Characterization of Ionomer Solutions. 2. Dynamic Light Scattering Studies on Sulfonated Polystyrene Ionomers in a Nonpolar Solvent

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ABSTRACT: The microphase behavior of lightly sulfonated polystyrene solutions in Decalin was investigated using dynamic light scattering. The nature of the aggregates formed in these solutions by the association of the sulfonic acid groups was dependent on the temperature and concentration. At high concentrations, aggregates persisted to temperatures far above the cloud point temperatures. At low concentrations, the aggregates were absent except near the cloud point temperatures. The aggregation increased as one approached the cloud point, thereby indicating that the extensive aggregation provides the driving force for phase separation in these solutions at temperatures higher than that for the precursor polystyrene solutions.

Introduction

Ionomers are macromolecules containing a small percentage of ionic groups chemically attached to a nonpolar backbone. The ionic groups aggregate to influence the structure and properties of ionomer solutions in nonpolar solvents.[1] For example, the association of the salt groups through ion−dipole interactions affects the dilute solution viscosity of sulfonated polystyrene (SPS) salts.[2,3] The association of sulfonic acid groups through hydrogen bonding in the case of the acid form of sulfonated polystyrene (HSPS)[3] gives rise to similar effects.

Lundberg and co-workers[2,3] observed that, at low polymer concentrations, the reduced viscosity of salts of SPS in nonpolar solvents was lower than that of the unmodified polystyrene. A crossover in the viscosities of the two solutions was observed at a certain polymer concentration and interpreted as a changeover from intramolecular association at low concentration to intermolecular association at higher concentrations.

Scattering studies in the low concentration regime (as determined by the previous viscosity measurements[2,3]) observed elevated apparent molecular weights. This indicated the presence of multichain aggregates in the regime where intramolecular associations were thought to dominate. Static light scattering[4] and SANS results,[5] for solutions of 1.39 mol % sulfonated NaSPS (M_w = 100 000) in xylene, were described by the *open association model*.[6] That is, the aggregation process was controlled by a series of equilibria between single chains and multichain aggregates of all sizes. At concentrations above 2 g/dL, the number of single chains decreased in favor of multichain aggregates containing two to six chains. Similar observations, based on the *open association* model, were made for 1.25 and 1.65 mol % NaSPS (molecular weight = 10^5) solutions in xylene.[7−9] At only a slightly lower sulfonation level of 0.95 mol %, the aggregation process of solutions of NaSPS (M_w = 100 000) in xylene was observed to be controlled by a *closed association mechanism*.[6] That is an equilibrium existed between single chains and aggregates of only one size (three chains per aggregate in that specific case).[7]

From dynamic light scattering experiments, the diffusion coefficients of solutions of 1.39 mol % NaSPS in xylene at 20 °C were found to be higher than that of the precursor polystyrene at concentrations below 0.1 g/dL.[4] This indicated that, in very dilute ionomer solutions, the ionic groups were intramolecularly associated to form isolated single coils. A single coil to aggregate transition was observed to occur for 1.3 mol % ZnSPS solutions in *m*-xylene at 20 °C at a concentration of 0.1 wt %.[10]

There have been very few studies on the aggregation behavior of the solutions of the acid forms of ionomers. This is surprising given the importance of ionomers and the relative ease with which the acid forms dissolve in nonpolar solvents. Dilute solution viscosity[3] and light scattering[11] experiments have indicated that the aggregation of the acid groups is weaker than that of the salt groups. A detailed study on the effect of the temperature and concentration on the mechanism of aggregation in these systems has not been done.

The phase behavior of solutions of the acid form of sulfonated polystyrene, HSPS, in Decalin was reported in a previous publication.[12] The cloud point temperatures were observed to increase dramatically with sulfonic acid group content. The higher cloud points of the HSPS solutions as compared to polystyrene were attributed to (i) the incompatibility of the polar sulfonic acid groups with nonpolar solvent Decalin and (ii) to the formation of multichain aggregates possessing a higher effective molecular weight than polystyrene due to the association of the sulfonic acid groups by hydrogen bonding. An investigation of aggregation process, especially near the critical region was considered necessary to fully understand the phase behavior and other solution properties of ionomers.

Dynamic light scattering (DLS) measurements were performed on ionomer solutions in order to better understand the nature of the association process of the sulfonic acid groups. The ability of dynamic light scattering to characterize a distribution of sizes makes it an ideal tool for the investigation of associating

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systems. The size, stability and hydrodynamic behavior of the ionomer aggregates as a function of temperature and concentration in solutions in nonpolar solvents was investigated. The DLS experiments were also conducted under conditions close to the phase boundary for the HSPS/Decalin system to study the solution behavior and the aggregation process just prior to phase separation.

Materials

Sulfonated polystyrene ionomer was synthesized from anionically polymerized polystyrene ($M_w = 24\ 150$, $M_w/M_n = 1.25$) using acetyl sulfate as the sulfonating agent.[13] This reaction yields the acid derivative with sulfonic acid groups randomly distributed at the para position of the styryl rings on the polystyrene chain. The sulfonated polystyrene ionomers in their acid form (HSPS) were recovered by solvent flashing in hot water and then dried under vacuum. The acid content of the HSPS polymer was determined by titration of the sulfonic acid groups using a standard methanolic sodium hydroxide solution with phenolphthalein as an indicator in a solvent mixture of toluene/methanol (90/10 v/v). The sulfonation level of the ionomer studied using DLS in this work was determined to be 1.9 mol %, i.e., 1.9 sulfonic acid groups per 100 styrene repeat units on the average. The nomenclature used is 1.9-HSPS-24K for the ionomer sample and PS-24K for the precursor polystyrene. The molecular weight of the precursor polystyrene was determined using size exclusion chromatography (SEC).

Using the synthesis procedure described above, it is not possible to control the placement of the sulfonic acid groups onto any particular styryl ring. However, the average sulfonation level of the SPS (hence, the average number of acid groups per molecule) can be controlled by the amount of acetyl sulfate added in the reaction step. The sulfonic acid groups will be distributed among the polystyrene chains randomly.

The probability, $P(x)$, of a chain having x sulfonic acid groups on a chain with degree of polymerization, N, is given by the binomial distribution

$$P(x) = \frac{N!}{(N-x)!\ x!}\, p^x (1-p)^{(N-x)} \tag{1}$$

where p is the probability of a monomer being sulfonated. In this study, $N = 232$ (from the precursor polystyrene molecular weight determined by SEC), and $p = 0.019$ (determined as the average sulfonation level by titration). The probability of a chain having one sulfonic acid group is $P(1) = 0.052$. There is a finite probability, $P(0) = 0.012$, of a chain having no sulfonic acid groups. Thus, the product of the sulfonation reaction will statistically yield some chains that have only one or no sulfonic acid groups.

Experiment

Stock solutions of the ionomer and polystyrene of various concentrations were prepared at room temperature in Decalin (Fisher Chemical Co.). The ratio of cis to trans isomers in Decalin was 54:46 as determined by GC−MS. The polymers were dried at 90 °C under vacuum for 48 h before they were used for making the solutions. All ionomer stock solutions were stirred using a magnetic stirrer for maximum agitation for at least one week to ensure complete dissolution. Solutions of concentration less than 4 g/dL were filtered into the scattering cells with 0.25 μm Gelman PTFE filters. The higher concentration solutions were filtered with 0.45 μm Gelman PTFE filters.

Dynamic light scattering measurements were performed with a BI-200SM goniometer (Brookhaven Instruments) using a 2.5 W Ar laser light source (Model Innova 70-3 from Coherent) operating at 514.5 nm and a BI-9000 AT digital correlator (Brookhaven Instruments) with 356 data channels. Eight delay channels were used for establishing a baseline (correlation function at infinite time). Before analysis, data sets were checked for interference from dust by comparing the measured and calculated baselines. When the difference was greater than 0.2%, the data were discarded. The delay time ranged from 0.025 to 10^7 μs. The laser intensities used at 514.5 nm ranged from 200 mW to 1.5 W. The detector aperture settings were optimized for all samples to obtain a photon count rate between 3×10^4 and 1×10^6 counts per second. The measurements were obtained at 10 angles ranging from 25 to 150°. For each concentration, the measurements were made in the temperature range 60 °C and below to about 0.5−1.0 °C above the cloud point (Figure 1). Details regarding the determination of the cloud point temperature for these solutions have been described elsewhere.[12]

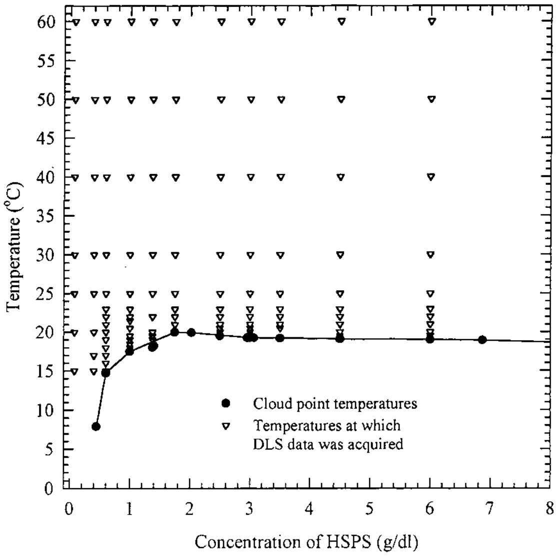

Figure 1. Dynamic light scattering (DLS) experiments: regions of the phase diagram studied for 1.9-HSPS-24K solutions in Decalin. The curve through the cloud points is a visual guide and has no physical significance.

The theory and applications of dynamic light scattering have been described in several publications.[14−16] The important physical relationships are presented below. The intensity autocorrelation function, $G^{(2)}(q,t)$, is formed from the measured intensities of scattered light and is expressed as:

$$G^{(2)}(q,t) = \langle I(q,t')I(q,t'+t)\rangle \tag{2}$$

$I(q,t')$ is the intensity measured at time t' and scattering vector $\mathbf{q}$, $I(q,t'+t)$ is the intensity measured at time $t'+t$, and $\mathbf{q}$, the scattering vector, is defined as follows: $(4\pi n_0/\lambda_0)\sin(\theta/2)$, where n_0 is the refractive index of the solvent, λ_0 is the wavelength of the incident light in vacuo, and θ is the scattering angle.

Intensity−intensity autocorrelation functions, $G^{(2)}(q,t)$, are related to the electric field autocorrelation functions, $g^{(1)}(q,t)$, through the Seigert relation[17]

$$G^{(2)}(q,t) = A(1 + \beta|g^{(1)}(q,t)|^2) \tag{3}$$

where the baseline term, A, approaches $\langle I(q,0)\rangle^2$ in the limit of long time averages. The amplitude β has a range of 0−1 and is related to experimental factors such as the finite area of the detector and the sampling time. For a monodisperse scatterer undergoing random Brownian motion, $g^{(1)}(q,t)$ is an exponential decay with a single relaxation time. Field autocorrelation functions derived from systems with multiple modes of relaxation may be represented as the convolution of a spectrum of relaxation times, $s(\tau)$, and an exponential decay:

$$g^{(1)}(q,t) = \int_0^\infty s(\tau,q)\exp(-t/\tau)\,\mathrm{d}\tau \tag{4}$$

This convolution is a Laplace transform which we invert to provide the spectrum of relaxation times using CONTIN, a constrained regularization method for inverting Laplace transforms provided by Provencher.[18] The spectrum of relaxation times from this inversion is represented as a series of amplitudes, $s(\tau)$, along a grid of relaxation time, τ, values. The amplitudes of the modes indicate the relative importance of different relaxations. The fits using CONTIN to several of the bimodal correlation functions were checked using a double exponential expression

$$g^{(1)}(q,t) = A \exp(-t/\tau_1) + B \exp(-t/\tau_2) \qquad (5)$$

where τ_1 and τ_2 are the relaxation times corresponding to the two relaxation modes.

An average value of the relaxation time, τ_w, from each peak in the spectrum was obtained as the ratio of the second to the first moment of that peak. The cooperative diffusion coefficient, D, was found as the slope of $1/\tau_w$ vs $\mathbf{q}^2$. An apparent hydrodynamic radius, R_H, was then calculated using the Stokes–Einstein equation, $D = kT/6\pi\eta_0 R_H$, where k is the Boltzman constant, η_0 is the solvent viscosity, and T is the temperature in Kelvin.

Results and Discussion

A. Polystyrene Solutions in Decalin. The field autocorrelation functions for the polystyrene solutions possessed a single relaxation mode at all concentrations and temperatures in this study. CONTIN analysis of the field autocorrelation function at each angle yielded one peak in the spectrum of relaxation times. The decay rates, Γ (where $\Gamma = 1/\tau_w$), obtained showed a linear relationship with $\mathbf{q}^2$, indicating that the exponential decay in the autocorrelation function was due to a diffusive process. Thus, the single relaxation is due to the diffusion of a single species in the polystyrene solutions. The cooperative diffusion coefficient of polystyrene in Decalin, D_{PS}, was obtained from the slope of the plot of Γ vs $\mathbf{q}^2$.

The values of the diffusion coefficient of polystyrene, D_{PS}, as a function of temperature for the various concentrations in Decalin is shown in Figure 2a. For all concentrations, D_{PS}, increases with temperature. At constant temperature, D_{PS}, decreases with increasing concentration (Figure 2b). The translational diffusion coefficient for dilute polymer solutions can be expanded to first order in concentration, C, as

$$D = D_0(1 + k_D C) \qquad (6)$$

where D_0 is the diffusion coefficient at infinite dilution and k_D is the second virial coefficient of the translational diffusion coefficient. The negative values of k_D obtained from Figure 2b are in agreement with previous results[19,20] on polystyrene solutions at concentrations below the overlap concentration. Decalin is a Θ solvent for polystyrene in the temperature range 15–20 °C depending on the cis–trans ratio.[21]

B. 1.9-HSPS-24K Solutions in Decalin. The goal of this study was to explore the structure of ionomer solutions in the single-phase region. Dynamic light scattering measurements were obtained at various temperatures for solutions of HSPS at concentrations ranging from 0.075 to 6.0 g/dL. Solutions in the single-phase region exhibited correlation functions with either one or two relaxation times depending on the temperature and concentration. Various regimes could be identified in the single-phase region by the differences in microphase separation behavior evidenced by single or multiple relaxations.

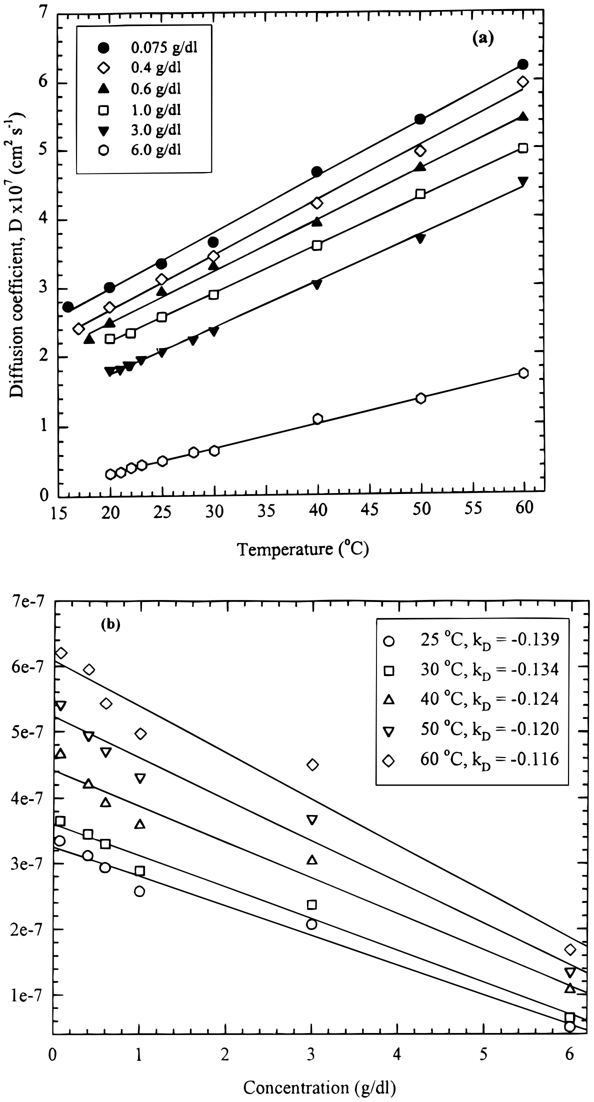

Figure 2. Diffusion coefficients of PS-24K solutions in Decalin at various concentrations and temperatures. The lines are least-squares fit to the data.

High Concentration Regime. Solutions with concentrations at and above 1.75 g/dL had correlation functions with two relaxation times at all temperatures and this concentration range is designated the "high concentration regime". Data for 3.0 g/dL solutions of HSPS-24K at 21.5 °C for 25 and 75° scattering angles is shown in Figure 3. Analysis of these correlation functions using CONTIN provided amplitude spectra with two well-separated peaks. These spectra are overlaid on the correlation functions in Figure 3, and the correspondence between the correlation functions and the spectra may be clearly seen. The bimodal spectra were observed at all scattering angles at which measurements were made. The correlation functions in Figure 3 were fit with a double exponential function (see eq 5), and the relaxation times determined were comparable to those obtained from CONTIN analysis. These are represented as solid vertical lines in Figure 3.

The decay rates, Γ, for both relaxation modes in Figure 3 showed a linear dependence with the square of the scattering vector, $\mathbf{q}^2$, indicating that both were due to diffusive processes (Figure 4). These bimodal spectra are evidence of two populations of diffusing species in this regime.

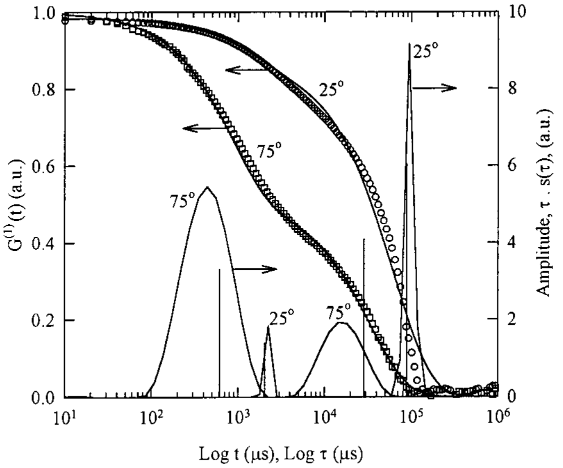

Figure 3. Field correlation functions and relaxation time spectra from dynamic light scattering data acquired at 25 and 75° scattering angles for a 3 g/dL solution of 1.9-HSPS-24K in Decalin at 21.5 °C. Two relaxation modes are observed. Amplitude curves are from fits using CONTIN. Results for double exponential function fits are included for comparison. Solid lines for fits and double exponential.

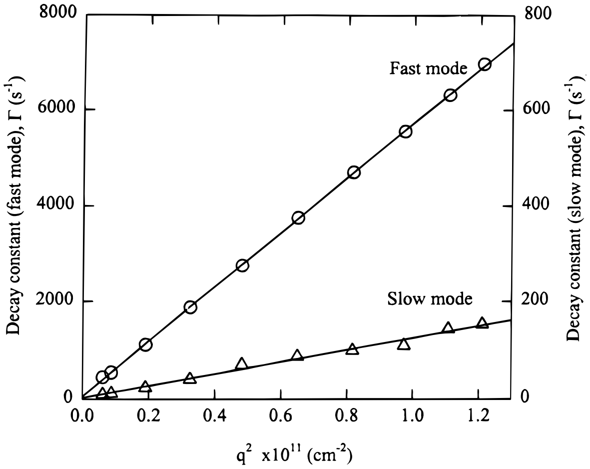

Figure 4. Γ vs $\mathbf{q}^2$ for the fast and slow relaxation modes of 3 g/dL solution of 1.9-HSPS-24K in Decalin at 21.5 °C. Diffusion coefficients of 5.67×10^{-8} and 1.22×10^{-9} cm^2/s are obtained from the slopes of the least-squares fit lines for the fast and slow relaxations, respectively.

The relaxation time spectra obtained using CONTIN analysis for various concentrations of 1.9-HSPS-24K in Decalin at 40 °C are shown in Figure 5. Two relaxation modes were observed for all concentrations investigated at or above 1.75 g/dL. The correlation functions for 1.75 g/dL solution at various temperatures, for the fixed scattering angle of 45°, are shown in Figure 6a. Inverse Laplace transform of all the correlation functions shown in Figure 6b yielded two peaks in the relaxation spectra. Two relaxation modes were previously reported for 1.3 mol % ZnSPS (M_w = 105 000) in *m*-xylene at 20 °C at concentrations between 0.1 and 0.5 wt %.[10]

Diffusion Coefficient from the Fast Relaxation Time. The diffusion coefficient values associated with both the fast and slow relaxation modes of 3 g/dL solution of 1.9-HSPS-24K are shown in Figure 7. The value of the fast mode diffusion coefficient, $D_{F,HSPS}$, is close to that of a 3 g/dL solution of PS-24K. Previous experiments with ionomer solutions[1–11] have revealed that at such high concentrations intermolecularly associated multichain aggregates predominate. However, the various species that can possibly still exist in these solutions include: unsulfonated polystyrene chains, intramolecularly associated chains and intermolecularly associated small or large aggregates. There will be some single chains present even at high concentrations because there is a nonzero probability for the existence of unsulfonated polystyrene chains in the sulfonation reaction product (see eq 1). These unsulfonated polystyrene chains will remain unassociated in solution. Nonetheless, from our experiments, the diffusion coefficient for the parent polystyrene is larger than that of the sulfonated material at all concentrations. Therefore the hydrodynamic volume associated with the fast relaxation of the sulfonated material is greater than that of the parent polystyrene at all concentrations. This must be the result of intermolecularly associating HSPS chains because intramolecularly associated chains would be expected to have a reduced hydrodynamic volume. Even the HSPS chains with one sulfonic acid group can participate in aggregates of at least two chains at any concentration. The intermolecularly associated aggregates responsible for the fast relaxation times are however small in size when compared to the multichain aggregates responsible for the slow relaxation time (see below). This is manifest in the value of $D_{F,HSPS}$ being larger but close to that of D_{PS}. The open association model that previously has been used to describe ionomers in solution considers the sulfonate pairs to be in dynamic equilibrium with the two chain dimer as the lowest stable state, however, multichain aggregates of all sizes are required to be in equilibrium with unassociated chains in this model.

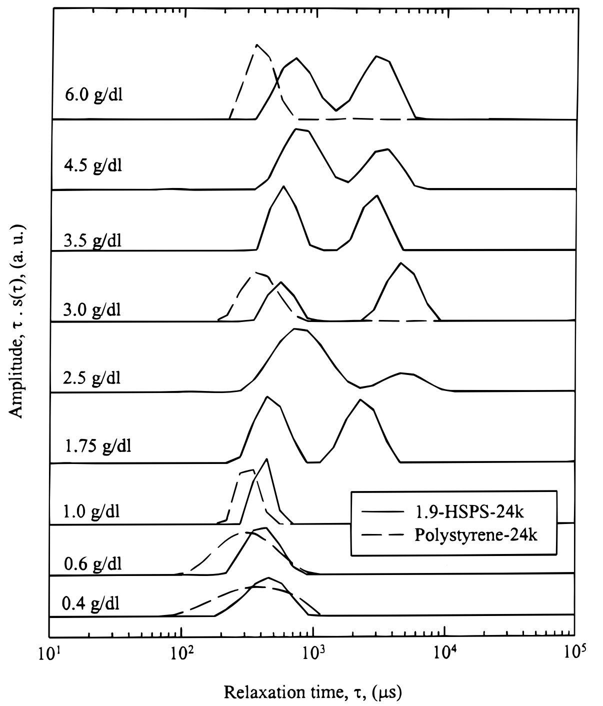

Figure 5. Relaxation time spectra for 1.9-HSPS-24K and PS-24K solutions in Decalin at 40 °C and 30° scattering angle.

The diffusion coefficients of both polystyrene (D_{PS}) and the fast mode species of HSPS ($D_{F,HSPS}$) each increase with temperature primarily as a result of changing solvent viscosity. The solubility of the parent PS backbone in the solvent provides the means to account for changes in solvent quality and viscosity in a self-consistent, model independent way and isolates the perturbation of chain conformation due to the associat-

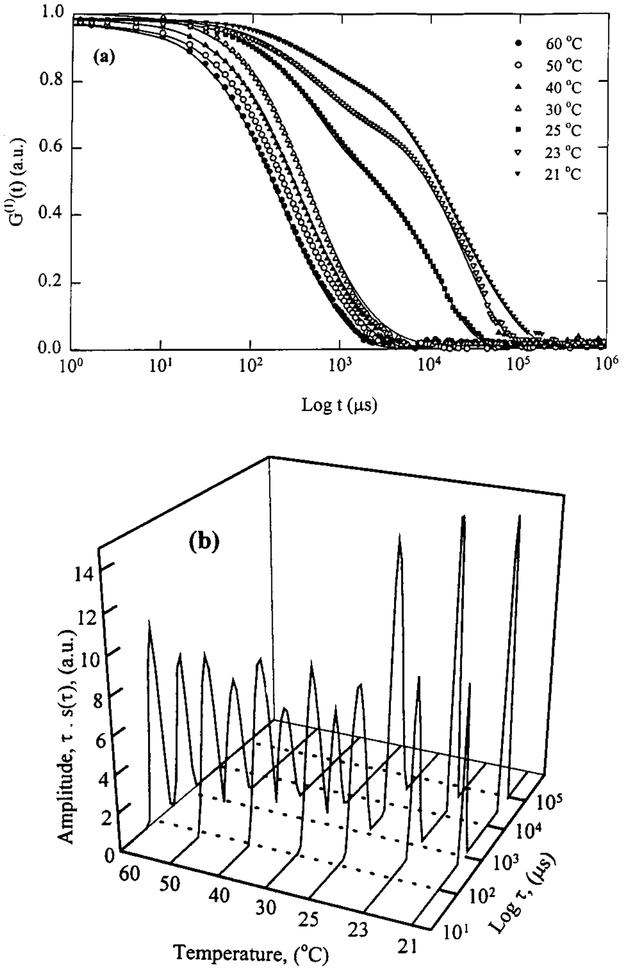

Figure 6. (a) Correlation functions and (b) relaxation time spectra, derived from DLS data of a 1.75 g/dL solution of 1.9-HSPS-24K in Decalin at temperatures ranging from 60 to 21 °C. Scattering angle is 45°. Cloud point temperature of this HSPS solution is 20 °C. Two modes of relaxation are observed in the entire temperature range.

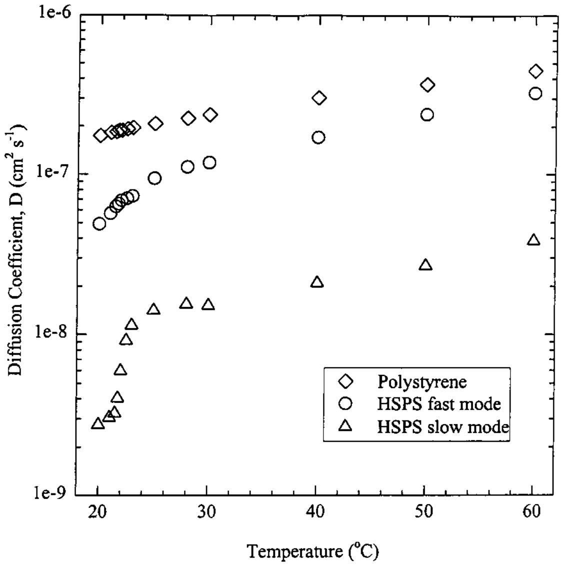

Figure 7. Diffusion coefficients of 3 g/dL solutions of PS-24K and 1.9-HSPS-24K in Decalin at various temperatures. Cloud point temperature for this HSPS solution is 19.2 °C.

ing groups. D_{PS} is always observed to be greater than $D_{F,HSPS}$ in the temperature range investigated. The ratio $D_{PS}/D_{F,HSPS}$ is shown in Figure 8 as a function of temperature. The value of the ratio is independent of solvent viscosity effects and also accounts for gross changes in solvent quality.

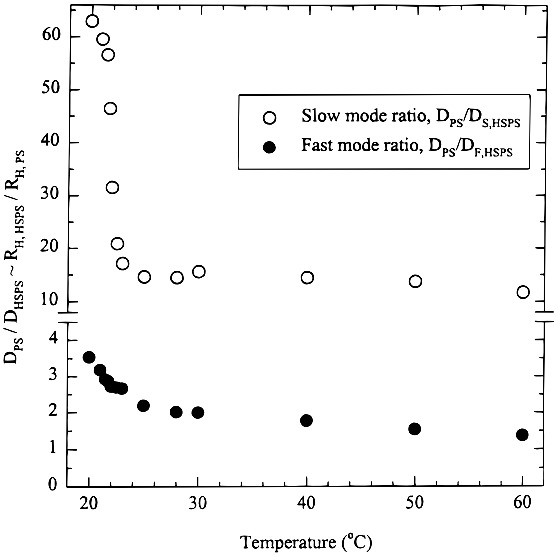

Figure 8. Ratio of diffusion coefficients of 3 g/dL solutions of PS-24K to 1.9-HSPS-24K. Cloud point temperature for this HSPS solution is 19.2 °C.

Significant differences in solvent quality between linear and cyclic polystyrenes near Θ conditions have been studied both experimentally[22] and theoretically.[23] Ring molecules had lower Θ temperatures than their linear counterparts. This result leads to the expectation that associating chains, which may have one or more loops in their configuration, will not shrink as rapidly as linear chains as the cloud point is approached. In fact, the ratio of D_{PS} to $D_{F,HSPS}$ is observed to vary from 1 to 3 as the temperature is varied from 60 °C to the cloud point. This ratio, after the application of the Stokes–Einstein equation, is also the ratio of the hydrodynamic radius of the HSPS to the hydrodynamic radius of the polystyrene. The relative change in solvent quality for linear and cyclic molecules reported previously may account for this variation, assuming that the aggregates responsible for the fast mode diffusion coefficient, $D_{F,HSPS}$, have a constant number of chains in the temperature range studied.

Diffusion Coefficient from the Slow Relaxation Time. Correlation functions obtained from solutions with concentrations at and above 1.75 g/dL show a second relaxation time at all temperatures studied. The value of the slow mode diffusion coefficient, $D_{S,HSPS}$, is an order of magnitude less than $D_{F,HSPS}$ (Figure 7). The slow mode diffusion coefficient is attributed to the presence of large multichain aggregates.

$D_{S,HSPS}$ decreases slowly with temperature above the cloud point for the 3 g/dL sample, but in the last 3 °C temperature range above the cloud point, an order of magnitude decrease in $D_{S,HSPS}$ is observed. In contrast, the rate of decrease in $D_{F,HSPS}$ with temperature is much less (although the rate of decrease also increases for this fast relaxation mode as the cloud point temperature is approached). The ratio of D_{PS} to $D_{S,HSPS}$ is observed to take values between 10 and 50 in the temperature range studied (Figure 8), and most of the increase occurs in the last 3 °C range above the cloud point. If the slow relaxation results from multichain aggregates and they experience the same or better solvent quality than the linear chains then the scaling relation $R \sim N^{\nu}$ can be

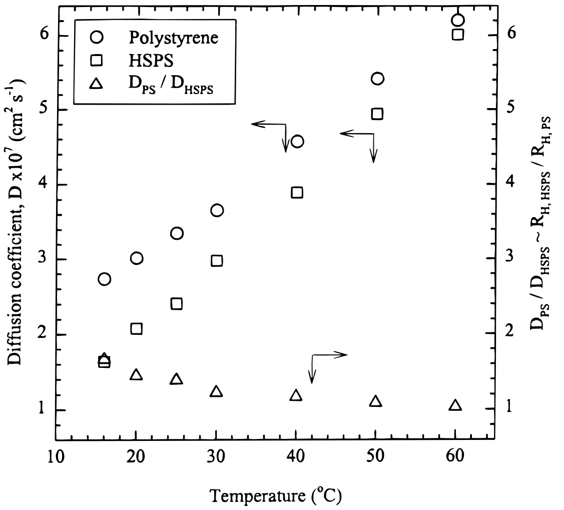

Figure 9. Diffusion coefficients of 0.075 g/dL solutions in Decalin of PS-24K and 1.9-HSPS-24K, and their ratio, at various temperatures.

used to estimate the minimum number of chains in such an aggregate. At high temperature where the ratio is 10 and the solvent quality is good (i.e. $\nu = 0.6$), the number of chains in an aggregate is on the order of 50. At lower temperatures, as solvent quality decreases and the value of ν approaches $^1/_2$, the minimum number of chains in an aggregate should increase toward 200. This is an estimate of a minimum value that considers the segment density of an aggregate to be about the same as that of a linear chain. We expect the segment density of an aggregate to be higher so that aggregates will have on the order of thousands of chains for the conditions where the ratio of D_{PS} to $D_{S,HSPS}$ is high (~50). This would especially occur in the narrow range of temperatures just above the cloud point, where aggregation becomes very extensive, and these very large sized aggregates are formed. The formation of these large molecular weight aggregates then provides the driving force for phase separation when the temperature is lowered further. The trends observed for the fast and slow mode diffusion coefficient values at other concentrations in this regime (1.75 g/dL to 6.0 g/dL) are similar to that seen for the 3 g/dL solution.

Low Concentration Regime. For temperatures more than 1 or 2 °C above the cloud point and concentrations at or below 1 g/dL, the field autocorrelation functions of 1.9-HSPS-24K exhibit a single relaxation. We designate this as the "low concentration regime". The values of the diffusion coefficients are shown in Figure 9 for 0.075 g/dL (the lowest concentration studied) solutions of both PS-24K and 1.9-HSPS-24K in Decalin, as functions of temperature. D_{PS} is always observed to be greater than D_{HSPS} in the temperature range investigated as seen for the fast relaxation time at higher concentrations. It was reported in previous work on ionomers in good solvents[4,10] that at very low concentrations, favorable hydrogen bonding interactions between sulfonic acid groups on the same chain reduced single coil dimensions giving the result $D_{HSPS} > D_{PS}$. However, in our experiments at low concentrations the ratio D_{PS}/D_{HSPS} takes on values between 1 and 2. Once again, these values indicate that the diffusing species in the HSPS solutions is larger than the PS at all temperatures studied. This is surprising in light of the poorer solvent quality of Decalin for HSPS as evidenced by the increased cloud point temperatures of sulfonated polystyrene[12] and can only be explained as further evidence of intermolecular aggregation.

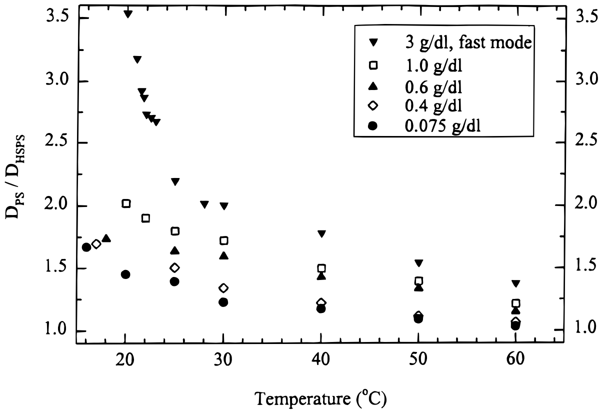

Figure 10. Ratio of diffusion coefficients of solutions in Decalin of PS-24K to 1.9-HSPS-24K for various concentrations in the "low concentration regime". The ratio for the fast mode of 3 g/dL solution is also shown for comparison.

Chains with two or more sulfonic acid groups will experience a competition between intra- and intermolecular hydrogen bonding. This competition will involve a balancing of lost conformational entropy due to the constraint imposed by the hydrogen bond and the unfavorable enthalpic interactions due to the increased local segment concentrations against the energy of stabilization of the fulfilled hydrogen bonds. As the temperature approaches the Θ condition the enthalpic contribution should become independent of concentration so that the configurational entropy loss will determine the distribution of associations between intra- and inter- molecular contacts. As $R_{H,\ HSPS} > R_{H,\ PS}$ some intermolecular hydrogen bonding must exist even at these "low concentrations". However, the fact that the ratio D_{PS}/D_{HSPS} never exceeds 2 and only one relaxation time is observed indicates that intermolecular aggregation is limited at these "low concentrations" in contrast to the "high concentration" data. The HSPS solutions have aggregates of 1 to 10 chains using the same scaling analysis as in the above discussion.

Our results are in contrast to the previous results for salt forms of SPS in xylene[4,10] where the data indicated that intramolecular associations dominated at concentrations below 0.1 g/dL. The previous results, however, were for SPS salts in xylene which is a good solvent for the polystyrene backbone at the temperature studied. Multichain aggregates were observed to have a greater effect on the dynamic light scattering results at higher concentrations in the case of SPS salts in xylene too.

In the "low concentration regime", the ratio D_{PS}/D_{HSPS} decreases from about 1.8 near the cloud point to about 1.1 at the higher temperatures (see Figure 9) but is never less than 1. Thus, intermolecular associations between the sulfonic acid groups persist in the entire temperature range investigated. Their effect on the diffusion coefficient is smaller, however, at the high-temperature end (between 50 and 60 °C). This temperature behavior was also observed for the fast mode diffusion coefficient at the other concentrations in this regime: 0.4, 0.6, and 1.0 g/dL (see Figure 10).

Behavior near the Cloud Point. At temperatures very near the cloud point, even solutions with concentrations at or below 1 g/dL, i.e., in the "low concentration regime", did exhibit two relaxations. This is in contrast to DLS results with the high concentration solutions

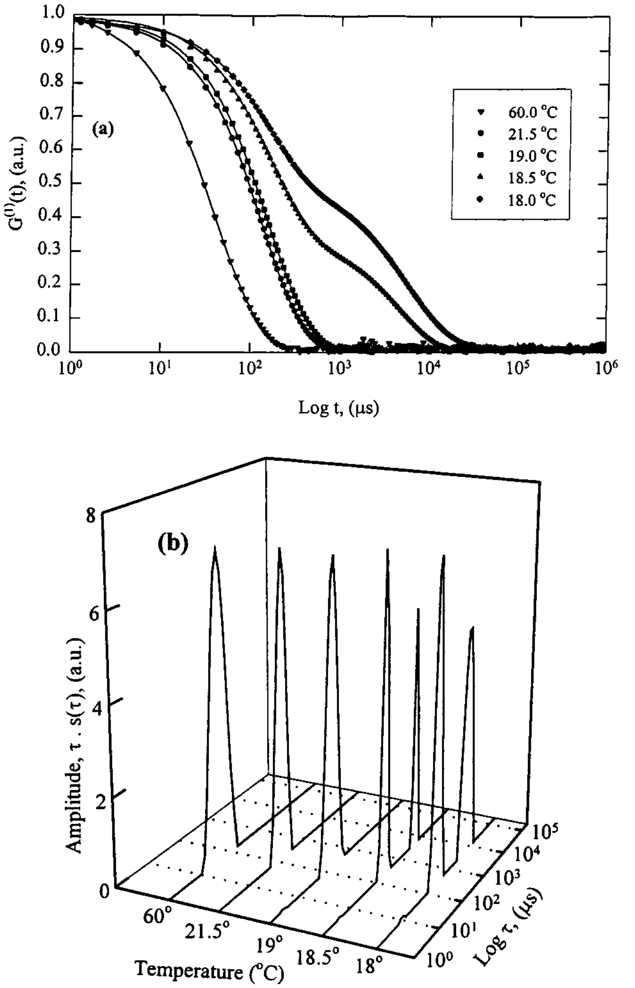

Figure 11. (a) Field correlation functions and (b) relaxation time spectra for a 1 g/dL solution of 1.9-HSPS-24K in Decalin at 60 °C and at temperatures near the cloud point of 17.5 °C. Scattering angle is 90°. The second relaxation mode appears for temperatures at and below 18.5 °C.

where multichain aggregates existed over the entire range of temperature and aggregate sizes increased dramatically near the cloud point. DLS experiments were conducted on the lower concentration HSPS solutions to see if a second mode of relaxation could also be observed for these if one approached close enough to the cloud point temperature. Here, 1.0 and 0.6 g/dL solutions of HSPS in Decalin were made at room temperature. DLS data were acquired at temperatures below room temperature to within 0.5 °C of the cloud point temperature of the solution. The solutions were stable for hours at these temperatures. Figure 11 shows the field correlation functions and the relaxation time spectra obtained from the DLS data acquired at a scattering angle of 90° for a 1 g/dL solution of 1.9-HSPS-24K in Decalin at temperatures near the cloud point. The second mode of relaxation is only observed at temperatures within 1 °C of the cloud point. The 0.6 g/dL solution also exhibits the slow relaxation mode at temperatures close to the cloud point (within 1 °C). Thus, in the “low concentration” regime, large aggregates are formed only near the phase boundary and they persist only up to a few degrees above the cloud point temperature. These results further substantiate the conclusion made in the preceding section that it is the formation of these large molecular weight aggregates that provides the driving force for phase separation of these solutions when the temperature is lowered.

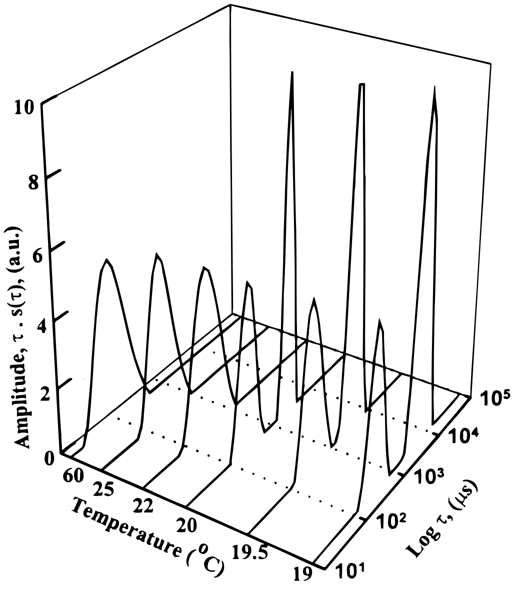

Figure 12. Relaxation time spectra for a 1.375 g/dL solution of 1.9-HSPS-24K in Decalin near the cloud point of 18 °C. Scattering angle is 75°. The second relaxation mode appears for temperatures at and below 20 °C.

Figure 12 shows the relaxation time spectra for a 1.375 g/dL solution of 1.9-HSPS-24K, which is a concentration intermediate to those shown in Figures 11 and 6. A comparison of Figures 11, 12 and 6, reveals that the second mode appears at higher temperatures as the concentration increases from the “low concentration” to the “high concentration regime”. The transition from the “low concentration” to the “high concentration” regime is sharp when measured by the appearance of the slow relaxation time. Below 1 g/dL, the slow mode does not appear until the temperature is within 1 °C of the cloud point, at 1.375 g/dL the slow mode does not appear until the temperature is within 2 °C of the cloud point, and at 1.75 g/dL the bimodal relaxation behavior is seen at all temperatures. Thus, small variations in concentration in this narrow region provide temperature dependent transitions between microphase regions that occur at progressively increasing temperatures from the cloud points.

Conclusions

The dynamic behavior of the HSPS ionomers in the nonpolar solvent Decalin is dominated by two diffusive relaxation modes. The fast diffusive relaxation mode is due to the presence of single chains, or small sized aggregates (of less than 10 chains), that are formed by the intermolecular association of the sulfonic acid groups. The slow diffusive relaxation mode is attributed to large multichain aggregates (containing hundreds of chains). Only the fast mode was observed at low concentrations (≤1 g/dL) at all temperatures that were at least 1 °C above the cloud point. Hence, at these low concentrations the predominant species appears to be single chains and small aggregates. At concentrations at or above 1.75 g/dL, both relaxation modes were observed at temperatures ranging from the cloud point to the highest temperature investigated (60 °C). It appears that at temperatures away from the phase boundary the formation of multichain aggregates becomes important only above a critical concentration. This is observed to be between 1 and 1.75 g/dL for 1.9 mol % HSPS ($M_w = 24\,000$).

Two relaxation modes was previously reported for 1.39 mol % Zn salts of SPS in *m*-xylene at concentrations between 0.16 and 0.5 wt % at 20 °C.[10] In that case, the fast relaxation times were lower than the precursor polystyrene relaxation times, whereas the slow relaxation times were larger. Thus, the difffusive species present were isolated single chains and multichain aggregates. In contrast, for the HSPS/Decalin system reported here, both the prevalent species clearly are aggregates. Of course, the aggregates differ in size and in the number of chains incorporated.

The fast and the slow relaxations in the HSPS/Decalin solutions occurred at progressively longer relaxation times with increasing ionomer concentrations and decreasing temperatures, indicating that aggregate formation was favored at high concentrations and low temperatures. Aggregate formation was observed to dramatically increase at temperatures very close to the cloud point. The dynamic behavior of the high concentration solutions at these temperatures was characterized by an order of magnitude decrease in the slow mode diffusion coefficients, and that of the low concentration solutions, by the appearance of a slow diffusive relaxation mode. It is proposed that this extensive aggregation provides the driving force for phase separation at temperatures that are much higher than the cloud point temperatures of the precursor polystyrene.

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