Polyurethane Interpenetrating Polymer Networks. I. Synthesis and Morphology of Polyurethane–Poly(methyl methacrylate) Interpenetrating Polymer Networks

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ABSTRACT: Two-component interpenetrating polymer networks (IPN's) of polyurethane–poly(methyl methacrylate) were prepared by the simultaneous polymerization process. The polyurethane network was cross-linked with trimethylolpropane and the poly(methyl methacrylate) network with trimethylolpropane trimethacrylate. The theoretical cross-link densities of the above networks were in the range of 20 000 to 27 000 molecular weight between the cross-link sites. Polyurethane–poly(methyl methacrylate) pseudo-IPN's, in which only one of the component polymers was cross-linked, were prepared for selected compositions as well as linear blends of the two polymers. Electron microscopy showed that phase separation resulted. However, the phase domains were finer in the IPN's than in the pseudo-IPN's or the linear blends of the corresponding polymers. Comparison with polyurethane–polystyrene IPN's, prepared in another study, showed that the phase domains were finer in the polyurethane–poly(methyl methacrylate) IPN's due to the higher compatibility of the polymer pairs. Phase inversion was observed to occur between 60 and 80% polyurethane concentration.

Interpenetrating polymer networks (IPN's) can be classified as polymeric catenanes if we envision a cross-linked polymer network to be composed of many macrocycles of varying sizes. The various techniques for preparing IPN's (sequential polymerization, latex blending, and simultaneous polymerization) can be viewed as statistical methods where a cyclization (cross-linking) of one component occurs in the presence of the other already cyclized component (cross-linked polymer network). The probability of forming polymeric catenanes (interpenetration) is, however, much greater than that of simple organic catenanes because of the larger covolume of the polymers available for threading by a chain. However, compatibility or degree of mixing affects the probability of threading in this case since generally most polymers are not compatible with each other.

IPN's were first prepared by Millar[2b] in 1960. A similar system was also evaluated by Shibayama et al.[3–6] Sequential IPN's (SIPN's) with different polymer entities have been investigated by Sperling et al.[7–15] with different polymer combinations generally based on chain-reaction polymerization.

Latex IPN's (LIPN's) were first reported by Frisch et al.[16] in 1969 by blending poly(urethaneurea) and polyacrylate latices. A number of different polymer combinations were also studied by Frisch et al. who were the first to prevent chain transfer between the networks.[17–19]

Simultaneous IPN's (SIN's) were first reported by Frisch et al.[20] by mixing a urethane prepolymer with a low molecular weight epoxy resin. The mixture was then cured simultaneously via independent (noninteracting) cross-linking reactions. Further SIN's were also studied by Frisch et al.,[21–24] which were prepared in a similar manner, and by Touhsaent et al.[25]

Most of the IPN's reported so far involve heterogeneous systems, usually one phase rubbery and the other phase glassy. This combination of rubbery and glassy polymer networks gives a rather interesting situation where a particular IPN system can range from a filler-reinforced elastomeric material to a leathery material, and to a rubber-reinforced (high impact) plastic material, depending on which component becomes the continuous phase. Since morphology plays a major role in affecting IPN properties, it has been extensively studied by electron microscopy and glass transition behavior. The morphology of IPN's depends on the method of synthesis, compatibility of the polymer systems employed, and on the relative rates of formation of each network. IPN's reported so far can be classified as having large domain structures with domain sizes of a few microns,[18] intermediate structures with sizes around 1000 Å,[10,12] fine structures with sizes around 100 Å,[12] and no resolvable domain structures at all.[2–6,23]

The nature of interpenetration is believed to vary systematically with the morphology, from partial interpenetration mostly at the boundaries of the dispersed phase (in the cases of large domain structure IPN's), to a super-molecular mixing where the domain size is in the same order of magnitude as the distances between the cross-links of the polymer network (a domain size of 100 Å corresponds roughly to a distance of about 200 mers between cross-links),[12] and to a molecular level mixing (homogeneous IPN's).

In sequential IPN's, the network first formed is most likely to be the continuous network. Its cross-link density is the controlling factor in determining the morphology of the system. Sperling et al.[27] observed a finer domain size (800–1000 Å) in their poly(styrene-*co*-butadiene)–polystyrene sequential IPN's when the first formed network, poly(styrene-*co*-butadiene), was cross-linked with 0.2% dicumyl peroxide, compared to a domain size of 1600–1800 Å when the first formed network was cross-linked with 0.1% dicumyl peroxide. The domain size was believed to be related to the distances between neighboring cross-link sites. Similar phenomena would occur in latex and simultaneous IPN's, although the relative rates of formation of each network would be the controlling factor in determining the morphology. It was also observed that the morphology of IPN's was slightly finer than the corresponding pseudo-IPN's (one polymer cross-linked and the other polymer linear).[27]

The major problems pending in the study of IPN's are that there is no general method to prove the existence of interpenetration and to measure the quantitative level of interpenetration. Equilibrium swelling and the apparent cross-link density measurements of Cluff et al.[29] would serve the purpose only when the IPN system is homogeneous and the statistical theory of rubber elasticity[30] is applicable. In heterogeneous systems, the compression modulus depends largely on the morphology, and the preference of the swelling solvent to one component network will gen-

Table I
Materials

Designation	Description	Source
Niax D-560	Poly(caprolactone) glycol mol wt = 1978, OH no. = 56.7	Union Carbide Corp.
TMP	Trimethylolpropane	Celanese Chem. Corp.
1,4-BD	1,4-Butanediol	GAF Corp.
MDI	4,4′-Diphenylmethane diisocyanate	Mobay Chem. Co.
MMA	Methyl methacrylate	Fisher Sci. Co.
TMPTMA	Trimethylolpropane trimethacrylate	Polyscience, Inc.
BPO	Benzoyl peroxide	Fisher Sci. Co.

erate cases where the swelling of the dispersed phase is restricted, thus making the apparent cross-link density measurements at best gross approximations.

The measurement of the shift in glass transition temperature can also be useful if the IPN system consists of a one-component network such as Millar's polystyrene–polystyrene sequential IPN's.[2b] If the IPN system employs two different polymer networks (actually most IPN's do), the shift of glass transition temperature should be compared to that of its topological isomers (both networks cross-linked but not interlocking). The topological isomers of IPN's are impossible to obtain at this stage due to the insoluble and infusible nature of cross-linked polymer networks and the incompatability of the formed networks. One alternative is to compare the shift of glass transition temperature of IPN's with its corresponding pseudo-IPN's (one polymer cross-linked and the other polymer linear) and linear polyblends (both polymers linear) provided that the cross-link densities of the IPN's are comparatively small. A similar approach would be to compare the morphology of IPN's to that of the corresponding pseudo-IPN's and linear polyblends by electron microscopy. This approach would be qualitatively possible but the quantitative analysis would be difficult because of the rather wide distribution of phase domain sizes and of the complexity of the morphology of the heterogeneous systems. Mechanical property measurements could also be used for proving the existence of interpenetration if a fair comparison of IPN's with the corresponding pseudo-IPN's and with linear polyblends is possible. The existence of interpenetration has been generally shown based on a combination of effects described above. In this paper we describe the synthesis of polyurethane–poly(methyl methacrylate) IPN's, pseudo-IPN's, and the preparation of linear blends and the subsequent investigation of their morphologies via electron microscopy.

Experimental Section

Materials. The raw materials used and their descriptions are shown in Table I. Poly(caprolactone) glycol with average molecular weight of 1978 (Niax D560), 1,4-butanediol (1,4-BD), and trimethylolpropane (TMP) were dried at 60 °C for 5 h under a vacuum of 2 mm. Methyl methacrylate (MMA) was washed with 5% aqueous potassium hydroxide solution, followed by washing with distilled water, dried over Linde 4A molecular sieves, and distilled at 40 °C under a vacuum of 2 mm to remove the stabilizer. Trimethylolpropane trimethacrylate (TMPTMA) was also distilled at 40 °C under 2 mm vacuum. 4,4′-Diphenylmethane diisocyanate (MDI) and benzoyl peroxide were used without further purification.

Preparation. Polyurethane (PU). The isocyanate terminated polyurethane prepolymer was prepared by reacting 2 equiv of 4,4′-diphenylmethane diisocyanate (MDI) with 1 equiv of poly(caprolactone) glycol (Niax D-560) at 60 °C. A resin kettle, equipped with a nitrogen inlet, stirrer, thermometer, and reflux condenser, was charged with 2 equiv of MDI. To this was added slowly with stirring 1 equiv of Niax D-560. The reaction was carried out under nitrogen at 60 °C until the theoretical isocyanate content (as determined by the di-*n*-butylamine titration method[28]) was reached. The prepolymer was stored under vacuum (not more than 2 days) because of its susceptibility to moisture. One equivalent of the PU prepolymer was heated to 80 °C and then homogeneously mixed with 1 equiv of a 1,4-butanediol (1,4-BD) and trimethylolpropane (TMP) mixture (4:1 equivalent ratio) for 5 min using a high torque stirrer. The air entrapped during mixing was removed by applying a vacuum for 5–10 min. The mixture was cast in a closed stainless steel mold (with polypropylene lining for easy demolding) at 80 °C for 16 h and 110 °C for 4 h on a platen press under 350 psi pressure.

Poly(methyl methacrylate) (PMMA). A resin kettle equipped with a nitrogen inlet, stirrer, thermometer, and reflux condenser was immersed in a water bath. It was charged with 118.3 g of distilled MMA monomer, 1.7 g of distilled TMPTMA, and 1.2 g of benzoyl peroxide. The mixture was stirred until the benzoyl peroxide was dissolved. The progress of the reaction was followed by placing a drop of mixture in isopropyl alcohol where the PMMA formed precipitated. The reaction was continued until 10–15% conversion and stopped by rapid cooling. The reaction mixture was cast in the same mold as used for the PU preparation and cured at 80 °C for 16 h and 110 °C for 4 h under 350 psi of pressure.

IPN's. One equivalent of the PU prepolymer was heated to 80 °C and then homogeneously mixed with 1 equiv of the 1,4-BD–TMP mixture (4:1 equivalent ratio) for 5 min. Then the MMA–TMPTMA prepolymer mixture was added in varying weight ratios and homogeneously mixed for 3 min using a high torque stirrer. The air entrapped during mixing was removed by applying a vacuum for 30 s. The mixture was then cast in the same manner as described above.

Linear Blends and Pseudo-IPN's. Linear PU was prepared in the same manner as for the polyurethane preparation, except that 1 equiv of PU prepolymer was reacted with 1 equiv of 1,4-BD instead of 1,4-BD–TMP mixture.

Linear PMMA was prepared in the same manner as for the PMMA preparation except that the cross-linking agent (TMPTMA) was omitted.

Linear polyblends were prepared for 75–25% and 50–50% PU–PMMA compositions in the same manner as the IPN preparation except that the 1,4-BD–TMP mixture was replaced by pure 1,4-BD in the PU network and the TMPTMA was omitted in the PMMA network.

Two pseudo-IPN's were prepared for the 75% PU–25% PMMA composition. They were prepared in the same manner as the IPN preparation except that one of the component networks was made linear by the procedure described above.

Samples prepared are listed in Table II.

Measurements. Electron micrographs were obtained on an AEI 6B and a Phillips 300 electron microscope. Samples were stained in osmium tetroxide for two weeks following Kato's staining technique,[31] after which they were embedded in epoxy resin. Sections 10 μ in thickness were cut using a Grand microtome and then embedded again in epoxy resin. The final specimens were cut in thicknesses of about 0.1 μ using a LKB Ultratome III. Electron micrographs were taken by the direct observation of the ultrathin sections.

Results and Discussion of the Morphology as Revealed by Electron Microscopy

In general, the polyurethane–poly(methyl methacrylate) IPN's were heterogeneous with phase domain sizes ranging from 500 to 5000 Å. The polyurethane phase showed staining by osmium tetroxide although the exact staining mechanism is not known. Previous work[18] on polyurethane latex IPN's and SIN's also showed staining of the polyurethane phase. Poly(methyl methacrylate) was not stained by osmium tetroxide.

Pure cross-linked polyurethane is partially crystalline (crystalline melting peak was observed in differential scanning calorimetry studies)[24,32] because of its low cross-link density. The electron micrograph of pure cross-linked polyurethane shows the nonstained (white) partially crystalline area (Figure 1). Linear polyurethane exhibits extensive crystalline structure (Figure 2).

Table II
Samples

Sample code		
UC100	Cross-linked PU 100%	Homopolymer
UL100	Linear PU 100%	Homopolymer
MC100	Cross-linked PMMA 100%	Homopolymer
ML100	Linear PMMA 100%	Homopolymer
UC85MC15	Cross-linked PU 85%, cross-linked PMMA 15%	IPN
UC75MC25	Cross-linked PU 75%, cross-linked PMMA 25%	IPN
UC60MC40	Cross-linked PU 60%, cross-linked PMMA 40%	IPN
UC50MC50	Cross-linked PU 50%, cross-linked PMMA 50%	IPN
UC40MC60	Cross-linked PU 40%, cross-linked PMMA 60%	IPN
UC25MC75	Cross-linked PU 25%, cross-linked PMMA 75%	IPN
UC15MC85	Cross-linked PU 15%, cross-linked PMMA 85%	IPN
UC75ML25	Cross-linked PU 75%, linear PMMA 25%	Pseudo-IPN
UL75MC25	Linear PU 75%, cross-linked PMMA 25%	Pseudo-IPN
UL75ML25	Linear PU 75%, linear PMMA 25%	Linear blend
UL50ML50	Linear PU 50%, linear PMMA 50%	Linear blend

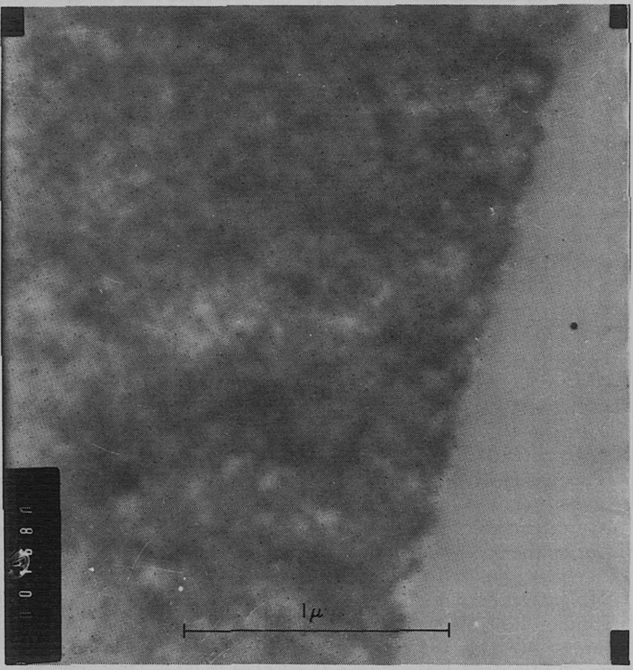

Figure 1. Electron micrograph of UC100.

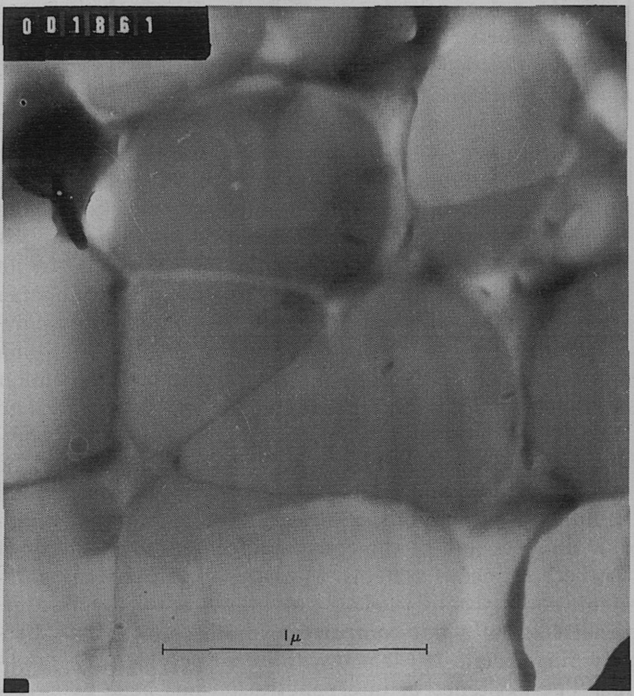

Figure 2. Electron micrograph of UL100.

Electron micrographs of polyurethane–poly(methyl methacrylate) IPN's (Figures 3–7) show finer phase domains than the polyurethane–polystyrene IPN's.[2a] This behavior is expected because of the higher compatibility in the polyurethane–poly(methyl methacrylate) system[24] (solubility parameters are closer). The phase inversion starts at 75% polyurethane (Figure 4) but is not as extensive as in the polyurethane–polystyrene system.[2a] Even at 60% polyurethane (Figure 5), the polyurethane phase retains the continuity, although the poly(methyl methacrylate) phase is becoming the continuous phase. At 40% polyurethane (Figure 6), the poly(methyl methacrylate) phase becomes the more continuous phase and the polyurethane phase becomes dispersed, although locally interconnected. The dispersed polyurethane phase is seen to be clearly isolated at 15% polyurethane (Figure 7). In general, it can be stated that the well-defined continuous-dispersed phase morphology occurs only when either polyurethane content or poly(methyl methacrylate) content exceeds 85%. The IPN morphology with polyurethane content less than 85% and higher than 15% becomes complicated, since both phases assume local or total continuity. This morphology would suggest that the relative rates of the two polymerizations would be about the same, since the network formed first would generally tend to be the more continuous one. Thus, the continuity here seems to be a function principally of concentration. This is borne out by cure time studies which indicated that both networks do form simultaneously. The relative reaction rates may also have some influence on the degree of phase separation (size of dispersed phase), since the polyurethane–polystyrene IPN's, reported earlier,[2a] do have larger domain sizes (the identical polyurethane was used). It was indicated that the polystyrene network formed first, since it assumed almost completely the continuous role sooner than the poly(methyl methacrylate) (became continuous at ~75% polyurethane and remained so). This is in agreement with the results of Touhsaent et al.[25] who found that the closer their epoxy–acrylic reactions were to simultaneity, the finer was the domain size.

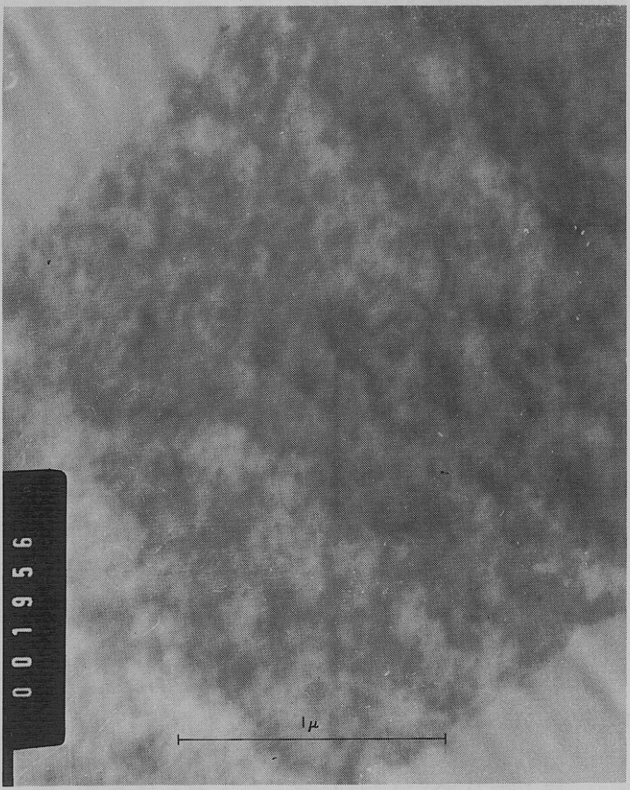

Figure 3. Electron micrograph of UC85MC15.

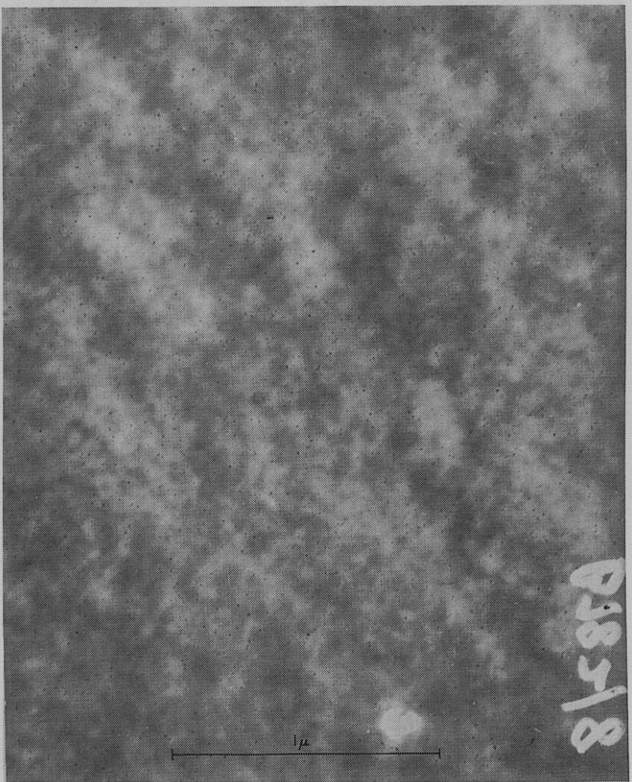

Figure 4. Electron micrograph of UC75MC25.

The electron micrographs of pseudo-IPN's (Figures 8 and 9) and the linear polyblend (Figure 10) of 75% polyurethane–25% poly(methyl methacrylate) show morphologies similar to the corresponding IPN system (Figure 4). It is difficult to identify the continuous and dispersed phase. The phase domain sizes in the pseudo-IPN's and linear blend systems are similar (2000–5000-Å range) but significantly larger than that of the corresponding IPN system (500–2000-Å range). This supports the contention that the interlocking of chains during polymerization and cross-linking of each polymer component prevents, to a certain extent, the demixing of the polymer chains, thus increasing the degree of mixing of the component networks. Note that in this simultaneous IPN process the starting material is a

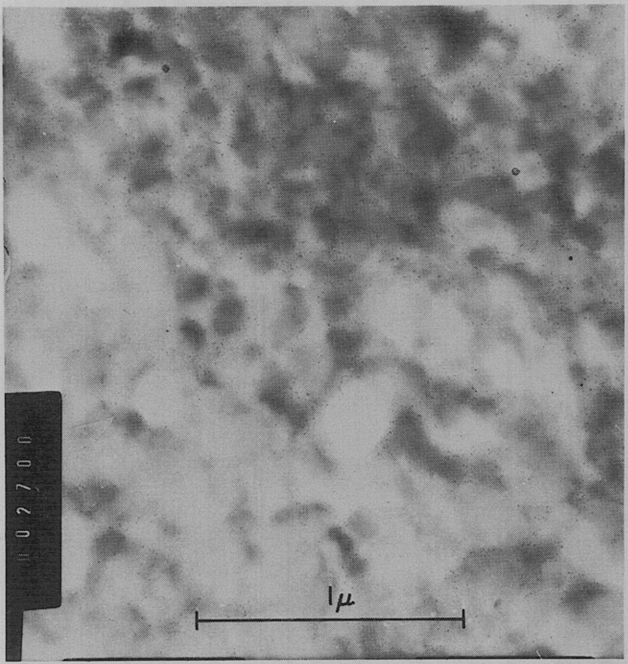

Figure 5. Electron micrograph of UC60MC40.

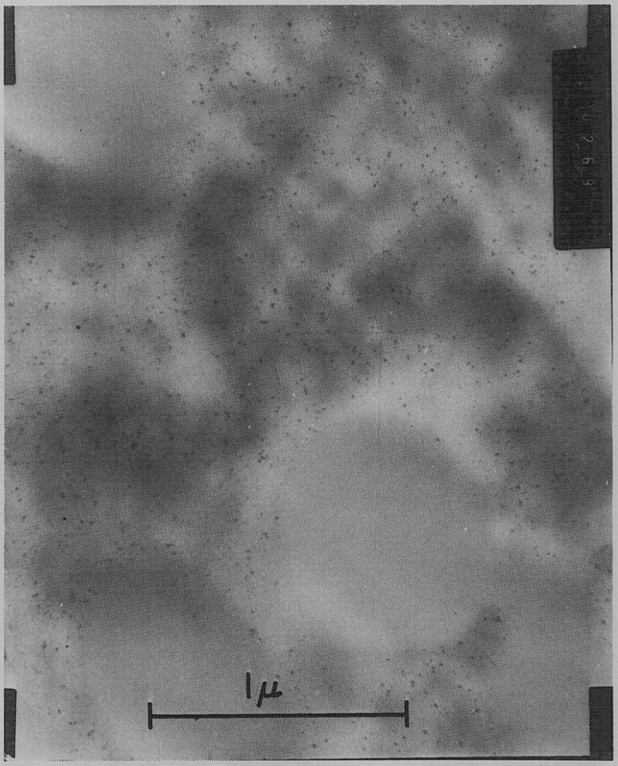

Figure 6. Electron micrograph of UC40MC60.

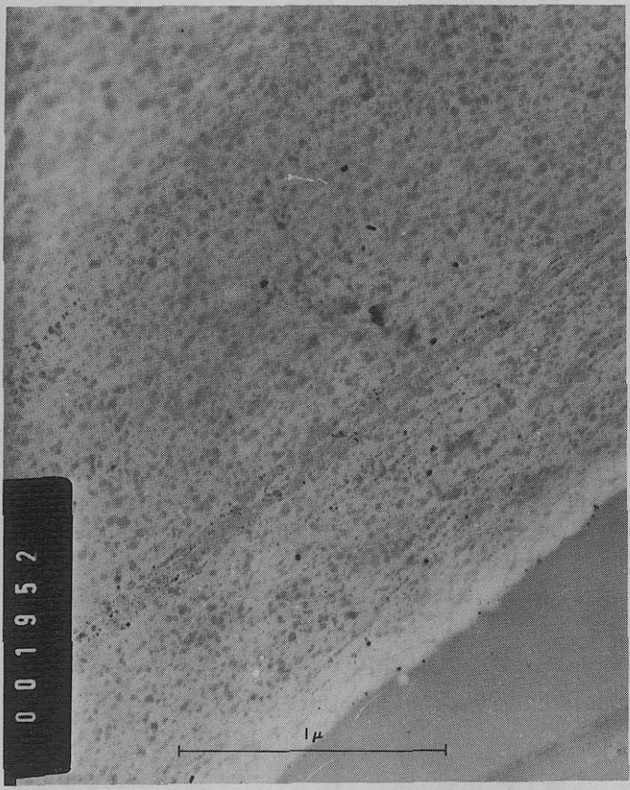

Figure 7. Electron micrograph of UC15MC85.

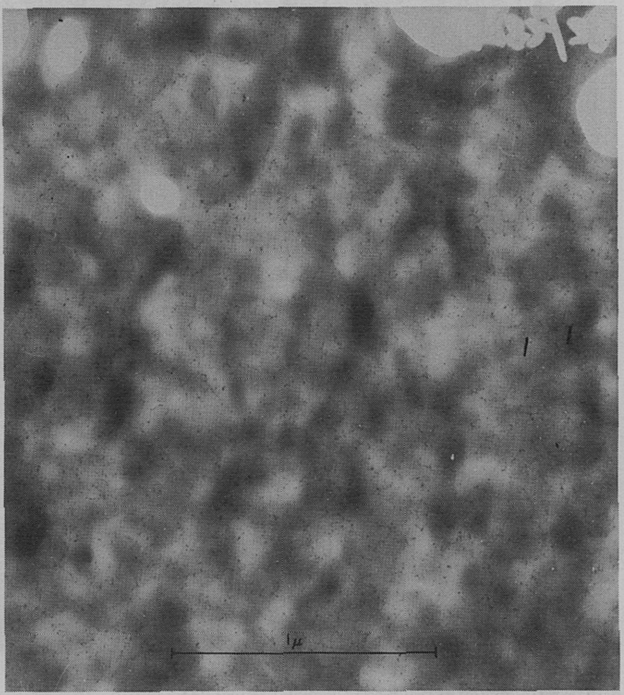

Figure 8. Electron micrograph of UC75ML25.

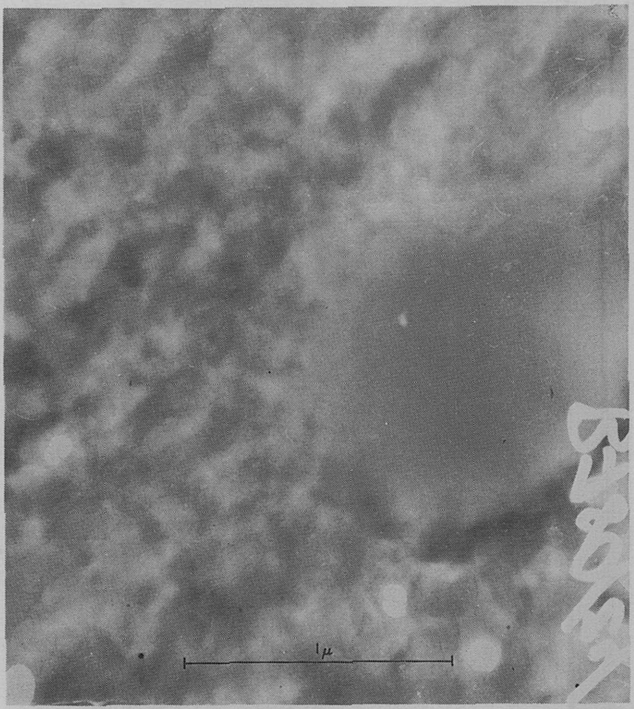

Figure 9. Electron micrograph of UL75MC25. w

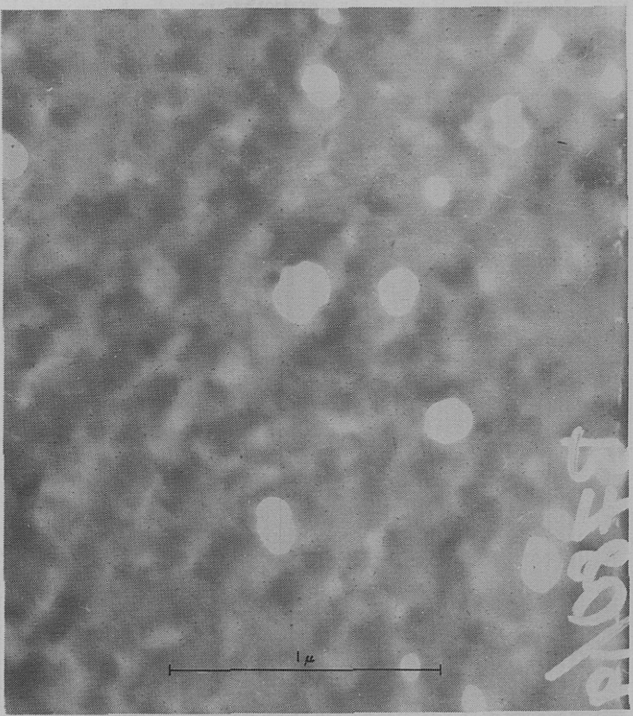

Figure 10. Electron micrograph of UL75ML25.

single phase low molecular weight prepolymer mixture. The compatibility of the system decreases with the increasing molecular weight of each network due to the decrease in the entropy of mixing. The system becomes two phase at the latter stages of polymerization and cross-linking. With the absence of interlocking of chains, extensive demixing during the polymerization process is expected to occur. This difference in phase domain size between the pseudo-IPN and IPN systems was also noted previously in a sequential IPN system.[27]

The actual domain size distribution is difficult to identify in the electron micrographs since it is possible that the smaller dispersed phases shown in the micrographs can be smaller sections of larger dispersed particles which were cut into ultrathin sections during the microtoming process. However, the relative comparison of the overall phase morphology is relevant and the general domain size distribution is shown to be relatively uniform.

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-