Polyurethane−Polyacrylate Interpenetrating Networks. 1. Preparation and Morphology

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ABSTRACT: Three types of urethane−acrylate IPN's, two sequential and one simultaneous, were prepared in which the urethane was formed under thermal polymerization; and the acrylate, by photopolymerization. The IPN morphologies were studied by transmission electron microscopy (TEM) and dynamic mechanical analysis (DMA). When the urethane was reacted to relatively high conversion prior to photoinitiation of the acrylate, the IPN's obtained were characterized by very small domain sizes (<20 nm) and a single T_g between those of the two components. When the acrylate polymerization was induced following much smaller conversion of the urethane, or if the acrylate was polymerized first, domains of larger size (>100 nm) were obtained. In these two instances, if the T_g's of the individual components are well separated, dynamic mechanical analysis indicated separate T_g values close to the T_g's of the individual components. The degree of phase mixing in each IPN was estimated from the T_g values from the Fox equation, and these correlate with the various processing conditions.

Introduction

This paper, and the companion paper which follows, represent attempts to understand the connection between processing conditions and morphology for a series of urethane−acrylate interpenetrating polymer networks (IPN's).[1−3]

IPN's are systems prepared by polymerizing a monomer and its cross-linking agent in the presence of a cross-linked polymer network of a different composition. Such systems can be prepared sequentially, in which one network is prepared and swollen with the second set of reactant (SeqIPN), or they can be prepared by simultaneous reaction of all of the constituents (SimIPN). Over the past quarter of a century, a substantial effort has gone into establishing that the detailed morphology, and the mechanical properties of the materials obtained, depend sensitively on the order in which the reactions are carried out and the details of the reaction conditions. This very complexity, which makes these systems difficult to study from an academic point of view, is particularly attractive from an industrial point of view.[4,5] The sensitivity of material properties to preparation conditions means that with a single set of reactants, one can in principle achieve materials with different properties by varying only the processing conditions.

To achieve appropriate control in such systems, it is important that the two polymerization reactions occur by different mechanisms. One of the classical examples satisfying this consideration is that of urethane−acrylate IPN's, in which the rate of condensation to form the urethane can be controlled by the amount of (typically tin) catalyst, and the rate of acrylate formation can be controlled by choice of the appropriate free radical initiator. In the various papers which describe controlling the rates of these polymerization reactions, the key variables were always the choice and amount of catalyst and variation of temperature.[6−11] Here we use light, i.e. photochemical initiation, to control the rate of acrylate polymerization, and temperature plus catalyst to vary the timing and the rate of urethane formation. We note that photochemical initiation of urethane polymerization in urethane−acrylate IPN systems has been described in both the patent[12] and scientific literature.[13]

The fundamental phenomenon associated with all IPN's is that phase separation occurs during the reaction. The timing and the extent of phase separation are determined by the thermodynamic immiscibility between the components, and this immiscibility changes during the course of the reaction.[11] The extent of phase separation is limited by the spatial scale over which interpenetration occurs at the onset of phase separation, and this in turn is related to the rates of polymerization in the system.

Generally speaking, in sequential IPN's, the first polymer network is thought to form the continuous phase, with the second polymer network as a dispersed phase. This may not remain true if the first-formed network is present as the minor component in the system. In some simultaneous IPN's, bicontinuous phases have been inferred from microscopy observations and mechanical measurements.[1−3] Compared with sequential IPN's, many simultaneous IPN's have been reported to yield a greater extent of molecular mixing and better mechanical properties. For example, Iisaka[14] reported that the simultaneous IPN of epoxy resin−bismaleimide allylester copolymer exhibited a maximum in glass transition temperature (T_g) and also in tensile strength, which was explained in terms of the greater extent of molecular mixing attained in simultaneous gelation of both networks. Zhou et al.[9] reported that in making polyurethane−poly(methyl methacrylate) (PMMA) IPN's, a well matched gelation time yielded an IPN with one T_g, and no observable phase separation by SEM, whereas under different reaction conditions in which the gelation times for the two cross-linking reactions were clearly different, they obtained IPN's with two T_g's and a heterogeneous phase morphology.

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Thus, as a general rule, one believes that the finest morphology, with the smallest phase domains will occur in simultaneous IPN's in which both systems reach their gel point at the same time. This conclusion is often difficult to assess. Gel points are often inferred from the kinetics of the polymerization process. Only recently have careful studies been reported of monomer conversion rates in IPN-forming systems.[6,11,15] It is not sufficient to employ conversion rates obtained from examination of the individual components. In the cases where careful studies have been carried out, as for example by the group of Meyer et al. in Strasbourg,[6,15] one learns that the other component can have strong effects on the polymerization of a given monomer. For example, in urethane–acrylate IPN's, the extent of urethane network formation has a profound influence on the onset of the Tromsdorrf effect in the acrylate conversion.

Beyond the questions of the domain size and mechanical properties of IPN's lie the more subtle and more important issues of domain composition and interface structure. In polymer blends, interfaces between the components are normally rather narrow and are determined almost entirely by the magnitude of the Flory–Huggins $\chi_{A/B}$ parameter, which describes the free energy of interaction between segments of the two polymers relative to those between two segments of the same polymer. Since interfaces tend to come quickly to equilibrium in simple blends of two polymers, there is normally reasonable agreement between interface thickness determined by scattering techniques and modern theories of the polymer–polymer interface. This situation is very different from that found in IPN's, where kinetic factors limit the extent of phase separation.

To address these issues, one needs new techniques. One approach reported recently by the Meyer group in collaboration with Weill involves NMR spin-diffusion experiments to estimate the degree of mixing in the various phases.[10] An alternative strategy could be based upon energy transfer measurements in which the individual components would be selectively labeled. This is our specialty. In the accompanying paper, we examine by energy transfer measurements a urethane–acrylate system characterized by very small domain size to estimate the composition of the urethane-rich phase. In this paper, we describe the synthesis of this class of IPN's, composed of 67 wt % urethane and 33 wt % acrylate (2-ethylhexyl and/or isobornyl acrylate), in which irradiation is used to initiate the acrylate polymerization. We describe the morphology and mechanical properties of the IPN's obtained as a function of the timing of the urethane cure and the acrylate network formation.

Experimental Section

1. Sample Preparation. All samples contain 67 wt % of polyurethane (PU) and 33 wt % of polyacrylates (PA). In the first set of IPN's, the acrylate monomer is 2-ethylhexyl acrylate (EHA) with 1,6-hexanediol diacrylate serving as the cross-linker. The acrylate/diacrylate ratio is 90/10 (wt/wt, Table 1). Three different IPN's of the same composition were prepared by different polymerization sequences, and these are referred to as two sequential IPN's (SeqIPN), $\mathrm{PU}_{g15}^{75\%}\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$ and $\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$, and one simultaneous IPN(SimIPN), $\mathrm{PU}^{50\%}\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$. A second set of IPN's were prepared in an identical manner, except that 35 wt % of the 2-ethylhexyl acrylate (EHA) was replaced with isobornyl acrylate (IBA), and these are referred to as $\mathrm{PU}_{g15}^{75\%}\mathrm{PA(EHA/IBA)}^{100\%}\mathrm{PU}^{100\%}$, $\mathrm{PA(EHA/IBA)}^{100\%}\mathrm{PU}^{100\%}$, and $\mathrm{PU}^{50\%}\mathrm{PA(EHA/IBA)}^{100\%}\mathrm{PU}^{100\%}$. By replacing all the EHA with IBA, a third set of IPN's were also prepared in the identical manner, which are named as $\mathrm{PU}_{g15}^{75\%}\mathrm{PA(IBA)}^{100\%}\mathrm{PU}^{100\%}$, $\mathrm{PA(IBA)}^{100\%}\mathrm{PU}^{100\%}$, and $\mathrm{PU}^{50\%}\mathrm{PA(IBA)}^{100\%}\mathrm{PU}^{100\%}$. Our notation for these IPN's is explained in Appendix A.

Table 1. Recipe for IPN Preparation

chemical	weight (g)	mmol
2-ethylhexyl acrylate[a]	5.40	29.3
1,6-hexanediol diacrylate	0.60	2.65
photoinitiator	0.015	0.0585
poly(tetramethylene glycol) ($M_n = 1000$)	9.00	9.0
Desmurdo N-100[b]	3.45	7.2

[a] Isobornyl acrylate was also used; see text for details. [b] NCO weight percent in N-100: 26.3% (calculated), 21.8–22.2% (actual).

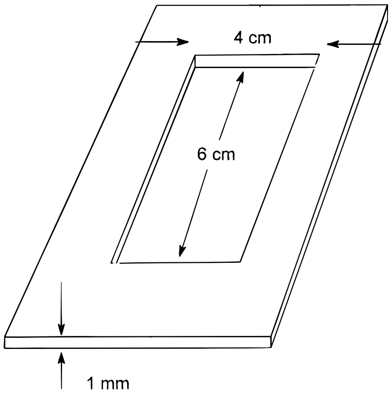

Figure 1. Mold for preparation of IPN samples.

(a) Preparation of SeqIPN $\mathrm{PU}_{g15}^{75\%}\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$. To a 50 mL Erlenmeyer flask were added the photoinitiator (15 mg, 2,2-dimethoxy-2-phenylacetophenone, Aldrich), 2-ethylhexyl acrylate (5.40 g, Fluka), and 1,6-hexanediol diacrylate (600 mg, Aldrich). After the photoinitiator had dissolved, poly(tetramethylene glycol) (9.00 g, $M = 1000$, Dupont) was added to the Erlenmeyer flask and thoroughly mixed with the acrylate monomers by stirring. Triisocyanate (Desmurdo N-100, 3.45 g, Miles Chemical Co.) was subsequently added to the above Erlenmeyer flask and stirred at 55 °C for 2 min to obtain a homogeneous solution (at room temperature, the mixture remained as two discrete liquid phases). Dibutyltin dilaurate (6 μL, 500 ppm based upon polyurethane, Polysciences Inc.) was added, and the resulting viscous liquid mixture was then transferred to sheets of biaxially oriented polypropylene film at 22 °C and then sandwiched between two polypropylene films to make 1 mm thick IPN samples in a mold of 1 mm thick silicon rubber (Figure 1). Under this condition, the PU network gelled in ca. 15 min. Gellation was noted as a rapid change in the sample from a fluid to a rubbery state. After 2 h at room temperature (ca. 75% PU conversion), these samples were photolyzed for 10 min (with 3000 Å lamps in a Rayonet photochemical reactor), conditions sufficient to cause complete polymerization of the acrylate. The sample was kept at 22 °C for at least another 46 h to allow the urethane polymerization to go to completion before any measurements on the system were carried out.

(b) Preparation of SeqIPN $\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$. As above, the photoinitiator (15 mg, 2,2-dimethoxy-2-phenylacetophenone), 2-ethylhexyl acrylate (5.40 g), and 1,6-hexanediol diacrylate (600 mg) were placed in a 50 mL flask. Poly(tetramethylene glycol) (9.00 g) was added with stirring. Triisocyanate (Desmurdo N-100, 3.45 g) was subsequently added, and the mixture was stirred at 55 °C for 2 min to make a homogeneous solution. Here a smaller amount of dibutyltin dilaurate (1.2 μL, 100 ppm based upon polyurethane) was subsequently added. The resulting viscous liquid mixture was then transferred immediately to the mold described in Figure 1 to form samples ca. 1 mm thick. These samples were photolyzed immediately for 20 min at 3000 Å and then placed in an oven at 60 °C for 4 h.

(c) Preparation of SimIPN $\mathrm{PU}^{50\%}\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$. The mixture described for sample $\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$ was prepared as described above and was heated with mixing for 2.0 min at 55 °C. Dibutyltin dilaurate (1.2 μL, 100 ppm based upon polyurethane) was added and, as before, the mixture was placed between sheets of polypropylene (cf. Figure 1) at 22 °C to form 1 mm thick IPN samples. After 90 min at room temperature (PU not gelled yet, ca. 50% PU conversioin at this point), these samples were photolyzed for 16 min at 3000 Å and then placed in an oven at 60 °C for 4 h.

(d) Preparation of SeqIPN$\mathrm{PU}^{75\%}_{\mathrm{g}15}\mathrm{PA(EHA/IBA)}^{100\%}\mathrm{PU}^{100\%}$, $\mathrm{PA(EHA/IBA)}^{100\%}\mathrm{PU}^{100\%}$, and SimIPN $\mathrm{PU}^{50\%}\mathrm{PA(EHA/IBA)}^{100\%}\mathrm{PU}^{100\%}$. These IPN's were prepared in an identical manner as was used for preparing $\mathrm{PU}^{75\%}_{\mathrm{g}15}\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$, $\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$, and $\mathrm{PU}^{50\%}\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$, respectively, except that isobornyl acrylate (1.89 g, Aldrich) and 2-ethylhexyl acrylate (3.51 g) were used instead of 5.4 g of 2-ethylhexyl acrylate.

(e) Preparation of SeqIPN $\mathrm{PU}^{75\%}_{\mathrm{g}15}\mathrm{PA(IBA)}^{100\%}\mathrm{PU}^{100\%}$, $\mathrm{PA(IBA)}^{100\%}\mathrm{PU}^{100\%}$, and SimIPN $\mathrm{PU}^{50\%}\mathrm{PA(IBA)}^{100\%}\mathrm{PU}^{100\%}$. These IPN's were prepared in an identical manner as was used for preparing $\mathrm{PU}^{75\%}_{\mathrm{g}15}\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$, $\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$, and $\mathrm{PU}^{50\%}\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$, respectively, except that isobornyl acrylate (5.4 g, Aldrich) was used instead of 5.4 g of 2-ethylhexyl acrylate.

(f) Preparation of SeqIPN $\mathrm{PU}^{100\%}_{\mathrm{g}15}\mathrm{PA(IBA)}^{100\%}$. This SeqIPN was prepared by using the same monomer composition and processing conditions as those used for $\mathrm{PU}^{75\%}_{\mathrm{g}15}\mathrm{PA(IBA)}^{100\%}\mathrm{PU}^{100\%}$, except that the photolysis was conducted after polyurethane reaction completion (48 h after film casting).

(g) Preparation of SeqIPN $\mathrm{PU}^{100\%}_{\mathrm{g}180}\mathrm{PA(IBA)}^{100\%}$. This IPN was prepared by following the same protocol for preparing $\mathrm{PU}^{100\%}_{\mathrm{g}15}\mathrm{PA(IBA)}^{100\%}$, except that 100 ppm tin catalyst was used instead of 500 ppm. Under this condition, the PU gelation time was ca. 180 min.

2. Transmission Electron Microscopy (TEM) Studies. All TEM specimens were prepared by microtoming at −100 °C to obtain slices with typical thickness of 60 nm. These samples were subsequently stained with $\mathrm{RuO_4}$ vapor. TEM photos were taken in a JEOL 1210 instrument operated at 120 kV. The highest magnification is 200 000.

3. DMA Measurements. IPN samples were cut to form strips 1 mm thick and 5 mm × 30 mm in size. Dynamic mechanical analyses were conducted at 1 Hz in the extension mode, using a Seiko DMS 110 Instrument System.

Results and Discussion

Sample Preparation. We consider an acrylate−urethane system in which the polyurethane (PU) is the major component and comprises 67 wt % of the system. By varying experimental conditions, we are able to polymerize either the urethane or the acrylate first. By reacting the urethane precursors to partial conversion before the acrylate is reacted and then completing the urethane polymerization, we obtain a third system. The acrylate polymerization is photoinduced, which provides particularly strong control over the timing of the creation of the urethane and acrylate networks. In some experiments, the acrylate monomer 2-ethylhexyl acrylate (EHA) was used. Here the electron microscopy experiments are informative, but because of the low T_g of the PEHA phase, no information about single or dual T_g's could be obtained from dynamic mechanical measurements. Therefore, we prepared a second set of IPN's in which part of the EHA was replaced by isobornyl acrylate (IBA) and also a third set of IPN's in which all of the EHA was replaced by isobornyl acrylate (IBA). In all instances, 10 wt % of 1,6-hexanediol diacrylate was employed as the cross-linking agent.

The structures of the monomers employed are shown in Figure 2, and the recipe is presented in Table 1. All three types of IPN's in a given set were prepared from the same mixture of reactants. Since the PU network was formed between a diol (poly(tetramethylene glycol)) and a triisocyanate, we estimate the molecular weight between cross-links (M_c) in the fully cured PU phase to be ca. 1200. The polyacrylate (PA) phase is composed of 90 wt % of 2-ethylhexyl acrylate (and/or isobornyl acrylate) and 10 wt % of 1,6-hexanediol diacrylate, from which we estimate $M_c = 1800$.

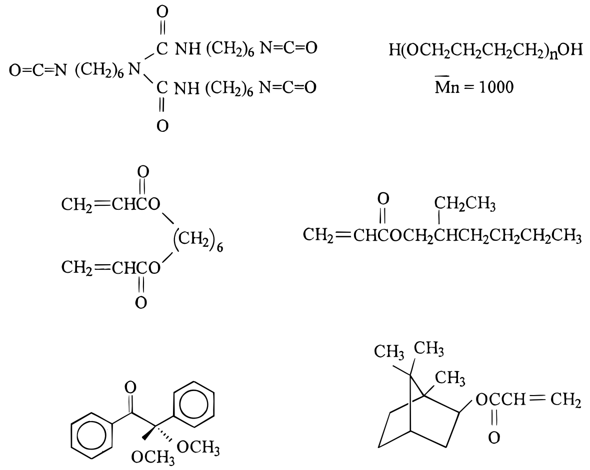

Figure 2. Structures of the monomers and the photoinitiator for IPN preparation.

Urethane polymerization was catalyzed by dibutyltin dilaurate and was followed by monitoring the isocyanate band in the infrared spectrum at 2270 cm^{-1}.[15,16] Acrylate polymerization was photoinitiated, with 2,2-dimethoxy-2-phenylacetophenone as the photoinitiator. Here the extent of polymerization was followed by monitoring the vinyl hydrogen out-of-plane vibration in the IR at 810 cm^{-1}.[15,16] In this and all other IPN's, gellation, particularly of the PU component, was inferred from monitoring the sharp transformation of the system from a fluid to a rigid state, which occurs over a short period of time. In the sample described in the following paragraph, the gel point for the PU phase was reached after 15 min, and this observation is included in the notation for the sample.

SeqIPN $\mathrm{PU}^{75\%}_{\mathrm{g}15}\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$ was prepared by first heating the mixture at 55 °C for 2 min and adding a relatively large amount of catalyst (500 ppm dibutyltin dilaurate based on urethane weight) to initiate polyurethane formation, followed by cooling to room temperature (to 22 °C, over 1−2 min) and continuing this polymerization at room temperature for another 2 h. These conditions carry the urethane polymerization to about 75% completion, well past the gel point (gelation at 15 min). This sample was then irradiated to complete the acrylate polymerization, and then the urethane polymerization was allowed to go to completion at room temperature over ca. 40 h. The other SeqIPN, $\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$, was prepared by irradiating the sample immediately after mixing and cooling the components (here with only 100 ppm dibutyltin dilaurate catalyst). In this way, we were able to polymerize the acrylate completely with minimal polyurethane formation (less than 10% conversion, estimated by IR). The sample was then heated in an oven for 4 h at 60 °C to polymerize the urethane. To obtain $\mathrm{PU}^{50\%}\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$, the monomer mixture was heated at 55 °C for 2 min and further reacted (with 100 ppm dibutyltin dilaurate catalyst) at room temperature for 90 min to effect a partial cure. This system did not pass the gel point of the urethane. From the NCO band in the IR, we infer about 50% conversion. The sample was then irradiated to complete acrylate conversion, followed by 4 h in an oven at 60 °C. $\mathrm{PU}^{50\%}\mathrm{PA(EHA)}^{100\%}\mathrm{PU}^{100\%}$ may be thought of as a kind of “simultaneous” IPN, since acrylate

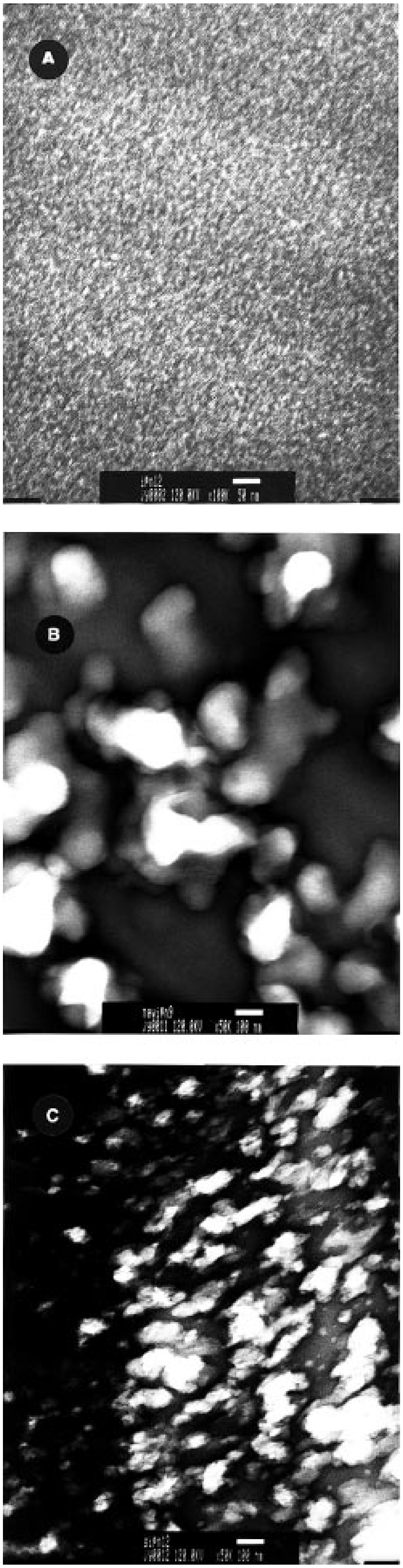

Figure 3. TEM images of (A) $PU_{g15}^{75\%}PA(EHA)^{100\%}PU^{100\%}$, (B) $PA(EHA)^{100\%}PU^{100\%}$, and (C) $PU^{50\%}PA(EHA)^{100\%}PU^{100\%}$. Marker bars: (A) 50 nm; (B) 100 nm; (C) 100 nm.

polymerization occurs in the half-polymerized but not yet gelled urethane phase. We refer to this sample as a SimIPN, keeping in mind its true nature.

Morphology As Seen by Transmission Electron Microscopy. In urethane–acrylate IPN's, the urethane phase is stained selectively with RuO_4 and appears as the dark phase in the images shown in Figure 3. Figure 3A is an image of a thin section of SeqIPN $PU_{g15}^{75\%}PA(EHA)^{100\%}PU^{100\%}$. The domain sizes are small and seem well mixed. In many instances, there is no clear boundary between the phases. The individual acrylate domains are smaller than 20 nm. In samples in which the phase domains are much smaller than the thickness of the TEM sample, unambiguous interpretation of the images in terms of domain shape, boundary diffuseness, and phase continuity is difficult.

In Figure 3B we see an image of another SeqIPN $PA(EHA)^{100\%}PU^{100\%}$ in which the acrylate network was polymerized first. Here the polyurethane is present as the continuous phase with large globules of the acrylate dispersed within it. Most of the PA domains are 100–300 nm in diameter, with relatively sharp boundaries on the TEM scale. The smaller objects seen in the image are likely due to off-center sections through much larger PA domains.

In the Introduction, we mentioned that the first network to be formed commonly becomes the continuous phase. Here the PA phase is clearly the dispersed phase. These types of dispersed phases occur when the first-formed polymer is not miscible with the second-stage precursors and phase separates after the first component polymerizes. We infer from the turbidity that the polyacrylate has phase separated during its formation. This is likely a consequence of immiscibility between the PA and the poly(tetramethylene glycol) component of the reaction mixture. This morphology is then locked in during the second-stage urethane polymerization.

It is rather remarkable to note the contrast in morphology between sample $PU^{50\%}PA(EHA)^{100\%}PU^{100\%}$ and that shown in Figure 3A representing $PU_{g15}^{75\%}PA(EHA)^{100\%}PU^{100\%}$. In these two samples, the order of polymerization is the same (urethane–acrylate–urethane), but the extent of urethane conversion prior to irradiation of sample $PU^{50\%}PA(EHA)^{100\%}PU^{100\%}$ was much smaller and did not reach the gel point. Here we observe that the acrylate appears as a dispersed phase, with domains ranging in size from 50 to 300 nm. While some distortion of the images may be due to the sample sectioning process, these domains are clearly irregular, rather than spherical in shape. By comparison with Figure 3B, we see that the phase boundaries here are often fuzzy or indistinct.

Dynamic Mechanical Analysis. IPN Set I with PA(EHA). Dynamic mechanical measurements were carried out in the extension mode to obtain the loss modulus E'', the storage modulus E', and their ratio, tan δ. The PU network itself exhibited a broad glass–rubber transition in the tan δ vs temperature plot with a maximum at −55 °C, which was taken to be the T_g of this PU. A similar plot for the PA(EHA) network showed a somewhat more symmetrical trace, with a maximum at −36 °C. These serve as the comparison for the tan δ vs T plots for the three IPN samples $PU_{g15}^{75\%}PA(EHA)^{100\%}PU^{100\%}$, $PA(EHA)^{100\%}PU^{100\%}$, and $PU^{50\%}PA(EHA)^{100\%}PU^{100\%}$, shown in Figure 4.

All three IPN samples show only a single glass transition region. Samples $PA(EHA)^{100\%}PU^{100\%}$ and

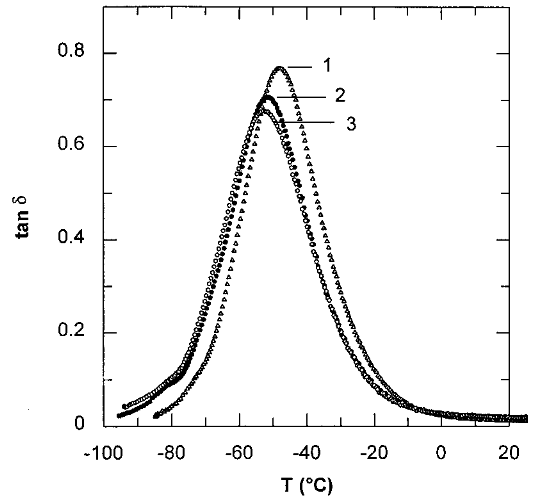

Figure 4. tan δ vs temperature plot for IPN's (1) PU$^{75\%}_{g15}$PA(EHA)$^{100\%}$PU$^{100\%}$, (2) PA(EHA)$^{100\%}$PU$^{100\%}$, and (3) PU$^{50\%}$PA(EHA)$^{100\%}$PU$^{100\%}$.

PU$^{50\%}$PA(EHA)$^{100\%}$PU$^{100\%}$ have peaks at almost the same location as that of the PU component. Since the TEM images show large-scale phase separation in these samples, it appears that the mechanical properties of the PU component dominate the measurement, and the contribution of the PA phase is not visible. By contrast, there is a shift in the maximum for PU$^{75\%}_{g15}$PA(EHA)$^{100\%}$PU$^{100\%}$ to higher temperature. This shift is consistent with considerable mixing of the two phases. However, none of these conclusions are unambiguous.

IPN Set II with PA(EHA/IBA). To resolve some of the outstanding issues, we prepared a new set of IPN's in which part of the EHA was replaced with isobornyl acrylate (IBA) to raise the T_g of the acrylate phase. The new acrylate monomer combination comprised 58.5 wt % EHA, 31.5 wt % IBA, and 10 wt % hexanediol diacrylate. A sample of this component PA(EHA/IBA) was prepared as a reference sample for dynamic mechanical analysis, and then three new IPN samples (PU$^{75\%}_{g15}$PA(EHA/IBA)$^{100\%}$PU$^{100\%}$, PA(EHA/IBA)$^{100\%}$ PU$^{100\%}$, and PU$^{50\%}$PA(EHA/IBA)$^{100\%}$PU$^{100\%}$) were prepared following the same protocol as for the samples described above.

In Figure 5, we plot tan δ vs T for PU$^{75\%}_{g15}$PA EHA/IBA)$^{100\%}$PU$^{100\%}$ as well as for PU ($T_g = -55$ °C) and PA(EHA/IBA) ($T_g = -17$ °C). Here we see clearly that the sample is characterized by a single T_g (−42 °C) which lies in between those of its individual components. This indicates good phase mixing of the two networks, which is consistent with the TEM result.

The other two IPN samples show two peaks in their dynamic mechanical spectra (cf. Figure 6). These appear at almost the same temperatures as those for the individual components, as expected for samples characterized by extensive phase separation and large domain sizes. This result is in accord with the TEM results. Closer inspection of the tan δ plots for these two IPN's reveals that there is a shift to lower temperature of the peak corresponding to the PU phase for PA(EHA/IBA)$^{100\%}$PU$^{100\%}$, which is due to incomplete reaction of the polymer−diol,[14] and the peaks corresponding to the PA phase are shifted to lower temperature (ca. 3 °C) in both IPN's, indicating a small amount of polyurethane mixed with the polyacrylate phase.

Despite the differences observed in the DMA traces for these three IPN's, they are all transparent. This is due to a match in the refractive indices of the polyurethane and polyacrylate components.

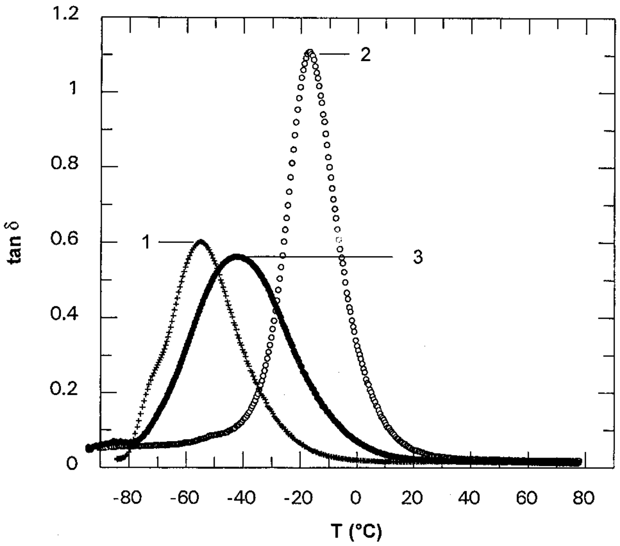

Figure 5. tan δ vs temperature plot for (1) PU, (2) PA(EHA/IBA), and (3) PU$^{75\%}_{g15}$PA(EHA/IBA)$^{100\%}$PU$^{100\%}$.

IPN Set III with PA(IBA). If monomer conversion can be driven to completion and the T_g's of the two components are well separated, one should in principle be able to use the shifts in T_g values found in the IPN to infer phase mixing among the components. One approach to using T_g values to infer the extent of mixing would employ the Gordon−Taylor[18] or the Fox equation.[19] These expressions, both based upon volume additivity, become identical if the polymer densities are not too different and if the ratio of the thermal expansion coefficients is inversely proportional to the ratio of the T_g's. For our system, the Fox equation can be expressed as

$$\frac{1}{T_{g_{\mathrm{IPNPU}}}} = \frac{W_{\mathrm{PU}}}{T_{g_{\mathrm{PU}}}} + \frac{1 - \mathrm{W}_{\mathrm{PU}}}{T_{g_{\mathrm{PA}}}} \qquad (1)$$

$$\frac{1}{T_{g_{\mathrm{IPNPA}}}} = \frac{\mathrm{W}_{\mathrm{PA}}}{T_{g_{\mathrm{PA}}}} + \frac{1 - \mathrm{W}_{\mathrm{PA}}}{T_{g_{\mathrm{PU}}}} \qquad (2)$$

For miscible polymer blends, many systems show deviation from this simple behavior, a topic reviewed recently by Schneider[20a] and by Schneider and Di Marzio.[20b] In these cases, the interactions between the polymers which lead to miscibility can lead to energetic and configurational entropic (free volume) effects that require additional terms to fit the plots of T_g vs blend composition. The additional parameters needed to fit the data[21] are, unfortunately, material parameters that cannot be determined independently.

The Fox equation has the merit that composition can be inferred from the two T_g values. This serves as a semiquantitative insight into the relationship between the phase behavior of the system and processing history. All of the samples have the same bulk composition but differ only in the number and location of cross-links in the system. Furthermore, in one instance where we are able to determine the composition of the phases using energy transfer measurements, the compositions inferred analyzing the DMA data in terms of eqs 1 and 2 are almost identical.

DMA data from the three IPN's in Set II, in which the two homopolymer networks have T_g's separated by 36 °C, are still not good enough for phase mixing

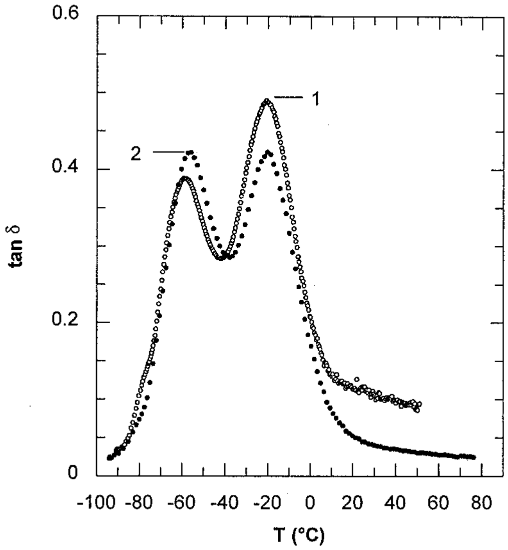

Figure 6. tan δ vs temperature plot for (1) PA(EHA/IBA)$^{100\%}$PU$^{100\%}$ and (2) PU$^{50\%}$PA(EHA/IBA)$^{100\%}$PU$^{100\%}$.

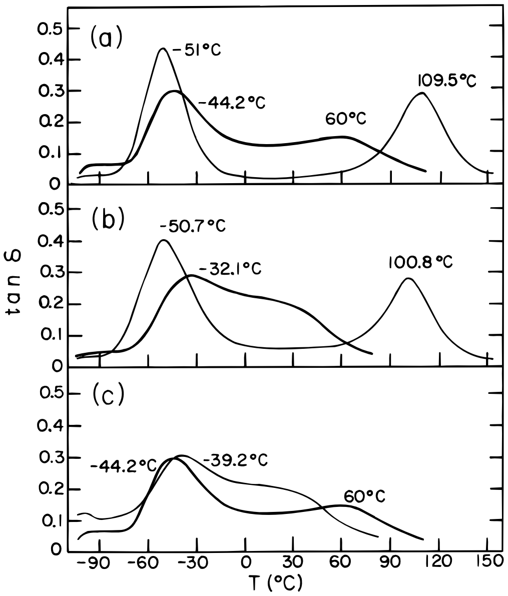

Figure 7. DMA plots for (a) seqIPN's PU$^{75\%}_{g15}$PA(IBA)$^{100\%}$PU$^{100\%}$ (thick line) and PA(IBA)$^{100\%}$PU$^{100\%}$ (thin line), (b) SimIPN PU$^{50\%}$PA(IBA)$^{100\%}$PU$^{100\%}$ (thin line) and SeqIPN PU$^{100\%}_{g180}$PA(IBA)$^{100\%}$ (thick line), and (c) SeqIPN's PU$^{75\%}_{g15}$PA(IBA)$^{100\%}$PU$^{100\%}$ (thick line) and PU$^{100\%}_{g15}$PA(IBA)$^{100\%}$ (thin line).

Table 2. IPN Set III Glass Transition Temperatures[a]

	T_g (°C)	
IPN	PU-rich phase	PA-rich phase
PA(IBA)$^{100\%}$PU$^{100\%}$	−51	109.5
PU$^{50\%}$PA(IBA)$^{100\%}$PU$^{100\%}$	−50.7	100.8
PU$^{75\%}_{g15}$PA(IBA)$^{100\%}$PU$^{100\%}$	−44.2	60
PU$^{100\%}_{g15}$PA(IBA)$^{100\%}$	−39.2	10−25,[b] shoulder
PU$^{100\%}_{g180}$PA(IBA)$^{100\%}$	−32.1	5−20,[b] shoulder

[a] From peak position in tan δ vs *T* plot. [b] Broad shoulder.

Table 3. Phase-Domain Composition in Set III IPN's As Calculated from tan δ

	PU phase		PA phase	
IPN	PU (wt %)	PA (wt %)	PU (wt %)	PA (wt %)
PA(IBA)$^{100\%}$PU$^{100\%}$	95.4	4.6	assume 0%	assume 100%
PU$^{50\%}$PA(IBA)$^{100\%}$PU$^{100\%}$	95.1	4.9	3	97
PU$^{75\%}_{g15}$PA(IBA)$^{100\%}$PU$^{100\%}$	88.6	11.4	20	80
PU$^{100\%}_{g15}$PA(IBA)$^{100\%}$	83.9	16.1	40[a]	60[a]
PU$^{100\%}_{g180}$PA(IBA)$^{100\%}$	77.6	22.4	46[b]	54[b]

[a] Estimated from the shoulder in the tan δ plot at 20 °C (T_g). [b] Estimated from the shoulder in the tan δ plot at 10 °C (T_g).

Table 4. IPN Turbidity

IPN type	name	turbidity
SeqIPN[a]	PU$^{75\%}_{g15}$PA(EHA)$^{100\%}$PU$^{100\%}$	transparent
	PU$^{75\%}_{g15}$PA(EHA/IBA)$^{100\%}$PU$^{100\%}$	transparent
	PU$^{75\%}_{g15}$PA(IBA)$^{100\%}$PU$^{100\%}$	transparent
	PU$^{100\%}_{g15}$PA(IBA)$^{100\%}$	transparent
	PU$^{100\%}_{g180}$PA(IBA)$^{100\%}$	transparent
SeqIPN[b]	PA(EHA)$^{100\%}$PU$^{100\%}$	cloudy
	PA(EHA/IBA)$^{100\%}$PU$^{100\%}$	transparent
	PA(IBA)$^{100\%}$PU$^{100\%}$	cloudy
SimIPN[c]	PU$^{50\%}$PA(EHA)$^{100\%}$PU$^{100\%}$	cloudy
	PU$^{50\%}$PA(EHA/IBA)$^{100\%}$PU$^{100\%}$	transparent
	PU$^{50\%}$PA(IBA)$^{100\%}$PU$^{100\%}$	cloudy

[a] Sequential IPN's are those in which the urethane component reached the gel point prior to initiation of acrylate polymerization. [b] Sequential IPN's here are those in which the acrylate component polymerized to completion first. [c] "Simultaneous IPN's" here refer to partial conversion of the urethane polymerization in which acrylate polymerization is initiated before the PU phase gels.

calculations with the Fox equation. To further increase the difference in T_g values, we prepared a third set of IPN's in which all the EHA was replaced by IBA. Here the T_g's of the two homopolymers are separated by 165 °C. DMA spectra are presented for these samples in Figure 7.

1. SeqIPN PU$^{75\%}_{g15}$PA(IBA)$^{100\%}$PU$^{100\%}$. As shown in Figure 7a, IPN PU$^{75\%}_{g15}$PA(IBA)$^{100\%}$PU$^{100\%}$ exhibits two T_g's at −44.2 °C (PU-rich phase) and 60 °C (PA-rich phase), respectively. The T_g for the pure homopolyurethane is −55.4 °C, and that for homopolyacrylate network PA(IBA) is $T_g = 109.5$ °C.

The inward shift of the T_g's in the IPN can be interpreted in terms of the degree of phase mixing in each component. As shown in eqs 1 and 2, W_{PU} is the weight percent of PU in the PU-rich phase, and we observed a T_g of −44.2 °C ($T_{g_{IPNPU}}$) in Figure 7a, compared to −55.4 °C for pure PU itself and 109.5 °C for the PA network. Similarly, W_{PA} is the weight percent of PA in the PA-rich phase (with $T_{g_{IPNPA}} = 60$ °C). The calculated compositions are presented in Table 3.

2. SeqIPN PA(IBA)$^{100\%}$PU$^{100\%}$. Sample PA(IBA)$^{100\%}$-PU$^{100\%}$ also gives two well-separated T_g's (Figure 7a), and the higher T_g (109.5 °C) is taken as that for cross-linked poly(isobornyl acrylate) network PA(IBA). This value is slightly higher than that of pure PIBA itself ($T_g = 94$ °C, ref 17), due to the influence of the 10 wt % diacrylate cross-linking agent. Attempts to prepare a model network by irradiation at room temperature of the acrylate monomer mixture itself did not work because the reaction would not go to completion. The monomer−polymer mixture obtained in this way had a T_g of 64 °C.

3. SimIPN PU$^{50\%}$PA(IBA)$^{100\%}$PU$^{100\%}$. The DMA plot for this sample (Figure 7b) resembles that of PA(IBA)$^{100\%}$PU$^{100\%}$ shown in Figure 7a. The main difference is in the T_g of the PA-rich phase, which is shifted to somewhat lower temperature. For the above IPN's, a summary of the T_g's in each phase is given in Table 2, and the phase mixing results are presented in Table 3.

Consider the PU-rich phase in these IPN's. In PA-(IBA)$^{100\%}$PU$^{100\%}$ and PU$^{50\%}$PA(IBA)$^{100\%}$PU$^{100\%}$, $T_{g_{PU}}$ is

Table 5. IPN Notation

acrylate monomer	IPN name	comments
EHA	PU$_{g15}^{75\%}$PA(EHA)$^{100\%}$PU$^{100\%}$	These are sequential IPN's. PU gelled at 15 min.
EHA/IBA	PU$_{g15}^{75\%}$PA(EHA/IBA)$^{100\%}$PU$^{100\%}$	
IBA	PU$_{g15}^{75\%}$PA(IBA)$^{100\%}$PU$^{100\%}$	
EHA	PA(EHA)$^{100\%}$PU$^{100\%}$	These are sequential IPN's. PA cured to completion first.
EHA/IBA	PA(EHA/IBA)$^{100\%}$PU$^{100\%}$	
IBA	PA(IBA)$^{100\%}$PU$^{100\%}$	
EHA	PU$^{50\%}$PA(EHA)$^{100\%}$PU$^{100\%}$	"Simultaneous" IPN's. PU reacted first to 50%, not gelled at this point.
EHA/IBA	PU$^{50\%}$PA(EHA/IBA)$^{100\%}$PU$^{100\%}$	
IBA	PU$^{50\%}$PA(IBA)$^{100\%}$PU$^{100\%}$	
IBA	PU$_{g15}^{100\%}$PA(IBA)$^{100\%}$	sequential IPN
IBA	PU$_{g180}^{100\%}$PA(IBA)$^{100\%}$	sequential IPN

shifted only 4 deg, corresponding to a ca. 5% of PA chains mixed in PU-rich phase. The third IPN, PU$_{g15}^{75\%}$PA(IBA)$^{100\%}$PU$^{100\%}$, with $T_{g_{PU}}$ shifted by 10 deg, indicates that more than 10 wt % of PA is mixed with the PU-rich phase. Turning to the PA-rich phase, only the last IPN (PU$_{g15}^{75\%}$PA(IBA)$^{100\%}$PU$^{100\%}$) shows a significant shift of $T_{g_{PA}}$ (here ca. 50 deg), corresponding to 20 wt % of PU in the PA-rich phase.

The greatest extent of phase mixing occurs in sample PU$_{g15}^{75\%}$PA(IBA)$^{100\%}$PU$^{100\%}$. For comparison, we prepared a new sample in which PU conversion was completed before photoinitiation of acrylate polymerization, sample PU$_{g15}^{100\%}$PA(IBA)$^{100\%}$. A second modification involved decreasing the amount of tin catalyst in the system to slow the amount of time needed for gelation of the PU component, sample PU$_{g180}^{100\%}$PA (IBA)$^{100\%}$. The DMA plots for these two IPN's are shown in Figures 7b and 7c.

4. SeqIPN PU$_{g15}^{100\%}$PA(IBA)$^{100\%}$ and SeqIPN PU$_{g180}^{100\%}$PA(IBA)$^{100\%}$. Here we observe a further inward shift of the two transition regions compared with that of PU$_{g15}^{75\%}$PA(IBA)$^{100\%}$PU$^{100\%}$, and these are also reflected in an increasing extent of phase mixing (Table 3). Based on these data, we conclude that gelation of PU prior to PA formation is essential for extensive phase mixing, that fully curing the PU gives better phase mixing than partial curing of PU before irradiation, and that slow reaction toward gelation of the PU yields even further phase mixing.

Turbidity of IPN's. Turbidity measurements are often useful as an empirical method of determining phase mixing. For example, a transparent IPN sample implies a better phase mixing compared with a cloudy IPN sample; phase domains in the transparent sample should be much smaller than the wavelength of light. There is, however, a description in the literature of a transparent IPN sample which exhibited two well-separated T_g's, an unusual observation reported without any explanation.[13] We also observe this phenomenon for samples containing the EHA/IBA mixture of Set II. Our observations of IPN turbidities are summarized in Table 4, in which the first five SeqIPN's (PU gelled first) are all transparent. These are consistent with the TEM results (very small phase domains, <20 nm) and the DMA data (one T_g). The rest of the IPN's in Table 4, with domains >100 nm (TEM) and two well-separated T_g's (DMA), with two exceptions, are turbid. The two exceptions, PA(EHA/IBA)$^{100\%}$PU$^{100\%}$ and PU$^{50\%}$ PA(EHA/IBA)$^{100\%}$PU$^{100\%}$ are transparent. This can only occur if the refractive indices of the two polymers match at this specific PA composition.

Summary

Eleven urethane−acrylate IPN's of both the sequential and simultaneous type, were prepared by varying the processing conditions and polyacrylate compositions. IPN morphology in these systems was examined by transmission electron microscopy (TEM) and dynamic mechanical analysis (DMA). Where possible, the degree of phase mixing was calculated from shifts in the tan δ maxima through the Fox equation. We conclude that sequential IPN's in which PU gels first have the finest phase domains (<20 nm) and greatest extent of phase mixing. A curious result is that in SeqIPN preparations where the PU gels first, lower amounts of tin catalyst, which lead to slower network formation, yield a greater extent of PA mixing into the PU-rich phase. Some samples are transparent, in spite of phase separation, due to index of refraction matching of the PU and PA phases. Further studies of phase mixing by the fluorescence energy transfer technique are presented in the following paper.

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Appendix A: Notation for IPN Preparation

The name of each IPN conveys information about the order of polymerization for each polymer, the conversion at each stage, the gelation time for the polyurethane network, and the polyacrylate composition. The superscript on the first polymer describes the fractional conversion; and the subscript, the measured gelation time. If no subscript is present, the reaction was carried to full conversion or, for partial conversion, gelation did not take place. For the second and third stages, only the conversion is given. For polyacrylate composition, EHA refers to 2-ethylhexyl acrylate and IBA to isobornyl acrylate. Two examples are explained below:

(a) PU$_{g15}^{75\%}$PA(IBA)$^{100\%}$PU$^{100\%}$ describes a sequential IPN in which the PU network reached the gel point after 15 min and further reacted to a conversion of 75%, followed by photolyzing to complete acrylate polymerization. Finally, urethane polymerization was run to completion before any testing of the sample. Here the PA network consists of 90 wt % of poly(isobornyl acrylate) and 10 wt % of cross-linking reagent. Because we always use 10 wt % of cross-linking reagent, we do not specify this information in the IPN name.

(b) PU$_{g180}^{100\%}$PA(IBA)$^{100\%}$ stands for a sequential IPN in which PU gelled first at 180 min and further reacted to

100% completion. PA is formed following PU polymerization. The PA network consists of (90 wt %) poly(isobornyl acrylate) plus cross-linking agent.

All IPN notations are summarized in Table 5.

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