

Block Copolymers Derived from 2,2' Azobis (2-Cyanopropanol). II. Morphologies and Properties of Poly(urethane-block-methyl methacrylate) and Poly(urethane-block-styrene)

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ABSTRACT: The two-phase structure of polymer blends or block copolymers prepared with polyurethane macroazo initiators and methyl methacrylate or styrene have been studied. The synthesis of these block copolymers was reported in a previous article (Cheikhalard, et al. *J Appl Polym Sci* 1998, 70, 613–627). One of the difficulties encountered with the copolymers is their characterization in order to know if the products of the syntheses of monomers A and B are true block copolymers P(A-*b*-B) or homopolymer blends Polymer A/polymer B (PA/PB) with a certain concentration of block copolymers. Preceding studies have shown that the polymers obtained previously with polyurethane macroazo initiators (reacted with methyl methacrylate or styrene) are primarily block copolymers. In the present study, the morphology, the thermal and the rheological properties of the crude block copolymers and of some of their fractionated products are investigated and compared with their corresponding blends of homopolymers having the same composition. Results displayed in this report show clearly that the shear storage modulus G' of our polymers at the rubbery plateau are higher than the corresponding polymer blends. They confirm previous analyses (by steric exclusion chromatography and nuclear magnetic resonance) (Cheikhalard, et al. *J Appl Polym Sci* 1998, 70, 613–627) aimed at proving the copolymer morphology of our polymers. The morphology of blends was first studied by optical microscopy. A decrease in the dispersed phase size is observed when the percentage of polyurethane content increases. Transmission electron micrographs obtained for mixtures and pure block copolymers show a microheterogeneous structure as seen by optical microscopy. These two structures were also characterized by differential scanning calorimetry and by dynamic viscoelastic measurements. A decrease in the glass transition temperature of hard blocks (polymethyl methacrylate or polystyrene), in comparison with the pure homopolymers, in polymer blends and in block copolymers was observed and can be attributed to the presence of a small amount of soft blocks in the hard phase. A quantitative evaluation of the degree of phase separation was obtained by differential scanning calorimetry showing the presence of an interphase. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 437–446, 2000

Key words: polyurethane; polymethyl methacrylate; polystyrene; block copolymers, morphology; phase separation

INTRODUCTION

Block copolymers represent an important class of multiphase materials and they have received con-

siderable attention in the last 30 years. Much of the interest in these polymers has arisen because of their rather remarkable microphase morphology. This structure imparts many of the interesting and desirable properties of these block copolymers. Several studies have been reported on the synthesis and the compatibilizing action of block

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copolymers in immiscible polymer blends. Emulsifying activity of diblock or triblock copolymers has been widely used to solve the usual problems linked to weak interfacial adhesion of polymer blends. The addition of a compatibilizer,² such as a diblock copolymer, to polymer blends, in which one or other segment is identical or miscible with one or other constituent of the blends may be a useful means for increasing the interaction between the phases by the formation of an interphase.³ Lowering the interfacial tension promotes more stable and finer dispersion, which improves the mechanical properties. Block copolymers consisting of soft and hard segments offer many possibilities for tailor-made copolymers. As reported by Leibler et al.^{4,5} and Noolandi and Hong,⁶⁻⁸ the concentration and the morphology of such multiphase systems influences their behavior and can be controlled by alternating the block lengths,⁹ the molar mass distribution, and the nature of the blocks.

The two-phase structure of block copolymers in the solid state is also influenced by the chain conformation during the solvent casting process which is responsible for the formation of definite structures that are maintained in the solid state. The effect of these preset structures is ultimately reflected in changes of mechanical properties of the material and demonstrates that the presence of a liquid must also be considered as a structure controlling parameter.

Thermoplastic elastomers such as styrene-butadiene or styrene-isoprene diblock and styrene-butadiene-styrene (SBS) or styrene-isoprene-styrene (SIS) triblock copolymers have attracted attention and have been widely studied.¹⁰⁻¹² Block copolymers composed of polyester,¹³⁻¹⁵ polyamide,¹⁵⁻¹⁷ polyurethane,^{18,19} or polysiloxane,²⁰ with an additional polymer segment (various types of vinyl polymers) are highly attractive polymer materials. These varieties of block copolymers were prepared using macroazoinitiators. Little attention has been given to the study of the microphase structure of such block copolymers. It is important from an application standpoint to be able to understand and control the degree of microphase separation and its relation to morphology. A preceding article¹ describes the synthesis of poly(urethane-*b*-methyl methacrylate) [P(U-*b*-MMA)] or poly(urethane-*b*-styrene) [P(U-*b*-S)] using polyurethane macroazo initiators based on polyester segments. Those copolymers are a combination of soft polyurethane (PU) ester and hard polystyrene (PS) or polym-

ethyl methacrylate (PMMA) segments. Phase separation can be expected if the solubility parameters of the soft and the hard segments are sufficiently different, but also depend on the length of the individual polymer sequences. Either of the two phases can form the continuous or matrix phase depending on the composition and length of each sequence. The phenomenon of phase separation for block copolymers containing soft and hard segments has been proven by electron microscopy²¹⁻²⁴ and small angle X-ray scattering.²⁵ The two-phase structure can also be observed by differential scanning calorimetry (DSC)^{10,26} and by dynamic mechanical spectroscopy. Examination of the morphology of the resulting block copolymers is a good means of critically assessing the effectiveness of the synthetic method because the production of a highly ordered dual-phase morphology requires a very uniform molecular architecture with minimal contamination.

The present work is centered on the study of the morphology, thermal and viscoelastic properties of crude block copolymers directly from the synthesis, some of their fractionation products P(U-*b*-MMA) and P(U-*b*-S), and the corresponding polymer blends having the same composition. A common approach for determining the extent of phase mixing is first to compare the glass transitions of the fully amorphous block copolymers with those of the corresponding homopolymers. Then it is necessary to determine quantitatively the phase segregation ratio of the crude block copolymers by DSC. The change in heat capacity (ΔC_p) and the loss factor amplitude ($\tan \delta$) during α relaxation of the soft and hard phase were measured and are compared with the ΔC_p and $\tan \delta$ of the pure soft and hard phase of homopolymers.

EXPERIMENTAL

Block copolymers, P(U-*b*-S) and P(U-*b*-MMA), and polymer blends PU/PS or PMMA, having the same composition as the block copolymers used are those prepared in our previous article.¹ Their purification was performed by fractionating the crude copolymers. Some of the characteristics of the crude block copolymers and of their fractions are summarized in Table I.

Morphologies of the blends were studied using a phase contrast optical microscope. Cast films were used for optical microscopy studies. They were obtained from copolymer solutions (10% by weight) in 2-butanone. Samples for rheological

Table I Percentage of PU in the Copolymer (% PU), and in the Homopolymer PU (% PU_h), Average Molar Masses of Crude Polymers and of Their Fractions¹

Copolymer	% PU	% PU _h	\bar{M}_n (g/mol)	\bar{M}_w (g/mol)	$I_p = \bar{M}_w/\bar{M}_n$
PU	100.0	100	27	66	2.4
PMMA-3	0.0	0	123	471	3.8
PS-1	0.0	0	16	42	2.6
P(U- <i>b</i> -MMA)-1	27.9	6.0	94	286	3.0
Fraction 3	63.0	35.9	111	509	4.6
Fraction 4	30.2	4.8	160	671	4.2
Fraction 5	15.0	0.9	192	367	1.9
Fraction 6	13.8	0.8	140	223	1.6
Fraction 7	19.2	4.2	91	130	1.4
P(U- <i>b</i> -MMA)-2	38	ND	69	194	2.8
P(U- <i>b</i> -S)-1	51.0	18.6	55	131	2.4
Fraction 3	61.0	14.4	67	158	2.4
Fraction 4	61.3	8.8	67	229	3.4
Fraction 5	24.8	6.2	74	181	2.4
Fraction 6	21.3	3.7	83	182	2.2
P(U- <i>b</i> -S)-2	82.7	66.2	30	93	3.1
Fraction 1	26.4	~0	121	244	2.0
Fraction 2	32.2	~0	106	225	2.1
Fraction 3	80.1	72.0	73	112	1.5

ND, not determined.

testing were prepared by slow evaporation of the solvent, 2-butanone, at room temperature for 3 days, then under vacuum at 60°C for 24 h and finally compression-molded at 150°C [above the glass transition temperature (T_g) of the PS or PMMA block] for 1 h.

The microdomain structures were examined by transmission electron microscopy (TEM). Ultrathin sections of ca. 70-nm thickness were obtained by microtoming at -100°C with a Reichert Ultracut E low-temperature sectioning system (Reichert, NY, US). Electron microscopic observations were made with a Hitachi H-600 transmission electron microscope (Hitachi, Japan) operated at 80 kV.

The T_g and the change of heat capacity, ΔC_p , at T_g were recorded using a Perkin Elmer Pyris calorimeter (Perkin Elmer, Norwalk, CT, US). Standard aluminum sample pans were used. Samples of ca. 10 mg were weighed directly in the pan, and an empty pan was used as a reference. Both pans were heated at a heating rate of 10°C/min in inert atmosphere (helium).

A Rheometrics Solid Analyzer (RSA II) (Rheometric Scientific, Piscataway, New Jersey, US) was used to obtain the dynamic mechanical spectra (elastic modulus E' , loss modulus E'' , and loss factor amplitude $\tan \delta$ as a function of temperature) from -100 to 150°C at 1 Hz. The tension

mode on 100- to 200- μ m thick films was considered for such studies. Measurements were done in a temperature steps mode (i.e., the properties were measured for a constant temperature after 3 min as soak time).

A Rheometrics Dynamic Analyzer (RDA II) (Rheometric Scientific, Piscataway, New Jersey, US) equipped with parallel plates was also used. The dynamic mechanical spectra (storage modulus G' , loss modulus G'' , and $\tan \delta$ as a function of temperature) from 170°C down to 100°C for polymers, based on PMMA segments, and from 150°C down to 80°C for polymers based on PS segments were recorded at 1 Hz with a cooling rate of 2°C/min. The plate diameter was 8 mm. The angular deformation was 0.3% when the matrix phase is PMMA or PS, and 1% when the matrix phase is soft PU.

RESULTS AND DISCUSSION

Block copolymers P(U-*b*-S) and P(U-*b*-MMA) were synthesized by radical polymerization with PU macroazoinitiator (PUMAI).¹ The synthesis yielded block copolymers P(U-*b*-S) and P(U-*b*-MMA) with more or less homopolymer PU (PU_h). The fractionation of the crude mixtures yielded

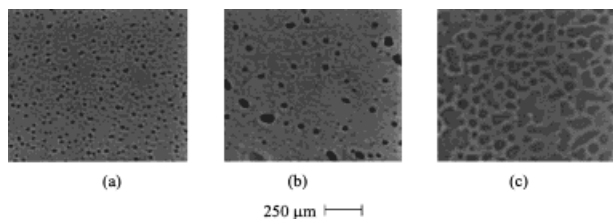


Figure 1 Morphologies of polymer blends obtained by optical microscopy. (a) PU/PMMA-1 (28/72, w/w); (b) (PU/PMMA)-2 (38/62 w/w); and (c) (PU/PS)-1 (51/49 w/w).

several fractions of pure block copolymers. Table I gives the percentage of PU in the copolymer PU (% PU) and in the homopolymer PU (% PU_h). It also gives the average molar mass of crude polymers and of their fractions. The morphologies of blends PU/PMMA and PU/PS and some of their corresponding crude block copolymers having the same mass composition were examined first by an optical microscope with a magnification of 500 and are shown in Figures 1 and 2. At this scale, no phase separations were observed for the three crude block copolymers. For polymer blends, the bright area represents the PMMA or PS-rich domain whereas the dark area indicates the PU-rich domain. In the case of PU/PMMA blends, the sizes of the dispersed domains were reduced when the PU content decreased [Fig. 1(a and b)].

The TEM micrographs of P(U-*b*-MMA)-1, P(U-*b*-S)-1 crude block copolymers and of fraction 4 of P(U-*b*-MMA)-1 and fraction 1 of P(U-*b*-S)-2 “pure block copolymers” are given in Figure 2. As observed in our previous work, crude block copolymers directly issued from the synthesis are in fact blends of block copolymers and homopolyurethane (Table I). Figures 2(a) and (c) correspond to crude block copolymer P(U-*b*-MMA)-1 containing 4.8% of homopolymer PU and to a fraction of this copolymer with almost the same composition but with larger average molar masses and a lower concentration of only 3% of homopolymer PU. Figure 2(a) shows dispersed phases for the crude block copolymer with sizes in the range 0.2–4 μm that are much bigger than those observed in Figure 2(c) (0.1 μm) for the purified fraction. According to these TEM observations, it can be assessed that the block copolymer could behave as if it were not miscible with the corresponding homopolymer PU. Some of the block copolymer should be present in the interfacial regions as a surfactant between the PU dispersed phase and the block copolymer. Moreover, by analogy with polymer mixtures,²⁷ the high polydispersity of the

fraction can also prevent the formation of a highly ordered structure even if its homopolymer PU_h content is lower than in the crude sample.

The electron micrograph of the crude block copolymer P(U-*b*-S)-1 (corresponding to 18.6 parts of PU and 81.4 parts of pure triblock copolymer) is shown in Figure 2(b) and shows PU-rich particles, with diameters in the range $\phi = 0.1 - 0.3 \mu\text{m}$, dispersed in a PS-rich continuous phase.

When the homopolymer PU_h has been removed as in fraction 1 of P(U-*b*-S)-2 [Figure 2(d)], the size of the dispersed phase decreases drastically even if the average molar masses \bar{M}_n and \bar{M}_w double. As two phase structures have been observed by OM and TEM, they can be characterized using other techniques such as DSC or thermomechanical analyses.

DSC measurements of crude block copolymers showed two T_g s corresponding to their hard and soft blocks. The T_g s of homopolymers PU (T_g^S) and PS or PMMA (T_g^H) were found by DSC at -32, 104, and 122°C, respectively (Table II). The T_g of the PU soft block in crude P(U-*b*-S) and P(U-*b*-MMA) block copolymers was found to be slightly higher than the one of the pure homopolymer whereas the values ob-

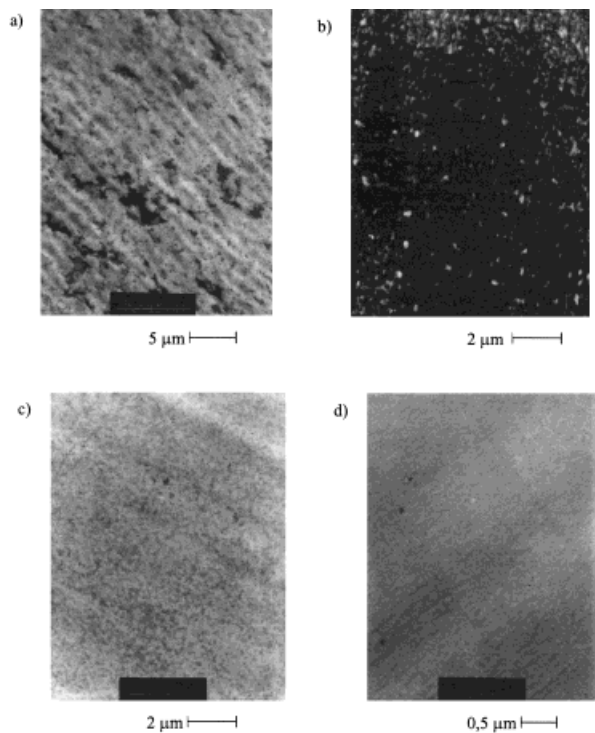


Figure 2 Micrographs of block copolymers obtained by transmission electron microscopy. (a) P(U-*b*-MMA)-1; (b) P(U-*b*-S)-1; (c) fraction 4 of P(U-*b*-MMA)-1; (d) fraction 1 of P(U-*b*-S)-2.

Table II T_g and ΔC_p of the Soft and Hard Segments of the Block Copolymers and of their Homologous Homopolymers

Copolymer	% PU	$T_g^{(S)}$	$\Delta C_p^{(S)}$	$T_g^{(H)}$	$\Delta C_p^{(H)}$
PU _h	100.0	-32	0.440	—	—
PMMA-3	0.0	—	—	122	0.194
PS-1	0.0	—	—	104	0.294
P(U- <i>b</i> -MMA)-1	27.9	-30	0.121	107	0.125
P(U- <i>b</i> -MMA)-2	38.0	-30	0.190	109	0.093
P(U- <i>b</i> -S)-1	51.0	-30	0.220	92	0.141
P(U- <i>b</i> -S)-2	82.7	-29	0.280	92	0.054

tained for the hard segments (PS and PMMA) were lower than their corresponding homopolymers (Table II). These differences indicate there is some PU in the PS or PMMA phases and PMMA or PS in the PU phase. These results are in agreement with TEM analyses of P(U-*b*-MMA)-1 and P(U-*b*-S)-1 [Fig 2(a and b)] which are showing two phases. Similar results have been found by elastic modulus measurements vs temperature at 1 Hz for P(U-*b*-MMA)-1 (28 wt % PU content), and P(U-*b*-MMA)-2 (38 wt % PU content) (RSAII measurements) (Fig. 3). These two α relaxation temperatures are separated by a pseudo plateau for E' . The level of this plateau decreased from 2×10^9 to 8×10^8 Pa when the PU content in the block copolymer increased. Similar results were found by Bhowmick et al.²⁸ for block copolyamides having soft and hard segments. The amplitude of the loss factor ($\tan \delta$) and the T_g for the hard segments for all samples with different percentage of PU can be better determined by the Rheometrics Dynamic Analyser (RDAII at 1 Hz) from 170°C down to 100°C for polymers contain-

ing PMMA segments and from 150°C down to 80°C for polymers containing PS segments. These results show the relaxation associated with the glass transition of the hard segment. As expected, the α relaxation of hard segments for crude block copolymers, as estimated from the curves in Figure 4, were a few degrees lower compared with PMMA or PS homopolymers (Table III and IV). Dynamic mechanical properties of crude block copolymers were compared with their corresponding blends having the same PU content. The behavior of block copolymers is similar to the polymer blends: the bigger the amount of PU, the smaller values for E' and a tendency for higher values for $\tan \delta$. Tables III and IV show clearly that the shear storage modulus G' of P(U-*b*-MMA)-1, P(U-*b*-MMA)-2, and P(U-*b*-S)-1 (crude block copolymers, having a high percentage of block copolymer in the mixture) (Table I) at the rubbery plateau is higher than the corresponding polymer blend having the same PU content. This difference in the behavior of each kind of sample having the same PU content and rather close

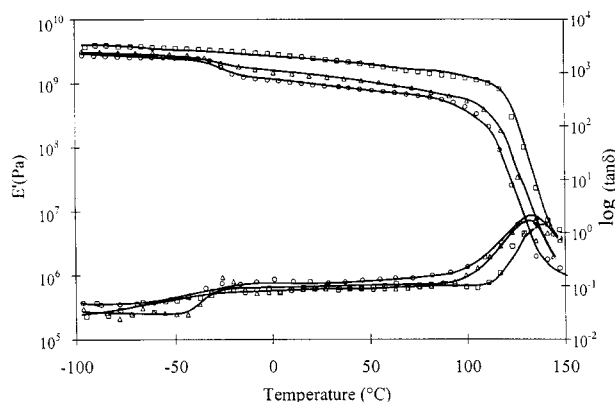
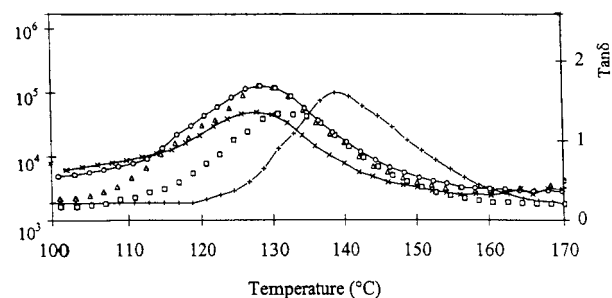
**Figure 3** Storage modulus E' and loss factor $\tan \delta$ curves for PMMA-3, P(U-*b*-MMA)-1, and P(U-*b*-MMA)-2 at 1 Hz. □, PMMA-3'; △, P(U-*b*-MMA)-1; ○, P(U-*b*-MMA)-2.**Figure 4** Dynamic mechanical spectra of the block copolymers based on polyurethane and polymethyl methacrylate and their corresponding polymer blends, having the same PU content, at 1 Hz. — + —, PMMA-3; — × —, (PU/PMMA)-1 blend 28 : 72 w/w; □, P(U-*b*-MMA)-1; — ○ —, (PU/PMMA)-2 blend 38 : 62 w/w; △, P(U-*b*-MMA)-2.

Table III G' Modulus and Maximum $\tan \delta$ Amplitude Values Measured at 170°C at 1 Hz for PMMA-3, Crude Diblock and Triblock Copolymer P(U-*b*-MMA) and Polymer Blends PU/PMMA

Copolymer	PU (%)	$\tan \delta$ Amplitude at T_α	T_α^H (Onset) (°C)	T_α (at $\tan \delta$ Maximum) (°C)	G' at 170°C (10 ⁵ Pa)	Continuous Phase
PMMA-3	0.0	1.66	125	139	5.03	PMMA
P(U- <i>b</i> -MMA)-1	27.9	1.32	113	128	1.48	PMMA
P(U- <i>b</i> -MMA)-2	38.0	1.68	109	133	1.29	PMMA
(PU/PMMA)-1	27.9	1.35	115	128	0.68	PMMA
(PU/PMMA)-2	38.0	1.68	112	128	0.81	PMMA

average molar masses is consistent with a difference in their morphologies. The $\tan \delta$ curves of polymer blends show a broader transition than the crude block copolymers indicating extensive phase mixing (Fig. 4).

The amplitude of $\tan \delta$ values and the physical aspect of blends and block copolymers based on PU and PS or PMMA are given in Tables III and IV. The continuous phase, observed by optical microscopy, for block copolymers and polymer blends based on PU and PMMA is formed by PMMA hard phase segments. Conversely, in the case of block copolymers and polymer blends based on PU and PS segments, the PS continuous phase is obtained only for P(U-*b*-S)-1. The blend (PU/PS)-1 having the same PU content as P(U-*b*-S)-1 exhibits a soft continuous phase (PU). A phase inversion seems to be induced by block copolymer effect.

The PMMA-1 and P(U-*b*-MMA)-1 samples, except fractions 3 and 4, were analyzed by a Rheometrics Dynamic Analyser (RDA II) measurements to determine the position and the amplitude of $\tan \delta$ related to the hard phase relaxation. From Figure 5 and Table V, it can be noted that the relaxation (T_α^H onset and at $\tan \delta$ maximum) of the hard phase is about 10°C lower than that of PMMA-3 homopolymer. This shows there is par-

tial miscibility between both phases. Values of the storage modulus G' of block copolymers are slightly lower than that of PMMA-3 because of the presence of PU segments. Comparing G' curves temperature of the crude block copolymer with fractions 5–7 we can conclude that viscoelastic properties of crude block copolymers are not significantly affected by the presence of 6% PU homopolymer. Therefore, the crude block copolymer P(U-*b*-MMA)-1 can be used in some cases without further purification.

G' and $\tan \delta$ curves vs temperature of crude block copolymers P(U-*b*-S)-1 and P(U-*b*-S)-2 and some of their fractionation products are compared with PS-1 homopolymer (Figs. 6 and 7). The beginning of the hard phase relaxation (T_α^H , onset value) of crude block copolymers and the fractions studied were 10°C lower than that of PS-1 homopolymer (Table VI). This is correlated with the presence of a certain degree of phase mixing. From G' and $\tan \delta$ curves vs temperature for P(U-*b*-S)-1 and some of its fraction (Fig. 6), it can be noted that the presence of 18.5% of PU homopolymer does not affect significantly the viscoelastic properties of the block copolymers in comparison with “pure” fractions (fractions 5–7). This was not the case for P(U-*b*-S)-2 having higher PU content (Fig. 7). From Figure 7, the

Table IV G' Modulus and Maximum $\tan \delta$ Amplitude Values Measured at T_α at 1 Hz for PS-1, Crude Triblock Copolymer P(U-*b*-S) and Polymer Blends PU/PS

Copolymer	PU (%)	$\tan \delta$ Amplitude at T_α	T_α^H (Onset) (°C)	T_α^H (at $\tan \delta$ Maximum) (°C)	G' at 150°C (10 ⁴ Pa)	Continuous Phase
PS-1	0.0	2.85	108	115	19.90	PS
P(U- <i>b</i> -S)-1	51.0	2.34	101	112	5.80	PS
P(U- <i>b</i> -S)-2	82.7	2.57	103	112	0.40	PU
PU/PS-1	51.0	2.43	100	111	1.53	PU
PU/PS-2	82.7	2.43	102	115	0.20	PU

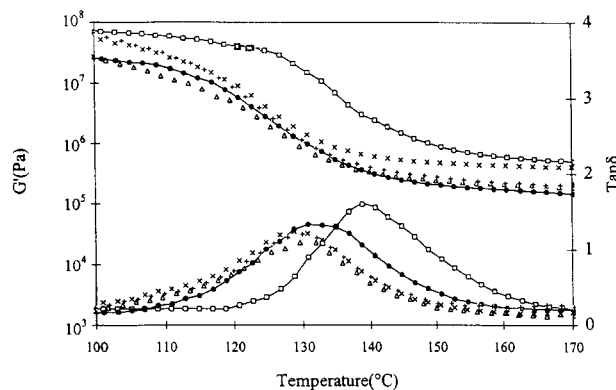


Figure 5 Dynamic mechanical spectra of PMMA-3, P(U-*b*-MMA)-1 and its corresponding fractions at 1 Hz. —□—, PMMA-3; —●—, P(U-*b*-MMA)-1; △, fraction 5; ×, fraction 6; +, fraction 7.

shear storage modulus of the crude block copolymer P(U-*b*-S)-2 and the fraction 3 are much lower than those of fractions 1 and 2. This phenomenon can be explained by the amount of PU content which is low for fractions 1 and 2 (26.4 and 32.2%, respectively) and higher, respectively 80.1 and 82.7%, for fraction 3 and the crude block copolymer. These results show clearly that dynamic mechanical measurements are in agreement with the percentage of PU in the copolymer that were found by previous SEC and ¹HNMR analyses.¹

The DSC, RSA, and RDA measurements show clearly that the T_g s of the styrene or methyl methacrylate segments in the copolymers are lower than those of homopolystyrene or homopolymethyl methacrylate. This behavior can be explained by phase mixing: some of the PU mixes in with the thermoplastic hard phase, lowering its glass transition. DSC measurements on the soft phase show a very slight increase in T_g value in comparison with the one of its corresponding homopolymer. We can therefore assume that the soft phase is formed by PU soft segments in which

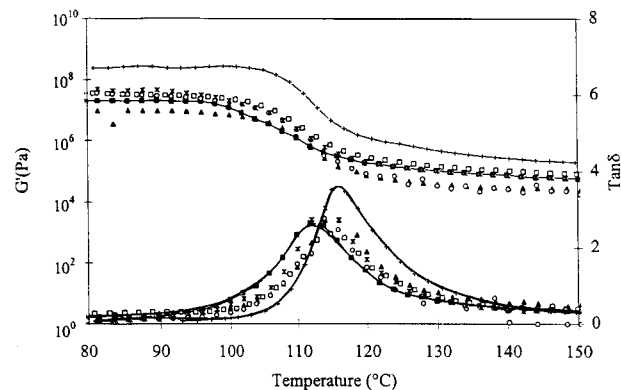


Figure 6 Dynamic mechanical spectra of PS-1, P(U-*b*-S)-1, and its corresponding fractions at 1 Hz. —+—, PS-1; —●—, P(U-*b*-S)-1; ▲, fraction 3; ○, fraction 4; □, fraction 5; ×, fraction 6.

a very small amount of hard segments is dissolved. These results are in agreement with other studies, such as the ones by Kim and Burns²⁹ on PS/polybutadiene blends; these authors have shown that the T_g of the PS phase in blends with polybutadiene is lower than the T_g of pure PS and varies. In the case of two-phase systems with partial miscibility, however, each phase consists mainly of one block, with only a small amount of the other block (composition close to 0 or close to 1). In the following discussion, the PU-rich phase is called the β soft phase whereas the PMMA-rich and PS-rich phases are the α hard phases. Taking into consideration that systems with partial miscibility usually do not have strong intermolecular interactions, the mass fraction of the β phase (M_β) can be determined using the Fox equation³⁰:

$$\frac{1}{T_g} = \frac{M_\beta^{(S)}}{T_g^{(S)}} + \frac{1 - M_\beta^{(S)}}{T_g^{(H)}} \quad (1)$$

where T_g is the glass transition temperature of the PU or thermoplastic rich phase in the blend or

Table V G' Modulus and Maximum $\tan \delta$ Amplitude Values Measured at 170°C at 1 Hz for PMMA-3, Crude Block Copolymer P(U-*b*-MMA)-1 and Its Fractions 5-7

Copolymer	PU (%)	$\tan \delta$ Amplitude	T_α^H (Onset) (°C)	T_α^H (at $\tan \delta$ Maximum) (°C)	G' at 170°C (10 ⁵ Pa)	Continuous Phase
PMMA-3	0	1.66	125	139	5.03	PMMA
P(U- <i>b</i> -MMA)-1	27.9	1.32	113	128	1.48	PMMA
Fraction 5	15.0	1.10	116	132	1.91	PMMA
Fraction 6	13.8	1.24	117	129	4.1	PMMA
Fraction 7	19.2	1.20	117	130	2.15	PMMA

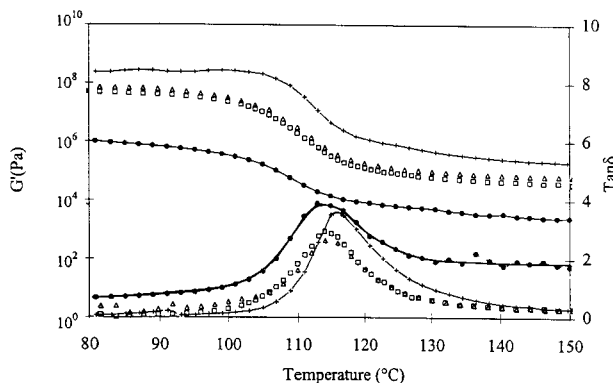


Figure 7 Dynamic mechanical spectra of P(U-b-S)-2 and its corresponding fractions at 1 Hz. — + —, PS-1; —●—, P(U-b-S)-2; Δ , fraction 1; \square , fraction 2; \circ , fraction 3.

block copolymer, $T_g^{(S)}$ and $T_g^{(H)}$ are the T_g s of the pure homopolymers.

Using the changes in heat capacities related to the two T_g s, we have attempted to determine quantitatively the phase segregation ratio. This method of calculation is the same as the one used by Wagener and Matayabas³¹ to determine the amount of segregated soft and hard segments in the case of microphase separation of segmented PUs.

For the β phase it can be written that the measured ΔC_p of the β phase $\Delta C_{p\beta}^{obs}$ results from a contribution of the PU segment $\Delta C_p^{(S)}$ and the thermoplastic (hard segment) $\Delta C_p^{(H)}$.

$$\frac{\Delta C_{p\beta}}{W_\beta} = M_\beta^{(S)} \Delta C_p^{(S)} + (1 - M_\beta^{(S)}) \Delta C_p^{(H)} \quad (2)$$

Where W_β = mass fraction of β phase and $M_\beta^{(S)}$ = mass fraction of PU in the β phase.

W_β can be determined using Eq. (2). $\Delta C_p^{(S)}$ and $\Delta C_p^{(H)}$ are obtained by measuring ΔC_p values for pure homopolymers and assuming that the values do not depend on the molar mass. We are also able to calculate the mass fraction of PU soft block in the β phase with respect to the total mass of PU in the mixture.

$$\% S_\beta = \frac{M_\beta^{(S)} / W_\beta}{M^{(S)}} \quad (3)$$

where $M^{(S)}$ is the mass fraction of PU (S) determined by $^1\text{H-NMR}^1$.

W_α , $M_\alpha^{(H)}$, and $\% H_\alpha$ can be obtained in the same manner, using Eqs.(1–3) for the α phase; $M_\alpha^{(H)}$ is the mass fraction of PMMA or PS in the α phase and W_α = mass fraction of α phase.

$$\% H_\alpha = \frac{M_\alpha^{(H)} W_\alpha}{M^{(H)}} = \frac{M_\alpha^{(H)} W_\alpha}{1 - M^{(S)}} \quad (4)$$

where $\% H_\alpha$ = the mass fraction of PMMA or PS^(H) in the α phase with respect to the total mass of PMMA or PS in the block copolymer and $1 - M^{(S)} = M^{(H)}$ is the mass fraction of PS or PMMA^(H) in the block copolymer determined by $^1\text{H-NMR}^1$.

Displayed in Tables II and VII are the T_g , ΔC_p , M_S , $M_\beta^{(S)}$, W_β , $\% S_\beta$, $M_\alpha^{(H)}$, W_α , and $\% H_\alpha$ for the crude block copolymers. Let us compare the mass fraction of PU^(S) in the β phase ($M_\beta^{(S)}$) in all crude block copolymers. All $M_\beta^{(S)}$ values obtained for the crude block copolymers studied are almost equal

Table VI G' Modulus and Maximum $\tan \delta$ Amplitude Values Measured at 150°C at 1 Hz for PS-1, P(U-b-S)-1 and Its Fractions 3–6, P(U-b-S)-2 and Its Fractions 1 and 2

Copolymer	PU (%)	$\tan \delta$ Amplitude	T_α^H (Onset) (°C)	T_α^H (at $\tan \delta$ Maximum) (°C)	G' at 150°C (10 ⁴ Pa)	Continuous Phase
PS-1	0	3.50	109	115	19.9	PS
P(U-b-S)-1	51.0	2.64	99	112	5.8	PS
Fraction 3	61.0	2.71	101	115	2.51	PS
Fraction 4	61.3	2.76	101	114	1.78	PS
Fraction 5	24.8	2.17	101	115	8.12	PS
Fraction 6	21.3	3.03	100	114	5.95	PS
P(U-b-S)-2	82.7	4.20	100	112	0.4	PU
Fraction 1	26.4	UD	104	114	6.4	PS
Fraction 2	32.2	UD	103	114	3.61	PS

UD, undetected.

Table VII Phase Composition of Crude Block Copolymers

Copolymer	$M_{\beta}^{(S)}$	$M_{\alpha}^{(H)}$	W_{β}	W_{α}	% S_{α}	% H_{β}
P(U- <i>b</i> -MMA)-1	0.98	0.95	0.28	0.60	97	78
P(U- <i>b</i> -MMA)-2	0.98	0.95	0.44	0.45	84	69
P(U- <i>b</i> -S)-1	0.97	0.94	0.50	0.47	96	89
P(U- <i>b</i> -S)-2	0.96	0.94	0.64	0.18	75	99

to 1 which means that the soft phase is formed essentially of PU soft blocks. In the same way, $M_{\alpha}^{(H)}$ values are ≈ 0.95 , showing that a small amount of PU segment is therefore dissolved in the hard phase.

The sum of the mass fraction of α and β phases, W_{α} and W_{β} , is below 1 for all crude block copolymers, which corresponds to a structure with two phases separated by an interfacial region. The percentage of hard segments in the α phase (% H_{α}) varies from 69 to 99% and the percentage of soft segments (% S_{β}) is in the range 75–97%. These values show that each phase is more or less partially miscible in the other. The percentages (% H_{α}) and (% S_{β}) seem to depend on the chain lengths, the PU content, etc.

CONCLUSIONS

Morphology and viscoelastic properties of crude block copolymers P(U-*b*-MMA), P(U-*b*-S) and some of their fractionation products were studied. The morphological structure of the materials is microheterogeneous with domain sizes depending on their homopolymer PU content and on the nature of the sequences (PU, PMMA, PS). The microphase separations were characterized by DSC. Two T_g s were observed and were slightly different from those of their respective homopolymers, indicating partial phase mixing. A description of phase composition was also performed using T_g and ΔC_p values of each segment and the results are also in agreement with a partial phase mixing.

Rheological studies showed that the presence of covalent bonds between both PU and PS or PMMA sequences in crude block copolymers increases their viscoelastic properties in comparison with polymer blends (PU/PS or PU/PMMA) with the same composition. Moreover, the presence of a small amount of PU homopolymer in crude block copolymers does not modify significantly their viscoelastic properties.

Because of C_p and T_g values obtained with DSC experiments, it was possible to calculate the compositions of the phases that are partially miscible. The percentage of hard segments in the α phase (% H) is in the range 69–99% and the one of soft segments in the β phase in the range 75–97%.

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REFERENCES

- Cheikhalard, T.; Massardier, V.; Tighzert, L.; Pascault, J. P. *J Appl Polym Sci* 1998, 70, 613–627.
- Thomas, S.; Prud'homme, R. E. *Polymer* 1992, 33, 4260–4268.
- Noolandi, J. *Polym Eng Sci* 1984, 24, 70–78.
- Leibler, L. *Makromol Chem, Macromol Symp* 1988, 16, 1–17.
- Ghosh, S.; Khastgir, D.; Bhowmick, A. K. *Polymer* 1998, 39, 3967.
- Noolandi, J.; Hong, K. M. *Macromolecules* 1984, 17, 1531.
- Noolandi, J.; Hong, K. M. *Macromolecules* 1982, 15, 482.
- Noolandi, J. *J Polym Sci* 1984, 24, 70.
- Creton, C.; Kramer, E. J.; Hadziioannou, G. *Macromolecules* 1991, 24, 1846–1853.
- Meyer, G. C.; Widmaier, J. M. *J Polym Sci, Polym Phys Ed* 1982, 20, 389–398.
- Aggarwal, S. L. *Polymer* 1976, 17, 938–956.
- Aggarwal, S. L.; Livigni, R. L. *Polym Eng Sci* 1977, 17, 498–505.
- Haneda, Y.; Terada, H.; Yoshida, M.; Ueda, A.; Nagai, S. 1994, 32, 2641–2652.
- Walz, R.; Heitz, W. *J Polym Sci, Polym Chem Ed* 1978, 16, 1807–1814.
- Matsukawa, K.; Ueda, A.; Inoue, H.; Nagai, S. *J Polym Sci, Part A: Polym Chem* 1990, 28, 2107–2114.
- Ueda, A.; Nagai, S. *J Polym Sci, Polym Chem Ed* 1984, 22, 1783–1787.
- Ueda, A.; Nagai, S. *J Polym Sci, Polym Chem Ed* 1984, 22, 1611–1621.

18. Kinoshita, H.; Tanaka, N.; Araki, T. *Macromol Chem* 1993, 194, 829–839.
19. Kinoshita, H.; Tanaka, N.; Araki, T. *Macromol Chem* 1993, 195, 413–425.
20. Elif Hamurcu, E.; Hazer, B.; Misirli, Z.; Baysal, B. M. *J Appl Polym Sci* 1996, 62, 1415–1426.
21. Aggarwal, S. L. *Shell Polym* 1979, 3, 42–44.
22. Aggarwal, S. L., Ed; *Block Polymers*; Plenum Press: New York, 1970; Vol. 52, pp. 137–151.
23. Odel, J. A.; Dlugosz, J.; Keller, A. *J Polym Sci, Polym Phys Ed* 1976, 14, 861–867.
24. Bradford, E. B.; Vanzo, E. *J Polym Sci, Part A1* 1968, 6, 1661–1670.
25. Fujimura, M.; Hashimoto, T.; Kawai, H. *Rubber Chem Technol* 1978, 51, 215–224.
26. Xie, R.; Yang, B.; Jiang, B. *J Polym Sci, Part B: Polym Phys* 1995, 33, 25–32.
27. Broseta, D.; Fredrickson, G. H.; Helfand, E.; Leibler, L. *Macromolecules* 1990, 23, 132–139.
28. Ghosh, S.; Khastgir, D.; Bhowmick, A. K. *Polymer* 1998, 39, 3969.
29. Kim, W. N.; Burns, C. M. *J Appl Polym Sci* 1986, 22, 2989–3004.
30. Fox, T. G. *Bull Am Phys Soc* 1956, 1, 123.
31. Wagener, K. B.; Matayabas, J. C., Jr. *Macromolecules* 1991, 24, 618–619.