5%. When C is large, the crystallinity determined by eq 10 is relatively insensitive to the previously discussed precision in measuring $V_g{}^b(1 - C)$ so that the overall precision in measuring C is of the order of 5%.

In conclusion, it is evident that with relatively polar polymers and sorbate vapors, GC retention data depend on the surface-to-volume ratio of the polymer in the column. This effect is quite marked at polymer transition temperatures. The simplified model presented here, which considers the effect of surface adsorption together with the exclusion of the sorbate vapor from the crystalline regions of the polymer, predicts a crystallinity for poly(ethylene oxide) in accord with recent literature data. The model also clarifies earlier results in the GC literature for retention of PEO below its melting temperature.

On a more speculative level, if it proves possible to characterize quantitatively the variation in polymer surface area with loading, then this GC technique may have some novel possibilities. For example, below T_m, a more detailed interpretation of the dependence of the retention volume on s/w should indicate whether very thin layers of the polymer exhibit different crystalline properties from the bulk polymer. Above T_m, the factoring of solution properties of thin layers into bulk and surface contributions may allow the surface excess concentration of solute in a polymer to be measured.[17,18] Thus, in principle, the GC method may be extended from studies on the adsorption of vapors on polymers where bulk absorption is negligible[26] to studies of adsorption with concurrent solution in the polymer.

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Morphological Characterization of Polyester-Based Elastoplastics

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ABSTRACT: Morphological and structural characterization of a series of elastoplastic materials based on a semicrystalline poly(tetramethylene terephthalate) hard segment and a poly(oxytetramethylene) soft segment have been performed. Results from low angle laser light scattering and polarized light microscopy demonstrate the presence of a spherulitic superstructure over a wide range of compositions. The direction of the optic axis within the spherulite is dependent on the average hard block length and sample preparation method. Evidence for chain folding within the lamellae has been obtained by the chemical etching technique. Mechanical relaxation measurements suggest that the noncrystalline soft phase is a mixed phase of the polyether soft segment and uncrystallized polyester hard segments. The response of this structure to uniaxial extension has also been determined using low angle laser light scattering. The spherulites deform into ellipsoids having their major axis in the stretch direction. This deformation is only partially recoverable on release of the load. The proposed model differs from the two-phase domain microstructure generally assumed for block copolymer systems, being more closely related to the structure of semicrystalline homopolymers.

Elastoplastics, or thermoplastic elastomers, are a class of materials in which an attempt is made to combine certain desirable properties of elastomers (primarily recovery and energy absorption) with those of plastics (modulus and strength). This has been done by block copolymerization, combining alternating segments of rigid "hard" polymer and flexible "soft" polymer. A level of rigidity, structural integrity, and thermal resistance are imparted by the hard segment, while elastic recovery is provided by the soft segment. Such polymers contain no chemical cross-links, and thus may be processed as conventional thermoplastics.

The most widely studied of these systems has been the styrene–butadiene–styrene and styrene–isoprene–styrene triblock copolymers. Here it was determined that the hard (styrene) and soft (butadiene or isoprene) segments undergo microphase separation to form individual domains largely composed of one type of segment. The geometry of the domain system is a function of the segment molecular weight and sample history[2a] but generally involves hard segment domains dispersed in a soft segment matrix. Arguments based on thermodynamic incompatibility of the hard and soft segments have been advanced to explain such behavior.[2b,3]

A similar sort of morphology was later proposed for more complex multiblock copolymers such as the polyurethanes[4] in which the blocks are shorter and more numerous. This was based on analogies between the viscoelastic properties of polyurethanes and the sytrene–butadiene types. It has become commonplace to speak of domain formation in these systems, with the underlying assumption that separation into discrete microphase regions of hard and soft segments is occurring. Recent experimental evidence and geometric calculations have suggested for the polyurethanes, however, that this is not the case.[5–7] Rather it was proposed that the hard segments form an interlocking network cocontinuous with regions rich in soft segments.

A similar model has been proposed for polyester-based elastoplastics in which the hard segments are partially crystalline poly(tetramethylene terephthalate) (PTMT).[8] The soft segment in these compositions is based on poly(oxytetramethylene) glycol (PTMG), generally of molecular weight about 1000. The model proposes a two-phase domain structure with randomly oriented interconnected lamellar hard segment domains approximately 100 Å in width. These domains, while not discrete as in the styrene–butadiene–styrene system, are still presumed to act as intermolecular tie points or physical cross-links. Later work on similar systems by Shen et al. reported the observation of spherulitic structures under certain sample preparation conditions.[9] It is the purpose of this paper to present a morphological model for such polyester-based elastoplastics based on analogies with common semicrystalline thermoplastics rather than with domain forming block copolymers.

Experimental Section

Polymers. All polymers were formed by the polyesterification of dimethyl terephthalate, butane diol and poly(oxytetramethylene) glycol. The number average PTMG molecular weight was either 1000, 2000, or 3400. The structure of the resultant polymer, as shown in Figure 1, consists of alternating segments of poly(tetramethylene terephthalate) and poly(oxytetramethylene) glycol terephthalate. The average length of the poly(tetramethylene terephthalate) segments, *x*, is determined by the mole percent PTMG incorporated into the copolymer. Samples containing 20 to 65 wt % PTMG of the three molecular weights were prepared. Typical results are presented for a limited number of these compositions. They are identified by the weight percent PTMG and molecular weight in thousands by a code such as 50-2 (50 wt % PTMG of molecular weight 2000).

Characterization. Low angle light scattering patterns were obtained on melt-pressed sample films using a He–Ne laser. The sample film was placed between crossed polaroids for the H_v scattering. Patterns were obtained on elongated films by use of a hand operated stretching jig.

Melting points were determined on a Perkin-Elmer DSC 1B at a heating rate of 20°C/min under an N_2 purge. Dynamic mechanical properties were measured using a Rheovibron DDV-II Dynamic Viscoelastometer. Samples were again in the form of melt-pressed films. Measurements were made at 110 Hz and a heating rate of about 2°C/min. Samples were initially cooled to ca. −175° with liquid nitrogen then heated slowly as measurements were made.

Chemical Etching. Samples to be examined were cryogenically ground to pass a 140 mesh screen and subsequently given the desired thermal treatment. Chemical etching was carried out in a pressure vessel at 90° for 16 hr with 40% aqueous methylamine. The insoluble residue from the reaction was washed with ethylene glycol and methanol, air dried, and weighed.

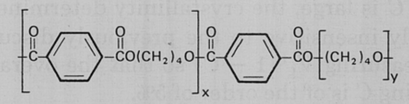

Figure 1. Chemical structure of polyester elastoplastics.

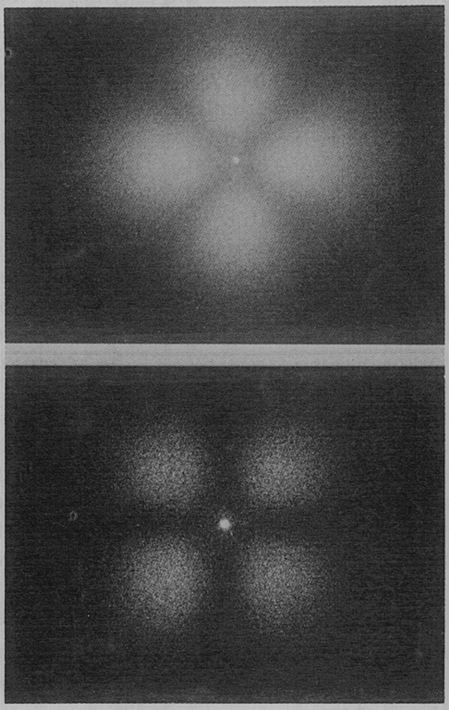

Figure 2. H_v low angle light scattering patterns: (top) sample 20-1; (bottom) sample 65-1.

The molecular weight and molecular weight distribution of the residue was determined by gel permeation chromatography. The chromatograph was operated at 125° using *m*-cresol as the solvent with columns having exclusion limits of 1.5 × 10⁴, 2 × 10³, 700, 250, and 100 Å, respectively. The system was calibrated with polystyrene standards obtained from Pressure Chemical Co. and with a set of previously characterized PTMT samples. The signal from the GC refractometer was monitored by a PDP-8I computer equipped with cathode-ray display.[10]

Results and Discussion

Superstructural Features. The previous morphological model for semicrystalline polyester elastoplastics suggests a two-phase structure of randomly oriented lamellar hard segment domains.[8] It is evident from the low angle light scattering patterns of Figure 2, however, that a spherulitic morphology is present. Both patterns show spherulitic scattering, with a maximum intensity at the center of each lobe. The difference in orientation of the pattern is due to a difference in orientation of the optic axis with reference to the spherulite radius. Whether the pattern of Figure 2 (top or bottom) is normally observed has been found to be a function primarily of the average polyester block length, though it may also be influenced by thermal history. It should be noted that the pattern of the top part of Figure 2 is characteristic of the poly(tetramethylene terephthalate) homopolymer.

The presence of well developed spherulitic structures across the entire composition range has also been confirmed by polarized light microscopy both in melt-pressed films and microtomed sections from injection molded bars. The familiar patée cross birefringence pattern is observed with an orientation corresponding to that found in the light

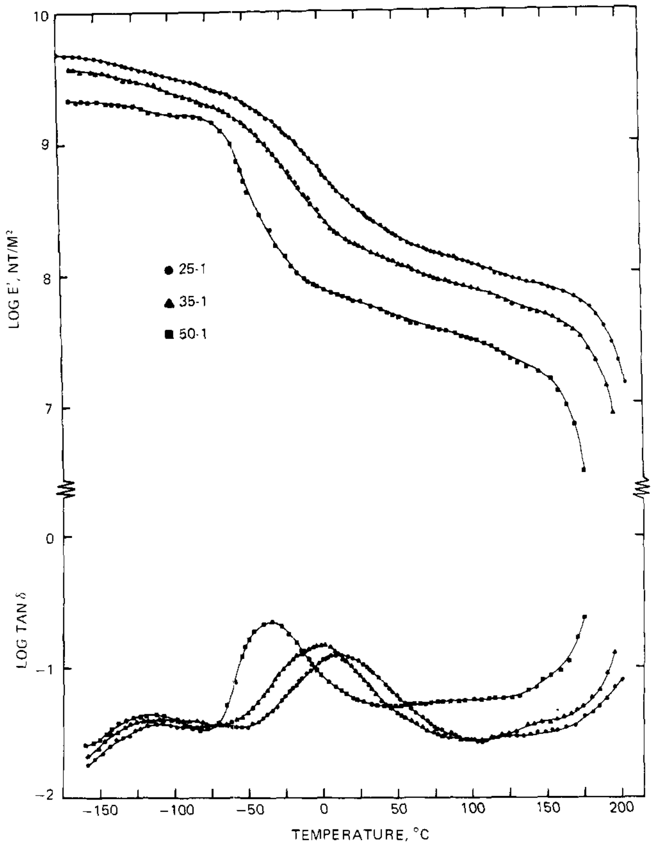

Figure 3. Dynamic mechanical properties for samples 25-1, 35-1, and 50-1.

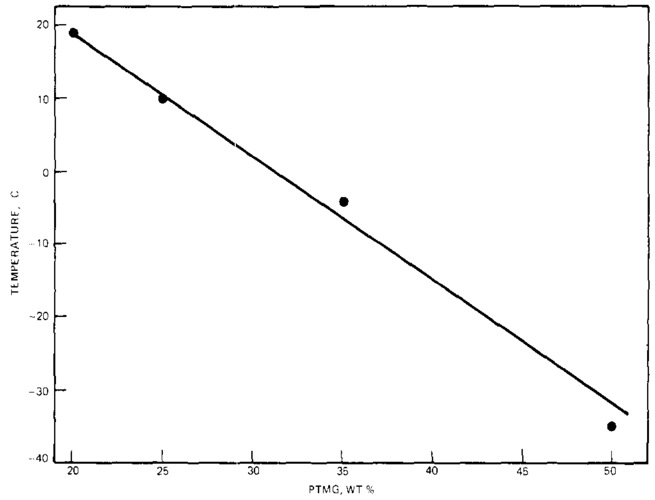

Figure 4. Dependence of primary loss peak temperature on wt % PTMG (PTMG mol wt = 1000).

scattering. Spherulites have also been found in solution cast films of similar composition.[9]

The skeleton of any spherulitic structure at ambient temperatures must of course be formed by the poly(tetramethylene terephthalate) segments. Because of the anticipated low degree of crystallinity of these segments, a relatively large amount of amorphous polyester will be rejected into the interradial regions of the spherulite. These regions must contain the amorphous PTMG segments as well, as they are covalently linked to the poly(tetramethylene terephthalate) segments. Phase separation in the sense applied to some block copolymer systems thus does not occur here. Rather, the structure is simple spherulitic crystallization in which the amorphous portion of the spherulite is a mixed phase of PTMG and uncrystallized poly(tetramethylene terephthalate).

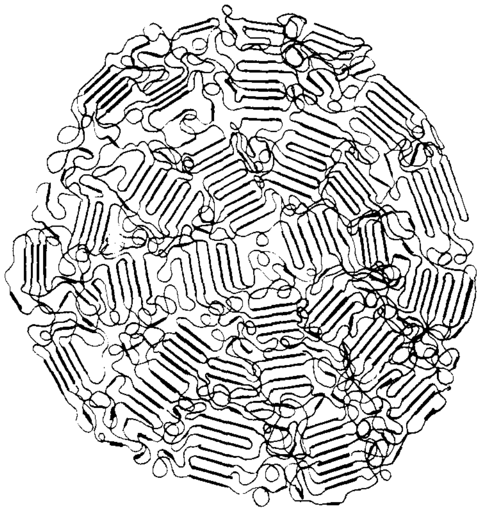

Figure 5. Schematic of proposed structure. Heavy lines represent polyester segments.

Support for this contention concerning the composition of the soft phase is obtained from dynamic mechanical properties. Modulus magnitude and loss tangent for three samples of varying PTMG content are shown in Figure 3. A single loss peak is observed, indicating that the PTMG and amorphous poly(tetramethylene terephthalate) do not exist in separate phases. The position of the primary loss peak shifts continuously with composition, as shown in Figure 4, where the loss peak temperature is plotted as a function of weight percent PTMG for the samples with 1000 molecular weight PTMG. Thus, varying the overall polymer composition causes a parallel change in the composition of the amorphous phase. These results are inconsistent with a model of phase separation based on hard and soft segments. However, they are the anticipated result for a simple semicrystalline copolymer in which the composition of the amorphous phase may be altered. Microphase separation occurs only into crystalline and amorphous regions, precisely as in common semicrystalline homopolymers. The question of compatibility of the hard and soft segments, of great importance in the styrene–butadiene system, is of little consequence here.

A schematic diagram of the proposed morphology is shown in Figure 5. The radial lamellae are crystallized poly(tetramethylene terephthalate), which account for only a minor fraction of the spherulite volume. This is due to the low overall degree of crystallinity resulting from copolymerization with PTMG. Between these crystalline radial fibrils is the amorphous "soft" phase, a mixture of uncrystallized poly(tetramethylene terephthalate) and the PTMG segments. This is a single phase showing one glass transition. As indicated in the figure and discussed below, chain folding may occur in the lamellae.

This morphology has some significant implications for the physical properties of these polymers. The hard segments cannot be said to act as physical cross-links in the sense applied to styrene–butadiene block copolymers. It is not possible to deform the soft segment without simultaneous deformation of the hard segment. The deformation mechanism is thus also quite analogous to that observed in other spherulitic, partially crystalline polymers. An example of this is found in Figure 6 where low angle light scattering patterns are shown for a sample under three condi-

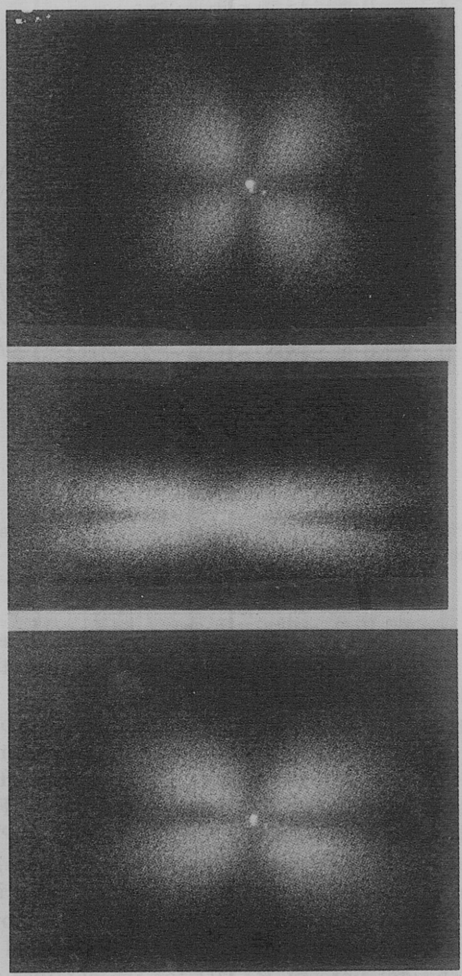

Figure 6. H_v light scattering patterns for sample 58-1: (top) control; (middle) under 200% extension; (bottom) relaxed from 200% extension.

tions. Figure 6 (top) is the undeformed polymer, showing a typical spherulitic scattering pattern. When deformed and held under strain (Figure 6, middle), the pattern elongates, indicating a deformation of the spherulites into the stretch direction. When the stress is released, there is residual deformation of the spherulites, evident in Figure 6 (bottom). Results similar to those of the top and middle parts of Figure 6 have also been observed in solution cast spherulitic films.[9] This results from the deformation of crystalline hard segments, which is largely irreversible. The materials thus bear little analogy to elastomers, where deformation occurs in rubbery segments between cross-links which act to prevent flow.

The morphology also affects the dynamic mechanical properties, as previously discussed. The results are consistent with the existence of a mixed amorphous soft phase containing both the PTMG and poly(tetramethylene terephthalate) segments. The latter serve to reinforce the soft phase, thus raising the glass transition from the value of pure PTMG (about −50°[11]) which would be observed in a hard–soft phase separated system. Further, under conditions of ideal microphase separation, the temperature of this loss peak would not change with copolymer composition, though the magnitude would. The T_g increases with decreasing PTMG content because at lower PTMG levels the average length of the polyester segment is greater. The longer segments are more effective as reinforcing agents in the soft phase, resulting in a more strongly elevated T_g.

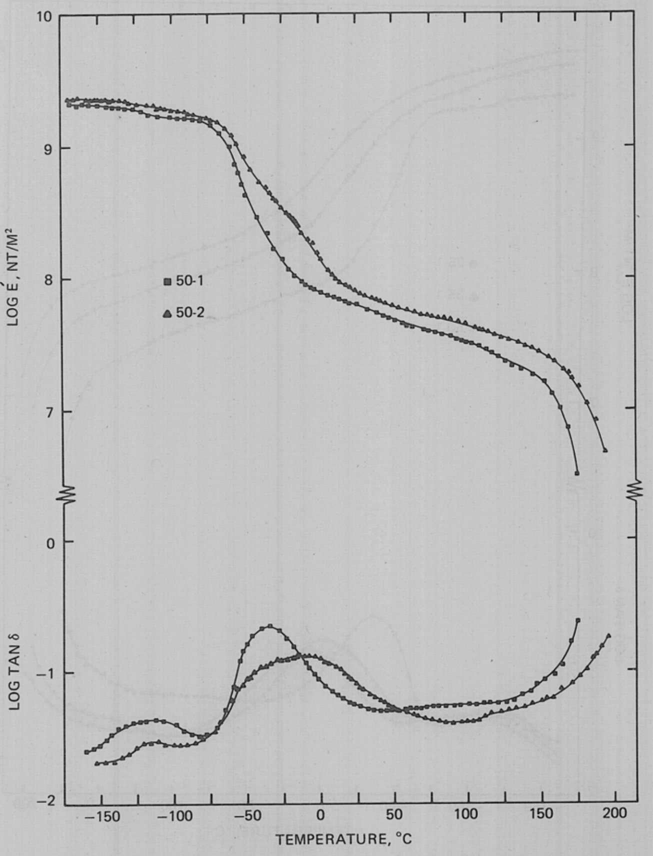

Figure 7. Dynamic mechanical properties for samples 50-1 and 50-2.

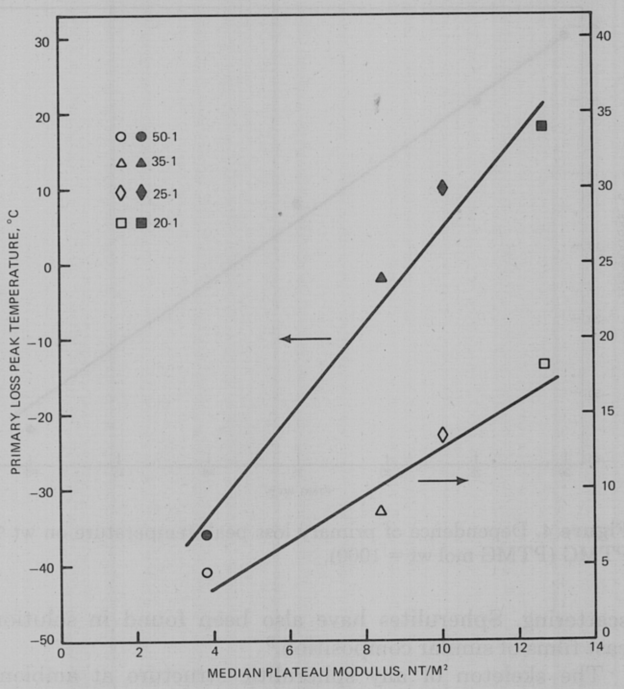

Figure 8. Dependence of median plateau modulus on average hard block degree of polymerization and primary loss peak temperature.

A similar effect may be noted on increasing the PTMG molecular weight from 1000 to 2000 (Figure 7). The loss peak temperature is raised from −36 to −12°, as doubling the PTMG molecular weight at a constant weight percent also doubles the number average polyester degree of polymerization (DP). The magnitude of the loss peak decreases

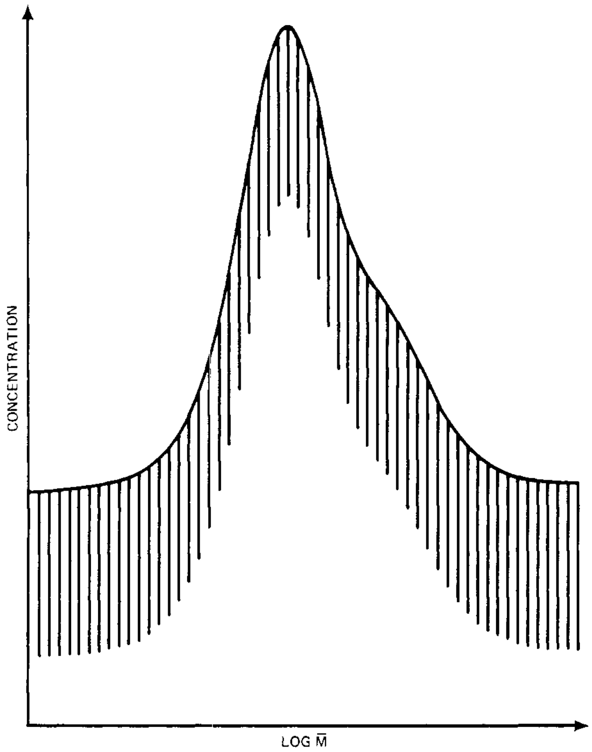

Figure 9. Molecular weight distribution of chemically etched hard segments, sample 20-1.

due to the lower mole percent PTMG at the higher molecular weight.

A "median plateau modulus" between the T_g and T_m has been estimated for each composition from the $|E^*|$ data. The modulus in this region is related to the stiffness of the material in the normal use temperature range. Figure 8 shows that this modulus varies directly with both the mean hard block DP and the primary loss peak temperature. The latter relationship is not unexpected in view of the spherulitic morphology and the fact that the soft phase is not pure soft segment. It does demonstrate, however, the important result that one cannot vary the T_g and modulus independently in this system.

Lamellar Structure. Information on the lamellar structure has been obtained by the chemical etching technique. Figure 9 shows a typical GC chromatogram of the residue from the aminolysis reaction. It has previously been shown that this reaction selectively degrades the amorphous regions of polyesters, including chain folds at the crystalline–amorphous interface.[12] The molecular weight of the residue is therefore representative of the molecular chain length which constitutes the lamellar fold period of the most perfect lamellae. Direct evidence of chain folding in these systems is given by the shoulder on the high molecular weight side of the distribution (see Figure 9). This shoulder occurs at exactly twice the peak molecular weight and is due to chains which traverse the lamellae twice. This shoulder disappears with reaction time as fold cleavage approaches completion, and in the limit one obtains essentially monodisperse poly(tetramethylene terephthalate) of lamellar origin. We find that the lamellar fold period of the reacted residue is equal to that of the polyester homopolymer, 7 to 8 monomer units, and is independent of PTMG content and PTMG molecular weight over the range studied. In this case of sample 20-2 we find that lamellar thickening occurs with increasing annealing temperature as one finds in more conventional semicrystalline polymers. The average fold period increases from 8 to 9 monomer units when the annealing temperature is increased from 140 to 200°. The structure of the most perfect lamellae in these copolymers, as determined by chemical etching, is thus indistinguishable from that of the poly(tetramethylene terephthalate) homopolymer.

Conclusions

The block copolymers studied are more analogous, both in morphology and properties, to common semicrystalline thermoplastics than to block copolymer systems which undergo microphase separation into hard and soft domains. Spherulitic crystallization persists even in samples having very short number average crystallizable block lengths. While incompatibility of the hard and soft segments does not lead to hard–soft phase separation in these polymers, it may serve as an added driving force for hard segment association and subsequent crystallization. The lamellar characteristics can thus be largely unaffected by copolymerization and unexpectedly high degrees of crystallinity (relative to that of the polyester homopolymer) may occur. While the spherulitic structure is well formed, the high volume fraction of amorphous segments implies the presence of a large amount of amorphous interradial material. This is apparently a single mixed phase of soft segment and uncrystallized hard segment. Thus, while the general principle of microphase separation in block copolymers is well established, its effects on morphology and structure must be understood in the context of the inherent properties of the individual segments. In the case of the present materials, the most important of these is the crystallization characteristics of the hard segment, which strongly influences the resultant morphology.

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