

EFFECTS OF SOLVENTS ON THERMOTROPIC
LIQUID CRYSTALLINE COPOLYESTERS

by

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INTRODUCTION

Polyethylene terephthalate (PET), $--[O-CH_2CH_2OC(=O)-\text{C}_6\text{H}_4-C(=O)--]_n$, is one of the most important commercial polymers in terms of both sales and range of application. As a fiber PET is used extensively in the area of textiles being commonly blended with cotton, wool or rayon. Not only do the PET fibers provide strength, they also contribute to the "permanent press" properties of the fabric. The strength of these fibers is very evident as a reinforcing material in automobile tires. As a film, PET is used in applications such as magnetic tapes, packaging materials, electrical insulation and backing of photographic films.

The versatility of PET, from an application standpoint, can be related to the different physical arrangements of the molecules, i.e., the morphology. Since the final material properties are directly related to the morphology, it is obvious that morphology (or structure)-property studies are of extreme importance. Also, the way in which the material is processed influences bulk properties and therefore becomes an important variable in structure-property relationships. The inter-relationship between processing, structure and bulk properties is best understood by looking at an example, the spinning of PET fibers. When PET is extruded through a spinneret from the melt and quickly quenched, an unoriented amorphous filament is obtained. This filament is weak and does not possess desirable fiber properties. However, when this randomly

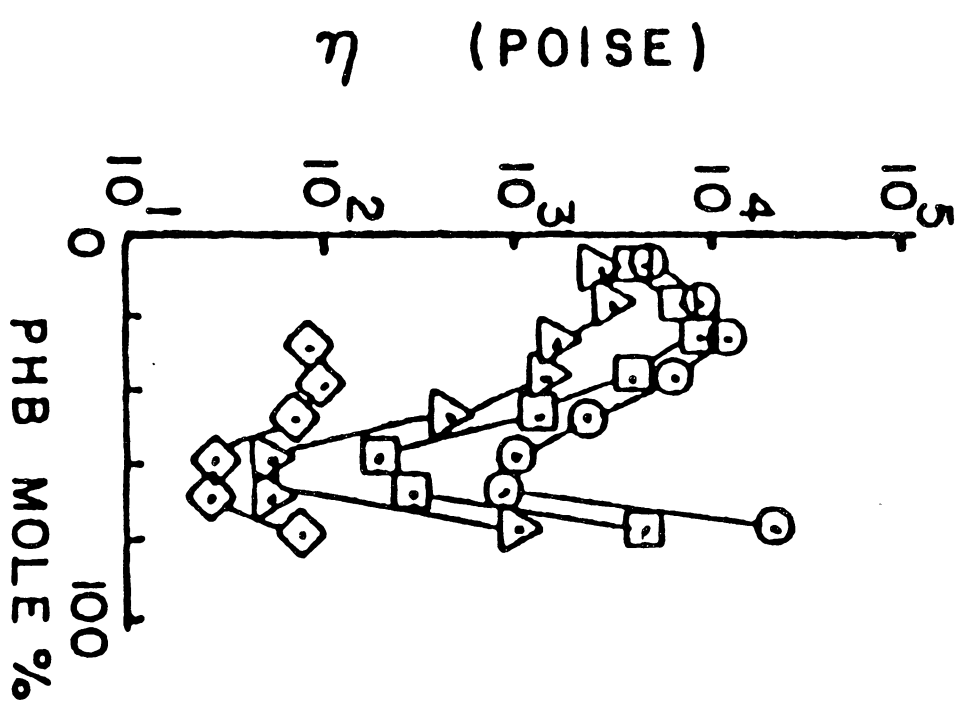
oriented amorphous fiber is drawn above its glass transition temperature, a substantial amount of molecular orientation is introduced and a semi-crystalline fiber with good properties is obtained. In order to stabilize the fiber dimension and reduce shrinkage, the filament is heat set at a high temperature which enables the release of internal strain and promotes further crystallization. The final fiber properties depend on the morphology (e.g. crystallinity and orientation) which in turn can be controlled by the processing conditions, for example, the draw ratio, draw rate, draw temperature et cetera. This clearly shows the need for systematic morphological studies which would then enable a broad field of applications.

Although PET is widely used as a fiber and film, it has had only limited acceptance as a molding plastic. One important reason for this is the need for hot molds (140-150°C) to allow the polymer to crystallize [6]. Also, the upper use temperature of the amorphous polyester is limited by its T_g (69°C) [7], whereas the heat deflection temperature of the semi-crystalline material is 85°C at 264psi load [8]. In an attempt to increase the T_g of the polyester and also to increase its flame resistance, researchers at Tennessee Eastman Company produced a copolyester by molding PET, which has a flexible chain conformation, with p-hydroxybenzoic acid (PHB), which has a stiff rodlike conformation. They have also reported that processing of these systems can lead to highly anisotropic fluids whose melt viscosity behaves in a rather

anomalous way when contrasted with conventional, thermally processable flexible chain polymers. Specifically, copolyesters with at least a PHB content of 35 mole percent have opaque melts and Figure 1 a-b shows some of the properties of these materials. Figure 1(a) shows that the melt viscosity starts to decrease at a PHB value of 30 mole percent due to the onset of liquid crystalline order, with the lowest viscosity being present at about 60 mole percent PHB. The anisotropic nature of these materials following injection molding and solidification is evident from the data presented in Figure 1(b) which were obtained on the 60 mole percent PHB copolymer. Specifically, the effect of specimen thickness on flexural modulus is obvious in this figure. While injection molding of conventional flexible chain polymers often leads, under similar molding rates, to anisotropic properties caused by molecular orientation, the level of anisotropy is never of the magnitude observed for these mesophase systems. The phenomena of the opaque melts, low viscosities and anisotropic properties can be explained on the basis of liquid crystal formation.

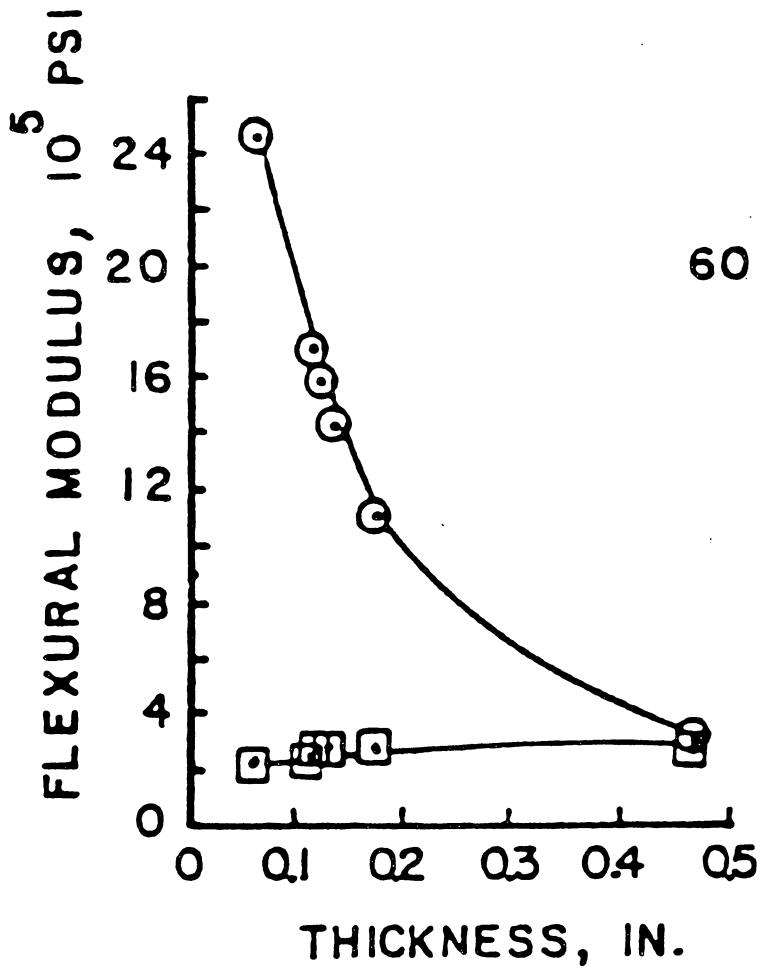
The objective of this research is to investigate these thermotropic liquid crystalline copolyester systems in order to achieve a better understanding of the range of morphologies that may be induced. A second purpose is to investigate the morphologies induced when these liquid crystalline systems are exposed to various solvents.

Figure 1. (a) Melt viscosity at 275°C of PET modified with different levels of p-hydroxybenzoic acid (from ref. 6); flow direction of PET modified with 60%PHB (from ref. 6).



○ 15 1/SEC
 □ 100
 △ 1600
 ◇ 54000

Figure 1. (b) Effect of specimen thickness on flexural modulus along the flow and across the flow direction of PET modified with 60%PHB (from ref. 6).



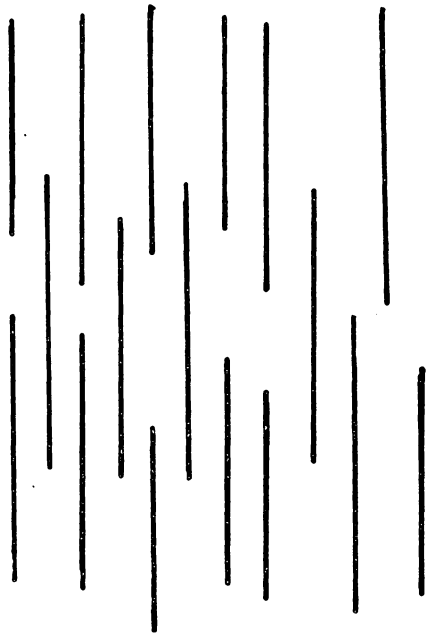
LITERATURE REVIEW

LIQUID CRYSTALLINE BEHAVIOR

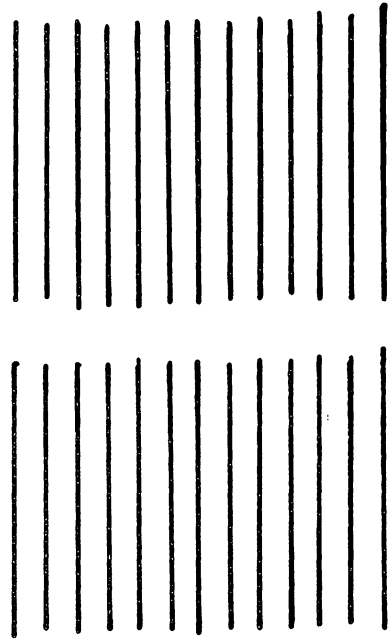
The term liquid crystal represents a morphological form intermediate between the isotropic fluid state and the three dimensionally ordered crystalline state [9]. The first observation of this phenomenon was made by Ritzner in 1888 [10] and the term liquid crystal behavior was introduced soon afterward by Lehmann [11]. A material that exhibits liquid crystalline order possesses many of the characteristic mechanical properties of fluids yet has a sufficient degree of molecular order so as to diffract x-rays according to Bragg's law. Hence, this texture is denoted as a mesophase originating from the Greek term "mesos" meaning "intermediate".

Generally liquid crystalline order is classified into three types of mesomorphic arrangements: nematic, smectic, and cholesteric. In the nematic phase as shown in Figure 2(a), the center of gravity of the molecules are arranged at random, but in localized regions these molecules have the same orientation. Hence, a rodlike system of preferential uni-directional order is established due to the nematic ordering. For those systems displaying high strength or high modulus, it is generally the nematic morphology that is preferably induced. Figure 2(b) schematically shows the smectic phase where

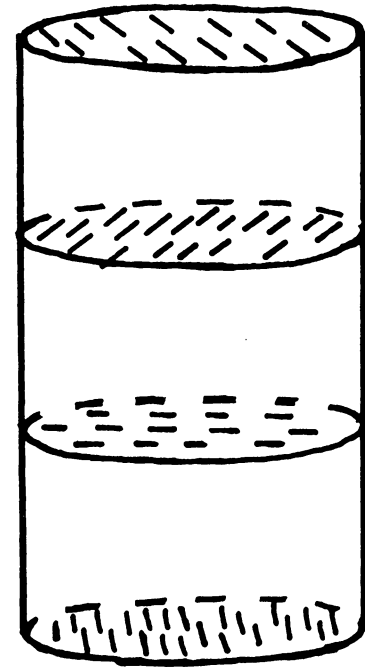
Figure 2. Three generalized forms of liquid crystalline order. (a) Nematic (b) Smectic, and (c) Cholesteric.



NEMATIC



SMECTIC



CHOLESTERIC

the molecules are arranged side by side in a series of stratified layers and the centers of gravities of these molecules are arranged in equidistant planes which make up the corresponding layers. There are several variations to the smectic arrangement which arise from tilting or periodic inclination of the molecules within the stratified layers [9]. As might be expected from the sketch for smectic morphology, this texture is not susceptible to high modulus performance due to the lack of molecular backbone overlap in the orientation direction. The third type of liquid crystalline order is that of the cholesteric mesophase and is schematically shown in Figure 2(c). It is similar to the nematic phase in that it appears to be made up of nematic layers that are then systematically rotated with respect to one another in successive planes, each of which lie perpendicular to the cylindrical axis as shown. Due to the lack of molecular overlap between the long axes of molecules arranged between two adjacent layers, it is unlikely that these structures would promote high strength or high modulus materials in contrast to that of purely nematic mesophase materials.

Liquid crystalline materials can be either thermotropic or lyotropic. Thermotropic liquid crystals are processed from the melt and are dependent on temperature, magnetic fields and electric fields. Lyotropic liquid crystals are processed from solution and depend on polymer concentration, temperature, magnetic fields, and electric fields. The PET/PHB copolyester materials developed at Tennessee Eastman by Jackson, which were referred to earlier in

this paper, is thermotropic in nature and are the first thermotropic liquid crystalline polymer system to be recognized. As mentioned earlier, these liquid crystal copolyesters have unique properties in the melt and solid state. However, very few morphological studies have been performed on these materials. The bulk structure of these materials is to be investigated in this study and the different type of techniques that can be utilized are now briefly reviewed now.

TECHNIQUES USED TO STUDY BULK MORPHOLOGY

The bulk morphology of polymeric materials can be investigated using indirect or direct techniques. Among the direct techniques, wide angle x-ray scattering (WAXS) and small angle x-ray scattering (SAXS) were utilized by Heffelfinger et al. [1,2] to study the bulk structure of PET. Also infrared dichroism and dynamic mechanical measurements have been used to obtain structural information for various polymeric systems [3,4]. In order to study the bulk morphology directly, two destructive techniques, namely fracturing and chemical etching, have been used frequently. The technique of fracturing is based on the idea that fracturing of a sample may take place at weak locations which are found along the boundary of some internal structure [5]. The fracture surface is then analyzed using microscopic techniques.

Chemical etching is a direct technique where a suitable chemical reagent is used to preferentially attack and degrade a

specific region and the etched specimen is then analyzed using a variety of techniques. The technique of chemical etching is based on the principle that a suitable chemical reagent can selectively degrade or etch away some given component or region faster than another. For example, in the case of a semi-crystalline polymer, the ideal reagent will degrade only the amorphous regions while leaving the crystalline structure undisturbed.

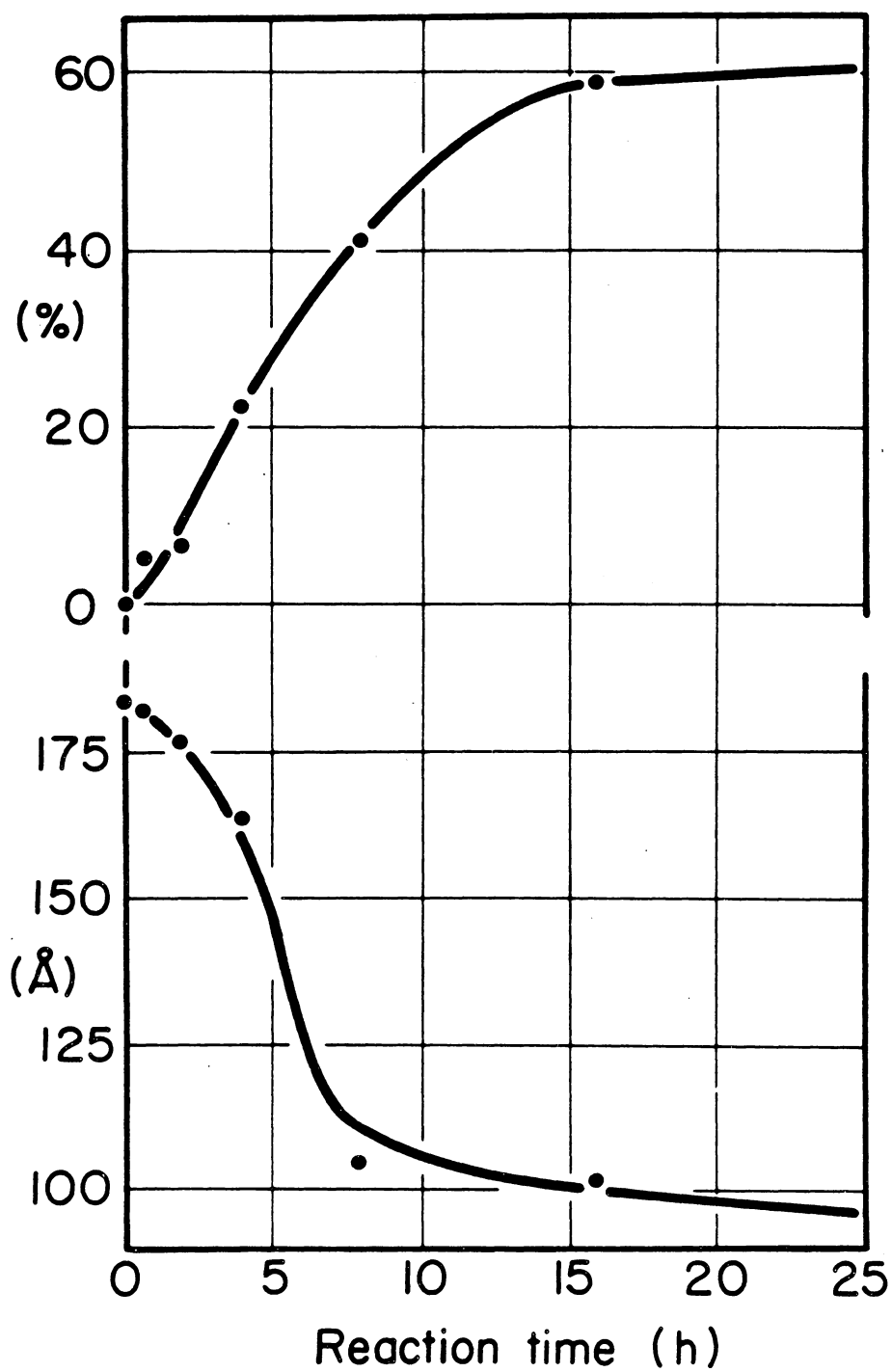
Chemical etching techniques were first developed for the analysis of cellulose where the material was etched by acid hydrolysis in water or ethanol at 80-100°C using, for example, 1-3N HCl or H₂SO₄[20]. Then using weight loss measurements and x-ray analysis Baudish et al. [21] obtained information about the crystal structure of native cellulose and regenerated cellulose. The native cellulose samples they found were of relatively perfect crystals and disordered material. During etching the disordered material gets etched away while the crystals remain without substantial change in perfection. The regenerated samples, on the other hand, were found to have less perfected crystals in addition to the disordered material. Upon etching, the disordered material is hydrolyzed away in addition to less perfect crystals becoming perfected.

In the case of semi-crystalline polyolefins, the polymeric backbone is highly stable and a different approach is required for etching. Palmer and Cobbold [22] discovered that when fuming nitric acid oxidized bulk samples of polyethylene crystallized from the melt, preferential attack on the links between the lamellar

crystals occurred. They investigated the textures of linear and branched polyethylene after etching with fuming nitric acid for different periods of time. For linear polyethylene, attack occurred preferentially at the available surface of the amorphous regions which are almost exclusively located between lamellar crystals. In branched materials, some amorphous material was present as defects within the lamellae. Similar morphological studies have been performed by Keller and Sawada [23] on polyethylene crystallized near the melting point and on polyethylene quenched from the melt. A detailed study of the factors influencing the oxidation of polyethylene by fuming nitric acid was done by Illers [24]. The weight loss and change in lamellar thickness of melt crystallized polyethylene on etching is shown in Figure 3. It shows that the major portion of the initial weight loss correlates well with the amorphous material in the starting polymer, while the crystallinity of the remaining etched sample after initial rapid decrease in weight is close to that of completely crystalline oligomer [25].

Chemical etching studies have also been performed on polyethylene terephthalate by Miyagi and Wunderlich [26], Farrow et al. [27], Baker [28], Adams [29] and by Chu and Wilkes [30]. While Miyagi and Wunderlich used water as the etching reagent, the other researchers used various amines, for example, n-propyl amine or butyl amine. Chu and Wilkes developed a new technique called "contact etching" to study the bulk morphology of semi-crystalline PET and this same technique, described in experimental techniques,

Figure 3. Weight loss and change in lamellar thickness of melt crystallized polyethylene on etching (from ref. 25).



was utilized in this present study as well. These researchers studied a variety of films and fibers with different mechanical and thermal histories. Depending on the degree of crystallinity, etching times of 4 hours to 36 hours were used and a "brick" structure at low magnifications and a "network" superstructure at higher magnifications was observed. The characteristic dimension of the super-structure varied from 700\AA to 3000\AA depending on the sample history; for example, the amorphous material had a ribbon thickness of 800\AA with the network randomly oriented while the sample drawn at 90°C had a ribbon thickness of around 3000\AA . The network structure on the etched surface of the fibers had a characteristic dimension of 600\AA which decreased as the draw ratio was increased. An important finding in these etching studies with amines was that all results are influenced by the phenomenon, etchant (solvent) induced crystallization. In other words, the etchant used initially crystallizes part of the amorphous polymer and then degrades or etches out the remaining amorphous regions.

In this study, the approach taken is to utilize the technique of contact chemical etching to study the bulk morphology of these liquid crystalline copolyesters. Specifically, using n-propyl amine as the etching reagent, can PET or PET rich regions be selectively removed by the etchant thereby revealing a better view of the morphological texture in these systems?

The effects of solvents on these copolyesters are also of interest and hence, it is appropriate to briefly review some of the relevant principles of polymer-solvent interaction.

POLYMER-SOLVENT INTERACTIONS

When one refers to interactions between a non-reactive liquid and a polymer, it becomes necessary to consider polymer solubility. The process of dissolving a polymer in a solvent is governed by the familiar free energy equation

$$\Delta G_M = \Delta H_M - T\Delta S_M \quad (1)$$

where ΔG_M is the change in free energy of the system upon mixing, ΔH_M is the enthalpy change, ΔS_M is the entropy change upon mixing and T is the absolute temperature. For any process to proceed spontaneously, the change in free energy must be negative. The means of achieving this are to induce a large increase in entropy coupled with a small increase in enthalpy or, to decrease enthalpy, which would then enhance the spontaneity of a process. Since a dissolution of a polymer is always connected with a small increase in entropy, the magnitude of the enthalpic term, ΔH_M , is the deciding factor in determining the sign of the free energy change. Many expressions have been developed for this enthalpy term and the most widely accepted one, proposed by Hildebrand and Scatchard [12,13] is

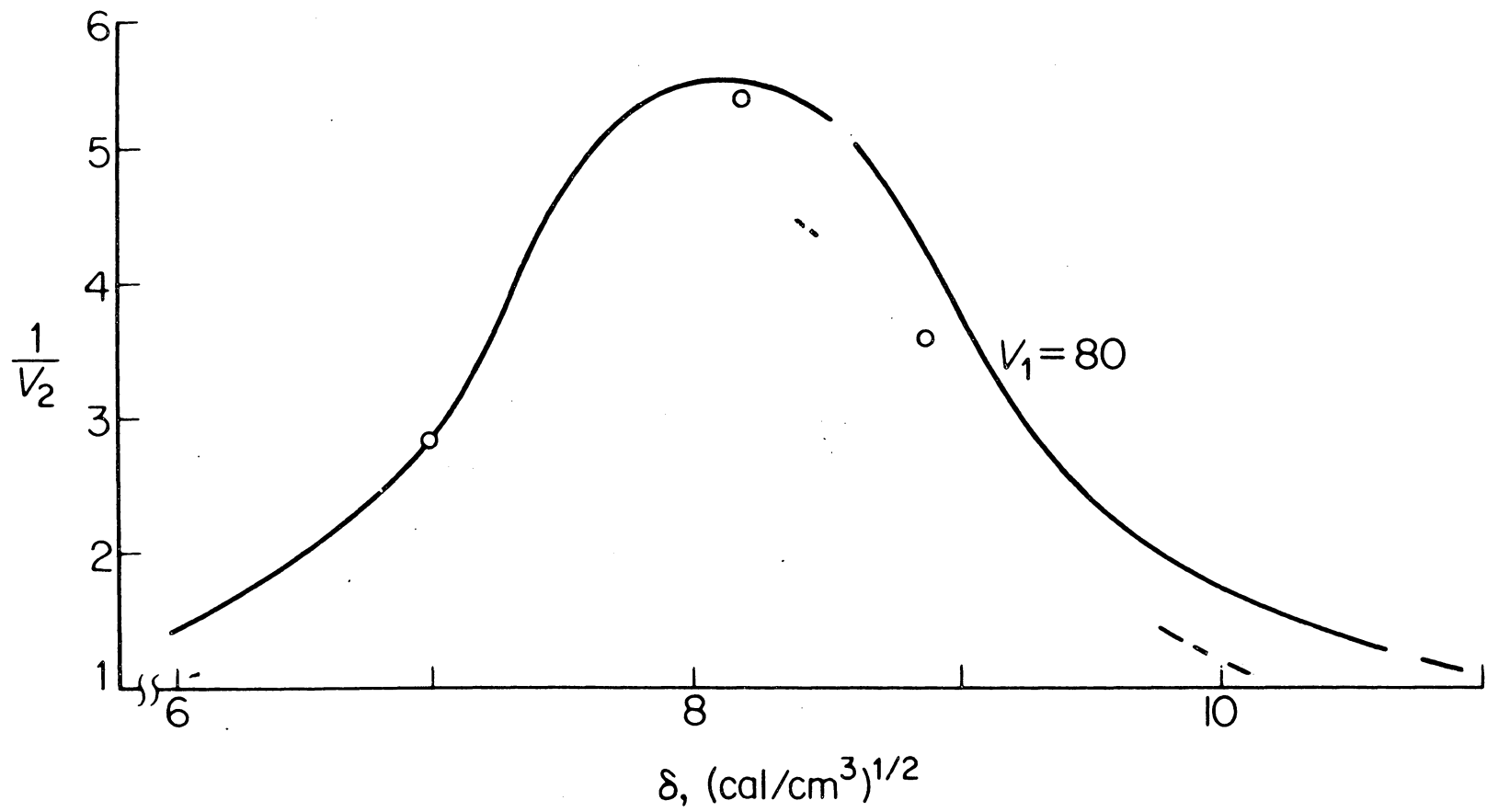
$$\Delta H_M = V_M [(\Delta E_1/V_1)^{\frac{1}{2}} - (\Delta E_2/V_2)^{\frac{1}{2}}] \phi_1 \phi_2 \quad (2)$$

where V_M is the total volume of the mixture, ΔE_1 & ΔE_2 are the energies of vaporization of each component, V_1 & V_2 are the molar

volumes of each component and ϕ_1 & ϕ_2 are the volume fractions of each component in the mixture. The term $(\Delta E/V)$ is called the "cohesive energy density" and physically signifies the amount of energy needed to overcome all intermolecular forces in one mole of liquid. Hildebrand gave the square root of the cohesive energy density, i.e. $(\Delta E/V)^{\frac{1}{2}}$, a special name, the solubility parameter, (δ) . The dimensions of δ are $(\text{cal}/\text{cm}^3)^{\frac{1}{2}}$. Hence, it can be seen that the mixing of two substances is dependent on $(\delta_1 - \delta_2)^2$. If the heat of mixing is not so large as to prevent mixing, then $(\delta_1 - \delta_2)$ has to be relatively small. In fact, if $(\delta_1 - \delta_2) = 0$, solution is assured by the entropy factor. In other words, if the δ values of the two substances are nearly equal, the substances will be miscible.

Equation 2 does not hold for crystalline polymers since it was assumed that no specific forces are active between the structural units of the substances involved. Also, if one of the substances involved contains strongly polar groups or hydrogen bonds, ΔH_M may become higher than predicted by equation 2, so that ΔG_M (in equation 1) becomes positive even for $\delta_1 = \delta_2$ and dissolution does occur [14]. On the other hand, if both substances contain polar groups or hydrogen bonds, solubility may be promoted. If the polymer comprises a cross-linked network, solution cannot occur but polymer segments can be solvated to give a swollen gel. In this case, maximum swelling occurs when δ of the polymer matches δ of the solvent. An example of this is seen in Figure 4, where the swelling of cross-linked butyl rubber is plotted for ten different

Figure 4. Swelling data for butyl rubber in solvents with (from ref. 40) V_2 = molar volume of solvent V_1 = volume fraction of rubber in the swollen sample.



solvents [15]. It is obvious that solvents having a value of δ between 8 and 9.5 swell butyl rubber the best.

Another approach to the thermodynamic description of polymer-solvent interaction is the Flory-Huggins theory [16,17]. This theory describes the free energy change on mixing a polymer and solvent, ΔG_M , as

$$\Delta G_M = RT[N_1 \ln(1-v_1) + N_2 \ln v_2 + \chi N_1 v_2] \quad (3)$$

where ΔG_M is the free energy of mixing, N_1 and N_2 are the number of moles of solvent and polymer, v_2 is the volume fraction of polymer in the mixture, R is the gas constant, T is the absolute temperature and χ is the polymer-solvent interaction parameter. In equation 3, the first two terms indicate the configurational entropy of mixing and are always negative. Hence, the third must be also negative or be a small positive number in order that ΔG_M can be negative. Therefore, χ must be either negative or a small positive number for polymer-solvent compatibility. For cross-linked polymer systems, the solvent cannot dissolve the polymer but can swell it. According to Flory and Rehner [18], a solvent with a low χ will induce maximum swelling.

In order to relate the interaction parameter, χ , to the solubility parameter, δ several semi-empirical approaches have been made. Bristow and Watson [19] found that,

$$\chi = \beta_1 + V_1/RT (\delta_1 - \delta_2)^2 \quad (40)$$

where δ_1 and δ_2 relate to the solvent and polymer respectively, R is the gas constant, V_1 is the molar volume of the solvent and T is the absolute temperature. β is a lattice constant, which is equal to the inverse of the number of nearest neighbors of a molecule or segment in solution and has a numerical value of about 0.35 ± 0.1 . Therefore, by knowing values for χ or δ , one can predict fairly well what type of interaction a solvent will have when it comes in contact with a polymer. One of the outcomes of polymer-solvent interaction is the inducement of crystallinity and this phenomena is addressed next.

SOLVENT INDUCED CRYSTALLIZATION

Polymeric materials can be crystallized in several ways. For example, thermal induced crystallization (from the melt) has been studied extensively, while strain induced crystallization has also received a substantial amount attention. Another way of introducing crystallinity in an amorphous polymer is by the use of appropriate solvents and is referred to as Solvent Induced Crystallization (SINC). The process of SINC can be explained in the following manner. When a polymer comes in contact with an interactive solvent, the solvent molecules diffuse into the polymer. The solvent-polymer interaction increases the mobility of the

polymeric segments by interrupting the segmental forces. This gives the polymeric molecules the capability of rearranging into a thermodynamically lower energy state, the crystalline state, if suitable molecular symmetry exists [26]. Thus, solvents that interact strongly with a polymer are capable of inducing crystallization. The basic mechanism for SINC is similar to that of thermal induced crystallization from the glassy state. While in thermally induced crystallization the inducement of segmental mobility is obtained by thermal energy, in SINC, chemical energy is used instead.

Most of the studies regarding SINC have been conducted on polyethyleneterephthalate, cellulose triacetate and poly-carbonate [27-30]. Wilkes and Desai [30] studied the morphology induced in amorphous PET film by various solvents and followed the kinetics of SINC by small angle light scattering, wide angle x-ray scattering, optical microscopy and scanning electron microscopy. They observed spherulites of few microns in diameter and that the rate of crystallization was controlled by the rate of solvent diffusion in the polymer. Also investigated in their studies was the effect of SINC on the glass transition temperature and the dynamic mechanical properties of PET in the presence of various solvents. Benecki and Turska [31,32] have studied the crystallization of polycarbonate using various solvents. They found that separate diffusion and crystallization fronts existed under certain experimental conditions and reported that the reason for these separate fronts was due to

the time required for significant conformational changes to take place in the polymer chain. Solvent induced crystallization studies performed on polyphenylene sulfide (PPS), which is a rapidly growing engineering thermoplastic, have shown that PPS can be crystallized by using solvents such as methylene chloride or dioxane and that the surface morphologies induced by these solvents were different when treated for long periods of time [33]. From WAXS studies it was speculated that the SINC process for this system occurred mainly at the surface.

In this present study, the objective is to determine whether the PET that is present in the copolyester system can crystallize upon treatment with solvent and if so, what types of morphologies are induced. Also, the aim is to see what effect, if any, certain types of dye carriers have on the morphology of these liquid crystalline systems.

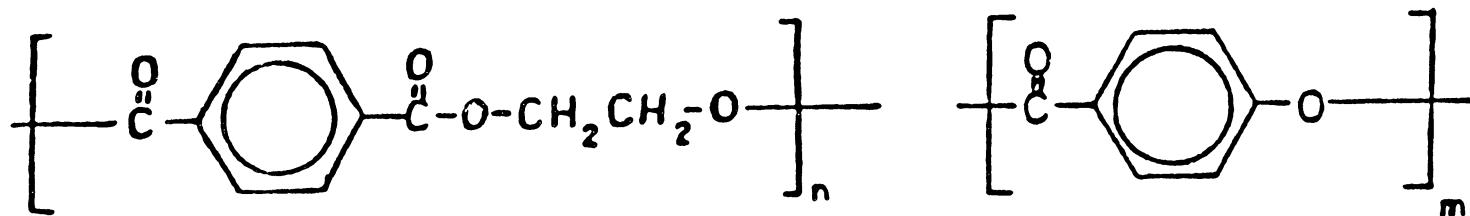
The chapters that follow give an account of the preparation of the thermotropic liquid crystal copolyesters, the techniques used to characterize these materials, as well as the analysis of the data.

EXPERIMENTAL METHODS

MATERIALS

The PET/PHB copolyester series, i.e., PHB content varying from 30 mole% to 80 mole%, used in this study was obtained directly in powder or pellet form from Tennessee Eastman Company. Pure PET obtained from Tennessee Eastman Company and PHB obtained from Carborundum Company were also used as controls. Details on the synthesis of the copolyesters appear in [6] and are summarized below.

A mixture of p-acetoxybenzoic acid (5-90 mole%) and polyethylene terephthalate particles was placed in a 500ml reaction flask. After the reaction flask was evacuated and purged with nitrogen to remove any traces of air, it was heated under vacuum in a metal bath at 110°C to dry the reactants. These dry reactants were placed in a bath at 275°C, stirred in a nitrogen atmosphere and acetic acid distilled out. When a low viscosity was obtained, a vacuum of about 0.5mm was applied for approximately 4 hours at 275°C (300°C for the higher melting compositions). Low melt viscosities were obtained with copolyesters prepared with 5-40 mole% p-acetoxybenzoic acid, high melt viscosities with 50-70 mole% p-acetoxybenzoic acid and the 80-90 mole% p-acetoxybenzoic acid copolyesters solidified during preparation. These copolyesters were further heated under vacuum (0.05-0.1mm) at 210-280°C for 4-16 hours in order to increase the



COPOLYESTER GEN. STRUCTURE

60 MOLE% PHB/PET	$n = .4$	$m = .6$
80 MOLE% PHB/PET	$n = .2$	$m = .8$

Figure 5. The general chemical structure of the PET/PHB copolyesters studied.

intrinsic viscosity by solid phase polymerization. The lower temperature was used for the lower PHB mole percent materials and the higher temperature for the higher PHB mole percent systems. Figure 5 shows the general chemical structure of the PET/PHB copolyester systems. Values for m and n vary as PHB content changes. For example, when $m=0.3$ and $n=0.7$, it would indicate a 30 mole%PHB/ 70 mole%PET material.

The solvents used in this study were reagent grade *n*-propylamine, butylamine, dioxane, methylene chloride and acetone. Two dye carriers, TANDEL(butyl benzoate) and CAROLID(ortho-phenylphenol) were kindly supplied by Sybron Tanatex Chemical Company.

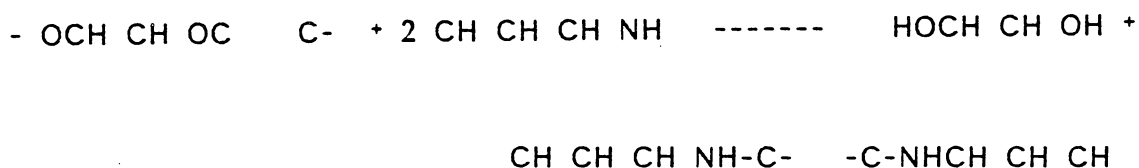
FILM PREPARATION

To minimize hydrolysis by moisture sorption, all samples were heated in a vacuum oven at 100°C for approximately 72 hours, prior to being pressed into thin films. The lower PHB content materials were pressed at temperatures around 230°C while temperatures of around 285°C were used for higher PHB content systems. The films were quenched in an ice-water bath after being pressed. For the etching studies, films that were pressed and quenched (PQ) and films that were pressed, quenched and annealed (PQA) were used. For the SINC studies pressed, quenched (PQ) films were utilized.

TECHNIQUES

(a) Etching Technique

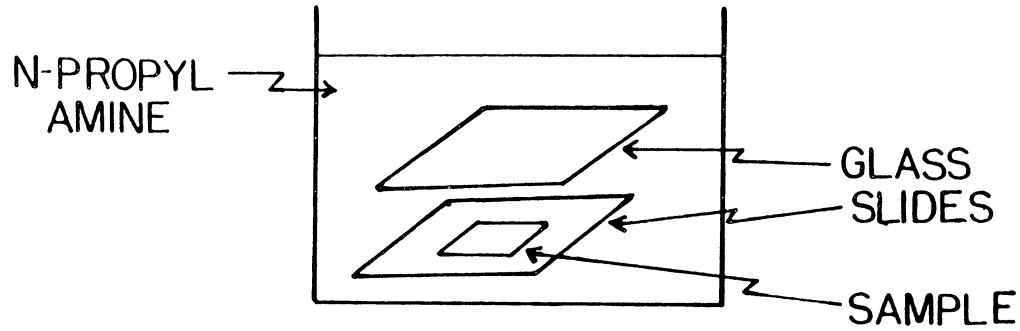
Figure 6 schematically shows the apparatus used for etching the films. The sample is sandwiched between two glass slides, which in turn is placed inside a petri dish containing n-propylamine. The petri dish is covered and due to the toxic nature of the fumes is allowed to sit in a hood for the desired amount of time. Finally, the sample is removed, rinsed in cold water and air dried. The stoichiometric equation which describes the chemical reaction of etching PET by n-propylamine is given below. Ethylene glycol and N,N-dipropylterephthalamide are formed and are soluble in the presence of excess amine.



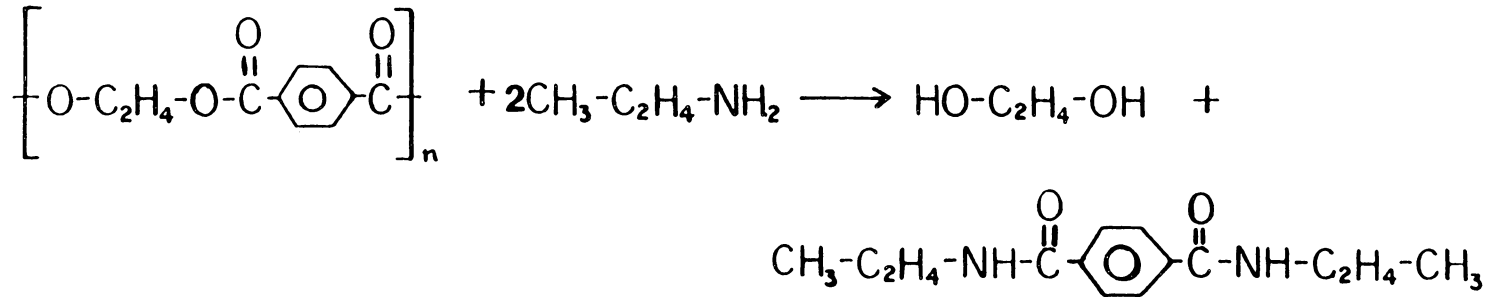
The copolyesters containing PHB up to 50 mole percent were etched for 2 hours, while the higher PHB content films were etched for 28 hours. The lower PHB content films disintegrated (but did not dissolve) when etched for longer periods of time and hence, were etched for only 2 hours in order to maintain integrity of the of the film for morphological studies. Contact etching was also performed on these samples for different periods of time. Etching times of 15 minutes, 30 minutes, 60 minutes and 120 minutes were utilized.

Figure 6. Schematic diagram for apparatus used for contact chemical etching and the chemical reaction for etching of PET by n=propylamine.

CHEMICAL ETCHING



CHEMICAL REACTION FOR ETCHING OF PET BY N-PROPYLAMINE



Butylamine, which is less reactive than n-propylamine was also used as the etching reagent but in this case the glass slides were not used. The sample was directly exposed to the amine and then rinsed in water and dried. By using a less reactive amine and no glass slides it was investigated if the etching behavior seen in contact etching with n-propyl-amine could be reproduced. Butylamine was used as the etchant for films that were pressed, quenched and annealed.

(b) Characterization Techniques

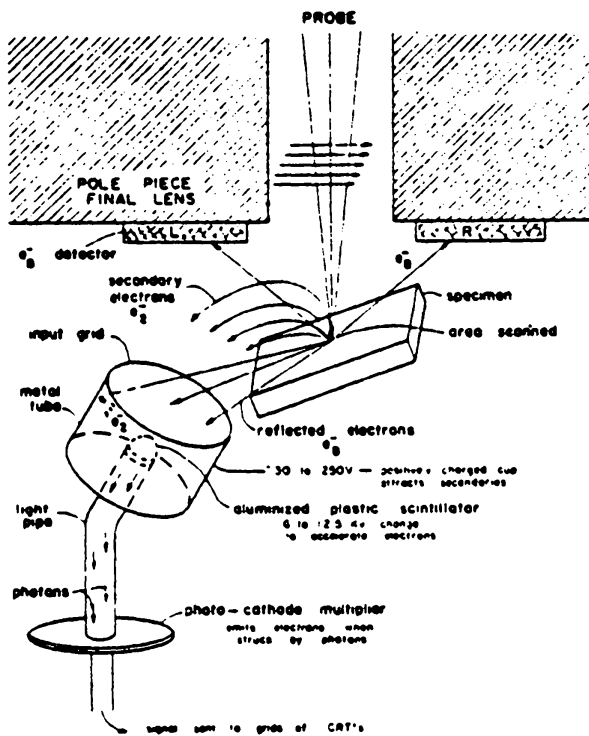
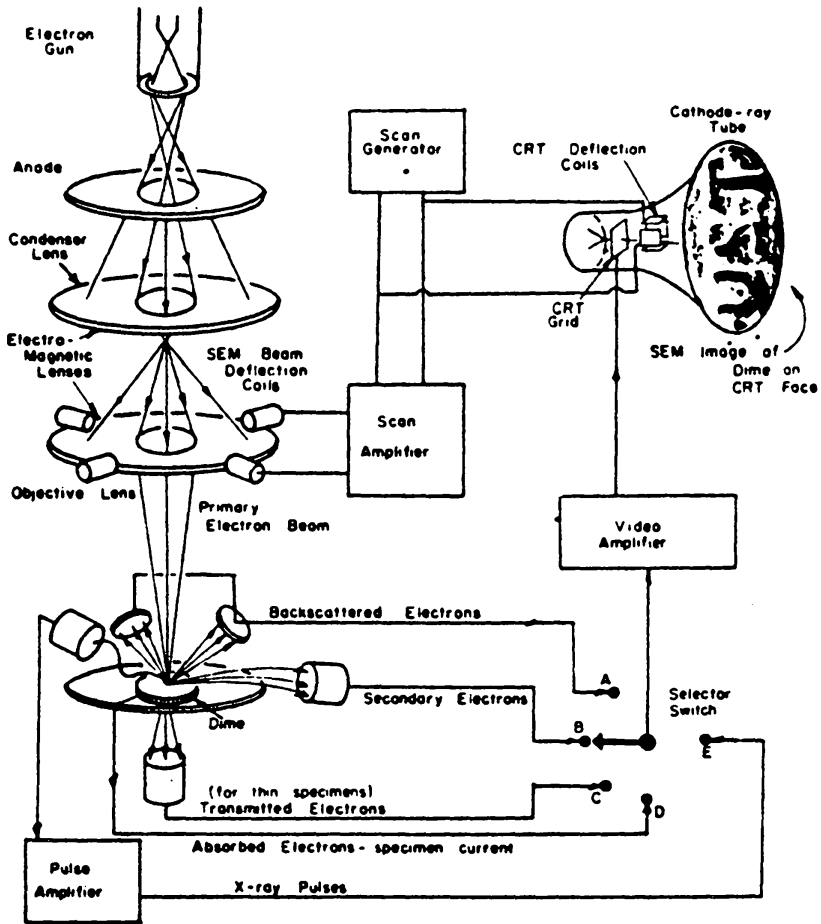
(1) Scanning Electron Microscopy (SEM)

The technique of scanning electron microscopy is an extremely useful tool and has become popular in the field of polymer science. The reason for this is twofold: (1) the ease with which samples can be prepared for viewing by this technique and (2) the high resolution and depth of focus that this technique offers.

Since SEM was utilized a significant amount in this study, some general aspects of the theory behind SEM are presented below. A more detailed discussion can be found in reference [34].

Figure 7 schematically shows the electron optics system, the sample stage and the detector system. A tungsten filament is usually the source of illumination in an SEM. When a current is passed through, the filament is heated and a stream of electrons is emitted. These electrons are accelerated by means of an applied voltage, typically on the order of 15kV. This accelerated beam of electrons then passes through a series of apertures and lenses

Figure 7. Schematic diagram of the electron optics system, the sample stage and the detector system for a scanning electron microscope.



which demagnify and focus the beam. The final lens that the beam passes through not only reduces the beam size but also has a set of scanning coils which forces the beam to continuously trace out a rectangular raster on the sample surface.

When the electron beam strikes the sample surface several events occur but the one of particular interest is the emission of secondary electrons. These secondary electrons are produced when the high energy electron beam penetrates the sample surface and loses its energy by ionizing atoms in the sample. The number of secondary electrons that can emerge from the sample surface decreases with the increase of path length it must travel. Since a secondary electron can lose its energy by the ionization of other atoms along the path, only those secondary electrons emitted near the surface, approximately 100^oA from the surface, can completely escape. The escaping secondary electrons are accelerated to a detector which has a positive potential. This detector is connected through a video amplifier to a cathode-ray tube, which in turn is scanned in synchronization with the beam striking the specimen. Thus, an image of the specimen surface is constructed point by point on the cathode-ray tube screen. The image can then be studied and recorded on photographic film.

For samples with a surface layer of uniform composition, it is the surface topography that dictates the contrast of the image. For example, if the sample surface is nearly perpendicular to the beam and hence a small incident angle, the path length for most

secondary electrons emitted is long; thus, low intensity is shown on the cathode-ray tube for that location. A steep surface on the other hand, would appear very bright.

The procedure for sample preparation is rather simple. Samples are placed on an aluminum stub and coated with a thin layer ($\approx 100\text{-}150\text{\AA}$) of gold. The main reason for coating polymeric samples with gold is because an electron rich surface layer will enable a higher quality image of the surface to be obtained rather than viewing the uncoated, low-electron density polymer directly. Resolution is also improved by the use of this electron rich metal surface layer. Another important reason for coating with gold is to avoid any "charging effects" that can be caused due to the fact that polymeric materials are poor conductors.

In these present studies an ISI Super 111-A scanning electron microscope along with a SPI sputter coater, T.M. Model 13131 (for coating the sample with a layer of gold) were used.

(2) Wide Angle X-ray Scattering (WAXS)

X-ray diffraction arising from periodic fluctuations in electron density that occur over small distances (approximately up to 20\AA) results in WAXS. Such scattering arising from crystals in semi-crystalline polymers can be utilized to determine the degree of crystallinity and sometimes obtain information regarding size, perfection and orientation of the crystals. WAXS studies were performed during the course of this investigation in order to obtain a qualitative estimate of the crystallinity level in the samples. While

detailed reviews of this topic and its applications to polymers can be found elsewhere [35,36,37], some of the concepts directly related to this study are mentioned below.

A typical WAXS pattern that results from an amorphous material is shown in Figure 8 where the characteristic diffuse halo is evident. If the diffraction pattern is taken of a sample consisting of a number of crystals with an overall random orientation with respect to the incident beam, the pattern will then consist of sharp rings (see Figure 9). The sharpness of these rings is related to the crystalline perfection. If the crystallites are not oriented at random but have their crystal axes oriented around a preferred direction, the WAXS pattern will take the form of arcs as shown in Figure 10.

A Phillips PW 1720 table-top x-ray generator equipped with Warhus cameras was used to obtain WAXS patterns of the thermally pressed films, the films treated with solvent and the films etched with n-propylamine. The operating voltage was 40kV and the beam current 25mA. Sample thickness varied from 5mils. to 15mils., while exposure times varied from 6 to 15 hours. Sample to film distances were either 7.1cm or 8.0cm depending on which camera was used.

(3) Differential Scanning Calorimetry (DSC)

A Perkin-Elmer DSC-2 was used for thermal analysis. DSC runs were performed at a heating rate of 10°min., starting from room temperature and ending at approximately 553°K. The glass transition temperature, the crystallization temperature, the melting temperature and the enthalpies of crystallization and fusion

Figure 8. Typical wide angle x-ray scattering pattern of an amorphous polymeric material (from ref. 42).

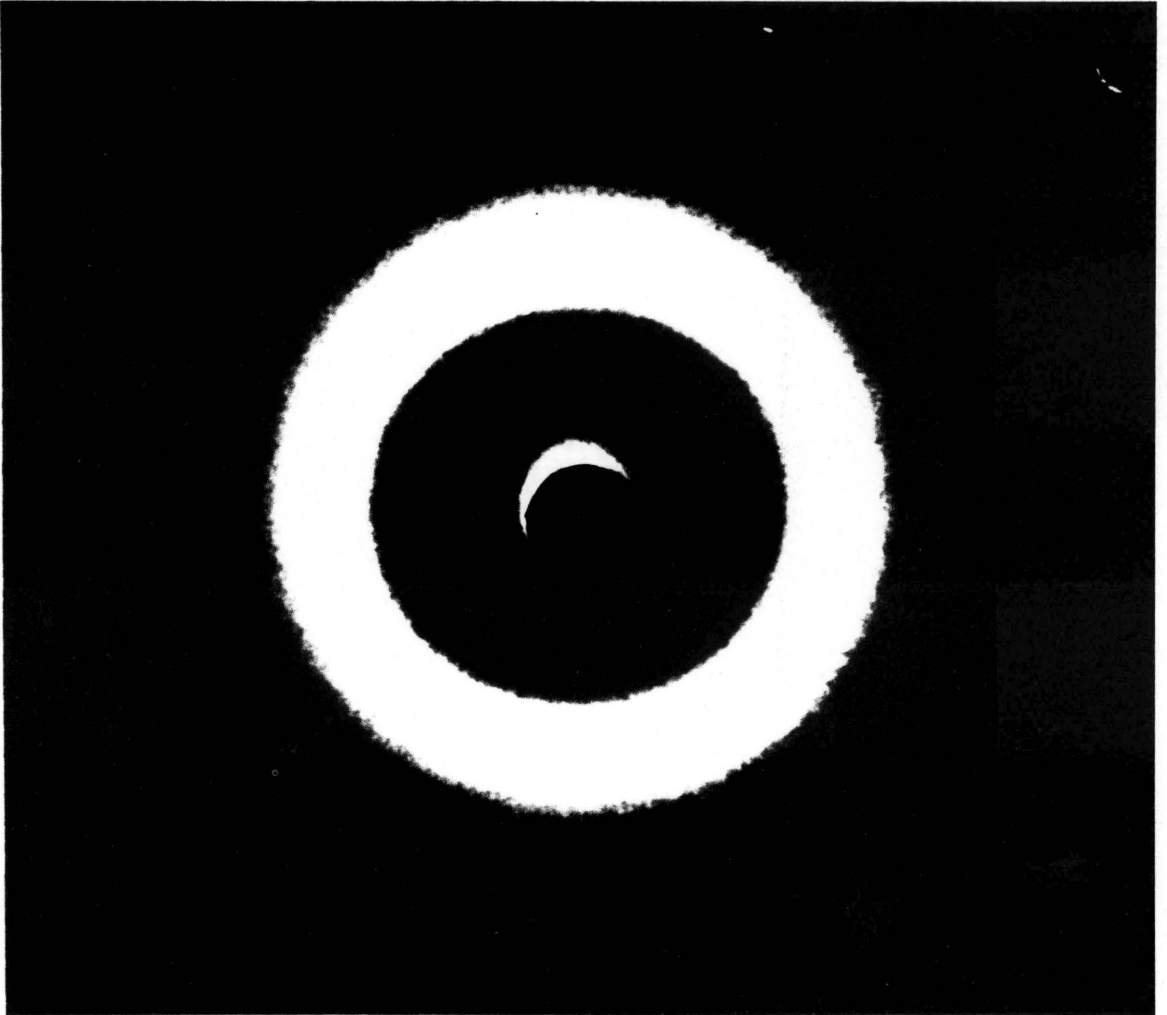


Figure 9. Wide angle x-ray scattering pattern of a semi-crystalline polymer (from ref. 42).

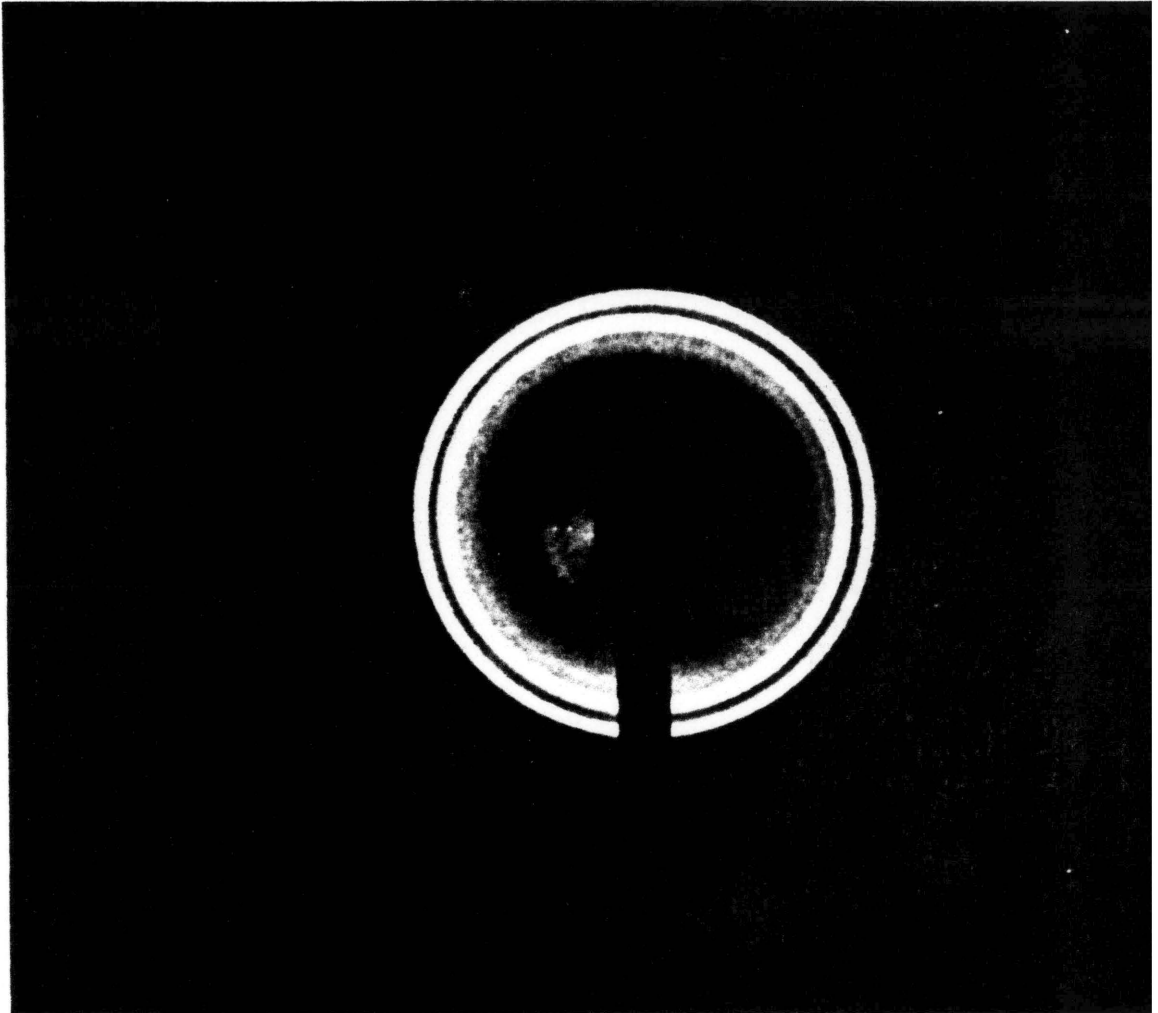
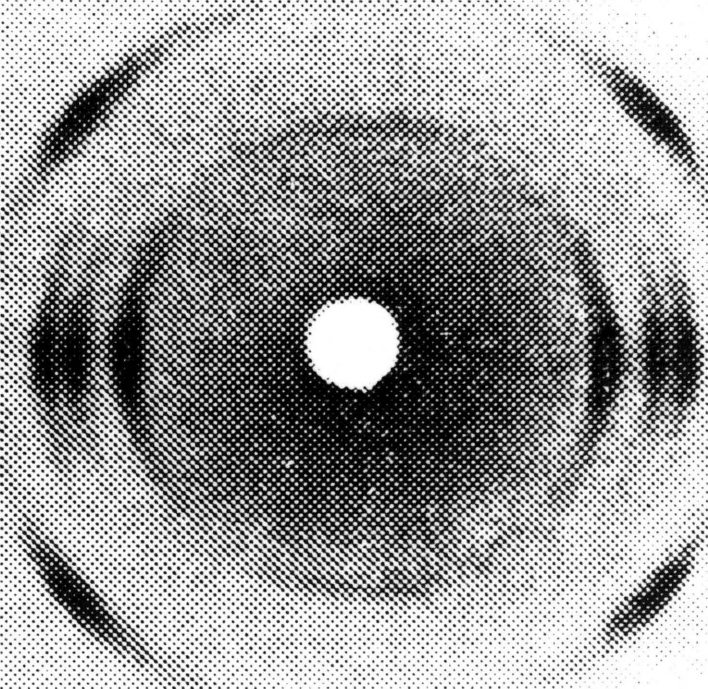


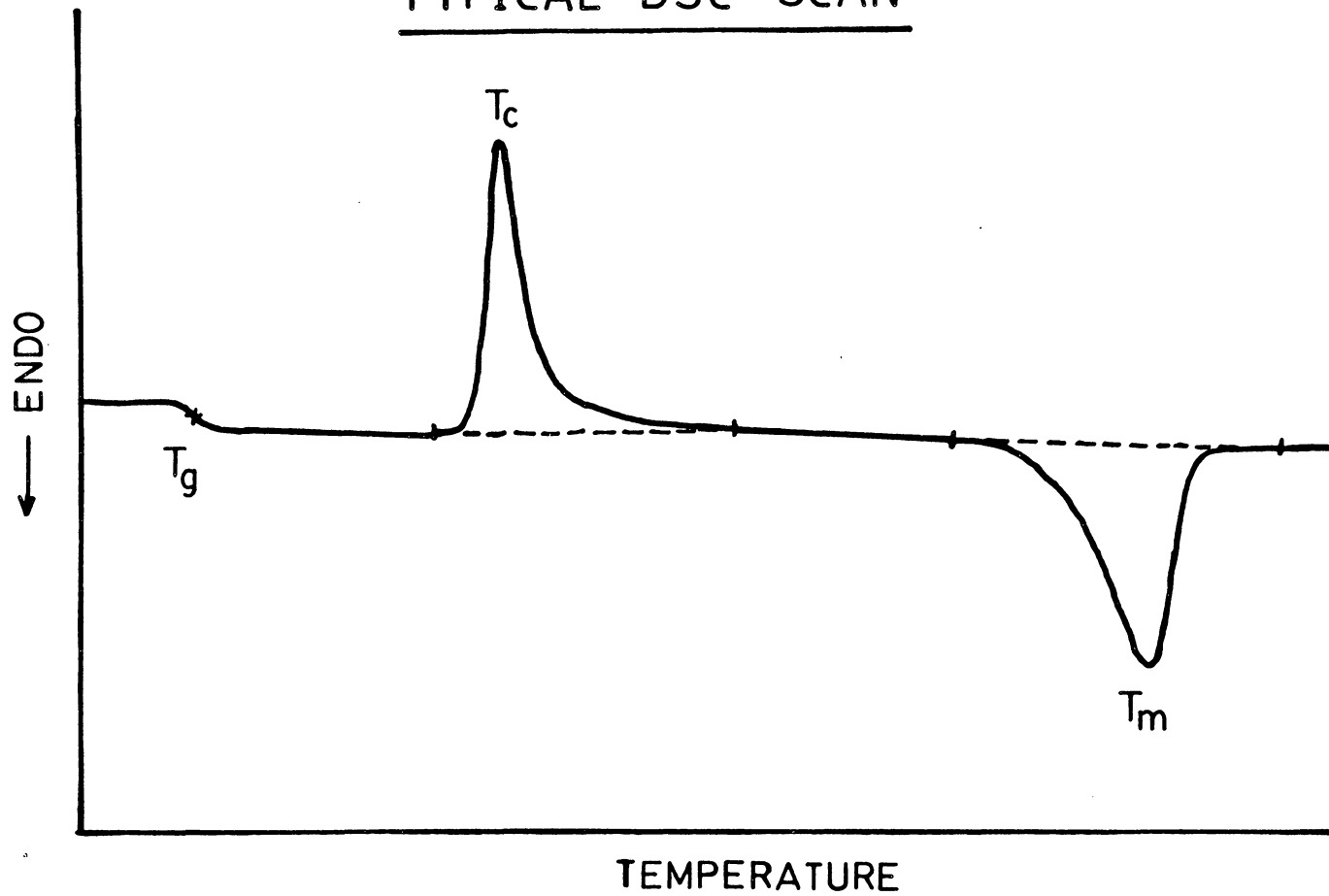
Figure 10. Wide angle x-ray scattering pattern of an oriented semi-crystalline polymer (from ref. 41).



were the parameters that were monitored. The area under the crystallization peak is a measure of the amount of heat that is liberated by the material upon crystallization while the area under the melting peak is a measure of the amount of heat that is absorbed by the material upon melting, i.e. heat of fusion. A typical DSC scan is shown in Figure 11 along with the parameters that are measured.

Figure 11. Typical DSC scan showing parameters of interest.

TYPICAL DSC SCAN



RESULTS AND DISCUSSION

DIFFERENTIAL SCANNING CALORIMETRY

DSC was performed on thermally pressed and quenched films of pure PET and the PHB/PET copolyester series. Figure 12 shows the DSC traces of PET and the PET/PHB copolyester series. Parameters of interest are the glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_M) and the areas under the crystallization and melting peaks. The small endothermic peak that appears near the glass transition temperature is associated with the non-equilibrium behavior or physical aging of the amorphous PET regions. This was verified by observing the DSC scans on materials that had been heated to 280°C, cooled back to room temperature and again heated in the DCS. The DCS traces of these scans are shown in Figure 13 and the endothermic peak no longer is present. A good overview on the non-equilibrium behavior of polymeric glasses is given by Tant and Wilkes [39]. The T_g 's of the copolyester system apparently do not change with the increase in PHB content. The crystallization temperature decreases with the increase in PHB levels. The crystallization process is associated with PET and it is presently speculated by the author that the PHB regions act as nucleating agents which would explain the lowering of T_c . Also seen in the DSC scans is the fact that as the mole percent of PHB increases, the melting temperature decreases. This is due

Figure 12. Differential scanning calorimetric scans of PET and the PET/PHB copolyester series. *-Scan at higher sensitivity.

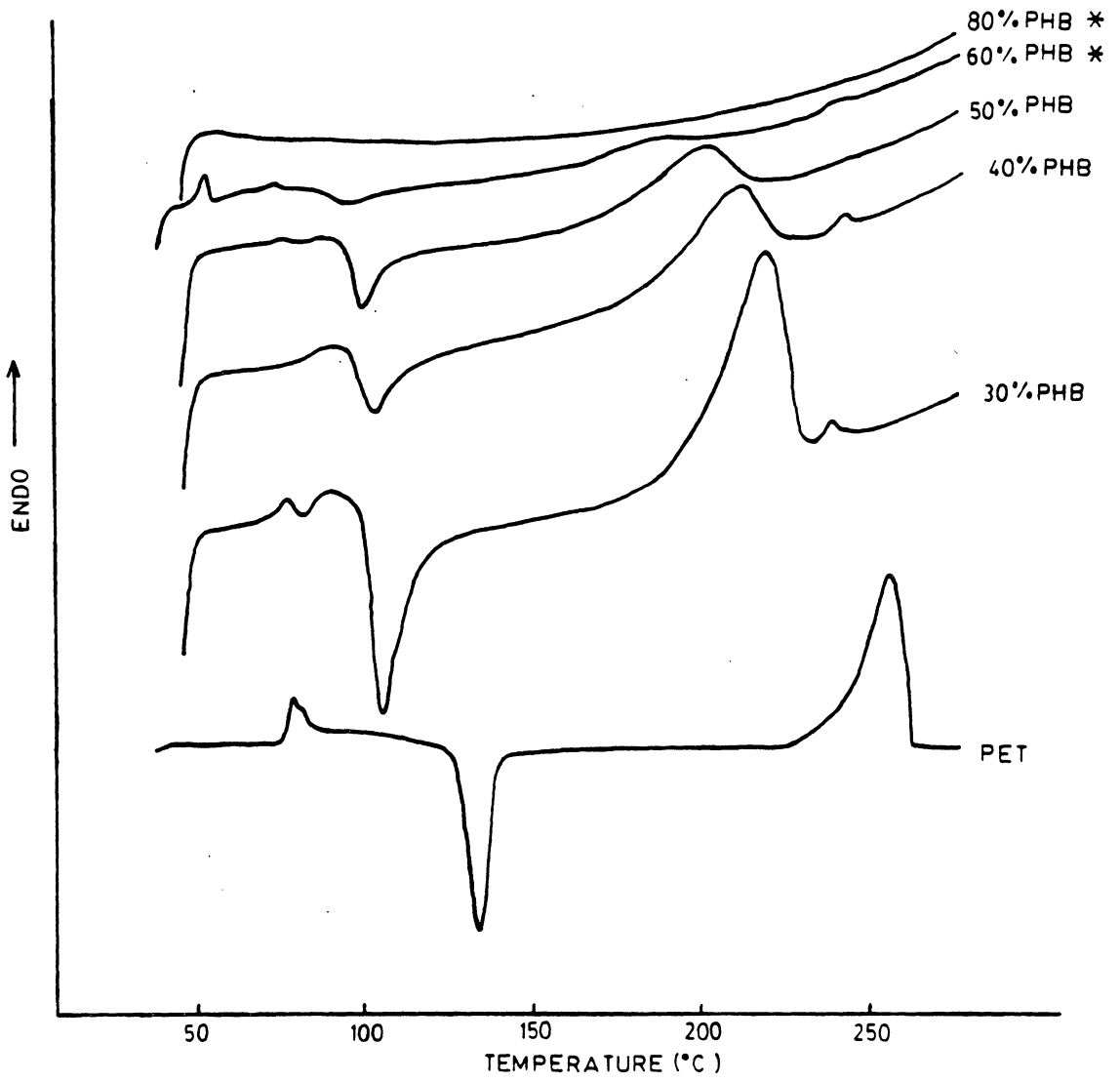
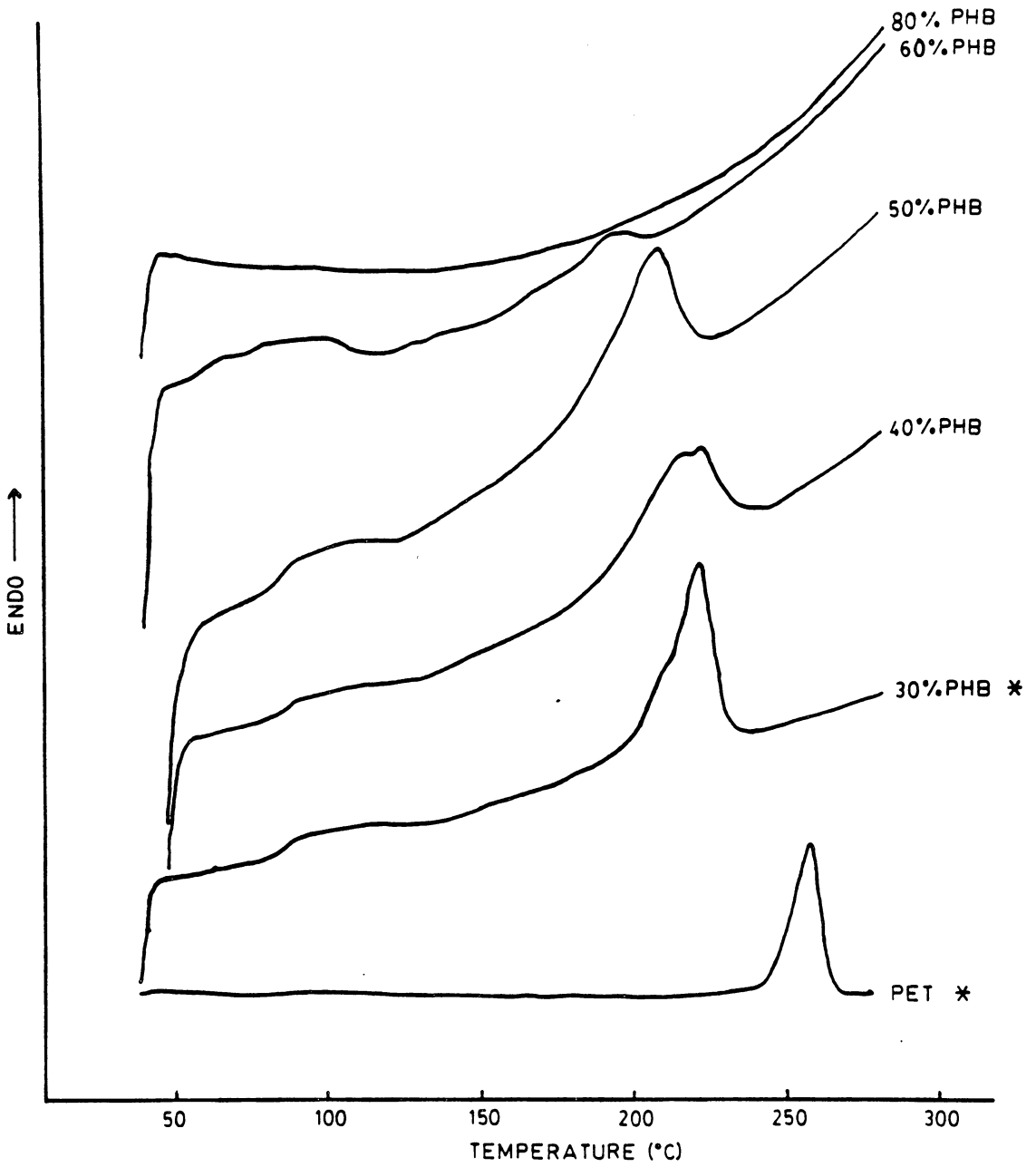


Figure 13. Differential scanning calorimetric scans of PET and the PET/PHB copolyester series that has been heated to 280°C in the DSC, cooled back to room temperature and then rescanned at 10°/min.



to the PHB segments acting somewhat as a diluent, which would then lower T_M . When the area under crystallization peak is compared to the area under the melting peak, it is seen that the area under the melting peak has a higher value. This would indicate that the starting material is semi-crystalline in nature. Also, as PHB content increases the heat of fusion is lowered indicating a decrease in PET crystallinity as expected. Table 1 summarizes the highlights of the DCS scans.

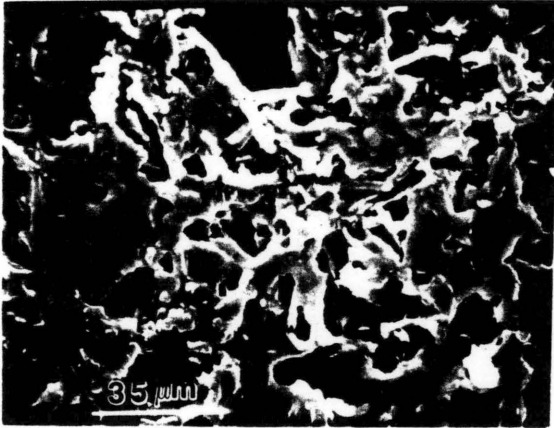
ETCHING STUDIES

(a) Chemical etching of pressed, quenched films

Etching studies were carried out on thermally pressed and quenched films of the PET/PHB copolyester series. Similar studies were also performed on pure PET and PHB for control purposes. The aim of this study is to see if PET or PET rich regions can be etched away by the amine and if so, can it selectively be etched out.

Figure 14 shows SEM micrographs of the contact etched materials as a function of PHB content. It is apparent that as PHB content increases less material gets etched away by the amine even though longer etching times were used for those materials with higher mole percentages of PHB. Also, qualitatively supporting this observation is the fact that as PHB content increases the amount of etched residue decreases. Specifically, at a PHB content of 40 mole percent, there appears to have been PET regions (regions that are

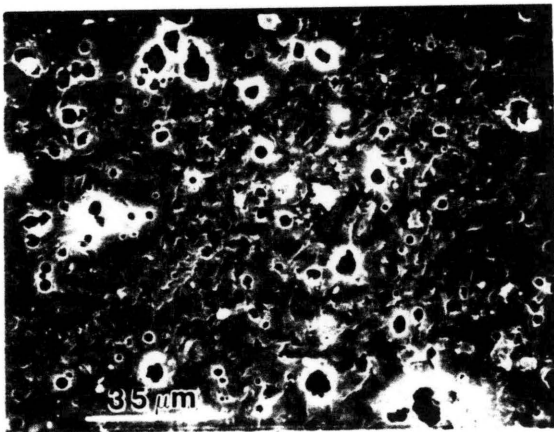
Figure 14. Scanning electron micrographs of PET/PHB copolyester pressed films etched in n-propylamine. (a)40% PHB, etched 2 hours; (b)50% PHB, etched 2 hours; (c)60% PHB, etched 28 hours and, (d)80% PHB, etched 28 hours.



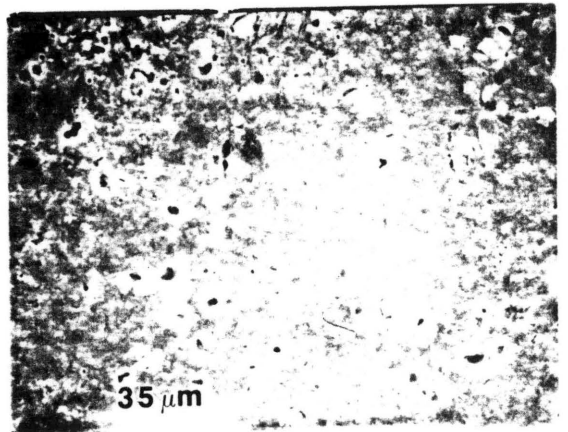
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D

etched away) that are approximately 14 microns in size while in the 80 mole percent PHB material the regions that have been etched away are the order of 3 to 6 microns. Qualitatively at least the degree of etched volume is decreased in line with PET content as it should be if selective etching occurs. Pure PHB could not be pressed into a thin film because of its extremely high melting temperature and was used in a powder form. When the PHB powder was contact etched by the amine for several hours and then observed under the scanning electron microscope it was found that no apparent etching occurred. From these observations it can be concluded that the material tends to be non-homogeneous in terms of dispersement of the PET and PHB components, and that PET rich regions are being selectively etched away by the amine. These observations are in line with those suggested by Wunderlich's earlier calorimetric studies in that the texture clearly appears to be that of a two phase nature in contrast to that of being homogeneous as suggested from the NMR studies by the Tennessee Eastman researchers [38].

Films containing less than 50 mole percent PHB could not be etched for long periods of time as indicated earlier since the films tended to degrade into a powder form. However, with the higher PHB content films (greater than 60 mole percent PHB) this was not the case. This fact along with the SEM micrographs suggests that at lower PHB levels, a PET rich phase seems to appear as the continuous phase. At mole percentages of the order of 60 percent

or higher for PHB, it is the PHB rich phase that forms the continuous phase. Figure 15 shows simplified models that are suggested for two different levels of PHB. They qualitatively account for the etching behavior of the compression molded copolyester films.

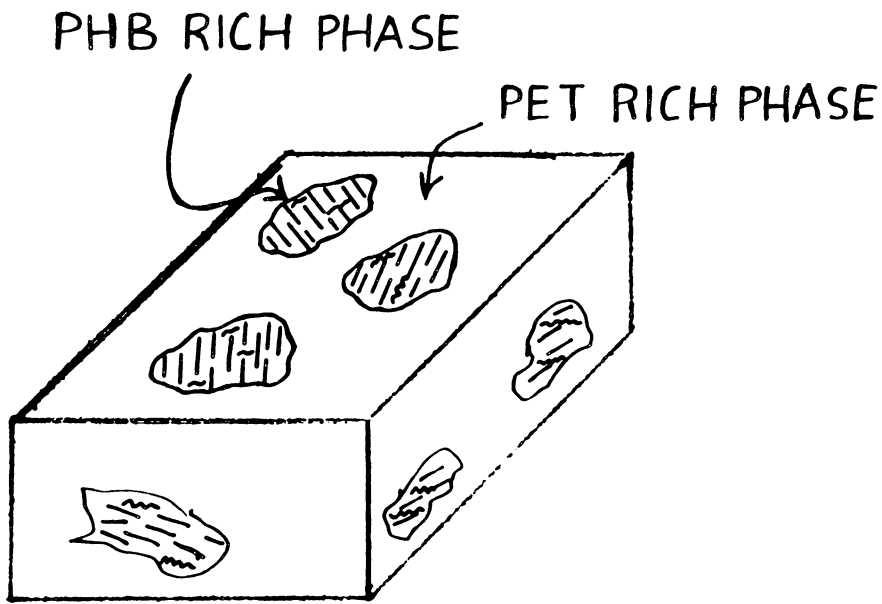
Preliminary etching work was also performed using different etchants. Specifically, butylamine and a 50 percent aqueous solution of n-propylamine were used. Also, these samples were not sandwiched between glass plates. SEM results showed that the overall etching effect was the same as that seen when the samples were contact etched with n-propylamine.

(b) Chemical etching of pressed, quenched and annealed films

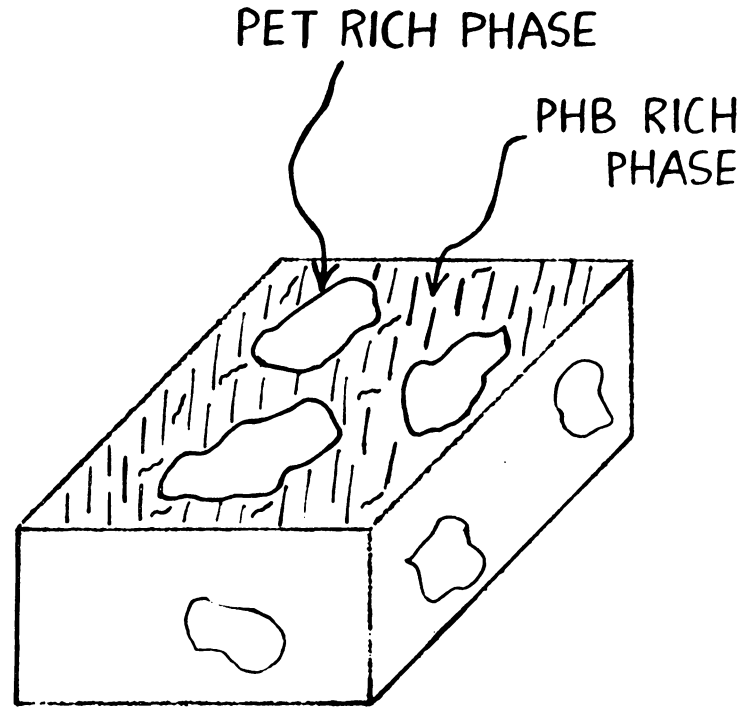
Etching studies were performed on thermally pressed, quenched and annealed films of the PET/PHB copolyester series. The films were annealed at 100°C for 60 minutes. The purpose of annealing the films was to enhance the degree of crystallization and the degree of perfection of the crystallites. Butylamine, which is a less reactive amine than n-propylamine, was used as the etchant and the sample was not sandwiched between glass slides during etching. This would therefore produce the same etching effect even though a less reactive amine was used.

Figure 16 shows low magnification SEM micrographs of the annealed films etched for six hours in butylamine. The 30%PHB, 40%PHB and 50%PHB samples show a "brick" like structure, while the 60%PHB film shows a structure similar to that of the unannealed

Figure 15. Simplified molecular model at (a) low levels of PHB (b) high levels of PHB, based on SEM studies of etched films.

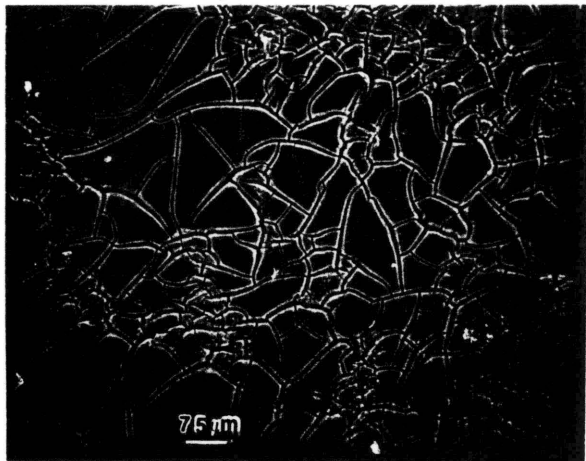


(A)

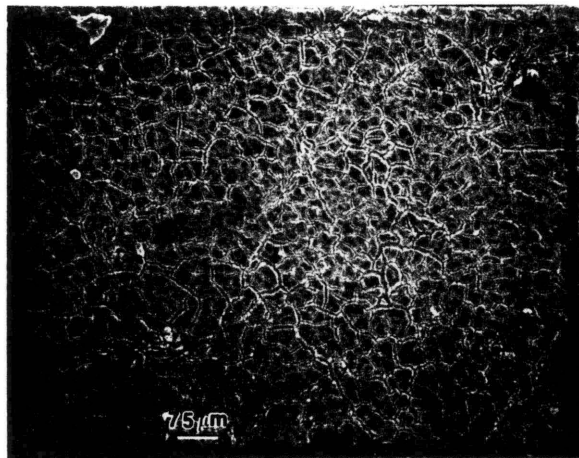


(B)

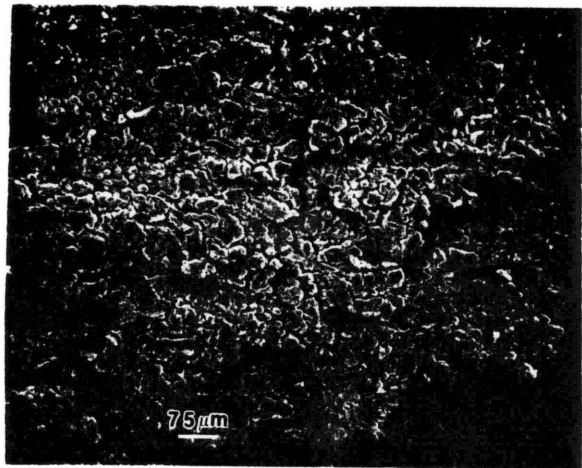
Figure 16. Low magnification scanning electron micrographs of pressed, quenched and annealed films of the PET/PHB copolyester series after being etched by butylamine for 6 hours. Films were annealed at 100°C for 1 hour. (a)30% PHB, (b)40% PHB, (c)50% PHB & (d)60% PHB.



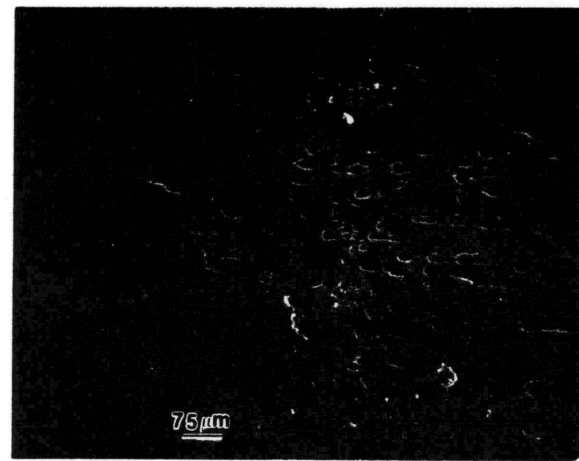
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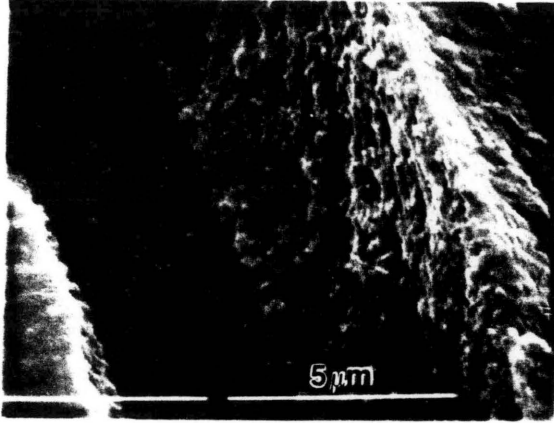
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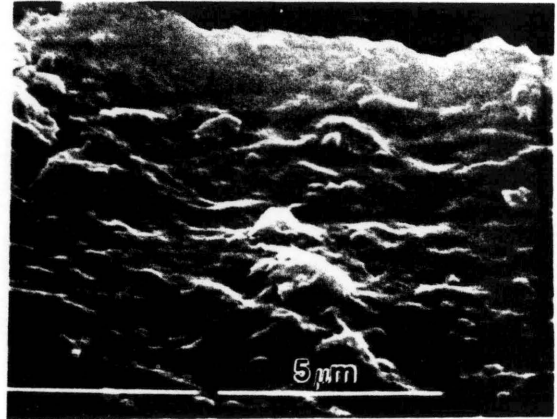
D

60%PHB film. The brick structure has also been seen by Heffelfinger [1] , Adams [29] and by Chu and Wilkes [5] when semi-crystalline PET is etched by an amine. For the materials showing brick structure, i.e. materials where PET is the continuous phase, the brick size appears to be largest in 30%PHB and the overall effect of etching most drastic in the 50%PHB. A possible explanation for this behavior could be the varying amount of PET. It has also been reported by Chu and Wilkes [5] that at high magnifications a "network structure" can be observed in pure PET. This network structure could not be found in the PET/PHB copolyester series at higher magnifications. High magnification SEM micrographs of the copolyesters are shown in Figure 17. One of the reasons why the network structure is not present may be due to the low annealing temperature used, 100°C in this case, which in turn will produce small but less perfect crystallites. This is so because 100°C falls in the temperature region where the rate of crystallization is not a maximum for PET. In the case of the 60%PHB material, it is PHB that is the continuous phase and there is no difference in the structure upon etching the pressed, quenched film and the pressed, quenched and annealed film. This can be attributed to very little crystallization of PET (which is confirmed by DSC results already presented) and upon etching, the PET rich regions which are mostly amorphous are removed by the amine. A comparison of the unannealed and annealed films after etching are shown in Figure 18 and the similarity in etching effects are shown at higher magnification.

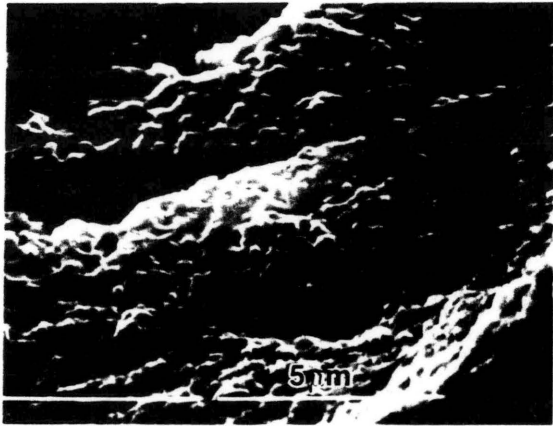
Figure 17. High magnification scanning electron micrographs of pressed, quenched and annealed films of the PET/PHB copolyester series after being etched with butylamine for 6 hours. The films were annealed at 100°C for 1 hour. (a)30% PHB, (b)40% PHB, (c)50% PHB and (d)60% PHB.



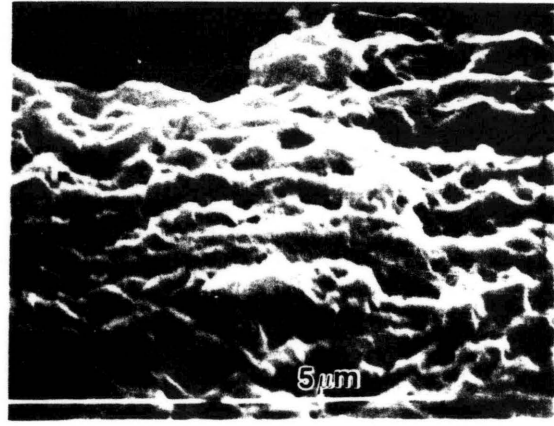
A



B

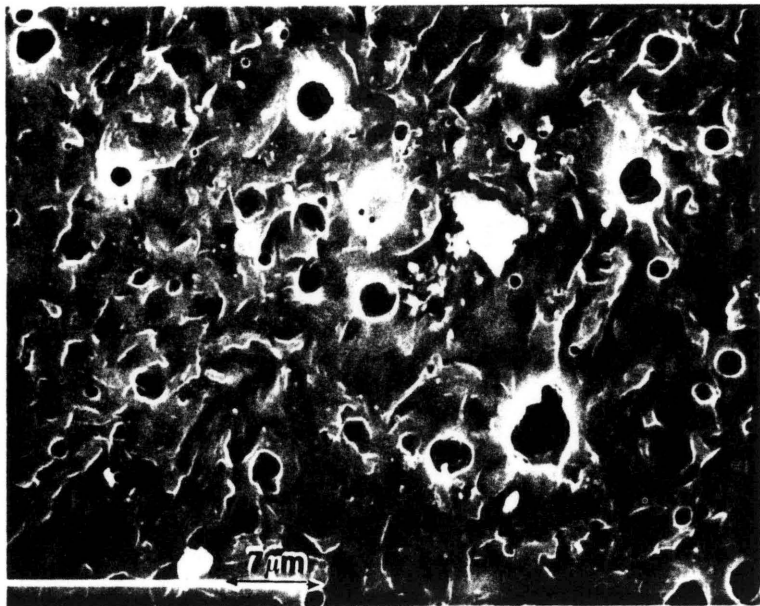


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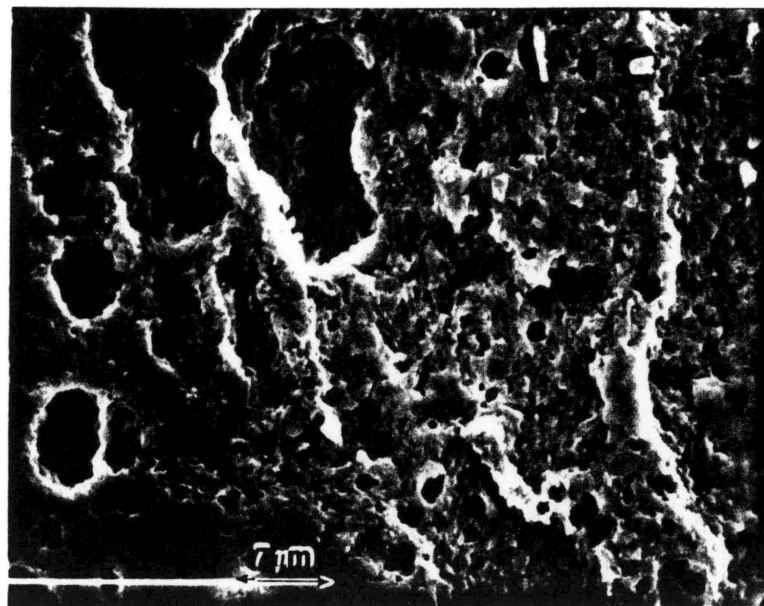


D

Figure 18. Scanning electron micrographs of the 60% PHB (a) pressed, quenched film and (b) pressed, quenched and annealed film. The films were etched for 6 hours in butylamine.



A



B

In order to see the effects of etching time, these annealed films were etched for a longer period of time, 9 hours, in butylamine. SEM micrographs of these etched surfaces are shown in Figure 19. In the case of the materials where PET is the continuous phase, it is seen that the brick structure is smaller in size. This probably is due to a kinetic effect of the reaction between PET and butylamine. No significant change is seen in the 60% PHB sample when it is etched for longer periods of time. Again, the PET rich regions are etched out by the amine.

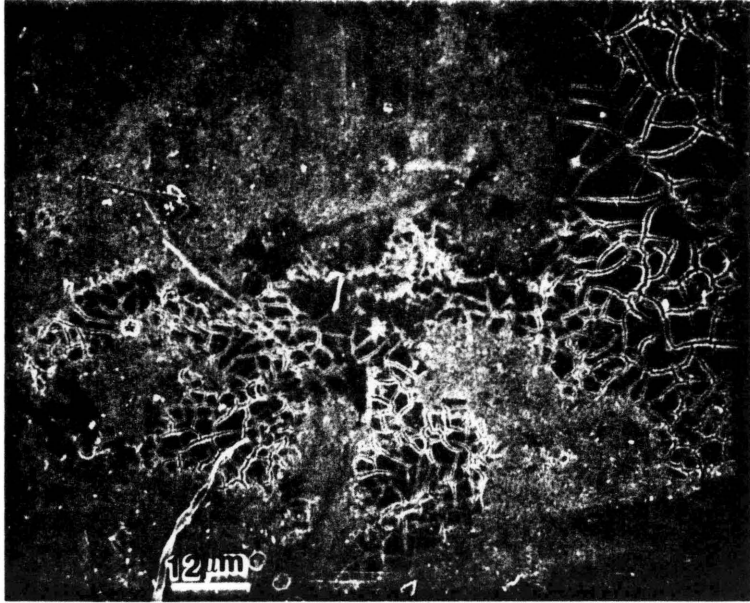
SOLVENT INDUCED CRYSTALLIZATION STUDIES

(a) SINC studies using common solvents

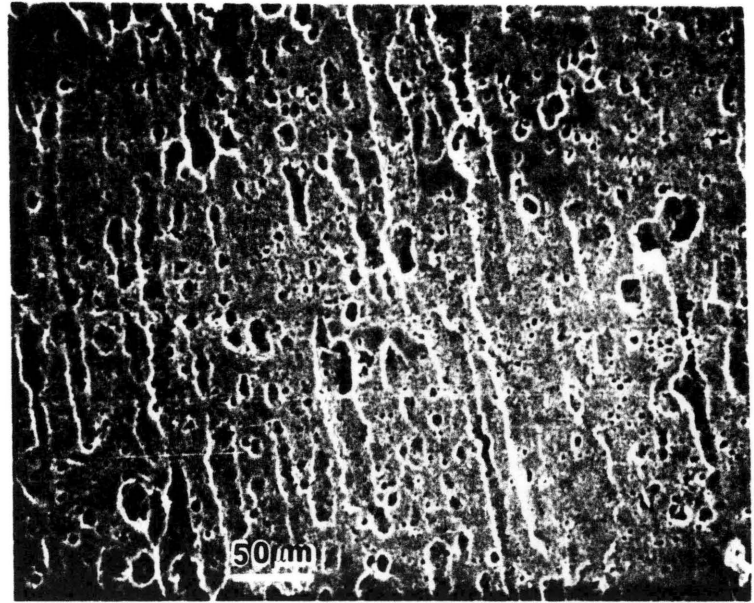
It is well known that crystallinity can be induced in PET by using appropriate solvents [27,30]. Since PET is one of the components in the copolyester used, these materials were treated with solvents that were known to induce crystallinity in PET to see if crystallinity could be induced.

SEM micrographs of the top surface of the thermally pressed, quenched films before exposure to solvent are shown in Figure 20. A slightly rough surface texture is seen due to the contact of the film surface with teflon sheets during film pressing. When PET is exposed to dioxane at room temperature for 1 minute, a spherulitic morphology results and the corresponding SEM micrographs are shown in Figure 21. The size of the spherulites range from 6-20 microns.

Figure 19. Scanning electron micrographs of the PET/PHB copolyester series. The films were etched for 9 hours using butylamine.

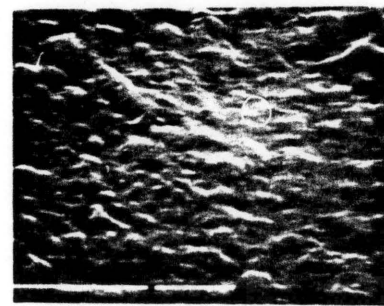
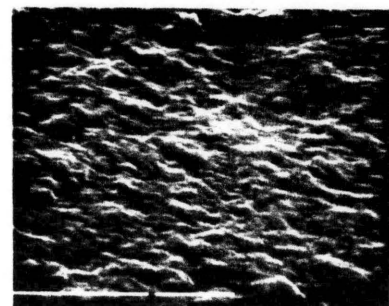
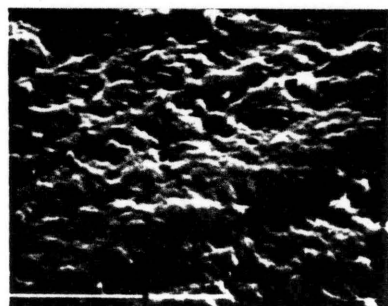
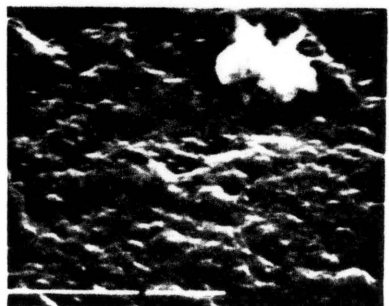
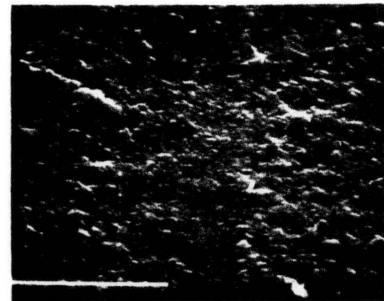
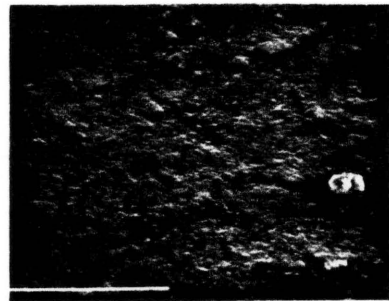
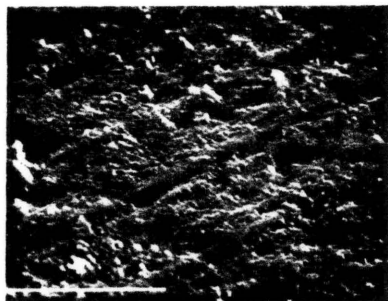
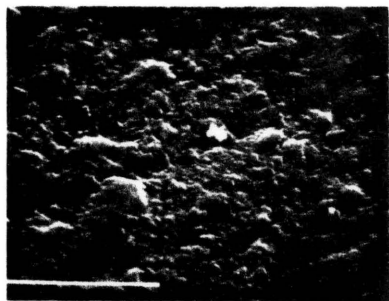


A



B

Figure 20. Scanning electron micrographs of the pressed, quenched films of the PET/PHB copolyester series. (a)30% PHB, (b)40% PHB, (c)50% PHB and (d)60% PHB.



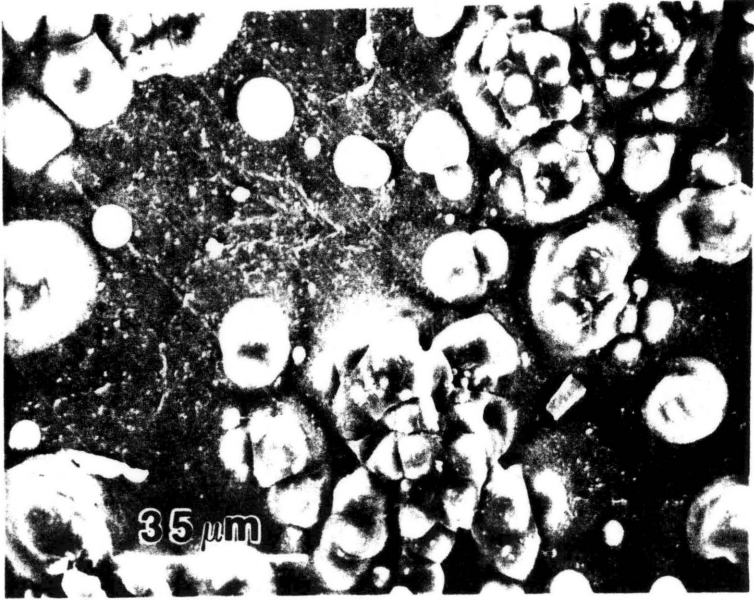
A

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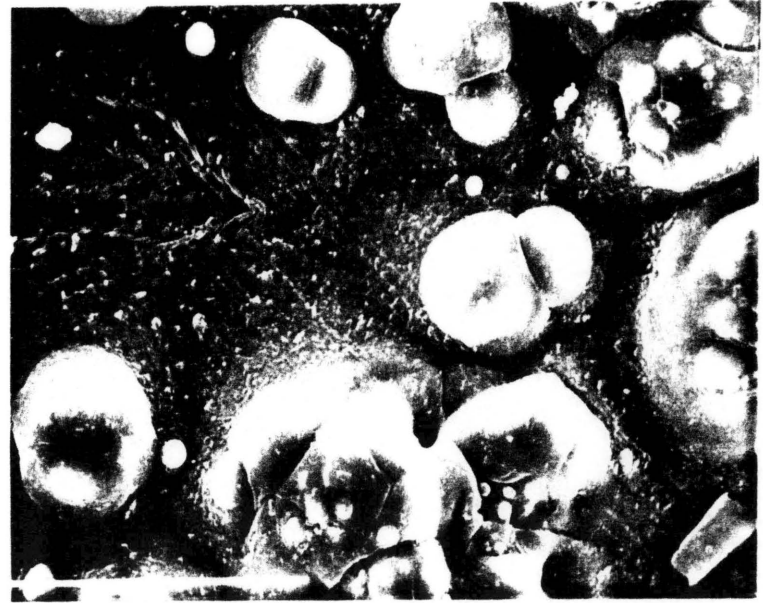
C

D

Figure 21. Scanning electron micrograph of PET that has been treated with dioxane for 1 minute.



A



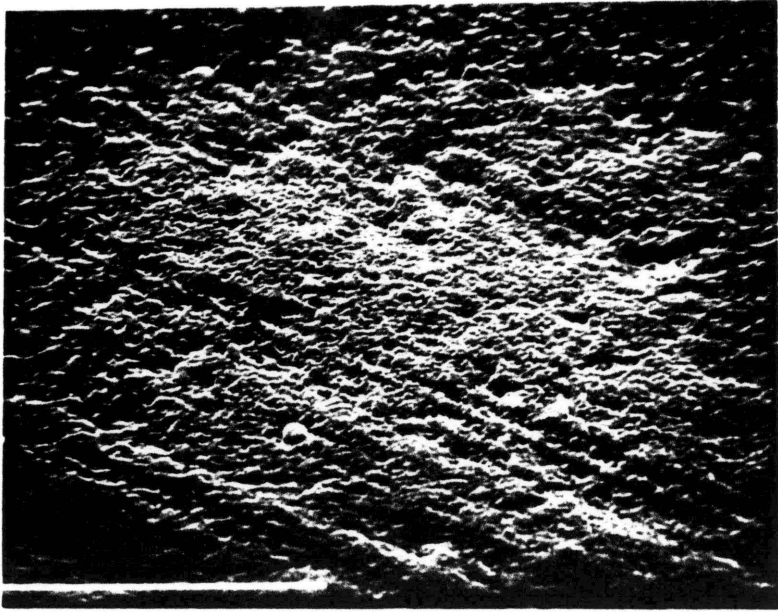
B

When the PET/PHB copolyester series was exposed to solvents like dioxane, methanol or methylene chloride for times short as 1 minute, the lower PHB content films formed a gel and then dissolved. One possible explanation is that the molecular weight of the PET rich regions is not as high as pure PET and therefore, the materials dissolve easily. Figure 22 shows the surface structure of a 50% PHB film that was dipped in dioxane, quickly removed and dried. Although the surface texture does not seem to be drastically different than the untreated material at low magnifications, at higher magnifications it appears that a surface texture that is swollen or "puffed up" randomly throughout the sample is induced.

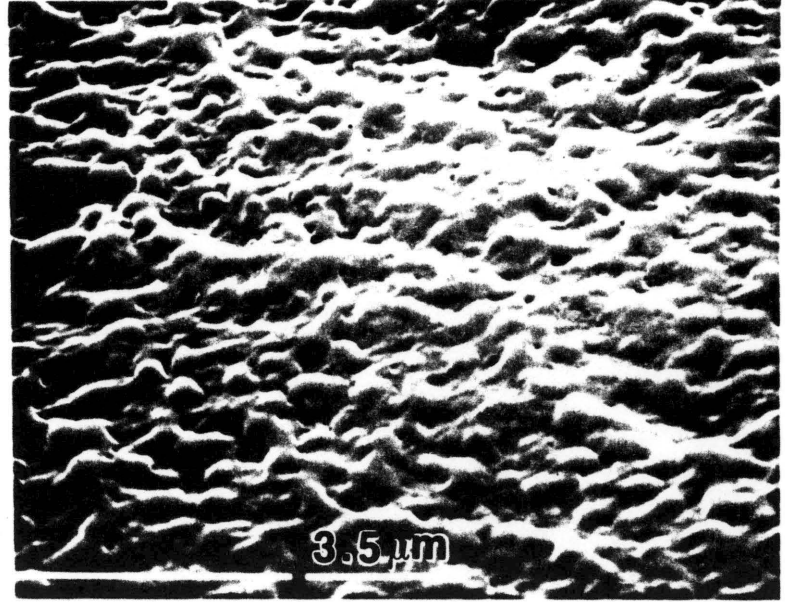
When the 60% PHB film was exposed to dioxane, the material did not dissolve. This is because the PHB rich phase is the continuous phase and it does not interact with the solvent in the given time frame. SEM micrographs of the 60% PHB film exposed to dioxane for 1 minute are shown in Figure 23. No significant change in surface texture can be detected. The effect of methanol on 60% PHB was verified by exposing a 60% PHB film to methanol for 1 minute. Figure 24 shows the surface texture of this solvent treated material and again no apparent change in surface morphology can be seen.

Acetone, which after long exposure times induces crystallinity in PET was found to be a solvent that did not dissolve the lower PHB content copolyester material. A 30% PHB film was exposed to acetone for 10 hours and the resulting surface texture is represented by the SEM micrographs in Figure 25. The texture

Figure 22. Scanning electron micrograph of the 50% PHB pressed, quenched film that has been dipped in dioxane.

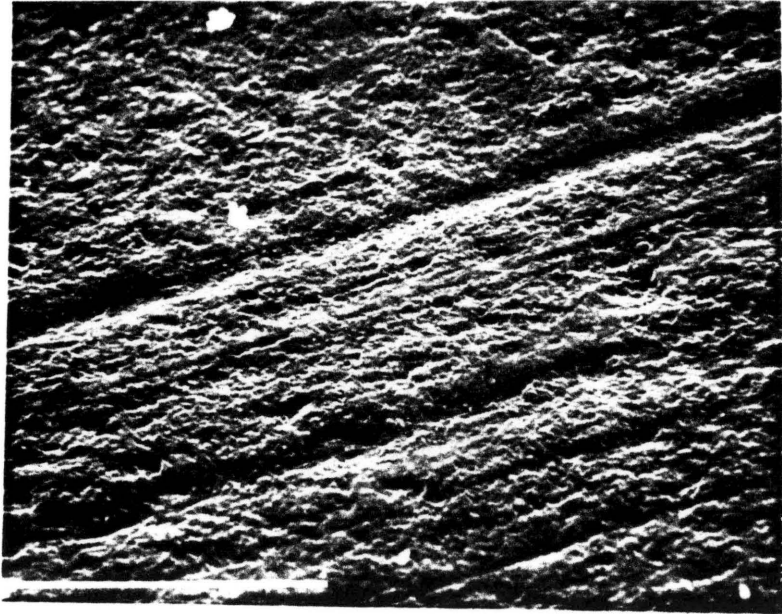


A

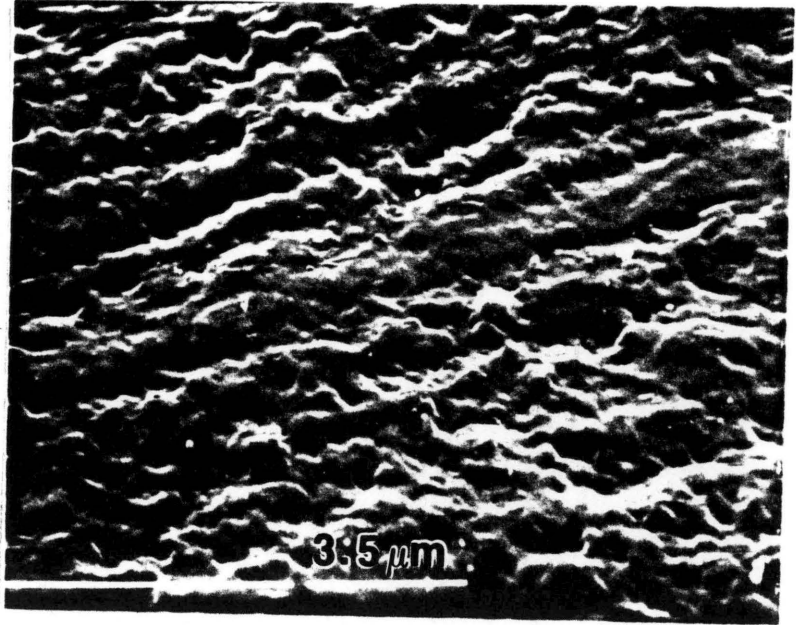


B

Figure 23. Scanning electron micrograph of a 60% PHB pressed, quenched film that has been treated with dioxane for 1 minute.

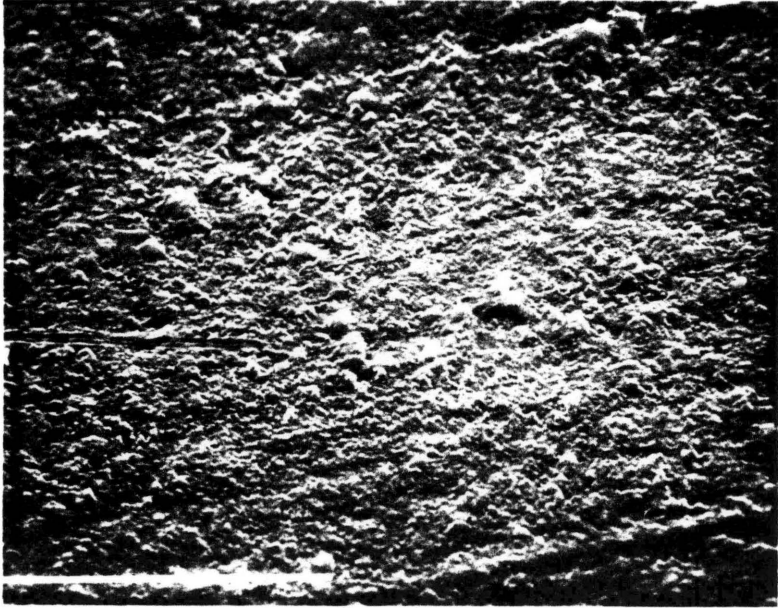


A

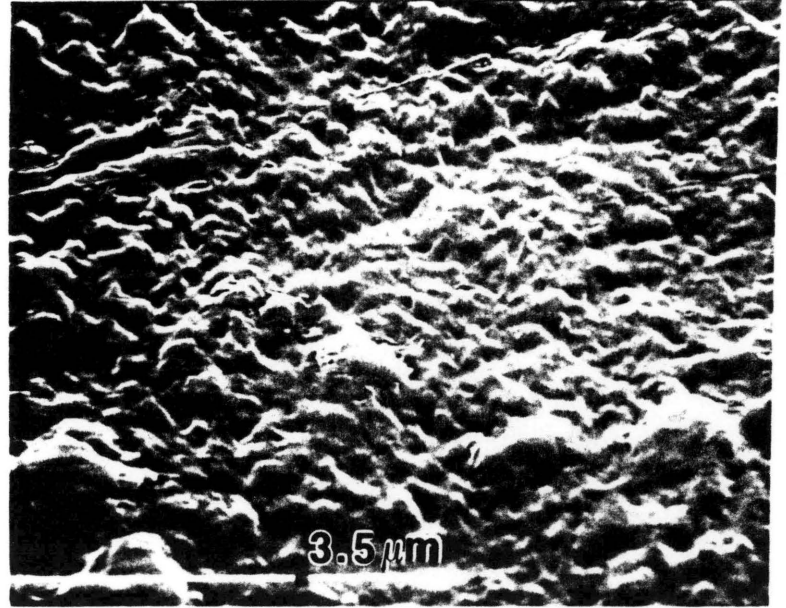


B

Figure 24. Scanning electron micrograph of a 60% PHB pressed, quenched film that has been treated with methanol for 1 minute.



A



B

appears slightly swollen but not drastically different than the original film texture.

These results imply that solvents which readily induce crystallinity in PET cannot be used for the same purpose in the PET/PHB copolyester materials. The polymer-solvent interaction is far greater than the intermolecular forces, which causes the polymer to dissolve.

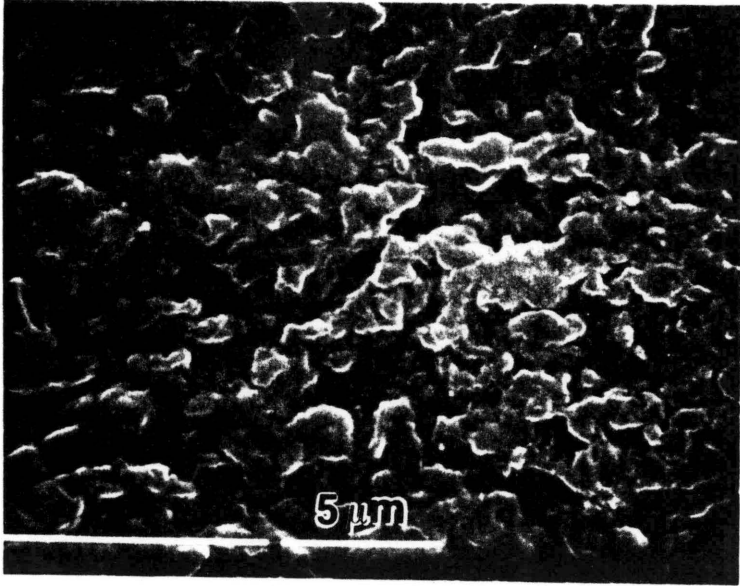
(b) Investigation of SINC caused by the etching reagent

It has been reported that when semi-crystalline PET is etched by an amine, a certain amount of crystallinity is induced by the amine prior to the etching process itself [5]. Since the morphological texture of the PET/PHB copolyester systems were investigated using an amine as the etchant, the solvent induced crystallization phenomena for these materials was also studied. The samples etched for different periods of time were analyzed using SEM and WAXS.

(1) Wide angle x-ray scattering studies

Wide angle x-ray scattering patterns of the thermally pressed and quenched films are given in Figure 26. All materials give rise to diffuse scattering patterns and as PHB content increases the diffuseness decreases. The diffuse scattering pattern in the 30% PHB sample can be attributed to the amorphous nature of the PET regions in this material while at higher PHB levels (e.g. 60%PHB) the scattering is associated with PHB.

Figure 25. Scanning electron micrograph of a 30% PHB pressed, quenched film that has been treated with acetone for 10 hours.

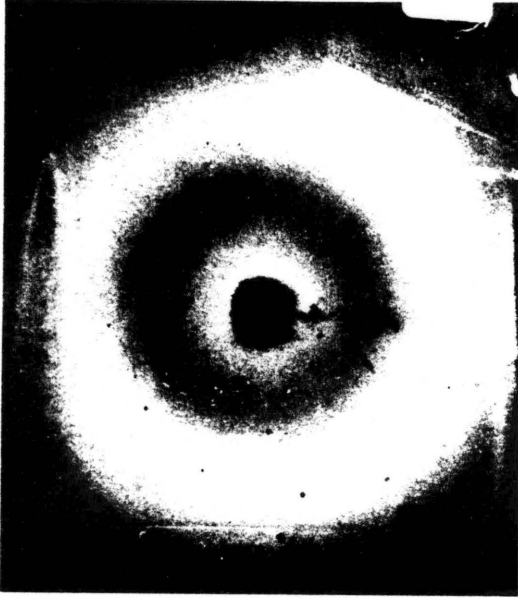


A

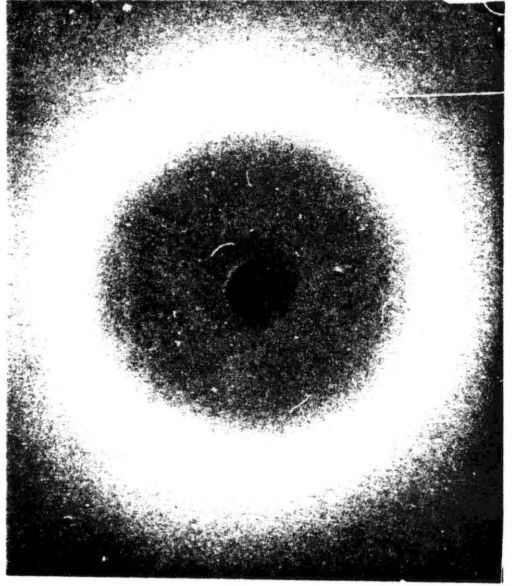


B

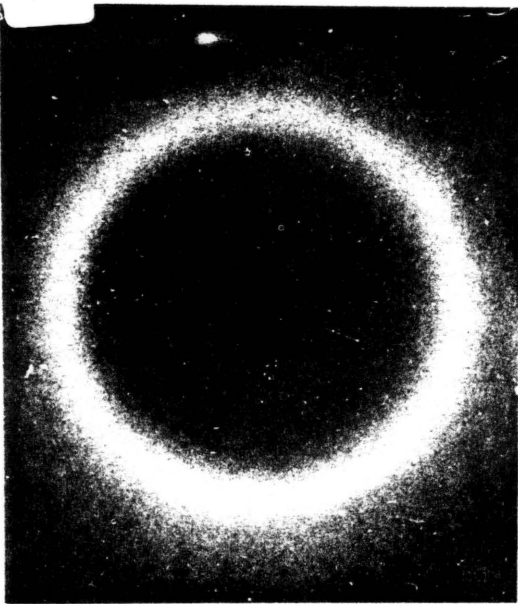
Figure 26. Wide angle x-ray scattering patterns of the pressed, quenched films of the PET/PHB copolyester series. (a)30% PHB, (b)40% PHB, (c)50% PHB and (d)60% PHB.



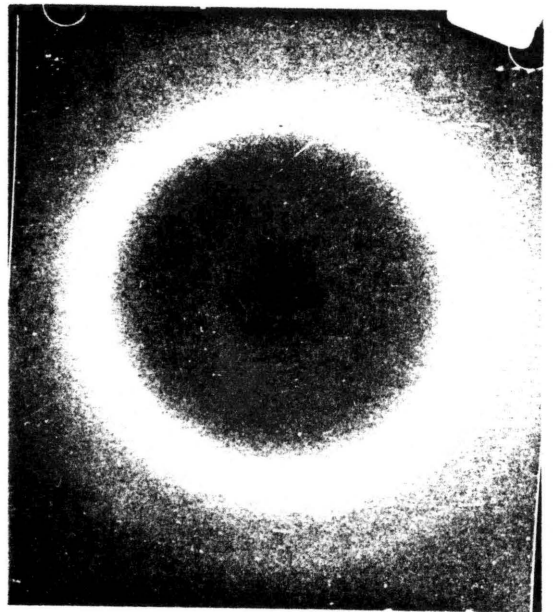
A



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C



D

Wide angle x-ray scattering patterns of the thermally pressed, quenched films after etching with n-propylamine for 15 minutes is shown in Figure 27. The 40%PHB sample has a scattering pattern consisting of multiple rings which indicates scattering from different planes. This additional scattering can be attributed to solvent induced crystallization of the PET segments. The 50%PHB sample has a scattering pattern consisting mainly of a slightly diffuse ring and a very weak, sharp ring. When this scattering pattern is compared to the scattering pattern of the unetched sample shown in Figure 27, it is clear that additional scattering is present in the etched sample. This is again due to the inducement of crystallinity by the solvent. There is no apparent change in the 80%PHB WAXS pattern after treatment with the amine and this is not surprising since only 20% of PET is present in this material.

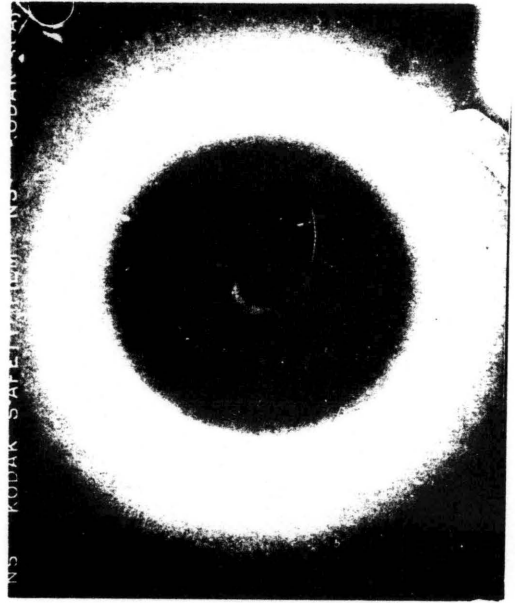
(2) Scanning electron microscopy

The thermally pressed, quenched and amine etched (for 15 minutes) films were studied under the SEM. Figure 28 shows the electron micrographs of these materials and in the lower PHB samples the inducement of a new morphological texture is evident. The structure observed is in order of 2-3 microns in size and is due to the inducement of crystallinity by the amine. Similar structures have been reported by Makarewicz and Wilkes [27] in their studies on the effects of solvents on PET. At higher PHB levels no apparent inducement of crystallinity by the amine is evident. This is in line with the WAXS results.

Figure 27. Wide angle x-ray scattering patterns of the pressed, quenched films of the PET/PHB copolyester series after etching with n-propylamine for 15 minutes. (a) 30%PHB, (b) 40%PHB, (c) 50%PHB, (d) 80%PHB.



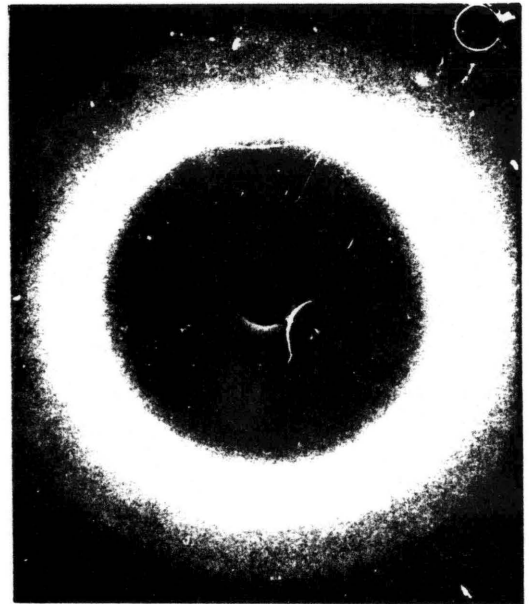
A



B

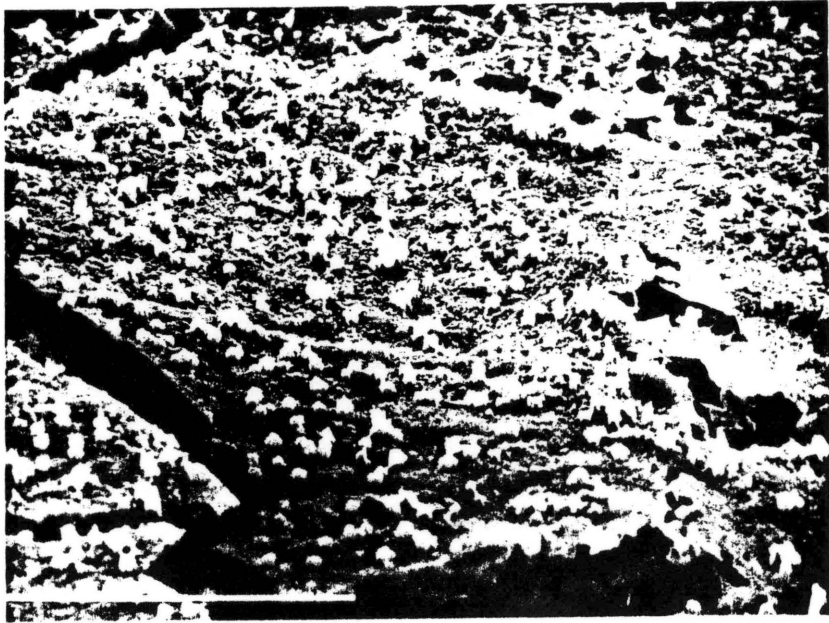


D

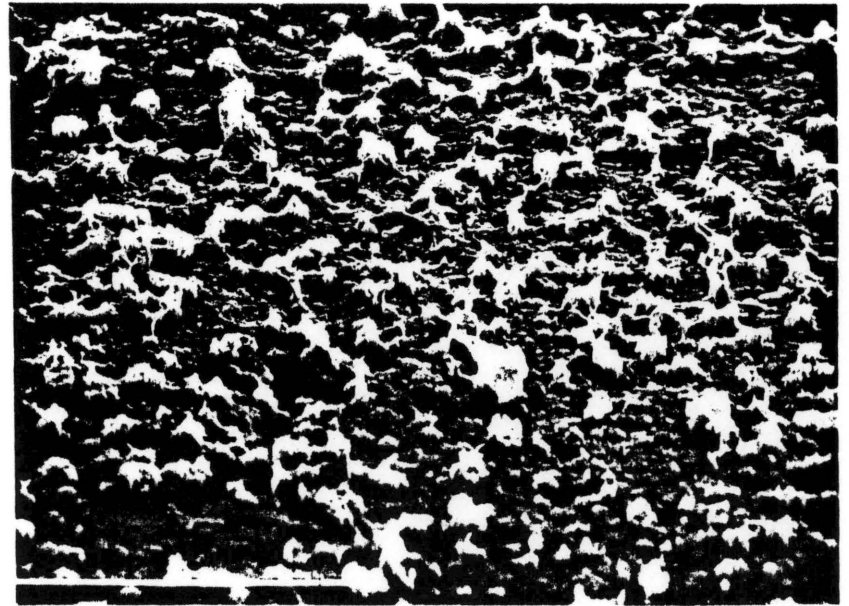


C

Figure 28. Scanning electron micrographs of the pressed, quenched films of the PET/PHB copolyester series etched with n-propylamine for 15 minutes.



60% PET - 40% PHB



50% PET - 50% PHB

From the WAXS and SEM results it can be concluded that when these PET/PHB copolyesters come in contact with either n-propylamine or butylamine, initially some crystallinity is induced by the amine. When the films are etched for longer periods of time chemical etching of the amorphous regions occurs and after even longer times the crystalline regions are degraded.

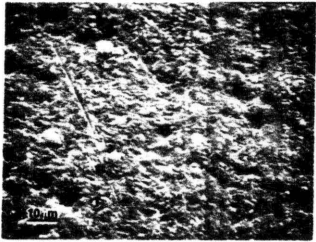
DYEING STUDIES

Dyeing studies on these copolyester materials were carried out using two different dye carriers, ortho-phenylphenol and butylbenzoate. The dyed samples were analyzed for amount of dye pick up and change in morphology. Typically some sort of color measuring device, for example, a Hunter color difference meter is used to measure dye pick up but in this study, due to small sample sizes this was not possible. Instead, the amount of dyeing as a function of PHB content was obtained qualitatively using the AATCC Gray Scale for evaluating staining.

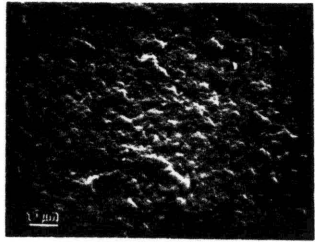
Data obtained from the gray scale evaluations are shown in Table 2 and Table 3. Results from the dyeing experiments performed at 80°C show that as PHB content increases the amount of dye absorbed by the sample decreases. For example, the 30%PHB sample absorbs a larger amount of dye compared to the 50%PHB sample. This trend in dyeing is seen for both dye carriers used. These results imply that the dye carriers and dye are preferential to the PET rich regions. Dyeing was also performed at room

temperature using butylbenzoate as the dye carrier and the amount of dye absorbed was visually found to be significantly lower than the amount absorbed at 80°C. The trend seen at 80°C, that is, higher dye pick up at lower PHB levels, was also seen in this case.

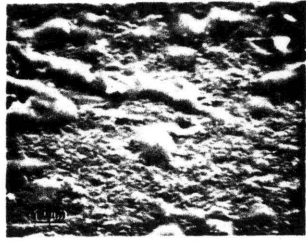
The surface morphologies of the dyed samples were analyzed by scanning electron microscopy and compared with the undyed materials. Figure 29 shows the SEM micrographs of the surface textures of the copolyester series dyed at room temperature using butylbenzoate as the dye carrier. The surface texture of the 50%PHB material appears to be randomly "puffed up" while the other materials do not show very significant differences. Figure 30 shows the SEM micrographs of the samples dyed at 80°C using butylbenzoate as the dye carrier. While at low magnifications there appears to be no significant change in surface texture, at higher magnifications a slightly swollen surface is present. The 50%PHB film does not show the "puffed up" texture as it did when dyeing was performed at room temperature. This is surprising since at higher dyeing temperatures one would expect a more drastic change in surface texture than at room temperature dyeing. Figure 31 shows the surface textures after dyeing with ortho-phenyl-phenol as the dye carrier. The 50%PHB sample has a randomly "puffed up" surface texture. The texture of the other materials does not change significantly but appears to be slightly swollen. A good explanation for the different behavior of the 50%PHB sample is not available at this time.



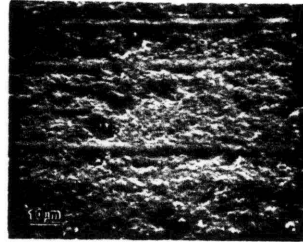
A



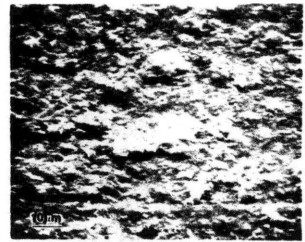
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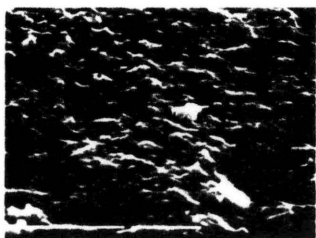


D

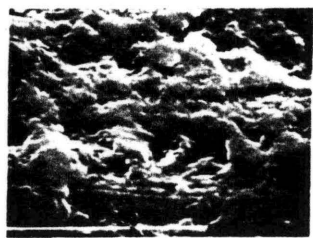


E

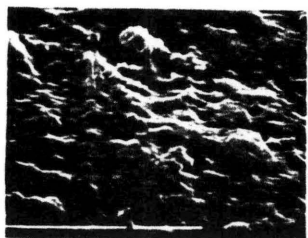
Figure 30. Scanning electron micrographs of the PET/PHB copolyester series that has been dyed at 80°C using butyl benzoate as the dye carrier. (a)30%PHB, (b)40%PHB, (c)50%PHB, (d)60%PHB and (e)80%PHB.



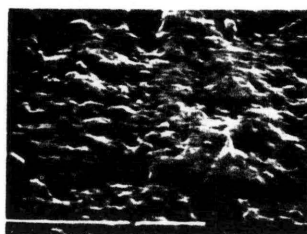
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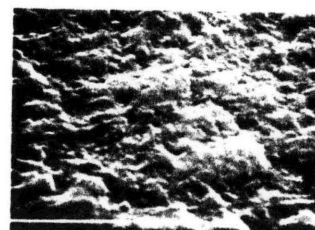
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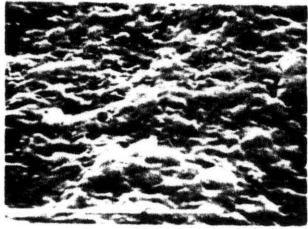


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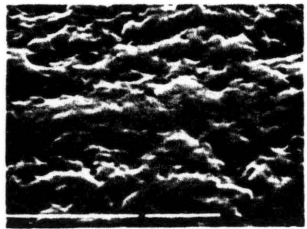


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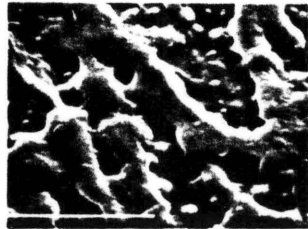
Figure 31. Scanning electron micrographs of the PET/PHB copolyester series that has been dyed at 80°C using ortho-phenyl phenol as the dye carrier. (a)30%PHB, (b)40%PHB, (c)50%PHB, (d)60%PHB and (e)80%PHB.



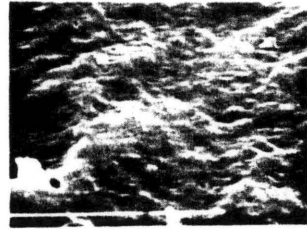
A



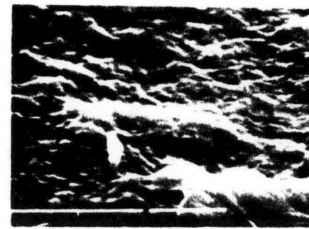
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CONCLUSIONS

1. Differential scanning calorimetric studies show that the crystallization temperature of the PET regions decreases with PHB content up to 60%PHB. It is speculated that the PHB regions act as nucleating agents for the crystallization of PET . Also, the melting temperature decreases as PHB levels are increased since the PHB segments act as diluents.

2. The technique of selective chemical etching is feasible to study the morphological textures of PET/PHB liquid crystalline copolyesters. Specifically, using an appropriate amine, PET rich regions can be etched away selectively within the time scale of etching.

3. Chemical etching studies on thermally pressed, quenched films show that at low PHB levels, a PET rich phase is the continuous phase. In the higher PHB content films (i.e. 60 mole percent PHB), it is the PHB rich phase that is the continuous phase and PET is the dispersed phase.

4. Etching studies strongly indicate that the thermotropic copolyester system is more non-homogeneous in nature, with blocks of PET rich regions and PHB rich regions being present.

5. Chemical etching studies on thermally pressed, quenched and annealed films show a different morphology than the corresponding unannealed films. This is due to the enhancement of crystallinity and crystal perfection in the annealed case. However, no change in morphological texture is seen at the 60%PHB level. This can be attributed to very little crystallization of the PET rich regions and the relative ease with which these regions can be etched out by the amine.

6. Time dependent etching studies coupled with WAXS results show that the mechanism for chemical etching at low PHB levels consists of two steps. Initially, solvent induced crystallization of PET occurs and after longer etching times the PET regions are degraded and etched out.

7. Dyeing studies at room temperature show very low dyeing rates as expected. When the dyeing temperature is raised to 80°C increased dyeing is obtained as shown by the AATCC Gray Scale results. As PHB content increases the amount of dye pick-up decreases, which indicates that dyeing is selective to PET only.

TABLE 1

Data Obtained from DSC Scans

	<u>T_g</u>	<u>T_c</u>	<u>T_m</u>
100%PET			
70%PET - 30%PHB	82 ^o C	104 ^o C	219 ^o C
60%PET - 40%PHB	81 ^o C	102 ^o C	212 ^o C
50%PET - 50%PHB	80 ^o C	99 ^o C	204 ^o C
40%PET - 60%PHB	--	93 ^o C	188 ^o C
20%PET - 80%PHB	--	--	---

TABLE 2

AATCC Gray Scale readings for evaluating staining of PET/PHB copolyesters using TANDEL (Butyl Benzoate) as the dye carrier.

	<u>Gray Scale Reading</u>
100%PET	1
70%PET - 30%PHB	1-2
60%PET - 40%PHB	2
50%PET - 50%PHB	3
40%PET - 60%PHB	3-4
20%PET - 80%PHB	4

TABLE 3

AATC Gray Scale readings for evaluating staining of PET/PHB copolyesters using CAROLID (Ortho-phenyl phenol) as the dye carrier.

	<u>Gray Scale Reading</u>
100%PET	1
70%PET - 30%PHB	1
60%PET - 40%PHB	1-2
50%PET - 50%PHB	2
40%PET - 60%PHB	2-3
20%PET - 80%PHB	3-4

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EFFECTS OF SOLVENTS ON THERMOTROPIC
LIQUID CRYSTALLINE COPOLYESTERS

by

Eugene Gregory Joseph

(ABSTRACT)

Morphological studies were carried out on thermotropic liquid crystalline copolyesters based on poly(ethyleneterephthalate) (PET) and para hydroxybenzoate (PHB), where PHB content varied from 0 mole percent up to 80 mole percent. The technique of chemical etching coupled with SEM and WAXS was utilized to obtain structural information. Morphological changes that occur when these materials are exposed to solvents such as dioxane or acetone and dye carriers were also studied using SEM.

Electron microscopy results on the thermally pressed, quenched and chemically etched films indicate that selective chemical etching, i.e. etching of PET rich regions, occurs. This indicates a heterogeneous structure. An oversimplified molecular model has been proposed based on these results where at low PHB levels a PET rich phase is the continuous phase and at higher PHB levels (≥ 60 mole%PHB) a PHB rich phase is the continuous phase. SEM results on pressed, quenched, annealed and etched films show a "brick-like" structure similar to that seen when pure PET is chemically

etched. WAXS studies show that crystallization is induced by solvent (etchant) at small etching times which indicates that the etching of PET rich regions is a two step process; (i) solvent induced crystallization, (ii) chemical etching. Dyeing studies carried out the PET/PHB systems using two different dye carriers indicate that dyeing occurs preferentially in the PET regions. Morphological studies on the dyed materials show a "puffed up" structure present only in the 50mole% PHB material.