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Single-Coil to Aggregate Transition of Sulfonated Polystyrene Ionomers in Xylene Studied by Dynamic Light Scattering

Kirill N. Bakeev,*,† Iwao Teraoka, William J. MacKnight, and Frank E. Karasz

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

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ABSTRACT: A single-coil to aggregate transition in the zinc salts of sulfonated polystyrene ionomers in xylene was studied by dynamic light scattering. As the polymer concentration was increased in the dilute regime, the measured average diffusion coefficient of the polymer molecules decreased, and it was accompanied by a broadening in the distribution of the coefficient. Spectral analysis of the light scattering autocorrelation function revealed a clear transition from a single- to a dual-decay rate mode with increasing solute concentration, the faster being identified as the diffusion of isolated coils. Thus the slowing-down of the average diffusion with increasing polymer concentration was ascribed to the emergence of aggregates. The overall weight fraction of the aggregates, however, remained low.

Introduction

Ionomers are generally defined as predominantly nonpolar hydrocarbon polymers containing small amounts, usually less than 10 mol %, of covalently bound salt groups present either as side groups or as end groups. The aggregation of ionomers in nonpolar media has been a subject of investigation for several years. It is known that the association of salt groups can result in the formation of intra- and interchain aggregates in nonpolar solvents and, in the solid state, in microscopically separated domains. These aggregates serve as physical cross-links, an arrangement that dominates the major properties of such polymers in nonpolar media and gives rise to the application of ionomers as thermoplastic and surface-active materials, oil viscosity modifiers, and so on.[1–5]

The investigation of ionomer aggregation in nonpolar solvents is much less advanced than that of ionomers in the solid state, because their poor solubility in nonpolar solvents restricts the number of ionomers available for study to samples that have a very low content of salt groups, about 1–4 mol %, depending on the ionomer and solvent type. Furthermore, the very low concentration of the ionomer required to obtain reliable information on the crossover from intra- to interchain aggregate formation is relatively difficult to study. Lundberg and co-workers studied ionomer aggregation of sulfonated polystyrene ionomers in various nonpolar solvents.[6–8] Crossover behavior was observed in the concentration dependence of the reduced viscosity, η_{red}, for the ionomer and that for unmodified polystyrene of the same degree of polymerization. At low concentrations η_{red} for the ionomer was smaller than that for the unmodified polystyrene, and, with an increase of ionomer concentration, η_{red} increased drastically, exceeding that of the polystyrene. The results suggested that an intra- to interchain interaction equilibrium that determines viscosity behavior of the ionomer exists in the ionomer solution. The crossover concentration for η_{red} of the ionomer–polystyrene has been roughly estimated to be equal to the overlap concentration of the polystyrene, which is defined as the reciprocal of the intrinsic viscosity. We have recently confirmed these data by applying a fluorescent molecular probe technique to the same ionomer system.[9] Recent data on both small-angle neutron and light scattering have shown the presence of intra- and interchain aggregates in the ionomer solution.[10–14] It was found[12,14] by light scattering that the single-chain dimension of the sodium salt of sulfonated polystyrene ionomer with 1.39 mol % salt groups at their lowest concentration (ca. 0.045 g/dL) in xylene was approximately 20% smaller than the single-chain dimension of the unmodified polystyrene in the same solvent. This contraction was attributed to the intrachain association of individual ionomer coils in the dilute solution regime.[12,14] However, it is not clear whether the chain further contracts or levels off as the polymer concentration decreases still further.

In this contribution we examine by dynamic light scattering (DLS) the aggregation of zinc salts of sulfonated polystyrene ionomers with 1.3 mol % salt groups for various ionomer concentrations in dilute solutions of xylene. We predict that further analysis of DLS data will yield a quantitative understanding of the equilibrium between single coils and multiple-coil aggregates in the dilute regime and will reveal a transition between the two states as the concentration changes.

Experimental Section

Zinc-neutralized sulfonated polystyrene ionomer, provided by R. D. Lundberg, was synthesized from anionically polymerized polystyrene with $M_w \sim 105\,000$ and $M_w/M_n \sim 1.05$ (M_n and M_w are number- and weight-average molecular weights, respectively) by a chemical transformation reaction as previously described.[11] The content of $-SO_3(Zn)_{1/2}$ groups was determined by elemental analysis. Polystyrene (PS) and ionomer (SPZn) solutions were prepared, using a magnetic stirrer for maximum agitation. Freshly opened *m*-xylene (99%; $\epsilon \sim 2.2$; Fisher) was used without further purification to dissolve the polymers. All ionomer stock solutions were stirred for a least 5–6 days to ensure complete dissolution. Prior to DLS measurements, polymer solutions were repeatedly filtered (normally three times) into dust-free Pyrex-glass test tubes through Millipore PTFE membrane filters with a 0.2-μm pore size.

Solution viscosities were measured with a standard Ubbelohde capillary viscometer in a temperature-controlled water bath at 20 °C. Each solution was temperature-equilibrated for about 20 min prior to viscosity measurements. An average value of viscosity was taken for 4–5 consecutive measurements of the same sample.

DLS measurements in the homodyne configuration were carried out with an Ar ion laser (Spectra-Physics Model 2020) operated at a light intensity of 100–250 mW and wavelength λ

[†] Current address: Polymer Science Department, Moscow State University, Leninskie Gory, Moscow V-234, Russia.

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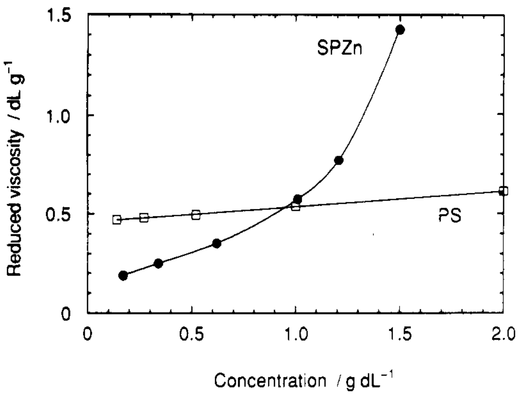

Figure 1. Reduced viscosity of *m*-xylene solutions of SPZn and PS as a function of polymer concentration.

~ 514.5 nm and with a digital correlator (Langley-Ford Instruments Model 1096). All measurements were conducted at 20 °C (refractive index $n_\lambda^{20} \sim 1.496$ and viscosity $\eta_0 \sim 0.6165$ cP for *m*-xylene). The scattering angle θ was 25.0°, unless otherwise specified.

A base-line-subtracted, normalized homodyne autocorrelation function (ACF) $g_2(t)$ for a delay time t was first converted to a normalized electric-field ACF $g_1(t)$. The two ACFs are related by the expression $g_2(t) = [g_1(t)]^2$. The ACF $g_1(t)$ was then analyzed by a second-order cumulant expansion $\ln[g_1(t)] \sim -\langle\Gamma\rangle t + (1/2)\mu_2 t^2$, where $\langle\Gamma\rangle$ is the average of a decay rate Γ, and $\mu_2 = \langle\Gamma^2\rangle - \langle\Gamma\rangle^2$ is the variance of Γ.[15] The same ACF was also analyzed by the CONTIN program originally provided by Provencher[16] as $g_1(t) \sim \int_{-\infty}^{\infty}\Gamma G(\Gamma)\exp(-\Gamma t)\, \mathrm{d}\ln\Gamma$ to obtain the spectrum $G(\Gamma)$.

When the polymer solution is dilute and the scattering angle θ is low, the decay rate Γ is related to the center of mass mutual diffusion coefficient, D_m, by $\Gamma = D_\mathrm{m}q^2$, where $q = (4\pi n/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector. The hydrodynamic radius, R_H, is the radius of a sphere that yields the same diffusion coefficient as the nonspherical scatterer in the dilute solution limit, $R_\mathrm{H} = k_\mathrm{B}T/(6\pi\eta_0 D_0)$, where $k_\mathrm{B}T$ denotes the thermal energy and D_0 is the value of D_m in the dilute solution limit.

Results and Discussion

Figure 1 shows a comparison of the concentration dependence of the reduced viscosity η_red for SPZn with that of an unmodified polystyrene (PS) of the same degree of polymerization in *m*-xylene. As found in previous reports,[6,8] there is a crossover in the concentration dependence of η_red. The crossover concentration is close to the overlap concentration $c^* \sim 0.9$ wt % of PS, a result that is also in agreement with the other reports.[6,8]

The ACF $g_2(t)$'s for SPZn solutions (0.10 and 0.50 wt %) and a PS solution (0.50 wt %) in *m*-xylene are shown in Figure 2. At concentration $c = 0.50$ wt % (below the crossover concentration of η_red; see Figure 1), the ACF of the SPZn solution follows a nonexponential decay, whereas that of the PS solution shows a nearly single-exponential decay. It is also evident that the initial decay rate of the ACF for SPZn is smaller than that for PS. As the polymer concentration decreases, the profile of the ACF for SPZn changes; and at 0.10 wt %, it appears to adopt a single-exponential decay, with a decay rate larger than that of the 0.50 wt % SPZn solution (Figure 2). There was no appreciable change in the profile of the ACF of PS solutions for various PS concentrations below 0.50 wt %. The decay rates of the ACFs for SPZn and PS were nearly the same at $c = 0.10$ wt %.

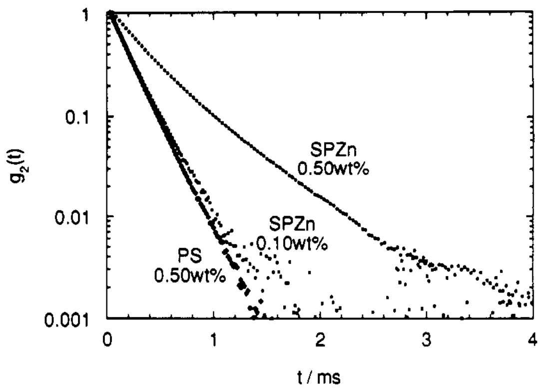

Figure 2. Homodyne autocorrelation functions $g_2(t)$ of SPZn solutions (0.10 and 0.50 wt %) and a PS solution (0.50 wt %) in *m*-xylene as a function of time t.

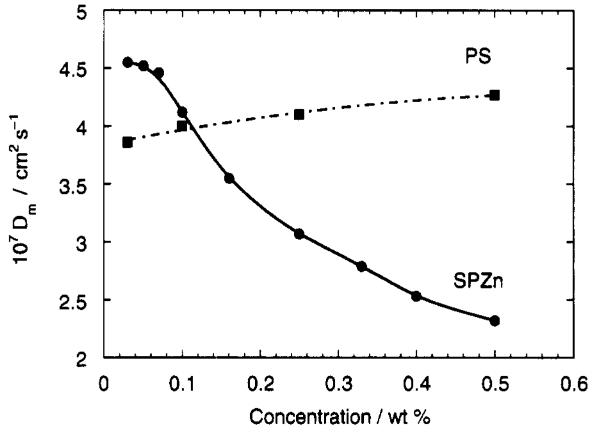

Figure 3. Center of mass diffusion coefficient D_m of *m*-xylene solutions of SPZn (circles) and PS (squares) as functions of the polymer concentration.

At the three scattering angles 25.0°, 35.0°, and 45.0°, the initial decay rates obtained in the second-order cumulant analysis were proportional to q^2, which allows us to estimate an average of D_m from an ACF measured at 25.0° alone. The estimated D_m values are shown in Figure 3 for both PS and SPZn solutions as functions of the polymer concentration. The D_m for PS solutions increases slightly with increases in c in the range $0.03 \le c \le 0.50$ wt %, a result consistent with the fact that *m*-xylene is a good solvent for PS.[12] As the SPZn ionomer concentration decreases to $c \sim 0.070$ wt %, D_m increases; below that concentration, it levels off. Upon extrapolation to zero concentration, we find that R_H of SPZn is smaller than that of PS. PS and SPZn have the same D_m at a concentration $c_\mathrm{D} \sim 0.12$ wt %. Above c_D, the average of D_m for SPZn is smaller than that for PS, whereas below c_D the opposite trend prevails. This result is consistent with the literature and suggests that there is a transition from the single coil to the multiple-coil aggregate as the polymer concentration exceeds c_D. The existence of this transition is also supported by a measured increase in the broadness index $\mu_2/\langle\Gamma\rangle^2$ for SPZn from 0.03–0.05 at $c \le 0.10$ wt % to 0.10–0.12 at $c = 0.50$ wt %.[17]

The transition characteristics of the distribution in Γ are optimally represented in the spectrum $G(\Gamma)$ calculated by CONTIN (Figure 4). In the logarithmic spacing for Γ, $\Gamma G(\Gamma)$ is proportional to a weight fraction of a decay component $\exp(-\Gamma t)$. As a reference, the spectra of PS are also shown for $c = 0.030$ and 0.25 wt %. Below c_D, there is only one peak in the spectrum of $G(\Gamma)$ for SPZn, and that peak is located very close to that for PS solutions, a result demonstrating that only single chains are present in SPZn solutions. An increase in the SPZn concentration above c_D leads to the appearance of a second peak with a smaller Γ, while the original peak, ascribed to diffusion of single coils, is retained with little change in the peak position. With further increase in c, the weight fraction of the second peak increases, and the positions of both

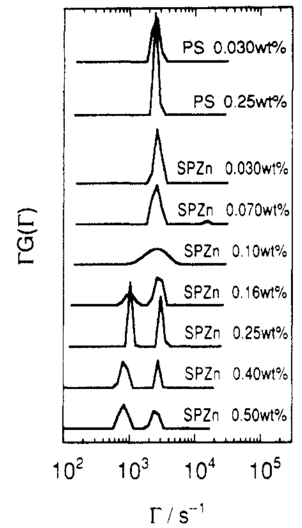

Figure 4. Decay rate spectrum $G(\Gamma)$ obtained in the CONTIN analysis for SPZn solutions at several polymer concentrations in *m*-xylene. For reference, the spectra of PS solutions are also shown for two concentrations. $\Gamma G(\Gamma)$ represents the relative weight of each decaying component in the logarithmic spacing of Γ.

Table I
CONTIN Analysis Results for Dynamic Light Scattering Measurements of SPZn Solutions in *m*-Xylene

concn/(wt %)	Γ_1/s^{-1} [a]	Γ_2/s^{-1} [a]	G_1/G_2 [a]	M_1/M_2 [b]	c_1/c_2 [b]
0.16	1024	2767	0.463	7.3	0.063
0.25	1048	3106	1.12	8.8	0.13
0.33	1023	2849	1.20	7.8	0.16
0.40	864	2755	1.33	10.2	0.13
0.50	830	2477	1.40	8.9	0.16

[a] Analysis by CONTIN. [b] Calculated.

peaks shift to smaller values of Γ. The shift suggests that *m*-xylene provides the SPZn molecules with near Θ conditions, in good agreement with the measurement[12] of the second virial coefficient for SPNa in *m*-xylene. The concentration 0.10 wt % that produced the apparent broad distribution, although still a single peak, in $G(\Gamma)$ for SPZn coincides with the c_D found in Figure 3 from the initial decay rate measurement.

The value qR, where R is the radius of a scatterer that produces the second (slower) peak in $G(\Gamma)$, is estimated to be ca. 0.21 for the scattering angle of 25° and the sample concentration of 0.50 wt %. Also from the fact that there was no appreciable change in the CONTIN spectrum for the ACFs measured at higher angles except for a shift factor by q^2, the slower decay in the ACFs is ascribed to the center of mass diffusion of the ionomers.

Let us assume that, at $c \geq 0.16$ wt %, there are two populations for SPZn molecules: isolated single coils and aggregates. We interpret the spectrum of $G(\Gamma)$ as comprising two δ-function spikes at Γ_1 and Γ_2 (averages of Γ for the slower and faster peaks) with heights G_1 and G_2, a spike at Γ_2 originating in the isolated coils. We then estimate the ratio of the molecular weights M_1 and M_2 and the ratio of weight concentrations c_1 and c_2 of the two populations. For a coil in a Θ solvent, $\Gamma_i \propto (M_i)^{-1/2}$ ($i = 1, 2$), and we assume, for simplicity, that the same relation holds for the aggregate. Then, $M_1/M_2 = (\Gamma_2/\Gamma_1)^2$. From $G_i \propto c_iM_i$,[18] we obtain $c_1/c_2 = (G_1/G_2)(M_2/M_1)$. The calculated data are summarized in Table I. An aggregate was found to consist of 8–10 ionomer coils. The fraction of the aggregates increases rapidly as the ionomer concentration increases above c_D, followed by a constant fraction at ca. 14% for $c \geq 0.33$ wt %.

There is a difference of a factor of about 10 between the crossover concentrations as observed for the viscosity (η_{red}; Figure 1) and for the diffusion coefficient (D_m; Figure 3). This large difference can be attributed to different types of averaging functions applied to a polydisperse system for η_{red} and D_m. The ACF in DLS is dominated by contributions from fractions of aggregates, whereas the viscosity is determined mostly by fractions that exist in a large number, i.e., isolated coils.[19]

In conclusion, investigation into aggregation equilibrium of sulfonated polystyrene ionomers in nonpolar solvents by DLS with CONTIN analysis has shown the presence of only isolated coils in solutions with $c \leq 0.1$ wt %. An increase in the SPZn concentration above a crossover concentration c_D around 0.12 wt % leads to formation of multiple-coil aggregates, but the weight fraction of the aggregates remains low. Detailed analysis of the DLS data has provided a quantitative picture of the ionomer aggregation in the nonpolar solvent on the molecular level that cannot be obtained by the measurement of average quantities.

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