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Dielectric Properties and Cocrystallization of Mixtures of Poly(butylene terephthalate) and Poly(ester–ether) Segmented Block Copolymers

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ABSTRACT: Measurements of the complex permittivity were used to assess the amorphous phase miscibility in blends of poly(butylene terephthalate) (PBT) and several poly(ester–ether) (PEE) segmented block copolymers. In addition, complex plane parameters were determined for the component polymers and certain blends and their variation with hard segment content or blend composition is discussed. It was found that larger hard segment (tetramethylene terephthalate) content in the segmented block copolymers favors increased amorphous phase miscibility and cocrystallization. Thermal analysis and morphological evidence point to extensive cocrystallization in PEE-84/PBT mixtures.

Introduction

In the past several years there has been considerable interest in polymer blends in which one or more of the component polymers are capable of crystallizing. Particularly intriguing examples are mixtures based on poly(butylene terephthalate) (PBT) and various poly(ester–ethers) (PEE) segmented block copolymers. The poly(ester–ethers) under consideration are comprised of a poly(tetramethylene oxide) "soft" segment and a "hard" segment that is chemically identical with PBT (i.e., tetramethylene terephthalate (4GT)). Since it has been demonstrated that the crystalline unit cell structure and interplanar spacings of PBT and the PEE segmented copolymers are identical,[1] it would seem possible that, given the opportunity (i.e., that there is at least some limited miscibility in the melt), the PEE hard segment and PBT would cocrystallize in the blended state to give labile intermolecular cross-links.

Although a rather large number of papers have appeared concerning crystallization, morphology, and solid-state properties of both PBT (e.g., ref 2–4) and the PEE segmented copolymers (e.g., ref 5–9), little attention has focused on blends of these two polymers. The one exception is a relatively recent study by Shih[10] in which mixtures of PBT and a PEE block copolymer containing 59 wt % 4GT (soft segment molecular weight of 1000 g/mol) were found to be immiscible at compositions from 10–90% PBT. The resulting blends contained four phases, two amorphous and two crystalline. In the present paper we report our initial findings on the phase behavior of mixtures of PBT and poly(ester–ether) segmented block copolymers containing a range of hard-segment concentrations. Particular attention is paid to the dielectric properties of the copolymers and blends. We show that amorphous phase miscibility increases as 4GT concentration in the block copolymer increases and that extensive cocrystallization appears to occur in blends containing the high 4GT content copolymer.

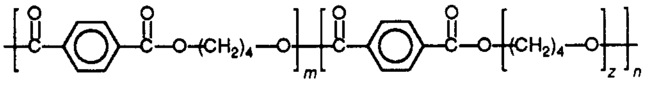
Table I
Characteristics of PBT and Segmented Block Copolymers

designation	hard seg (4GT), wt %	T_g, °C	T_m, °C	W_c, %	av 4GT seg length
PEE-44	44[a]	−40	146	13	5
PEE-58	58	−30	198	19	8
PEE-84	84	~30 (br)	214	26	31
PBT	100	60	223	31	

[a] Also contains ~7 wt % isophthalate residues.

Experimental Section

Materials. The PBT used in our experiments was provided by General Electric (Valox 310) and is reported to have a number-average molecular weight of ca. 33 000 g/mol. The poly(ester–ethers) were obtained from E. I. du Pont de Nemours and Co. and had overall molecular weights of 25–30 000 g/mol. The three copolymers used in our experiments have the general chemical structure



The characteristics of the copolymers and PBT can be seen in Table I. The 4GT contents range from 44 to 84 wt % (80–97 mol %) as determined from ^{1}H NMR. NMR also showed that PEE-44 contained ~7 wt % isophthalate residues. If one assumes a most probable distribution (random polymerization), then the average 4GT segment length can be estimated and this is found

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to vary from 5 to 31. It is well-known that the copolymers are semicrystalline. The prevailing morphological view (cf. ref 1, 7) is one of chain fold lamallae of the hard segment (ca. 30–100 Å) in an amorphous matrix composed of a mixture of the soft and any uncrystallized hard segments (i.e., they will exhibit a single T_g). This is despite the fact that the high molecular analogues of the hard and soft segments are apparently not miscible. On a larger scale, the crystalline lamallae are generally organized into spherulites.

As expected, the glass transition temperature (T_g), melting point (T_m), and degree of crystallinity (W_c) decrease with decreasing hard-segment concentration (the values in Table I were obtained from melt-processed samples that had been air cooled from the melt). If one normalizes the degree of crystallinity to the weight of 4GT in the copolymer, the values for the copolymers and PBT are identical, indicating that the decrease in degree of crystallinity is directly proportional to the 4GT content.

Sample Preparation. The PBT and copolymers were dried in a dehumidified tray for 16 h before melt processing at ~238 °C in a twin- or single-screw extruder (polymer residence time 50–70 s). In addition, blends and pure polymers were cast from 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). Blends were cast into aluminum pans, allowed to air dry then dried under vacuum at 70 °C for 3–5 days. Blends were also solution cast from a 60/40 mixture of phenol and tetrachloroethane; the behavior (i.e., the miscibility and melting behavior) of these samples is very similar to those cast from HFIP and will not be discussed further.

To obtain uniform films for dielectric measurements, samples were initially dried at ca. 100 °C for 24 h, then hot pressed at 250 °C for 3–8 min, and then quenched to room temperature. Gold electrodes were applied to the resulting films (70–100 μm thick) by vacuum evaporation. The electrode diameter was approximately 10.2 mm.

One concern when dealing with blends of polyesters is the possibility of transesterification during melt processing. The results for the solution-cast (either from HFIP or phenol/tetrachloroethane) and melt-processed samples were identical within experimental error and indicate the lack of significant transesterification of our melt-processed blends.

Characterization. Measurements of glass transition temperatures and melting behavior were performed with a Perkin-Elmer differential scanning calorimeter (DSC-2) at a heating rate of 20 deg/min. For measurement of T_g's, sample sizes of 13–21 mg were used, whereas sizes for characterization of heats of fusion (ΔH_f) and T_m's were 2.50–4.0 and 0.3–1.0 mg, respectively. The small sample sizes were used for measurement of T_m in order to minimize problems associated with low polymer thermal conductivity.[11] Endothermal areas and peak temperatures where calibrated with an indium standard. Base lines defining endothermal areas were constructed by drawing a line from a temperature below which melting was observed to begin to a temperature slightly higher than the last traces of melting. Degrees of crystallinity were calculated by using a perfect crystal heat of fusion for PBT of 34 cal/g.[12]

Measurements of the dielectric constant and loss from −150 to 150 °C and 0.1 to 100 kHz were made by using a Hewlett-Packard Model 4274A multifrequency LCR meter. A heating rate of 2 deg/min was used in all experiments. The dielectric constant was calculated by treating the sample as a parallel plate capacitor and from knowledge of the area-to-thickness ratio of the specimen. The phase angle is measured directly, and its complement δ gives the loss tangent, tan δ.

Some limited research on the morphology of the blends and pure polymers was conducted by using optical microscopy and low-angle laser light scattering. Polarizing microscopy was performed with an Olympus BHSP-300 microscope which was equipped with a Mettler FP82 hot stage. The light scattering was done under crossed polars and the scattered intensity was detected photographically or with a Model 1216 Princeton Applied Research (PAR) Vidicon detector, coupled to a PAR Model 1460 optical multichannel analyzer.

Results and Discussion

The results of the DSC experiments regarding blend T_g's were largely inconclusive. For example, DSC thermograms for melt-processed and solution-cast PEE-44/PBT mixtures indicate a multiphase system; i.e., they exhibit two T_g's. The lower transition temperature is located at approximately the same temperature as the T_g of pure PEE-44, while the location of the higher temperature transition is more difficult to assess due to the low magnitude and breadth of the heat capacity change. The thermograms in the temperature range near T_g for the PEE-58 and PEE-84 mixtures were equally or more difficult to interpret. The PEE-58 mixtures exhibit two T_g's, but their precise location is difficult to judge accurately.

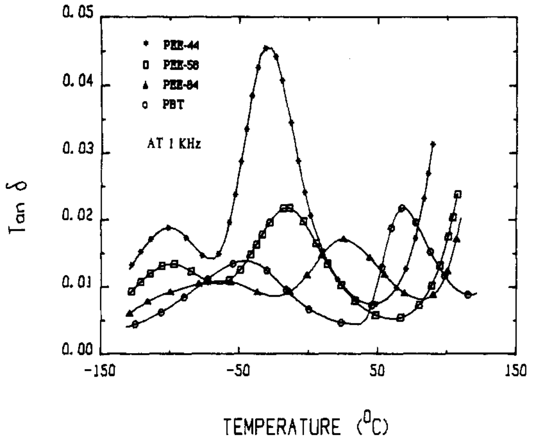

Figure 1. Loss curves at 1 kHz for PBT and segmented block copolymers.

Table II
Activation Energies for the β- and γ-Relaxations of PBT and the Segmented Block Copolymers

	β-relaxation	γ-relaxation
PEE-44	28	8
PEE-58	41	11
PEE-84	55	11
PBT	68	15

Dielectric Measurements. a. Pure Polymers. Since both PBT and the copolymers are relatively polar, dielectric loss measurements were undertaken in an attempt to gain greater insight into the amorphous phase behavior. PBT and the copolymers exhibit two dielectric transitions in the temperature range of interest (see Figure 1). The higher temperature relaxation (which we will term the β-transition) is associated with large-scale (T_g-like) motion in the amorphous phase. The low-temperature relaxation (γ) has been assigned to motions of the COO moiety in noncrystalline regions for PBT, while for the copolymers it has been assigned to either local mode motions of the soft segment or a combination of these motions and COO motions from noncrystalline hard segments.[13] Apparent activation energies (E_a) for each of these relaxations can be derived from the appropriate Arrhenius plot (Table II). E_a for the β-relaxation was found to vary from 68 to 28 kcal/mol when going from PBT to PEE-44 and from 15 to 8 kcal/mol for the γ-transition. These values are near those derived previously for similar copolymers by Lilaonitkul and Cooper.[13]

In an effort to explore the relative local (amorphous phase) molecular environments of the copolymers and PBT, we constructed normalized loss curves, i.e., plots of the normalized loss factor ϵ''/ϵ''_m (where ϵ''_m is the maximum value of ϵ'') versus log f/f_m (where f is the frequency and f_m the frequency at which ϵ''_m occurs). The distribution of relaxation times can be qualitatively assessed by comparing half-widths and other shape factors, graphically. Because of the limited frequency range used in our experiments (ca. 3 decades), in order to construct a normalized loss curve that encompasses a reasonably wide

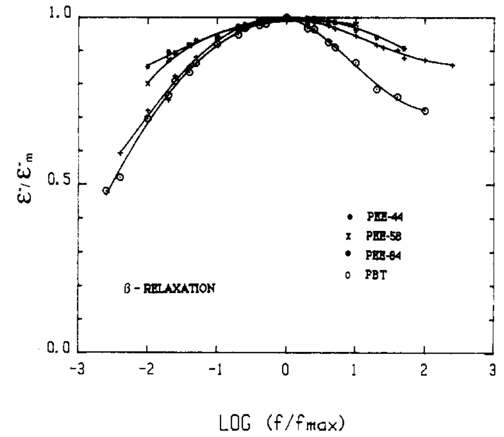

Figure 2. Normalized loss curves (β-transition) for PBT and segmented block copolymers.

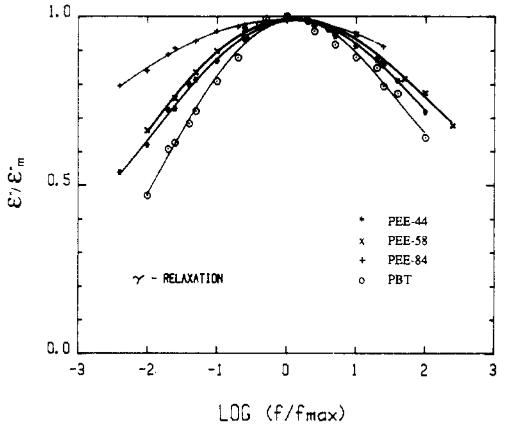

Figure 3. Normalized loss curves (γ-transition) for PBT and segmented block copolymers.

frequency range, it was necessary to shift the partial curves obtained at different temperatures to construct a single master curve. The normalized loss curves for the β and γ relaxations of the copolymers and PBT are shown in Figures 2 and 3 (using averaged data for a clearer representation). All of the curves for the β-transition are quite broad, which is typical of semicrystalline polymers. The usual view is that the crystals restrict long-range motion in the amorphous phase. The high-frequency skewing, particularly evident for the copolymers, is typical for many polymer systems.

For the β-relaxation we find that the normalized loss curves for the copolymers become increasingly broad with increasing 4GT content, indicating an increase in the range of local molecular environments or distribution of relaxation times. PBT shows the narrowest relaxation time distribution. The degrees of crystallinity of the PBT and copolymers are different but the breadth of the β-process, although certainly perturbed by the presence of crystallinity, does not appear to be sensitive to changes in degree of crystallinity.[14,15] The subglass γ-relaxation, if associated with the amorphous phase as in poly(ethylene terephthalate)[15] and PBT,[13] is generally thought to be insensitive (except for the intensity or relaxation strength) to either the presence or the degree of crystallinity. This is presumably a consequence of the local character of the motions associated with the γ-process. The relative broadening of the β-relaxation can be rationalized by considering the mixing of unlike segments in the amorphous component in the copolymers. In this scenario, PBT exhibits a relatively uniform molecular environment. Mixing of short PBT blocks with the soft-segment blocks (as in PEE-44) apparently results in a somewhat broader distribution. Since the respective homopolymers are not miscible, we might except that increasing the average molecular weight of a 4GT block from ca. 1000 to 7000 g/mol (i.e., on going from PEE-44 to PEE-84) would result in greater difficulties in mixing and a broadening of the relaxation time distribution.

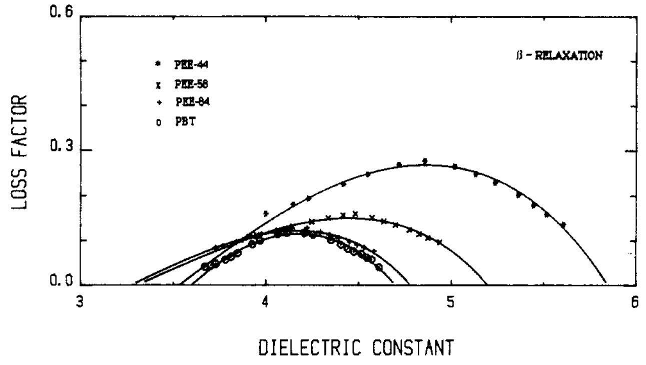

Figure 4. Argand diagrams for the β-process of PBT and segmented block copolymers.

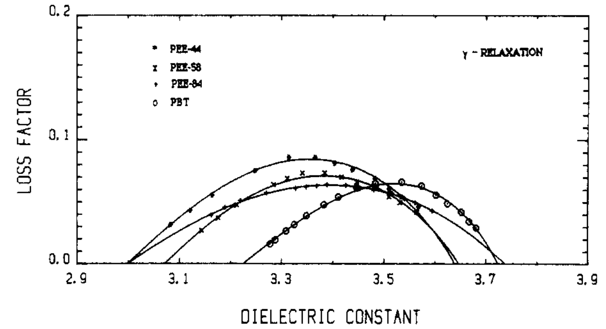

Figure 5. Argand diagrams for the γ-process of PBT and segmented block copolymers.

On a relative basis, the γ-relaxation broadens in the same fashion with copolymer content; however, this is less likely to be associated with mixing/molecular weight considerations due to the local character of the relaxation. The explanation for the observed behavior more likely lies in the dual nature of the γ-process for the copolymers. The γ-relaxation in PBT has been associated with motions of the COO group in different conformations in noncrystalline regions.[13] For the copolymers, the γ-process will likely be composed of a combination of this motion with local motions of the soft-segment repeat units ($(CH_2)_4O$). As 4GT content increases, one would expect an increasingly large contribution from γ_{COO} at low frequencies (high temperatures) and this is consistent with the behavior seen in Figure 3.

To quantitatively describe the relaxation processes of the copolymers and PBT, we utilized the empirical Havriliak–Negami model, which describes a given relaxation process in terms of five complex plane parameters.[16]

$$\frac{\epsilon^*(\omega) - \epsilon_u}{\epsilon_r - \epsilon_u} = [1 + (i\omega\tau_0)^{1-a}]^{-b} \qquad (1)$$

$\epsilon^*(\omega)$ is the complex dielectric permittivity at the angular frequency ω; ϵ_u and ϵ_r are the unrelaxed (high frequency) and relaxed (low frequency) dielectric constrants, respectively; τ_0 is the central relaxation time; and a and b are empirical parameters, $0 \leq a \leq 1$ and $0 \leq b \leq 1$. The parameter a represents the symmetric broadening of the relaxation time distribution; the width increases as parameter a increases. The parameter b describes the high-frequency skewness of the relaxation distribution. When $b = 1$, eq 1 is equivalent to the Cole–Cole equation.

Table III
Complex Plane Parameters for PBT and Block Copolymers

sample	T, °C	ϵ_u	ϵ_r	a	b
		β-Relaxation			
PEE-44	-8	3.35	5.85	0.63	0.50
PEE-58	0	3.31	5.20	0.71	0.40
PEE-84	51	3.28	4.78	0.72	0.43
PBT	100	3.60	4.70	0.71	0.75
		γ-Relaxation			
PEE-44	-81	3.00	3.64	0.61	0.60
PEE-58	-81	3.07	3.65	0.65	0.69
PEE-84	-47	3.00	3.74	0.75	0.70
PBT	0	3.23	3.72	0.56	0.45

Time–temperature superposition was utilized to construct complex plane plots at a given reference temperature for each sample. These are shown in Figures 4 and 5 for the β- and γ-processes, respectively. For the β-transition, the reference temperature was chosen as the tan δ maximum at 100 kHz ($T_{\max_\beta}$) plus 10 °C; for the δ relaxation, we chose $T_{\max_\gamma}$.

Although new statistical methods are available,[17,18] the complex plane parameters were determined graphically[16] and are listed in Table III. ϵ_r, ϵ_u, and the relaxation strength (ϵ_r–ϵ_u) for PBT are all nearly the same as that reported for PET of comparable degree of crystallinity and at a comparable temperature.[15] The relaxation strength increases as more soft segment is added to the copolymer and this is generally consistent with the decreasing crystallinity and larger β-process relaxation strength of high molecular weight poly(tetramethylane oxide) reported by Wetton and Williams (ϵ_r–ϵ_u ~ 2.4).[19] The symmetric broadening parameter a is near 0.6–0.7 for all samples, compared to values near 0.2, which are typical for noncrystalline polymers.[14] There is some indication of increased broadening with copolymer 4GT content, in agreement with implications from the normalized loss curves. However, the derived a for PBT is near those for PEE-58 and -84, in contrast to what is expected from the normalized loss curves. The reason for this discrepancy is unknown at the present time. The value of b for PBT is 0.75, indicating some high-frequency skewness. For comparison, it was found recently that the shapes of the complex plane plots for a number of semicrystalline PET's were nearly symmetric and could be adequately described by the Cole–Cole equation. The values of b for the copolymers are near 0.4–0.5 (significant high-frequency skewing), values which are typical for amorphous polymers.[14]

Within experimental error, no systematic change in the relaxation strength of the γ relaxation was observed. The variation in a is in excellent agreement with the normalized loss curves. The significant high frequency skewness of the γ-process for PBT is presumably related to the fact that the PBT γ process involves local motions of the COO units in different conformations (i.e. gauche and trans) (13). The addition of the soft segment causes an increase in symmetry.

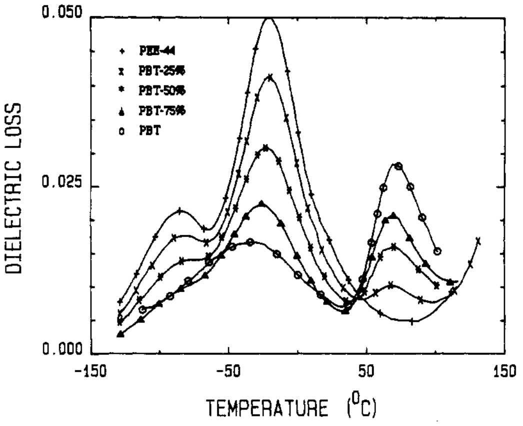

Figure 6. Loss curves at 10 kHz for PBT, PEE-44, and three blends.

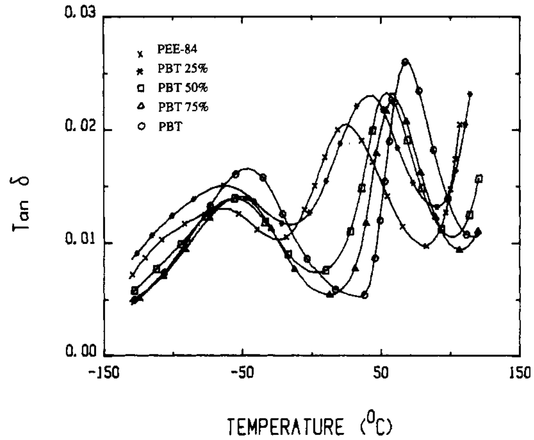

Figure 7. Loss curves at 1 kHz for PBT, PEE-84, and three blends.

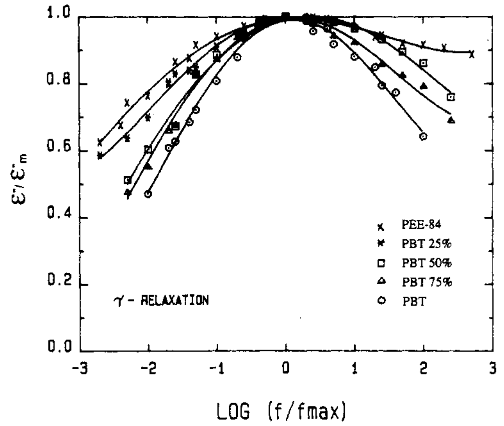

Figure 8. Normalized loss curves (γ-process) for PBT, PEE-84, and blends.

b. Polymer Blends. Figure 6 shows the dielectric loss as a function of temperature for PBT, PEE-44, and three blends at 10 kHz. Two β-transitions are observed for all blends: one near 70 °C corresponding to an essentially pure PBT phase and a second at lower temperatures. Unfortunately there is considerable overlap of the PEE-44 β-relaxation and γ-transition of PBT, making it difficult to ascertain what is happening in the low-temperature region. However, DSC observations of the lower T_g, in combination with the results of the dielectric experiments, lead to the conclusion of amorphous phase immiscibility over the range of compositions studied. The results for the PEE-58/PBT mixtures were similar although there does appear to be some limited miscibility as evidenced by movement of the β-relaxation of PBT to lower temperatures upon blending (e.g., a depression of 8 deg for the blend containing 25% PBT). When the hard-segment content of the copolymers increases to 84% (Figure 7), one finds single β- and γ-relaxations, indicating a miscible amorphous phase, at least at the level at which we are probing. Arrhenius plots for the β- and γ-transitions were also constructed for the PEE-84/PBT mixtures and, not surprisingly, the calculated activation energies varied between those of the pure components. Normalized loss curves were constructed for the PEE-84/PBT blends and pure polymers for both the β- and γ-transitions. The

Table IV
Complex Plane Parameters for PEE-84/PBT Blends

sample	T, °C	ϵ_u	ϵ_r	a	b
		β-Relaxation			
PBT	100	3.60	4.70	0.71	0.75
PBT-75%	90	3.82	4.98	0.74	0.80
PBT-50%	80	3.60	4.79	0.72	0.70
PBT-25%	58	3.65	5.14	0.76	0.70
PEE-84	50	3.50	4.83	0.74	0.60
		γ-Relaxation			
PBT	0	3.23	3.72	0.56	0.45
PBT-75%	-13	3.37	3.91	0.51	0.32
PBT-50%	-23	3.19	3.74	0.61	0.40
PBT-25%	-30	3.28	4.00	0.71	0.60
PEE-84	-49	3.14	3.77	0.73	0.64

curves for the γ-transition are shown in Figure 8; the general character of those for the β-relaxation is similar. For both relaxations, the breadth varies more or less regularly from PBT (the narrowest) to PEE-84. This is similar to the results on other[20,21] (but not all (e.g., ref 22)) miscible blends and indicates a relatively uniform microscale environment in the blends.

Complex plane plots were also constructed for the β- and γ-relaxation of the PEE-84 blends and pure polymers at the appropriate reference temperature (as described earlier). The complex plane parameters were derived from a fit of the Havriliak–Negami expression and are listed in Table IV. There is no systematic change in the relaxation strength of either transition with blend composition. For the β-relaxation, the degree of symmetric broadening was found to be virtually identical for all specimens (i.e., ~0.7) while the relaxation becomes increasingly symmetric upon addition of PBT. Generally, the relaxation time distribution for the γ-process was found to become broader (and more symmetric) with increasing PEE-84 concentration, in line with indications from the normalized loss curves. It must be noted that the complex plane parameters listed for PEE-84 in Tables III and IV are somewhat different, presumably due to the slightly different thermal histories of these two specimens. The values listed in Table IV are for a sample that was prepared under identical conditions as the blends and PBT.

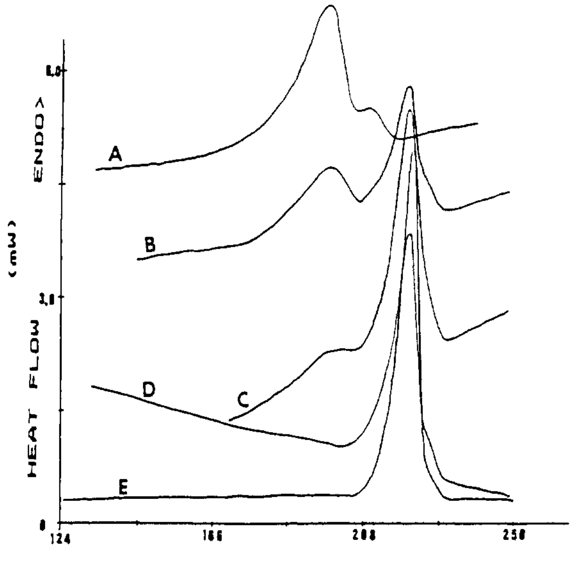

Figure 9. DSC thermograms of (A) PEE-58; (B) 75/25, PEE-58/PBT blend; (C) 50/50; (D) 25/75; (E) PBT.

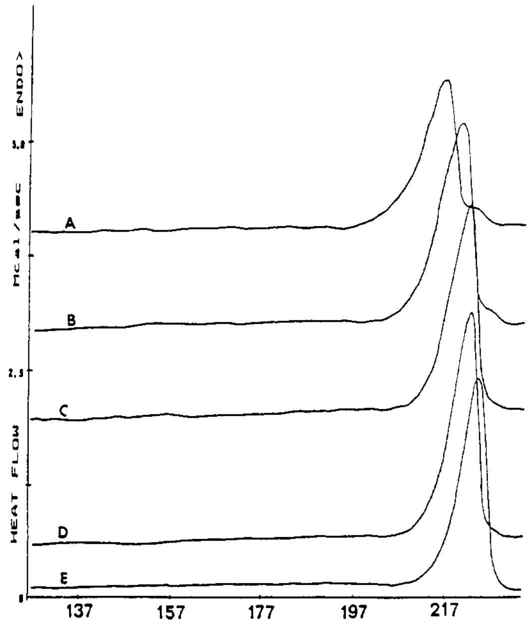

Figure 10. DSC thermograms of (A) PEE-84; (B) 75/25, PEE-84/PBT blend; (C) 50/50; (D) 25/75; (E) PBT

Cocrystallization. As noted recently, cocrystallization between two crystalline polymers in a single crystalline lattice is extremely rare.[23] However, due to the identical chemical structures of the crystallizable units in PBT and the poly(ester–ether) block copolymers under consideration here, as well as the partial or complete miscibility indicated from our dielectric measurements, we felt that certain of these mixtures would be excellent candidates to exhibit cocrystallization. For blends of PEE-44 and PBT we observed two distinct melting transitions whose T_m's are the same as those of the unblended polymers. In addition, the relative magnitudes of the melting endotherms in the mixtures change as one would expect for individual crystallization of the two polymers. For PEE-58/PBT blends we also observe two melting endotherms (see Figure 9). [For the present purposes, we will ignore the second, higher temperature endotherm that is observed for PEE-58, which presumably arises from lamellar reorganization during heating in the DSC.[24,25]] The lower T_m for the blends (not seen in Figure 9 for the 25/75 PEE-58/PBT blend due to the scale used) is identical with that of the primary melting endotherm of PEE-58. However, the higher temperature endotherm is shifted slightly to lower temperatures (~3 deg for the highest PEE-58 content blend), and this is consistent with the partial miscibility indicated from dielectric measurements. The total degree of crystallinity varies more or less uniformily with blend composition, but it does appear that the changes in the relative magnitudes of the endotherms are not entirely consistent with individual crystallization of the component polymers. Experiments are in progress in an attempt to clarify the situation.

As noted earlier, PBT and PEE-84 are miscible and it is in this situation that we expect the greatest probability of cocrystallization. This is supported by the observation of a single melting transition from DSC (Figure 10) and optical microscopy for all blend compositions and a uniform variation in T_m and degree of crystallinity. Verification of cocrystallization using wide-angle X-ray diffraction was not possible since the lattice parameters of 4GT-based copolymers are independent of 4GT content and identical with those of PBT.[1] Optical microscopy and small-angle light-scattering experiments were conducted to see if separate crystallization of the component polymers could be detected. As noted previously for unblended PBT and PEE copolymers, we observed usual and/or unusual spherulitical morphologies, depending on the crystallization conditions.[4,26,27] No indication of separate crystallization was detected and we therefore conclude at this time that cocrystallization is likely in blends of high 4GT content copolymers and PBT.

Conclusions

Measurements of the complex dielectric permittivity show clearly that larger 4GT contents in the poly(ester-ether) segmented block copolymers under consideration favor increase amorphous phase miscibility in blends with PBT. Thermal analysis and morphological evidence suggest that there is extensive cocrystallization in blends of PEE-84 and PBT.

Registry No. PBT, 26062-94-2; PBT (SRU), 24968-12-5; (1,4-butanediol)(polytetramethylene glycol)(terephthalic acid) (block copolymer), 106159-00-6; (1,4-butanediol)(isophthalic acid)(polytetramethylene glycol)(terephthalic acid) (block copolymer), 106159-01-7.

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Mechanistic Investigation of the Photochemistry of Thiosulfate Functional Zwitterions

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ABSTRACT: The synthesis and characterization of a water-soluble zwitterionic polymer that is photochemically reactive is described. The polymer contains reactive thiosulfate groups that upon photolysis undergo sulfur-sulfur bond cleavage and subsequent loss of water sensitivity. Direct photolysis of model compounds clearly indicates the formation of disulfide photoproducts which can also be identified in the polymer films by FTIR analysis. The quantum efficiency for loss of thiosulfate groups, at least in a model compound study, is about 0.2. Preliminary results show that the primary sulfur-sulfur bond cleavage of the thiosulfate chromophore is readily sensitized by a standard triplet sensitizer.

Introduction

Organic thiosulfates were first synthesized by Bunte in 1874[1] by the reaction of alkyl halides with sodium thiosulfate and are often referred to as Bunte salts. Bunte determined that alkyl thiosulfates are quite sensitive to heat and hydrolysis, especially in the acid form:

$$C_2H_5Br + Na_2S_2O_3 \rightarrow C_2H_5SS(=O)_2O^-Na^+ + NaBr$$

Alkyl thiosulfates are known[2-4] to photodegrade by a homolytic cleavage at the S-S bond caused by exposure to ultraviolet light. The photoproducts have been shown to initiate free-radical polymerizations of methyl methacrylate, styrene, and acrylonitrile.[2,3] Further, alkyl thiosulfate salts bound to a polymer backbone have been photolyzed as supports for graft polymerizations.[4] Unfortunately, there is only limited information about the nature of the photolysis mechanism(s).

One interest in developing thiosulfate-functional polymers results from the ability of the Bunte salt group to impart water solubility to an otherwise hydrophobic moiety, coupled with the potential to degrade to disulfide cross-links. Early work showed that copolymers of (*N*-(acrylamido)amino)ethyl thiosulfate with vinyl acetate and methyl acrylate could be cross-linked by the addition of

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