Miscibility Enhancement via Ion-Dipole Interactions. 2. LCST Behavior of Polystyrene Ionomer/Poly(alkylene oxide) Systems

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ABSTRACT: A study of LCST behavior is used to show that ion-dipole interactions can lead to truly thermodynamic miscibility in polymers which are immiscible in their absence. Blends of polystyrene (PS) ionomers with poly(propylene oxide) (PPrO) at low PPrO contents are miscible at low temperatures: they undergo phase separation and become opaque upon heating but recover their transparency upon cooling. The degree of miscibility enhancement (related to the strength of the interaction) can be compared in different systems by comparing the positions of the cloud point curves. Thus, an increase in the ion content of the PS ionomer shifts the cloud point curve to higher temperatures. A decrease in the counterion size in the PS ionomer (i.e., K > Na > Li) also increases the strength of the interaction and leads to an upward shift of the cloud point curves. The effect of molecular weight is similar to that seen in nonionic blends. The phase separation is a relatively fast process in a blend of styrene containing 10.4 mol % lithium methacrylate copolymer (S-0.104MAA-Li) mixed with PPrO and is completely reversible; a decrease in the ion content or an increase in the radius of the counterions slows down the phase-separation process and is accompanied by incomplete recovery of transparency upon cooling. This suggests that the lower the miscibility, the slower the phase separation process. Transparency measurements are also used to compare the strengths of the interactions between PS ionomers and PPrO on the one hand and PS ionomers and poly(ethylene oxide) (PEO) on the other. Finally, the relative strengths of ion-dipole interactions and of hydrogen bonds are also compared by transparency measurement.

Introduction

Thermodynamic considerations as well as a wide range of experiments have suggested that some type of attractive interaction is usually required if two polymers are to be miscible.[1,2] Because the mixing of different polymers of high molecular weights leads to a very small positive entropy of mixing, the "entropic stabilization", which is the driving force for mixing of two solvents or of a polymer and a solvent, is no longer operative. In order to find miscible polymer systems, combinations of polymer pairs which show a negative enthalpy of mixing must be found. Examples of interactions which have been widely studied as miscibility enhancers in polymer blends are hydrogen bonding,[3-8] donor-acceptor interactions,[9-11] and dipole-dipole interactions[12-14] among others. The properties of ionomers have been explored for some time in this laboratory, and recently studies of ionomeric blends have been undertaken. Several immiscible polymer pairs have been made miscible by utilizing anion-cation interactions;[15-20] when one polymer with proton-donating groups (e.g., $-SO_3H$) is mixed with another containing proton-accepting groups (e.g., pyridine), polycations and polyanions are formed by proton transfer. For example, the polystyrene/poly(ethyl acrylate) and the polystyrene/polyisoprene systems have been made miscible at a functional group content of ca. 5%.

Miscibility enhancement via ion-dipole interactions has also been reported recently.[20-23] Ion-dipole interactions play an important role in inorganic chemistry:[24] they are responsible for the dissolution of ionic crystals in water, and numerous ion-dipole complexes like hydrates and ammoniates have been studied in the solid state as well as in solution. Ion-dipole interactions between polar polymers and small ions have also been investigated by Moacanin and Cuddihy[25] and other groups.[26-29] The viscosity and the glass transition temperature of poly(alkylene oxide) increase appreciably on mixing with $LiClO_4$ due to the strong interaction between the polymer and the cations. While ion-dipole interactions in small molecule/small molecule and polymer/small molecule systems are well-known, ion-dipole interactions in polymer/polymer system have not been studied systematically.

Because interaction energies for ion-ion interactions and ion-dipole interactions are proportional to r^{-1} and r^{-2}, respectively, for any given ion, the interaction for the former is stronger than for the latter. However, ion-dipole interactions are strong enough to enhance miscibility of otherwise immiscible polymers, as was pointed out in a previous paper.[21] The miscibility of a blend consisting of PS and poly(alkylene oxide) was enhanced by introducing small percentages of ions into the PS. Ion-dipole interactions of this type were shown to be effective for many systems.[22,23] Although it is important to understand whether the miscibility enhancement due to ion-dipole interactions leads to truly thermodynamic miscibility, the methods employed to date do not always give this information. In previous studies, the techniques used to evaluate miscibility were related to such properties as the glass transition temperature, transparency of the samples at room temperature, and mechanical properties. However, the miscibility of the blend has to be understood in terms of thermodynamic stability.[30] It has been recognized from thermodynamic considerations that miscible blends must show LCST behavior,[30-33] and cloud point curves have, indeed, been obtained for several miscible blend systems.[34-39] In typical experiments, miscible transparent blends at low temperature undergo phase separation and become opaque upon heating, and the process is frequently reversible. Of course, a cloud point cannot be found if the chemical decomposition temperature is lower than the cloud point or if the cloud point is below the glass transition temperature of the system. In general, however, a thermodynamic assessment of the miscibility of a blend sample can be made by studying the LCST behavior. Furthermore, the strengths of various interactions can be compared by comparing the positions of the cloud point curves. For example, it was pointed out from thermodynamic theory[31] that the position of the cloud point curve should shift to higher temperature with an increase in the strengths of the attractive interactions.

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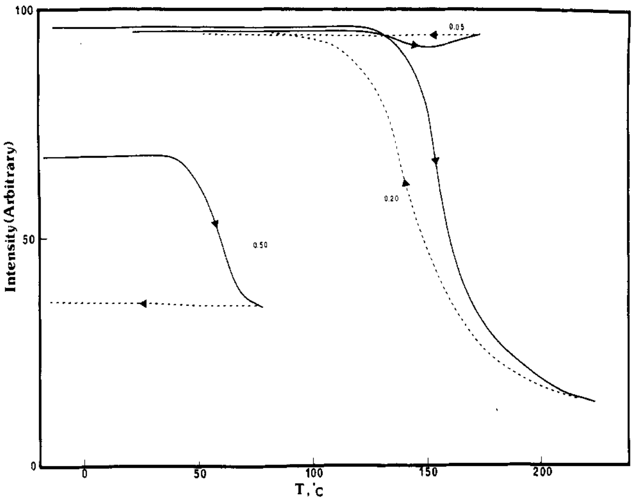

Figure 1. Variation of transmitted light intensity (arbitrary units) with temperature for S-0.104MAA-Li/PPrO(l) systems at w_{PPrO} = 0.05, 0.20, and 0.50: (—) heating; (---) cooling.

In this work, the LCST behavior of blends of PS ionomers and poly(alkylene oxides) was studied in order to obtain a thermodynamic assessment of miscibility. In a recent study,[20] it had been found that in systems which were rendered miscible by ion–ion interactions, no LCST behavior was observed below the decomposition temperature of the polymers because of the high strength of these interactions. However, since the strength of ion–dipole interactions is expected to lie between that of ion–ion and van der Waals interactions, cloud point curves might be observed below the decomposition temperature. This is, indeed, the case. Furthermore, in this study, the effect of ion content, and that of the size of counterion on the cloud point curves, is also explored to compare the strengths of the attractive interactions; the molecular weight effect is also investigated. Finally, the kinetics of phase separation of the PS ionomer/PPrO blends are discussed qualitatively.

Experimental Section

Samples. The samples and the preparation methods were described in a previous paper.[21] Disk samples for transparency measurements were compression molded at temepratures slightly above T_g. Typical dimensions of the disk samples were radius = 6.5 mm and thickness = 0.5 mm. It is characteristic of polymer blends that the thermal history influences the results appreciably.[34] In our case, the molding temperature depended on the composition. Therefore, in order to maintain the same thermal history, all samples were annealed at 70 °C for 3 days before transparency measurements were started.

Measurements. To observe the phase-separation behavior, a disk sample was mounted on a 1-mm-thick microscope glass slide and covered with a 0.2-mm-thick cover glass. The assembly was then placed on a Mettler FP52 hot stage mounted on a microscope. It was observed that the heating or cooling rate influenced the results;[34] thus, the heating or cooling, regulated by a Mettler FP5 unit, was performed at 3 deg/min for all samples. The thermocouple was placed near the disk sample, and the temperature were read directly from a digital thermocouple thermometer. The transmitted light intensity was recorded as an output voltage on a recorder by using a photocell at the eyepiece position. The cloud point was obtained from the point where the scattered light intensity began to increase in the τ vs. T plot. τ is the turbidity (total scattered intensity) defined by $\tau = -(1/d) \ln (I/I_0)$, where I and I_0 are the transmitted light intensity with and without the sample, respectively, and d is the thickness of the disk sample. The transparency measurments below room temperature were performed in a nitrogen atmosphere by passing a stream of nitrogen cooled by liquid nitrogen through the hot stage. The minimum temperature obtained by this method was -20 °C.

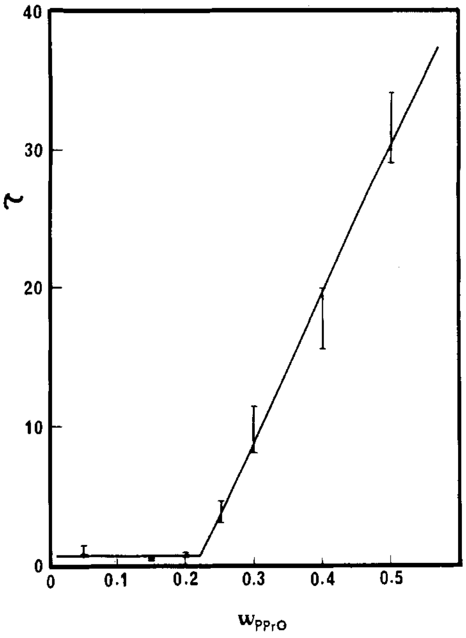

Figure 2. Turbidity at room temperature for S-0.104MAA-K/PPrO(l) system.

Results and Discussion

Figure 1 shows the temperature dependence of the transmitted light intensity for S-0.104MAA-Li/PPrO(1)(40) system. Because the 5 wt % sample underwent only very small scale microphase separation, the transmitted light intensity, I, did not decrease appreciably. The 20 wt % sample showed typical phase-separation behavior. I began to decrease at 124 °C on heating and continued decreasing gradually until it leveled off at about 220 °C, where the sample was opaque. Upon cooling, I began to increase until it returned almost to the initial value. This figure shows that the phase separation process for this sample is reversible and thus thermodynamic. The 50 wt % sample was partially transparent and I changed slightly upon heating. Figure 2 shows the composition dependence of turbidity at room temperature. The size of the bars represents the variation of the transmitted light intensities caused by changes in the position of the light rays traversing the sample. This difference is a result of the molding process since the temperature of the center of the disk is slightly higher than that of the edge. It can be seen from the figure that the sample is transparent at $w_{\mathrm{PPrO}} < 0.23$ and turns rapidly opaque beyond this value. Consequently, LCST behavior above room temperature was observed only for $w_{\mathrm{PPrO}} < 0.25$ for this system.

PEO (Crystalline Polymer/Amorphous Polymer). It was shown in the previous paper[21] that the PS ionomer/PEO system was miscible at low PEO contents ($w < 0.1$). The conclusion was based on the presence of a single glass transition and on the transparency of the samples. For $0.1 < w_{\mathrm{PEO}} < 0.5$, the blend was partially miscible, showing two glass transitions, as well as partial transparency. Analysis of the PS ionomer/PEO system at high PEO contents is complicated because of the crystallinity of PEO. However, the miscibility enhancement of PS ionomers with amorphous PEO can still be studied by transparency measurements at temperature higher than the melting point of PEO.

Figure 3 shows the temperature dependence of the transmitted light intensity for the S-0.104MAA-Li/PEO(1) system at 90% PEO content. The step seen at around 55 °C is undoubtedly related to the melting of the PEO. On further heating, the transmitted light intensity increases

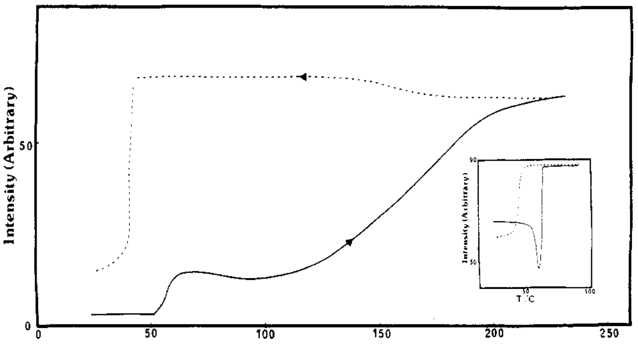

Figure 3. Variation of transmittted light intensity (arbitrary units) with temperature for S-0.104MAA-Li/PEO(l) system at w_{PEO} = 0.90. Insert shows the data for pure PEO(h): (—) heating; (- - -) cooling.

further, as the styrene ionomer dissolves progressively. The disk sample is almost transparent at around 220 °C. Upon cooling, the transmitted light intensity stays at a constant high value until it suddenly decreases at 40 °C due to the recrystallization of PEO. The temperature dependence of the transmitted light intensity for pure PEO is also shown in the same figure for comparison.

PPrO System (Amorphous Polymer/Amorphous Polymer). As was shown in Figure 1, the PPrO(l) system shows the transition between complete transparency and opacity at low PPrO contents (w_{PPrO} = 0.20), while a exhibiting corresponding change only over much smaller ranges of transparency at high PPrO contents (w_{PPrO} = 0.50). The reason for this decrease in I is that the samples of high PPrO contents consist of two phases already at low temperatures. The S-0.104MAA-Li/PPrO(h) system is also phase separated at low temperatures and exhibits a two-step change in the I vs. T plot, suggesting the existence of two distinct points at which phase changes occur.

Below w_{PPrO} = 0.25, only one step is observed. These findings parallel those of Nishi and Kwei[35] who observed a two-step change in the cloudiness of their samples. In the S-0.104MAA-Li/PPrO(h) system, two-step changes in τ vs. T plot are observed at a PPrO content of more than 0.25. These two steps correspond to the cloud points of each phase.

Figure 4 shows the effect of ion content on the cloud point curves. The ion contents of PS ionomer are 4%, 7%, and 10%. It can be seen in the figure that the higher the ion content, the higher the cloud point curve. In other words, the higher the ion content, the stronger the total interaction between PS ionomer and PPrO. In order to show that this is not due to a change of the strength of ion–dipole interaction but to the change of total interactions between ions and dipoles, the cloud points were plotted against the mole fraction of dipoles of total interacting groups [i.e., [–O–]/([COO$^-$] + [–O–])] (Figure 5). All points fall on a single straight line, with a correlation coefficient of –0.98. The samples with different ion contents have the same cloud point if the mole fractions of dipoles are the same. Because the number ratio of ions to dipoles, [COO$^-$]/[–O–], is the same at the same mole fractions of dipoles, the strength of one set of ion–dipole interactions[41] is the same as for all blends. However, since the ratio [COO$^-$]/[–O–] becomes larger for blends of higher ion content at the same weight fraction, the total interactions between molecules becomes stronger and leads to the shift of cloud point curve to higher temperatures if the data are plotted in Figure 4.

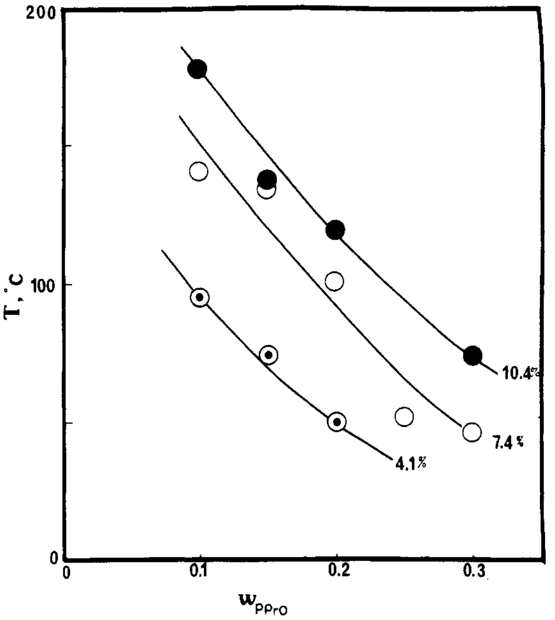

Figure 4. Effect of ion content on cloud point curves for S-MAA-Li/PPrO(l) systems.

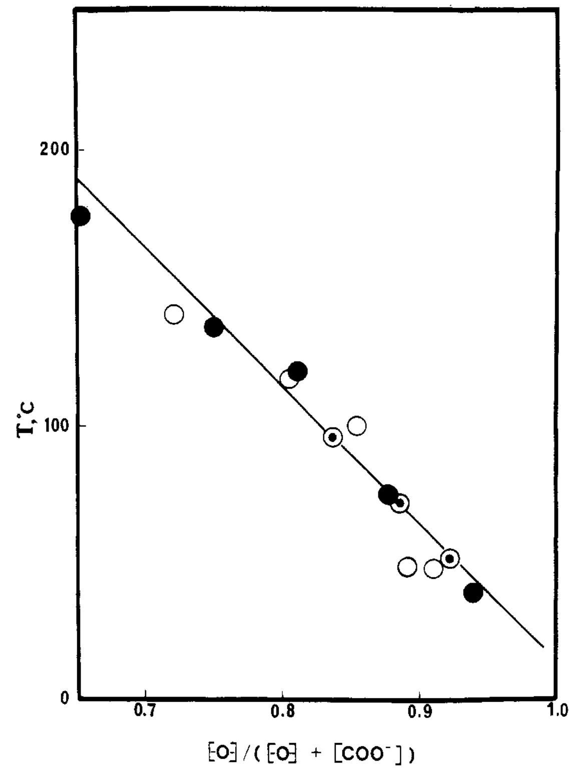

Figure 5. Cloud points plotted against mole fraction of total interacting groups present as dipoles (i.e., [–O–]/([COO$^-$] + [–O–])) for S-MAA-Li/PPrO(l) systems.

Figure 6 shows the effect of the counterions on the cloud point curves. The position of the cloud point curves increases in the order Li > Na > K, which is inversely proportional to the size of the counterions. It is well-known that in the case of ion–dipole complexes involving small molecules (e.g., alkali halides) the stability of the complex increases with decreasing ionic radius.[24] For example, of all the alkali halides, only those containing lithium give stable hydrates at room temperature. It has also been shown that the T_g of ionomers increases with decreasing size of the counterions of same valency.[42] These phenomena are due to the fact that the interaction energy between ions or ions and dipoles increases with decreasing ionic radius of cations. Figure 6 also shows that the interactions become stronger as the size of counterions decreases.

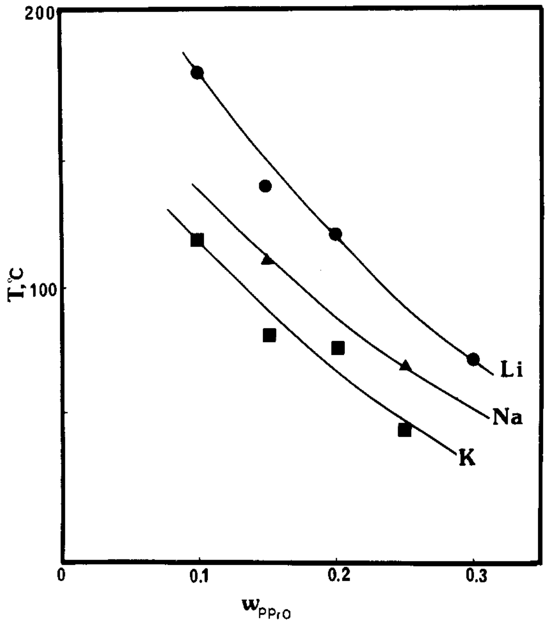

Figure 6. Effect of counterions on cloud point curves for S-0.104MAA-M/PPrO(l) systems.

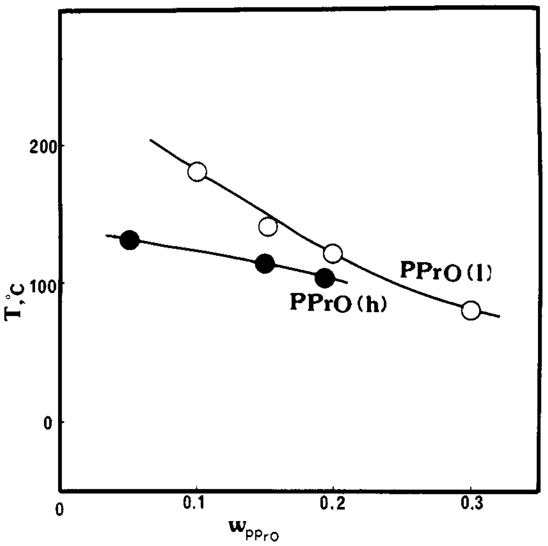

Figure 7. Effect of molecular weight on cloud point curves for S-0.104MAA-Li/PPrO systems.

Figure 7 shows the molecular weight dependence of the cloud point curve for the PPrO systems of low PPrO content. The lower the molecular weight, the higher the position of cloud point curve, i.e., the higher the miscibility. This trend was indicated before[21] from the shift of glass transition temperature. This is as expected from the thermodynamic theory[31] and parallels the results for the PS/poly(vinyl methyl ether) (PVME) system,[35] as well as those for other blends.

The LCST behavior of hydrogen-bonded systems was also studied by using unneutralized PS–MMA. At least for the S-0.104MAA/PPrO(l) system, the blend samples were completely transparent up to the decomposition temperature (ca. 230 °C) at $w_{PPrO} < 0.5$. This result indicates that hydrogen bonding is stronger than the ion–dipole interaction in the PS ionomer/PPrO(l) system. Although no great difference was observed in terms of the T_g shift between systems subject to hydrogen bonding and ion–dipole interactions,[21] the cloud point curves show a clear difference. Shibayama et al.[43] recently reported that the deuteriated PS(PSD)/PVME system showed a cloud point curve ca. 40 °C higher than that of PS/PVME system, although both systems had the same glass transition temperatures. From a measurement of the volume of mixing, it was observed that the PSD/PVME system had greater miscibility than the PS/PVME system. These results show that the cloud point curves are much more sensitive to the difference of the strength of interactions than the glass transitions.

Kinetics of Phase Separation. The kinetics of phase separation were studied qualitatively for the PS ionomer/PPrO(l) systems. It was observed that the phase separation of S-0.104MAA-Li/PPrO(l) system at low PPrO contents was a relatively fast process. For example, for the 15% sample, when the temperature was increased suddenly (over ca. 20 s) from 80 °C (below cloud point) to 180 °C (above cloud point), the time needed to complete the phase separation process was about 2 min; while when the temperature was decreased suddenly from 180 to 80 °C, the time needed to recover the transparency was about 4 min. However, the process became slower with increasing PPrO contents, so that at a high enough PPrO contents ($w_{PPrO} > 0.25$), complete recovery of transparency upon cooling was not observed with a cooling rate of 3 deg/min. It was also observed that the recovery was slower and less complete with decreasing ion content, as well as with increasing size of the counterions, or with increasing molecular weight. In other words, the lower the miscibility (or weaker the interactions), the slower the less complete the recovery of transparency upon cooling. Nishi and Kwei[36] reported that the recovery was incomplete near the minimum of the cloud point curve. Yang et al.[44] recently reported that the kinetics of phase separation of the PSD/PVME system were about 10 times faster than those of the PS/PVME system. These data are consistent with our data.

Conclusions

This study of the LCST behavior in blends shows that ion–dipole interactions lead to truly thermodynamic miscibility. The strengths of the attractive interactions can be compared by using the positions of the cloud point curves. The cloud point curve shifts to higher temperatures with increasing ion contents from 4% to 7% to 10%. The cloud point curve also shifts to higher temperature with decreasing size of counterions (i.e., K > Na > Li). Thus, the strength of the interactions is strongest for high ion contents and for small counterions.

The blend samples with crystalline PEO at high PEO contents become almost transparent above the melting point of PEO and show no cloud points up to the decomposition temperature (ca. 230 °C). Thus, the interactions of the PEO system are stronger than those in the PPrO system. Because blend samples involving hydrogen bonding for the PPrO system do not show cloud points up to the decomposition temperature, these interactions are stronger than the ion–dipole interactions. Thus, the strength of the ion–dipole interaction lies between that of ion–ion interactions and hydrogen bonding on one hand and van der Waals interactions on the other. Due to the relatively weak ion–dipole interactions, LCST behavior is observed below the decomposition temperature for the PS ionomer/PPrO(l) system.

The molecular weight effect on the cloud point curve is the same as that seen in neutral blends; the lower the molecular weight, the higher the cloud point curve.

The kinetics of phase separation show that the phase-separation process is faster for the system with the higher cloud point curve. For the S-0.104-MAA-Li/PPrO(l) system, the phase separation and the recovery of transparency occurs in 2–4 min at low PPrO content, becoming slower with increasing PPrO content. The same trend is observed when the molecular weight is increased, when the size of counterions becomes larger, or when the ion content becomes lower. Thus, the phase separation process slows down with decreasing degree of miscibility (or the strength of interactions).

Finally, it should be emphasized that ion–dipole interactions provide a high degree of control in miscibility enhancement, in that not only the molecular weight but also the ion content, nature of the counterion, and the degree of neutralization can be changed in these blends, all of which lead to different degrees of miscibility enhancement.

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Registry No. (MAA-Li)(S) (copolymer), 40904-02-7; (MAA-Na)(S) (copolymer), 31227-13-1; (MAA-K)(S) (copolymer), 25068-00-2; PPrO, 25322-69-4; PEO, 25322-68-3.

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