Phase Behavior of Blends of Poly(ethylene glycol) and Partially Neutralized Poly(acrylic acid)

Xinya Lu and R. A. Weiss*

Polymer Science Program and Department of Chemical Engineering, The University of Connecticut, Storrs, Connecticut 06269-3136

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ABSTRACT: Blends of poly(acrylic acid), PAA, and poly(ethylene glycol), PEG, are miscible over the entire range of composition as a result of hydrogen-bonding between the acids and ether oxygens. Infrared analysis showed that the formation of acid–ether complexes is preferred over that of cyclic acid dimers formed from self-association of the carboxylic acid groups. Miscibility decreased as the extent of neutralization of acrylic acid (AA) to the lithium salt (LiA) increased, and lower critical solution temperatures (LCST) were observed for blends made with AA-LiA copolymers containing 0.1–0.4 mole fraction LiA. Pairwise interaction energies between the different chemical species were calculated from equilibrium melting point depression data and a binary interaction model. Favorable interactions between AA and ethylene glycol (EG) promoted miscibility, while an unfavorable interaction between LiA and EG favored demixing. Infrared analysis showed that neutralization of the acid reduced the concentration of acid–ether complexes and promoted formation of acid cyclic dimers that favored phase separation.

Introduction

The phase behavior of binary polymer blends has been a popular research topic over the past two decades.[1–4] Miscibility of two high molecular weight polymers usually requires the presence of exothermic interactions, since the combinatorial entropy of mixing is small for polymer mixtures. Examples of specific, attractive *inter*molecular interactions that have been used to develop miscible blends include hydrogen-bonding,[5] dipole–dipole interactions,[6] ion–dipole interactions,[7] acid–base interactions,[8] transition-metal complexation,[9] and charge-transfer complexation.[10] Recently, it was shown that *intra*polymer repulsive interactions are also effective for producing miscible blends from copolymer/homopolymer mixtures.[11–15]

Examples of systems exhibiting strong polymer–polymer interactions are the hydrogen-bond complexes of poly(ethylene glycol) and poly(carboxylic acid) mixtures[16,17] though studies of those systems have focused primarily on their solution behavior. Complexation of poly(methacrylic acid) (PMAA)/poly(ethylene glycol) (PEG) in acidic aqueous solutions occurs at a 1:1 stoichiometric ratio based on the repeating units, but the stability of the hydrogen bond is sensitive to the solvent used and the degree of neutralization of the poly(carboxylic acid). For example, aqueous PMAA/PEG complexes dissociate when PMAA is partially neutralized with NaOH (PMAA-*co*-Na-MA), which suggests that the carboxylate salt does not interact, or does so only very weakly, with PEG in water. Similar phase behavior was also observed for poly(acrylic acid) (PAA)/PEG mixtures in water.[18,19] Neat PAA/PEG blends are miscible because of the formation of hydrogen bonds between the carboxylic acid and ether groups, but the Na salt of PAA is immiscible with PEG.

In contrast to the immiscibility of PEG/(PMAA-*co*-Na-MA) solutions, a poly(alkylene oxide), which was essentially poly(ethylene oxide) (PEO), and poly(styrene-*co*-Li-methacrylate) ionomers (PS-LiMA) were reported to be miscible, presumably because of ion–dipole interactions between ethylene oxide and the metal carboxylate groups.[20] {Note that the ethylene oxide is the repeat unit for both PEG and PEO; the only differences between the two polymers are the end groups. It is assumed here that the end groups play a negligible role in the phase behavior of blends of PEG or PEO with a poly(carboxylic acid) or its salts.} Two possible reasons for differences in the miscibility of the polyether/poly(metal carboxylate) solutions and blends are (1) the ion–dipole interactions responsible for mixing of the neat polymers are solvated by the polar solvent, i.e., the acidic water, in the solutions and (2) the miscibility enhancement observed for the neat blends might result either fully or partially from *intra*molecular repulsion effects in the ionomer.

In this paper, the effects of partial neutralization on the miscibility of neat (i.e., solventless) PAA/PEG blends is described. The mechanism of miscibility enhancement was identified by using melting point depression measurements to calculate the binary interaction parameters between all combinations of the different repeat units in the copolymer/homopolymer mixture. The blends exhibited lower critical solution temperature (LCST) type liquid–liquid phase behavior, and the cloud point as a function of neutralization level was measured for several compositions by optical microscopy. Fourier transform infrared (FTIR) spectroscopy was used to examine possible specific interactions between the blend components.

Experimental Details

PAA with M_w = 50 000 and PEG with M_w = 5000 were purchased from Polysciences, Inc. Copolymers of acrylic acid (AA) and lithium acrylate (Li-A) were prepared by partially neutralizing aqueous solutions of PAA with an appropriate amount of lithium hydroxide. The partially neutralized polymers were cast from solution at room temperature and dried under vacuum at 50 °C for 1 week. The nomenclature used here for the partially neutralized PAA is x-Li-PAA, where x is the extent of neutralization in mol % of PAA repeat units.

Polymer blends were prepared by codissolving the two polymers in a mixed solvent of water/methanol (50/50 v/v) to produce a 4% (wt) polymer solution. The solutions were stirred overnight, and films of the blends were cast from solution at 5 °C, air-dried for a few days and finally dried to constant mass under vacuum at about 40 °C for 1 week.

A Perkin-Elmer DSC-7 was used to measure the glass transition temperature(s) (T_g) and the melting point (T_m) of

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the PEG using a heating rate of 20 °C/min. The T_g and T_m were taken as the midpoint of the change in the specific heat and the maximum of the melting endotherm, respectively. Isothermal crystallization of the PEG component was carried out in aluminum sample pans in the DSC-7. The samples, weighing 3–4 mg, were held at 75 °C for 5 min and then quenched quickly to the desired crystallization temperature (T_c). After crystallization was allowed to proceed for at least 30 min, the samples were rapidly cooled to −50 °C and then reheated to 100 °C and 20 °C/min to obtain the melting point. Temperature calibrations were carried out using the melting points of cyclohexane and indium.

Cloud-point measurements were made by visually observing the clarity of thin films with a Nikon optical microscope equipped with a Linkan-TH600 hot stage. A thin film was cast from solution onto a glass slide and covered with a cover glass. The approximate location of the cloud point was located by visually observing when the film became cloudy when it was heated at 10 °C/min, and a more precise determination was made by repeating the experiment over a smaller temperature range using a heating rate of 2 °C/min. The cloud point was defined by the first sign of cloudiness in the film; the measurement was reproducible to within 2 °C.

Infrared spectra were measured with a Nicolet Model 60SX FTIR spectrometer. Each spectrum was signal averaged over 128 scans with a resolution of 2 cm^{-1}. The infrared samples were cast from solution onto NaCl plates and dried at ca. 75 °C under vacuum.

Results and Discussion

Blend Miscibility. *Inter*molecular interactions between Li-A and ethylene oxide (EG) may affect the free energy of mixing for partially neutralized PAA/PEG blends in one of two ways: (1) if the interaction between Li-A and EG is endothermic, the free energy increases and the blend should become less miscible with increasing neutralization as long as no other *intra*molecular effects occur, and (2) if the Li-A/EG interaction is exothermic, the free energy decreases and miscibility will become more favorable with increasing neutralization. Because the T_g's of the two component polymers are appreciably different, miscibility of the blends may be assessed from T_g measurements; i.e., a single composition-dependent T_g is taken here as the criterion for miscibility.

The effect of composition on the T_g of x-Li-PAA/PEG blends (x = the mole fraction of Li-A groups in the copolymer) for three different neutralization levels of the PAA is shown in Figure 1. The data in Figure 1 represent the state of the samples at the drying temperature, i.e., nominally at 40 °C. Because the temperature gradients in the vacuum oven used for drying the samples were large, the actual annealing temperature was probably more like 40 ± 10 °C, so that the phase behavior shown by the data in Figure 1 has the same uncertainty with respect to temperature. These data qualitatively demonstrate the perturbation that the copolymer composition has on the phase behavior. A quantitative assessment of the phase diagram for these blends is provided by the cloud-point measurements that are described later in this paper.

The PAA/PEG (i.e., 0.0-Li-PAA/PEG) and the 0.05-Li-PAA/PEG blends (Figure 1a and 1b) exhibited a single, composition-dependent T_g that was intermediate between those of the neat constituent polymers. This indicates that these blends were miscible in the amorphous phase over the entire range of composition at the annealing temperature used, i.e., the vacuum oven temperature.

When the concentration of the Li salt increased to x = 0.20, phase separation was observed over the com-

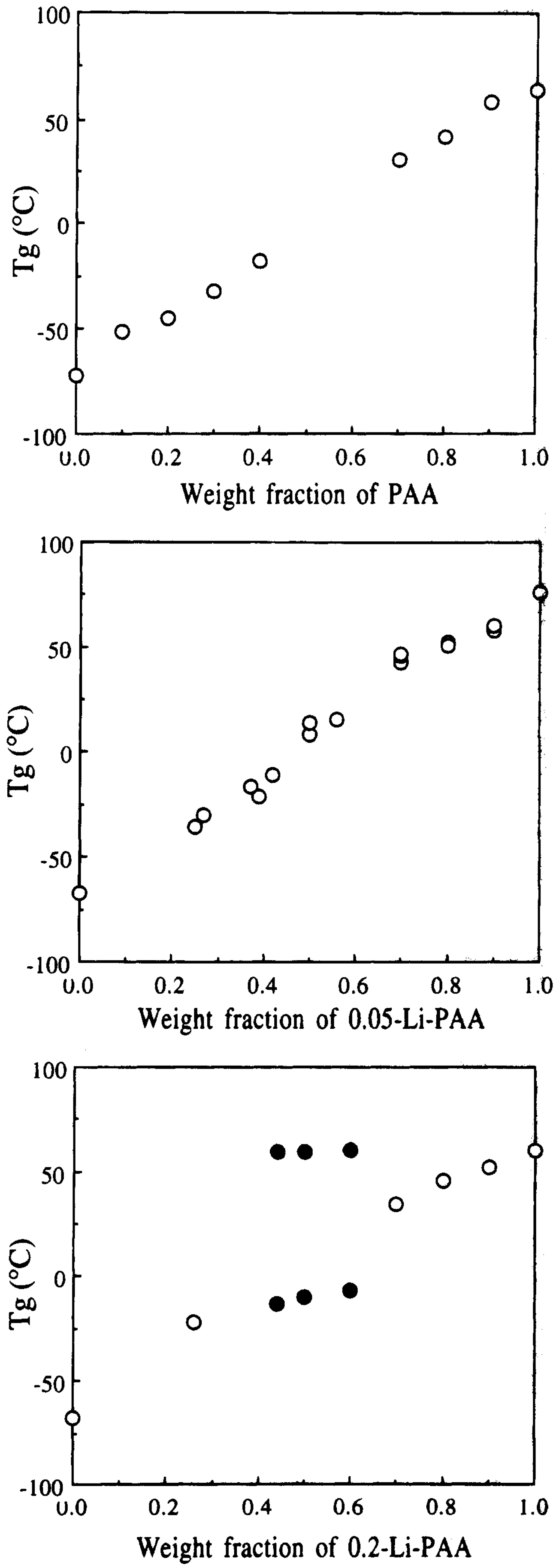

Figure 1. Glass transition temperature vs composition for (a, top) 0-Li-PAA/PEG, (b, middle) 0.05-Li-PAA/PEG, and (c, bottom) 0.2-Li-PAA/PEG blends.

position range of ca. $w_1 = 0.40-0.60$, where w_1 denotes the weight fraction of Li-PAA, as indicated by the presence of two T_g's, Figure 1c. The temperatures of the two T_g's indicate the presence of two amorphous phases: one of almost pure 0.20-Li-PAA and a second of ca. 60% (wt) PEG and 40% (wt) 0.20-Li-PAA mixture. It is not apparent from these data, however, whether phase separation occurred at the annealing temperature or during the DSC scan. In either case, it is clear that the boundary between the one-phase and two-phase regions for the 0.2-Li-PAA/PEG blends was significantly lower than for the PAA/PEG blends. The decrease in miscibility of the PEG/PAA blends with increasing neutralization of the PAA is similar to the reported solution behavior of similar blends; e.g., aqueous PAA/PEG complexes completely dissociate when the PAA is neutralized to ca. 30 mol %.[17,18]

When the composition of the copolymer was $x \geq 0.20$, the optical clarity of the freshly cast films was sensitive to the temperature used to prepare the films, which is also consistent with a perturbation of the phase boundary by neutralization of the PAA. For example, a 50/50 PEG/0.20-Li-PAA blend cast at 5 °C was optically clear and remained clear when annealed at ca. 40 °C. In contrast, the same sample was opaque, indicating a phase-separated morphology, when cast at 50 °C. The observation indicates that the blend exhibits lower critical solution temperature (LCST) behavior; i.e., it becomes less miscible as temperature increases. Although the 50/50 PEG/0.20-Li-PAA blend sample cast at 5 °C was clear, its DSC thermogram revealed two T_g's, which indicates two phases. The lower T_g, however, was very close to the interpolated value expected for a miscible 50/50 blend, and we believe that the as-cast blend was miscible and phase separation of a 0.20-Li-PAA-rich phase actually occurred during the DSC heating scan as an LCST was exceeded. In that case, the LCST must occur below the T_g of 0.20-Li-PAA, ca. 70 °C. This hypothesis was confirmed by the cloud-point measurements described below.

The DSC results indicate that neutralizing the PAA reduces the favorable interaction responsible for the miscibility of PAA and PEG. Since hydrogen-bonding between acrylic acid and the ether groups favors mixing, the interaction between the lithium acrylate and the ether must be weaker than the hydrogen bond and may be repulsive, i.e., have a positive interaction energy. Otherwise, little change in the phase behavior would be expected.

Interaction Parameters from Melting Point Depression Measurements. Quantitative information about the thermodynamic interactions in miscible blends containing a crystallizable polymer can be obtained from melting point depression measurements. Changes in the melting point of the crystallizable component may arise for either morphological or thermodynamic reasons. The thermodynamic effect may be described by the equation of Nishi and Wang:[21]

$$T_{\mathrm{mo}} - T_{\mathrm{m}} = -T_{\mathrm{m0}}B(V_{2\mathrm{u}}/\Delta H_{2\mathrm{u}})\phi_1^{\,2} \qquad (1)$$

where B is an interaction energy density. The subscript 1 denotes the noncrystallizable polymer (x-Li-PAA) and 2 denotes the crystallizable polymer (PEG). T_{m} and T_{m0} are the equilibrium melting temperatures of the crystallizable component in the blend and the neat polymer, respectively. ϕ_i, $\Delta V_{i\mathrm{u}}$ and $\Delta H_{i\mathrm{u}}$ are the volume fraction, molar volume, and molar enthalpy of fusion of component i. $\Delta H_{2\mathrm{u}}$ and $\Delta V_{2\mathrm{u}}$ were taken as 8.29 kJ/mol and 38.9 cm^3/mol, respectively.[22]

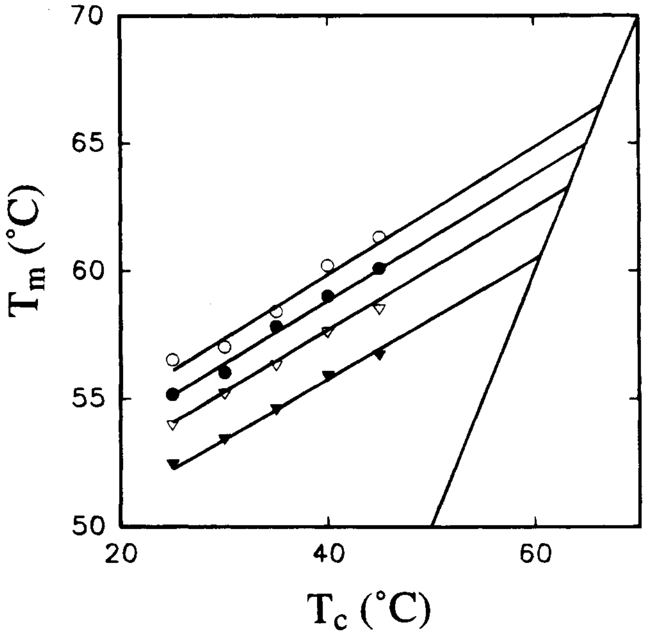

Figure 2. Hoffman–Weeks plots for 0.05-Li-PAA/PEG blends. Equilibrium melting points were obtained by extrapolation of data to $T_c = T_m$.

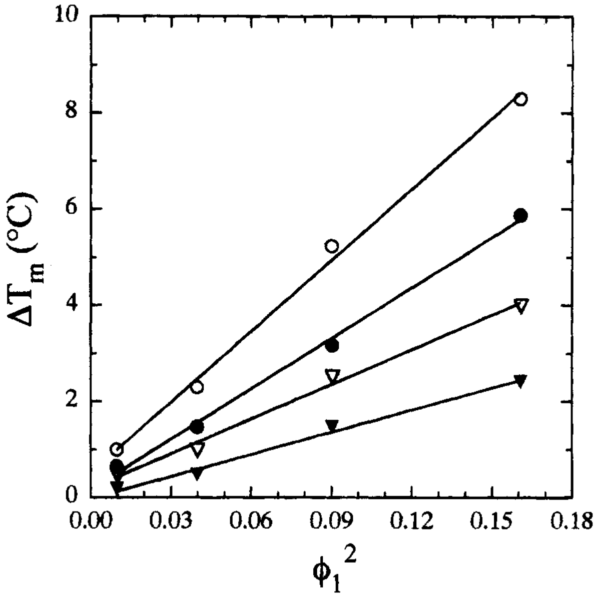

Figure 3. Equilibrium melting point depression vs $\phi_1^{\,2}$ for (○) 0-Li-PAA/PEG, (●) 0.05-Li-PAA/PEG, (▽) 0.1-Li-PAA/PEG, and (tds) 0.15-Li-PAA/PEG blends.

Equilibrium melting points were determined by using the procedure of Hoffman and Weeks,[23] which eliminates the influence of morphology on T_{m}. Figure 2 shows an example Hoffman–Weeks plot for the 0.05-Li-PAA/PEG blends. Similar plots were obtained for other blends. The melting point depression, $\Delta T_{\mathrm{m}} = T_{\mathrm{m}} - T_{\mathrm{m0}}$, is plotted as a function of $\phi_1^{\,2}$ in Figure 3 for 0.0-Li-PAA/PEG, 0.05-Li-PAA/PEG, 0.1-Li-PAA/PEG, and 0.15-Li-PAA/PEG blends. The following values for B were calculated from eq 1:

blend	B (cal/cm^3)
0.0-Li-PAA/PEG	−7.8
0.05-Li-PAA/PEG	−5.2
0.10-Li-PAA/PEG	−3.7
0.15-Li-PAA/PEG	−2.4

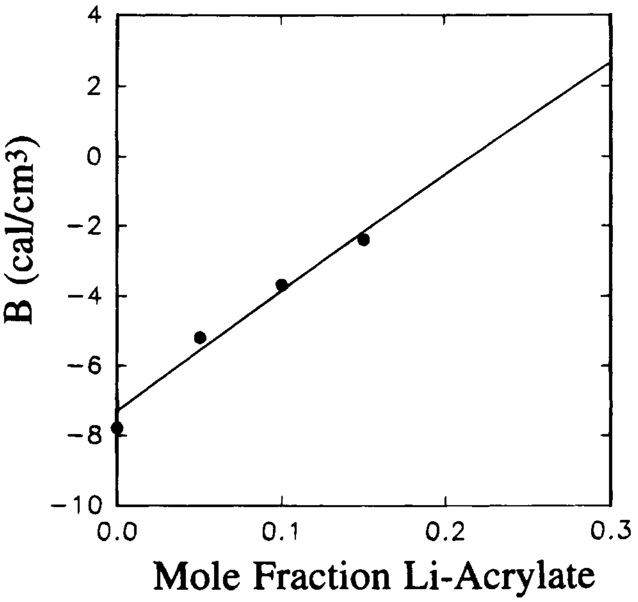

Figure 4. Fit of the binary interaction model to the B values obtained of the x-Li-PAA/PEG blends.

The interaction energy density, B, for PAA/PEG is negative, which indicates an attractive interaction. Neutralization of the PAA with lithium increases B, which indicates a less favorable interaction. The increase in B also suggests lower miscibility for the blends when the Li^+ salt is formed, which is consistent with the T_g data discussed above.

For the blends containing the partially neutralized PAA, the B calculated from the melting point depression data actually represents an average interaction energy for all pairwise interactions, i.e., interactions between acrylic acid and ethylene glycol ($B_{AA/EG}$), Li^+ acrylate and ethylene glycol ($B_{LiA/EG}$), and Li^+ acrylate and acrylic acid ($B_{LiA/AA}$). The individual binary interaction energies, $B_{i/j}$ may be calculated by applying the binary interaction model[11,12] to the B data tabulated above, i.e.,

$$B = vB_{LiA/EG} + (1 - v)B_{AA/EG} - v(1 - v)B_{LiA/AA} \quad (2)$$

where v is the volume fraction of Li^+ acrylate in the partially neutralized PAA. The first two terms of eq 2 represent the contribution of interpolymer interactions, while the last term reflects the contribution of intrapolymer interactions within the ionic copolymer. For the 0.0-PAA/PEG blends, $v = 0$, and B in eq 2 reduces to $B_{AA/EG}$. The application of eq 2 assumes that Li^+ acrylate and acrylic acid occupy similar volumes, i.e., $v \approx x$. This assumption is reasonable because the size of Li^+ is only slightly larger than that of H^+, and the volume change due to the neutralization is probably small for the relatively low neutralization levels considered here.

For the blends and interaction energies tabulated above, the best fit of eq 2 provides the following binary interaction energy densities:

$$B_{LiA/EG} = 22.8 \text{ cal/cm}^3$$

$$B_{AA/EG} = -7.5 \text{ cal/cm}^3$$

$$B_{LiA/AA} = -6.4 \text{ cal/cm}^3$$

The negative value of $B_{AA/EG}$ indicates that an exothermic interaction, in this case, hydrogen-bonding, occurs between AA and EG. The binary interaction model yields a relatively large positive value for $B_{LiA/EG}$, indicating a repulsive interaction between these groups. That result is surprising in that it is well-known that ion–dipole interactions take place between PEG and monomeric salts, though the strength of the interaction depends on the nature of the anion and cation pair.[24] The negative value for $B_{LiA/AA}$ results from either dipole–dipole interactions or ion–dipole interactions between the acid and salt groups.

Equation 2 predicts that a negative $B_{AA/EG}$ promotes miscibility, i.e., a negative B, which explains the miscibility of PAA and PEG. The negative $B_{LiA/AA}$ and the positive $B_{LiA/EG}$, however, increase B and reduce the miscibility of the partially neutralized poly(carboxylic acid) and PEG, which is consistent with the experimental observations described above.

Note that for this system of a copolymer/homopolymer blend, an attractive *intra*molecular interaction between the two polar components of the copolymer suppress miscibility. This is in contrast to systems in which repulsive interactions between components of a copolymer may enhance miscibility. An example of the latter effect that is germane to the PAA/PEG blends is a blend of poly(styrene-*ran*-methacrylic acid) (PS-*co*-MAA) and poly(ethylene oxide) (PEO). In that case, the intramolecular interactions between the polar MAA groups and the nonpolar S groups is repulsive, and $B_{MAA/S} \approx 100$ cal/cm³.[25] This large repulsive energy promotes the miscibility of PS-*co*-MAA with PEG. A similar explanation may apply to the observation of miscibility of blends of PEG and poly(styrene-*ran*-lithium methacrylate).[20] Like $B_{S/MAA}$, $B_{S/LiMAA}$ is probably large and positive, and *intra*polymer repulsive interactions would be expected to dominate the overall value of B. As a result, it is not surprising that blends of PEG and poly(styrene-*ran*-lithium methacrylate) are miscible over a specific range of copolymer composition.[20]

Phase Behavior. Polymer mixtures may exhibit either upper or lower critical solution temperature behavior (UCST or LCST, respectively). Because of equation of state effects that are prevalent in systems in which there are attractive intermolecular interactions, the latter type of phase behavior is most common for polymer blends.[26] An LCST for a miscible blend is sensitive to the energies of the different interactions in the blend,[27] and generally, the LCST increases as the overall interaction parameter becomes more negative. For systems with very strong attractive *inter*molecular interactions, such as polyelectrolyte complexes, the LCST may exceed the chemical decomposition temperature and not be observed. For copolymer/homopolymer blends where miscibility stems from *intra*molecular repulsion in the copolymer, an LCST is also sometimes observed.[28,29] The LCST in those systems depends on the composition of the copolymer, which affects the overall interaction energy, or the interaction parameter. Therefore, measurements of the LCST for a series of blends of similar chemistry provides a sensitive method for assessing their relative overall interaction parameters. In the present study, the phase behavior was studied for PAA/PEG blends with varying amounts of the PAA neutralized to LiA.

The effect of the degree of neutralization, x, on the LCST for 28/72 (w/w) and 50/50 x-Li-PAA/PEG blends is shown in Figure 5. When $x < 0.10$, the blends were miscible and no LCST was detected up to the decomposition temperature of the blend, ca. 150 °C. The high

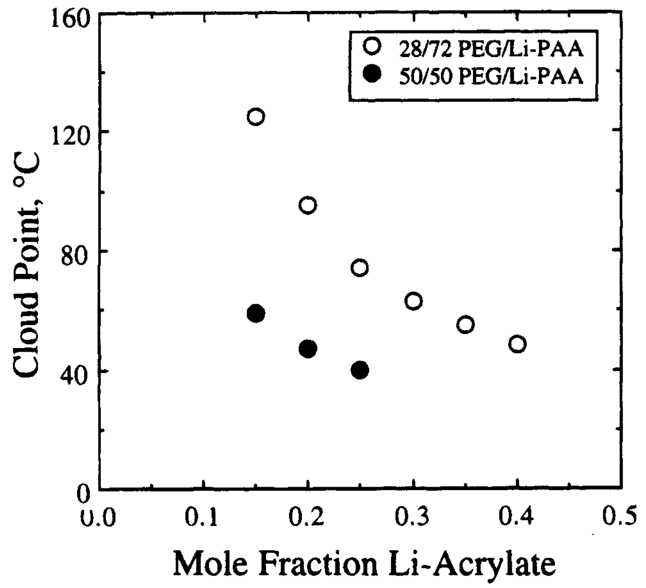

Figure 5. LCST behavior of the *x*-Li-PAA/PEG blends as function of the neutralization level.

LCST, or absence of one, is a result of the extensive hydrogen-bonding between MAA and EG. For $x \geq 0.15$, the LCST decreases as the degree of neutralization increases. These results are consistent with the interaction energy densities calculated from the binary interaction model and support the conclusion that a less negative overall interaction energy results when the acrylic acid is converted to the Li^+ salt.

Figure 5 also indicates that the effect of neutralization on the LCST becomes less significant at the higher neutralization levels studied. The diminishing effect of neutralization at the higher salt concentrations may be explained qualitatively by the differences in the temperature dependencies for the various interactions that occur in these blends. The interaction parameter can be divided into two terms:[30] one for favorable interactions, in this case, hydrogen-bonding, B_H, and the other for unfavorable interactions, B_{Dis}. The favorable and unfavorable interaction terms decrease with increasing temperature. The latter effect promotes phase-mixing, and the former favors phase-demixing. At a lower degree of neutralization, the phase-separation temperature of the blend is controlled by the stability of the hydrogen bonds, and when additional neutralization takes place, a relatively large decrease in the LCST occurs as a result of lowering the concentration of hydrogen bonds. At higher degrees of neutralization, however, the dispersive term also exerts a tangible influence on the LCST, and as temperature increases, the decrease of this effect counters the decrease in the favorable interaction term. The competing effects effectively cancel, so at the higher neutralization levels studied here, the LCST becomes relatively insensitive to incremental changes in the degree of neutralization.

Specific Interactions. FTIR spectroscopy is useful for characterizing hydrogen-bonding in polymer blends. For the present system, two absorption bands, the C=O stretching near 1700 cm^{-1} and the O—H stretching near 3000–3500 cm^{-1}, are particularly sensitive to hydrogen-bonding. Figure 6 shows the FTIR spectra for PAA/PEG blends and the two component polymers in the spectral region 1500–2100 cm^{-1}. For the neat PAA, two C=O stretching bands were observed at 1706 and 1732 cm^{-1}. The lower frequency band corresponds to hydrogen-bonded C=O in intermolecular cyclic acid dimers and the higher frequency one is due to free C=O (hereafter referred to as "free acid" groups).[31]

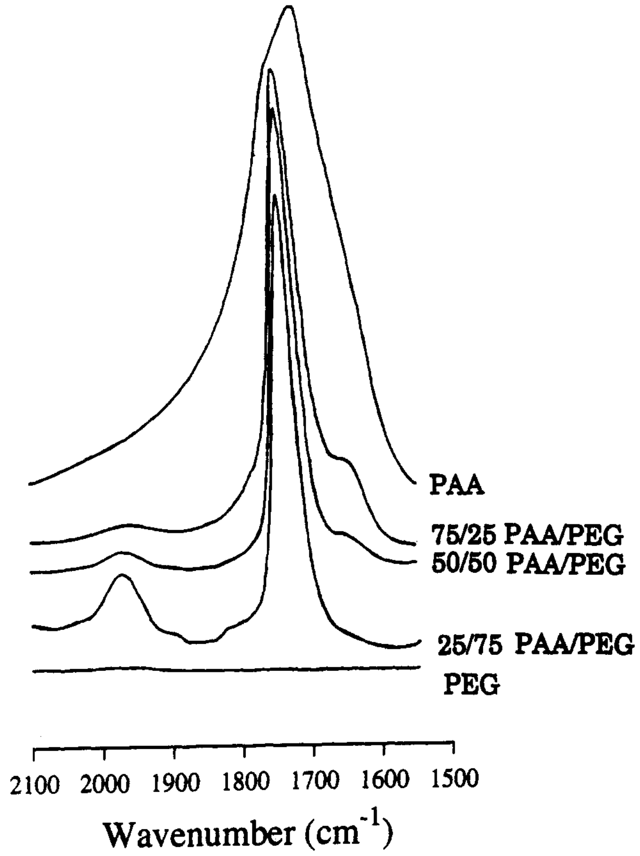

Figure 6. FTIR spectra in the C=O stretching region for the PAA/PEG blends.

Upon addition of 25 wt % PEG, the band associated with the intermolecular cyclic dimers decreased significantly, and the band for the free C=O increased and narrowed, which indicates that an exchange of hydrogen bonds from acid cyclic dimers to acid–ether complexes occurred when the two polymers were mixed. A new absorption band also occurred at ~1955 cm^{-1} in the blends, and it increased in intensity as the PEG concentration increased. That new band, which is indicative of strong hydrogen bonds, is a satellite band of a hydrogen-bonded hydroxyl group,[32] which is discussed below.

One might expect the exchange from cyclic acid dimers to acid–ether hydrogen bonds if the latter were a stronger interaction. That assumption is consistent with the observations that PAA is water-soluble, while complexes of PAA and PEO are not.[18,19] In the former case, the self-hydrogen-bonding of the poly(carboxylic acid) is solvated by water, whereas in the latter system, water does not displace the acid–ether hydrogen bond. Coleman et al.,[33] however, reported that the enthalpy of the hydrogen bond for self-associated methacrylic acid groups in ethylene–methacrylic acid copolymers (EMAA) was 14.4 kcal/mol and the corresponding enthalpy for a carboxylic acid–ether interaction was only 6 kcal/mol. On that basis, those authors attributed the miscibility of EMAA and PEO to the entropy gained by the PEO in mixing rather than to a decrease in the free energy from enthalpic effects.

An important difference between the EMAA/PEO system studied by Coleman et al.[33] and the blend considered in the present paper is the equilibrium concentration of free acid in the neat PAA compared

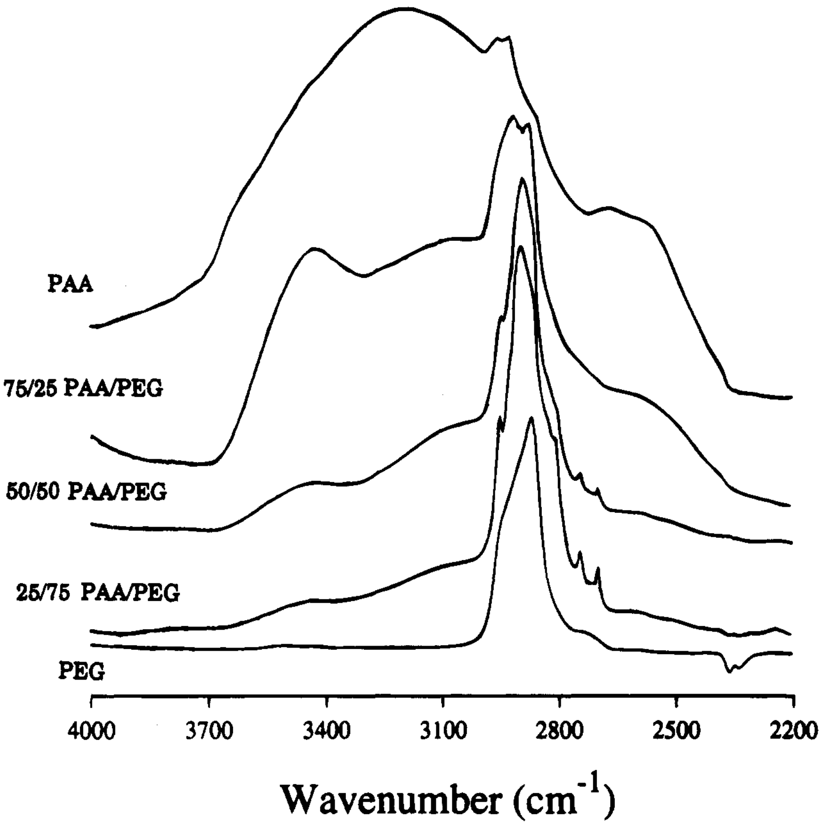

Figure 7. FTIR spectra in the O–H stretching region for the PAA/PEG blends.

with EMAA. For EMAA, the infrared spectrum of the C=O region (Figure 2 in ref 33) and the theory developed by Coleman et al.[33] for the equilibrium concentration of free acid groups indicate that neat EMAA contains little or no free acid. Figure 6 of this paper, however, clearly shows that the intensity of the 1706 cm^{-1} IR absorption due to free carbonyl for PAA is comparable to that of the 1732 cm^{-1} band for hydrogen-bonded carbonyl. The reason for the discrepancy between these results and those in ref 33 may be a result of less segmental flexibility in the PAA. A critical assumption of the Coleman model is that the acid groups have "...sufficient flexibility to follow their intrinsic proclivities in forming hydrogen bonds".[33] While, for EMAA, the separation of the acid groups by flexible methylene sequences may be sufficient to allow complete dimerization of the acid groups, an equivalent result in PAA would require in effect a complete loss of conformational entropy. As a result, a significant concentration of free acid was observed in the neat PAA and complexation of these groups with the polyether presumably is enthalpically favored.

The question of why there is a reduction of cyclic acid dimers upon mixing PAA with PEO is still a troublesome one if indeed the hydrogen bond of the dimer is significantly more enthalpically favored than is the acid–ether hydrogen bond. Lee et al.[33] conclude that the free energy lost by the carboxylic acid copolymer upon exchange of hydrogen bonds from the acid dimers to the ether is offset by the grain in entropy of the polyether. Although this may explain the miscibility of EMAA and PEO and may also be an important factor in the mixing of PAA and PEO, the loss of miscibility upon conversion of the acid to its Li$^+$ salt indicates that the increase in entropy of the PEO is no longer sufficient to drive mixing. This may be explained by the Coleman model as a weaker interaction between LiA and EG than between AA and EG, so that the entropic contribution is no longer able to compensate for the gain in free energy associated with breaking acid dimers. The acid concentrations studied here were, however, much greater than those considered by Coleman et al.,[33] even in the partially neutralized blend. Therefore, unless the LiA/EG interaction were highly repulsive, the Coleman model would still seem to favor mixing. A repulsive LiA/EG interaction is consistent with the results of the binary interaction model described above.

Hydrogen-bonded complexes formed in water generally have a 1:1 stoichiometry.[13,14] The blend containing 25% (wt) PEG was completely amorphous, and therefore all the ether groups were available for forming hydrogen bonds. That blend composition corresponds to a molar ratio of [ether]/[acid] $\approx$ 2. If a 1:1 acid–ether complex occurred in the blend, as it does in aqueous PAA/PEG solutions, half of the acid groups would not be complexed with the polyether. The uncomplexed acids would be expected to form acid cyclic dimers. However, the spectrum shown in Figure 6 indicates a lower than expected concentration of acid cyclic dimers and the presence of free acid groups (i.e., the band at 1732 cm^{-1}).

When the PEG concentration increased, the infrared band due to the acid cyclic dimers continued to decrease and the band for free C=O increased (see Figure 6). At 75% PEG, the absence of the band at 1710 cm^{-1} indicates no acid cyclic dimers remained. At that composition the blend was crystallizable, but the PEG concentration in the amorphous phase was sufficiently high relative to the PAA concentration so that enough ether groups were available to complex with all the acid groups in the blend.

More direct evidence for the hydrogen bonding between the acid and ether groups is provided by the spectral changes of the O–H stretching vibration. Figure 7 shows the FTIR spectra for the blends in the

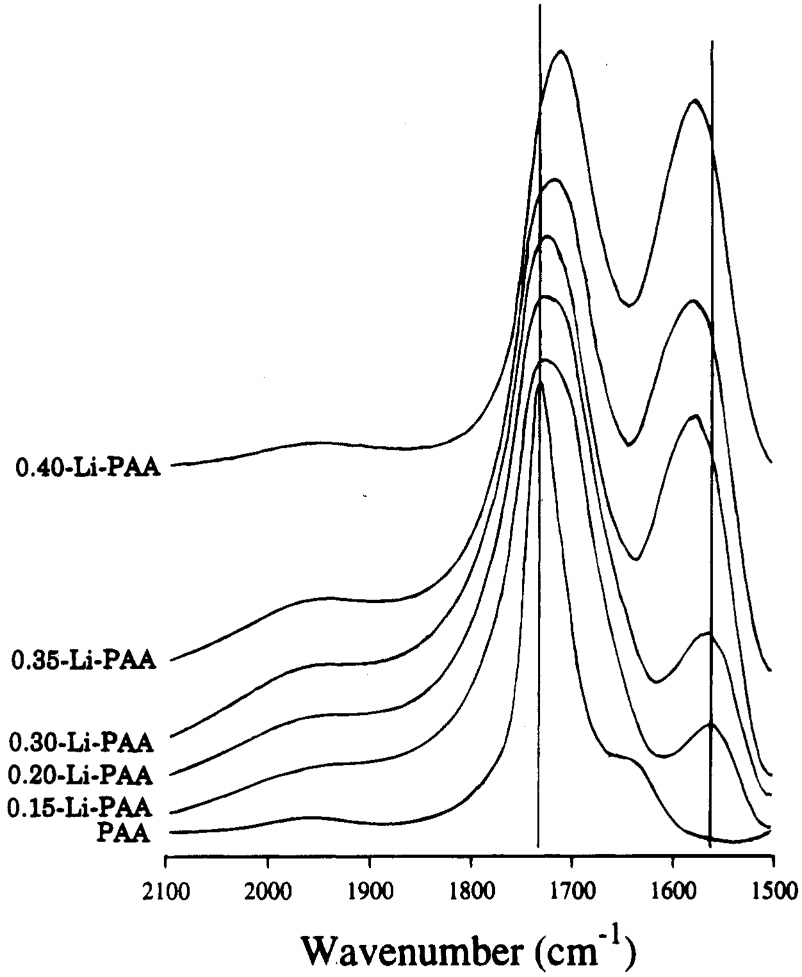

Figure 8. Effect of the neutralization of the C=O stretching for the 75/25 x-Li-PAA/PEG blends.

hydroxyl stretching region. For aliphatic acids, the O—H stretching vibrations usually occur at ~3490–3570 cm^{-1} for free hydroxyl groups and at ~3000 cm^{-1} for acid cyclic dimers.[34] The O—H stretching absorption for the neat PAA was a broad band centered at ~3200 cm^{-1}, which indicates a distribution of environments for the O—H groups, e.g., free hydroxyl groups, noncyclic single and multiple hydrogen bonds, and cyclic dimers. A satellite O—H band was observed at ~2650 cm^{-1} for PAA. When PAA was blended with PEG, the broad O—H band was resolved into two bands centered at ~3450 and ~3100 cm^{-1}. The band at 3450 cm^{-1} is consistent with the stretching vibration of free O—H in an aliphatic carboxylic acid, and the relatively broad band ~3100 cm^{-1} may be a composite of vibrations due to hydrogen-bonded O—H groups in the acid–ether complex and in the acid cyclic dimers. The contribution from the acid cyclic dimers should be small, however, based on the intensity of the C=O absorptions in Figure 6. With increasing PEG content, the hydrogen-bonded O—H band shifted slightly to lower frequency. This small shift was probably due to a decrease in the concentration of the acid cyclic dimers, whose absorption frequency is somewhat higher than that of the acid–ether hydrogen bond. As seen in Figure 6, acid cyclic dimers were not detected in the 75% PEG blend. For that blend, the hydrogen-bonded O—H band should only be due to the acid–ether complex. The band frequency was ~100 cm^{-1} lower than for the maximum frequency of the hydrogen-bonded O—H absorbance for the neat PAA, which further suggests that the hydrogen bonds between PEG and PAA are stronger than the self-hydrogen-bonding in PAA. The increased hydrogen-bond energy of the acid–ether complex favors mixing of the two polymers.

Changes in the satellite bands, which are very sensitive to the strength of hydrogen bonds,[35] support the conclusions above. For the O—H stretching mode, a structureless band centered near 3300 cm^{-1} corresponds to weak hydrogen bonds. For relatively strong hydrogen bonds, the O—H stretch shifts to lower frequency and a satellite band at 2650 cm^{-1} is observed, e.g., for the neat PAA shown in Figure 7. When the hydrogen bonds in PAA are replaced by the acid–ether hydrogen bond, two satellite bands at ~2600 and ~1950 cm^{-1} and an O—H stretching band at ~3100 cm^{-1} are observed.

Figure 8 shows the effect of neutralization of the PAA on the FTIR spectra of 75/25 x-Li-PAA/PEG blends in the C=O stretching region. The band at ~1560 cm^{-1} is due to the C=O stretching absorption for the LiA, and the intensity of this band increases as the degree of neutralization increases. As discussed earlier, the carboxylic acid may exist as either a free acid ($\nu_{C=O}$ = 1732 cm^{-1}) or a cyclic dimer ($\nu_{C=O}$ = 1710 cm^{-1}). Neutralization of the PAA results in significant broadening of the C=O bands and changes their peak positions. The peak positions of the two C=O bands for AA and LiA are plotted in Figure 9 as a function of the extent of neutralization. The LiA band shifts to higher frequency with increasing neutralization of the PAA, while the AA band shifts to lower frequency. A significant change in the band positions occurred over the neutralization range of 20–30% (mol), which corresponds to the neutralization level for which the more

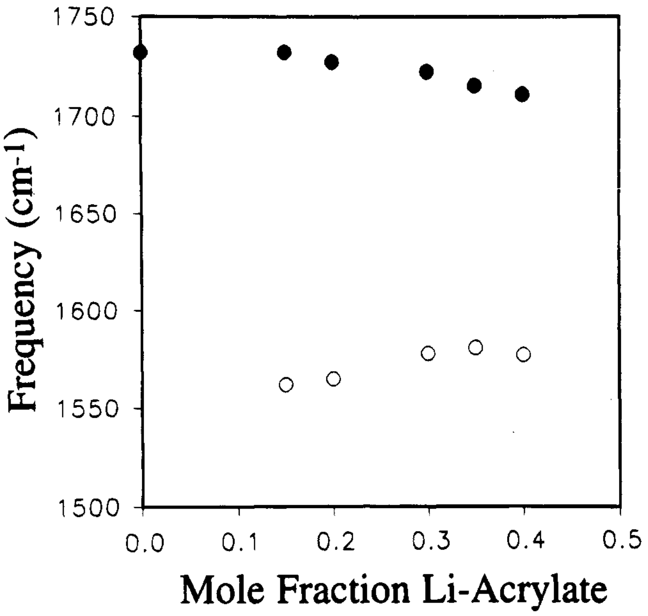

Figure 9. C=O stretching frequencies of the 75/25 *x*-Li-PAA/PEG blends vs the degree of neutralization.

noticeable effects on phase separation were observed. Since the C=O band of the acid cyclic dimers is at a lower frequency (~1710 cm^{-1}), the low-frequency shift of the C=O band for the acid form suggests that a larger fraction of the acid cyclic dimers existed at a higher neutralization level—presumably, as a consequence of phase separation of the blends. The shift to higher frequency of the C=O band for LiA may arise from the stronger interactions between the Li carboxylate dipoles in microphase-separated aggregates. That is, the frequency of the C=O vibration increases as the dipole–dipole interactions become stronger.[35]

Conclusions

The miscibility of PAA and PEG decreased upon neutralization of the PAA to its lithium salt. For annealing temperatures of 40–50 °C, the critical level of neutralization below which the blends were miscible was ca. 20 mol %. These blends exhibit LCST phase behavior, and the LCST decreases as the extent of neutralization of the PAA increases. The interaction parameters calculated from melting point depression data indicate that favorable segmental interaction between the acrylic acid and ethylene glycol promotes phase mixing, while an unfavorable segmental interaction between the Li^+ acrylate and ethylene glycol favors demixing.

Spectral changes of the C=O stretching infrared bands indicate that a hydrogen-bond exchange from the acid cyclic dimers in the neat PAA to acid–ether complexes occurs upon blending PAA and PEG. Neutralization of the acid inhibits formation of the acid–ether complexes and results in an increased fraction of acid cyclic dimers. The most significant changes in the FTIR spectra occurred when the level of neutralization was about 20 mol %, which corresponds to the critical neutralization level for phase separation found by thermal analysis.

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