

Phase Separation and Mechanical Properties of an Amorphous Poly(ether-b-ester)

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The dynamic mechanical properties and phase separation of a series of amorphous condensation multiblock polymers, poly(oxypropylene-b-oxypropylene oxyterephthaloyl), was studied. Samples prepared from poly(oxypropylene) with a molecular weight of 3000 showed clear evidence of block phase separation from small angle x-ray scattering and two transition regions in torsional braid analysis. As the molecular weight of the poly(oxypropylene) was reduced, the stages between clear phase separation and formation of a homogeneous mixture were observed. The size and shape of the mechanical damping peaks could be controlled by the block size, the weight fractions of the two components, and the chemical composition of the components.

Polymers are often used in sound absorption and vibration damping applications (1), for example, in reducing hull noise in ships (2) and in sound-proof helmets (3). Their efficiency in these applications is related to the $\tan \delta$ of the polymer in the range of frequencies and temperatures found in the particular application. A major limitation of conventional amorphous homopolymers is that the region of high $\tan \delta$ (> 0.8) extends over only 20°–30°C, at 1 Hz, in the glass-rubber transition region (4). There have been many attempts to broaden this damping peak by the addition of plasticizers and fillers, but with only limited success (5, 6). However, the width of the peak can be readily controlled in polymer blends (7, 8, 9). Recently, interpenetrating networks (IPN) have been prepared that show exceptionally broad and high $\tan \delta$ maxima,

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and they have properties in damping applications that are significantly better than other commercially available damping materials (5). It is thought that the broad maxima in $\tan \delta$ observed in IPNs arises from a partial phase separation of the network chains such that regions of continuously varying composition are found rather than the regions of pure homopolymer normally observed in polymer blends. Each volume element with a given composition contributes to the overall properties, leading to a broad $\tan \delta$ peak.

The tendency of an amorphous multicomponent polymer system to phase separate is driven by the large negative enthalpy of the phase-separated state relative to a homogeneous mixture (11). In terms of the Scott-Hildebrand solution theory (10), this negative enthalpy is related to the difference in solubility parameter of the components and their molecular weight. The tendency to phase separate is opposed by the loss in entropy caused by the reduction in chain configurations on phase separation. In principle, polymer blocks, grafts, blends, and IPNs could all show partial phase separation with a suitable choice of polymers and chain topology.

The remarkable properties of amorphous block polymers, particularly poly(styrene-*b*-diene), have been studied extensively in recent years. Many studies (10, 35, 36, 37, 38) suggest that the degree of phase separation depends on the length of, the number of, and the chemical composition of the blocks.

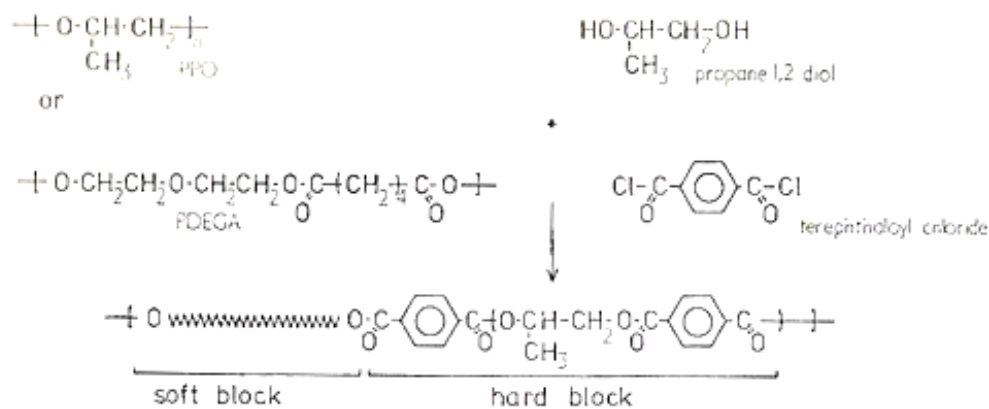
The aim of the present study was to prepare multiblock polymers having a suitable combination of these three variables so that the change between a polymer showing phase separation to one behaving as a homogeneous mixture could be observed in a thermoplastic. In this intermediate region, properties similar to those of IPNs might be expected. The properties of these materials also would be of interest in comparison with the semicrystalline multiblock polymers such as the segmented polyurethanes and poly(ether-*b*-ester)s that are available commercially.

Approach

A series of amorphous condensation multiblock polymers were prepared comprising poly(oxypropylene oxyterephthaloyl) (3IGT), a brittle glassy solid, as the hard block and poly(oxypropylene) (PPO) or poly(di(oxyethylene)oxyadipoyl) (PDEGA) as the soft block.

Polymer Preparation

The polymerization method used was a polycondensation of terephthaloyl chloride, propane 1,2-diol, and the appropriate soft block (Figure 1) in a 20% solution in dry 1,2-dichloroethane at 85°C for 48 hours.



Block molecular weights

soft block MW = prepolymer MW = x

wt % prepolymer 25 50 75

hard block MW $2x$ x $\frac{1}{2}x$

Figure 1. Preparation of the multiblock polymers

The molar ratio of soft block to propane 1,2-diol and terephthaloyl chloride was $A:B:(A+B) \times 1.01$. Four moles of pyridine per mole of acid chloride was added to react with the HCL produced in the polymerization. Pyridine hydrochloride was removed at the end of the reaction by washing with dilute HCl.

Multiblock polymers were prepared from PPO prepolymers with molecular weights 400, 1000, 2000, 3000, and weight fractions of PPO 25, 50, and 75%. PPO "homopolymers" were prepared by reacting PPO prepolymer with terephthaloyl chloride alone. A sample also was prepared containing 50% PDEGA of mol wt 2550.

The polymers were characterized by viscometry and GPC analysis. The viscosities were measured as 0.5 g dl⁻¹ solutions in 1,1,2,2-tetrachloroethane at 25°C. Gel permeation chromatograms were measured in dimethylacetamide solution at 80°C. A typical chromatogram of 3IGT homopolymer is given in Figure 2. There is a small secondary peak at high elution volume. This secondary peak appeared in all of the polymers prepared from terephthaloyl chloride, and the elution volume of the maximum was constant, independent of the presence of PPO. This secondary peak is thought to be attributable to residual terephthalic acid and cyclic dimer and trimer that are formed in the early stages of polycondensation reactions (15). The simple construction shown in Figure 2 was used to remove the low-molecular-weight peak, and the chromatograms were converted to poly(styrene) molecular weight using a computer program supplied by the Department of Chemistry, University of Manchester. All results are given in Table I. The overall molecular weight of these polymers is estimated as 12,000–20,000 from viscosity

Table I. Data

Polymer	Soft Block		Wf_{PPO}	Wf_{TE}	\bar{S}
	(mol wt)	(approx wt frac)			
PPO/3IGT	400	100	0.720	0.280	
		75	0.526	0.420	2.03
		50	0.421	0.500	1.53
		25	0.215	0.637	1.17
	1000	100	0.869	0.131	
		75	0.678	0.266	1.65
		50	0.469	0.415	1.22
		25	0.226	0.584	1.08
	2000	100	0.930	0.070	
		75	0.724	0.216	1.35
		50	0.548	0.341	1.15
		25	0.314	0.511	1.06
3000	100	0.951	0.049		
	75	0.680	0.242	1.18	
	50	0.486	0.380	1.08	
	25	0.255	0.544	1.03	
PDEGA/3IGT	2550	100	0.944	0.059	
		50	0.55	0.329	1.11
3IGT/C	—	—	0	0.718	

^a T_g of 3IGT homopolymer with the same molecular weight as the hard block.

^b Single-point viscosities $0.5 \text{ g} \cdot \text{dl}^{-1}$ in tetrachlorethane at 25°C .

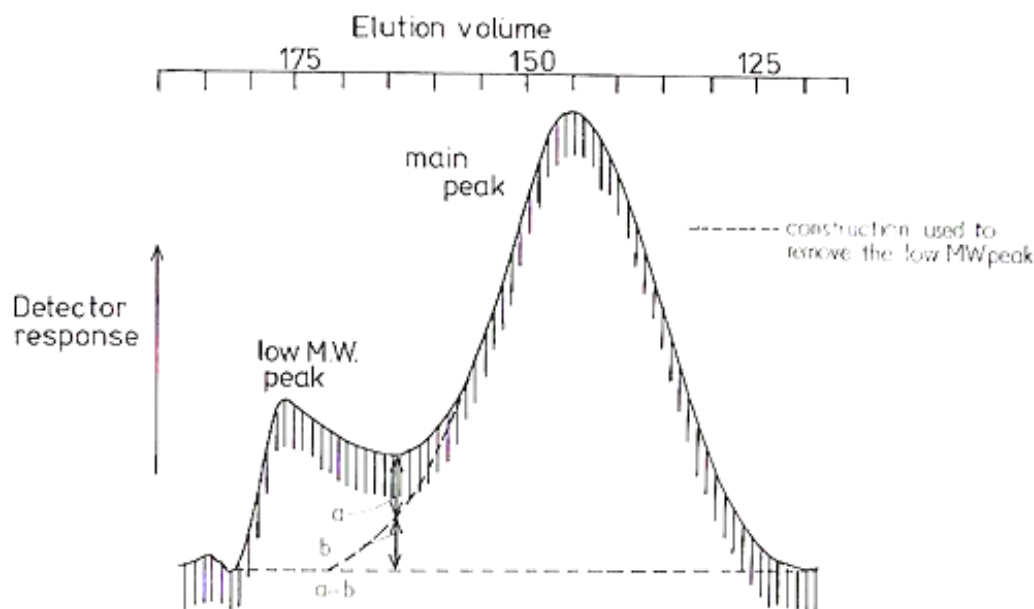


Figure 2. GPC chromatogram of 3IGT prepared using terephthaloyl chloride (3IGT/C)

for the Polymers

\bar{g}	Hard Block		Tetrachloroethane $0.5/\text{dl } g^{-1}$	GPC in DMA ^c ($\bar{M}_n \times 10^{-3}$ \bar{M}_w/\bar{M}_n)		T_g/K ($\tan \delta$ max)
	\bar{H}_n	$T_g/^\circ C^a$				
			0.401	56	2.03	251
2.04	536	8	0.615	71	2.26	271
2.96	728	13	0.548	59	2.18	283
7.39	1640	12	0.375	29	1.97	315
			0.550			229
2.59	643	9	0.842	92	1.49	248
5.54	1260	32	0.556	63	2.61	267
16.39	3607	71	0.455	54	2.28	308
			0.423	34	2.03	221
3.98	926	22	0.502	49	2.46	235
8.38	1820	46	0.490	39	2.22	260
21.84	4553	78	0.413			308
			0.425	30	1.83	219
				(14.30) ^d	(2.99) ^d	
7.13	1566	41	0.398	33	2.06	234
15.77	3368	68	0.494	52	2.29	—
43.02	8852	90	0.391	64	2.12	317
			0.415	31	1.74	241
10.25	2199		0.425	37	2.16	261
			0.319	51		363 (DSC)

^c GPC in dimethyl acetamide solution at 80°C, poly(styrene) calibration.

^d GPC in dimethyl acetamide solution at 80°C, poly(oxyethylene) calibration.

and GPC data (16, 17). The ratio of \bar{M}_w/\bar{M}_n in terms of poly(styrene) molecular weight was 1.7/2.6; a similar range has been reported for poly(oxytetramethylene oxyterephthaloyl-co-oxysebacoyl) random copolymers (22).

Naming System

The multiblock polymers are distinguished by soft-block type, the molecular weight of the soft block, and the appropriate weight fraction of the soft block. Therefore, PPO 3000/50 refers to a PPO/3IGT block polymer, prepared from a PPO prepolymer with molecular weight of 3000 and containing approximately 50% by weight of PPO. PPO 3000/100 represents a PPO "homopolymer" prepared by linking a PPO prepolymer mol wt 3000 with terephthaloyl chloride. 3IGT/C refers to 3IGT prepared from terephthaloyl chloride and 3IGT/M to melt-polymerized 3IGT using dimethyl terephthalate.

Block Molecular Weights

The sequence distribution of monomer residues in copolycondensation reactions of this type has been studied in detail by Peebles (18, 39). If all monomers are assumed to have equal reactivity and if the reaction has gone to completion, the number-average sequence length of 3IG residues (\bar{g}) is given by:

$$\bar{g} = \frac{[3IG]_0 + [PPO]_0}{[PPO]_0} \quad []_0 = \text{initial concentration}$$

Similarly, for PPO residues:

$$\bar{s} = \frac{[3IG]_0 + [PPO]_0}{[3IG]_0}$$

The sequence lengths follow a "most probable" distribution; values of \bar{s} and \bar{g} for each polymer are given in Table I. Because of the high molecular weight of PPO, \bar{s} is generally less than two, so the molecular weight of the soft block will be taken as the molecular weight of the PPO prepolymer. The molecular weight of the hard block (\overline{Hn}) is given by:

$$\overline{Hn} = 206 \bar{g} + 148$$

206 = mol wt of repeat unit

148 = mol wt of oxyterephthaloyl residue

To a first approximation, a multiblock polymer prepared from PPO with molecular weight x containing 50% PPO by weight will have a hard-block molecular weight of x ; one containing 25% will have a hard-block molecular weight of $2x$; and one containing 75% PPO a hard-block of $x/2$ (Figure 1).

Melt Polymerization of 3IGT

Low-molecular-weight 3IGT homopolymers (1000–8000) were prepared by melt polycondensation (19) using dimethyl terephthalate, and the T_g s were measured using DSC. Molecular weights up to 4000 were measured by end-group analysis, higher molecular weights were estimated by extrapolation of the T_g /mol wt curves (16, 17). An attempt was made to prepare PPO 3000/50 by the same method, but the PPO formed a separate layer in the melt before high-molecular-weight polymer was formed and the attempt was abandoned.

Mechanical Testing

The room-temperature properties of the polymers varied from viscoelastic liquids for 100% PPO through soft (50% PPO) and tough (25% PPO) solids to a brittle glass (3IGT). A torsional braid pendulum was used as the dynamic mechanical-test method, because only with a supported sample could the polymers be tested on one apparatus, and only small amounts of the polymers were available. The torsional pendulum was based on Gillham's design (20), with the inertia disc motion being detected by a Hall-effect device. The glass substrate consisted of two glass rovings twisted around each other by "doubling" to give a uniform bundle of 1680 filaments that acted as support for the polymer, with the ends of the glass trapped in crimp tags. The polymer was cast onto the braid as a 30% solution in a suitable solvent, and the solvent removed slowly at atmospheric pressure and under vacuum to leave a composite consisting of a polymer matrix and the glass support. The volume fraction of polymer in the braid (ϕ_p) was calculated from the weight per unit length of the braid, knowing the amount of glass present and assuming a polymer density of 1.0.

The braids were tested from -100°C upwards at a heating rate of 1°C min^{-1} and a frequency of ≈ 1 Hz, using an inertial weight of 4.55×10^{-5} kg m^2 . The damped sine waves were processed by hand to give log decrement and modulus. The radius of the sample was calculated from the weight per unit length, as above, with the additional assumption that the sample was a right circular cylinder and that there were no voids in the sample.

The Torsional Braid as a Composite Material

In any discussion of the results from torsional braid analysis it is important to establish what contribution the glass will make to the properties of the composite. The principal effects of the glass are illustrated in Figure 3. The modulus and log-decrement curves for a sample of poly(styrene) and a braid of poly(styrene) were cast from a toluene solution and tested using two different inertia weights. The sample of pure poly(styrene) was tested on a conventional inverted torsional pendulum (21). The modulus and damping curves are in fairly close agreement at low temperatures and in the first part of the transition region but beyond the maximum in log decrement, there are major differences between the curves. Most important is in the observation that at high temperatures the modulus of the composite tends to a constant limiting value. Above the glass-transition temperature, the modulus of the poly(styrene) matrix becomes very small, so this limiting

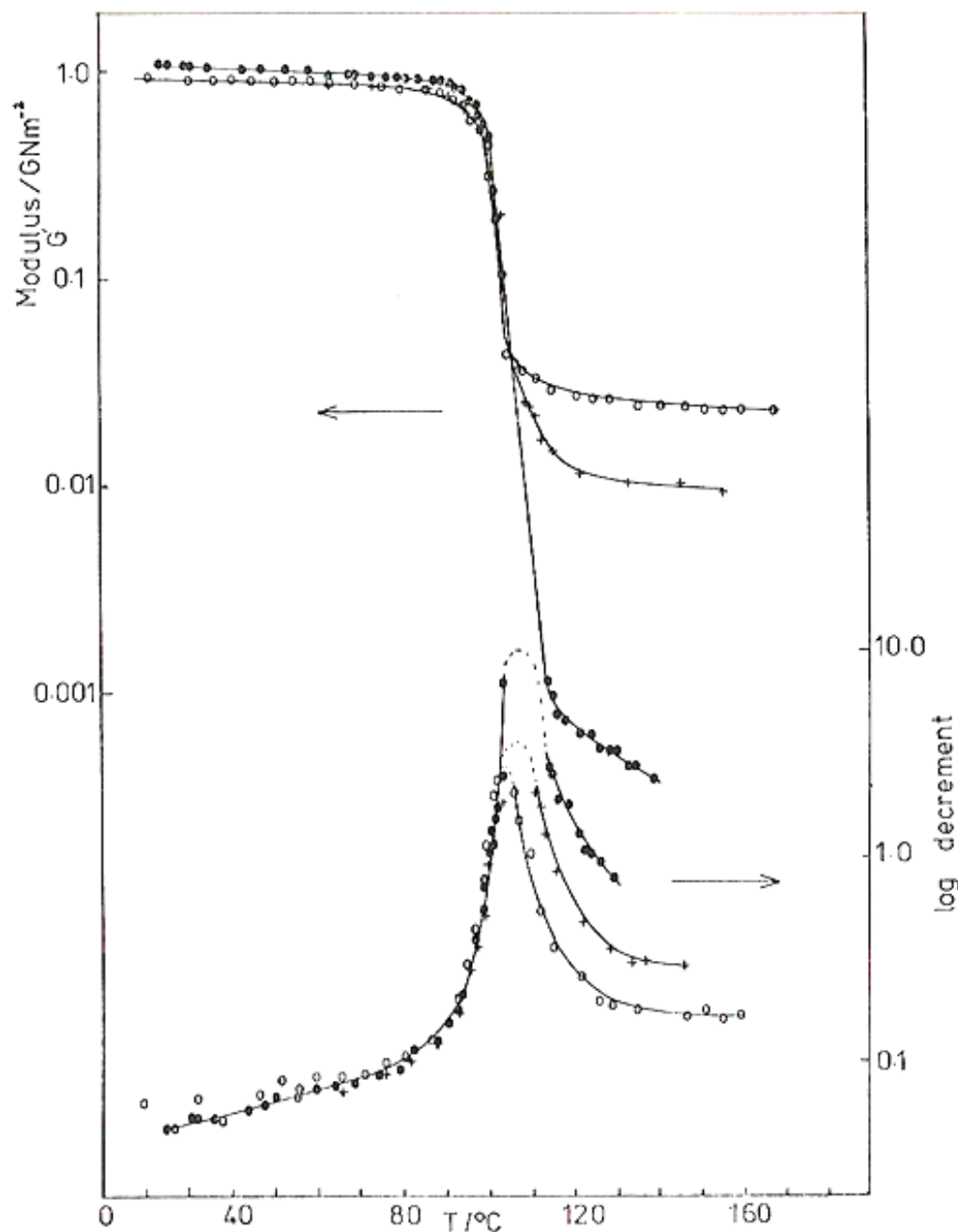


Figure 3. A comparison between the mechanical properties of poly(styrene) and a poly(styrene) braid. (●) Compression-molded sample of PS. PS braid cast from toluene, $\phi_p = 0.78$. (○) $I_1 = 4.55 \times 10^{-5} \text{ kg m}^{-2}$. (+) $I_2 = 8.8 \times 10^{-6} \text{ kg m}^{-2}$.

modulus must correspond to the torsional rigidity of the glass trapped between the two crimp tags. The damping of the braid also tends to a low constant value at high temperatures for the same reason. The effect of the different inertia weights (I_1 , I_2) is probably a result of the change in tension in the sample, altering the configuration of the glass. As a result of the change in the damping curves at high temperatures, the T_g as defined by the maximum in log decrement has been shifted down in

temperature by about 5°C. The important conclusion of this discussion is that below the maximum in log decrement the results from the braid are comparable with a sample of pure polymer, but above the maximum the properties of the glass substrate dominate the composite braid.

The value of the modulus of the poly(styrene) braid at low temperature is smaller than the sample of pure poly(styrene) because the cross-section of the braid is rather irregular, and the approximation of an irregular cross-section by a circular one will inevitably lead to an underestimate of modulus (21). For this reason, the absolute values of the modulus of the multiblock polymers in Figures 4–10 are unreliable.

It should be noted that a $T_{L, L}$ would not be expected in this poly(styrene) braid sample because of its high molecular weight (approximately 100,000) (46). Also, this analysis of the composite structure of the braid supports Nielsen's (47) suggestion that $T_{L, L}$ arises solely from the residual elasticity of the glass. The torsional pendulum, braid, and $T_{L, L}$ will be discussed in more detail elsewhere (16, 17).

Properties of the Multiblock Polymers

Figure 4 shows the properties of PPO 3000/50 cast from methyl ethyl ketone (MEK) and toluene. The sample cast from MEK shows two equal-sized peaks in log decrement but in the sample cast from toluene, the high-temperature peak is much larger than the low-temperature peak. These variations are typical of a two-phase composite in which the morphology is controlled by the casting solvent (21). All of the other samples were cast from solutions in MEK. The results for all of the other samples are summarized in Figures 5, 6, 7, 8, and 9. The series of polymers prepared from PPO mol wt 400 all showed a sharp transition region similar to poly(styrene). A sample of melt polymerized 3IGT of mol wt 2750 also is shown. As the block molecular weight increases, the transition region becomes progressively broader until in PPO 3000/50 a double peak is formed. The breadth of the transition region in the samples prepared from high-molecular-weight PPO may be taken as evidence of some form of phase separation.

Small Angle X-Ray Results

Small angle x-ray pictures of melt-pressed films of PPO 3000/50 and 3000/25 cast from MEK showed a well-defined diffraction ring giving a measure of the size of the inhomogeneities in the material. A MEK-cast film of PPO 3000/50 gave identical results. A sample of PPO 2000/25 gave a diffuse scattering after three times the exposure of the PPO 3000/50, indicating the presence of irregular inhomogeneities with less difference in electron density between the scattering regions (Figure 10).

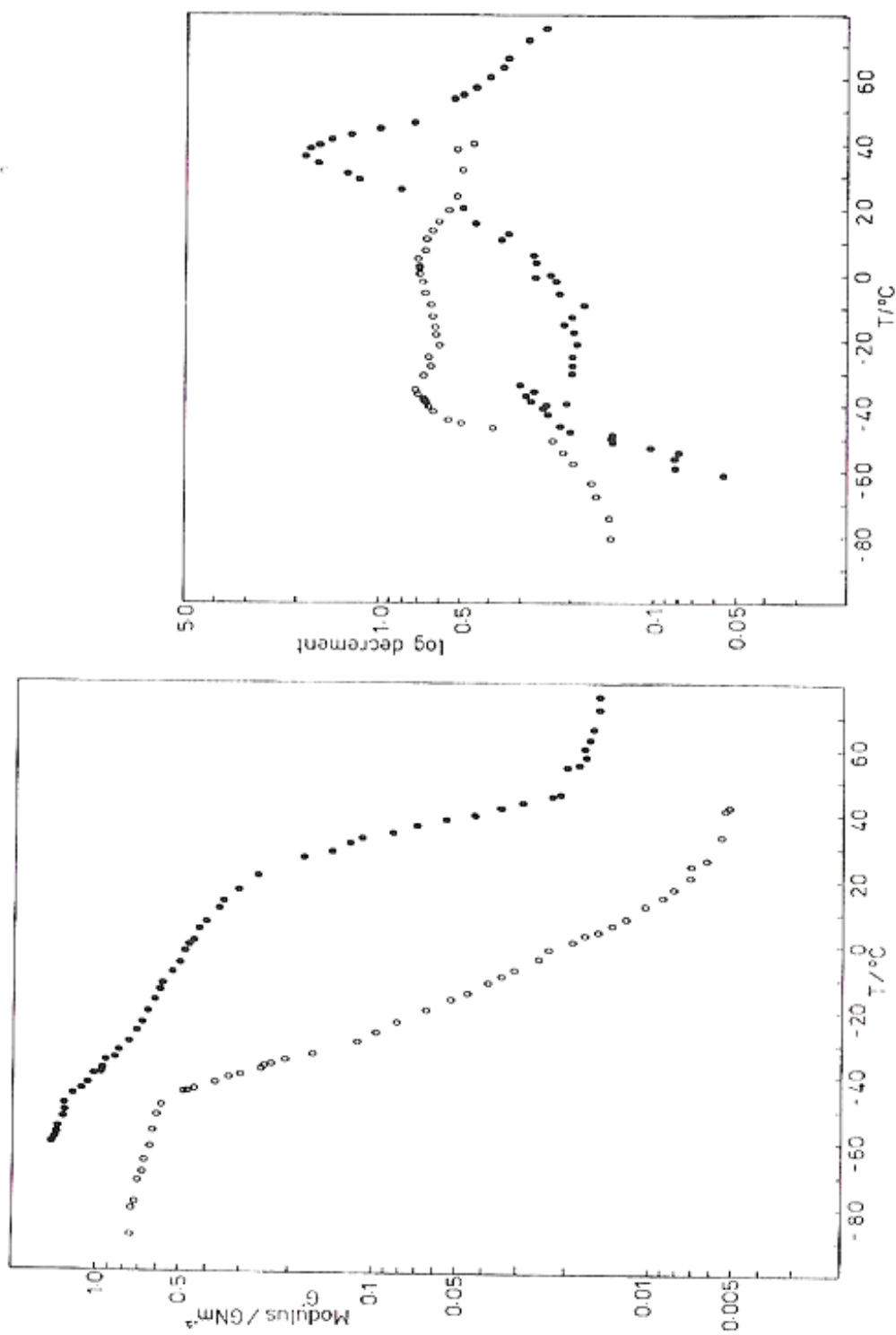


Figure 4. The effect of casting solvent on the properties of PPO 3000/50. (○) Cast from MEK, $\phi p = 0.87$. (●) Cast from toluene, $\phi p = 0.66$.

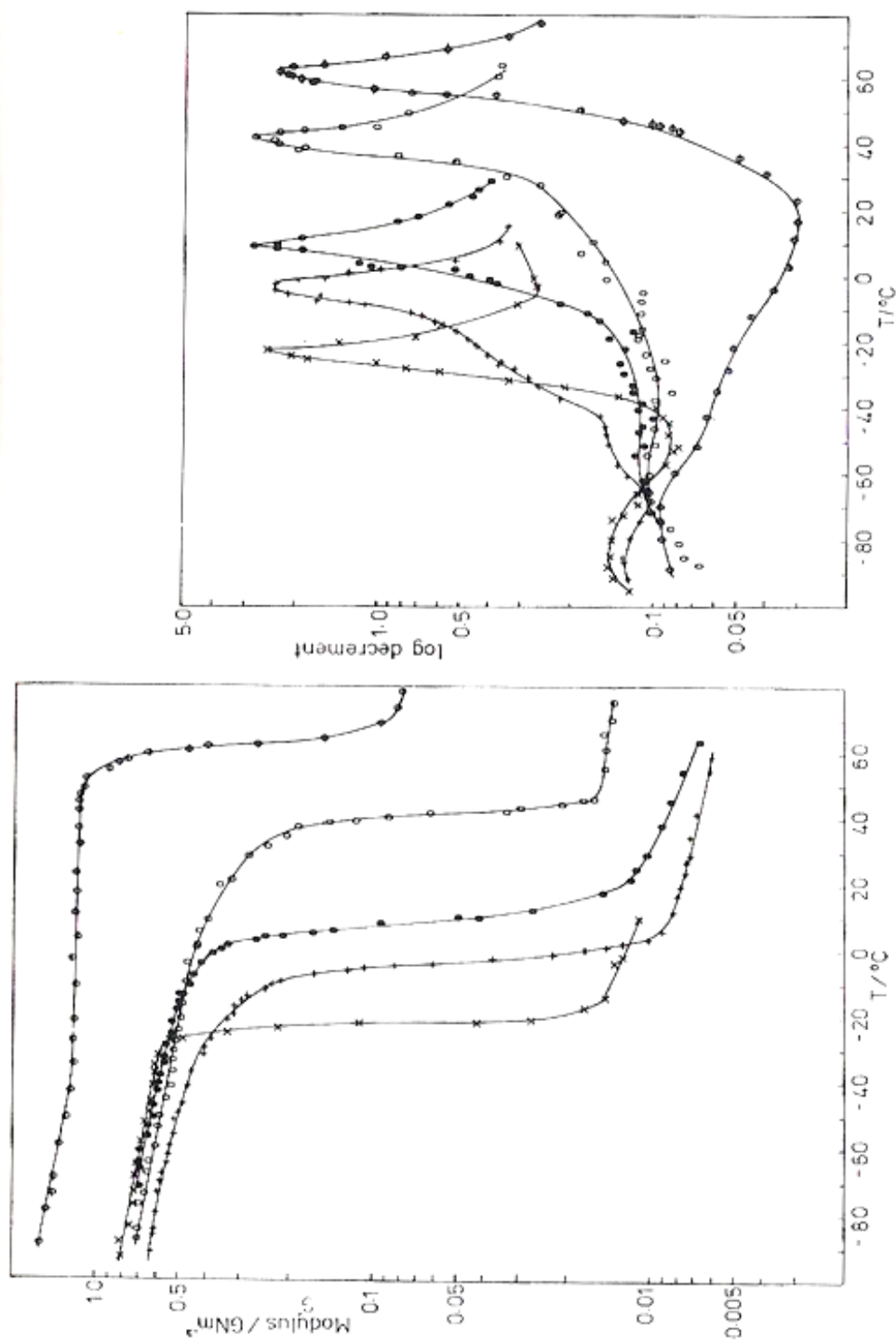


Figure 5. The properties of polymers prepared from PPO of mol wt 400. (x) PPO 400/100, $\phi p = 0.84$. (+) PPO 400/75, $\phi p = 0.86$. (●) PPO 400/50, $\phi p = 0.83$. (○) PPO 400/25, $\phi p = 0.8$. (○) 3IGT/
 $M \phi p = 0.61$.

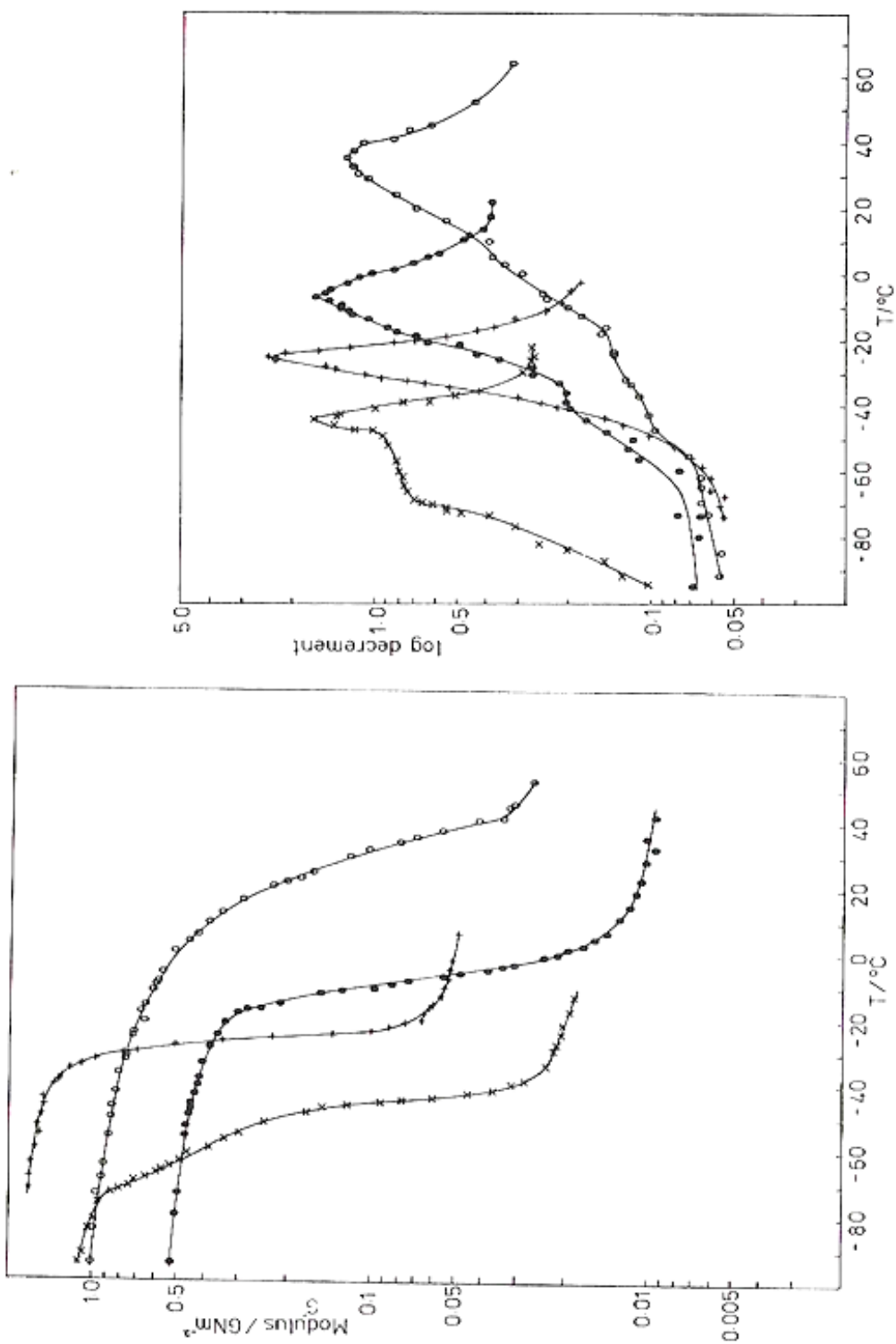


Figure 6. The properties of polymers prepared from PPO of mol wt 1000. (\times) PPO 1000/100, $\phi_p = 0.79$. ($+$) PPO 1000/75, $\phi_p = 0.86$. (\bullet) PPO 1000/50, $\phi_p = 0.85$. (\circ) PPO 1000/25, $\phi_p = 0.79$.

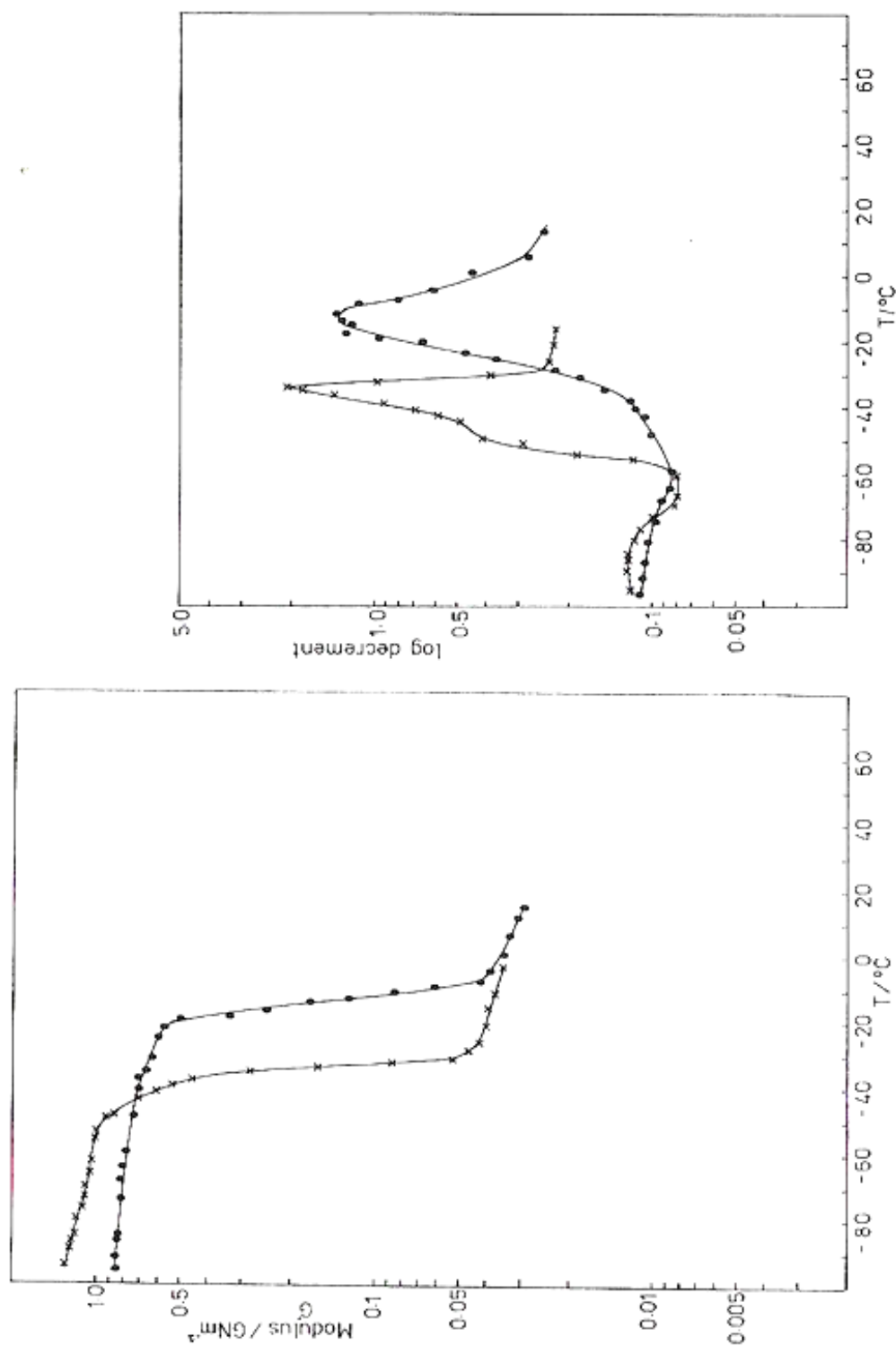


Figure 8. The properties of polymers prepared from PPO of mol wt 3000. (x) PPO 3000/100, $\phi_p = 0.68$. (+) PPO 3000/75, $\phi_p = 0.68$. (●) PPO 3000/50, $\phi_p = 0.87$. (○) PPO 3000/25, $\phi_p = 0.79$.

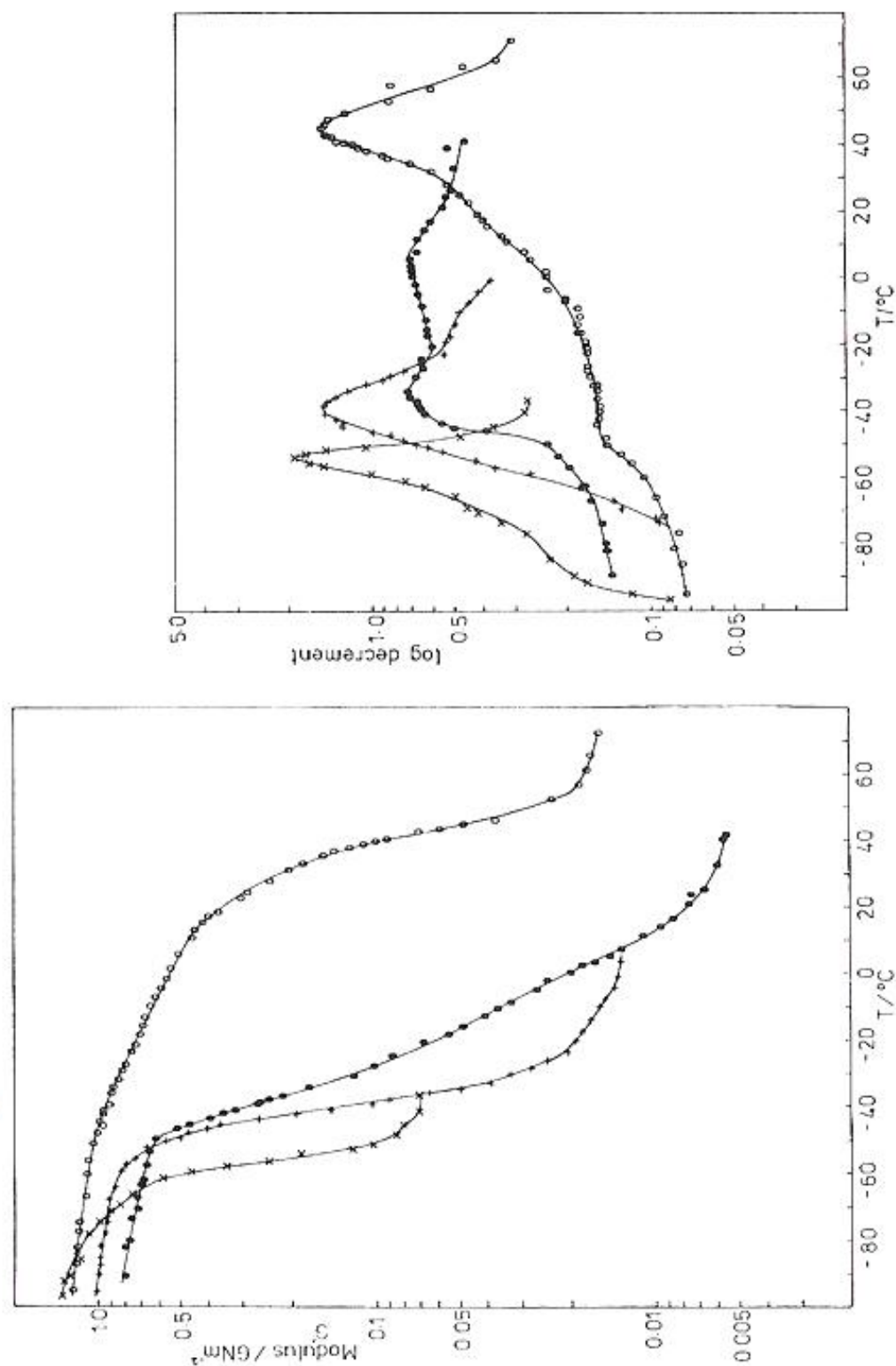


Figure 9. The properties of polymers prepared from PDEGA of mol wt 2550. (X) PDEGA 2550/100, $\phi_p = 0.74$, (●) PDEGA 2550/50, $\phi_p = 0.79$.

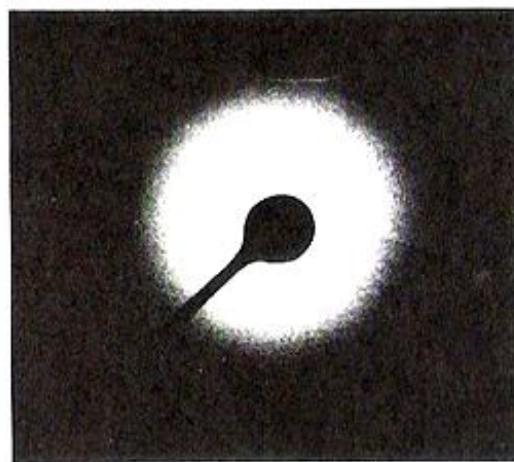
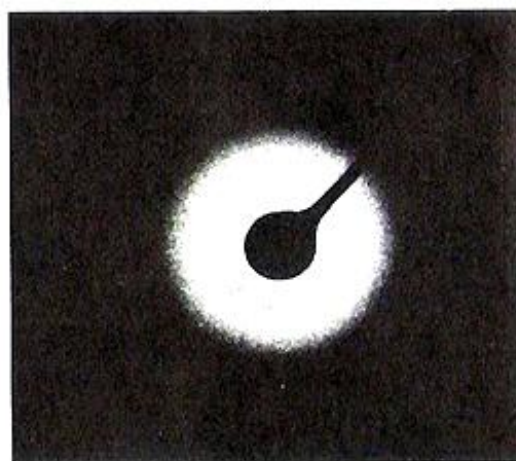
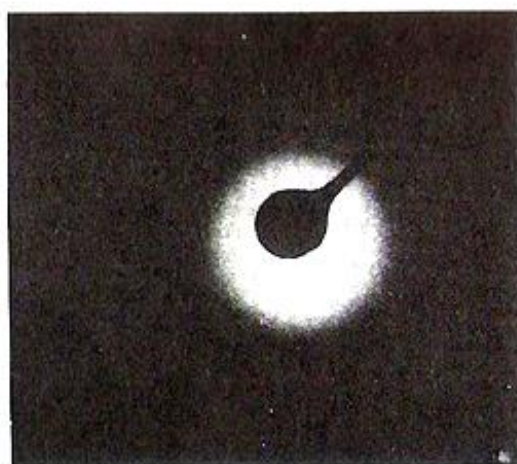


Figure 10. Small angle x-ray pictures of the multiblock polymers. (top) PPO 3000/25, 24-hr exposure. (middle) PPO 3000/50, 24-hr exposure. (bottom) PPO 2000/25, 50-hr exposure.

Discussion

The small angle x-ray results show that regular inhomogeneities were present in samples PPO 3000/50 and 3000/25. The crucial question in any study of this type is what sort of phase separation has occurred in these polymers? The blocks, whole chains with slightly different composition, or low-molecular-weight impurities could have separated out. It is well established that the size of the inhomogeneities produced by phase separation of the blocks in a block copolymer are controlled by the molecular weight of the blocks (24, 25) because the joints between the blocks must lie in the interfacial region between the domains (Figure 11).

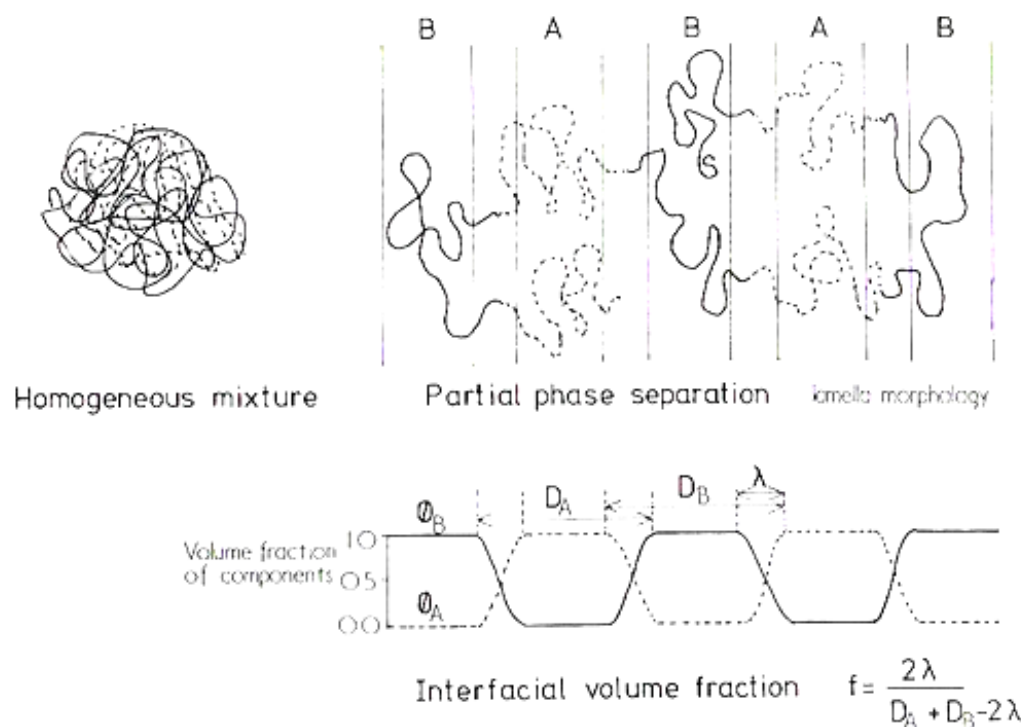


Figure 11. Diagram of phase separation of a multiblock polymer

Table II shows the Bragg spacing and the sum of the unperturbed block dimensions for PPO 3000/50 and 3000/25, $\langle r_o \rangle$ was estimated from the values for PPO, and poly(oxyethylene oxyterephthaloyl) given in the literature (26). As the average block molecular weight increased, the Bragg spacing also increased and is the same order of magnitude as the unperturbed block dimensions. This can be taken as a clear indication that phase separation of the blocks has occurred in PPO 3000/50 and 3000/25.

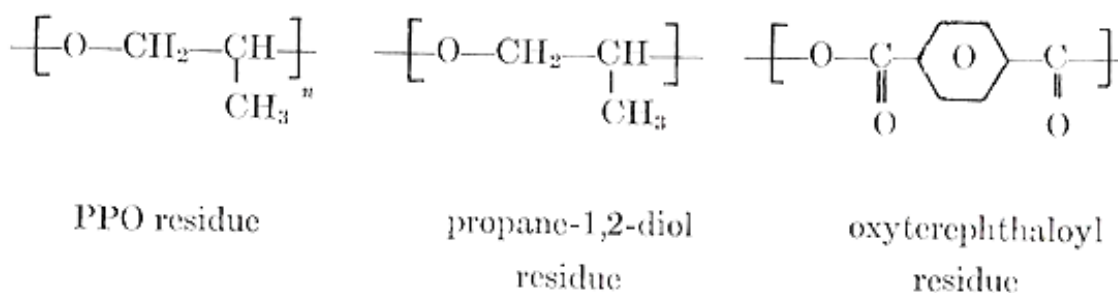
Table II. Small Angle Scattering Data

Polymer	PPO (mol wt)	3IGT (mol wt)	Average (mol wt)	R ^a	Bragg Spacing
PPO 3000/50	3000	3368	3184	10.09 nm	14.4 nm
PPO 3000/25	3000	8852	5926	13.3 nm	19.2 nm

$$^a R = \langle r_o \rangle_{\text{PPO}} + \langle r_o \rangle_{\text{3IGT}}; \frac{\langle r_o \rangle}{M^{1/2}} = 0.087 \text{ nm.}$$

T_g/Composition Relation

If the polymers do not show phase separation they can be considered as random copolymers. The T_g of a random copolymer solely depends on composition if the molecular weight is sufficiently high for T_g to be independent of molecular weight (27). It has been established that the molecular weight of 3IGT/C is high enough to make the T_g independent of molecular weight (16, 17). In these copolymers the residues of three monomers appear. To define the composition of all of the PPO-based copolymers by one weight fraction, the contributions of the other two components must be added together.



Defining T_g by the maximum in $\tan \delta$, a plot of T_g vs. weight-fraction PPO residues (Wf_{PPO}) and T_g vs. weight-fraction oxyterephthaloyl residues (Wf_{TR}) can be compared in Figure 12. The plot against Wf_{TR} shows the majority of the points lying on a curve; those lying off the curve are indexed and correspond to those polymers with unsymmetrical maxima in log decrement. The points lying on the line are those with single, sharp maxima in log decrement and the 50% copolymers that have symmetrically broadened peaks in log decrement. The simple T_g -composition relationship for polymers with a single sharp maxima in log decrement is evidence that they are behaving like homogeneous random copolymers. Similarly, those polymers that do not lie on the line must be phase separated because the regions producing the maxima in log decrement have a different composition to the original polymer. The

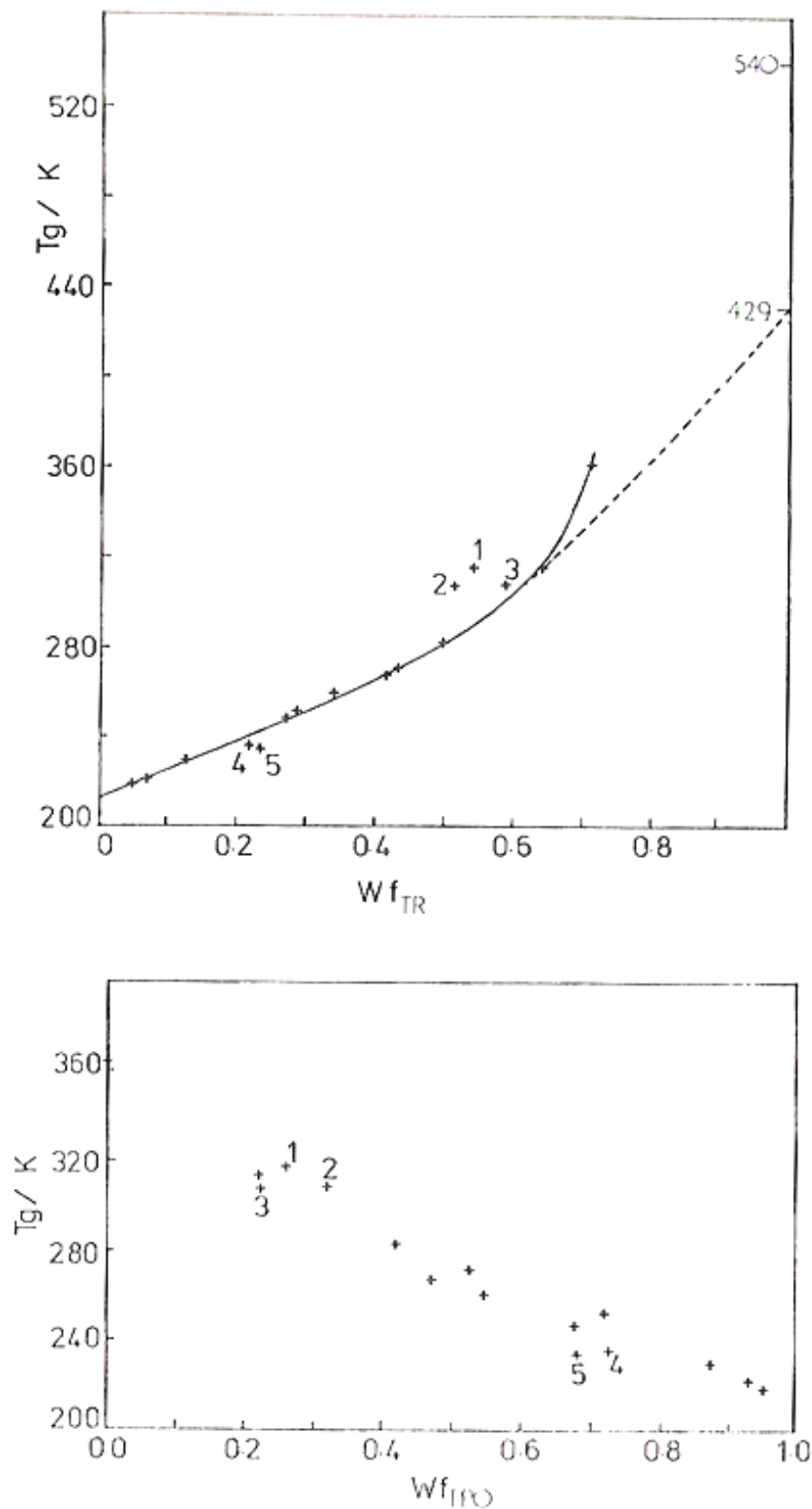


Figure 12. T_g against copolymer composition defined by weight fraction oxyterephthaloyl and PPO residues. (1) PPO 3000/25, (2) PPO 2000/25, (3) PPO 1000/25, (4) PPO 2000/75, (5) PPO 3000/75.

T_g of poly(1,4 phenylene terephthaloyl) has been reported as 540 K (41). All of the points could not be fitted by the general T_g /composition formula by Wood (27), even when the T_g of poly(oxyterephthaloyl) was allowed to float. If the point for 3IGT was omitted, the rest of the points were fitted by the Fox equation (40), shown as a dashed line in Figure 12.

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

The T_g against weight-fraction PPO-residues graph shows a general T_g /composition curve with significantly more scatter than the Wf_{TR} plot (Figure 12). In defining the copolymer by Wf_{PPO} , the T_g is assumed independent of variations in the ratio of terephthaloyl-to-diol residues. In the case of Wf_{TR} , the T_g is assumed independent of variations in the ratio of PPO to diol by weight. Because PPO and propane 1,2-diol have the same repeating unit, their contribution to chain flexibility will be the same and hence Wf_{TR} provides the best measure of the composition of the polymers.

Analysis of the Mechanical Properties

The morphology and composition variation found in the phase-separated materials can be deduced from the shape and position of the damping curves. Two-phase composites are generally found in three basic morphologies: phase 1 dispersed in a matrix of phase 2, phase 2 dispersed in a matrix of phase 1, and a lamella morphology in which both phases are continuous. If phase 1 is a rubber and phase 2 a glass, then the modulus of the composite depends crucially on the morphology. If one of the phases is dispersed, the continuous phase dominates the dispersed phase, leading to an impact-resistant glass in the first case and a filled rubber in the second. In the case of a lamella morphology, both phases contribute equally to the modulus of the composite in a logarithmic law of mixing. Consequently, the size of the $\tan \delta$ peaks corresponding to the T_g of the phases also will depend on the morphology. The $\tan \delta$ peak for the continuous phase is larger than that of the dispersed phase, and a lamella morphology will lead to two equally sized peaks. This may be seen in the experimental data on poly(styrene-*b*-diene) polymers (28, 45) and follows from the relationship between $\tan \delta$ and the differential of the log of the real modulus. The relationship between $\tan \delta$ and the viscoelastic functions is discussed in Refs. 6, 16, 21, and 44, and the properties of composites have been reviewed in Ref. 21.

The following assumptions are made in analyzing the mechanical property results. In a completely phase-separated system, the T_g of the soft block is the same as the T_g of the PPO "homopolymers," e.g., PPO 3000/100. The T_g of the hard block of a given molecular weight is the same as the T_g of the free homopolymer with same molecular weight. The overall glass-rubber transition is considered to arise from incremental contributions of regions of different composition combined together as in a conventional composite.

PPO 400/75/50/25, 1000/75 (Figures 5 and 6)

These all show a single sharp maxima in log decrement and a simple relationship between T_g and composition, indicating that they are homogeneous materials.

PPO 1000/50, 2000/50 (Figures 6 and 7)

Both samples show a symmetrically broadened peak in log decrement. The width of the peak in PPO 2000/50 indicates that regions with widely varying composition are present and the narrower peak in PPO 1000/50 indicates that less phase separation has occurred in this sample. The fact that the maxima of the log-decrement peaks lie on the T_g /composition curve and these peaks are symmetrically broadened indicates that regions with the same composition as the original polymer are most common and the regions of varying compositions are arranged in a lamella morphology in which they all contribute equally to the overall properties of the composite.

PPO 3000/50 (Figures 4 and 8)

The presence of two peaks in log decrement shows that phase separation has developed sufficiently for regions rich in PPO and 3IGT to be most common. The differences between the temperatures of these two maxima and the T_g s of the blocks if complete phase separation had occurred are shown in Table III. The two peaks in the MEK-cast sample are indicative of a lamella-like morphology. The difference in the size of the peaks in the toluene-cast sample indicates a 3IGT matrix containing PPO-rich dispersed regions.

This dependence of block polymer property on casting solvent also is seen in poly(styrene-*b*-diene) polymers (28). Theoretical work (23) has shown that the thermodynamically most stable morphology for a diblock polymer containing 50% of each component is a lamella morphology. For this reason MEK was chosen for the tests on all other polymers.

Table III. T_g Values of the Phase-Separated Regions

Sample	Maxima in Log. Dec.	
	High Temp (°C)	Low Temp (°C)
PPO 3000/50: MEK Cast	5	-35
PPO 3000/50: Toluene Cast	35	-40
PPO 3000/100	—	-54
3IGT/M mol wt 3368	68	—

PPO 3000/25 (Figure 8)

PPO 3000/25 produces a small angle x-ray diffraction ring but only a single maxima in log decrement with a long, low-temperature tail. The composition of the regions producing the maximum in log decrement are different from the composition of the parent polymer. The fact that a second peak in log decrement is not observed for the PPO-rich regions would suggest that there is a 3IGT-rich matrix that dominates the mechanical properties, with PPO-rich dispersed regions producing the long, low-temperature tail. Block copolymers containing 25% of one component generally form dispersed phases (23, 29); also, the low-temperature transition in PPO 3000/50 cast from toluene is only just visible, so it is reasonable that the reduction in PPO weight fraction would lead to the disappearance of this transition.

PPO 2000/25, 1000/25 (Figures 6 and 7)

From the same evidence as above it may be deduced that there is a continuous 3IGT matrix with dispersed PPO-rich regions. The narrowing of the $\tan \delta$ maxima indicates that the differences in composition get progressively smaller with lower PPO molecular weight, in line with the small angle x-ray results.

PPO 3000/75, 2000/75 (Figures 7 and 8)

The shifting of the maxima in log decrement to low temperatures is the evidence for phase separation. These polymers probably show a long low-temperature tail that has been obscured by the limiting modulus of the braid.

Sources of Uncertainty

The major source of uncertainty in these results comes from the influence the glass substrate might have on phase separation; preferential absorption of one of the blocks onto the surface of the glass (32) would obviously affect phase separation. The low-molecular-weight peak observed in the GPC curves also could affect the results. In so far as the T_g /composition curve (Figure 12) shows a direct T_g /composition relation with symmetrical displacement of the 25% and 75% copolymers above and below the line, there is no evidence to suggest that these other factors are affecting phase separation. The detailed analysis of torsional pendulum data is also rather uncertain at high damping values (33), as is the analysis of multiphase systems by single-frequency isochronal data (34). For most of the curves discussed here, the maximum in log decrement is about 1.0, and these effects are likely to be "second order" compared with the effect of the braid and the large differences observed between the samples.

Conclusions

The sequence of curves in Figures 5-11 shows the stages of partial phase separation that occur in an amorphous multiblock polymer with polydisperse hard blocks. By systematically varying the block molecular weights and copolymer composition, the breadth and shape of the damping peaks changed in a systematic and predictable way. Controlled partial phase separation would appear to be a powerful way to tailoring polymer properties for a particular application.

The difference between these polymers and conventional Hytrel-type poly(ether-b-esters) is emphasized by the attempt to polymerize PPO 3000/50 by melt polycondensation, the method normally used for Hytrel (42). Complete phase separation occurred, showing that the incompatibility between PPO/3IGT is much greater than poly(oxytetramethylene-b-oxytetramethylene oxyterephthaloyl).

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Literature Cited

1. Ungar, E. E., Hatch, D. K., *Prod. Eng.* (1961) 32, 41.
2. Ball, G. L., Salyer, I. O., *J. Acoust. Soc. Am.* (1966) 39, 663.
3. Sperling, L. H., Thomas, D. A., *National Technical Information Service Tech. Bull.* (1975) AD/A-003 852.

4. Hiejbocur, J., "Physics of Non-crystalline Solids," p. 231, J. A. Prins, Ed., North Holland, Netherlands, 1965.
5. Manson, J. A., Sperling, L. H., "Polymer Blends and Composites," Plenum, New York, 1976.
6. McCrum, N. G., Read, B. E., Williams, M. L., "Anelastic and Dielectric Effects in Polymeric Solids," Wiley, New York, 1967.
7. Kollinsky, F., Markert, G., "Multicomponent Polymer Systems," N. A. Platzer, Ed., *ADV. CHEM. SER.* (1971) **99**, 175.
8. Kraus, G., Rollman, K. W., "Multicomponent Polymer Systems," N. A. Platzer, Ed., *ADV. CHEM. SER.* (1971) **99**, 189.
9. Mizumachi, J., *Adhesion* (1970) **2**, 292.
10. Meier, D. J., *Polym. Prepr.* (1974) **15**, 171.
11. Helfand, E., *J. Chem. Phys.* (1975) **62**, 99.
12. Krause, S., *Macromolecules* (1970) **3**, 84.
13. Leary, D. F., Williams, M. C., *J. Polym. Sci., Polym. Phys. Ed.* (1974) **12**, 265.
14. Allport, D. C., James, W. H., "Block Copolymers," p. 208, Applied Science, United Kingdom, Division of Elsevier, New York, 1973.
15. Flory, P. J., "Principles of Polymer Chemistry," Cornell University, Ithaca, NY, 1953.
16. Watts, M. P. C., Ph.D. Thesis, University of Manchester, Institute of Science and Technology, 1977.
17. Watts, M. P. C., White, E. F. T., unpublished data.
18. Peebles, L. H., *Macromolecules* (1974) **9**, 58.
19. Goodman, I., Rhys, J. H., "Polyesters," Vol. 1, IUIfe Books, London, 1965.
20. Gillham, J. K., *A.I.Ch.E. J.* (1974) **20.6**, 1066.
21. Neilsen, L. E., "Mechanical Properties of Polymers and Composites," Vol. 1, Dekker, 1974.
22. Marrs, W., Still, R. H., Peters, R. H., *J. Appl. Polym. Sci.*, in press.
23. Meier, D. J., "Block and Graft Copolymers," J. J. Burke, V. Weiss, Eds., Syracuse University, Syracuse, NY, 1973.
24. Kromer, H., Hoffmann, M., Kampf, G., *Ber Bunsenges. Phys. Chem.* (1970) **74**, 859.
25. Helfand, E., Wasserman, Z. R., *Polym. Eng. Sci.* (1977) **17**, 73.
26. "Polymer Handbook," 2nd ed., J. Brandrup, E. H. Immergut, Eds., Wiley-Interscience, 1975.
27. Wood, L. A., *J. Polym. Sci.* (1958) **28**, 319.
28. Miyamoto, S., Kodama, K., Shibayama, K., *J. Polym. Sci., Polym. Phys. Ed.* (1970) **8**, 2095.
29. Folkes, M. J., Keller, A., "Physics of Glassy Polymers," R. N. Howard, Ed., p. 548, Applied Science, 1973.
30. Yip, H. K., Williams, H. L., *J. Appl. Polym. Sci.* (1976) **20**, 1217.
31. Sacher, E., *J. Polym. Sci., Polym. Phys. Ed.* (1968) **6**, 1935.
32. Lipatov, Y. S., *Adv. Polym. Sci.* (1977) **22**, 1.
33. Struick, L. C. E., *Rheol. Acta.* (1967) **6**, 119.
34. Tschoegl, N. W., Cohen, R. E., *175th National ACS Meeting, California, 1978*.
35. Toporowski, G. M., Roovers, J. E. L., *J. Polym. Sci., Polym. Chem. Ed.* (1976) **14**, 2233.
36. Kraus, G., Rollman, K. W., *J. Polym. Sci., Polym. Phys. Ed.* (1976) **14**, 1133.
37. Senich, G. A., Macknight, W. J., *ADV. CHEM. SER.* (1979) **176**, 97.
38. Matzner, M., Noshay, A., Robeson, L. M., Merriam, N., Barclay, R. McGrath, J. E., *App. Polym. Symp.* (1973) **22**, 143.
39. Peebles, L. H., *Macromolecules* (1974) **7**, 872.
40. Fox, T. G., *Bull. Am. Phys. Soc.* (1956) **1**, 123.

41. Frosina, V., Levita, G., Landis, J., Woodward, A. E., *J. Polym. Sci.* (1977) **15**, 239.
42. Cella, R. J., *J. Polym. Sci., Part C* (1973) **42**, 727.
43. Sperling, L. H., "Recent Advances in Polymer Blocks, Blends and Grafts," p. 152, Plenum, New York, 1974.
44. Schwartzl, F. R., Struick, L. C. E., *Adv. Mol. Relaxation Processes* (1967) **1**, 210.
45. Robinson, R. A., White, E. F. T., "Block Copolymers," S. L. Aggarwal, Ed., p. 123, Plenum, New York, 1970.
46. Stadniki, S. J., Gillham, J. K., Boyer, R. F., *J. Appl. Polym. Sci.* (1976) **20**, 1245.
47. Neilsen, L. E., *Polym. Eng. Sci.* (1977) **17**, 713.

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