In summary, we have prepared IPN's, pseudo-IPN's, and linear blends of a polyurethane and poly(methyl methacrylate). Electron microscopy shows that phase separation occurs, with the domain sizes in the IPN's being significantly smaller than those of the pseudo-IPN's and linear blends, demonstrating the role played by interpenetration in compatibilizing these polymers.

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Polyurethane Interpenetrating Polymer Networks. II. Density and Glass Transition Behavior of Polyurethane–Poly(methyl methacrylate) and Polyurethane–Polystyrene IPN'S

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ABSTRACT: The density and glass transition behavior of simultaneous interpenetrating networks (SIN's) of polyurethane and poly(methyl methacrylate) were evaluated. The densities were measured by the hydrostatic method. The glass transition behavior was studied by differential scanning calorimetry and by dynamic mechanical spectroscopy (torsional pendulum). Increased densities, due to the partial mixing of the component networks, were observed in the IPN's. This effect was more pronounced in the polyurethane–polystyrene IPN's. The increased density effect agreed well with the specific volume hypothesis of Kwei for a compatible polymer pair. Two glass transition temperatures corresponding to the component networks were observed in the IPN's, which further substantiated the phase separation observed with electron microscopy. However, the two glass transition temperatures were shifted inwardly, indicating some interpenetration. The pseudo IPN's (only one polymer cross-linked) and the linear blends did not exhibit this inward shift.

The density behavior of IPN's has been controversial. Millar[4] observed increased densities in his polystyrene–polystyrene sequential IPN's. It was suggested that some of the "holes" in the comparatively loosely packed[5] amorphous polystyrene structure were filled by self-entanglement of the growing network. However, Shibayama and Suzuki[6] observed no difference in density between IPN's and the constituent networks in a similar system of polystyrene–polystyrene sequential IPN's. Frisch et al.[7,8] also observed no difference in density in their polyurethane–polyacrylate latex IPN's.

Recently in a study on compatible polystyrene–poly(vinyl methyl ether) linear blends, Kwei et al.[2] observed densities higher than the theoretical densities based on volume additivity of the two-component polymers. The following approach was proposed and agreed well with the experi-

Table I

Composition	Density, g/cm^3	
	Actual	Calcd[a]
Homopolymers		
UC100	1.146	
UL100	1.148	
MC100	1.193	
ML100	1.190	
SC100	1.050	
IPN's		
UC85MC15	1.153	1.153
UC75MC25	1.165	1.158
UC60MC40	1.163	1.165
UC50MC50	1.181	1.169
UC40MC60	1.189	1.174
UC25MC75	1.186	1.181
UC15MC85	1.180	1.186
UC95SC5	1.152	1.141
UC90SC10	1.159	1.136
UC85SC15	1.158	1.131
UC75SC25	1.152	1.121
UC50SC50	1.128	1.096
Pseudo IPN's		
UC75ML25	1.154	1.157
UL75MC25	1.156	1.158
Linear Blends		
UL75ML25	1.158	1.158
UL50ML50	1.175	1.169
Average error range	0.012	

[a] Based on the volume additivity of the components.

mental results. If the system consists of two polymer components, A and B, whose glass transition temperatures, T_g(A) and T_g(B), differ widely, T_g(A) located above and T_g(B) below the test temperature, the chains of the glassy polymer A (at test temperature) molecularly mixed with the rubbery polymer B will be in a rubbery environment. The specific volume at test temperature of the glassy polymer chains A will be close to the specific volume of A in the rubbery state. Similarly, the specific volume at test temperature of the rubbery polymer chains B which are molecularly mixed with the chains of the glassy polymer A will be close to the specific volume of B in the glassy state. Both will contribute to the density increase. They also suggested that the partial mixing of polymer components would also result in increased densities. If a certain IPN system is composed of a rubbery and glassy component network, the interpenetration of each network should result in a similar density effect, if any interpenetration of the chains occurs.

The glass transition behavior of the IPN's depends on their morphology. Four situations have been observed: first, two distinct T_g's corresponding to each network;[7] second, two distinct but inwardly shifted T_g's;[9,10] third, one broad T_g intermediate to the T_g's of each network;[11] and finally, one sharp T_g intermediate to the T_g's of each network.[12] The inward shift or the merger of the glass transition temperatures has been used as partial evidence of interpenetration. However, this required careful comparison of the glass transition behavior of the IPN's with their topological isomers (blends of cross-linked polymer networks without interpenetration). The topological isomers of IPN's are impossible to obtain due to the intractable nature of the cross-linked polymers. The alternatives to the topological isomers of IPN's are pseudo-IPN's (only one network cross-linked) and linear blends, as well as, of course, the homopolymers. The comparison of the glass transition behavior should be made when the glass transition shift due to the cross-link density difference is known.

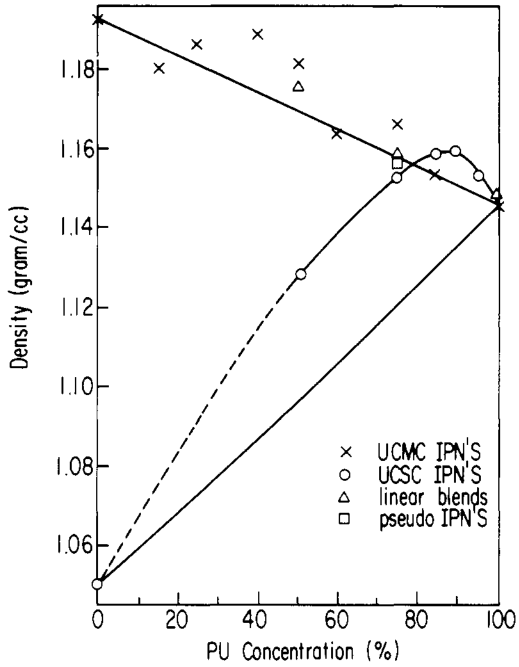

Figure 1. Density vs. polyurethane concentration (straight lines are based on volume additivity).

In this paper the density and glass transition behavior of the polyurethane–poly(methyl methacrylate) IPN's, pseudo-IPN's, and linear blends are reported. They are also compared with the polyurethane–polystyrene IPN's. The synthesis and morphology of the IPN's, pseudo-IPN's, and linear blends are reported elsewhere.[2a,3]

Experimental Section

Materials. The raw materials and the synthesis of the polymers described in this paper are reported elsewhere.[2a,3] The sample compositions are coded for the convenience of presentation. The first letter denotes the polymer type (U for polyurethane, S for polystyrene, and M for poly(methyl methacrylate)); the second letter denotes the nature of the network (L for linear and C for cross-linked); and the third numeral denotes the weight percentage of the polymer.

Measurements. The density at room temperature was obtained according to the ASTM hydrostatic procedure.[13] Glass transition temperatures were determined on a Perkin-Elmer DSC II differential scanning calorimeter. Measurements were carried out from −100 to +150 °C under nitrogen at a scanning rate of 10 °C/min. Low-temperature glass transition was also measured by a torsional pendulum at 0.2 Hz frequency from −100 to 20 °C. The glass transition temperature was noted as the peak in the loss modulus temperature curves. Details of the torsional pendulum experiment are reported elsewhere.[14]

Results and Discussion

Density. The actual densities and the calculated densities based on the volume additivity of the components are listed in Table I. The density–composition curve (Figure 1) shows significantly increased density in polyurethane–polystyrene IPN's, while this increase was less pronounced in polyurethane–poly(methyl methacrylate) IPN's. The maximum increase in the polyurethane–poly(methyl methacrylate) IPN system is at 40% polyurethane concentration. This increase of 0.015 g/cm^3 only slightly exceeds the maximum experimental error range of 0.012. The maximum increase in the polyurethane–polystyrene IPN system is observed at 75 and 50% polyurethane concentration. This increase is 0.032 g/cm^3. This seems to contradict the morpho-

Table II
Glass Transition Temperature, T_g (°K)

	Low T_g		High T_g
Composition	DSC	Torsion	DSC
	Homopolymers		
UC100	224	219	
UL100	224	218	
MC100			382
ML100			382
SC100			375
	IPN's		
UC85MC15	228	229	
UC75MC25	230	227	
UC60MC40	226	225	366
UC40MC60	227	227	367
UC25MC75	224		371
UC15MC85	224		379
UC80SC20	228		372
UC75SC25	226		372
UC60SC40	226		366
UC20SC80	228		369
	Pseudo-IPN's		
UC75ML25	226	219	
UL75MC25	224	219	
	Polyblends		
UL75ML25	224	219	

logical and glass transition behavior of the two IPN systems where the degree of mixing in polyurethane–poly(methyl methacrylate) IPN's was shown to be higher than that of the polyurethane–polystyrene IPN's (from the observed dispersed phase domain sizes[2a,3] and the shift in glass transition temperature). However, the coefficient of thermal expansion of poly(methyl methacrylate) in the rubbery state (above its glass transition temperature) is lower than that of polystyrene (poly(methyl methacrylate) 4.8×10^{-4}[15] and polystyrene 5.5×10^{-4} K^{-1})[16] while the coefficient of thermal expansion in the glassy state (below its glass transition temperature) is similar for both polymers (poly(methyl methacrylate) 2.25×10^{-4}[15] and polystyrene 2.285×10^{-4} K^{-1}).[16] Thus the difference in specific volumes of the rubbery poly(methyl methacrylate) chains and the glassy poly(methyl methacrylate) chains, both at room temperature, is smaller than for polystyrene. Hence the density effect of mixing in poly(methyl methacrylate) is smaller, based on the theory of Kwei et al.[2b] mentioned in the introduction. Also the smaller density differences between pure polyurethane and poly(methyl methacrylate) make the density effect less noticeable.

The density of the 75% polyurethane–25% poly(methyl methacrylate) IPN is slightly higher than that of its corresponding pseudo-IPN's and linear blends. The 50% polyurethane–50% poly(methyl methacrylate) IPN also shows a slight increase in density compared to its linear blends. The density measurement in the polyurethane–poly(methyl methacrylate) IPN system was not sensitive enough to detect the increased mixing effect of interpenetration (which was evidenced by the shift in glass transition temperature and finer domain sizes in the electron micrographs),[3] due to the small density effect of mixing in the system, although there is an overall trend of increased density. The polyurethane–polystyrene IPN's show a significant density increase compared to the theoretically calculated densities based on volume additivity.

Glass Transition Behavior. The glass transition temperatures of the samples are listed in Table II. The low T_g corresponds to the polyurethane phase transition and the high T_g corresponds to the poly(methyl methacrylate) or polystyrene phase transition. The onset temperature was compared in the DSC measurement due to the difficulties in obtaining the medium point in some of the thermograms. The maximum peak temperature in the G'' vs. temperature plot was taken as T_g in the torsion pendulum measurements. The experimental error range in the DSC measurement was ±2 and ±3 °C in the torsional pendulum measurements.

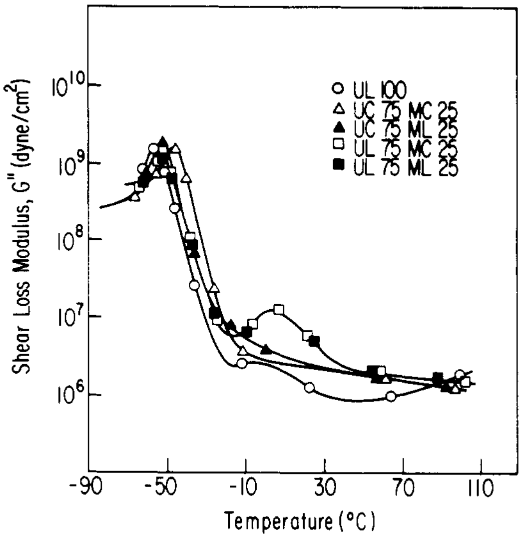

Figure 2. Shear loss modulus, G'', vs. temperature.

In general, the polyurethane–poly(methyl methacrylate) and the polyurethane–polystyrene IPN's exhibit two distinct glass transition temperatures corresponding to the respective component networks (Table II). However, they are shifted inward. The shift is more prominent in the high T_g than in the low T_g. The shift is more prominent in the polyurethane–poly(methyl methacrylate) IPN's than in the polyurethane–polystyrene IPN's. This is consistent with the compatibility and morphology of the two IPN's.[2a,3] The solubility parameter of poly(methyl methacrylate) is closer to the polyurethane than is that of polystyrene. The glass transition behavior indicates "impure" phases present in both IPN's due to interpenetration, presumably around the phase boundaries. It also indicates higher content of impure phases in the polyurethane–poly(methyl methacrylate) IPN's (compared to polyurethane–polystyrene IPN's) since the probability of interlocking is enhanced due to the higher compatibility of the polymer chains during the statistically controlled simultaneous interpenetration process. The interpenetration effect on the glass transition behavior is shown in the 75% polyurethane–25% poly(methyl methacrylate) samples (Figure 2 and Table II). Only the IPN sample exhibits a significant shift in the low T_g. The pseudo-IPN's and the linear polyblend show nearly identical T_g's with the pure polyurethane. There was no significant difference in T_g's observed between the linear and the cross-linked networks due to the light cross-link density (calculated $\bar{M}_c$ is in the range of 20 000). The difference in T_g's obtained from the DSC and the torsion pendulum measurement is relatively small, although the low T_g shift is more pronounced in the torsion pendulum measurements.

A seeming contradiction occurs here, i.e., the density increase implies a decrease in the free volume, which should yield an increase in T_g. However, the T_g's of the glassy polymer decrease. The authors feel that the interpenetration effect on shifting the T_g's inward is greater than the density effect on T_g.

In summary, the density and glass transition behavior agree with the electron microscopy[2a,3] and indicate that the phase separation is not complete, with "permanent" interpenetration being responsible for increased interaction between the phases (smaller domain sizes). Studies on the viscoelastic properties of these IPN's (which will be reported later) support these results.

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Structures of Two Crystalline Forms of Poly(butylene terephthalate) and Reversible Transition between Them by Mechanical Deformation

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ABSTRACT: For poly(butylene terephthalate) ($[\text{-O(CH}_2)_4\text{OCOPhCO-}]_n$) two crystal modifications (α and β forms) were found and their crystal structures were analyzed by x-ray diffraction. The transition between two modifications takes place reversibly by mechanical deformation: from the α form to the β form by elongation and inversely by relaxation. Two modifications belong to the triclinic system with the space group $P\bar{1}\text{-}C_i^1$. Each unit cell contains one molecular chain; the cell dimensions are a = 4.83 Å, b = 5.94 Å, c (fiber axis) = 11.59 Å, α = 99.7°, β = 115.2°, and γ = 110.8° for the α form; and a = 4.95 Å, b = 5.67 Å, c (fiber axis) = 12.95 Å, α = 101.7°, β = 121.8°, and γ = 99.9° for the β form. Several plausible molecular models obtained by the intramolecular potential energy calculation were examined by x-ray analysis, and finally the refinement of the proper models was carried out by the constrained least-squares method. The difference in fiber periods of two crystalline forms is ascribed majorly to a conformational change of a four-methylene group sequence in both forms: approximately $\bar{G}\bar{G}TGG$ for the α form and $TST\bar{S}T$ for the β form. The phenomena of the double orientation and tilting were observed as in the case of poly(ethylene terephthalate) and discussed in connection with the crystal structures.

Among the polyesters of the type $[\text{-O(CH}_2)_m\text{OCOPhCO-}]_n$, crystal structure of poly(ethylene terephthalate) [PET] (m = 2) was determined,[2] but for other members (m = 3–10), only the lattice dimensions or the fiber identity periods have been reported.[3-5] The present paper deals with poly(butylene terephthalate) [PBT] $[\text{-O(CH}_2)_4\text{OCOPhCO-}]_n$ (m = 4). We have found two crystal modifications, the α and β forms; the latter form exists only under tension and consists of more extended molecular chains. The transition between the α form and β form takes place reversibly by stretching and relaxation. The crystal structures of both forms were determined by x-ray analysis with the help of conformation energy calculation. Moreover, the phenomena of double orientation and tilting were observed as in the case of PET and will be discussed later, being correlated to the crystal structures.

After almost completion of the present study, the authors were informed the investigation of Professor Ward's group[6,7] had found the existence of two modifications in PBT and discussed the crystal deformation due to the transition.

Experimental Section

Samples. The preparation methods of the samples are summarized in Figure 1. The white opaque polymer was heated to become a transparent molten sample (mp 224 °C). The molten sample was drawn quickly soon after quenching in ice-water giving amorphous sample (observed density, 1.30 g/cm^3). Then the sample was further elongated at room temperature and was subjected to heat treatment at 200 °C in vacuo for 2 h under tension. The crystal form thus obtained in the uniaxially oriented fiber was named the β form. It was found that this modification exists only under tension and is transformed into another highly crystalline modification, the α form, by removing the tension. When the sample of the α form is again stretched about 12%, a pure β form is obtained. When the elongation is less than 12%, both modifications coexist. A doubly oriented specimen of the α form was prepared by rolling the uniaxially oriented α form fiber along the drawn direction. As to the β form, no doubly oriented specimen could be obtained.

Measurements. X-ray photographs were taken by using nickel-