Time- and Shear-Rate-Dependent Rheology of Ionomer Solutions

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ABSTRACT: The effect of dissolution time and shear rate on the viscosity of a lightly sulfonated polystyrene ionomer (sulfonation level, 1.18 mol %; molecular weight, 105 300) has been examined in a nonpolar solvent (xylene). In contrast to the time-independent properties of the same ionomer in a somewhat higher dielectric constant solvent, marked reduction in dissolution kinetics and pronounced shear thickening are observed. Surprisingly, these properties are a strong function of the sample preparation. Several orders of magnitude change in viscosity occurs under the appropriate experimental conditions. Based on previous small-angle light and neutron scattering measurements, a qualitative model emerges of ionomer chains in relatively dilute nonpolar solvents under both quiescent and shear conditions.

Introduction

It is widely recognized that polymeric materials are especially effective in controlling the rheology of fluid systems. Rather broad control is achievable due to the long contour length of the polymer chains and their unique ability to entangle with each other. If the degree of polymerization is high, then relatively low levels of polymer are required to establish the appropriate rheological characteristics.

In recent years low levels of ionic groups have been introduced into a variety of polymer chains, resulting in substantial change in physical properties, especially in comparison to the nonionic polymeric precursors.[1-5] A sufficient number of studies have been performed to clearly confirm that these ionic moieties establish a degree of control over the polymer physical properties not easily achieved with nonionically interacting chains. These property changes are due to the ability of these ionic groups to form microphase-separated regions containing either multiplets or higher order aggregates of the ionic materials (i.e., low dielectric bulk systems)[6,7] or intra- and interionic associations in dilute and semidilute nonpolar solutions[3], respectively. A direct consequence of these ion pair interactions is their exceptional thickening behavior in the semidilute polymer regime and a reduction in the reduced viscosity in dilute solution as compared to its nonionic counterpart.

The mechanism by which the reduced viscosity is markedly diminished in nonpolar solvents was reexamined in view of recent light[8-10] and neutron scattering[11] results. These measurements confirm that in the dilute solution regime aggregation of the ionomer chains occurs. The average number of coils within an aggregate is a strong function of sulfonation level, molecular weight, and concentration. Furthermore, the individual ionomer coils within an aggregate do not expand when associated with other coils but rather they retain their unperturbed dimensions. However, since aggregation is found, intermolecular ionic associations are assumed to dominate the solution rheology, but in addition some intramolecular associations should be superimposed on this picture. The reduction in the reduced viscosity in dilute solution is attributed to the existence of multichain aggregates and therefore the ineffectiveness of the individual ionomer coils within an aggregate to fully contribute to the reduced viscosity.

In this paper, we report our preliminary results on the rheological behavior of a monodisperse sodium-neutralized styrenesulfonate (Na–SPS) copolymer in a low dielectric constant solvent, xylene ($\epsilon = 2.4$). It is assumed that in this solvent the aggregation phenomena will be more pronounced, and therefore its effect on rheological properties can be more easily examined with respect to a number of factors such as time and shear rate. Changes in the rheological properties should be strongly associated with aggregate dissociation and/or formation.

Experimental Section

Our results are extremely dependent on the conditions (primarily polymer concentration) under which we prepare the sulfonated ionomer; therefore, it is important to carefully describe the specific synthesis procedure.

Anionically polymerized polystyrene was purchased from Polymer Laboratories, Ltd. The molecular weight of the polymer was 105 300 as determined by gel permeation chromatography. The preparation of the sodium-neutralized sulfonated polystyrene ionomer is similar to that described previously.[12] Polystyrene (30 g) was dissolved in 500 mL of 1,2-dichloroethane (1,2-DCE) at 25 °C (i.e., the polymer concentration is 6.0 g/dL). The solution was then heated to 50 °C, and the appropriate amount of acetyl sulfate was added, in this instance, 1.11 mL of acetic anhydride and 0.75 mL of concentrated sulfuric acid. The solution is continually stirred for 60 min at 50 °C, the reaction is terminated, and all free acids are neutralized with the addition of 1.4 g of sodium acetate dissolved in a mixture of 24 mL of methanol and 1.2 mL of water. It is noted that the free acid copolymer is completely soluble in 1,2-DCE, while a marked turbidity change occurs with the addition of the sodium acetate solution. The polymer was subsequently filtered and the sodium-neutralized ionomer isolated by stream stripping. This latter process lasts 60 min. The sulfonated polymer was vacuum-dried for 24 h at 100 °C. The sulfur content was determined by Dietert sulfur analysis and was used to calculate the sulfonation level. In this specific procedure, the sulfonate content was 1.18 mol % (0.36 wt ; sulfur).

Xylene solutions containing the above-described copolymer were prepared at room temperature with a conventional magnetic stirring apparatus. In all instances, clear "gel-free" solutions were obtained between 15 and 30 min depending on the polymer level.

Low-shear-rate viscosity measurements (25 °C) were performed on a Contraves low shear 30 instrument with the low-shear-rate data extrapolated to zero-shear-rate conditions or a Brookfield viscometer (Model LVT) utilizing a UL adapter for low-viscosity measurements and various size spindles for the higher viscosity solutions. These latter viscosity values correspond to 0.2 s^{-1}. Shear-rate-dependent viscosity measurements (25 °C) were performed on a Haake CV-100 viscometer using ME type couette cells.

A computerized Brookhaven Instrument Model BI-2030 goniometer with a digital correlator was used for quasi-elastic light

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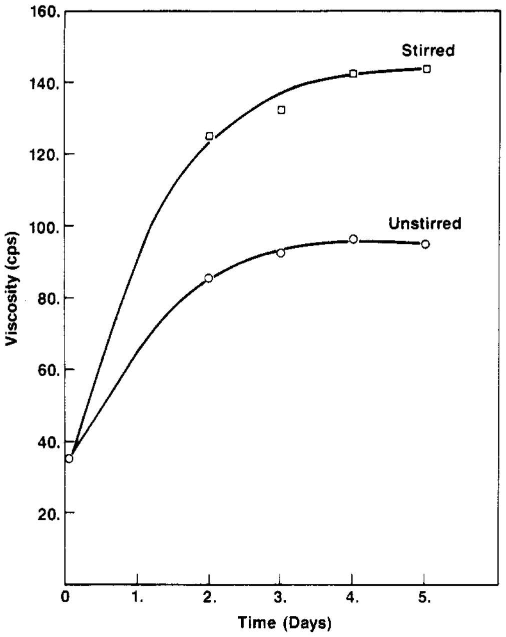

Figure 1. Viscosity–time profiles of a 3.0 g/dL sodium-neutralized sulfonated polystyrene ionomer (1.18 mol %) in xylene: (○) continuously stirred during storage; (□) quiescent conditions after a 2-h stirring period.

scattering (QELS) measurements (25 °C). The data presented here were all obtained at 90 ° scattering angle. The light source was a Spectra Physics Model 124B He–Ne laser operated at 35-mW power at 632.8 nm. The photon correlation function was fitted to a single-exponential function utilizing the half-width of the distribution of scattered electric field frequencies. This is subsequently used to determine tthe diffusion coefficient, which, in turn, is used to calculate the hydrodynamic radius from the well-known Stokes–Einstein relationship.

Results and Discussion

Results obtained with sodium sulfonate ionomers reveal complex solution behavior due primarily to the dielectric constant (ϵ) of the solvent.[3] Relatively complete counterion dissociation from the vicinity of chain backbone occurs in high-ϵ environments, while ion pair formation dominants low-ϵ solvents. This, of course, is a direct consequence of the strength of interaction which is inversely related to ϵ. However, only a single-component solvent possessing ϵ values of 7.4 (i.e., tetrahydrofuran (THF)) have been explored in a systematic manner. In this particular solvent, rapid dissolution kinetics are found. Further lowering of the value of ϵ results in a dissolution behavior illustrated in Figure 1 (xylene, ϵ = 2.4).

Contrary to the rapid dissolution of the ionomer into THF, markedly slower kinetics are found in xylene. Although conventional, low-shear-rate stirring enhances the dissolution process, "complete solubilization" takes place only over an extended period of time. Stirring simply increases the dissolution kinetics and the viscosity value at sufficiently long times.

Parallel behavior is observed at higher ionomer levels (Figure 2).

It is quite apparent in view of the previously described aggregation phenomena (light and neutron and scattering results) that the initially large aggregates are transformed into increasingly smaller entities. At the present time, it is not known whether the individual coils disengage from the aggregates, subsequently re-forming smaller aggregates (with some remaining individually dispersed), or simply the large aggregates disintegrate directly into smaller entities, or a combination of both mechanisms occurs. Since it is difficult to envision a cooperative process involving multichain disentanglement motions, the first mechanism suggested above is preferred from a simple probability viewpoint. Whatever the chain redistribution mechanism, the overall result is an increase in the fluid viscosity since the larger number of smaller aggregates and individualized ionomer chains will perturb the flow stream lines within the fluid to a greater extent than the much smaller number of larger aggregates due to the formation of a more uniform ionically associating pseudo network structure.

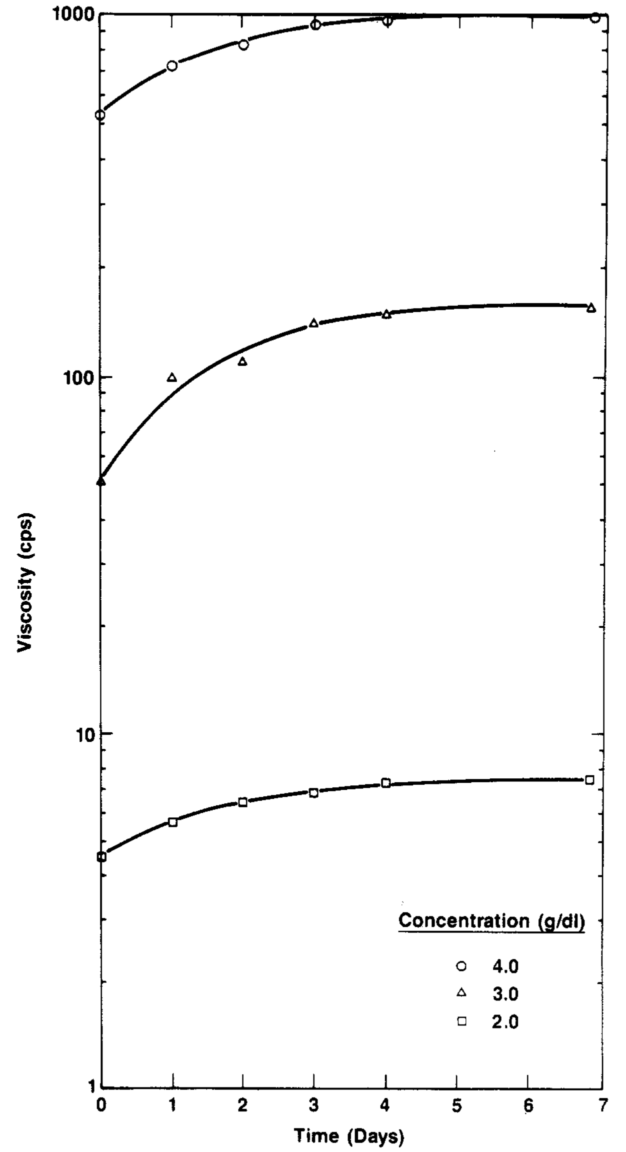

Figure 2. Viscosity–time relationships of a 2.0 (□), 3.0 (△), and 4.0 g/dL (○) Na–SPS ionomer (1.18 mol %) in xylene. The solution was unstirred after a 2-h stirring period.

Dissociation of large aggregates into smaller entities is clearly observed in the QELS measurements as presented in Figure 3. These results follow the corresponding increase in viscosity shown in Figure 2 (lower curve).

An additional aspect of this study is the dependence of solution properties on shear rate. The previously described data were obtained at a low shear rate (0.2 s^{-1}) or were extrapolated to zero shear rate. A dramatic rise in viscosity occurs as the shear rate is increased. This shear rate effect is superimposed on the kinetics for the aggregate dissociation process as shown in Figure 4. The shear thickening demonstrated in Figure 4 starts at lower shear rates for longer dissociation times. It is known[13] that increasing the ionomer concentration substantially reduces the shear rate

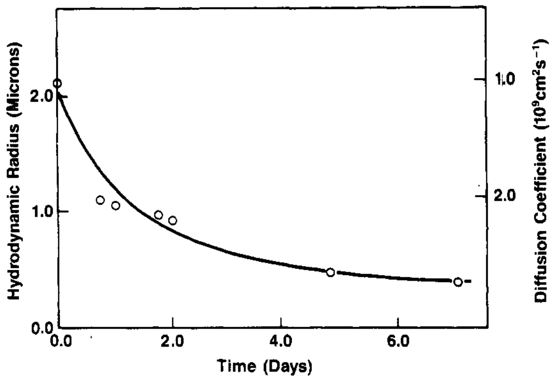

Figure 3. Hydrodynamic radius (and diffusion coefficient) of a 2.0 g/dL Na–SPS ionomer (1.18 mol %) in xylene as a function of time. The solution was stirred for 2 h and then remained unstirred.

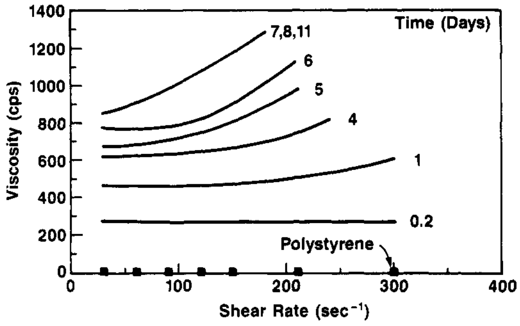

Figure 4. Viscosity–shear rate–time profiles of a 4.0 g/dL Na–SPS ionomer (1.18 mol %) in xylene. A polystyrene solution (4 g/dL) is shown for comparison purposes. These solutions were not stirred during storage.

for the onset of shear thickening. Therefore, this observation parallels the increased dissolution of the aggregates at the longer times. Our measurements also confirmed that unfunctionalized polystyrene and its ionomeric counterparts exhibit no time dependencies or shear thickening in a less nonpolar solvent, tetrahydrofuran (ϵ = 7.4), under identical experimental conditions. Furthermore, the viscosity in the xylene solutions rises very rapidly into a gel state with increased shear rate. This process is completely reversible upon release of the shear stress. Figure 4 also confirms the dissolution kinetics presented in the previous figures, where dissolution seems to be virtually complete after approximately 7 days.

The appearance of a gel at high shear rates indicates that the aggregates have linked into a three-dimensional network. A highly probable mechanism for this occurrence is the conversion of some intraaggregate to interaggregate ionic associations. This would result in a gellike structure if the interaggregate associations spanned a substantial portion of the solution. This is, of course, anticipated to occur in a more facile manner at longer dissociation times, as is observed. Therefore, aggregate formation and aggregate dissociation can simultaneously occur under appropriate experimental conditions.

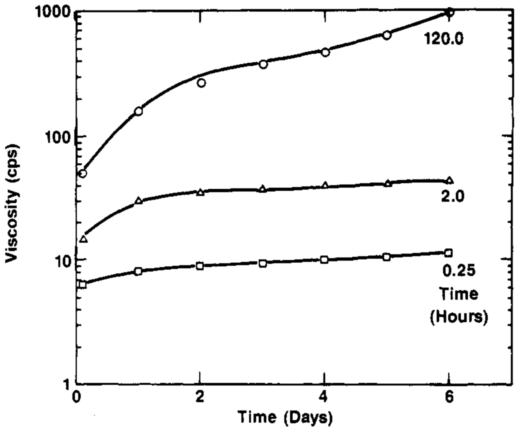

Figure 5. Influence of freeze-drying a stirred 3.0 g/dL xylene solution on the viscosity–time profiles of a Na–SPS ionomer (1.18 mol %). The initial ionomer solution was agitated for (□) 0.25, (△) 2.0, and (○) 120 h prior to freeze-drying.

Finally, a significant degree of control over the aggregate dissociation process is attained with conventional (i.e., solid carbon dioxide) freeze-drying of the ionomer solutions (and melts[14]) "aged" to varying degrees. Typical data are shown in Figure 5. These solutions were prepared directly from the synthesized ionomer powder which was added directly to xylene for a predetermined time and freeze-dried. The resulting freeze-dried powder was subsequently added again into xylene under agitation and the viscosity measured. At an equivalent ionomer concentration of 3 g/dL, long dissolution times produce the expected viscosity rise, although somewhat higher values are noted. Increasingly short times produce dramatically lower viscosity values. For example, a reduction of about 2 orders of magnitude occurs at 0.25 h. This viscosity reduction and the accompanying very slow dissociation kinetics are not presently understood. However, it is quite apparent that freeze-drying at short dissolution times produces a marked reduction in the aggregate dynamics and possibly structure. A clearer picture will undoubtedly emerge by utilizing such techniques as quasi-elastic light scattering, neutron spin-echo, and small-angle neutron scattering.

Conclusion

These rheological and quasi-elastic light scattering studies of a sodium-neutralized sulfonated polystyrene in a low dielectric constant solvent verify the unexpected time and shear-rate dependencies of these interesting associating-type polymers. In conjunction with the recent small-angle neutron and light scattering measurements on similar ion-containing polymers, a mechanism for this unique behavior can be qualitatively understood. Although the individual ionomer coils retain, to a good approximation, their unperturbed dimensions, multichain aggregates are formed even in very dilute solution. The dissociation of these aggregates with time and their reaggregation under shear profoundly influence rheological properties. This latter effect may be directly attributed, in part, to the conversion of some intraaggregate associations to interaggregate linkages forming a three-dimensional network, i.e., a gel. This process reverses with removal of the shear stress. Finally, freeze-drying of these nonpolar solutions under specific conditions produces a marked reduction in the aggregation dynamics. Although the changes in rheological properties are substantial and controllable, the underlying mechanism for this behavior remains a matter of speculation at the present time. Further structural, rheological, and scattering studies are currently in progress and will be reported in the near future.

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Osmotic Second Virial Coefficient and Two-Parameter Theories

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ABSTRACT: Literature data on polystyrene in toluene show that the molecular weight dependence of the interpenetration function, Ψ, does not follow the dependence on chain expansion factor, α_s, that would be predicted by two-parameter theory for Gaussian chains; there is an increase of Ψ at low molecular weight which can be explained by the non-Gaussian dependence of chain dimensions on M caused by local chain stiffness. A different kind of deviation from two-parameter theory is seen under Θ-solvent conditions: for polystyrene in cyclohexane at the Θ-temperature, second virial coefficients at low M do not vanish and can be rationalized as due to three-body interactions within the overlap region of two polymers.

Small Molecular Weights in Good Solvents

Interactions in dilute solutions of flexible high polymers are often discussed in terms of the interpenetration function,[1] Ψ. This dimensionless quantity is defined in relation to the osmotic second virial coefficient, A_2 (for two identical chains), by

$$\Psi = (A_2M^2/4\pi^{3/2}N_A\langle S^2\rangle^{3/2}) \tag{1}$$

where M is the polymer molar weight, $\langle S^2\rangle$ the mean square radius of gyration, and N_A Avogadro's number. Several approximate expressions[2] have been derived for Ψ as a function of the excluded volume parameter.

$$z = \left(\frac{3}{2\pi a^2}\right)^{3/2}\beta n^{1/2} \tag{2}$$

Here β is the binary cluster integral and n the number of statistically independent segments of effective bond length, a. The so-called two-parameter theories[3] based on the Gaussian chain model involve the only combinations na^2 and $n^2\beta$, where n is proportional to M.

It is well-known that z cannot be determined directly by experiment. However, the experimentally accessible expansion coefficient, α_s, for the rms radius of gyration can also be expressed as a function of z. Therefore, a plot of $\Psi(z)$ vs. $a_s(z)$ eliminates z and provides a valuable test for two-parameter theories. As is the case for $\Psi(z)$, several theoretical approximations are available[4-7] for α_s as a function of z. It is important to find self-consistent pairs of functions $\Psi(z)$ and $\alpha_s(z)$. Though several papers[8-13] deal with this test of the two-parameter theories, it appears helpful to add further comments.

As one example, the treatments according to Kurata et al.,[14] Yamakawa,[15] and Yamakawa and Tanaka[16] give the relations

$$\alpha_s^2 = 0.541 + 0.459(1 + 6.04z)^{0.45} \tag{3a}$$

$$\Psi = 0.547[1 - (1 + 3.903z/\alpha_s^3)^{-0.468}] \tag{3b}$$

These equations, like other combinations, yield reasonable agreement with many experimental results[9,10] but only under certain circumstances, as will be seen below. We do not suggest that they should necessarily be preferred to other such combinations.

Apart from numerical differences, all but two[17a,b] of the approximate theories of Ψ yield monotonically increasing functions of z. In the limit of high z, they attain constant values. This behavior has been confirmed only by experiments with relatively high molecular weight samples, in which the excluded volume parameter, $z(\alpha_s)$, was varied by *changing the temperature*.[9,10,18] An example, Figure 1 represents such measurements by Berry[18] with different polystyrene (PS) samples in *trans*-decalin.

In good solvents, a limiting plateau value is also found experimentally for high molecular weights.[18-23] According to eq 3b, the limiting value is 0.547, which is significantly larger than any experimental data, available in the high z range. However, more recent theoretical predictions, 0.231 by Oono and Freed[24] and 0.268 by Witten and Schäfer[25], are in closer agreement with experiment. The crucial point here is that the shape of $\Psi(\alpha_s)$ is completely different from that of Figure 1. This is seen in Figure 2, which represents Ψ isothermally over a wide range of α_s^3 for PS in the good solvent toluene and employs several sets of literature data.[21-23,26] In this case, z is varied at constant β by *changing the molecular weight*.

This behavior has already been mentioned by Miyaki[19] et al. We offer further evidence from small-angle neutron scattering experiments[21,27] with four very low molecular weight PS samples in toluene-d_8 and cyclohexane-d_{12}. These provide us with the complete set of data necessary to calculate Ψ and α_s essentially down to the limit $\alpha_s \to 1$. For the other literature data,[22,23,26] $\langle S^2\rangle$ values for unperturbed PS were calculated with the equation of Benoit

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