Simultaneous Interpenetrating Networks of a Polyurethane and Poly(methyl methacrylate). II. Partitioning of MMA Monomer in the Last Stages of Polymerization

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SYNOPSIS

In a model polyurethane/poly(methyl methacrylate) (PU/PMMA) system, the partitioning of unreacted methyl methacrylate monomer (MMA) is studied in the late stages of its polymerization, simulated by incorporating controlled amounts of MMA in otherwise fully cured simultaneous interpenetrating networks (SIN) samples. Glass transitions temperatures (T_g) were determined using dynamic mechanical spectroscopy and differential scanning calorimetry as a function of MMA content of the SINs. The lowering of T_g in each phase due to the plasticization effect of MMA is used to calculate a plasticization coefficient for each phase, finally allowing calculation of the partition coefficient of MMA between the two phases. It is found that the MMA monomer distributes itself almost uniformly across the two phases of the current SIN system, leading to speculation as to the locus of late SIN polymerization. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Interpenetrating polymer networks (IPNs) are a special class of polymer blends in which the polymers are crosslinked.[1,2] Like most blends, IPNs phase separate at some point during the polymerization of their monomers and/or prepolymers. Since crosslinking generally limits the phase domain size, domains are small compared to blends of the corresponding linear polymers. Crosslinking, generally, forms the basis for the interesting properties of IPNs, e.g., improved mechanical properties like toughness and fatigue, sound and vibration damping capabilities, and reduced swelling in solvents. These and other properties, sometimes unique to specific systems, allow for IPN applications as damping materials, automotive parts, ion-exchange resins, artificial teeth, medical wound dressing, etc.[1]

Sequential IPNs are obtained by swelling a polymer network I with a monomer mixture II, which is polymerized *in situ.*[1,2] In contrast, *simultaneous interpenetrating networks* (*SINs*) are made when all monomers or prepolymers and the corresponding crosslinkers are mixed together, before either polymer is formed.[1,2] Subsequent polymerizations require that the two polymers should be formed by noninterfering mechanisms. SIN systems prominent in the literature emphasize *cross*-polyurethane-*inter-cross*-poly(methyl methacrylate) (PU/PMMA).[2] The PU is generally formed by step-polymerizing a polyether or polyester diol with a diisocyanate, while PMMA is formed by the free-radical polymerization of methyl methacrylate (MMA) monomer initiated by thermal- or photoinitiators. The networks are crosslinked typically by employing controlled amounts of a triol or a triisocyanate for the PU and a dimethacrylate for the PMMA network.

The ubiquitous PU/PMMA system serves as an excellent model SIN system while giving good mechanical and damping properties. For example, Allen et al.[3] found that semi-I IPNs of cross-PU/linear

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PMMA at 20:80 compositions had impact strengths of 10 times those of pure linear PMMA. Although the modulus was reduced by a factor of about 2, the optical transmission of these semi-IPNs was the same as that of pure PMMA. Kim et al.[4,5] found that phase domains were finer in PU/PMMA SINs than in the corresponding linear blends and that the two glass transitions (T_g's) were shifted inward. Later, Hur et al.[6,7] obtained extremely broad, single glass transitions indicating a microheterogeneous morphology in their fatigue behavior studies of PU/PMMA SINs. Frisch and co-workers[8] found that poly(carbonate–urethane)/PMMA SINs had single T_g's in all compositions, which combined with transmission electron microscopy (TEM)-based studies, indicated single-phase morphologies even though the linear polymer blends were immiscible. Besides showing superior solvent and heat resistance as compared to the linear blends, these SINs also exhibited a tensile strength–synergism at intermediate compositions.[8] Zhou et al. studied pseudo IPNs of PU/PMMA (with PMMA as linear or star polymer chains).[9] Phase behavior of these materials and full IPNs was studied via glass transition behavior and scanning electron microscopy with respect to aging.[10,11] Recently, Akay and Rollins[12] recorded unusually high elongations at failure in their PU/PMMA SINs and synergism in various mechanical properties, with maximum improvements in the PU/PMMA composition range 30/70 to 40/60.

In almost all SINs and IPNs, gelation of at least one polymer and/or phase separation occurs while the polymerizing system still contains a significant amount of unreacted monomer and/or functional groups. For example, in the 70/30 PMMA/PU SINs investigated at 60°C in this laboratory,[13] phase separation occurred at about 11% conversion of MMA (the PMMA having gelled at about 8% conversion). Therefore, all of the remaining MMA monomer must be partitioned between the two phases after phase separation. However, the rates of MMA polymerization in the two phases may be different, e.g., due to concentration and viscosity differences, and particularly, after vitrification of the PMMA-rich domains, which occurs at about 90% MMA conversion at 60°C.[13] Glass transition measurements indicated that in the fully cured SINs,[13] each phase contained less than 1% of the "other" polymer. This also means that some of the PMMA produced after phase separation may be selectively transported by diffusion. Any new PMMA formed in the PMMA-rich phase may stay there, whereas linear PMMA formed in the PU-rich phase may be driven to the other, PMMA-rich, phase, following the laws of thermodynamics and kinetics. Of course, branching and crosslinking severely limit diffusion.

Naturally, as more monomer polymerizes, the morphology continues to develop in such SIN systems. In the current study, a partition coefficient for the MMA in the SIN will be developed. It is known that the presence of unreacted monomer (like MMA) in any polymer will tend to decrease the glass transition temperature (T_g) through a plasticization effect. Thus, the drop in T_g in both polymers of an SIN may be correlated to the concentration of the MMA present in the corresponding phase, allowing the partition of the MMA in the two phases to be addressed. A possible method for doing this involves determining the glass transitions of an IPN/SIN as a function of conversion of unreacted MMA. However, this method has some practical limitations because it requires quenching the reaction very sharply, at a precisely known conversion. Furthermore, it is important to ensure that minimum MMA loss occurs (evaporation or polymerization) during the subsequent T_g determination.

An alternative technique was, therefore, adopted in this study. Fully cured PU/PMMA SINs were swollen with controlled amounts of MMA monomer, inhibited with 10 ppm of hydroquinone monomethyl ether, followed by determination of the T_g's, as described below.

THEORY

Gordon and Taylor[14] proposed an empirical equation relating the T_g of a binary polymer system to its composition, which was approximated to a linear form by Koleske and Lundberg.[15] Later, Couchman[16] derived these equations by treating the entropies of mixing. The simplest, linear equation among these is written as

$$T_g = M_1 T_{g1} + M_2 T_{g2} \qquad (1)$$

where T_g equals glass transition temperature of the blend of polymers 1 and 2; T_{g1} and T_{g2} equal glass transition temperatures of polymers 1 and 2, respectively; M_1 and M_2 equal mass fractions of polymers 1 and 2, respectively, in the blend. (See the List of Symbols for these and following symbols.)

There are two important assumptions involved in the derivation of Eq. (1). First, both the pure components were assumed to have nearly the same heat capacity increments through their glass transitions, i.e., $\Delta C_{p1} \approx \Delta C_{p2}$. Second, it was assumed

that the T_g's of the two components are not greatly different from each other, i.e., $T_{g1}/T_{g2} \approx 1$.

Equation (1) may be applied to the current system, where "component 2" is a small molecule (MMA), a plasticizer for "component 1" (polymer: PU or PMMA). The low "T_g" of component 2 challenges the second assumption made above ($T_{g1}/T_{g2} \approx 1$) in the derivation of Eq. (1), making its logarithmic precursor equation more suitable for analysis.[16] However, the logarithmic equation predicts a convex relationship between T_g and composition,[15] and therefore, Eq. (1) was chosen in this study, since its linear form makes the subsequent data analysis much simpler. Indeed, in the limited plasticizer concentration range studied ($\leq 25\%$), Eq. (1) will be shown to fit reasonably well. The literature too, in several cases,[17-19] shows a nearly linear dependence of T_g on plasticizer content. For poly(vinyl chloride) plasticized by tritolyl phosphate, a straight line is observed up to 50% plasticizer content.[17]

In the following generalized treatment, PU is denoted by A, PMMA by B, and MMA by letter P, for plasticizer.

Pure Polymers

Rearranging Eq. (1) and rewriting in terms of more suitable notation gives

$$T_{gA} = T_{gA,0} + w_{pA}p_A \qquad (2)$$

which is similar to the equation form used by Koleske and Lundberg.[15] Here,

$$p_A = \frac{T_{gp} - T_{gA,0}}{100} \qquad (3)$$

and $T_{gA,0}$ equals T_g of pure PU (polymer A); T_{gA} equals T_g of PU in presence of plasticizer P, T_{gp} equals T_g of plasticizer P, i.e., MMA; w_{pA} equals weight percent of plasticizer P in polymer A, or 100 times the mass fraction of MMA in the swollen sample; and p_A equals the plasticization coefficient of MMA for polymer A (PU) (= slope of T_{gA} vs. w_{pA} plot).

Similarly,

$$T_{gB} = T_{gB,0} + w_{pB}p_B \qquad (4)$$

where the subscript B denotes PMMA, polymer B, and all terms have the same corresponding meaning as above with subscript A, for PU. Thus,

$$p_B = \frac{T_{gp} - T_{gB,0}}{100} \qquad (5)$$

where p_B equals plasticization coefficient of MMA for polymer B (PMMA) (= slope of T_{gB} vs. w_{pB} plot).

Simultaneous Interpenetrating Networks

Glass transition data of fully cured SIN materials show two distinct peaks in tan δ vs. temperature curves corresponding to the pure polymers PU and PMMA with no measurable inward shifting or broadening of the transitions. This indicates that Eqs. (2) and (4) should also hold in the two phases of the SIN since the phases are primarily composed of the corresponding pure polymers. Furthermore, the symbol T_{gA}, used above for pure PU can, therefore, also be used to denote the T_g of the PU-rich phase of the SINs. Same is true in using the symbol w_{pA} for mass fraction of MMA in pure PU (polymer A) as well as the PU-rich phase of the SINs. The symbols T_{gB} and w_{pB} may similarly be used for pure PMMA (polymer B) as well as the PMMA-rich phase. Therefore, in SINs, the plasticizer MMA will partition between the two polymers A and B such that

$$K_{A/B} = \frac{w_{pA}}{w_{pB}} \qquad (6)$$

and

$$W_p = w_{pA}a + w_{pB}b \qquad (7)$$

where W_p equals the overall weight percent of plasticizer P in the SIN; a and b equal the weight fractions of polymers A and B, respectively, in the unplasticized SIN (note: $a + b = 1.0$); and $K_{A/B}$ equals the partition coefficient of the plasticizer between phases A and B. The goal of this study, then, becomes the determination of the quantity $K_{A/B}$. For the SIN domains, the drop in T_g may be expressed as, following Eq. (2),

$$T_{gA} = T_{gA,0} + W_p p_{A,a} \qquad (8)$$

where $p_{A,a}$ is the plasticization coefficient of MMA for polymer A (PU) in the SIN containing polymers A and B in the ratio (a/b) ($p_{A,a}$ = slope of T_{gA} vs. W_p plot). Comparing Eqs. (2) and (8),

$$w_{pA}p_A = W_p p_{A,a} \qquad (9)$$

or, for polymer A,

$$w_{pA} = W_p\left(\frac{p_{A,a}}{p_A}\right) \qquad (10)$$

Similarly, for polymer B,

$$w_{pB} = W_p\left(\frac{p_{B,b}}{p_B}\right) \qquad (11)$$

Applying Eqs. (10) and (11) to Eq. (6), then provides

$$K_{A/B} = \frac{p_{A,a}}{p_A}\bigg/\frac{p_{B,b}}{p_B} = \frac{p_{A,a}p_B}{p_{B,b}p_A} \qquad (12)$$

Since all of the four parameters on the right-hand side of Eq. (12) can be experimentally determined, the partition coefficient, $K_{A/B}$, can easily be estimated for the SINs.

EXPERIMENTAL

Synthesis

The PU/PMMA SIN system was identical to the one described in the first paper[13] of this series. Table I summarizes all materials used and their sources. The samples were synthesized in the manner described before.[13] In brief, the PPG polyether diol and TMP triol were mixed and dried at 60°C in vacuum for ca. 30 min, in a 1:1 equivalent ratio. Upon cooling to room temperature, the H_{12}MDI diisocyanate and T-12 catalyst (as a 5% solution in toluene) were mixed with it, also in vacuum to avoid any air intake. The resulting PU–reaction mixture is referred to as "U" in this paper. For the PMMA–reaction mixture (denoted by MMA), the monomers MMA and TEGDM were passed through neutral aluminum oxide (Brockmann Activity I) to remove the dissolved inhibitor. Both LPO initiator and TEGDM crosslinking monomer were dissolved in MMA in the required concentration, and the mixture was flushed with nitrogen (N_2) gas to remove all dissolved oxygen (O_2), which acts as an inhibitor. To obtain the SIN–reaction mix, the above two mixtures were mixed in the desired proportion, followed by a final flushing with N_2. All mixtures were polymerized in poly(tetrafluoroethylene) (TFE)-coated glass molds at 60°C for 10 h, followed by postcuring in a vacuum oven at 100°C for 4 h and then at 120°C for another 10 h. This polymerizes or removes all MMA monomer below detection levels.

Table II lists the three SINs prepared for this study and their overall PU/PMMA composition. The PU networks in all the samples were prepared using the same crosslinker amounts (1.0 equivalent TMP triol). The PMMA networks in SIN-2, SIN-3, and pure PMMA samples were made by using 0.5% (by weight of final PMMA network) TEGDM crosslinker, whereas for SIN-1, 3.0% TEGDM was used. Table II also lists the number-average molecular weight between crosslinks (M_c, g/mol) for the

Table I SIN Materials and Recipes Used[a]

Compound	Class	Amount	Supplier
PU, Polymer A			
Poly(oxypropylene) glycol (PPG); MW = 2000	Polyether diol	1.0 equiv.	Polysciences
Dicyclohexylmethane-4-4'-diisocyanate (H_{12}MDI), Desmodur W	Aliphatic diisocyanate	2.0 equiv.	Miles, Inc.
2-Ethyl-2-(hydroxymethyl)-1,3-propane diol, or, Trimethylolpropane (TMP)	Crosslinker (triol)	1.0 equiv.	Aldrich
2-Butyl-2-ethyl-1,3-propanediol (BEPD)	Chain extender (diol)	1.0 equiv.	Eastman Chemical
Dibutyl tin dilaurate (T12)	Tin catalyst	0.05% (w/w PU)	Aldrich
PMMA, Polymer B			
Methyl methacrylate (MMA)	Monomer	96.5–99.0%	Aldrich
Tetraethylene glycol dimethacrylate (TEGDM)	Crosslinking monomer	0.5–3.0%	Polysciences
Lauroyl peroxide (LPO)	Initiator	0.5%	Aldrich

[a] Polymerization temperature = 60°C.

Table II   Molecular Weights Between Crosslinks for the Individual Networks and SINs

Sample	PU/PMMA Ratio	M_c, PU (g/mol)	M_c, PMMA (g/mol)
XPU	100/0	2600	—
XPMMA	0/100	—	5200
SIN-1	50/50	2600	3600
SIN-2	20/80	2600	5200
SIN-3	10/90	2600	5200

PU and PMMA networks in the three SINs. The M_c values were obtained from the pure PU and PMMA networks with the same crosslinker levels as in the SINs, determined[13] by the rubbery plateau shear modulus values [from Rheometrics Dynamic Analyzer (RDA-II)] and applying the theory of rubber elasticity.

Swelling in MMA

The MMA used for swelling the samples was not treated with alumina, so that it still contained ca. 10 ppm of hydroquinone monomethyl ether inhibitor. This reduced the possibility of undesired polymerization of MMA during the determination of T_g's of the swollen samples.

Fully polymerized and postcured SINs and homopolymer networks were cut into sizes slightly smaller than those suitable for the dynamic mechanical spectroscopy (DMS) measurements and soaked in MMA with periodic weighing for varying lengths of time so as to incorporate controlled amounts of MMA into them. After the desired amount of MMA was incorporated, the sample was wrapped in a 0.05-mm-thick polyethylene (PE) film and sealed using an adhesive tape. The sealed sample was kept at room temperature for 6–12 h to reach equilibrium.

Glass Transitions

Glass Transitions (T_g's) of samples were determined by differential scanning calorimetry (DSC) and DMS which were done, respectively, on a Mettler DSC30 and a Rheometrics Dynamic Analyzer (RDA-II) in the rectangular torsion mode.

For DSC, a 15- to 20-mg sample was sealed in an aluminum pan and heated from 130 to 200°C at the rate of 10°C/min. The point of inflection during the glass transition in the heat capacity vs. temperature plot was taken as the T_g. The loss of MMA from the sample sealed in the aluminum pan was about 1.3% in 30 min at room temperature.

For DMS, the specimens were approximately 3 × 12 × 40 mm in size which were heated from the glassy state measurements being made in temperature steps of about 5°C. The strain level was 0.2–1.0% at a frequency of 1.0 Hz. In this way, the shear storage modulus G', the shear loss modulus G'', and tan $\delta = G''/G'$ were determined vs. temperature. Peaks in G'' were taken as the T_g's. These values seemed to coincide with the T_g values determined from the DSC at the experimental conditions employed. For MMA-swollen samples, DMS was done with the sample wrapped in the PE film in order to reduce the evaporation of MMA during the experiment. Separate experiments on pure polymer networks showed that the presence of this PE film had no measurable influence on the observed glass transition temperature of the sample.

RESULTS

Figure 1 shows the plots of loss moduli (G'') vs. temperature for a 100% PU network swollen to various extents with MMA solvent, indicating the T_g's at G'' peaks. While the PE film does not change the observed T_g, the absolute values of both G' and G'' are probably somewhat erroneous. Figure 2 shows the DSC scans on the same 100% PU network, swollen to different extents with MMA, indicating
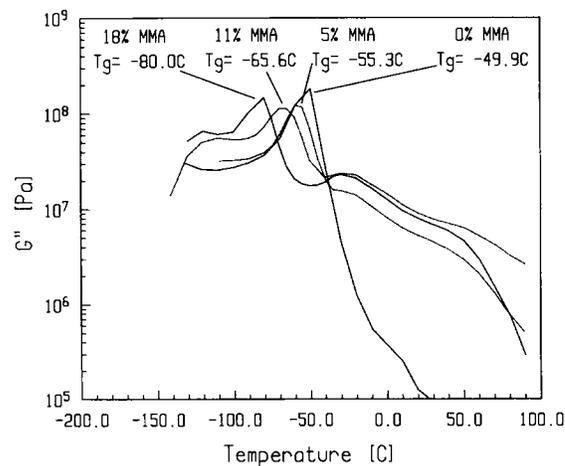
Figure 1   Loss moduli (G'') plots vs. temperature for the pure PU network swollen with different amounts of MMA. The samples were wrapped and sealed with a thin PE film to retard evaporation of MMA during experiments, conducted at a frequency of 1.0 Hz on the Rheometrics RDA-II.
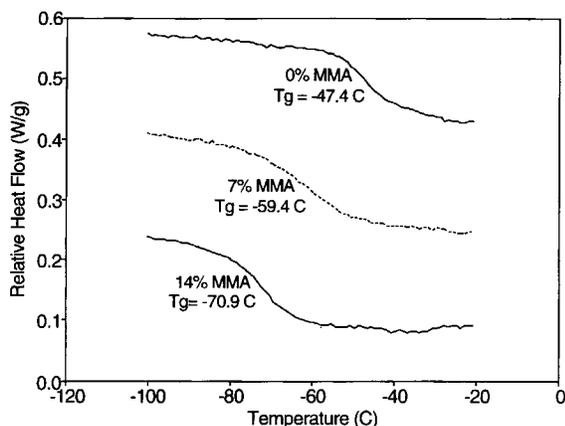
Figure 2 DSC scans on the pure PU network swollen with different amounts of MMA. The samples were heated in sealed aluminum pans at a rate of 10°C/min.

the points of inflection as T_g's. Figure 3 plots these data points (DMS and DSC combined) vs. the percentage of MMA, showing a good linear fit between T_{gA} and w_{pA} according to Eq. (2). The plasticization coefficient for PU is, p_A = slope equal to -1.70 [°C/(weight percent of plasticizer)]. In the same way, PMMA was shown to have $p_B = -3.68$ [°C/(weight percent of plasticizer)].

For SINs, which were phase separated, the decrease in each of the two glass transitions was followed as a function of overall percentage of MMA in the sample (W_p). Figure 4 plots the T_g values (G'' peaks and DSC) for SIN-2 (20/80 PU/PMMA) vs.

the percentage of MMA absorbed, W_p. The drop in each T_g (T_{gA} and T_{gB}) of the SIN is fitted to a straight line of the form of Eq. (8). The slopes of the linear fits provide values of the plasticization coefficients of MMA for the phase in question ($p_{A,a}$ and $p_{B,b}$).

Table III summarizes the plasticizer coefficients determined for all the samples. Using these numbers, and Eq. (12), the values of the partition coefficient ($K_{A/B}$) of MMA between the PMMA- and PU-rich phases for the three SIN samples are calculated and also tabulated in Table III. Since the average of the partition coefficients, $K_{A/B}$, is close to unity, it appears that MMA is distributed nearly equally between the two phases.

Glass Transition of the Plasticizer, MMA

From the above analysis, it is also possible to estimate a "glass transition," T_{gP} value for MMA (plasticizer). From Eqs. (3) and (5), respectively,

$$T_{gP} = p_A \times 100 + T_{gA,0} \tag{13}$$

$$T_{gP} = p_B \times 100 + T_{gB,0} \tag{14}$$

Table IV shows the T_{gP} of MMA using these equations and the plasticization coefficients values for pure PMMA and PU, from Table III. An average value of -239°C (34 K) is found.
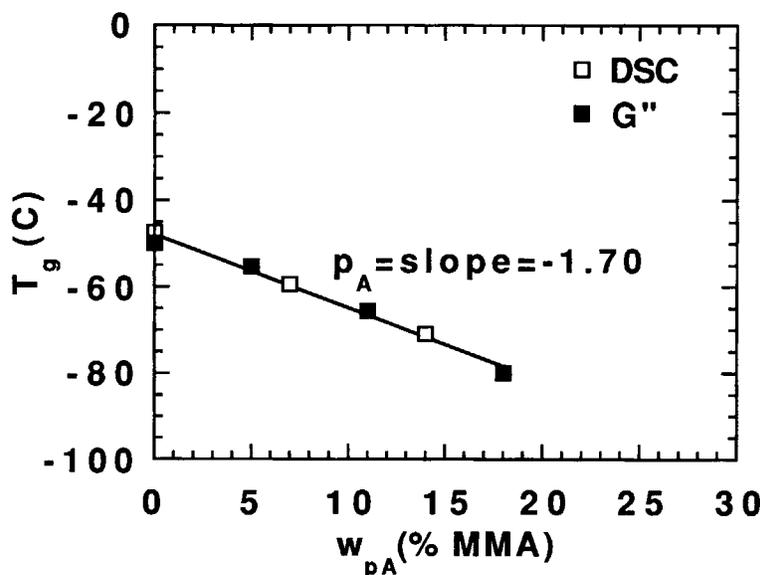
Figure 3 Plot of T_g's determined from Figures 1 and 2 for the pure PU network (T_{gA}) vs. percent MMA by weight (w_{pA}). (□) DSC data, (■); DMS data. Combined data are fitted to a straight line.
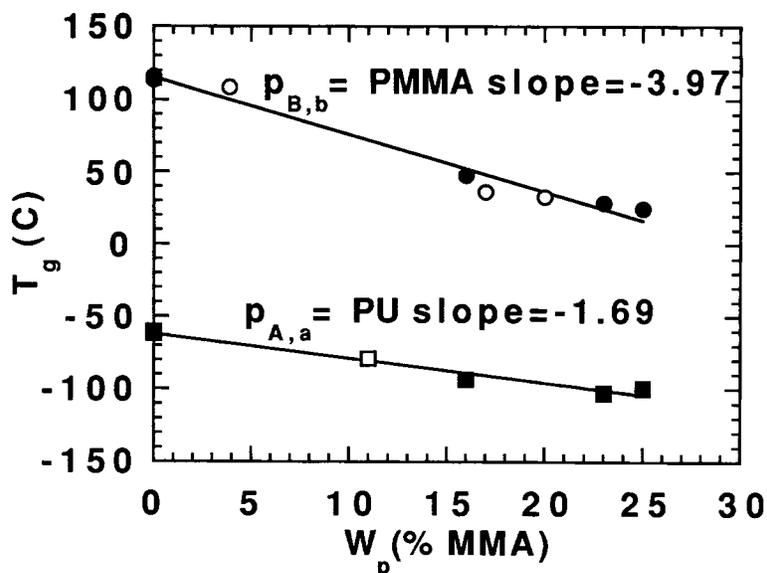
Figure 4 Plots of T_g's determined from DSC and DMS for SIN-2 (20/80 PU/PMMA) vs. overall percent MMA by weight (W_p). ($\square$, $\blacksquare$) T_{gA} (PU); (O, $\bullet$) T_{gB} (PMMA). ($\square$, O) DSC data; ($\blacksquare$, $\bullet$) DMS data. Combined data are fitted to straight lines for each polymer (phase).

DISCUSSION

Table III shows that the partition coefficients $(K_{A/B})$ of MMA in all the PU/PMMA SINs are near unity, the slight differences being within experimental error. SIN-2 has the farthest $K_{A/B}$ value from unity, 0.921, corresponding to an MMA distribution of 48/52 between the PU/PMMA phases. Therefore, it is evident that MMA is distributed nearly equally between the two phases of the current system, rather than showing a strong preference for a single phase. This result is consistent with the fact that the solubility parameters of PU and PMMA are fairly close to each other (see Table V). In the first paper[13] of this series, a metastable phase dia-

gram for the ternary system MMA–PMMA–PU was developed as a triangle. The present results indicate that the tie lines for the phase separation curve in that triangle would be almost parallel to each other, and to the line "PMMA–PU," at least in the region of less than 25% MMA, studied in this paper.

In comparing the $K_{A/B}$ values for the three SINs, it may be important to consider the differences in the tightness of the PU and PMMA networks from one sample to another. Table II shows that the PU network in all the samples has the same crosslink density. But, the PMMA network is more densely crosslinked in SIN-1 (using 3.0% TEGDM crosslinker) than in SIN-2, SIN-3, and pure PMMA (each using 0.5% TEGDM). With the limited cur-

Table III Plasticizer Coefficients of MMA in PU and PMMA in Various Samples and the Resulting Partition Coefficient ($K_{A/B}$) of MMA in PU and PMMA for the SIN Samples[a]

Sample	% PU (Polymer A)	% PMMA (Polymer B)	$p_{A,a}$	$p_{B,b}$	Partition Coefficient $K_{A/B} = (p_{A,a} \times p_B)/(p_A \times p_{B,b})$
XPU	100	0	−1.70 ($=p_A$)	—	—
XPMMA	0	100	—	−3.68 ($=p_B$)	—
SIN-1	50	50	−1.67	−3.54	1.021
SIN-2	20	80	−1.69	−3.97	0.921
SIN-3	10	90	−2.00	−4.06	1.066

[a] A = PU; B = PMMA.

Table IV   Glass Transition of MMA Calculated from Its Plasticization Coefficients for Pure PMMA and PU Networks

Plasticized Polymer	Polymer T_g	Plasticization Coefficient	T_g (MMA)
PU (A)	−49°C	−1.70 (=p_A)	−219°C
PMMA (B)	110°C	−3.68 (=p_B)	−258°C
			Average = −239°C = 34 K

rent data, however, it is difficult to say whether crosslink density affects the partition coefficient, and further work is therefore required to clarify this aspect. Nevertheless, for the low swelling levels (≤ 25%) employed here, and the corresponding low monomer contents in late SIN polymerizations, such effects are probably not very large.

In a study by Jin et al.,[20] discussing an almost identical PU/PMMA SIN system as the present one, it was proposed that in the later stages of polymerization, the remaining MMA reaction takes place primarily at the interphase, where MMA arrives by diffusion. The presence of radicals in the PU phase was ignored based on an earlier study,[21] resulting in the conclusion that the polymerization of MMA in the PU-rich phase was negligible. However, in light of the present results, some modifications to those conclusions can be proposed. Given that the unreacted MMA distributes almost evenly between the PU- and PMMA-rich phases, and comparing the solubility parameter values of PU, PMMA, and LPO, listed in Table V, it is likely that the LPO initiator also gets distributed more or less evenly among the two phases or perhaps slightly more in the PU phase. If present, LPO would surely

Table V   Solubility Parameters for the Relevant SIN Components

Component	Solubility Parameter δ $(cal/cm^3)^{1/2}$
PU[a]	9.5
PMMA[b]	9.3
MMA[c]	8.8
LPO[d]	9.6

[a] Determined by the maximum swelling method using numerous solvents.

[b] Average of all listed values in Table V of Section IV, *Polymer Handbook*, 2nd edition, J. Brandrup and E. H. Immergut, Eds., IV, Wiley, New York, 1974, pp. 357.

[c] Table II of Section IV, p. 346, in *Polymer Handbook* (see footnote b for bibliographic information).

[d] Calculated using Small's table on p. 339 of *Polymer Handbook* (see footnote b for bibliographic information).

decompose to initiate polymerization of the remaining MMA monomer in each phase, including the PU-rich phase.

In the PMMA-rich phase, which is vitrified at ca. 90% conversion of MMA,[13,20] subsequent polymerization of MMA is slowed considerably. However, complete conversion of MMA has been noted using Fourier transform infrared (FTIR) spectroscopy in such SINs (even greater than the limiting conversion due to vitrification in pure PMMA samples).[13,20] This requires the remaining MMA in the PMMA phase to diffuse out to the interphase where it can polymerize due to the lower T_g and lower viscosity, as proposed by Jin et al.[20] However, the PU-rich phase has an even lower viscosity and therefore, should *also* allow continued polymerization of the MMA contained within, based on the current results.

In either case, it seems reasonable that the MMA present in the PMMA domains would polymerize primarily at the interphase, once vitrification of the PMMA domains has occurred. This may cause broadening of the interphase, since diffusion of the newly formed PMMA to the PMMA-rich domains may be restricted by the vitrified state. At the same time, any new PMMA formed in the PU-rich domains should be driven toward the PMMA-rich domains, but may also be stopped at the interphase itself. Thus, the interphase region may be significantly broadened in such situations. In some cases, the interphase region may be substantial enough to have its own T_g. This may explain the weak peak observed occasionally between the PU and PMMA T_g peaks in the tan δ vs. temperature curves.[22] As an example, Figure 5 plots tan δ vs. temperature for SIN-1 (50/50 PU/PMMA, prepared simultaneously), along with that for a 50/50 polyurethane-polystyrene sequential IPN, prepared in a related study.[13] Both samples show a very faint peak between 0 and 30°C, sometimes observed in these and other systems.[22]

An alternate hypothesis suggests that the main locus of polymerization is within the PU-rich phase,
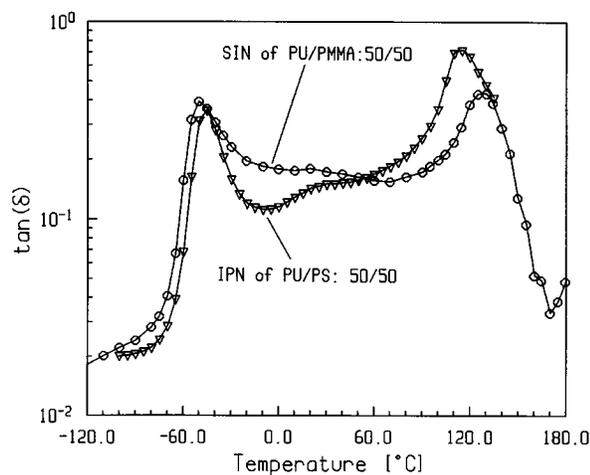
Figure 5 Tan δ vs. temperature for SIN-1 (50/50 PU/PMMA) and for a sequential IPN (50/50 PU/PS) at 1.0 Hz on the RDA-II. Besides the two peaks corresponding to the homopolymers, note a faint third peak in each sample between 0 and 30°C.

with partial diffusion of the PMMA formed toward the domain boundaries. In the polybutadiene–polystyrene sequential IPNs, for example, incomplete diffusion resulted in "snow-storm" appearing morphologies.[23,24]

CONCLUSIONS

Utilizing the T_g data determined for MMA-plasticized PU/PMMA SINs, the partition coefficients ($K_{A/B}$) of MMA between PU and PMMA phases were calculated. The $K_{A/B}$ values were nearly 1.0 ($\pm$ 0.1), which implies that any unreacted MMA monomer will be distributed between the two phases almost uniformly, up to 20–25% MMA content. This also means that the tie lines for the ternary metastable phase diagram of the system MMA–PMMA–PU[13] would be almost parallel to each other, and to the line PMMA–PU, up to 20–25% MMA in the system.

NOTE ADDED IN PROOF

The entropic contribution to $K_{A/B}$ is treated by V. Mishra, D. A. Thomas, and L. H. Sperling in an article to be submitted to *Macromolecules*.

LIST OF SYMBOLS

A   polymer A, PU
B   polymer B, PMMA

a	weight fraction of polymer A (PU) in the unplasticized SIN
b	weight fraction of polymer B (PMMA) in the unplasticized SIN (Note: $a + b = 1.0$)
$K_{A/B}$	partition coefficient of the plasticizer P between phases A and B
M_1	mass fraction of polymer 1 in the blend
M_2	mass fraction of polymer 2 in the blend
M_c	number-average molecular weight between crosslinks for the PU and PMMA networks (in g/mol)
p_A	plasticization coefficient of MMA for pure polymer A (PU); slope of T_{gA} vs. w_{pA} plot
p_B	plasticization coefficient of MMA for pure polymer B (PMMA); slope of T_{gB} vs. w_{pB} plot
$p_{A,a}$	plasticization coefficient of MMA for polymer A (PU) in the SIN containing polymers A and B in the ratio (a/b); slope of T_{gA} vs. W_p plot
$p_{B,b}$	plasticization coefficient of MMA for polymer B (PMMA) in the SIN containing polymers A and B in the ratio (a/b); slope of T_{gB} vs. W_p plot
T_g	glass transition temperature of the blend of polymer 1 and polymer 2
T_{g1}	glass transition temperature of polymer 1
T_{g2}	glass transition temperature of polymer 2
$T_{gA,0}$	T_g of pure PU (polymer A)
T_{gA}	T_g of PU (or PU-rich phase, in the SIN) in presence of plasticizer
T_{gB}	T_g of PMMA (or PMMA-rich phase, in the SIN) in presence of plasticizer
T_{gP}	T_g of plasticizer, P (i.e., MMA)
w_{pA}	weight percent of plasticizer P in pure polymer A (or in the phase rich in polymer A)
W_p	overall weight percent of plasticizer P in the SIN

Note: Subscript B denotes PMMA, polymer B, and all terms have the same corresponding meaning as with subscript A, for PU.

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