

# Miscibility of Some Methacrylate and Acrylate Homopolymer Blends

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**ABSTRACT:** The miscibility of three binary blends, poly(methyl methacrylate) with poly(methyl acrylate), poly(ethyl methacrylate) with poly(ethyl acrylate), and poly(methyl methacrylate) with poly(ethyl acrylate) has been examined using narrow molecular weight distribution samples prepared by the group-transfer polymerization technique. The structural difference of the  $\alpha$ -methyl group is sufficient to limit one-phase behavior to mixtures of polymers of low molecular weight only. A similar situation is found for mixtures of the isomers poly(methyl methacrylate) and poly(ethyl acrylate). Analysis of the molecular weight miscibility limits yields the segmental interaction energy density values; although, a fuller description of the effect of blend composition on miscibility requires these to be composition variables.

## Introduction

The phase behavior of polymer and copolymer blends can be described<sup>1-10</sup> by an extension of the Flory expression for the free energy of mixing in which the (nominally enthalpic) segmental interaction energy density  $B_{12}$  is replaced by a composition weighted term  $B_{\text{blend}}$ . For a generalized binary copolymer mixture  $A_xB_{1-x} + C_yD_{1-y}$ , where  $x$  and  $y$  are segment volume fractions, this is given by

$$B_{\text{blend}} = xyB_{AC} + (1-x)yB_{BC} + x(1-y)B_{AD} + (1-x)(1-y)B_{BD} - x(1-x)B_{AB} - y(1-y)B_{CD} \quad (1)$$

The various  $B_{ij}$ s are segmental contact energy densities which are regarded as being temperature and composition independent. The critical value of  $B_{\text{blend}}$  for phase separation is expressed in terms of the blend component molar volumes  $V_i$  by

$$B_{\text{crit}} = 0.5RT(V_1^{-0.5} + V_2^{-0.5})^2 \quad (2)$$

Phase boundaries, for given copolymer molar volumes, can then be described in  $x$ - $y$  composition space using eq 1. Successive simplifications of eq 1 apply to binary copolymer mixtures with a common monomer, to homopolymer-copolymer mixtures, and to homopolymer mixtures.

Since eq 1 is in point of fact a form of the equation of a general conic section, it followed that all predicted phase boundaries in such systems are themselves conic sections, or portions of conic sections. Data fitting procedures based on the properties of conic sections have been demonstrated by us<sup>7,11</sup> for several experimental phase boundaries. Given one of the system  $B_{ij}$  values, these permit the evaluation of all the remaining  $B_{ij}$  values. Nevertheless, theoretical exploration of possible phase behavior in untried systems, and subsequent correlation with experiment, does rely on the availability of a database of segmental  $B_{ij}$  values. In this context the miscibility of three methacrylate/acrylate homopolymer combinations is examined in order to derive the segmental interaction values involved.

## Experimental Section

**Solvents and Monomers.** Tetrahydrofuran (THF) was treated successively with ferrous sulfate and potassium hydroxide

and then distilled. It was further redistilled from sodium-benzophenone prior to use. Acetonitrile (AN) was dried with molecular sieves and distilled from calcium hydride prior to use.

Methyl methacrylate (MMA), ethyl methacrylate (EMA), methyl acrylate (MA), and ethyl acrylate (EA) were washed with aqueous sodium hydroxide and then water and dried first over calcium chloride and then over calcium hydride. The monomers were finally distilled under a partial atmosphere of nitrogen.

1-Methoxy-1-(trimethylsilyl)-2-methyl-1-propane (MTS) and tris(dimethylamino)sulfonium trimethylsilyl difluoride (TASF<sub>2</sub>) were purchased from Polysciences and Aldrich, respectively, and used as received.

**Group-Transfer Polymerization.** Polymers were synthesized using the group-transfer polymerization technique. Reactions were carried out using MTS as initiator and TASF<sub>2</sub> as catalyst in nitrogen-blanketed prebaked glassware using dried syringes to transfer reagents. Typically, monomer, THF as solvent, and then initiator were introduced into the reaction flask and stirred. A solution (0.01 mol dm<sup>-3</sup>) of catalyst in a 9:1 (by volume) mixture of THF and AN was then added, resulting in a steady temperature rise of 35–50 °C. The temperature was allowed to fall back to 20 °C when the reaction mixture was treated with methanol and the solvent evaporated to obtain the polymer, which was finally reprecipitated from toluene solution into hexane.

**Characterization.** Molecular weights were determined for THF solutions of the polymers using gel permeation chromatography with polystyrene standards as calibrants. Glass transition temperatures ( $T_g$ ) were measured using a Perkin-Elmer DSC-4 calorimeter scanning at 20 K/min. Table I shows polymerization and characterization data for all the samples.

**Blend Preparation.** The miscibility of a blend was assessed by determining whether one or two  $T_g$ s were present. Blends were prepared by dissolving the two components in toluene in the desired proportions to a total of 5 wt %. The solutions were cast onto microscope slides, and the solvent was allowed to evaporate at room temperature. The resulting films were then vacuum dried at 30 °C for 24 h prior to examination in the DSC-4 calorimeter as above.

## Results and Discussion

As will be apparent from the results that follow, one-phase behavior is restricted to blends of short chain length polymers, and, in order adequately to establish interaction parameters from the limits of miscibility, group-transfer polymerization methods were chosen to facilitate the synthesis of a series of well-defined low molecular weight samples. Table I shows the details of the samples used in phase studies.

Tables II–IV summarize the  $T_g$  data obtained for 50/50 wt % blends of poly(methyl methacrylate) (PMMA) with

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Table I  
Polymerization and Characterization Data for Polymer Samples Used

sample design	monomer, mol dm <sup>-3</sup>	MTS, mmol dm <sup>-3</sup>	TASF <sub>2</sub> , mmol dm <sup>-3</sup>	yield, %	$M_n^b$	$M_w/M_n^c$	$T_g$ , K
PMMA24	0.80	91	0.40	21	2400	1.1	331
PMMA32	0.31	40	5.00	73	3200	1.3	350
PMMA49	1.34	66	0.21	89	4900	1.4	367
PMMA119	4.80	170	0.72	82	11900	1.3	371
PMMA226	3.10	54	0.37	83	22600	1.3	381
PMA50	4.20	63	0.28	33	5000	1.6	268
PMA65	7.93	79	0.49	47	6500	1.7	270
PEA37	2.69	70	0.19	70	3700	2.2	238
PEA47	2.66	75	0.30	70	4700	2.0	239
PEA58	1.74	60	0.33	48	5800	1.4	239
PEA77	3.90	60	0.27	53	7700	1.6	241
PEA268 <sup>a</sup>					26800	3.0	252
PEMA32	1.61	102	0.20	81	3200	1.1	300
PEMA70	1.52	76	0.33	62	7000	1.2	324
PEMA118	2.30	56	0.24	91	11800	1.1	327
PEMA276	3.80	52	0.26	74	27600	1.3	337

<sup>a</sup> Purchased from Polysciences. <sup>b</sup> Apparent molecular weight from GPC. <sup>c</sup> From GPC measurements.

Table II  
 $T_g$  Values for 50/50 wt % Blends of PMMA with PMA

blend components	$T_g$ , K
PMMA24/PMA50	291
PMMA24/PMA65	292
PMMA32/PMA50	277
PMMA32/PMA65	271
PMMA49/PMA50	287 + 352
PMMA49/PMA65	270 + 341
PMMA119/PMA50	263 + 333
PMMA119/PMA65	268 + 338
PMMA226/PMA50	264 + 340
PMMA226/PMA65	250 + 316

Table III  
 $T_g$  Values for 50/50 wt % Blends of PMMA with PEA

blend components	$T_g$ , K
PMMA32/PEA37	249
PMMA32/PEA77	249
PMMA32/PEA108	263
PMMA49/PEA47	255
PMMA49/PEA77	248
PMMA119/PEA37	249
PMMA119/PEA47	243 + 338
PMMA119/PEA58	244 + 340

Table IV  
 $T_g$  Values for 50/50 wt % Blends of PEMA with PEA

blend components	$T_g$ , K
PEMA32/PEA77	246
PEMA70/PEA37	248
PEMA70/PEA47	248
PEMA70/PEA58	247
PEMA70/PEA77	248 + 293
PEMA118/PEA37	249 + 303
PEMA118/PEA77	250 + 297
PEMA118/PEA108	238 + 303
PEMA276/PEA37	237 + 293

poly(methyl acrylate) (PMA), of PMMA with poly(ethyl acrylate) (PEA), and of poly(ethyl methacrylate) (PEMA) with PEA, and from these the molecular weight limits for miscibility are obtained. At a phase boundary the condition  $B_{\text{blend}} = B_{\text{crit}}$  is met. For these present systems eq 1 reduces to its simplest possible form  $B_{\text{blend}} = B_{AC}$ , where A and C are the two homopolymer repeat units, and  $B_{\text{crit}}$  will lie between adjacent one-phase and two-phase blends on a scale of increasing blend component molecular weight. For example, the value of the segmental interaction  $B_{\text{MMA-MA}}$  will be bounded by " $B_{\text{crit}}$ " values calculated via eq 2 where  $V_1$  and  $V_2$  are given by PMMA32 and PMA65, respectively, and by PMMA49 and PMA50,

Table V  
Segmental Interaction Energy Densities Obtained from 50/50 wt % Blend Behavior and the Values of  $\alpha$ ,  $B_0$ , and  $B_1$  Which Describe the Phase Boundaries in Figures 2-4

segments		$B_{ij}$ , J cm <sup>-3</sup>	$B_0$ , J cm <sup>-3</sup>	$B_1$ , J cm <sup>-3</sup>	$\alpha$
MMA	MA	1.09-1.27	1.47	-0.78	-0.1
MMA	EA	0.78-0.91	0.57	0.42	0.55
EMA	EA	0.73-0.85	0.68	0.60	1.1

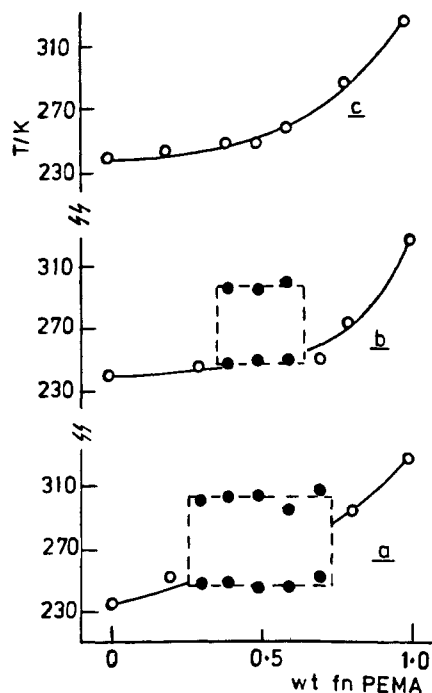
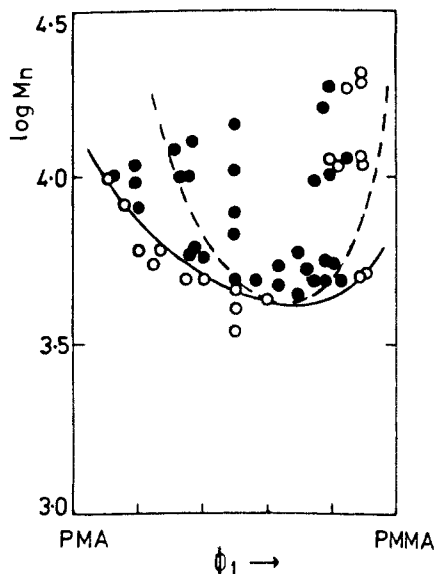


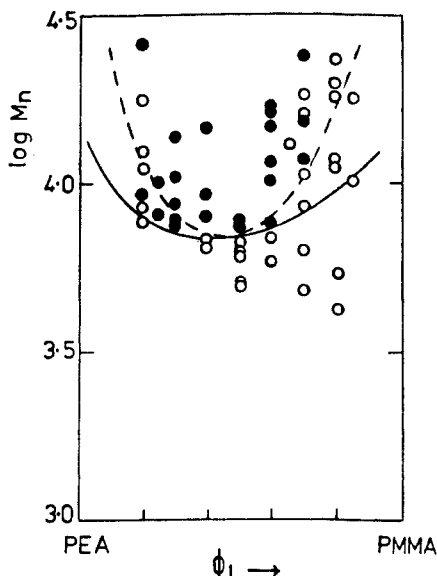
Figure 1. Glass transition values vs composition for representative PEMA/PEA blends: (O) one-phase blend; (●) two-phase blend. (a) PEMA70/PEA108, (b) PEMA70/PEA77, (c) PEMA70/PEA58.

respectively. (Polymer molecular weights were converted to molar volumes using group additivity estimated densities.<sup>12</sup>) The segmental interaction energy densities calculated in this way for each of the three blends examined are collected in Table V.

A broader picture is obtained from the composition-molecular weight dependence of miscibility, as exemplified by the representative data for PEMA/PEA shown in Figure 1. Phase diagrams may then be constructed by plotting the one- $T_g$  and the two- $T_g$  compositions on tie lines joining



**Figure 2.** Composition-molecular weight phase behavior for PMMA/PMA blends: (O) one-phase blend; (●) two-phase blend.  $\phi_1$  is the volume fraction of PMMA in the blend. (—) Binodal. (---) Spinodal calculated from eq 3 and 5 with  $\alpha$ ,  $B_0$ , and  $B_1$  given in Table V.



**Figure 3.** Composition-molecular weight phase behavior for PMMA/PEA blends: (O) one-phase blend; (●) two-phase blend.  $\phi_1$  is the volume fraction of PMMA in the blend. (—) Binodal. (---) Spinodal calculated from eqs 3 and 5 with  $\alpha$ ,  $B_0$ , and  $B_1$  given in Table V.

pairs of molecular weights as described previously,<sup>13,14</sup> and these are shown for the three systems in Figures 2–4.

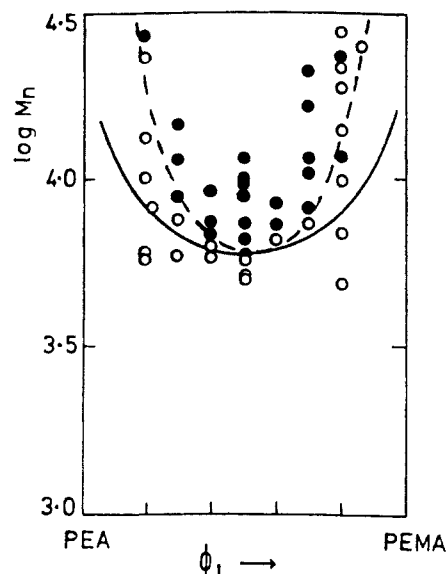
When the expression<sup>15</sup>

$$\Delta\mu_i = RT\{\ln \phi_i + \phi_j(1 - V_i/V_j)\} + V_i\phi_j^2 B_{ij} \quad (3)$$

is employed for the chemical potential  $\Delta\mu_i$  ( $i = 1$  and  $2$ ;  $j = 2$  and  $1$ ), binodal phase boundaries in terms of blend composition volume fraction  $\phi_i$  and molar volume  $V_i$  (i.e., molecular weight) may be determined by applying the condition that the chemical potentials in each phase (primed and unprimed) are equal

$$f_i = (\Delta\mu'_i - \Delta\mu_i)/(\phi'_2 - \phi_2) = 0 \quad (4)$$

The form of eq 4 avoids the trivial solution  $\phi'_2 = \phi_2$  and thus may be solved using standard nonlinear methods. Using the  $B_{ij}$  values in Table V, we were unable to reproduce with any accuracy the two-phase regions shown



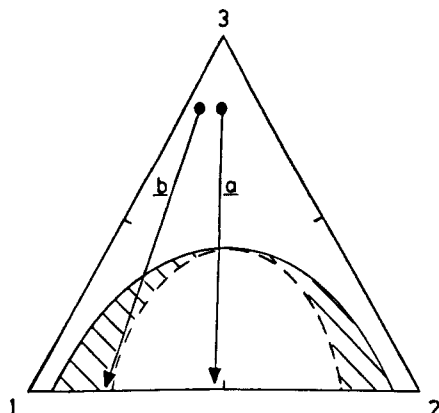
**Figure 4.** Composition-molecular weight phase behavior for PEMA/PEA blends: (O) one-phase blend; (●) two-phase blend.  $\phi_1$  is the volume fraction of PEMA in the blend. (—) Binodal. (---) Spinodal calculated from eqs 3 and 5 with  $\alpha$ ,  $B_0$ , and  $B_1$  given in Table V.

in Figures 2–4, the calculated boundaries being very much flatter and more symmetrical than the experiments suggest. Somewhat improved fits to the data may be obtained by allowing  $B_{ij}$  to take an empirical composition dependence such that

$$B_{ij} = B_0 + B_1\phi_2 + \alpha B_1\phi_2^2 \quad (5)$$

and consequently replacing the second term on the right-hand side of eq 3 with  $V_i\phi_j^2(B_{ij} - \phi_i\partial B_{ij}/\partial\phi_j)$ . The values of  $\alpha$ ,  $B_0$ , and  $B_1$  which give reasonable overall fits to each of the systems are included in Table V. For the PMMA/PMA system  $\alpha = -0.1$  and here essentially a compositionally linearly dependent  $B_{\text{MMA-MMA}}$  suffices, whereas for the other two systems  $\alpha > 0$  and strong quadratic dependences are required. In all three cases the calculated binodals adequately represent the data in the midcomposition regions but are somewhat less than satisfactory at the composition extremes (most noticeably for the PEMA/PEA system).

Figures 2–4 also show the spinodal condition ( $\partial\Delta G^2/\partial\phi_i^2 = 0$ ). Interestingly, this appears to provide a better overall description of the data—certainly for the PEMA/PEA and the PMMA/PEA blends. Discrimination of the state of a blend is inherently less sure at the composition extremes where the minor component  $T_g$  may be difficult to discern, and so it may be unwise to place undue reliance on data in this region. However, we have observed that spinodals in other polymer mixtures also fit experiment better than the corresponding binodals.<sup>16</sup> A rationale for this may be proposed by recalling that solvent-cast binary blends result from traversing a polymer (1) + polymer (2) + solvent (3) ternary phase diagram, such as that shown schematically in Figure 5. On loss of solvent, mixtures close to 50/50 compositions cross the ternary binodal and become immediately unstable with respect to phase separation. On the other hand, blends at the composition extremes traverse a region of metastability where phase separation is controlled by nucleation and growth kinetics. Since the viscosity increases rapidly as the polymer (1) + polymer (2) binary line is approached, there is a consequent greater possibility of “locking-in” a metastable one-phase blend here.



**Figure 5.** Schematic ternary phase diagram for polymer (1) + polymer (2) + casting solvent (3). (—) Ternary binodal. (---) Ternary spinodal. The metastable area is hatched. *a* and *b* are traverses for a 50/50 and a 20/80 1 + 2 blend during casting and loss of solvent.

Returning now to the actual values summarized in Table V, the energy densities obtained for these quasi-homologue interactions are in some respects surprisingly adverse, certainly if regarded from a consideration of the types of possible surface contacts in the bulk mixtures. Each of the repeat units offers the choice of only an aliphatic-and/or an ester-type surface to a potential nearest neighbor, which in turn is similarly endowed. Such a simplistic argument is valid up to a point. It is, nevertheless, the philosophy underlying group additivity methods which take account of contact areas as well as contact types.<sup>17,18</sup> Complete matching of like-like interactions at the intersegmental level, to the exclusion of unlike interactions, denies the accompanying entropy penalty, especially in polymeric mixtures, and indeed the basic assumptions of random mixing.

The spread of the values in Table V is not large in the general context of  $B_{ij}$  data which range from zero to that, for example, of acrylonitrile-butadiene<sup>7,19</sup> of  $36 \text{ J cm}^{-3}$ . Any internal comparisons of the data (in terms of structure) are probably a fruitless exercise. A point of comparison, however, is the effect of an  $\alpha$ -methyl group, as quantified here in the PMMA/PMA and PEMA/PEA pairings and in the much-examined styrene/ $\alpha$ -methylstyrene (S/MS) system.  $B_{S-MS}$  has been determined by us<sup>20</sup> and by others<sup>21</sup> from phase studies to be ca.  $0.01 \text{ J cm}^{-3}$ , an order of magnitude less than either  $B_{MMA-MA}$  or  $B_{EMA-EA}$ . All three interactions notionally arise only from the exchange of an  $\alpha$ -hydrogen for an  $\alpha$ -methyl on the same backbone. The difference between the styrenic and the acrylic blends must reflect subtleties in the interaction energetics which are lost within the embrace of a single interaction term. An appeal to entropic effects, at least those associated with differences in free volume as measured by the relative  $T_g$  values of the blends' components, does not appear to provide an explanation since in all three cases a difference of 70–80 K exists.

The compositional variation of each of the three parameters shown in Figures 2–4 is rather greater than

the bounds of the 50/50 wt % -derived values.  $B_{ij}$ s obtained from the behavior of 50/50 test blends contain inherent compositional information, and in turn this will place a constraint on their realistic predictive use to broadly similar compositions. We have already alluded<sup>9,20</sup> to possible criticisms to this approach to polymer miscibility which is an amalgam of the rigidity of the lattice theory<sup>16</sup> (eq 1) and the single liquid approximation<sup>22</sup> (eq 2). Not only may the influence of composition be significant, but refinements may be required to account for the effect of temperature and molecular weight.<sup>23,24</sup> Undoubtedly these reflect the "portmanteaux" nature of  $B_{ij}$  terms. However, these are purely empirical embellishments of a basic simplicity, whose retention can be justified<sup>25</sup> on these grounds alone and on consequent practical utility.

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## References and Notes

- (1) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* 1983, 16, 753.
- (2) Paul, D. R.; Barlow, J. W. *Polymer* 1984, 25, 487.
- (3) Shiomi, T.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* 1986, 19, 2274.
- (4) Cowie, J. M. G.; Lath, D. *Makromol. Chem., Makromol. Symp.* 1988, 16, 103.
- (5) Chien, Y. Y.; Pearce, E. M.; Kwei, T. K. *Macromolecules* 1988, 21, 1616.
- (6) Litauzski, G.; Schmidt-Naake, G.; Kressler, J.; Kammer, H. W. *Polym. Commun.* 1989, 30, 359.
- (7) Cowie, J. M. G.; Elempuru, E. M.; Harris, J. H.; McEwen, I. J. *Makromol. Chem., Rapid Commun.* 1989, 10, 691.
- (8) Zhu, K. H.; Chen, S. F.; Ho, T.; Pearce, E. M.; Kwei, T. K. *Macromolecules* 1990, 23, 150.
- (9) Cowie, J. M. G.; McEwen, I. J.; Reid, V. M. C. *Polymer* 1990, 31, 905.
- (10) Cowie, J. M. G.; McEwen, I. J.; Nadvornik, L. *Macromolecules* 1990, 23, 5106.
- (11) Cowie, J. M. G.; Elempuru, E. M.; McEwen, I. J. *J. Polym. Sci., Part B: Polym. Phys.* 1991, 29, 407.
- (12) van Krevelin, D. W. *Properties of Polymers*; Elsevier Scientific Publishing Co.: Amsterdam, The Netherlands, 1976.
- (13) Saeki, S.; Cowie, J. M. G.; McEwen, I. J. *Polymer* 1983, 24, 60.
- (14) Cowie, J. M. G.; McEwen, I. J. *Polymer* 1985, 26, 1662.
- (15) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
- (16) Cowie, J. M. G.; Ferguson, R.; Li, G.; McEwen, I. J., submitted to *J. Polym. Sci., Polym. Phys. Ed.*
- (17) Manzini, G.; Crescenzi, V. *J. Phys. Chem.* 1977, 81, 431.
- (18) Price, G. J.; Ashworth, A. J. *Polymer* 1987, 28, 2105.
- (19) Cowie, J. M. G.; Harris, J. H.; McEwen, I. J., submitted to *Macromolecules*.
- (20) Cowie, J. M. G.; Fernandez, M. D.; Fernandez, M. J.; McEwen, I. J. *Polymer*, in press.
- (21) Widmaier, J. M.; Mignard, G. *Eur. Polym. J.* 1987, 23, 989.
- (22) Scott, R. L. *J. Chem. Phys.* 1949, 17, 268.
- (23) Lin, J.-L.; Roe, R.-J. *Macromolecules* 1987, 20, 2168.
- (24) Lin, J.-L.; Roe, R.-J. *Macromolecules* 1988, 21, 1227.
- (25) Nishimoto, M.; Keskkula, H.; Paul, D. R. *Polymer* 1989, 30, 1279.

**Registry No.** PMMA (homopolymer), 9011-14-7; PMA (homopolymer), 9003-21-8; PEMA (homopolymer), 9003-42-3; PEA (homopolymer), 9003-32-1.