigate the morphological difference between films formed by melting and solution casting. Because PEO-4000 is soluble in water, the PEO solutions used for film casting did not contain any LiCl. The composition used was 15% PEO-4000 with 85%

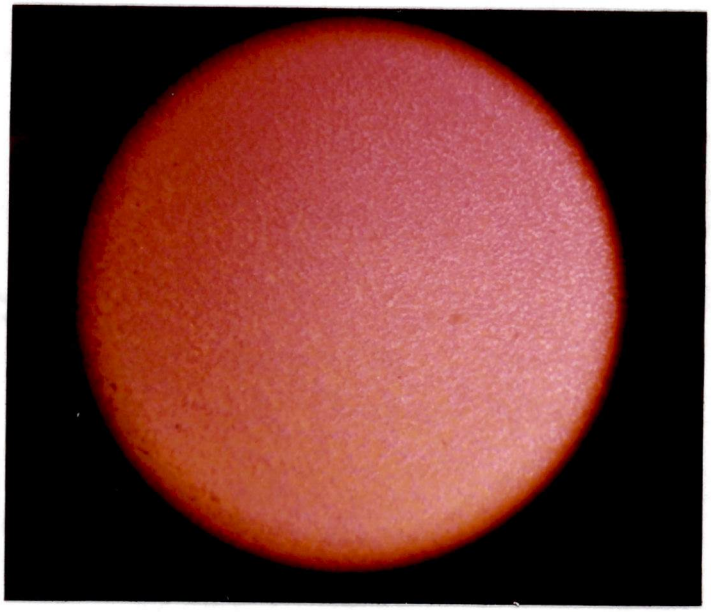
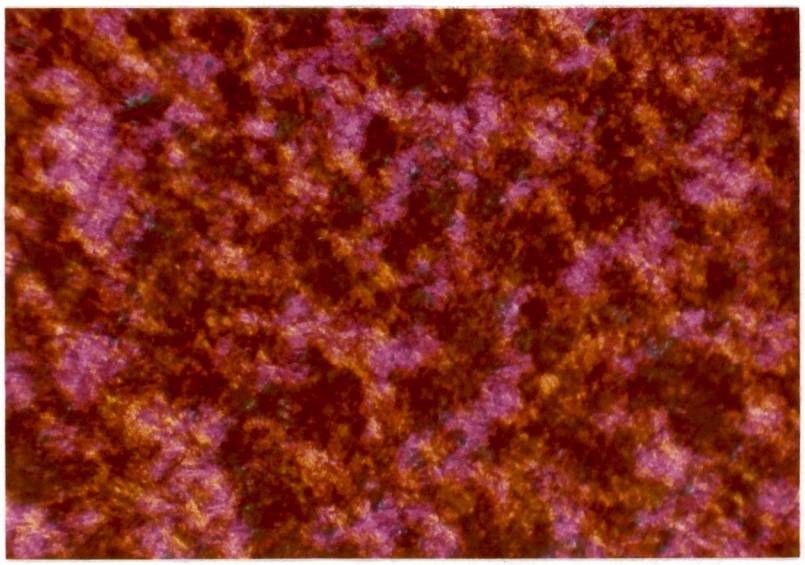
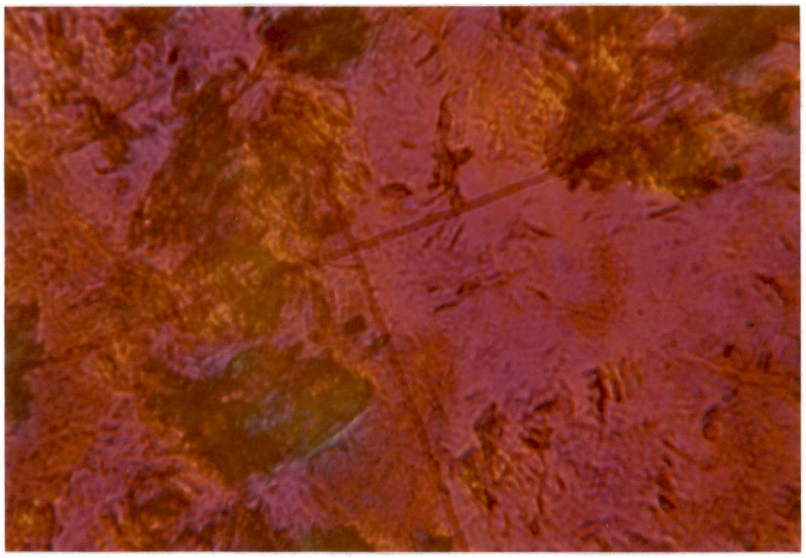


Figure 16. Typical Morphology of Poly(m-phenylene isophthalamide). 100X.

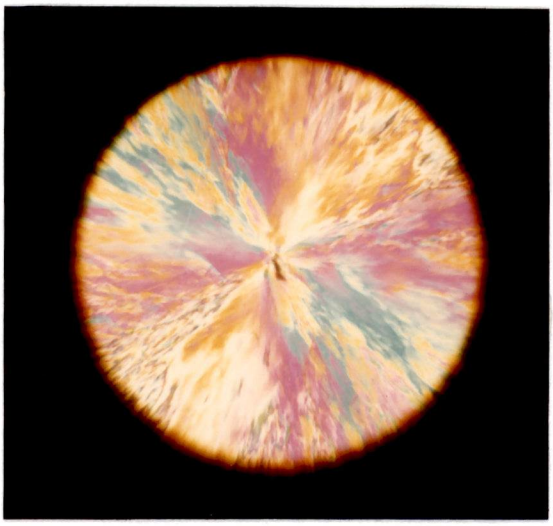


(a)

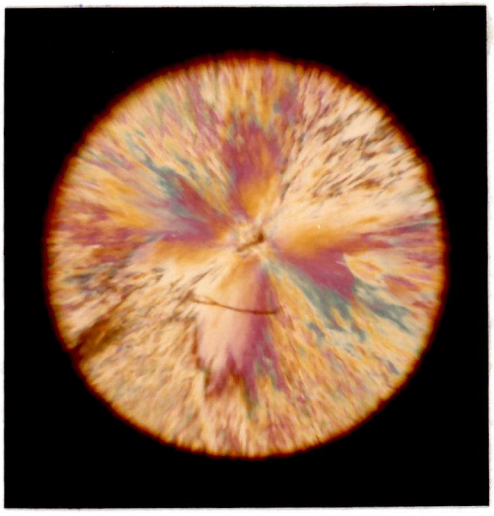


(b)

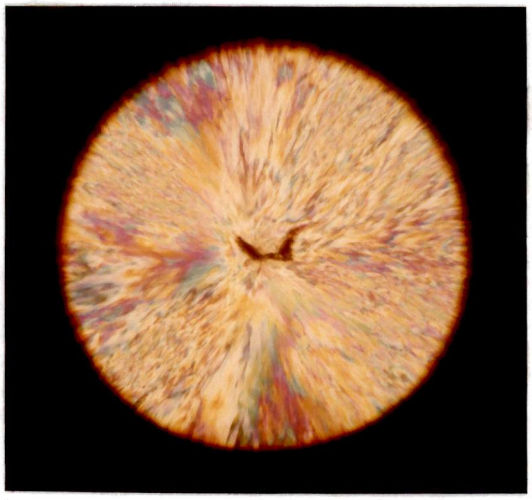
Figure 17. Optical Micrographs of the Block Copolymers. (a) ABA type; (b) BAB type. 500X.



(a)

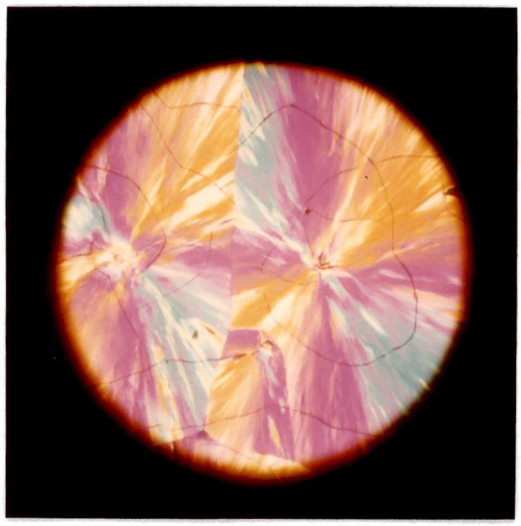


(b)

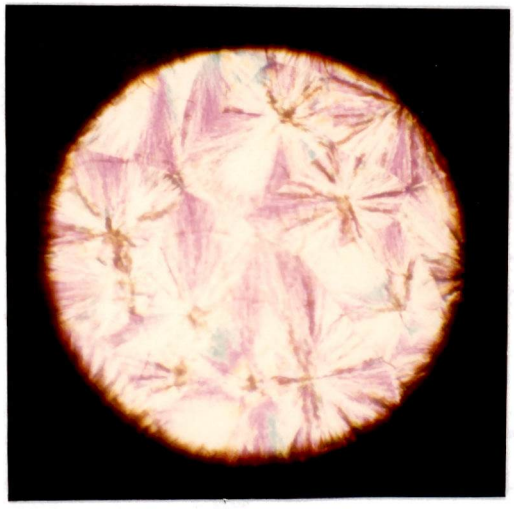


(c)

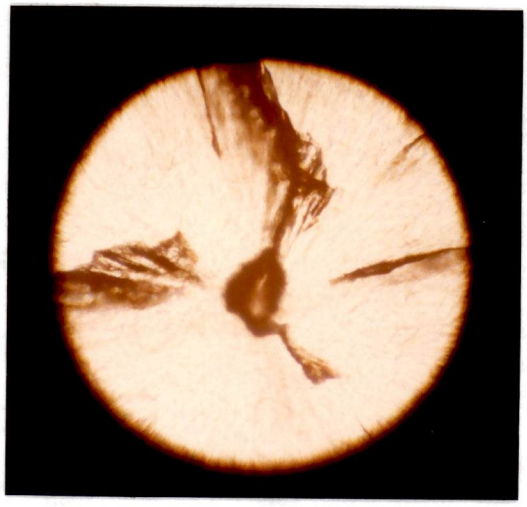
Figure 18. Morphology of Melted and Recrystallized PEO-4000. Cooled in the Air. Film thickness increases from (a) to (c). 100X.



(a)



(b)



(c)

Figure 19. Morphology of Melted and Recrystallized PEO-4000. Quenched in Dry Ice Bath. Film thickness increases from (a) to (c). 100X.

pure DMAc. The solution cast films, after being dried in vacuum oven at room temperature, did not show up any sharp Maltese cross pattern. Instead, only very colorful, randomly scattered images were observed (see Figure 20). However, when these films were heated up, melted and then cooled down in the air, the morphology changed and became similar to those in Figure 18. Very sharp Maltese cross developed. Therefore, the history of film formation and thermal treatment does have much influence on the morphology.

V.3. ISOPHTHALIC ACID

The morphology of isophthalic acid was also studied by solution cast films. These included the material obtained by reacting isophthaloyl chloride with distilled water and also that obtained by reacting isophthaloyl chloride with PEO-4000. Both materials exhibited the same morphological features. The compositions were 15% solid/5% LiCl/80% DMAc and 15% solid/85% DMAc.

When the above solutions were cast and dried, they did not form a continuous phase. Instead, powder-like "particles" stayed on the glass plates. All of them showed very colorful images. Needle-like structures and dendritic structures were observed (see Figure 21).

V.4. PHYSICAL MIXTURES OF BLOCK COPOLYMERS WITH ISOPHTHALIC ACID

From the description in Sections V.1 and V.3, we know that block copolymers, either ABA or BAB, and isophthalic acid do not develop

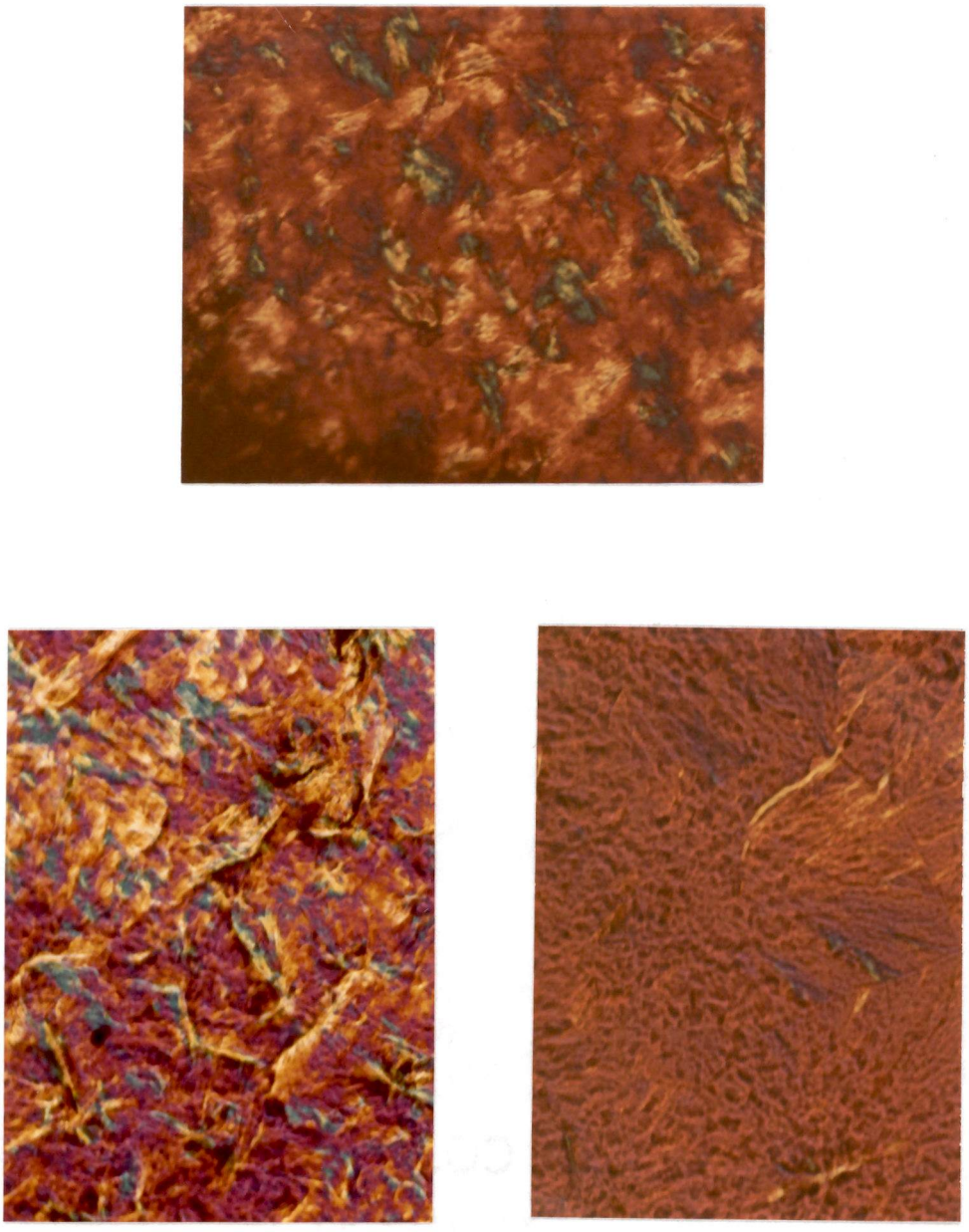
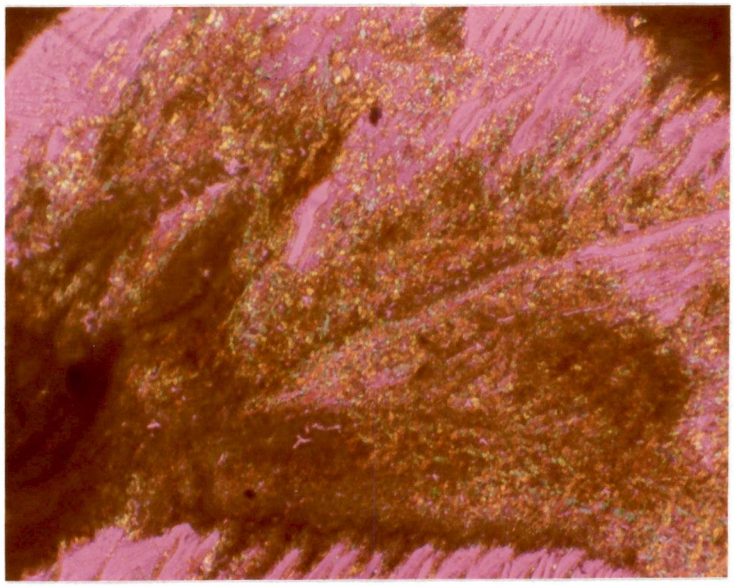
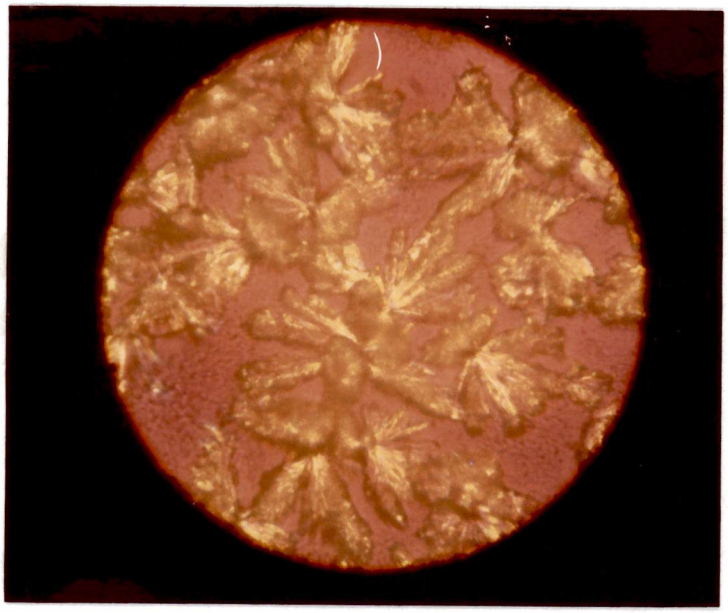


Figure 20. Morphology of Solution Cast Films of PEO-4000. Composition: 15% PEO-4000/85% DMAc. 100X.



(a)



(b)

Figure 21. Morphology of Isophthalic Acid. (a) Needle-like structure, 100X; (b) dendritic structures, 500X.

spherulitic structures when cast from solutions. However, when isophthalic acid was physically mixed with block copolymers, spherulitic crystallization occurred.

The casting solutions were prepared at the same composition as those in previous sections, i.e., 15% organic solid/5% LiCl/80% DMAc. In the 15% organic solid content, 60% of it was block copolymer, and 40% was isophthalic acid. Both BAB and ABA block copolymers gave Maltese cross patterns when mixed with isophthalic acid, indicating the spherulitic crystallization in the films (see Figures 22 and 23).

On the other hand, when there was no LiCl in the casting solution, the block copolymers did not dissolve completely in the solvent and the resulting films showed the growth of coarse spherulites (see Figures 24 and 25) and dendritic structures (see Figure 26).

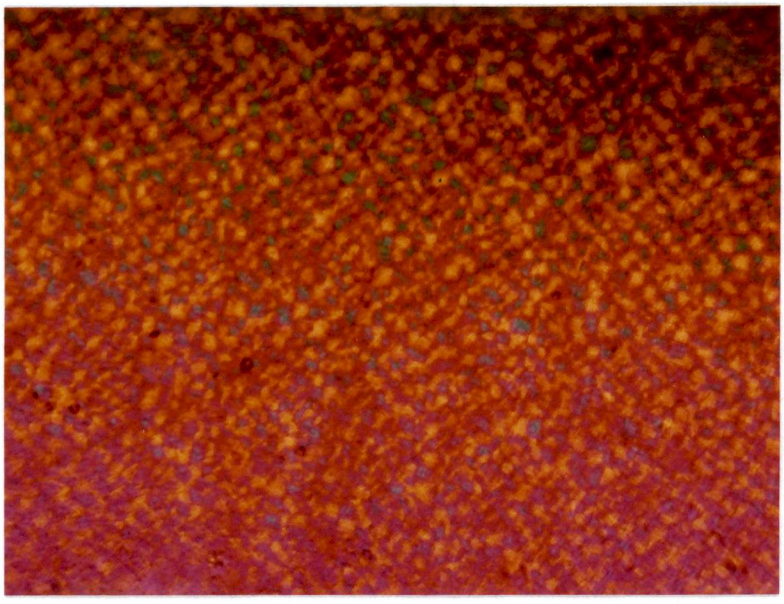
Several other unique and interesting morphological features were also found in these mixtures. These included needle-like crystals, row-like structures and various dendritic structures (see Figures 27-29).

V.5. PHYSICAL MIXTURES OF POLY(M-PHENYLENE ISOPHTHALAMIDE) AND PEO-4000

Mixtures of poly(m-phenylene isophthalamide) with PEO-4000 were prepared. The compositions were 20 and 40% of poly(m-phenylene isophthalamide) with 80 and 60% of poly(ethylene oxide)-4000, respectively.

Both showed spherulitic crystallization. The spherulites in the 80% PEO-4000 mixture were especially well defined.

It should be pointed out that PEO-4000 alone, when cast from solution, did not demonstrate any spherulite growth. Therefore, in the

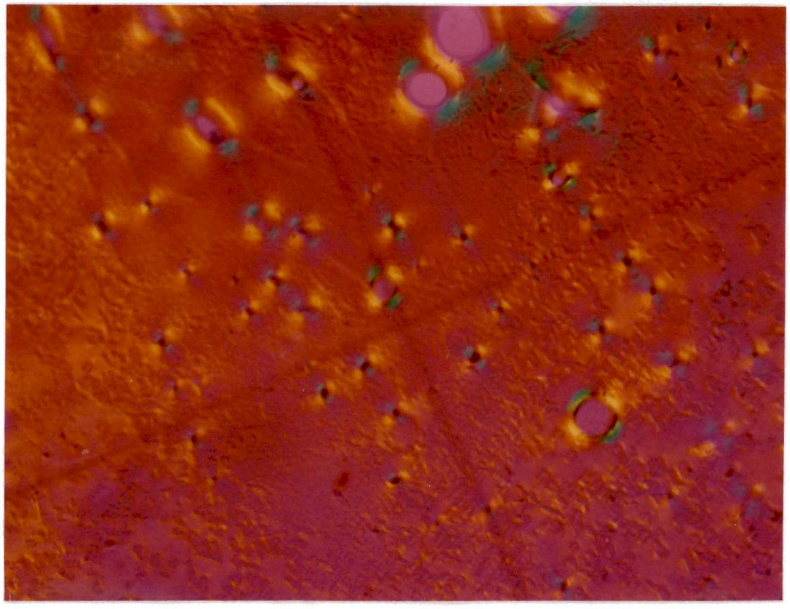


(a)

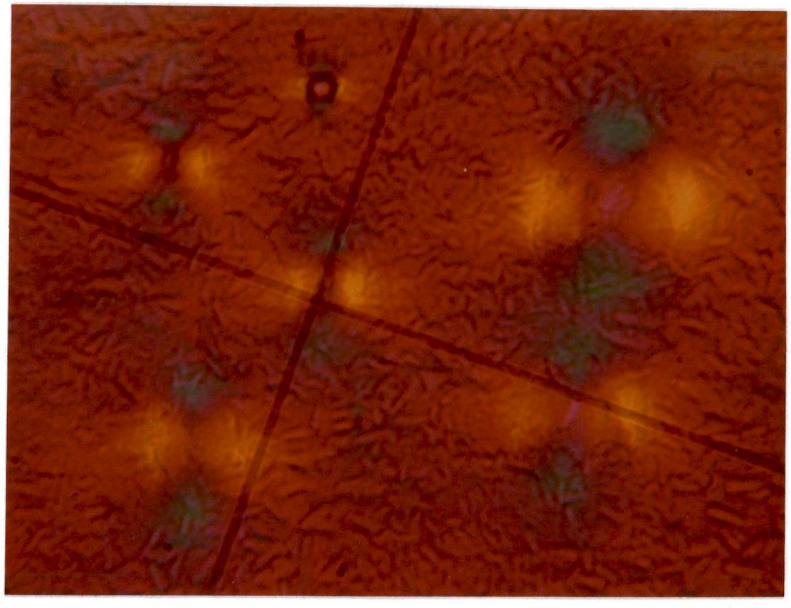


(b)

Figure 22. Optical Micrographs Showing the Development of Maltese Cross Pattern in 60% BAB Copolymer/40% Isophthalic Acid Mixture. Film cast from solution with LiCl. (a) 100X, film is thicker in the top region; (b) 500X.

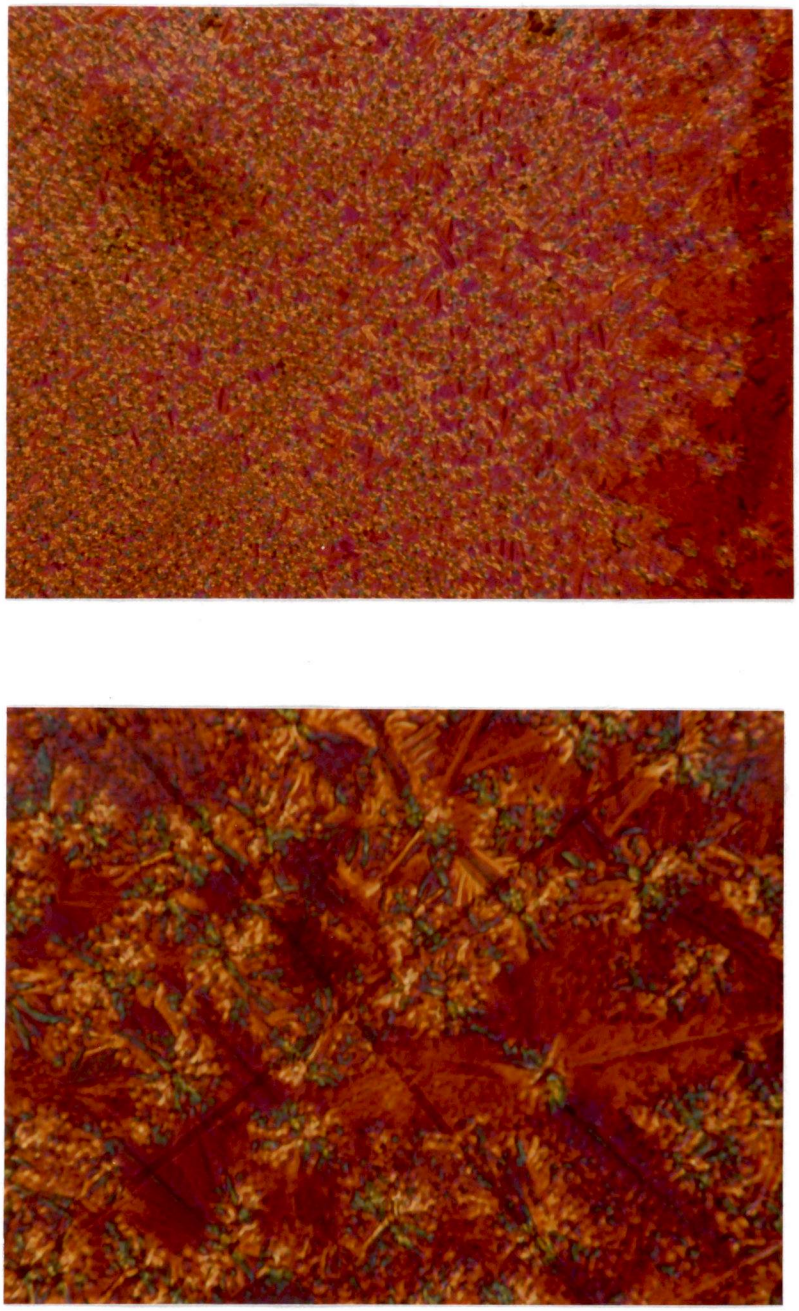


(a)



(b)

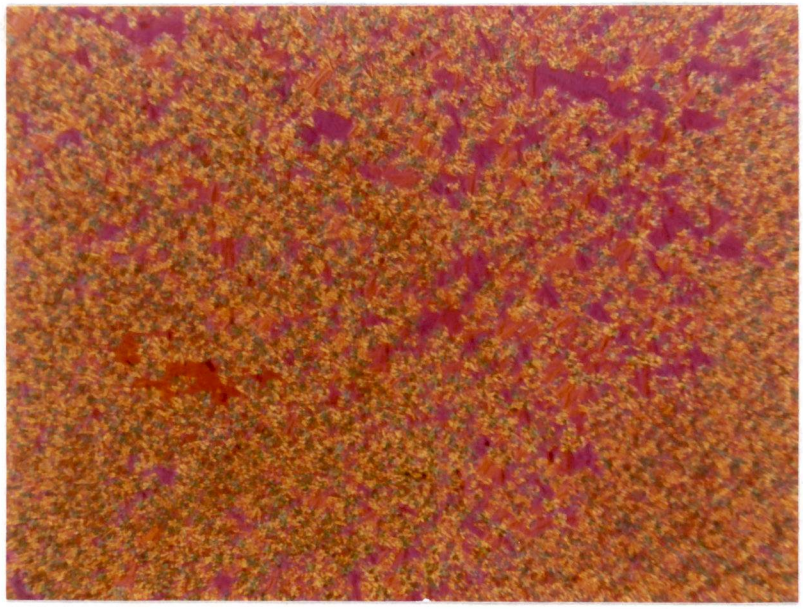
Figure 23. Optical Micrographs Showing the Development of Maltese Cross Pattern in 60% ABA Copolymer/40% Isophthalic Acid Mixture. Film cast from solution with LiCl. (a) 100X; (b) 500X.



(a)

(b)

Figure 24. Optical Micrographs of the Coarse Spherulites Formed in 60% BAB Copolymer/40% Isophthalic Acid Mixture. Film cast from solution without LiCl. (a) 100X, film thickness increases from left to right; (b) 500X.

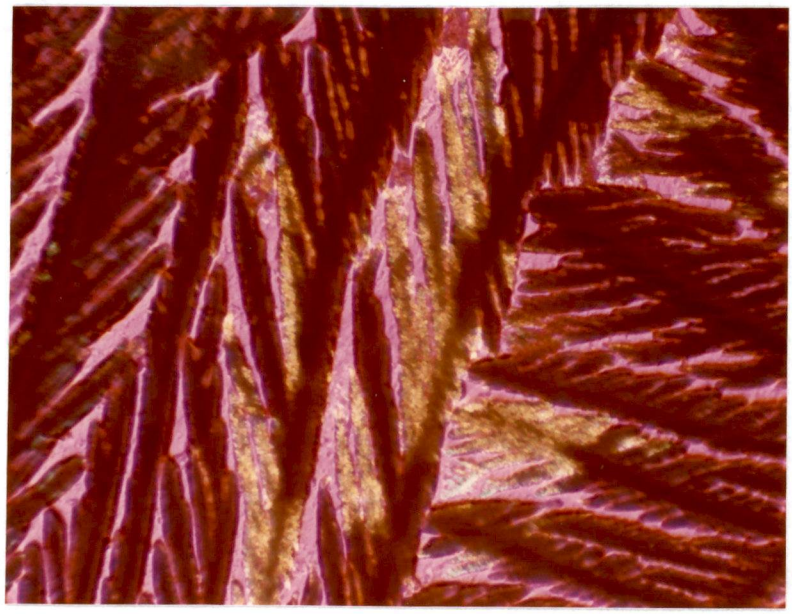


(a)

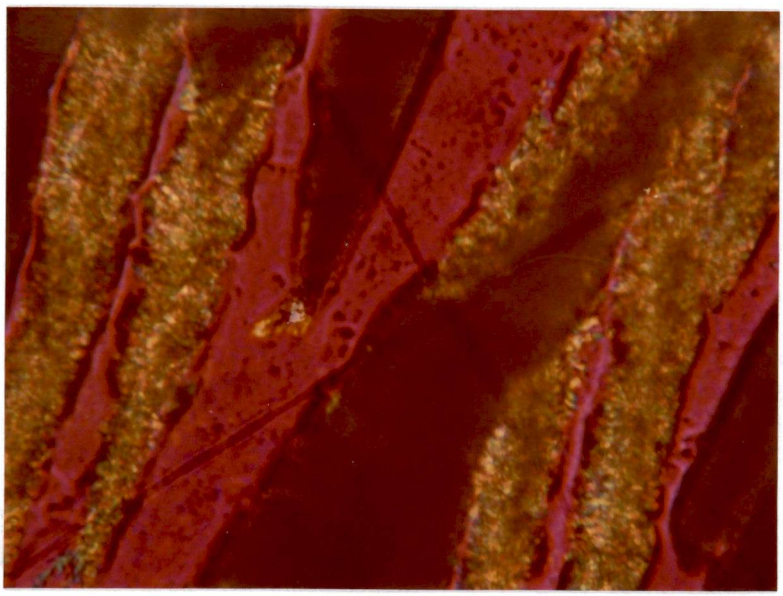


(b)

Figure 25. Optical Micrographs of the Coarse Spherulites Formed in 60% ABA Copolymer/40% Isophthalic Acid Mixture. Film cast from solution without LiCl. (a) 100X; (b) 500X.

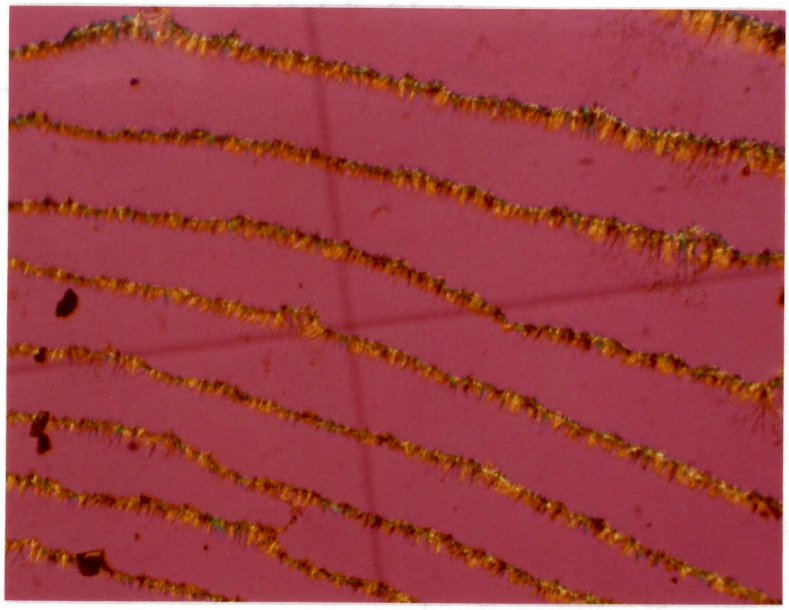


(a)

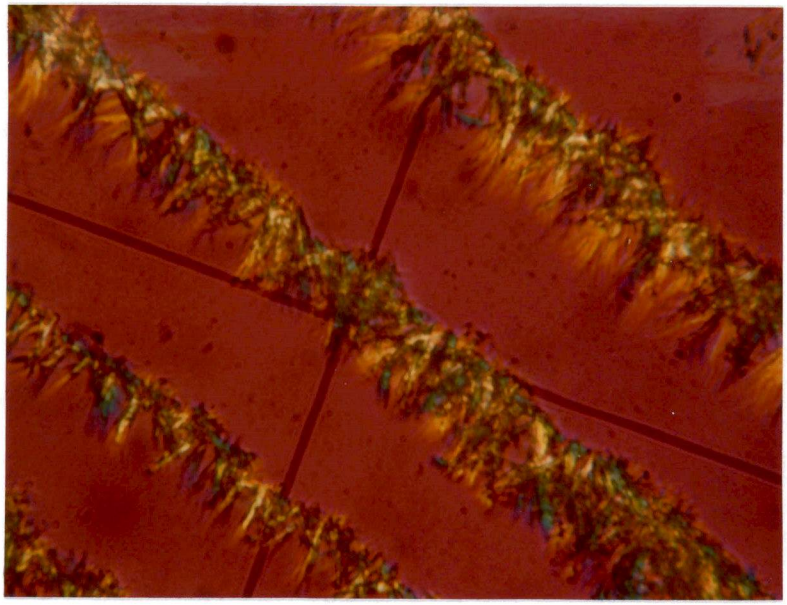


(b)

Figure 26. Dendritic Structures Developed in 60% ABA Copolymer/40% Isophthalic Acid Mixture. Film cast from solution without LiCl. (a) 100X; (b) 500X.

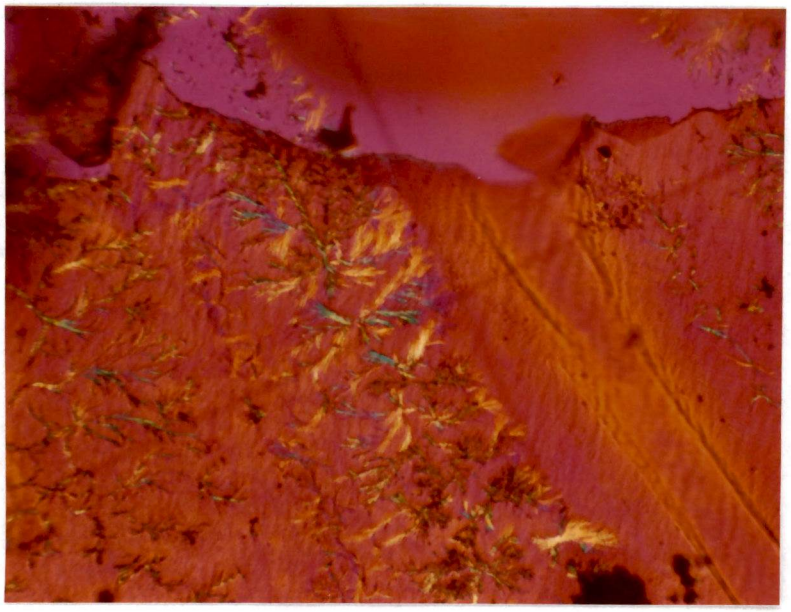


(a)

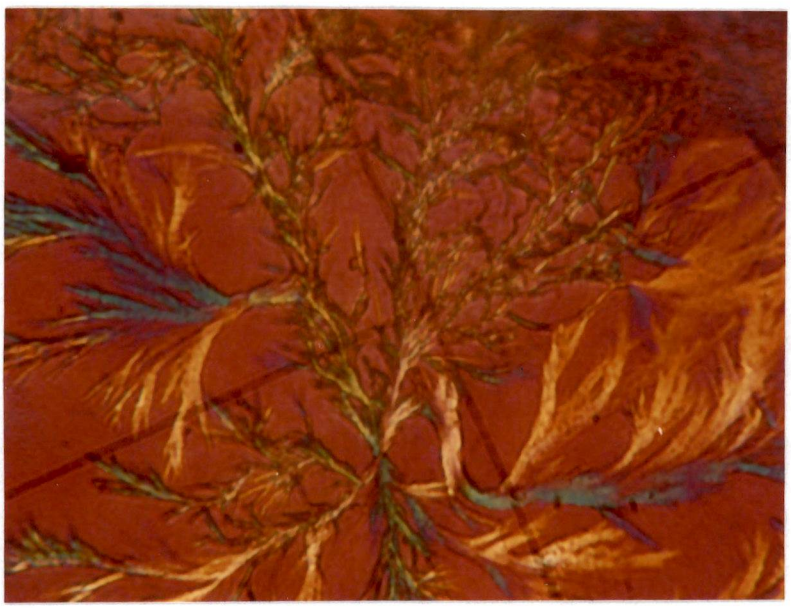


(b)

Figure 27. Row-Like Structures Developed in 60% BAB Copolymer/40% Isophthalic Acid Mixture. Film cast from solution with LiCl. (a) 100X; (b) 500X.



(a)



(b)

Figure 28. Dendritic Structures Developed in 60% BAB Copolymer/40% Isophthalic Acid Mixture. Film cast from solution with LiCl. (a) 100X; (b) 500X.

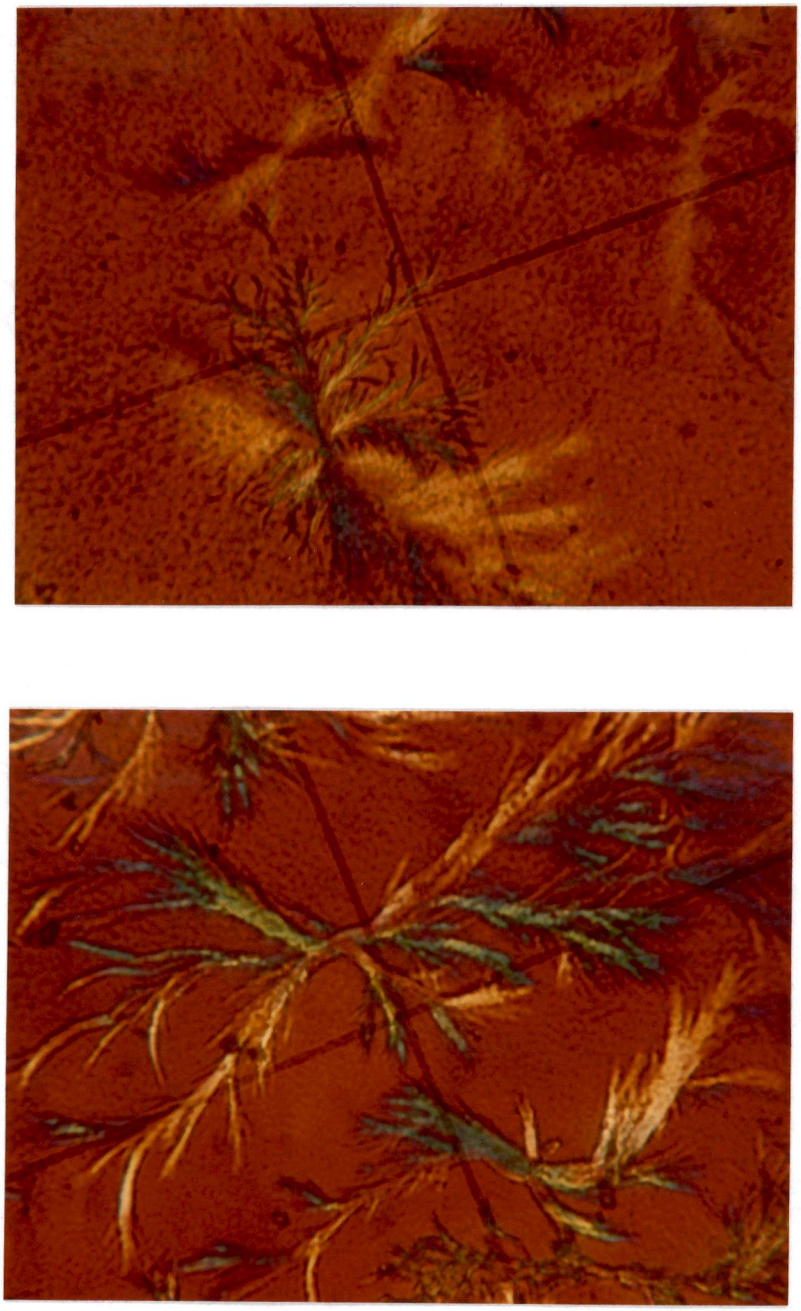
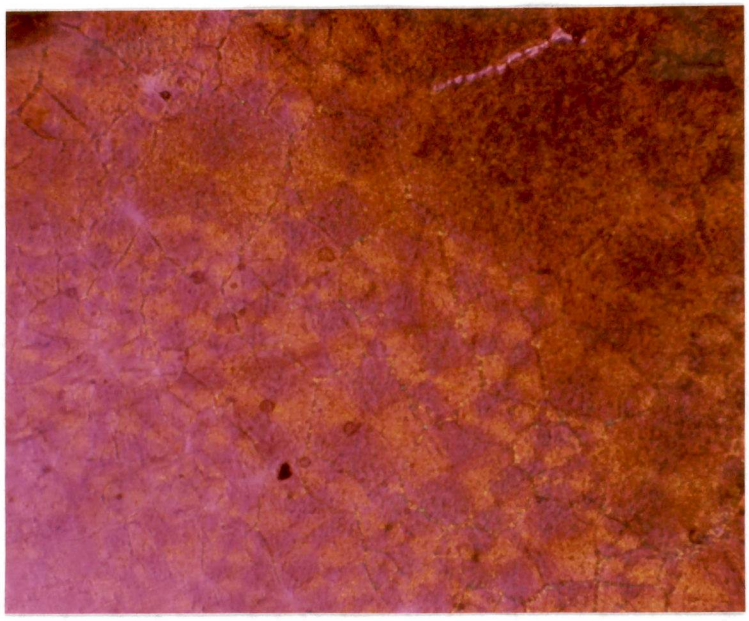


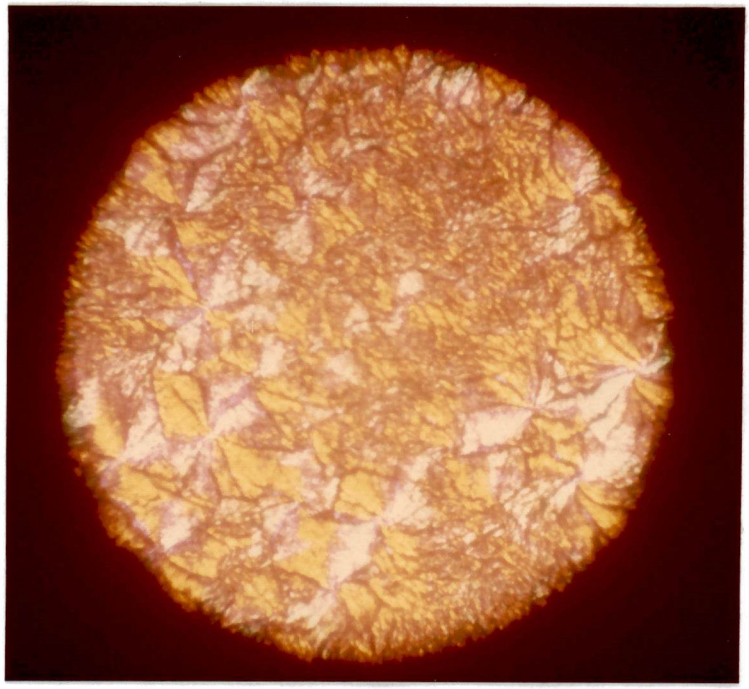
Figure 29. Dendritic Structures Developed in 60% BAB Copolymer/40% Isophthalic Acid Mixture. Film cast from solution with LiCl. 500X.

present case, poly(m-phenylene isophthalamide) seems to help the spherulitic crystallization. A similar situation existed in the mixtures of block copolymers with isophthalic acid. The more viscous high molecular weight polymers seem to play an important role in the film morphology.

The observed morphologies are presented in Figure 30.



(a)



(b)

Figure 30. Development of Maltese Cross Patterns in Poly(m-phenylene isophthalamide)/PEO-4000 Mixtures. Weight ratio: (a) 40:60; (b) 20:80. 500X.

CHAPTER VI

DISCUSSION

VI.1. THE SYNTHESIS

In the synthesis of poly(m-phenylene isophthalamide) homopolymers, care was taken to synthesize the homopolymers with an inherent viscosity greater than 1.0. There are several factors which determine the possibility of getting high molecular weight polymers. In order to get high molecular weight, the following precautions should be observed:

1. The purity of monomers, solvent and dry nitrogen gas should be as high as possible.
2. The reaction temperature at the beginning should be lowered to -40°C to prevent any side reaction.
3. The amounts of monomers employed should be in stoichiometrical balance, and the concentration of monomers in the solvent should preferably be in the range of 0.3 to 1.0 moles per liter (96).
4. Since longer reaction time in polycondensation usually results in more complete reaction, the reaction time should be extended, if necessary.

Generally speaking, the purification of the monomers is the most time-consuming step in the homopolymer synthesis. Both monomers are very reactive and unstable, therefore the purification was always finished on the same day or one day before the synthesis was conducted, and dry nitrogen gas blanket was provided to prevent the purified materials from

getting in contact with the air. Usually, m-phenylene diamine needs to be purified by vacuum sublimation for three to four times to get rid of the impurities. The isophthaloyl chloride can be recrystallized from dry n-hexane. However, some batches contained too much impurities to be purified in this way. Vacuum sublimation was found to be a good method to purify these batches.

In total, six batches of poly(m-phenylene isophthalamide) were synthesized during this research. Most of them gave inherent viscosity greater than one.

The block copolymer syntheses were also conducted. Infrared spectroscopy was used to measure the weight percent incorporation of poly(ethylene oxide) segment. The results showed that the ABA type triblock copolymer has 5.1% incorporation and the BAB type has 13.2% incorporation.

The reaction between isophthaloyl chloride and PEO-4000, originally designed to investigate the morphology of block copolymer/homopolymer mixtures, seemed to be a simple one at first glance. The reaction product was expected to be a high molecular weight polymer. However, due to the presence of water in the extraction step, the already-formed ester linkage was broken down and isophthalic acid was obtained as the final product. Many efforts were made to characterize this material. These included light scattering, wide-angle x-ray diffraction, infrared spectroscopy, solubility behaviors, and morphological studies. The details can be found in Section IV.4.

VI.2. THE MORPHOLOGY

As having been pointed out, the morphological interest in BAB type block copolymers was the major motivation for carrying out this research. However, the present work showed no Maltese cross development in poly(m-phenylene isophthalamide) and its ABA and BAB block copolymers. Therefore, the morphological studies were extended to include PEO-4000 and mixtures of PEO-4000 with poly(m-phenylene isophthalamide). An effort was also tried to study the morphology of block copolymers mixed with high molecular weight PEO extended by isophthaloyl chloride. Accidentally, the mixtures of isophthalic acid with block copolymers were studied instead. Nevertheless, the morphological features shown by isophthalic acid/block copolymer mixtures, together with those shown by PEO-4000/poly(m-phenylene isophthalamide) mixtures, eventually enable us to compare these observations with the spherulitic crystallization phenomena reported by Bernauer (68) and Keith and Padden (47).

Bernauer, for example, studied the spherulitic crystallization brought about in organic compounds by the addition of a few percent of impurities. The impurities he added were mainly resins which acted as a thickener to increase the melt viscosity. Bernauer concluded that, when the temperature is lowered, these impurities separate out in the melt as fine droplets which cause extensive crystalline disorder and break the growing crystals up into fibers.

On the other hand, Keith and Padden also studied the organic compound/organic compound mixtures and low molecular weight homopolymer/high molecular weight homopolymer mixtures. The mixtures they studied

were resorcinol-tartaric acid, isotactic polypropylene-atactic polypropylene, isotactic polystyrene-atactic polystyrene and high molecular weight poly(ethylene oxide)-low molecular weight poly(ethylene oxide).

The resorcinol-tartaric acid mixtures were melted and homogeneously mixed, and then the solidified masses were ground into fine powders, small samples of which were then fused between glass cover slips to provide thin films of melt in which spherulitic crystallization was observed. On the other hand, the polymer blends were dissolved to form 1% solution in solvents. Thin films were then cast on heated cover slips. After evaporation of solvent, the films were covered with further slips, remelted, and recrystallized.

Keith and Padden proposed a phenomenological theory of spherulitic crystallization. They emphasized that spherulite-forming materials are multicomponent systems in which certain components are likely to be rejected preferentially by growing crystals. The term "impurity" is used to refer to all such crystallization-rejected species. Among the above studied mixtures, tartaric acid, atactic polymers and low molecular weight poly(ethylene oxide) are regarded as impurities which induce the spherulitic crystallization. The hosts in which spherulitic crystallization occur are resorcinol, isotactic polymers and high molecular weight poly(ethylene oxide), respectively.

In the present work, the mixtures studied are low molecular weight poly(ethylene oxide)-high molecular weight poly(m-phenylene isophthalamide)

and isophthalic acid-aromatic polyamide block copolymer. Films were prepared by casting from concentrated solutions (15-20% solid content). However, no remelting was conducted after the films were cast. (Keith and Padden remelted the films after casting from 1% solution.)

By applying Keith and Padden's theory, the hosts in the present work are low molecular weight poly(ethylene oxide) and isophthalic acid. The impurities are high molecular weight poly(m-phenylene isophthalamide) and its block copolymers, respectively. Therefore, the roles of the impurity and the host are reversed in the present work if compared with Keith and Padden's. In this sense, the present work is closer to Bernauer's cases in which the hosts are low molecular weight organic compounds and the impurities are resins. However, there are still some differences. In Bernauer's work, films are prepared by melting the organic compounds. The concentration of the impurity is low, only a few percent. In the present work, films are cast from concentrated solution and the impurity contents are much higher, ranging from 20% to 60%.

Despite these differences, the spherulitic crystallization theories proposed by Bernauer and Keith and Padden seem to be all applicable to the present work.

First of all, we must realize that, in the present work, films are prepared from solutions in which the components have higher mobility than in the melt. When the solution is cast on the glass plate, the host (low molecular weight PEO or isophthalic acid) diffuses more quickly than the impurity (high molecular weight aromatic polyamide homopolymer or its

block copolymer). Therefore, during the solvent evaporation process, phase separation occurs and some host-rich regions are formed. In these regions, the concentration of the impurity is accordingly lowered. The more viscous poly(m-phenylene isophthalamide) and its block copolymers then act as "thickeners" (as in Bernauer's work) or "impurities" (as in Keith and Padden's work) which induce the spherulitic crystallization.

Therefore, this research presents a new spherulitic crystallization example in the polymer blends and organic compound/resin systems.

It seems to the author that, in addition to the spherulitic crystallization mechanism proposed by Keith and Padden, the much more viscous materials, i.e., poly(m-phenylene isophthalamide) and its block copolymers, all being high molecular weight polymers, also play an important role in the morphology development of the solution cast films.

It has been shown that, when PEO-4000 is cast from solution with 15% solid content, the resulting films do not exhibit the same morphology as that shown by the PEO melt. The films seem to be too thin to allow prominent spherulitic crystallization. When the films are heated, remelted, and then cooled down in the air, the area of the film shrinks, the film thickness increases and well-defined Maltese cross patterns are observed. Therefore, a critical thickness seems to be essential for the spherulitic crystallization.

However, when PEO-4000 is cast with the much more viscous poly(m-phenylene isophthalamide), spherulitic crystallization occurs readily. Therefore, the more viscous poly(m-phenylene isophthalamide) seems to have two-fold functions: First of all, it acts as the impurity

to induce the fiber-forming habit, thus giving rise to spherulitic crystallization. Secondly, it also restricts the flow of the low viscosity PEO-4000 and enables PEO-4000 to maintain enough thickness during solvent evaporation for spherulitic crystallization.

A similar situation exists in the isophthalic acid/block copolymer mixtures. It has been shown that, when isophthalic acid is cast from solution (15-20% solid content), the resulting "film" is actually composed of powder-like particles. Only needle-like and dendritic structures are observed. However, well-defined Maltese cross patterns are also observed when it is cast with the more viscous block copolymers.

VI.3. CONCLUSION

There are surely many factors controlling the morphology of the solution cast films. As we have learned from the literature, one single material such as polyethylene can show up several different morphological features depending on the experimental conditions. In the present work, the following factors have been proved to have influence upon the morphology:

1. the chemical nature of the material;
2. the composition of the solution;
3. the thermal history of film preparation;
4. the thickness of the film;
5. the presence of LiCl in the casting solution; and
6. the presence of a more viscous material.

It is also learned from this research that a low molecular weight crystalline polymer or a crystalline organic compound can exhibit spherulitic crystallization in the presence of a more viscous high molecular weight noncrystalline polymer.

LIST OF REFERENCES

LIST OF REFERENCES

1. Triggs, W. W., Brit. Patent 525,516.
2. Pease, D. C., U. S. Patent 2,516,585 (to DuPont).
3. Wittbecker, E. L., P. W. Morgan, J. Polymer Sci., 40, 289 (1959).
4. Magat, E. E., U. S. Patent 2,831,834 (to DuPont).
5. E. I. DuPont de Nemours, Inc., Brit. Patent 871,581.
6. Kwolek, S. L. et al., U. S. Patent 3,063,966 (to DuPont).
7. Preston, J., F. Dobinson, J. Polymer Sci., Pol. Lett. Ed., 2, 1171 (1964).
8. Preston, J., R. W. Smith, J. Polymer Sci., Pol. Lett. Ed., 4, 1033 (1966).
9. Preston, J., J. Polymer Sci., A-1, 4, 529 (1966).
10. Preston, J., R. W. Smith, C. G. Sthman, J. Polymer Sci., C, 19, 7 (1967).
11. Weiss, J. O., H. S. Morgan, M. R. Lilyquist, J. Polymer Sci., C, 19, 29 (1967).
12. Preston, J., R. W. Smith, S. M. Sun, J. Appl. Polym. Sci., 16 (12), 3237 (1972).
13. Campbell, C. R., M. J. Mathews, R. W. Smith, French Patent 1,577,262 (to Monsanto).
14. Beste, L. F., C. W. Stephens, German Patent 1,107,399 (to DuPont).
15. Hill, H. W., S. L. Kwolek, U. S. Patent 3,006,899 (to DuPont).
16. Pease, D. C., U. S. Patent 3,197,443 (to DuPont).
17. Hill, W. H. et al., U. S. Patent 3,349,062 (to DuPont).
18. Morgan, P. W., U. S. Patent 3,354,123 (to DuPont).
19. Bair, T. I., P. W. Morgan, Belgian Patent 726,050 (to DuPont).
20. Kuznetsov, G. A. et al., Vysokomol. Soedin., 7 (9), 1592 (1965).

21. Black, W. B., Trans. N. Y. Acad. Sci., Ser. II, 32, 765 (1970).

22. Butta, E., S. DePetris, V. Frosini, M. Pasquini, Eur. Polym. J., 7, 387 (1971).

23. Gan, L. H., P. Blais, D. J. Carlsson, T. Suprunchuk, D. M. Wiles, J. Appl. Polym. Sci., 19, 69 (1975).

24. Preston, J., J. Polym. Sci., A-1, 4, 529 (1966).

25. Hummel, D. O., H. Siesler, E. Zoschke, I. Vierling, U. Morlock, T. Stadtlander, Milliand Textilber., 54, 1340 (1973).

26. Wurtz, A., Compt. Rend., 49, 619 (1859).

27. Staudinger, H., Die Hochmolekularen Organischen Verbindungen, Springer, Berlin, 1932.

28. Staudinger, H., H. Lohmann, Ann., 505, 41 (1933).

29. Miller, R. A., C. C. Price, J. Polym. Sci., 34, 161 (1959).

30. Hill, F. N., F. E. Bailey, Jr., J. T. Fitzpatric, Ind. Eng. Chem., 50, 5 (1958).

31. Gaylord, N. G., Polyethers, Part I, Polyethylene Oxides and Other Polyethers, Interscience Publishers, New York, 1963.

32. Smith, K. L., R. Van Cleve, Ind. Eng. Chem., 50, 12 (1958).

33. Robertson, N. C., R. L. Mitchell, U. S. Patent 2,689,253 (to Celanese Corp. of America).

34. Sauter, E., Z. Physik. Chem., B21, 161 (1933).

35. Barnes, W. H., S. Ross, J. Am. Chem. Soc., 58, 1129 (1936).

36. Smith, K. L., R. Van Cleve., Ind. Eng. Chem., 50, 12 (1958).

37. Kuroda, Y., M. Kubo, J. Polymer Sci., 26, 327 (1957).

38. Hummel, D. O., Infrared Spectra of Polymers, Interscience Publishers, New York, 1966.

39. Todokoro, H., J. Polymer Sci., Part C, 15, 1 (1966).

40. Collins, E. A., J. Bares, F. W. Billmeyer, Jr., Experiments in Polymer Science, Wiley-Interscience, New York, 1963.

41. Geil, P. H., Polymer Single Crystals, Wiley-Interscience, New York, 1963.

42. Livingston, H. K., R. L. Gregory, J. Polymer Sci., Part A-2, 9, 2081 (1971).

43. Lee, Yu-der, "Solution Properties, Crystallinity and Morphology Studies of Aromatic Polyamides and Its Block Copolymers," Ph.D. dissertation, The University of Tennessee, Knoxville, 1976.

44. Wunderlich, B., Macromolecular Physics, Vol. 1, Academic Press, Inc., New York, 1973, p. 298.

45. Saratovkin, D. D. (1959), "Dendritic Crystallization." (Translated from the Russian by J. E. S. Bradley), Consultants Bureau, New York, Russian ed.,: 1950 and 1953, Metallurgizdat.

46. Wunderlich, B., A. Mehta, J. Materials Sci., 5, 248 (1970).

47. Keith, H. D., F. J. Padden, Jr., J. Appl. Physics, 34, 2409 (1963); 35, 1270, 1286 (1964).

48. Eppe, R., E. W. Fisher, H. A. Stuart, J. Polymer Sci., 34, 721 (1959).

49. Geil, P. H., J. Polymer Sci., 44, 449 (1960).

50. Eppe, R., E. W. Fischer, H. A. Stuart, J. Polymer Sci., 34, 721 (1959).

51. Keller, A., J. Polymer Sci., 36, 361 (1959).

52. Geil, P. H., "Morphology of Amorphous Polymers." In Polymeric Materials, by American Society of Metals, 1975.

53. Keller, A., J. Polymer Sci., 15, 31 (1955).

54. Pennings, A. J., A. M. Kiel, Z. Z. Kolloid, Polymere, 205, 160 (1965).

55. Pelzbauer, Z., R. St. J. Manley, J. Macromol. Sci., B4, 761 (1965).

56. Pennings, A. J., J. M. A. A. van der Mark, H. C. Booij, Kolloid Z. Z. Polymere, 236, 99 (1970).

57. Dreyfuss, P., ACS Symposium Series 6, "Polyethers," edited by E. J. Vandenberg, 1975, p. 72.

58. Wunderlich, B., P. Sullivan, Polymer, 3, 247 (1962).

59. Flory, P. J., Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953.

60. Geil, P. H., Experiments in Polymer Science, Wiley-Interscience, New York, 1963.

61. Yeh, G. S. Y., Crit. Rev. Macromol. Sci., 1, 173 (1972).

62. Geil, P. H., F. R. Anderson, B. Wunderlich, T. Arakawa, J. Polymer Sci., A2, 3707 (1964).

63. Hildebrand, J. H., R. L. Scott, The Solubility of Non-electrolytes, Reinhold, New York, 1950.

64. Scott, R. L., J. Chem. Phys., 17, 279 (1949).

65. Bohn, L., Kolloid-Z., 213, 55 (1966); Rubber Chem. Technol., 41, 495 (1968).

66. Johannsen, A., A Descriptive Petrography of Igneous Rocks, University of Chicago Press, Chicago, Illinois, 1931.

67. Wallerant, F., Bull. Soc. Franc. Mineral., 30, 43 (1907).

68. Bernauer, F., Gedrillte Kristalle, Borntrager, Berlin, 1929.

69. Morse, H. W., J. D. H. Donnay, Am. Mineralogist, 18, 66 (1933).

70. Buckley, H. E., Crystal Growth, John Wiley & Sons, Inc., New York, 1951, Chapter 12.

71. Rinne, F., Trans. Faraday Soc., 29, 1016 (1933); C. Robinson, ibid., 52, 571 (1956); H. D. Keith and F. J. Padden, Jr., unpublished results.

72. Ceresa, R. J., Block and Graft Copolymers, Butterworths, Washington, 1960.

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

74. Battaerd, H., G. W. Tregear, Graft Polymers, Polymer Reviews, Vol. 10, Interscience, New York, 1964.

75. Morton, M., L. J. Fellers, Macromol. Reviews, 2, 71 (1967).

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

77. Allport, D. C., A. A. Mohajer, in Block Copolymers, D. C. Allport, W. H. Janes, eds., Halstead Press, New York, 1973.

78. Zdrahala, R. J., "Block Copolymers Based on Wholly Aromatic Polyamide and Poly(ethylene oxide) or Poly(dimethyl siloxane) Segments." Ph.D. dissertation, The University of Tennessee, Knoxville, 1975.

79. Krause, S., J. Polymer Sci., A-2, 7, 249 (1969).

80. Matsuo, M., T. Ueno, H. Horino, S. Chujyo, H. Asai, Polymer, 9, 425 (1968).

81. Meir, D. J., J. Polymer Sci., C26, 81 (1969).

82. Matsuo, M., S. Sagae, H. Asai, Polymer, 10, 79 (1969).

83. Sloniskii, G. L., J. Polymer Sci., 30, 625 (1958).

84. Hughes, L. J., G. L. Brown, J. Polymer Sci., 5, 580 (1961).

85. Inoue, T., T. Soen, T. Hashimoto, H. Kawai, J. Polymer Sci., A-2, 7, 1283 (1969).

86. Inoue, T., T. Soen, T. Hashimoto, H. Kawai, Block Copolymers, S. L. Aggarwal, ed., Plenum Press, New York, 1970, p. 53.

87. Lotz, B., A. J. Kovacs, Kolloid-Z, 209, 97 (1966).

88. Lotz, B., A. J. Kovacs, G. A. Bassett, A. Keller, Kolloid-Z, 209, 115 (1966).

89. Riess, G., J. Kohler, C. Journut, A. Banderet, Macromol. Chem., 101, 58 (1967).

90. Kohler, J., G. Riess, A. Banderet, Eur. Polymer J., 4, 173, 187 (1968).

91. Molau, G. E., W. M. Wittbrodt, Macromolecules, 1, 260 (1968).

92. Inoue, T., T. Soen, T. Hashimoto, H. Kawai, Macromolecules, 3, 87 (1970).

93. Iwakura, Y., Y. Tanaka, S. Uchida, J. Appl. Polym. Sci., 5, 108 (1961).

94. Baer, M., J. Polymer Sci., A2, 417 (1964).

95. Childers, C. W., G. Krause, Rubb. Chem. Technol., 40, 1183 (1967).

96. Preston, J., Polymer Engr. & Sci. 15 (3), 199 (1975).

97. Manson, J. A., L. H. Sperling, Polymer Blends and Composites, Plenum Press, New York, 1976.

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