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Characterization of Ionomer Solutions. 1. Phase Behavior and Gelation of Sulfonated Polystyrene Ionomers in Decalin

K. Chakrabarty,[†] T. A. P. Seery,[†,‡,§] and R. A. Weiss*,[†,‡]

Polymer Science Program, Department of Chemical Engineering, and Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269

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ABSTRACT: The phase behavior of solutions of the acid form of lightly sulfonated polystyrene in Decalin was affected by the total acid group concentration and by the number of acid groups per molecule. The upper critical solution temperatures (UCST) increased with total acid group content as a consequence of poorer solvent quality. The UCST also increased with increasing number of acid groups per molecule, which was attributed to a loss of configurational entropy due to the aggregation of the acid groups by hydrogen bonding.

Introduction

Random ionomers are macromolecules containing a small percentage of ionic groups placed randomly and covalently attached to a nonpolar backbone. In relatively nonpolar solvents, the ionic species, e.g. sodium sulfonate salt groups in the sodium salt of lightly sulfonated polystyrene (NaSPS), associate due to electrostatic attraction between the ion-pair dipoles. In the case of the free acid derivative, HSPS, the associations involve hydrogen bonding of the sulfonic acid groups.

Association of the acid or salt groups has a significant influence on the solution properties of ionomers.[1−9] For example, aggregation of the dipolar groups increases the solution viscosity in nonpolar solvents,[2−3] and at a sufficiently high polymer concentration, a physically associated network may produce gelation.[4] Hydrocarbon-soluble ionomer complexes based on sulfonated EPDM and styrene−4-vinyl pyridine copolymers exhibit shear thickening viscosity behavior.[10] Because of these unusual properties, ionomers have been used as viscosity-index improvers.[11−15] The effectiveness of the ionomer in that application, as well as its potential use in other solution-based applications, is inherently linked to its aggregation behavior.

Despite the numerous experimental reports of ionomer solution behavior, a fundamental understanding of ionomer solutions is incomplete. To gain such an understanding, one must first understand the effect of aggregation of the dipolar groups on the thermodynamics and phase behavior of ionomer solutions. Specific interactions produce nonrandom mixing, which common thermodynamic theories for polymer solutions[16−19] do not consider. Experimental phase diagrams for ionomer solutions in nonpolar solvents are conspicuously absent in the literature, and no systematic investigation of gelation in random ionomers with respect to changes in temperature, concentration and the strength of the ion−dipole interactions has been reported.

Joanny[20] formulated a theory for ionomer solutions that predicts that random ionomer solutions exhibit two phase transitions: demixing and gelation (see Figure 1). At low polymer concentrations and temperatures below the Θ temperature of the nonionic base polymer, phase separation should occur in accordance with Flory's solution theory.[16] The only effect of the randomly distributed dipoles is a renormalization of the second virial coefficient, A_2, to take into account the effect of dipolar interactions

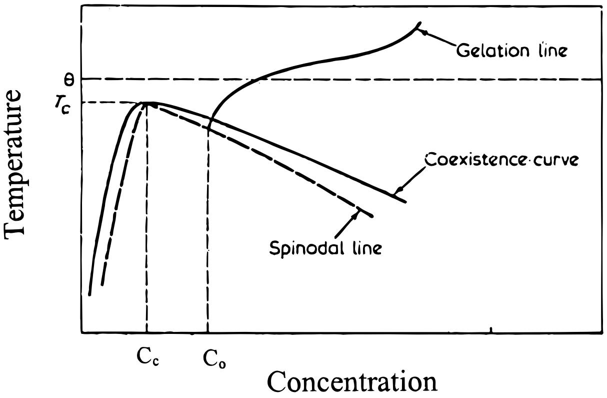

Figure 1. Theoretical temperature concentration phase diagram of random ionomer solutions. T_c and C_c are the critical temperature and concentration, respectively. C_o is the point where the gelation line and the coexistence curve meets. (Reprinted with permission from ref 20. Copyright 1980 Elsevier Science.)

$$A_2 = A_2' + f^2 A_2'' \qquad (1)$$

where A_2'' results from the attraction of the ionic dipoles and is always negative and f is the fraction of dipoles along the polymer chain. Joanny[20] attributed A_2' only to the excluded volume of the nonionic part of the backbone chains, but Hara and Wu[5] argued that this term should also include the interaction between the ionic groups and the solvent. Since nonpolar solvents are generally poor solvents for the ionic species, A_2' decreases with increasing ionic content, and eq 1 predicts that A_2 decreases with increasing ionic content. This has been confirmed by SALS experiments with NaSPS ionomers in THF[5,6] and xylene.[7,8] The Joanny model, however, precludes microdomain formation.

Joanny's theory predicts gelation at higher polymer concentration and temperature (see Figure 1), and the

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[†] Polymer Science Program.
[‡] Department of Chemical Engineering.
[§] Department of Chemistry.

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Table 1. Sulfonated Polystyrene Ionomer (HSPS) Samples

sample I.D.	M_w	M_n	M_w/M_n	sulfonation level (mol %), *x.y* =
x.y-HSPS-335	335 000	287 500	1.17	0.8
x.y-HSPS-120	120 500	107 500	1.12	0.4, 2.0, 2.8
x.y-HSPS-49	49 200	41 050	1.20	0.5, 2.0, 2.7, 3.6
x.y-HSPS-24	24 150	19 400	1.25	1.9, 2.3, 3.6, 4.7

concentration at which gelation occurs, c_{gel}, decreases as the concentration of the ionic dipoles increases. To date, however, there has been no experimental confirmation of the phase diagram proposed by Joanny.

The objective of the research described in the present paper was to determine how specific interactions perturb the phase behavior of random ionomer solutions. This paper focuses on the phase diagrams for sulfonated polystyrene solutions in Decalin using light scattering. The nature of the aggregation process as determined by dynamic light scattering is the subject of a second paper.

Experimental Details

Narrow molecular weight distribution polystyrenes synthesized by anionic polymerization were lightly sulfonated at 50 °C in 1,2-dichloroethane using acetyl sulfate as the sulfonating agent according to the procedure of Makowski et al.[21] The free-acid derivative of the sulfonated polystyrene ionomer (HSPS) was recovered by solvent flashing in boiling water and then dried under vacuum. The average sulfonation level of the SPS was controlled by the amount of acetyl sulfate used in the sulfonation reaction, though because the sulfonation is a random substitution reaction, the number of sulfonic acid groups on each chain varies.

The nomenclature used for the ionomers was *x.y*-HSPS-*n*, where *x.y* is the sulfonation level in mole percent of styrene substituted and *n* is $M_w \times 10^{-3}$. The samples are summarized in Table 1. The molecular weights given are for the precursor polystyrenes as determined by size exclusion chromatography. The sulfonation level was determined by titrating HSPS in toluene/methanol (90/10, v/v) solution with methanolic NaOH to a phenolphthalein end point. The uncertainty in the sulfonation level was ca. ±0.05 mol %.

Polystyrene and HSPS solutions were prepared in Decalin (40:60 cis−trans mixture, Eastman Chemical Co.) by weighing the polymer and solvent into glass vials. The vials were then heat sealed to prevent solvent loss. The polymers were dried at 90 °C under vacuum for 48 h before preparing the solutions. The solvent was used as received.

Phase diagrams of the ionomer solutions were determined with a light scattering apparatus built by Shaw and coworkers.[22] The polymer solutions in the glass vials were cooled at a constant rate while the vial was oscillated and the backscattered light intensity was measured. The cloud point was defined as the onset of deviation from the baseline of the average backscattered light intensity. The gel point was taken as the onset of a large increase in the amplitude of the oscillation of the backscattered light intensity.[22]

Results and Discussion

The phase diagrams of the HSPS solutions in Decalin exhibited upper critical solution temperature (UCST) type behavior. For low polymer concentrations, only a cloud point was observed for the solutions when they were cooled from the one-phase region, but at higher polymer concentrations the solution gelled before phase separation occurred (see Figure 2). The cloud points for the HSPS solutions were much higher than for solutions of the precursor polystyrene over the entire concentration regime investigated. The gel point temperature increased monotonically with increasing ionomer concentration. A similar effect of ionomer concentration on the gel formation temperature was previously reported for halato−telechelic ionomer (α,ω-Mg dicarboxylato polybutadiene) solutions in toluene.[23]

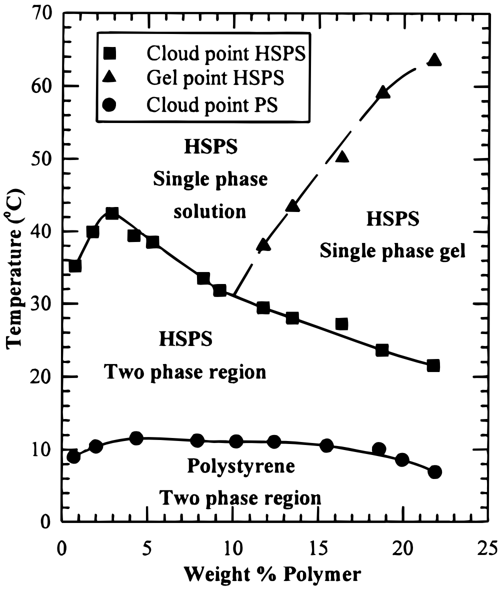

Figure 2. Phase separation and gelation of 0.8 mol % HSPS solutions in Decalin. The cloud point temperatures of the precursor polystyrene (M_w = 335 000) solutions in Decalin are also shown. The lines are for visual guide and have no physical significance.

The phase diagram shown for the HSPS solutions were in qualitative agreement with Joanny's theory, cf. Figures 1 and 2, though in contrast to the theory, phase separation occurred above the Θ temperature of polystyrene, which is ca. 15 °C in Decalin.[24] Quantitative comparisons with Joanny's theory were not attempted in this work, partly because the calculation of the binodal and the gel point curve require the dipole moment of the monomer (styrene sulfonate), which was not available. Also, Joanny's theory assumes that microdomains are not formed in random ionomer solutions, and it is well-known from the literature[1] and the dynamic light scattering work done in the current investigation that microdomains form in HSPS solutions. Metal salts of SPS of sulfonation level greater than 0.5 mol % were insoluble in Decalin above 2 wt % concentration, which prevented determination of their phase behavior.

The phase diagram in Figure 2 indicates that when an HSPS/Decalin gel is diluted with solvent at constant temperature, a homogeneous viscous solution should result. Jerome et al.[25,26] reported that ionomer gels formed from salts of α,ω-dicarboxylato-polybutadiene in nonpolar solvents became single-phase solutions upon dilution only if the cation was monovalent. Gels formed from Al^{3+}, Ti^{4+}, and Be^{2+} salts of α,ω-dicarboxylato−polybutadiene phase-separated in toluene at 25 °C when diluted to concentrations below 1 g/dL. They speculated that for a gel formed from an ionomer with a monovalent cation, the addition of the solvent sufficiently weakened the dipolar interactions so that the gel dissolved. However, the stronger interactions that occurred with higher valence metal cations precluded additional swelling by dilution, and in that case phase separation occurred. Dilution of the 0.8-HSPS-335 gels produced single phase viscous solutions (see Figure 2), which is consistent with the result obtained by Jerome

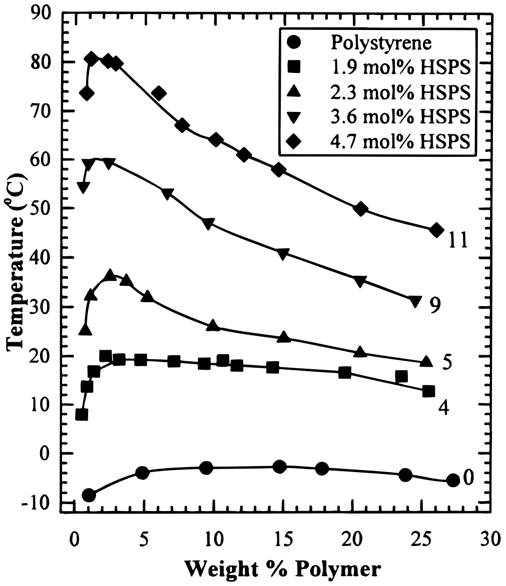

Figure 3. Cloud point temperatures of HSPS-24 and precursor polystyrene (M_w = 24 000) solutions in Decalin. The numbers in the figure indicate the average number of acid groups per molecule. The lines are for visual guide and have no physical significance.

et al.[25,26] for the monovalent cation salts of telechelic ionomers. The agreement between the behavior of the two systems is probably due to the relatively weak hydrogen bonding interactions in the HSPS/Decalin solutions that are analogous to the more labile dipolar interactions in the telechelic ionomers with monovalent cations.

Figure 3 shows the effect of sulfonation level on the phase diagram for HSPS solutions prepared with ionomers with M_w = 24 000. Increasing the sulfonation level raised the UCST and shifted the critical point to lower ionomer concentrations. Similar results were obtained for the ionomers with molecular weights of 49 000 and 120 000. The critical point (T_C) for the ionomer solutions for each molecular weight increased nearly linearly with increasing sulfonation level (see Figure 4). The term critical point is used here to denote the maximum cloud point temperature, though strictly speaking the critical point does not necessarily correspond to the maximum cloud point for a polydisperse system. The conclusions of this work are not affected by this approximation.

The increase in the critical point with sulfonation is consistent with the expectation that an ionomer with a higher content of acid groups will form more interchain aggregates by hydrogen bonding and thus exhibit a higher effective molecular weight. However, the increase in the UCST exhibited by the ionomers cannot be explained solely on the basis of increasing apparent molecular weight. According to the Flory–Huggins theory,[16] a polystyrene with infinite molecular weight should have a critical point coincident with the Θ temperature in Decalin, i.e., 15 °C.[24] As shown in Figures 3 and 4, the critical points for some of the ionomer solutions greatly exceeded that value. A more plausible explanation for the increase in the UCST is that Decalin becomes increasingly poorer as a solvent for sulfonated polystyrene as the sulfonation level increases. The Θ temperatures for polystyrene and HSPS in Decalin were determined from the intercept at infinite molecular weight of a plot of $1/T_c$ vs $1/M_n$,[16] (see Figure 5). The Θ temperature calculated for polystyrene in Decalin was 18.5 °C, which is comparable to the values reported in the literature.[24] The calculated Θ temperature for HSPS increased with sulfonation level (see Figure 5). For example, the Θ temperature for 2 mol % sulfonation HSPS was 151 °C.

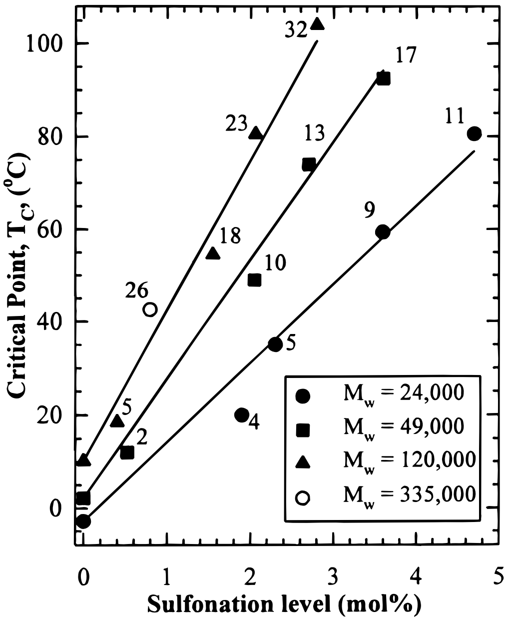

Figure 4. Critical points for the HSPS solutions of various molecular weights as a function of sulfonation level. The lines are least-squares fit to the data. The numbers next to the symbols indicate the average number of acid groups per molecule.

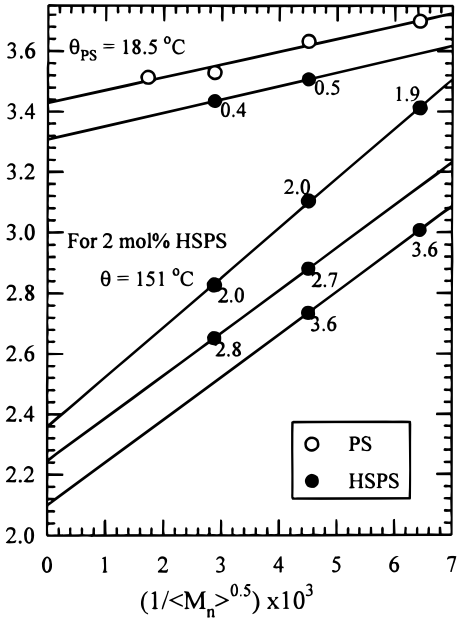

Figure 5. Calculation of the Θ temperatures of polystyrene and HSPS in Decalin. The numbers next to the symbols indicate the mole percent sulfonation level.

For a fixed sulfonation level, the critical point of the ionomer solutions increased with molecular weight as shown in Figure 4. This difference between the critical points of the ionomers with the same sulfonation level but different molecular weight may be due to the difference in the molecular weights of the nonionic backbone and/or differences in the average number of acid groups per molecule. Unfortunately, it is not

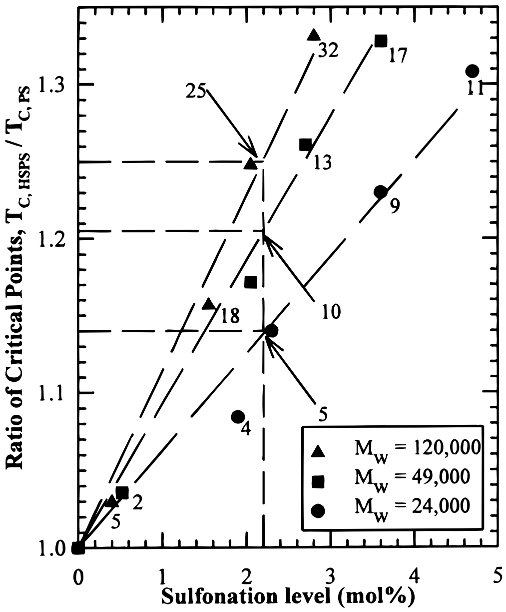

Figure 6. Ratio of critical points of HSPS to polystyrene as a function of sulfonation level. The lines are least-squares fit to the data. The numbers next to the symbols and the arrows indicate the average number of acid groups per molecule.

Table 2. Comparison of Critical Point Ratio for HSPS of Various Molecular Weights

mol wt	critical point ratio	mol % sulfonation	no. of acid groups per chain
24 000	1.14	2.2	5
49 000	1.20	2.2	10
120 000	1.25	2.2	25

possible to separate the effects of the molecular weight and the average number of acid groups per chain while keeping the total acid group content constant.

The ratio of the critical point of HSPS to that of the parent polystyrene is plotted as a function of sulfonation level in Figure 6. We assume that normalizing the critical point of HSPS by that of the parent polystyrene removes the effect of the molecular weight of the chain. A comparison of this ratio at a fixed sulfonation level (2.2 mol %) for the three molecular weights in Figure 6 is shown in Table 2. Since the critical points for these HSPS solutions occur at the same concentration (2 wt %), the *total number* of styrene sulfonic acid groups in these solution samples at their respective critical points is the same. Consequently, the “unfavorable” (for solubility purposes) enthalpic interactions are also the same in these samples. But the critical point ratio is highest for the HSPS-120, which also has the highest number of *acid groups per chain*. Thus, more segments of the HSPS-120 molecules are restrained by hydrogen bonding than in the HSPS-49 or the HSPS-24 solutions. This results in a greater loss of configurational entropy and hence poorer solubility for the HSPS-120. This phenomenon is not restricted to the critical point. For a fixed sulfonation level, the cloud points are higher for a higher molecular weight ionomer over the entire range of concentrations studied, (see Figure 7).

Conclusions

HSPS/Decalin solutions exhibit UCST-phase behavior. At low polymer concentrations, the solution goes directly from a single phase, viscous liquid to phase separation as the solution is cooled. At higher ionomer concentrations, a transformation from a viscous solution to a single-phase gel precedes phase separation. The cloud point temperatures are affected by the total concentration of acid groups in the solution, the number of acid groups per molecule, and the molecular weight of the ionomer. In general, the cloud point temperatures and the critical temperature increased with increasing sulfonation of the polymer. The increase in the UCST due to sulfonation was attributed to a decrease in the quality of the solvent for the ionomer, though aggregation of the ionomer due to hydrogen bonding probably also plays a role. When normalized for the critical point of the parent polystyrene solution, the enhancement of the critical point by sulfonation appeared to be greatest for the higher molecular weight polymers. This was attributed to greater loss of configurational entropy for the higher molecular weight polymers, because of the greater number of acid groups per chain. Gelation was observed only for the higher molecular weight ionomers, though the absence of gelation for the lower molecular weight ionomers may simply be due to the limited concentrations studied.

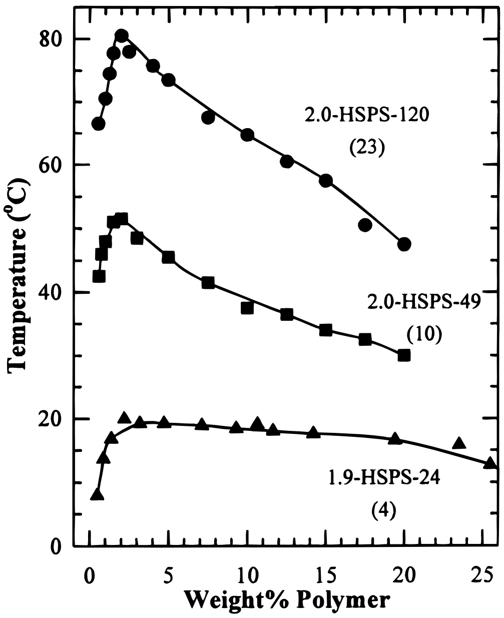

Figure 7. Effect of molecular weight on the cloud point temperatures of HSPS solutions in Decalin. The numbers in parentheses indicate the average number of acid groups per molecule. The lines are for visual guide and have no physical significance.

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