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Blends of Poly(styrene-*co*-acrylonitrile) and Methyl Methacrylate Based Copolymers

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ABSTRACT: The phase behavior of binary blends of styrene–acrylonitrile copolymers and methyl methacrylate copolymers with cyclohexyl methacrylate, phenyl methacrylate, and *tert*-butyl methacrylate has been determined as a function of composition of each copolymer. From these miscibility maps, binary interaction energy densities, B_{ij}, have been calculated for various monomer unit pairs. The interaction of acrylonitrile with styrene, methyl methacrylate, cyclohexyl methacrylate, and phenyl methacrylate is strongly repulsive (positive) in each case. The interaction of styrene with the methacrylate monomer units used here is weakly repulsive except in the case of cyclohexyl methacrylate where it is very weakly negative—polystyrene is miscible with the homopolymer of this methacrylate. Other recent reports have noted some miscibility of polystyrene with poly(ethyl methacrylate) and poly(*n*-propyl methacrylate). Interactions between the various methacrylate monomer units are modestly repulsive. The effects of these issues on phase behavior are discussed.

Introduction

Extensive observations over the years have shown that blends of random copolymers often have more interesting phase behavior than do the corresponding homopolymers.[1-66] Simple binary interaction models[28-30] with various extensions provide a simple way to rationalize these effects through the concept of intramolecular interactions within copolymers and a framework for designing blends with controlled phase behavior.[57-60,62] To accomplish the latter requires quantitative information about binary interaction energies for the various monomer unit pairs involved. A fruitful route to this information turns out to be the reverse procedure in which blend miscibility is experimentally mapped as a function of copolymer composition and then interaction energy values are calculated by fitting model equations to this information.[34-36,57-60]

In a recent paper,[57] we demonstrate the usefulness of a quantitative interaction energy database in searching for all miscible binary blends formed from homopolymers, copolymers, or terpolymers made from the monomers styrene, acrylonitrile, and methyl methacrylate (MMA). The interesting blends identified in that study all stem from the basic fact that poly(methyl methacrylate) homopolymer forms miscible blends with styrene–acrylonitrile copolymers (SAN) for a certain range of AN content. In this paper, we expand on this general scheme by examining the phase behavior of SAN copolymers with some MMA-based copolymers. In each case the new comonomer introduced is also a methacrylate. An interesting result is that poly(cyclohexyl methacrylate) has been found to form miscible blends with polystyrene. This enriches the possibilities for achieving miscibility among the various copolymers examined.

Background

The Flory–Huggins theory[67] provides a simple expression for the free energy of mixing of two polymers A and B (per unit volume of mixture)

$$\Delta G_{\mathrm{mix}} = RT\left\{\frac{\varphi_A \ln \varphi_A}{\tilde{V}_A} + \frac{\varphi_B \ln \varphi_B}{\tilde{V}_B}\right\} + B\varphi_A\varphi_B \qquad (1)$$

where φ_i is the volume fraction and $\tilde{V}_i$ is the molar volume of component i. In this model, the enthalpic contribution is given by a Van Laar type expression with an interaction energy density B for mixing of the segments of the component polymers. A stability analysis shows that the pair is miscible provided B is less than a critical value defined as follows

$$B_{\mathrm{crit}} = (RT/2)[\tilde{V}_A^{-1/2} + \tilde{V}_B^{-1/2}]^2 \qquad (2)$$

which is zero in the limit of high molecular weights. If B is temperature independent, then this model does not predict the lower critical solution temperature, LCST, behavior that is characteristic of most polymer blends. If a temperature dependence is assigned to B, this limitation can be overcome; however, we do not make any attempt here to model phase diagrams. Rather we rely on the fact that the LCST is such an extremely sensitive function of the interaction energy that borders between miscible and immiscible behavior in blends are a very strong function of copolymer composition.

When a binary interaction model is used, the net interaction energy, in the treatment outlined above, for mixing a copolymer of monomers 1 and 2 with a copolymer of 3 and 4 can be written as eq 63

$$B = (B_{13}\varphi_1' + B_{23}\varphi_2')\varphi_3'' + (B_{14}\varphi_1' + B_{24}\varphi_2')\varphi_4'' - B_{12}\varphi_1'\varphi_2' - B_{34}\varphi_3''\varphi_4'' \qquad (3)$$

where the B_{ij}s are parameters describing interactions between various i and j monomer units and φ_i' is the volume fraction of i monomer units in the copolymer. This manner of subdividing the net interaction energy into those of groups comprising the polymers is not limited to the Flory–Huggins theory but can be suitably incorporated into more sophisticated models when actual prediction of phase diagrams is the objective.[14,68] Here we are interested in the case of blending two copolymers having no common monomer, i.e., copolymer 1 + 2 and copolymer 3 + 4, where 1 = styrene, 2 = acrylonitrile, 3 methyl methacrylate, and 4 = the monomer to be varied. In the approach used here, the boundary of copolymer compositions dividing those that form miscible blends from immiscible ones, i.e., when

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Table I
Interaction Energy Density, B_{ij}, of Various Monomer Pairs

monomer pair	interaction energy density, cal/cm^3 this work	Nishimoto et al.[57]	Brannock et al.[58]	Cowie et al.[52]
S–AN	6.7	6.74	8.14	4.99
S–MMA	0.18	0.181[a]	0.181	0.181[a]
AN–MMA	4.1	4.11	5	2.78
CHMA–S	–0.03			
CHMA–AN	5.9			
CHMA–MMA	0.8			
PhMA–S	0.2			
PhMA–AN	4.0			
PhMA–MMA	0.3			

[a] Note that the S-MMA interaction energy is from the work of Fukuda et al.[69–71] in all cases.

Table II
Miscibility of Polystyrene with Various Methacrylate Polymers

polymer	CH_x/COO	miscibility	cloud point, °C	B, cal/cm^3
PMMA	4	immiscible		0.181[a]
PEMA	5	miscible	100–110	–0.036[b]
PnPrMA	6	miscible	100–110	–0.031[b]
PnBMA	7	immiscible		
PCHMA	9	miscible	230–240	–0.03[c]

[a] At 30 °C from Fukuda et al.[69–71] [b] From the cloud point temperature. See Brannock et al.[59] [c] From analysis of the miscibility region of blends of SAN with MMA–CHMA copolymer in this work.

$B = B_{crit}$, can be used to obtain information about the B_{ij}. In principle, these boundaries depend on temperature, but as stated earlier this is usually ignored since the limitations of the techniques employed do not readily encourage such refinement.

The first three rows in Table I summarize B_{ij} values from various sources for binary pairs of styrene (S), methyl methacrylate (MMA), and acrylonitrile (AN). A key issue here is the small but repulsive interaction between the S–MMA pair. The interaction energy for this pair, given in Table I, was determined by Fukuda et al.[69–71] from concentrated ternary solution measurements. Recently we found[58,59] that the styrene–methacrylate interaction becomes weakly negative when the alkyl group is an ethyl or an *n*-propyl unit. Thus, polystyrene is miscible with poly(ethyl methacrylate) and poly(*n*-propyl methacrylate); although, the LCST is very low in each case (see Table II). However, polystyrene appears to be immiscible[50,58,59] with poly(*n*-butyl methacrylate), which means the B_{ij} for this pair is positive. In what follows we find that poly(cyclohexyl methacrylate) is miscible with polystyrene and that the B_{ij} is slightly negative. At this point, there are some interesting questions about how the size or structure of the methacrylate alkyl group affects the interaction energy with styrene monomer units (see Table II).

Experimental Section

The SAN copolymers, including the polystyrene, used in this work are described in Table III while the MMA-based polymers are listed in Table IV. The former were all obtained from industrial sources while most of the latter were synthesized in this laboratory. The MMA-based polymers were prepared by free-radical polymerization at 75 °C using azobis(isobutyronitrile) as initiator. All of the copolymers contain 2–4% of methyl acrylate to help prevent depolymerization by unzipping. Copolymer compositions shown in Table IV were determined by ^1H NMR and are expressed on an acrylate-free basis. As an indicator of molecular weight, viscosities of their solutions (10% by weight) in methyl ethyl ketone were measured.

Blends of the copolymer were prepared by solution casting from tetrahydrofuran onto glass plates. The cast films were dried under a stream of dry nitrogen at ambient temperature for 1 day followed by further drying at 130 °C for 2 days under vacuum. This condition proved adequate to remove the solvent as confirmed by various thermal analyses while also serving to establish blend phase equilibrium at this temperature, which is above the glass transition temperature of all the polymers used in this investigation.

The homopolymers of the various methacrylate monomers used here all have glass transitions in the range 105–120 °C; thus, the methacrylate copolymers have glass transition temperatures that are not far enough separated from those of the SAN copolymers to make this a uniformly useful way of exploring phase behavior for their blends. Fortunately, the refractive indices are different enough in most of the cases considered that optical methods yield equivalent information. Depending on the compositions of the copolymers, films cast from their blends proved to be essentially transparent or opaque after the thermal treatment at 130 °C. Many of the transparent blends underwent reversible phase separation on heating and cooling above 130 °C. This behavior was especially prominent near the border of the composition boundaries between transparent and opaque blends; whereas, well inside these regions, no indication of phase separation could be detected up to temperature where decomposition became severe. These simple observations indicate that the boundaries between the transparent and opaque blends are caused by lower critical solution temperatures, LCST, that drop below the equilibration temperature of 130 °C as copolymer compositions are changed. Cloud points were quantitatively determined by isothermally annealing samples for 15 min in the sample holder of a Perkin-Elmer DSC-7 at various temperatures followed by observation for clarity or by DSC for glass transition behavior. In this way, the coexistence temperature could be bracketed.

Results and Discussion

PS–P(MMA–CHMA). Blends of polystyrene (PS) and poly(cyclohexyl methacrylate) (PCHMA) were transparent as prepared. They became cloudy when heated to 240 °C or above. This phase-separation process could be reversed by cooling. Similar behavior was found for a wide range of P(MMA–CHMA) copolymers when blended with polystyrene. Figure 1 illustrates phase diagrams, determined in the manner described above, for two particular copolymers. Figure 2 shows how the cloud points for blends containing 50% PS vary with the composition of the P(MMA–CHMA) copolymer. Interestingly, as MMA is introduced into PCHMA, the cloud point first increases, then declines very steeply, and evidently goes to some value below T_g in the limit of pure PMMA.

SAN–P(MMA–CHMA). Figure 3 shows how the miscibility of as-cast blends of SAN and P(MMA–CHMA) copolymers depends on the composition of the two copolymers. This map may be interpreted as an isothermal plane, T = 130 °C, defined by the drying temperature. For 0% CHMA, the well-known miscibility window for SAN copolymers with PMMA[42–45,49,52] is observed. PS is miscible with a very wide range of P(MMA–CHMA) copolymers, while, some SAN copolymers, including PS, are miscible with PCHMA.

Following previous examples, we assume here that the styrene–methyl methacrylate interaction is well-represented by the value B_{13} = 0.18 cal/cm^3, given by Fukuda et al.[69–71] Furthermore, we use the results of an analysis of phase behavior of polymers based on styrene, methyl methacrylate, and acrylonitrile[57] to set B_{12} = 6.7 and B_{23} = 4.1 cal/cm^3. Thus, only three other parameters in eq 3 are unknown. These can be estimated by fitting eqs 2 and 3 to the miscibility boundaries observed for blends of SAN copolymers with P(MMA–CHMA) copolymers, i.e., 4 = CHMA, and the results are listed in Table I. The following gives some physical feel for what experimental facts are involved in the fitting process to

Table III
Styrene–Acrylonitrile Polymers Used in This Study

polymer	descriptn	MW informn[a]	designatn	source
polystyrene	0% AN	$\bar{M}_w = 350\,000$ $\bar{M}_n = 100\,000$	PS	Cosden
poly(styrene-*co*-acrylonitrile)	3.5% AN	$\bar{M}_w = 211\,000$ $\bar{M}_n = 96\,400$	SAN3.5	Asahi
poly(styrene-*co*-acrylonitrile)	6.3% AN	$\bar{M}_w = 343\,000$ $\bar{M}_n = 121\,000$	SAN6.3	Asahi
poly(styrene-*co*-acrylonitrile)	9.5% AN	$\bar{M}_w = 195\,600$ $\bar{M}_n = 94\,700$	SAN9.5	Asahi
poly(styrene-*co*-acrylonitrile)	14.7% AN	$\bar{M}_w = 182\,000$ $\bar{M}_n = 83\,000$	SAN14.7	Asahi
poly(styrene-*co*-acrylonitrile)	19.5% AN	$\bar{M}_w = 178\,700$ $\bar{M}_n = 84\,300$	SAN19.5	Asahi
poly(styrene-*co*-acrylonitrile)	25% AN	$\bar{M}_w = 152\,000$ $\bar{M}_n = 77\,000$	SAN25	Dow
poly(styrene-*co*-acrylonitrile)	30% AN	$\bar{M}_w = 168\,000$ $\bar{M}_n = 81\,000$	SAN30	Dow
poly(styrene-*co*-acrylonitrile)	34% AN	$\bar{M}_w = 145\,000$ $\bar{M}_n = 73\,000$	SAN34	Asahi
poly(styrene-*co*-acrylonitrile)	40% AN	$\bar{M}_w = 122\,000$ $\bar{M}_n = 61\,000$	SAN40	Asahi

[a] From GPC calibrated by using polystyrene standards.

Table IV
Methyl Methacrylate Copolymers Used in This Study

polymer[a]	descriptn	solution viscosity[b]	designatn
poly(methyl methacrylate)	Plexiglas V811[c]	3.3	PMMA
poly(MMA-*co*-CHMA)	6.1% CHMA	10.3	MCH6.1
poly(MMA-*co*-CHMA)	11.2% CHMA	7.5	MCH11.2
poly(MMA-*co*-CHMA)	14.7% CHMA	5.3	MCH14.7
poly(MMA-*co*-CHMA)	21.1% CHMA	4.0	MCH21.1
poly(MMA-*co*-CHMA)	28.5% CHMA	3.8	MCH28.5
poly(MMA-*co*-CHMA)	34.4% CHMA	3.0	MCH34.4
poly(MMA-*co*-CHMA)	43.8% CHMA	3.7	MCH43.8
poly(MMA-*co*-CHMA)	56.7% CHMA	3.2	MCH56.7
poly(MMA-*co*-CHMA)	64.1% CHMA	2.5	MCH64.1
poly(MMA-*co*-CHMA)	80.7% CHMA	2.1	MCH80.7
poly(MMA-*co*-CHMA)	83.4% CHMA	3.0	MCH83.4
poly(MMA-*co*-CHMA)	86.8% CHMA	4.2	MCH86.8
poly(MMA-*co*-CHMA)	91.4% CHMA	4.0	MCH91.4
poly(cyclohexyl methacrylate)		5.1	PCHMA
poly(MMA-*co*-CHMA)	16.0% PhMA	5.0	MPh16.0
poly(MMA-*co*-CHMA)	28.3% PhMA	3.4	MPh28.3
poly(MMA-*co*-CHMA)	39.2% PhMA	2.7	MPh39.2
poly(MMA-*co*-CHMA)	51.1% PhMA	2.2	MPh51.1
poly(MMA-*co*-CHMA)	63.0% PhMA		MPh63.0
poly(MMA-*co*-CHMA)	81.0% PhMA		MPh81.0
poly(phenyl methacrylate)			PPhMA
poly(MMA-*co*-tBMA)	10.6% tBMA	16.8	MtB10.6
poly(MMA-*co*-tBMA)	21.9% tBMA	31.2	MtB21.9
poly(MMA-*co*-tBMA)	33.8% tBMA	28.7	MtB33.8
poly(MMA-*co*-tBMA)	45.0% tBMA	16.9	MtB45.0

[a] MMA = methyl methacrylate. CHMA = cyclohexyl methacrylate. PhMA = phenyl methacrylate. tBMA = *tert*-butyl methacrylate. [b] Viscosity of 10 wt % solution in methyl ethyl ketone (cP). [c] Commercial product of Rohm and Haas Co.

yield these parameters. One of these parameters is essentially specified by the percent of AN at which SAN copolymers become immiscible with PCHMA while a second is fixed by the percent of CHMA at which P(MMA–CHMA) copolymers become immiscible with polystyrene. The third unknown parameter relates to the curvature of the borders of the miscibility map. It is hard to place meaningful error limits on parameters obtained by fitting the model to the experimental data; however, a perturbation analysis that varies one parameter at a time showed that relatively small changes led to unacceptable fits of the data. The solid lines in Figure 3 correspond to the calculated loci of compositions where $B = B_{\text{crit}}$ using the B_{ij} values listed in Table I. The S–CHMA interaction energy is a small negative value while the MMA–CHMA interaction is repulsive but not to the extent observed for AN with S or with MMA. This interaction is the reason for the concave shape of the upper line in Figure 3. This line would be linear if the MMA–CHMA interaction energy were zero.

Copolymers of MMA–CHMA containing 21.6% or more of CHMA are miscible with PS. Since the B_{ij} values for all three monomer pairs involving S–MMA–CHMA are small, the net B for mixing PS with MMA–CHMA copolymers containing 21.6% or more CHMA is negative but small in magnitude. Therefore, the cloud point curve for 50/50 PS–P(MMA–CHMA) blends shown in Figure 2 is not as steep as that for SAN–PMMA blends[50] even though the miscibility window is wider in the present case.

Figure 4 shows how the AN content of SAN copolymers affects the cloud point for 50/50 blends, with P(MMA–CHMA) copolymers having the compositions shown. These diagrams might be compared with the well-known limiting case (% CHMA = 0) of PMMA–SAN mixtures.[42–45,49,52] For 21.1% CHMA the right edge of the miscibility window occurs at almost the same location as that for PMMA; however, the left edge is shifted to lower AN levels. As the level of CHMA in the copolymer increases, the miscibility window shifts to the left (lower AN levels) and eventually includes pure polystyrene since the latter is miscible with pure poly(cyclohexyl methacrylate). In all cases, the edges of the miscibility window are quite steep because of the strong repulsion (6.7 cal/cm^3) between styrene and arylonitrile units in SAN. The MMA–CHMA intramolecular repulsion is considerably smaller at 0.8 cal/cm^3. The interaction of styrene units with MMA units is weakly repulsive (0.18 cal/cm^3) while that with CHMA is weakly attractive (−0.03 cal/cm^3). It is interesting that Goh et al.[61] estimated the interaction between methyl methacrylate and ethyl methacrylate units to be about +3.25 cal/cm^3.

SAN copolymers have been found to be miscible with certain poly(n-alkyl methacrylates)[50] and certain aliphatic polyesters.[63] The limits of miscibility in these systems have been mapped two dimensionally in terms of the number of aliphatic carbons (CH_x) per ester group (COO) in the repeat units of the methacrylate and the esters versus the percent of AN of the SAN (see Figure 5). For comparison,

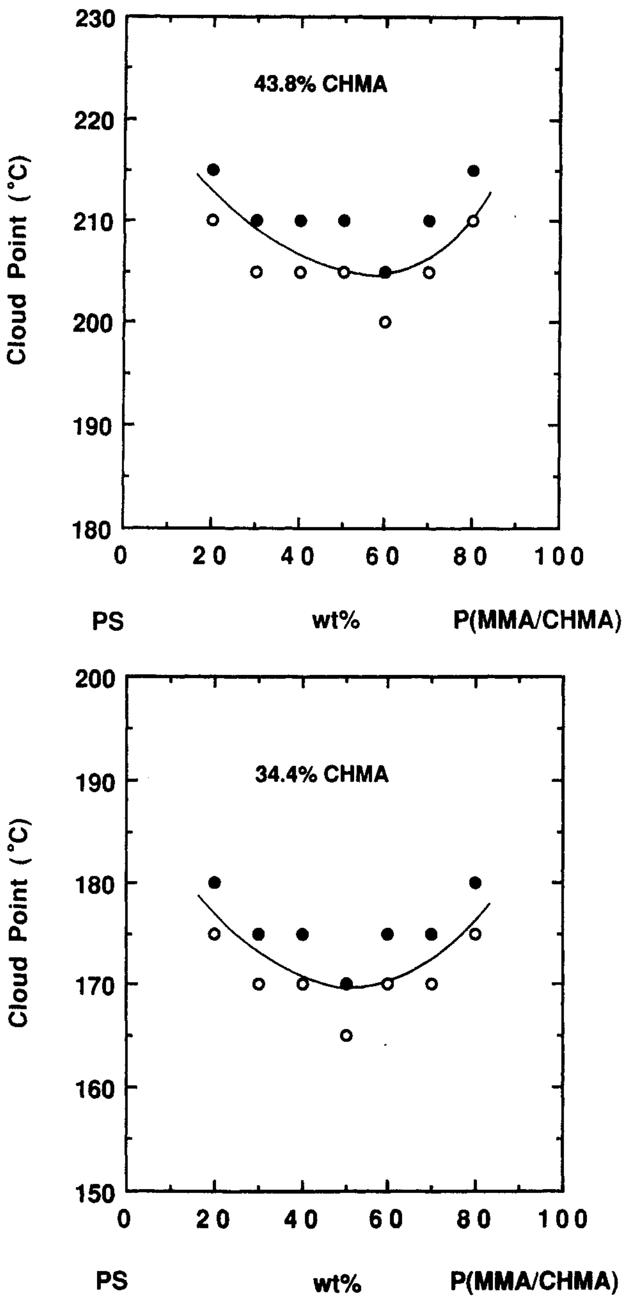

Figure 1. Cloud point curves for blends of polystyrene and MMA-CHMA copolymer: (○) clear, (●) cloudy after annealing for 15 min.

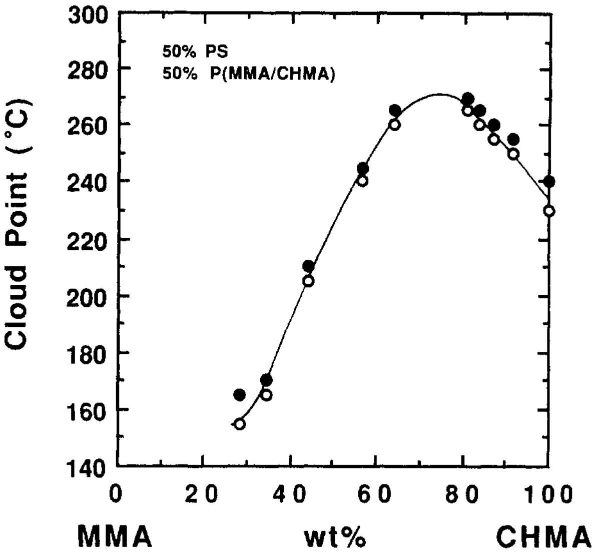

Figure 2. Cloud point of 50/50 blends of polystyrene with MMA-CHMA copolymers as a function of copolymer composition: (○) clear, (●) cloudy after annealing for 15 min.

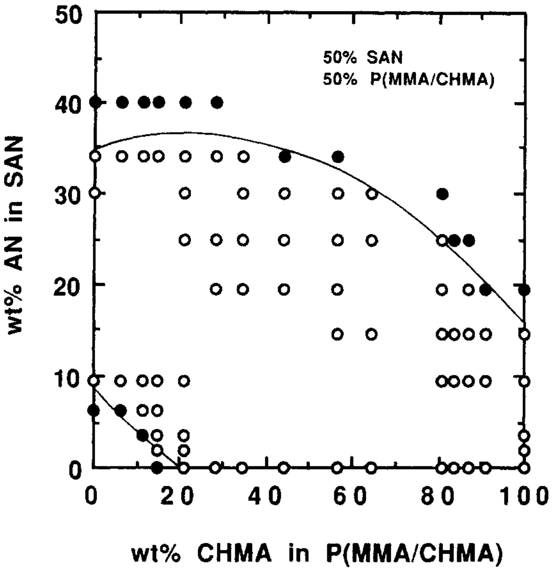

Figure 3. Miscibility map of 50/50 SAN copolymer and MMA-CHMA copolymer blends at 130 °C: (○) clear, (●) cloudy.

we have made a similar map for SAN blends with P(MMA-CHMA) copolymers. There are some broad similarities of the three maps as seen in Figure 5, which reflects the extent that miscibility (or polymer-polymer interactions) is determined solely by the content of CH_x, COO, AN, and styrene units in the polymers. There are some striking differences, which no doubt reflect issues of placement (in-chain vs pendent), structure (linear vs cyclic), etc. Perhaps the most noteworthy difference is that for the P(MMA-CHMA) copolymers the region of miscibility extends to higher CH_x/COO ratios and lower percent of AN levels than found for the polymethacrylates or the polyesters. The reasons for this are not clear at the present time, and a better understanding of such effects is needed in order to enhance our ability to forecast phase behavior from molecular structure. Any thorough approach to this question ought to focus on comparison of the quantitative features of the interaction energy surface[63] rather than simply a certain projection on to the composition plane, i.e., the miscibility envelope.

SAN-P(MMA-PhMA). Copolymers of methyl methacrylate and phenyl methacrylate (PhMA) were also blended with the SAN copolymers. The miscibility map is shown in Figure 6. No cloud point curves were determined for these blends. The dotted line in Figure 6 approximates the loci of copolymer compositions that have identical refractive indices. Therefore, near this line it is difficult to determine blend phase behavior by optical observations.

When eqs 2 and 3 plus the first three B_{ij} values in Table I were used the data in Figure 6 were fitted as mentioned earlier to obtain the estimates of the interaction energies for PhMA with styrene, MMA, and AN listed at the bottom of Table I. The curvature of the upper boundary in Figure 6 is somewhat less than that in Figure 3, which leads to the conclusion that the repulsion between MMA and PhMA is somewhat weaker than that with CHMA (0.3 vs 0.8 cal/cm^3). The styrene-PhMA interaction is repulsive and slightly larger than that for S-MMA. Consequently, PPhMA is not miscible with polystyrene, a fact that greatly restricts the region of miscibility seen in Figure 6 compared

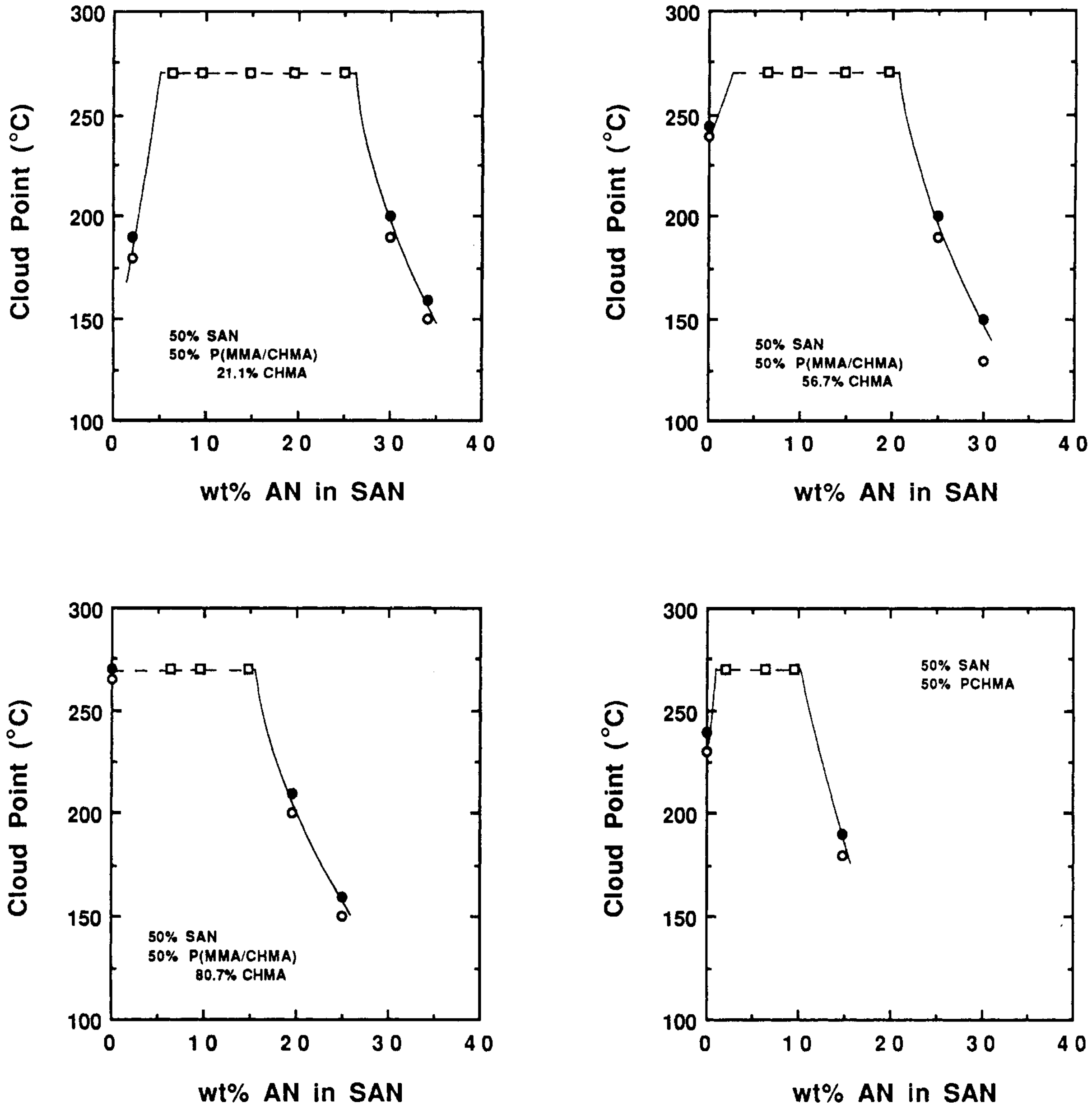

Figure 4. Cloud points for 50/50 blends of SAN and MMA-CHMA copolymers as a function of composition of each copolymer: (○) clear, (●) cloudy, (□) blends still clear at 270 °C; however, these compositions were not heated to higher temperatures because of decomposition.

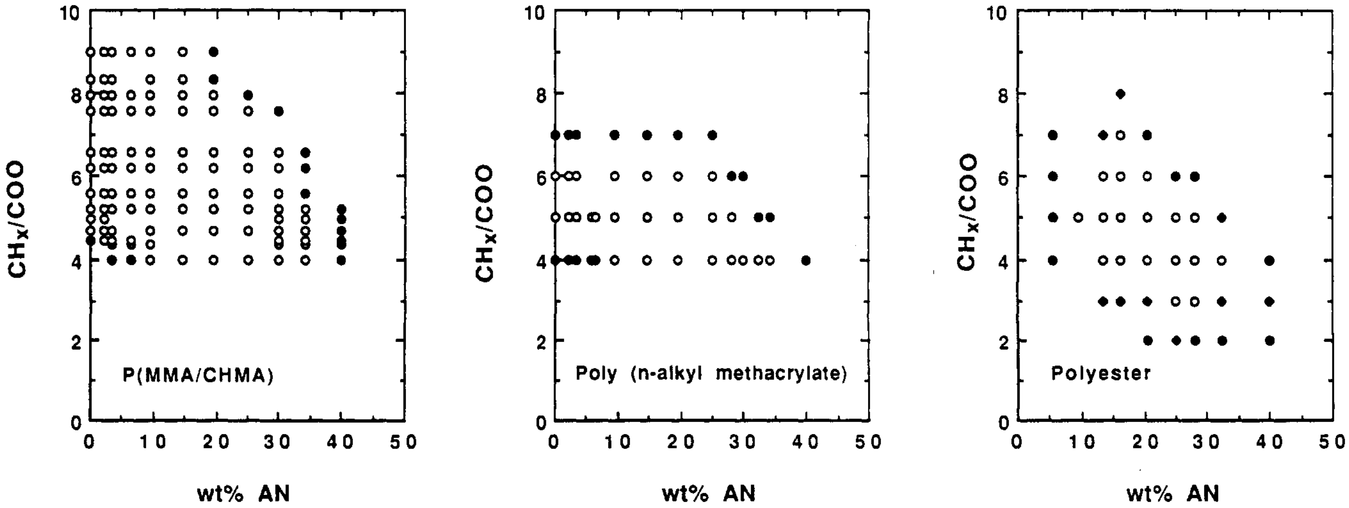

Figure 5. Miscibility maps of SAN blends with MMA-CHMA copolymers, poly(n-alkyl methacrylates), and polyesters: (○) clear, (●) cloudy. CH$_x$/COO is the ratio of aliphatic carbons per ester group.

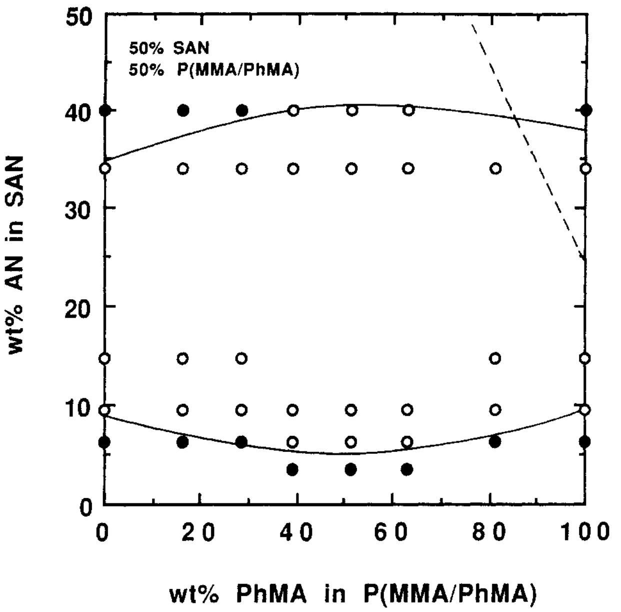

Figure 6. Miscibility map of 50/50 blends of SAN and MMA–PhMA copolymers: (○) clear, (●) cloudy. The dashed line approximates the compositions that have identical refractive indices.

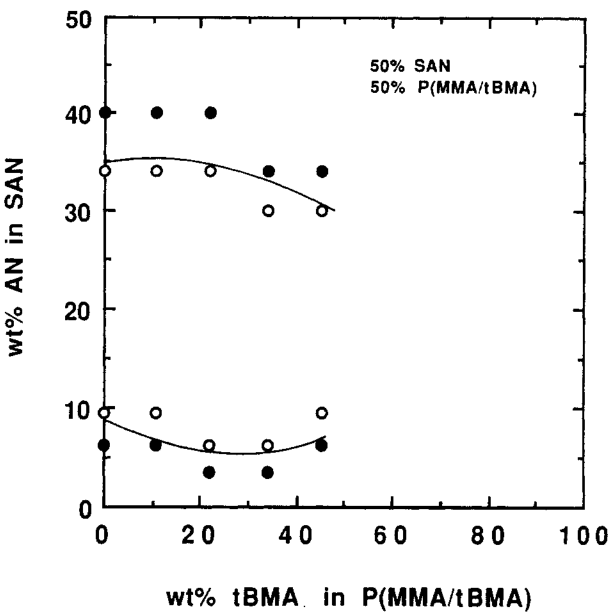

Figure 7. Miscibility map of 50/50 blends of SAN and MMA–tBMA copolymer: (○) clear, (●) cloudy.

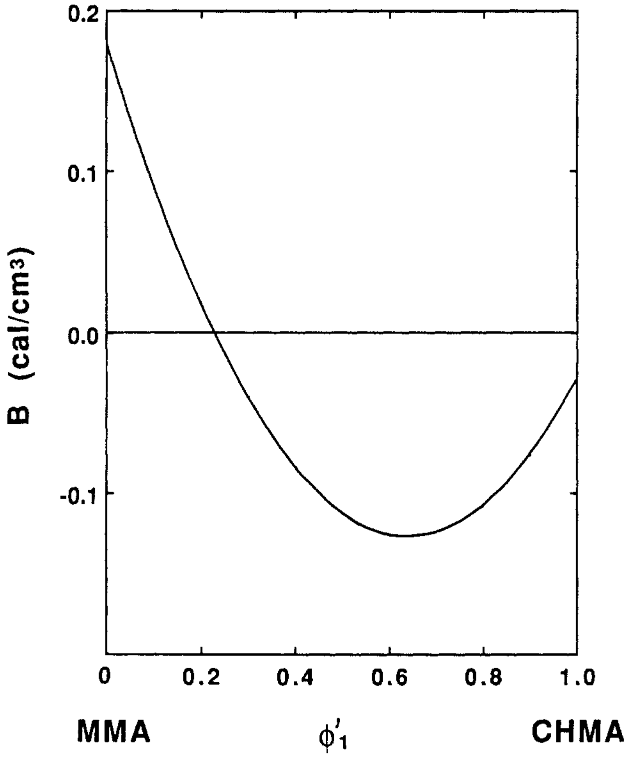

Figure 8. Net interaction energy, B, of polystyrene (monomer 3) and MMA (monomer 2)–CHMA (monomer 1) copolymers. Calculated from eq 3 by using B_{ij} values from Table I.

to that in Figure 3. There is, however, a region of AN contents where SAN copolymers are miscible with P(MMA–PhMA) copolymers regardless of the composition of the latter. The miscibility window for PPhMA is rather similar to that for PMMA with SAN copolymers since the interactions of S and AN with PhMA are very similar to those for MMA. The miscibility window with SAN copolymers is not much broader for P(MMA–PhMA) copolymers than it is for PMMA or for PPhMA homopolymers simply because the MMA–PhMA interaction is only weakly repulsive (0.3 cal/cm^3).

The consequences of the different interactions of CHMA and of PhMA with the other units in this system are quite striking and need to be understood at a more fundamental level.

SAN–P(MMA–tBMA). Four copolymers of *tert*-butyl methacrylate (tBMA) and MMA were made and blended with SAN copolymers. The results are shown in Figure 7. With these limited data, it is not possible to evaluate interaction parameters with any certainty. On the basis of previous work,[50,58,59] we do not believe that poly(*tert*-butyl methacrylate) has any region of miscibility with SAN copolymers. The shape of the data in Figure 7 suggests that a pinch off of the miscibility region will occur prior to reaching the limit of PtBMA; however, unfortunately the available copolymer compositions did not extend to high enough tBMA levels to encompass the proposed pinch off.

Summary

It is clear that the styrene–methacrylate interaction is weak and may be positive or negative depending on the structure of the methacrylate pendent group. Similar conclusions may be reached by examining the heats of mixing for liquids having molecular structures analogous to these monomer units.[58,59] The homopolymer of cyclohexyl methacrylate has a small favorable interaction with polystyrene, and miscible blends are formed. For *n*-alkyl methacrylate, these appear to be an optimum alkyl size for favorable interaction with polystyrene that contains fewer carbons than the cyclohexyl unit. When the cyclic pendent group is aromatic, the methacrylate–styrene interaction is unfavorable; thus, polystyrene and poly(phenyl methacrylate) are not miscible.

Because of the above, SAN copolymers exhibit strikingly different miscibility maps with MMA–CHMA copolymers compared to MMA–PhMA copolymers. The former has a broad band of miscibility that connects the PMMA–SAN miscibility window to the PS–PCHMA apex. For the latter, there is a PPhMA–SAN miscibility window similar to that for PMMA–SAN and the two connect with only minor broadening as the proportion of MMA and PhMA is varied in the copolymers. Tentative data for MMA copolymers with *tert*-butyl methacrylate suggest a more limited range of miscibility with SAN copolymers, but further work is needed for this system.

Binary interaction energy densities, without temperature dependence, were deduced from these miscibility–composition diagrams. These values should be useful in the design of other copolymer and terpolymers for blending and should help sharpen our understanding, even if only intuitively, of polymer–polymer interactions.

The present results confirm in a more quantitative way, a notion we have suggested in other recent papers.[23-25,62,64,65] Blends of polystyrene and poly(cyclohexyl methacrylate) exhibit LCST behavior. Adding methyl methacrylate to the cyclohexyl methacrylate polymer *raises* the cloud point for blends with polystyrene even though the interaction of MMA units with polystyrene is unfavorable. The issue is the larger effect of the intramolecular repulsion between MMA and CHMA that makes the net interaction more favorable and the cloud point higher. The net interaction can be calculated by using eq 3 and appropriate parameters from Table I. The result of this calculation is shown in Figure 8. This variation in B is no doubt the cause for the trends in phase behavior shown in Figure 2.

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References and Notes

(1) Paul, D. R.; Barlow, J. W.; Keskkula, H. *Encyclopedia of Polymer Science and Eng.*: John Wiley and Sons: New York, 1988; Vol. 12, p 399.

(2) Krause, S. *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Chapter 2.

(3) Fried, J. R.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1978**, *11*, 150.

(4) Vuković, R.; Karasz, F. E.; MacKnight, W. J. *Polymer* **1983**, *24*, 529.

(5) Vuković, R.; Karasz, F. E.; MacKnight, W. J. *J. Appl. Polym. Sci.* **1983**, *28*, 219.

(6) Vuković, R.; Kureševič, V.; Karasz, F. E.; MacKnight, W. J. *J. Appl. Polym. Sci.* **1985**, *30*, 317.

(7) Vuković, R.; Kureševič, V.; Šetgudović, N.; Karasz, F. E.; MacKnight, W. J. *J. Appl. Polym. Sci.* **1983**, *28*, 1379.

(8) Alexandrovich, P.; Karasz, F. E.; MacKnight, W. J. *Polymer* **1977**, *18*, 1022.

(9) Maeda, Y.; Karasz, F. E.; MacKnight, W. J. *J. Appl. Polym. Sci.* **1986**, *32*, 4423.

(10) Kressler, J.; Kammer, H. W. *Acta Polym.* **1987**, *38*, 600.

(11) Keskkula, H.; Paul, D. R. *J. Appl. Polym. Sci.* **1986**, *31*, 1189.

(12) Kressler, J.; Kammer, H. W.; Schmidt-Naake, G.; Herzog, K. *Polymer* **1988**, *29*, 686.

(13) Aoki, Y. *Macromolecules* **1988**, *21*, 1277.

(14) Kim, J. H.; Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 233.

(15) Chiu, S. C.; Smith, T. G. *J. Appl. Polym. Sci.* **1984**, *29*, 1781.

(16) Chiu, S. C.; Smith, T. G. *J. Appl. Polym. Sci.* **1984**, *29*, 1797.

(17) Jo, W. H.; Cruz-Ramos, C. A.; Paul, D. R. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 1057.

(18) Kim, J. H.; Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 2211.

(19) Kim, J. H.; Barlow, J. W.; Paul, D. R. *Polym. Eng. Sci.* **1989**, *29*, 581.

(20) Zakrzewski, G. A. *Polymer* **1973**, *14*, 347.

(21) Shiomi, T.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1986**, *19*, 2644.

(22) Kenney, J. F. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 123.

(23) Min, K. E.; Paul, D. R. *Macromolecules* **1987**, *20*, 2828.

(24) Min, K. E.; Paul, D. R. *J. Appl. Polym. Sci.* **1989**, *37*, 1153.

(25) Min, K. E.; Paul, D. R. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 2257.

(26) Goh, S. H.; Paul, D. R.; Barlow, J. W. *Polym. Eng. Sci.* **1982**, *22*, 34.

(27) Suess, M.; Kressler, J.; Kammer, H. W.; Heinemann, K. *Polym. Bull.* **1986**, *16*, 371.

(28) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.

(29) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.

(30) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.

(31) Shiomi, T.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1986**, *19*, 2274.

(32) ten Brinke, G.; Rubinstein, E.; Karasz, F. E.; MacKnight, W. J.; Vuković, R. *J. Appl. Phys.* **1984**, *56*, 2440.

(33) Balazs, A. C.; Sanchez, I. C.; Epstein, I. R.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1985**, *18*, 2188.

(34) Karasz, F. E. In *Polymer Blends and Mixtures*; Walsh, D. J., Higgins, J. S., Maconnachie, A., Eds.; NATO Advanced Study Institute Series E89; Martinus Nijhoff Publisher: 1985; p 25.

(35) Karasz, F. E.; MacKnight, W. J. *Adv. Chem. Ser.* **1986**, *211*, 67.

(36) Kang, H. S.; MacKnight, W. J.; Karasz, F. E. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1987**, *28*, No. 2, 134.

(37) Hunsel, J. V.; Balazs, A. C.; Koningsveld, R.; MacKnight, W. J. *Macromolecules* **1988**, *21*, 1528.

(38) Balazs, A. C.; Karasz, F. E.; MacKnight, W. J.; Ueda, H.; Sanchez, I. C. *Macromolecules* **1985**, *18*, 2784.

(39) Cantow, H. J.; Schulz, O. *Polym. Bull.* **1986**, *15*, 449.

(40) Pfennig, J. L. G.; Keskkula, H.; Barlow, J. W.; Paul, D. R. *Macromolecules* **1985**, *18*, 1937.

(41) Kammer, H. W. *Acta Polym.* **1986**, *37*, 1.

(42) Fowler, M. E.; Barlow, J. W.; Paul, D. R. *Polymer* **1987**, *28*, 1177.

(43) Stein, V. D. J.; Jung, R. H.; Illers, K. H.; Hendus, H. *Angew. Makromol. Chem.* **1974**, *36*, 89.

(44) Suess, M.; Kressler, J.; Kammer, H. W. *Polymer* **1987**, *28*, 957.

(45) Schmitt, B. J.; Kirste, R. G.; Jelenic, J. *Makromol. Chem.* **1980**, *181*, 1655.

(46) McBrierty, V. J.; Douglass, D. C.; Kwei, T. K. *Macromolecules* **1978**, *11*, 1265.

(47) Naito, K.; Johnson, G. E.; Allara, D. L.; Kwei, T. K. *Macromolecules* **1978**, *11*, 1260.

(48) Kruse, W. A.; Kirste, R. G.; Haas, J.; Schmitt, B. J.; Stein, D. J. *Makromol. Chem.* **1976**, *177*, 1145.

(49) Kressler, J.; Kammer, H. W.; Klostermann, K. *Polym. Bull.* **1986**, *15*, 113.

(50) Fowler, M. E.; Barlow, J. W.; Paul, D. R. *Polymer* **1987**, *28*, 2145.

(51) Ikawa, K.; Hosoda, S. *Polym. Prepr. Jpn.* **1988**, *27Q*, 1a49.

(52) Cowie, J. M. G.; Lath, D. *Makromol. Chem., Macromol. Symp.* **1988**, *16*, 103.

(53) Cowie, J. M. G.; Lath, D. *Polym. Commun.* **1987**, *28*, 300.

(54) Molau, G. E. *J. Polym. Sci., Polym. Lett. Ed.* **1965**, *3*, 1007.

(55) Shiomi, T.; Suzuki, M.; Tohyama, M.; Imai, K. *Macromolecules* **1989**, *22*, 3578.

(56) Kammer, H. W.; Kressler, J.; Kressler, B.; Kroschwitz, H.; Schmidt-Naake, G. *Acta Polym.* **1989**, *40*, No. 2, 75.

(57) Nishimoto, M.; Keskkula, H.; Paul, D. R. *Polymer* **1989**, *30*, 1279.

(58) Brannock, G. R.; Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Part B: Polym. Phys* **1990**, *28*, 871.

(59) Brannock, G. R.; Barlow, J. W.; Paul, D. R., to be published in *J. Polym. Sci., Part B: Polym. Phys.*

(60) Brannock, G. R.; Paul, D. R., to be published in *Macromolecules*.

(61) Goh, S. H.; Siow, K. S. *Polym. Bull.* **1988**, *20*, 393.

(62) Paul, D. R. In *Functional Polymers*; Bergbreiter, D. E., Martin, C. E., Eds.; Plenum Press: New York, 1989; p 1.

(63) Fernandes, A. C.; Barlow, J. W.; Paul, D. R. *J. Appl. Polym. Sci.* **1986**, *32*, 5357.

(64) Nishimoto, M.; Keskkula, H.; Paul, D. R., to be published in *Polymer*.

(65) Fernandes, A. C.; Barlow, J. W.; Paul, D. R. *Polymer* **1986**, *27*, 1788.

(66) Cruz-Ramos, C. A.; Paul, D. R. *Macromolecules* **1989**, *22*, 1289.

(67) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, New York, 1953.

(68) Sanchez, I. C. *Encyclopedia of Physical Science Technology*; Meyers, R. A., Ed.; Academic Press: New York, 1987; Vol. 11, p 1.

(69) Fukuda, T.; Inagaki, H. *Pure Appl. Chem.* **1983**, *55*, 1541.

(70) Fukuda, T.; Nagata, M.; Inagaki, H. *Macromolecules* **1984**, *17*, 548.

(71) Fukuda, T.; Nagata, M.; Inagaki, H. *Macromolecules* **1986**, *19*, 1411.

Registry No. PS, 9003-53-6; (MMA)(CHMA) (copolymer), 27517-36-8; (MMA)(PhMA) (copolymer), 59407-29-3; (MMA)(*t*BMA) (copolymer), 28549-51-1; PCHMA, 25768-50-7; (S)(acrylonitrile) (copolymer), 9003-54-7.