Miscibility Enhancement via Ion–Dipole Interactions. 1. Polystyrene Ionomer/Poly(alkylene oxide) Systems

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ABSTRACT: It is shown that ion–dipole interactions can lead to miscibility enhancement in polymer blends. While polystyrene is not miscible with poly(ethylene oxide) or poly(propylene oxide), styrene ionomers show very high miscibility with these materials at low alkylene oxide contents (10 wt %) and high, though not complete, miscibility at higher loading levels. For these systems it is seen that the glass transition temperature (from G'' peak positions) of the styrene ionomer is depressed dramatically with increasing alkylene oxide contents and that the glass transition of the alkylene oxide rises appreciably (in most cases) with increasing styrene ionomer content. Increases in ion content at constant styrene levels increase the miscibility. The degree of miscibility enhancement is comparable to that achieved in hydrogen-bonded systems. Finally, molecular weight effects observed here are quite similar to those seen in other blend systems.

Introduction

It is generally recognized that the vast majority of polymer pairs are not miscible. To achieve miscibility, the presence of specific interactions is usually required.[1-3] These interactions include hydrogen bonding in bulk or solution,[4-9] as well as a range of others, such as those giving rise to charge-transfer complexes.[10-12] Very recently, several studies have been performed on anion–cation interactions as miscibility enhancers, and several systems have been subjected to these studies,[13] including the styrene–ethyl acrylate system[14] and the styrene–isoprene system.[15] The polyelectrolyte complexes[16,17] are a well-known family of materials produced by ionic interactions at very high ion concentrations.

In this publication, the results of a study will be presented in which ion–dipole interactions are used as miscibility enhancers. Ion–dipole interactions are moderately strong and are responsible for such phenomena as the dissolution of salts in water.[18] They have not, as yet, been investigated as miscibility enhancers in polymer blends. In the present system, the ionomer selected is a styrene–lithium methacrylate copolymer with the ionic comonomer concentration in the range of 2–20% to be mixed with a poly(alkylene oxide), i.e., poly(ethylene oxide) (PEO) or poly(propylene oxide) (PPrO).

In the first part of the study, a 9.5 mol % lithium methacrylate copolymer in styrene will be mixed with various concentrations of high molecular weight PEO. The miscibility enhancement in this system will be compared with that found in styrene methacrylic acid (the ionomer precursor) using the same high molecular weight PEO. Therefore, the effect of ion–dipole interactions will be compared with that achieved by hydrogen bonding. Subsequently, the molecular weight effect will be explored by comparing the same styrene ionomer in a mixture with a low molecular weight PEO. Still other aspects of the investigation will include the study of other dipolar chains such as poly(propylene oxide) of both high and low molecular weights. In all of these studies, the 9.5% methacrylic acid or ionomer will be utilized. However, a brief study will also be devoted to the exploration of the effect of ion content on miscibility enhancement by exploring 2.3, 6.6, 9.5, and 16.7% ionomers at a constant PEO loading level. Naturally, the results of the ionomer or acid studies will be compared with those involving pure polystyrene mixed with the same poly(alkylene oxide) chains.

A very wide range of experimental techniques has been used to study miscibility in polymers.[1-3] In this work, three will be utilized. The first and most extensively used method involves the study of dynamic mechanical properties utilizing a torsion pendulum at an approximate frequency of 1 Hz. These studies will be supplemented by more qualitative studies involving transparency of the samples as well as brittleness of the resulting materials. Transparency, while qualitative, is a very sensitive method for detection of heterogeneity in polymers. It has been shown, for example, that only 0.01% of poly(methyl methacrylate) in polystyrene leads to the presence of cloudiness,[19] a characteristic feature of immiscible materials in which the refractive index difference is 0.1 or greater, which is the case in the PS–PPrO system. Brittleness in blends is usually indicative of poor mixing and will be utilized here also, although only on a qualitative basis.

Previous studies relevant to the present investigation include the work of Pearce and co-workers who have shown that the presence of short perfluorinated alcohol side chains in PS leads to dramatic miscibility enhancement with PEO.[6] It should be stressed that these are nonionic systems relying purely on hydrogen bonding for miscibility enhancement. A wide range of other studies of blends of ionomers with nonionic materials have been reported, but with few exceptions,[20] the vast majority of these are given in the patent literature.

Finally, it should be mentioned that ion–dipole interactions between poly(alkylene oxide) and small ions have been investigated in the past. These studies include the investigation of the dynamic mechanical properties of poly(propylene oxide) with dissolved lithium perchlorate by Moacanin and Cuddihy,[21] subsequent studies on similar systems by Wetton et al.,[22] and an investigation from this laboratory.[23] All these studies conclude that salts of low lattice energies dissolve in poly(alkylene oxide)s and that the dissolution of the salts leads to a dramatic increase of the glass transition temperature, viscosity, and other properties which can be expected from the presence of strong interactions.

Experimental Section

A. Materials. The styrene–methacrylic acid copolymers were synthesized in connection with another project[24] by a procedure described elsewhere.[25] The neutralization was carried out by adding the predetermined amount of methanolic LiOH. The molecular weights, sources, and sample designations are shown in Table I.

B. Sample Preparation. The styrene or styrene copolymer samples were dissolved in a mixture of benzene/methanol (90/10)

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Table I
Molecular Weights and Sources of Polymers

polymer	symbol	MW	source
polystyrene	PS	$(1.25–2.5) \times 10^5$	Polysciences
PS ionomer with 9.5 mol % MAA	S-0.095MAA-Li	1×10^5	this lab[a]
poly(ethylene oxide)	PEO(h)[b]	4×10^6	Polysciences
poly(ethylene glycol)	PEO(l)[b]	3.4×10^3	Polysciences
poly(propylene oxide)			
elastomer[c]	PPrO(h)	6×10^5	Hercules
liquid	PPrO(l)	4×10^3	Polysciences

[a] Estimated from previously calibrated preparation conditions. [b] "h" refers to high molecular weight (>10^5) and "l" refers to low molecular weight (<10^4). [c] The sample of "PARAL 58" contains ca. 6% of allyl glycidyl ether. It was kindly provided by Dr. E. J. Vandenberg.

at concentrations of ca. 1 g/dL. The PEO or PPrO samples were also dissolved in the same solvent. The solution of the latter was added to the former solution slowly with stirring, and stirring was continued overnight. All the solutions were clear. The solutions were freeze-dried and then kept under vacuum at high temperatures (close to the glass transition temperature of PS or PS copolymers) for at least 1 day.

The samples used for the measurements were prepared by compression molding. The polymers were heated in the mold to a temperature slightly higher than T_g under an applied load of 4000 lb/in.^{2} for 1 h, before being cooled slowly down to room temperature. Typical dimensions of the rectangular specimens for torsion pendulum studies were 3.0 × 6.0 × 50 mm and those of the disk samples used for transparency determination were radius = 6.5 mm and thickness = 0.5 mm.

C. Dynamic Mechanical Measurements. Dynamic mechanical studies of the blend samples were undertaken by using a computerized torsion pendulum, an early version of which is described elsewhere.[26] The frequencies varied from ca. 3 Hz for the glassy region to ca. 0.1 Hz for the low-modulus region. The heating rate was usually 0.6 °C/min with a temperature control of ±1 °C. The vibrating reed instrument was also described elsewhere.[27]

D. DSC. The thermal analysis were made with a Perkin-Elmer differential scanning calorimeter (Model DSC-1).

Results and Discussion

The computerized torsion pendulum utilized in this study produces a large number of data points for the moduli G' and G'' and for tan δ for each sample. Since in the subsequent description comparisons will be made involving several different materials on one graph, it is useful, instead of presenting individual data points, to present a smooth line for all the results. Furthermore, the peak in G'' is far better developed than in the tan δ plots. This is quite a general phenomenon for these materials, and for this reason G'' plots will be given along with G' data.

In the complete absence either of hydrogen bonding or of ion–dipole interactions, PS and PEO are immiscible. This can be seen quite clearly in Figure 1, which presents a plot of the storage modulus, G', and the loss modulus, G'', as a function of temperature for blends of PS and PEO containing, respectively, 0, 10, 20, 50, and 100% of the latter. It seems clear that the drop in the G' and the peak in G'', indicative of the glass transition temperature, occur for all the materials containing PS at approximately the same temperature, indicating the absence of interactions. In the G' plots, the intermediate step, occurring at approximately 64 °C, is a reflection of the crystalline melting point of the PEO. It is noteworthy that in this system the samples containing both PS and PEO are quite opaque and that the glass transition temperature and crystalline melting point, as determined by differential scanning calorimetry, do not change as a function of sample composition.

The behavior of PEO in the presence of PS ionomers is completely different. In these systems, ion–dipole interactions play a major role, as can be seen in a dramatic

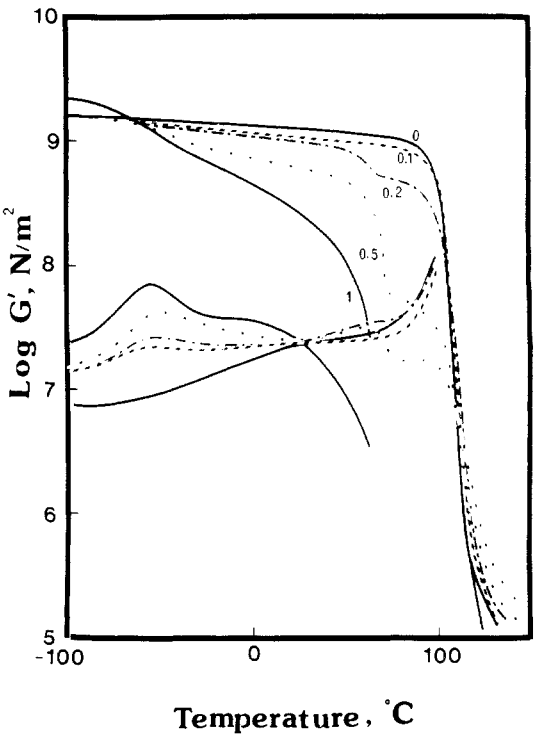

Figure 1. Variation of the shear storage modulus, G', and the shear loss modulus, G'', with temperature for blend PS/PEO(h) of various PEO fractions.

lowering of the primary glass transition temperature with increasing PEO content. This is shown in Figure 2 for G' and G'' as a function of a temperature. The lowering of the glass transition temperature reflects a dramatic enhancement in miscibility in the presence of ionic groups. It is also noteworthy that the high-temperature modulus, for example at 160 °C, which in pure PS ionomers is indicative of the existence of ionic aggregates,[28,29] decreases with increasing PEO content. In Figure 2, it drops by more than 1 order of magnitude on going from the pure PS ionomer to the 50% blend. It can be seen that as the PEO content decreases, the peak height of this low-temperature peak decreases as well and moves to slightly higher temperatures.

In terms of the optical properties, the pure PS ionomer, as well as the 10% blend, are completely clear. Some cloudiness is observed for the 20% sample, and the cloudiness increases progressively with increasing PEO content. DSC data show absolutely no crystallinity for the 10 and 20 wt % blends; for the higher PEO contents, considerably less crystallinity is seen than in the corresponding PS/PEO systems. Storage of the 10% sample at 150 °C for 1 week does not affect the transparency. At that temperature, the modulus of the sample is 7×10^5 N/m^2; thus, if demixing or ripening of small heterogeneous regions were to occur, it most likely would have occurred under those conditions.

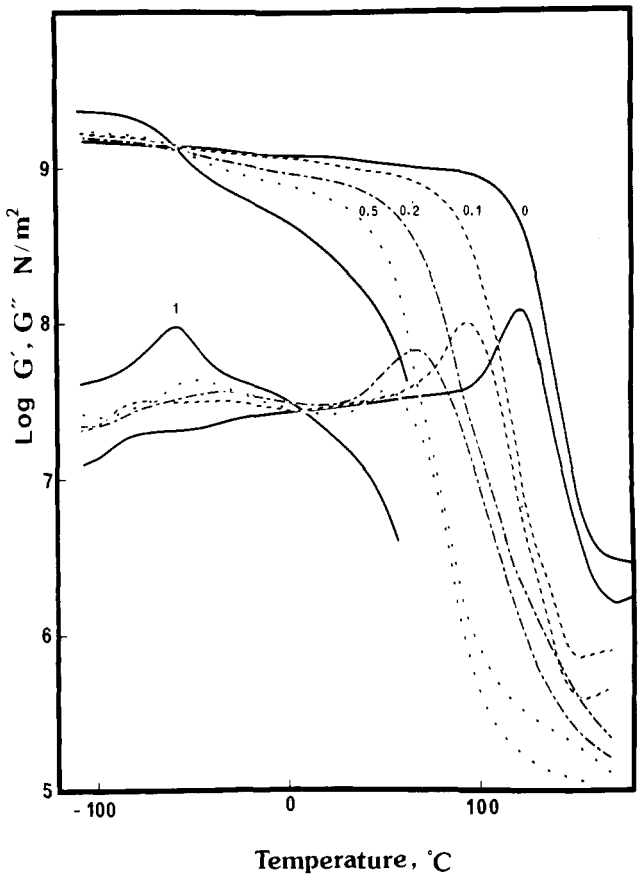

Figure 2. Variation of the shear storage modulus, G', and the shear loss modulus, G'', with temperature for blend S-0.095MAA-Li/PEO(h) of various PEO weight fractions.

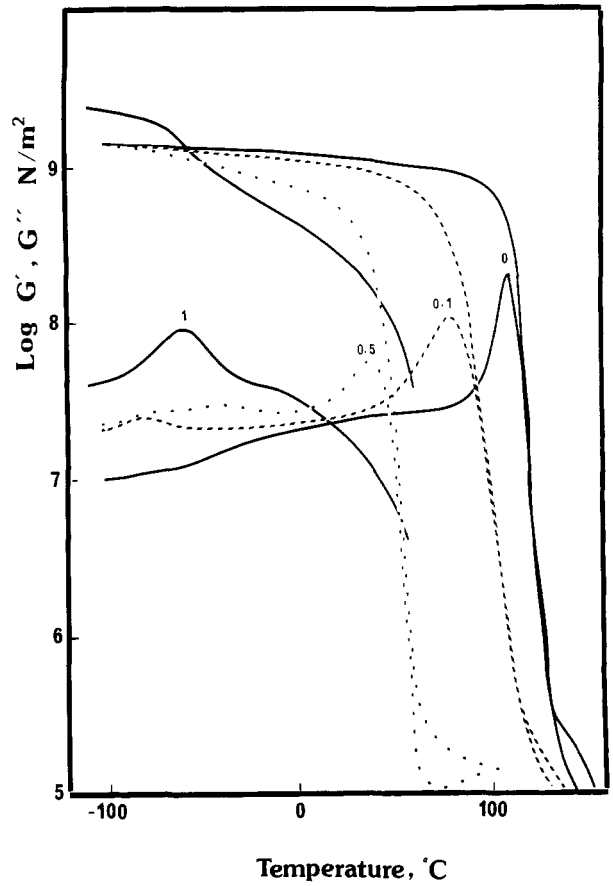

Figure 3. Variation of the shear storage modulus, G', and the shear loss modulus, G'', with temperature for blend S-0.095MAA/PEO(h) of various weight fractions.

Thus, the material seems to be truly thermodynamically miscible.

In order to compare the miscibility enhancement resulting from ion–dipole interactions with that obtained by hydrogen bonding in the same system, blends of PEO with the styrene–methacrylic acid copolymers were studied. Figure 3 shows the plots of log G' and log G'' vs. temperature, showing that the trends in behavior are quite similar for the acid as for the ionomer. It is seen very clearly that here, as in the ionomer case, the glass transition of the PS copolymer is depressed dramatically. Unlike the ionomer situation, however, the high-temperature modulus (specifically the inflection point) characteristic of entanglements or of ionic interactions, occurs in this system at ca. 2×10^5 N/m^2, reflecting the absence of ionic interctions. It is also noteworthy that the steepness of the G' curve in the glass transition region is much greater in the acid case than it was in the ionomer system in G' plots.

In order to study the generality of the effects described above, another polar nonionic chain analogous to PEO was investigated. The system PPrO was selected for this purpose. Both dynamic mechanical and DSC data show that PS and PPrO are immiscible in all composition ranges. By contrast, in the presence of ionomer, considerable miscibility enhancement is observed. This is shown in Figure 4 in the plot of log G' and log G'' vs. temperature. At low PPrO content, depression of the glass transition temperature is observed as before. However, at 50% of the PPrO, a characteristic double peak transition is observed suggesting that the miscibility is not as high as in the PEO case. However, some miscibility is still observed, because the glass transition temperature of the PS ionomer, although seen only as broad peaks in Figure 4, is depressed considerably below that of the pure ionomer.

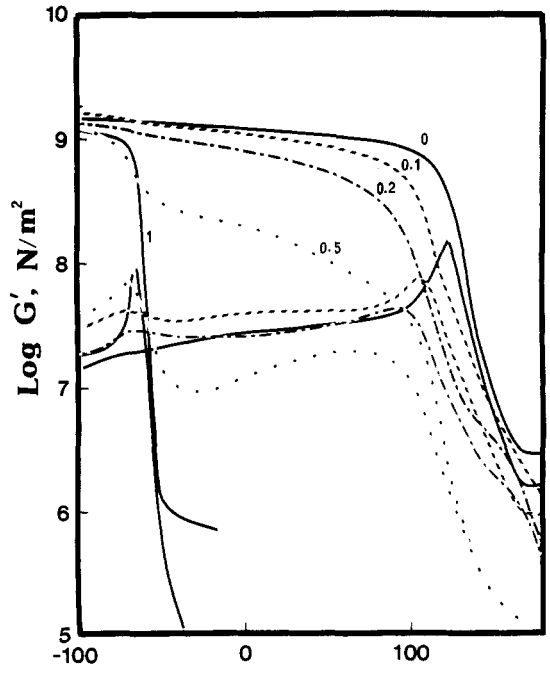

Figure 4. Variation of the shear storage modulus, G', and the shear loss modulus, G'', with temperature for blend S-0.095MAA-Li/PPrO(h) of various weight fractions.

The samples of low PPrO content are quite transparent; however, already at 20 wt % of PPrO, considerable cloudiness is seen in the samples. The 30 wt % sample is very

Table II
Molecular Weight Dependence of G'' Peak Position in the S-0.095MAA/PEO and PPrO (Acid and Salt) Systems

		high molecular weight		low molecular weight	
system	w	high T_g peak, °C	low T_g peak, °C	high T_g peak, °C	low T_g peak, °C
salt–PEO	0.0	120		120	
	0.1	94	−40, −72		
	0.2	68	−32	77	40
	0.5	52	−52		
	1.0		−56		
salt–PPrO	0.0	120		120	
	0.05			100	
	0.1	108	−70	84	
	0.2	90	−70	58	−34
	0.5	broad	−66		
	1.0		−66		
acid–PEO	0.0	110		110	
	0.1	78	−80		
	0.2			55	−30
	0.5	38	−40, −80		
	1.0		−56		
acid–PPrO	0.0	110		110	
	0.1	90	−30	90	−10
	0.2			78	−20
	0.5	88	−40		
	0.7	broad	−56		
	1.0		−66		

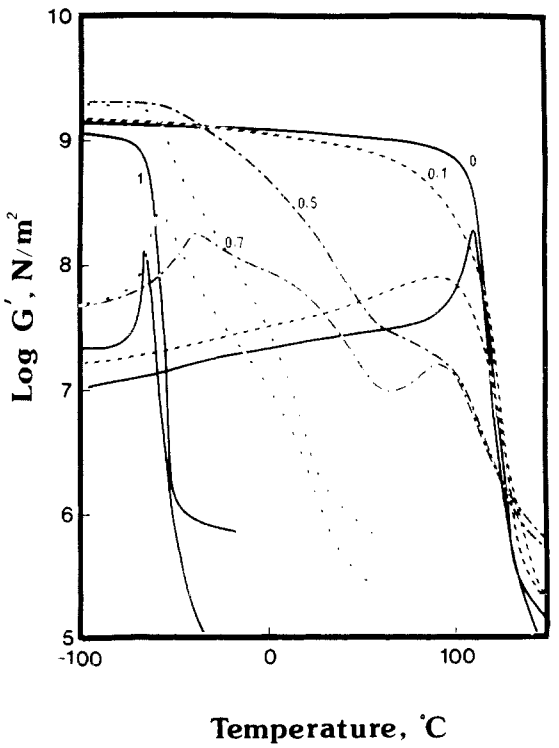

Figure 5. Variation of the shear storage modulus, G', and the shear loss modulus, G'', with temperature for blend S-0.095MAA/PPrO(h) of various weight fractions.

cloudy and quite characteristic of a phase-separated system. The same is true for the 50% sample. Similar behavior is seen when the ionomer is replaced by acid samples, as can be seen in Figure 5.

It is generally recognized that a decrease of the molecular weight leads to considerable miscibility enhancement in polymer blends.[30] To explore this effect in the present system, blends of both PEO and PPrO of low molecular weight were investigated here also. The storage modulus as a function of temperature is shown in Figure 6 for the low molecular weight PPrO. Again the same general trends are observed as before (compare Figure 4). The glass

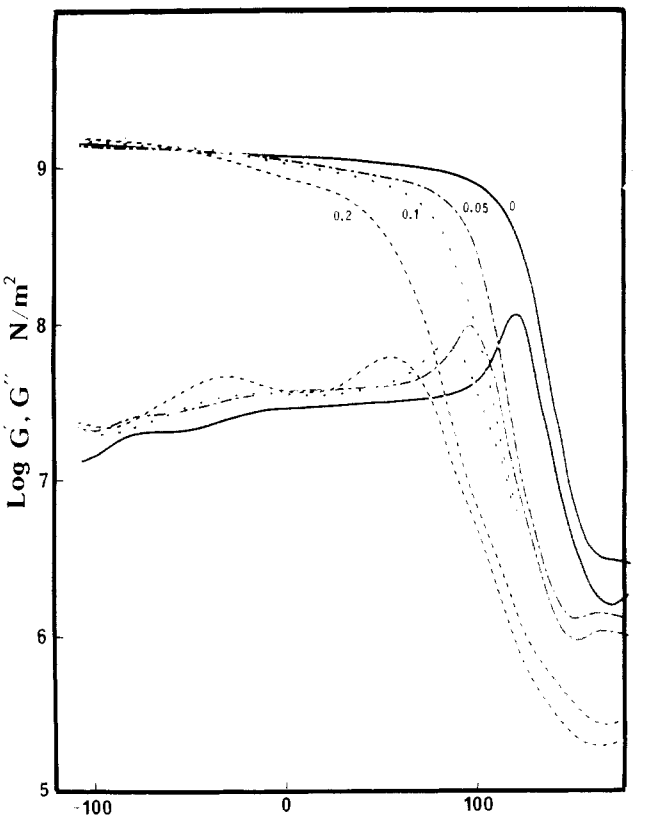

Figure 6. Variation of the shear storage modulus, G', and the shear loss modulus, G'', with temperature for blend S-0.095MAA-Li/PPrO(l) of various weight fractions.

transition temperature of the PS ionomer is depressed considerably with increasing PPrO content. Here, however, in contrast to Figure 4, the depression of the glass transition temperature is considerably higher than in the high molecular weight case. Sample transparency is also very much better in this system. Thus, the 20% sample is still transparent, and only the 30% sample begins to

Table III
Effect of Ion Content on the G'' Peak Positions in the S-xMAA/PEO (Acid and Salt) Systems at $w = 0.5$

ion content, %	salt			acid		
	high T_g peak, °C	T_m peak, °C	low T_g peak, °C	high T_g peak, °C	T_m peak, °C	low T_g peak, °C
0	99	64	−56	99	64	−56
2.3	90	64	−47	96	65	−44
6.6	67		−44	48		−31
9.5	53		−49	40		−42
16.7	44		−42			

show the first indication of cloudiness. The same general trends are observed in the case of the acid. The molecular weight effects are summarized in Table II for both the PEO and PPrO systems studied.

Finally, a brief study was performed on the effect of ion content. The results of that study are shown in Table III, in which the G'' peak positions are tabulated for 50% mixtures for both acids and salts at different ion contents. It is seen that in the salt the high T_g peak decreases with increasing ion content, as might be expected, while the low T_g peak increases only slightly with increasing ion content. In the acid, the same general trend is observed, the high T_g peak decreases with increasing ion content, and the low T_g peak increases also, possibly even slightly more effectively than was seen in the salt. Most of the samples in this range are not transparent because of the very high PEO content.

Summary and Conclusions

This study has clearly demonstrated that the presence of ion–dipole interactions enhances the miscibility of otherwise immiscible polymers in the PS–poly(alkylene oxide) blend system. In the complete absence of ionic groups, PS and PEO or PS and PPrO are immiscible, as is clearly seen in Figure 1 for the PS–PEO blend. This immiscibility is seen by the constancy of the glass transition temperature and melting point as a function of alkylene oxide content, as well as the opacity of the samples and their brittleness. The presence of 9.5 mol % of lithium methacrylate in PS, however, leads to a dramatic increase in miscibility. This miscibility is demonstrated in Figure 2 in a dramatic downward shift of the glass transition temperature of PS ionomer, the shift being proportional to the amount of alkylene oxide present. It is also confirmed by the transparency of the samples and the absence of crystallinity, especially in the low alkylene oxide content region, as well as by a dramatic improvement in the fracture properties of the materials, i.e., the absence of brittleness. As might be expected, the higher the ion content, the better the miscibility. This is clearly seen in the glass transition of PS copolymers with increasing ion contents at the 50% loading level (Table III). A parallel study of PS containing methacrylic acid without neutralization demonstrates that, for all practical purposes, ion–dipole interactions in this system are as effective as hydrogen bonds in enhancing the miscibility.

It should be stressed that complete miscibility is not observed over the entire region of alkylene oxide content studied here. At low loading levels, i.e., 5–10 wt % of the oxide, the samples are completely transparent. However, at higher loading levels, the samples show some opacity and a low-temperature peak, identified with the glass transition of the alkylene oxide rich phase, is seen. The loss peak has been identified as a glass transition peak from its activation energy of 37 kcal/mol, which was obtained by dynamic mechanical measurements at various frequencies. This is very close to the activation energy of 39 kcal/mol at the glass transition of −32 °C calculated from the universal WLF parameters. The glass transition of the PS ionomer is depressed, however, over the entire range, showing that miscibility is extensive though not complete.

The molecular weight dependence of the miscibility enhancement phenomenon described here is exactly as expected.[30] Thus, in general, the high molecular weight PEO or PPrO seems to be less miscible with the PS ionomer than the low molecular weight analogues. This is seen most clearly in Table II. As a matter of fact, in the high molecular weight PPrO system, while the glass transition temperature of PS copolymer goes down with increasing PPrO content, the glass transition temperature of the PPrO-rich phase does not increase. In all the other systems, however, it does. This table, incidentally, also suggests that the PEO system is more miscible at comparable loading and ion content levels than the PPrO system. This is seen in the lower glass transition temperature for comparable PS ionomer–PEO blends than for the PS ionomer–PPrO blends.

As a final confirmation that the ion–dipole interaction is indeed involved in the miscibility enhancement found here, it should be noted that the high-temperature shear modulus of the ionomeric blends decreases with increasing alkylene oxide content. The high-temperature modulus is a reflection of the degree of ionic interactions.[28,29] The lower the modulus, the more effective the breakup of the aggregates which are responsible for the high level of the modulus. In Figure 2, it is clearly seen that the high-temperature modulus decreases with increasing alkylene oxide content, confirming that the ionic aggregates are progressively disrupted as the polar polymer is added.

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Registry No. (Methacrylic acid)·(styrene) (copolymer), 9010-92-8; (methacrylic acid)·(styrene) (copolymer) lithium salt, 40904-02-7; PEO, 25322-68-3; PPrO, 25322-69-4.

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Xanthan Fractionation by Surface Exclusion Chromatography

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ABSTRACT: In chromatographic columns packed with nonporous particles, entropic effects exclude macromolecule centers of mass from the vicinity of pore walls over a distance closely related to the dimensions of these molecules; this causes a size fractionation based on surface exclusion. The efficiency of such a method for characterizing samples of high-molecular-weight xanthan depends on both shear rate and polymer concentration. The relation between polymer velocity and the molecule length–pore size ratio can be predicted by using a capillary model. The molecular weight distribution of two xanthan samples ($\bar{M}_w \simeq 2 \times 10^6$ and 3×10^6) was determined with good reproducibility.

Some recent papers[1,2] have suggested that conventional chromatographic techniques such as gel permeation chromatography (GPC) fail when applied to the characterization of very large macromolecules. Such polymers are easily oriented or deformed by hydrodynamic forces occurring in columns. Hence, steric pore exclusion mechanisms are disturbed, separation efficiency is poor, and the relationship between elution volume and molecular weight is found no longer to be valid for the highest molecular weight polymers.

A new technique based on surface exclusion, commonly called hydrodynamic chromatography, has been developed for rigid-particle size determination.[3] This technique, using nonporous column packing, has been shown to be efficient for size separation of proteins[4] and latexes.[5-8]

In a polymer solution near a repulsive wall such as a nonabsorbent solid surface, macromolecule centers of mass are sterically excluded from the wall vicinity over a distance related to macromolecule size. This phenomenon, which was theoretically predicted in static conditions for both flexible[9] and rodlike[10] polymers, leads to a depletion layer at the solid interface where polymer solution viscosity is lower than in the bulk.[11] During flow, this exclusion of macromolecules from the slowest stream lines near the wall induces a mean polymer velocity higher than the solvent one, thus giving a chromatographic polymer size fractionation. In this way, Prud'homme[12] eluted large macromolecules on a nonporous chromatographic packing and showed that macromolecules move ahead of solvent and that their velocity increases with their molecular weight. Nevertheless, the efficiency of the size fractionation observed was poor due to the too high flow rates used.

Table I
Chromatographic Column Characteristics

SiC packing, μm	length, cm	diameter, cm	permeability, 10^{11} cm^2	porosity
18	65	2.7	78	0.47
8	90	2.6	29	0.48

Table II
Characteristics of Xanthan Samples and Solutions

sample	mol wt[a]	intrinsic visc, cm^3/g	equiv molecular length, μm
I	1.8×10^6	4300	0.7
II	2.8×10^6	6900	1.0

[a] Light scattering.

This paper describes the first results of a study of shear rate and polymer concentration effects on the efficiency of xanthan fractionation by hydrodynamic chromatography. At sufficiently low shear rates and polymer concentrations, efficient separation is reached and the complete molecular weight distribution can be determined.

Experimental Section

The characteristics of the chromatographic columns used are given in Table I. They were dry packed with sharp-edged SiC particles, the mean dimension of which was 8 and 18 μm according to the manufacturer. Particle size distribution is relatively narrow as revealed by Coulter counter analysis (reduced standard deviation $\bar{\sigma}_r \simeq 0{,}25$).

Two xanthan microgel-free samples, the characteristics of which are given in Table II, were studied. The solutions obtained by

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