High-Pressure Viscosity of an Associating Polymer System: Zinc Sulfonated Polystyrene/Poly(styrene–4-vinylpyridine) Copolymer Solution

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ABSTRACT: Measurements made on nonassociating polystyrene-based polymers in tetrahydrofuran, THF, reveal that the intrinsic viscosity $[\eta]$, remains virtually constant with increasing pressure from 0 to 20 kbar. An associating polymer system of a 1:1 blend of zinc sulfonated polystyrene and poly(styrene–4-vinylpyridine) copolymer in THF shows a decrease in $[\eta]$ not seen in the nonassociating analogues. In addition, the associating system shows an unusual, abrupt, reversible rise in viscosity as pressure is increased to ca. 2 kbar and the viscosity exhibits a slow pressure response ($\approx$30 min equilibrium times) at this pressure, seemingly indicating some type of cooperative effect. We attribute both the pressure-induced decrease of $[\eta]$ and this abrupt viscosity rise to pressure-driven changes in the degree of association. We apply the Flory equation to model the high-pressure behavior of $[\eta]$ on changing effective molecular weight; we find that, for the 1.0 g/dL system, M_{eff} decreases by $\approx$29% from ambient pressure to 10 kbar. The abrupt viscosity rise corresponds to a $\approx$10% increase in M_{eff} at 2 kbar. When the concentration is reduced from 1.0 to 0.5 g/dL, the abrupt viscosity rise is eliminated and the decline in the effective molecular weight is diminished.

Introduction

Understanding the molecular basis of pressure-induced viscosity changes is a long-standing problem of both fundamental and practical interest. For simple, hard-sphere liquids much of the essential molecular architecture can be captured in the "free volume" of the fluid.[1] More complex molecular shapes and intermolecular interactions are difficult to treat rigorously, but the high-pressure viscosity of these systems can often be approximated by modification of the hard-sphere model such as is done in the rough-hard-sphere model.[2] For polymer solutions we have no clear understanding of how the high-pressure viscosity changes are related to molecular configurations. At least one reason for this is a lack of experimental studies from which to draw generalizations.

Associating polymers are among those most likely to exhibit significant viscosity effects connected with a pressure-induced configuration change. It is well-known that the incorporation of small amounts of ionic groups, typically <10 mol %, in a polymer chain has a profound influence on solution and bulk properties.[3,4] Depending upon the level of ionic functionality and counterion type, the ionic groups aggregate and can form a relatively strong network structure. As a result, these associating-type polymers have a variety of enhanced physical properties. These phenomena are both scientifically intriguing and technologically useful. The solution properties are of particular interest since the rheology of the fluid is now strongly modified through changes in the degree of association, and this can be controlled through manipulation of the chemical makeup of the polymer. Marked viscosity enhancements with an increase in polymer concentration, temperature, and shear rate, i.e., shear thickening, have been observed.

One would expect these associations to also be pressure dependent. An analogous system has already demonstrated that pressure-induced association changes can lead to unusual viscosity behavior. Water at $T < 15$ °C exhibits a *decreasing* viscosity with increasing pressure which is attributed to the breakup of the hydrogen-bonded associations present at ambient pressure.[5] The driving force for this breakup comes from a PV contribution to the free energy. In terms of molecular arrangements one can envision this as a competition between two effects. Hydrogen-bonded associations favor particular local coordinations, and we can conclude from the well-known phenomena of ice expanding upon freezing that these local ordering effects favor a low-density, open structure. Nondirectional closest packing effects, of course, favor high density. In associating polymer systems we can expect the same sort of competition between local ordering and packing effects, but it is difficult to estimate their relative contribution to the PV energy term. We do not have an equivalent bulk phase to examine such as we do for water. The experiments described here demonstrate that applied pressures do indeed affect the associations. Through such experiments we can gain a greater understanding of the energetics driving the formation of polymer associations. In addition, data on the viscosity variation with pressure are useful in technical applications where such polymers are used under high-pressure conditions.

The few previous studies on polymer solutions under pressure have been limited to nonassociating systems. These workers[6–8] have found a small increase in the specific viscosity with increasing pressure over the limited range of the studies (0–1 kbar). However, the small pressure range of these studies makes it difficult to interpret the meaning of this behavior. The data reported here were taken with a new diamond-cell viscometer[9] which allows a much wider range of investigation (0–20 kbar), limited only by the crystallization pressure of THF.

Materials

Our experiments were performed on tetrahydrofuran (THF) solutions of zinc sulfonated polystyrene (ZnSPS) and poly(styrene–4-vinylpyridine) (PSVP).[10,11] We studied solutions containing ZnSPS and PSVP individually and mixed 1:1 by weight (AP). The solutions ranged in concentration from 0.5 to 2 g/dL. At concentrations above $\approx$0.75 g/dL the 1:1 solutions exhibit a viscosity enhancement over the individual polymer solutions (Figure 1) indicating a relatively strong association between the two polymers. To aid in interpreting the influence of the

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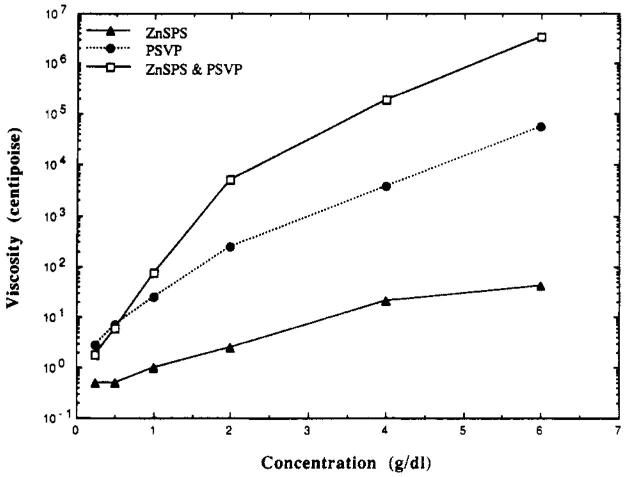

Figure 1. Concentration dependence of the viscosity of ZnSPS, PSVP, and 1:1 ZnSPS/PSVP in THF. Measurements were taken at a shear rate of 0.2 s^{-1}. Note the crossover in the 1:1 viscosity at ≈0.75 g/dL showing the importance of associations at higher concentrations.

association, we also measured THF itself and a THF/monodispersed polystyrene (PS) solution (M_w = 300 000, M_w/M_n = 1.06, obtained from Pressure Chemical Co., Pittsburgh, PA).

The ZnSPS was prepared by neutralizing a sulfonated polystyrene, prepared by sulfonating a commercial polystyrene (PS) (Styron 666, Dow Chemical Co.), with zinc. It had an intrinsic viscosity of 1.1 dL/g in xylene at 25 °C, giving an approximate viscosity-average molecular weight of 300 000. The nominal sulfonation level was 1.4 mol % as determined via sulfur analysis (0.42 wt %). Neutralization was accomplished with zinc acetate. An excess of neutralization agent was used in order to ensure complete neutralization of all sulfonic acids present.

The PSVP copolymer was prepared through the emulsion copolymerization of styrene and 4-vinylpyridine using potassium persulfate as the initiation agent, sodium lauryl sulfate as the surfactant, and dodecylthiol as the chain-transfer agent. The weight- and number-average molecular weights as determined by gel permeation chromatography in THF were 1 670 000 and 930 000, respectively. (The polydispersity index was 1.8, and the M_v was calculated to be 1 500 000.) The vinylpyridine content was 8.55 mol % based on nitrogen analysis (1.15 wt %).

Experimental Section

The viscosity measurements were made by recording the velocity of a falling ball inside a diamond anvil cell. A full report describing this device will be published elsewhere,[9] and only a brief description is given here. The pressure chamber consists of a 500 μm diameter hole drilled in a 250 μm thick piece of stainless steel which is compressed between two flat diamond surfaces. The ball, a nickel alloy about 50 μm in diameter, is allowed to roll down the surface of one of the diamonds. A video camera relays the image of the ball to a video dimension analyzer (VDA) which returns a voltage proportional to the displacement of the ball. A computer makes periodic readings of the VDA output, thus giving displacement and time. The slope of the line thus obtained yields the velocity of the ball, which can be converted into viscosity (η) by a modified Stokes equation

$$\eta = \gamma[2R^2 g(\rho_s - \rho_f) \cos \theta]/9v \qquad (1)$$

where R = sphere radius, g = acceleration of gravity, ρ_s = sphere density (7.6 g/mL), ρ_f = fluid density, θ = tilt angle of the cell, v = velocity of the ball, and γ = wall correction.

All of the parameters in eq 1 can be measured directly except for the wall correction. This correction, expressed as a ratio between the observed velocity and that expected from Stokes drag, arises from the close proximity of the diamond surface. Our previous work has shown that γ can be calculated from a comparison of our ambient-pressure measurements with those from an independent determination of viscosity.[9]

Table I
Tetrahydrofuran (THF)

temp, °C	presure, kbar	density,[a] g/mL	viscosity,[b] P	error,[c] %
22.0	0.00	0.886	0.00479	3.2
22.3	1.55	0.973	0.00914	4.6
22.6	2.02	0.991	0.01261	2.9
22.8	3.20	1.030	0.02046	2.4
22.8	4.09	1.055	0.02771	2.5
23.0	5.84	1.097	0.04670	3.2
23.1	7.99	1.139	0.08461	2.9
23.2	10.56	1.182	0.15149	2.8
23.2	13.12	1.219	0.25677	3.2
23.3	16.85	1.265	0.53226	2.8
23.3	18.83	1.287	0.78745	2.9

[a] Calculated from the Birch–Murnaghan equation of state,[15] K_0 = 10.8 kbar, K_0' = 9.7. [b] $\eta = \gamma[2R_s^2 g(\rho_s - \rho_f) \cos \theta]/9v$; γ = 0.1285, R_s = 24 μm, ρ_s = 7.6 g/mL, tilt angle (θ) = 55°. [c] Calculated from 1σ standard deviation.

The above equation is, however, only strictly applicable to a Newtonian fluid, and we have noted in our current experiments an indication that shear thinning occurs. We find for one of the polymer solutions, 1 g/dL of ZnSPS/PSVP, an apparent wall correction greater than unity, clearly not physically possible since it would imply an observed velocity larger than the Stokes velocity. This is a result of shear thinning. The shear rate in our experiment can be approximated by taking the ratio of the forward velocity of the rolling ball (330 μm/s) to its distance from the wall (≈1 μm), giving a shear rate of ≈300 s^{-1}. Measurements made in a Couette viscometer showed that the polymer solution shear thins by a factor of 6.4 over the range of 0.2–300 s^{-1}. This reduces the γ of 2.688 to 0.42, an entirely reasonable value. However, this shear thinning is unimportant in the following high-pressure measurements for two reasons. First, data taken on polymer–oil solutions show that the pressure variation of the viscosities at 300 s^{-1} and those at low shear are essentially identical.[12] Second, the total variation of viscosity with shear rate is only a small percentage (2%) of the total viscosity variation with pressure.

One should note that this concept of shear in our experiment is a simplified approximation to the actual shear effects in such a rolling-ball geometry. Even if a full description of the simple shear response of the fluid were available, a complete rheological constitutive relation (the form of which is at present unknown) is needed to obtain a unique solution of the resulting velocity field surrounding the sphere.[13]

The pressure in the diamond cell is calibrated by use of the ruby fluorescence peak, λ = 694.26 nm at ambient pressure, which shifts in frequency under pressure.[14] The measurements on the polymer solutions were in the 0–20 kbar range, with many interesting results occurring around 1 kbar. Diamond-cell experiments in such a low-pressure range are a technical challenge, and we have devised some specialized techniques. Data taken on materials with known η vs p behavior confirm the accuracy of our data in this region.[9]

Results and Discussion

Tables I–VI list the high-pressure viscosity data. As the density of the fluid changes under pressure, the buoyancy term (represented by ($\rho_s - \rho_f$) in the Stokes

Table II
Monodispersed Polystyrene (1 g/dL in THF, MW = 300 000)

temp, °C	pressure, kbar	density,[a] g/mL	viscosity,[b] P	error,[c] %
22.6	0.00	0.893	0.0142	3.8
21.5	1.96	0.997	0.0416	4.6
21.8	9.14	1.168	0.3527	3.0
22.0	17.18	1.279	2.1719	3.1
22.1	3.70	1.053	0.0733	4.1
22.0	13.32	1.231	1.0084	2.6
22.0	0.00	0.893	0.0146	8.2
22.0	0.81	0.946	0.0229	3.4
22.3	1.19	0.965	0.0263	2.2
22.2	2.82	1.027	0.0530	3.3

[a] Calculated from the Birch–Murnaghan equation of state;[15] K_0 = 10.8 kbar, K_0' = 9.7. [b] $\eta = \gamma[2R_s^2g(\rho_s - \rho_f)\cos\theta]/9v$; γ = 0.1588, R_s = 25 μm, ρ_s = 7.6 g/mL, tilt angle (θ) = 45°. [c] Calculated from 1σ standard deviation.

Table III
Zinc Sulfonated Polystyrene (1 g/dL in THF)

temp, °C	pressure, kbar	density,[a] g/mL	viscosity,[b] P	error,[c] %
23.3	0.00	0.893	0.01000	7.5
23.1	0.38	0.921	0.01149	4.9
23.1	0.99	0.955	0.01895	2.0
22.8	2.64	1.021	0.03851	3.9
22.9	4.00	1.061	0.06369	2.4
23.0	6.28	1.115	0.11824	0.8
23.0	11.15	1.200	0.35748	3.1
23.1	11.90	1.211	0.39499	3.5
23.0	14.90	1.251	0.79743	3.2
23.0	16.32	1.269	1.01065	3.4
23.0	18.73	1.296	2.00519	2.9
23.0	4.66	1.078	0.07075	1.6
22.5	0.70	0.940	0.01526	7.2

[a] Calculated from the Birch–Murnaghan equation of state;[15] K_0 = 10.8 kbar, K_0' = 9.7. [b] $\eta = \gamma[2R_s^2g(\rho_s - \rho_f)\cos\theta]/9v$; γ = 0.1538, R_s = 22.5 μm, ρ_s = 7.6 g/mL, tilt angle (θ) = 15°. [c] Calculated from 1σ standard deviation.

Table IV
Poly(styrene–4-vinylpyridine) Copolymer (1 g/dL in THF)

temp, °C	pressure, kbar	density,[a] g/mL	viscosity,[b] P	error,[c] %
22.3	0.00	0.893	0.2172	1.2
22.5	0.47	0.926	0.3154	1.2
22.8	6.10	1.111	4.4096	1.4
22.9	10.90	1.196	16.7375	1.2
22.9	19.44	1.304	112.3201	3.0
22.9	7.80	1.145	7.1729	1.0
21.8	0.00	0.893	0.2400	1.8
21.9	0.16	0.905	0.2682	2.5
22.0	0.33	0.917	0.2835	2.8
22.2	0.84	0.947	0.4060	1.8
22.3	1.13	0.962	0.4778	2.3
22.5	1.65	0.985	0.5764	1.8
22.6	1.93	0.996	0.7187	1.3
22.6	2.61	1.020	1.0713	0.9
22.7	3.40	1.044	1.4719	0.7

[a] Calculated from the Birch–Murnaghan equation of state;[15] K_0 = 10.8 kbar, K_0' = 9.7. [b] $\eta = \gamma[2R_s^2g(\rho_s - \rho_f)\cos\theta]/9v$; γ = 0.4081, R_s = 21 μm, ρ_s = 7.6 g/mL, tilt angle (θ) = 55°. [c] Calculated from 1σ standard deviation.

Table V
1:1 ZnSPS/PSVP Polymer Mixture (0.5 g/dL in THF)

temp, °C	pressure, kbar	density,[a] g/mL	viscosity,[b] P	error,[c] %
21.8	0.00	0.893	0.0580	1.7
21.8	0.29	0.915	0.0675	2.5
22.0	0.50	0.928	0.0759	2.3
22.1	0.75	0.942	0.0823	1.0
22.1	1.44	0.976	0.1162	2.4
22.2	1.82	0.991	0.1452	1.7
22.3	2.38	1.012	0.1750	0.9
22.3	3.11	1.036	0.2535	0.9
22.3	6.60	1.121	0.9459	2.7
22.3	8.84	1.163	1.6424	3.2
22.6	12.46	1.219	4.2976	2.5
22.6	16.18	1.267	8.4477	2.3
22.7	19.86	1.308	25.3633	7.1

[a] Calculated from the Birch–Murnaghan equation of state,[15] K_0 = 10.8 kbar, K_0' = 9.7. [b] $\eta = \gamma[2R_s^2g(\rho_s - \rho_f)\cos\theta]/9v$; γ = 0.5035, R_s = 25.5 μm, ρ_s = 7.6 g/mL, tilt angle (θ) = 15°. [c] Calculated from 1σ standard deviation.

Table VI
1:1 ZnSPS/PSVP Polymer Mixture (1 g/dL in THF)

temp, °C	pressure, kbar	density,[a] g/mL	viscosity,[b] P	error,[c] %
22.0	0.00	0.893	0.6802	4.0
22.0	0.26	0.913	0.8879	5.5
22.2	0.44	0.924	0.8945	2.7
22.3	0.56	0.932	0.9913	4.1
22.3	0.62	0.935	0.9908	5.2
22.4	0.68	0.939	1.0364	2.4
22.4	0.71	0.940	1.0876	2.5
22.4	0.76	0.943	1.0926	4.0
22.6	0.89	0.950	1.1294	5.0
22.6	1.01	0.956	1.1852	1.8
22.2	1.15	0.963	1.6517	2.6
22.3	2.31	1.009	2.6412	1.8
21.8	0.00	0.893	0.7056	4.1
22.3	1.82	0.991	2.3120	3.5
22.6	4.83	1.082	5.9276	4.2
22.7	5.48	1.097	7.5773	2.9
22.7	7.27	1.135	13.0449	2.1
22.1	8.50	1.157	18.8717	2.4
22.7	10.57	1.191	30.1987	4.1
23.0	11.87	1.211	44.2113	3.3
22.9	16.25	1.268	115.4082	4.4
23.0	18.60	1.295	219.3095	5.1
22.0	19.55	1.305	274.8465	4.2
22.8	17.23	1.279	128.7662	5.0
23.0	3.21	1.039	3.4098	3.8
22.1	0.00	0.893	0.6329	5.1
23.0	3.36	1.043	3.5383	3.5
22.8	1.98	0.998	2.3820	5.3
22.0	1.22	0.966	1.6725	1.4

[a] Calculated from the Birch–Murnaghan equation of state;[15] K_0 = 10.8 kbar, K_0' = 9.7. [b] $\eta = \gamma[2R_s^2g(\rho_s - \rho_f)\cos\theta]/9v$; γ = 2.688, R_s = 24.5 μm, ρ_s = 7.6 g/mL, tilt angle (θ) = 15°. [c] Calculated from 1σ standard deviation.

equation, eq 1) changes. The calculated viscosity in these tables accounts for this effect, with the density of the fluid being calculated from the Birch–Murnaghan equation of state[15] using data for THF from the literature.[16] For the polymer solutions their compressibility was taken as equal to that of the solvent which is a good approximation for these low polymer concentrations. The relative incompressibility of nickel made it unnecessary to correct the sphere density for pressure effects. The absolute viscosity is calculated using a wall correction, obtained as previously mentioned. These wall corrections are given as footnotes to the data tables. The errors in η/γ come from the variation observed in the sphere velocity. We typically measured 6–12 ball transverses of the pressure chamber at each pressure and from this data calculated the mean velocity and its standard deviation. These error estimates, which average about 1–4%, are given in the tables. The data are listed in the order in which the points were taken. These results are plotted in Figures 2 and 3. In Figure 3 we plot the relative viscosity, the high-pressure viscosity divided by the ambient-pressure viscosity. There is a definite advantage in using such a ratio. The actual values of the wall correction and ball radius become unimportant, and any uncertainty in the fluid density only weakly affects

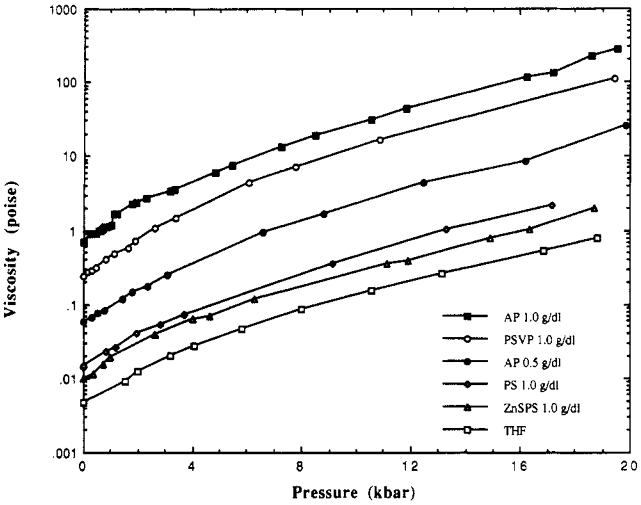

Figure 2. Absolute viscosities for all the solutions studied. A curvilinear viscosity vs pressure curve is typical for simple fluids when viewed over a wide pressure range. Nonassociating polymer solutions have the same shape as the solvent, but associating solutions deviate. See text for details.

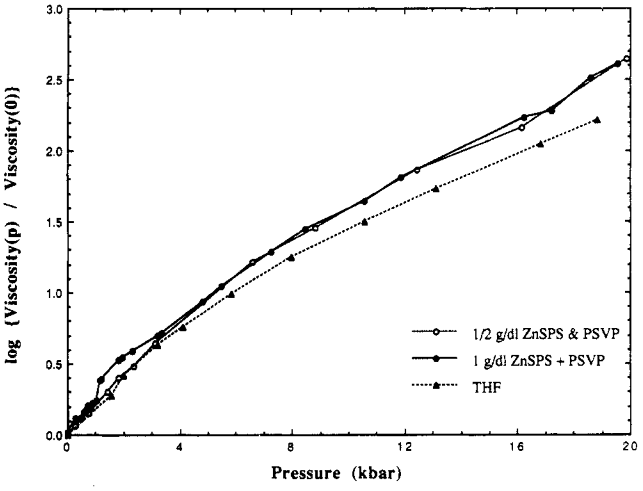

Figure 3. Abrupt viscosity rise between 1 and 3 kbar for 1.0 g/dL 1:1 ZnSPS/PSVP (AP) which disappears for a 0.5 g/dL concentration. Viscosities are shown relative to ambient-pressure viscosity.

the relative viscosity.[9]

Figure 1 shows the ambient-pressure viscosity of the polymer solutions. The associating polymer samples selected for high-pressure studies were 0.5, 1, and 2 g/dL, which, as can be seen in Figure 1, span the region where the onset of associations begin to influence the viscosity. We studied the nonassociating polymer components at 1.0 g/dL to provide a direct comparison.

Tetrahydrofuran (Table I) was chosen as the solvent for this experiment for two reasons: First, it has a quite high equilibrium freezing pressure determined to be 14.2 kbar at 22 °C. In addition it can be raised to a pressure of ca. 20 kbar without crystal nucleation. Many other common solvents freeze at a lower pressure. Second, it has a relatively slow viscosity change with respect to pressure (see Figure 2). THF displays a distinct curvature on a semilog plot of viscosity vs pressure typical of high-pressure viscosity for simple fluids when measured over a wide pressure range.[17]

Initial experiments sought to establish the behavior of nonassociating solutions. We measured THF itself and solutions of PS, PSVP, and ZnSPS, each at a concentration of 1 g/dL. Figure 2 shows the viscosity of all the solutions

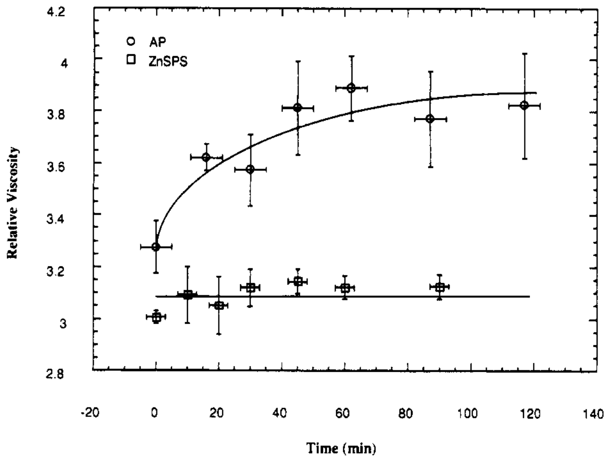

Figure 4. Equilibrium time after a pressure increase from 0 to 2 kbar. Note that approximately 30 min is required for equilibration of viscosity for 1:1 ZnSPS/PSVP (AP) at pressures near the viscosity jump. The nonassociating polymer shows no time dependence.

reported here. The nonassociating polymer solution curves have shapes nearly identical to those of the THF curve except for an offset resulting from their higher ambient-pressure viscosity. All of the data reported here were completely repeatable with respect to increasing and decreasing pressure, indicating that the high pressures do not in some manner irreversibly alter the polymer-chain structure. We would expect the 1.0 g/dL 300 000 M_v ZnSPS viscosity to be essentially the same as the 1.0 g/dL 300 000 M_v PS viscosity in the absence of interactions. The fact that the ZnSPS viscosity is slightly lower can be explained by intramolecular associations leading to denser polymer coils and aggregates.[18-22] The higher viscosity for PSVP is, in part, attributable to its 5-fold greater molecular weight. However, as explained below, the concentration is greater than c^* while ZnSPS and PS are at or below c^*.

The associating 1:1 ZnSPS/PSVP solution data (AP) show two types of behavior. At a concentration of 0.5 g/dL (Table V), its ambient-pressure viscosity lies between the viscosity of its components (PSVP and ZnSPS, Figures 1 and 2) and the trend of the pressure dependence is similar to those of the nonassociating polymers. However, at 1.0 g/dL (Table VI) the ambient-pressure viscosity exceeds that of its components (due to intermolecular associations) and the pressure dependence displays an unusual abrupt rise. The onset for this is just over 1 kbar, and the total increase is by about a factor of 2. This is better seen in Figure 3. This behavior is completely repeatable in both increasing and decreasing pressure.

In addition to this viscosity rise the AP solution exhibits an unusual long-time equilibration. This is shown in Figure 4. The pressure was quickly incremented from zero to ≈2 kbar, and viscosity was measured as a function of time. For the 1:1 copolymer solution, there is a distinct rise of viscosity with time which is not observed for the individual ZnSPS polymer solution. It appears that it takes 30–45 min for the 1:1 copolymer solution to reach its equilibrium value of the viscosity. Both solutions have approximately the same bulk viscosity; thus, individual molecular diffusion times should be similar. Therefore, it seems likely that the viscosity rise with time arises from some type of cooperative effect such as could come from polymer associations. It is well-known that shear thickening, a similar cooperative effect, can take several minutes to appear.[19] It should be noted that all of the viscosity values given in this study are steady-state values. In cases

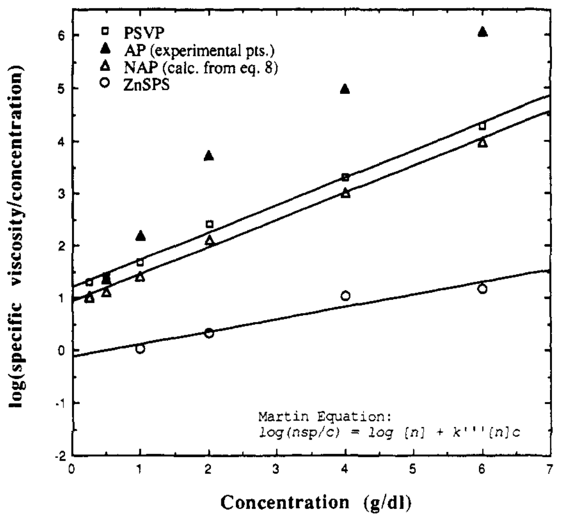

Figure 5. Martin equation used to calculate $[\eta]$ from η_{sp}. Values obtained are $[\eta]_{ZnSPS} = 0.7472$ dL/g, $[\eta]_{PSVP} = 16.05$ dL/g, and $[\eta]_{NAP} = 8.224$ dL/g.

where relaxation could be important, a period of at least 30 min from pressure change to data collection was allowed.

We attempted to run the associating polymer solution at a concentration of 2 g/dL and observed gellike or glassy behavior that prevented a determination of the viscosity. The origin of this effect is presently under investigation.

Intrinsic Viscosity and Effective Molecular Weight. Polymer solutions are usually described in terms of the intrinsic viscosity in order to separate the effect of the polymer on the viscosity from that of the solvent. Intrinsic viscosity is defined as

$$\eta_{rel} = \eta/\eta_0 \tag{2}$$

$$\eta_{sp} = \eta_{rel} - 1 \tag{3}$$

$$[\eta] = \lim_{c \to 0} (\eta_{sp}/c) \tag{4}$$

where η = solution viscosity, η_0 = solvent viscosity, η_{rel} = relative viscosity, η_{sp} = specific viscosity, and $[\eta]$ = intrinsic viscosity. The intrinsic viscosity is calculated by extrapolating η_{sp}/c to zero concentration. Three commonly used methods of doing this are

Huggins equation[23] $$\eta_{sp}/c = [\eta] + k[\eta]^2c \tag{5}$$

Kraemer equation[24] $$\{\ln (\eta_{rel})/c\} = [\eta] + k[\eta]^2c \tag{6}$$

Martin equation[25] $$\log (\eta_{sp}/c) = \log [\eta] + k[\eta]c \tag{7}$$

Our η_{sp} vs c data (Figure 5) best fit the Martin equation. For PSVP the concentrations we used to calculate $[\eta]$ are higher than those normally used for Huggins plots; we are well above c^* for this molecular weight. Thus we are forced to use the Martin equation, and our extrapolation to zero concentration yields a higher $[\eta]$ than we would expect. However, it should be noted that, in the following discussion, it is not the absolute $[\eta]$ that is important; rather it is the way that $[\eta]$ varies with pressure that is relevant to our calculations.

For the associating ZnSPS–PSVP mixture, the highly curved behavior exhibited in Figure 5 clearly indicates that $[\eta]$ for that mixture cannot be obtained by such an extrapolation. This is consistent with the change in degree of association that occurs with changing concentration. Therefore, to obtain $[\eta]$ for a hypothetical, nonassociating ZnSPS–PSVP mixture (NAP), we assume that the total specific viscosity in such a mixture would be equal to the sum of the specific viscosity of the two components:

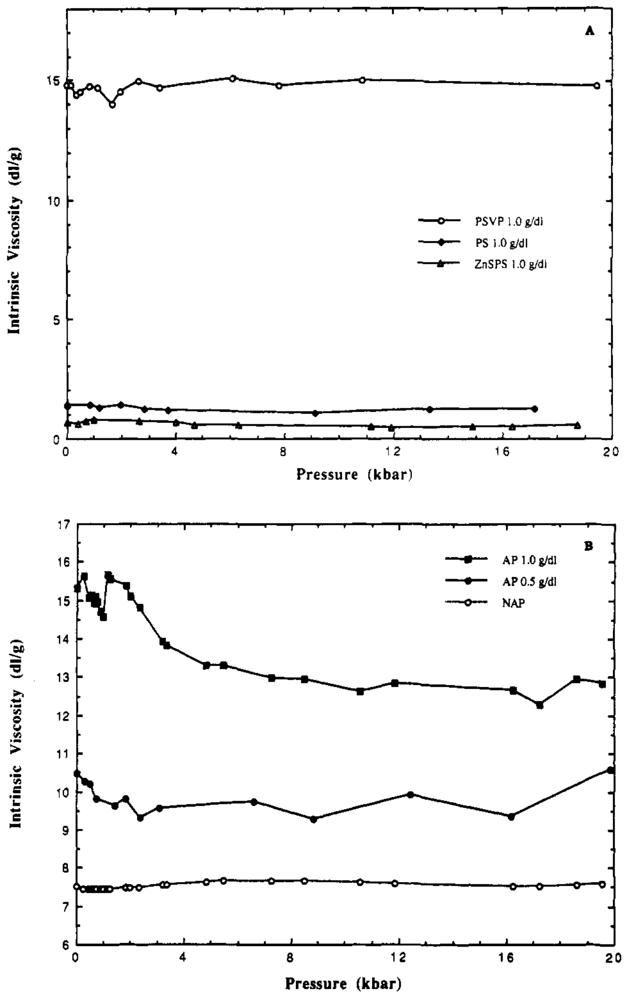

Figure 6. (A) Intrinsic viscosity for the nonassociating polymer solutions which is virtually independent of pressure after correcting the concentration for changing fluid density. (B) Intrinsic viscosity for the associating polymer solutions which declines with increasing pressure. In the 1.0 g/dL solution a sharp rise between 1 and 3 kbar is superimposed upon this trend.

$$\eta_{sp}^{NAP} = 1/2\eta_{sp}^{ZnSPS} + 1/2\eta_{sp}^{PSVP} \tag{8}$$

One would expect the η_{sp} for the actual associating polymer system (AP) to approach that for the NAP as $c \to 0$. Indeed, this is observed, suggesting that the assumption in eq 8 is valid and that the requirements for the calculation of $[\eta]$ are fulfilled. The Martin equation constants and corresponding values of $[\eta]$ calculated at ambient pressure are as follows: ZnSPS, $[\eta] = 0.7472$ dL/g and $k = 0.3161$; PSVP, $[\eta] = 16.05$ dL/g and $k = 0.032\,53$; NAP, $[\eta] = 8.224$ dL/g and $k = 0.063\,30$. We obtained values for PS from an analysis by Fetters[26] using the Huggins equation. These values are as follows: PS, $[\eta] = 1.5$ dL/g and $k = 0.36$.

Our next task is to calculate $[\eta]$ as a function of pressure. As η_{rel} contains both η and η_0 (both of which are functions of pressure), it is necessary to have the value of η_0 at the pressure of every data point for η. These were obtained by interpolation of the THF data. Thus we obtain $\eta_{sp}(p)$. $[\eta](p)$ is then calculated by substituting these $\eta_{sp}(p)$ values back into the Martin or Huggins equations using the previous, fitted constants (above) obtained at ambient pressure. (Of course, this assumes that the Martin or Huggins k remains constant with pressure, a reasonable assumption once concentration is adjusted for changing fluid density—see below.) For the individual ZnSPS and PSVP solutions, these were the experimentally derived values, but for the mixtures we used the Martin parameters based on the theoretical NAP η vs c behavior. All of these results are plotted in Figure 6A,B. Note that for nonassociating polymers $[\eta]$ is virtually independent of pressure.

We should comment here about the effect of pressure on concentration in the above calculations. As density changes with pressure, so does concentration when measured as mass/volume. Because we are using mass/volume as our units of concentration, we feel it is most appropriate to apply a concentration correction when calculating $[\eta]$ to account for the change of volume with pressure. This is most noticeable in the PSVP solution (whose concentration is well above c^*) which has an $[\eta]$ that increases by 25% with increasing pressure to 18 kbar when no concentration correction is applied but that remains virtually invariant when the correction is applied (Figure 6A). The $[\eta]$ calculations which follow include this concentration correction.

Flory has shown that for linear-chain polymers the intrinsic viscosity is dependent upon the radius of gyration and molecular weight of a dissolved polymer.[27]

$$[\eta] = \Phi'(\langle s^2\rangle)^{3/2}M^{-1} \tag{9}$$

$\Phi' = 6^{3/2}\Phi = 3.7 \times 10^{22}$ dL mol^{-1} cm^{-3}, with Φ = Flory constant, $\langle s^2\rangle^{1/2}$ = radius of gyration, and M = molecular weight. While Flory developed this equation for use under Θ conditions, Fetters has demonstrated its validity for PS in THF under good solvent conditions (25 °C). Using experimental values of $[\eta]$, M, R_G, and R_H and fitting the constants K and a, the following relationships were established:[26]

$$[\eta] = K\{R_G{}^3/M\}^a \tag{10}$$

$$K = 2.5 \times 10^{22}\ \text{dL mol}^{-1}\ \text{cm}^{-3} \qquad a = 0.998$$

$$[\eta] = K\{R_G{}^2R_H/M\}^a \tag{11}$$

$$K = 3.6 \times 10^{22}\ \text{dL mol}^{-1}\ \text{cm}^{-3} \qquad a = 1.018$$

where R_G = radius of gyration and R_H = hydrodynamic radius. As the values of a observed are close to unity, the validity of the Flory equation is established for PS in THF. The ambient-pressure values for $\langle s^2\rangle^{1/2}$ can be easily calculated from eq 9 given the molecular weights (ZnSPS = 300 000, PSVP = 1 500 000): $\langle s^2\rangle^{1/2}{}_{\text{ZnSPS}}$ = 182 Å, $\langle s^2\rangle^{1/2}{}_{\text{PSVP}}$ = 866 Å, and $\langle s^2\rangle^{1/2}{}_{\text{PS}}$ = 232 Å. To calculate the nominal $\langle s^2\rangle^{1/2}$ for the NAP, we assumed the ZnSPS and PSVP components were monodispersed (which is only a computational device, the solutions are both polydispersed) and used the well-known viscosity average molecular weight formula

$$M_v = \{(\textstyle\sum n_iM_i^{1+a})/(\sum n_iM_i)\}^{1/a} \tag{12}$$

where a is taken to be 0.731, experimentally determined for PS in THF.[28] This yields M_{NAP} = 840 000 and $\langle s^2\rangle^{1/2}{}_{\text{NAP}}$ = 554 Å.

In Figure 6A it is seen that, for the nonassociating polymers, $[\eta]$ is pressure independent; hence, the radius of gyration, $\langle s^2\rangle^{1/2}$, will also be constant. However, in Figure 6B one sees that $[\eta]$ for the associating polymer solutions varies. Because $\langle s^2\rangle^{1/2}$ for the individual polymer components is constant, we can infer that this variation in $[\eta]$ comes from a change in the degree of association. Using the experimentally determined dependence of $\langle s^2\rangle^{1/2}$ on M for PS in THF[28]

$$(\langle s^2\rangle)^{1/2} \propto M^{0.578} \tag{13}$$

we can then solve eq 9 for M as

$$[\eta] = K(M)^{0.734} \tag{14}$$

where $K = \Phi'\langle s^2\rangle^{3/2}{}_{\text{NAP}}/M_{\text{NAP}}{}^{1.734}$. The molecular weight in eq 14 is a measure of the effective molecular weight of the associating units, designated as M_{eff} hereafter.

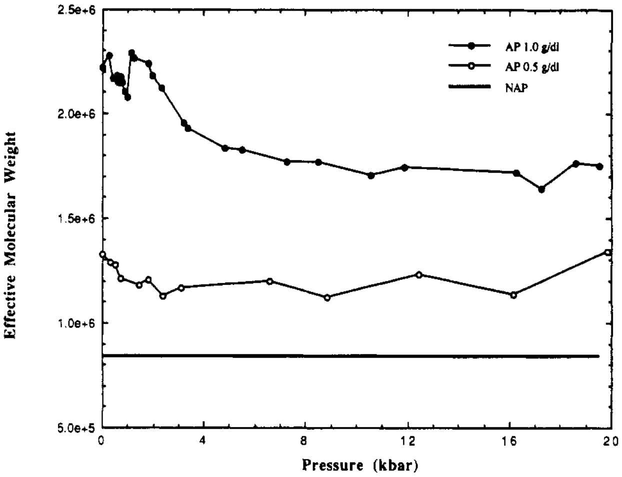

Figure 7. Effective molecular weight proportional to the degree of association which shows an overall decline in the 1.0 g/dL solution and to a lesser extent between 0 and 3 kbar in the 0.5 g/dL solution. The sharp rise is absent in the lower concentration solution.

The close chemical similarity of the ZnSPS and PSVP polymers to PS suggests that it is appropriate to apply this modified Flory equation (eq 14) to these polymers. For the associating mixtures we must recognize that the random distribution of the associating groups along the ZnSPS and PSVP polymer chains will make the polymer starlike rather than linear in the region of the associating groups. Thus, the Flory equation (eq 14) is not strictly applicable in estimating the relationship between $[\eta]$ and M_{eff}. An estimate of this effect can be obtained by comparing linear and star chains in dilute solutions. One sees that for polystyrene in good solvents[29] a star polymer exhibits an approximately 50% lower $[\eta]$ for a given molecular weight than that of a linear chain. (The Mark–Houwink K would be reduced by that amount.) However, the change in $[\eta]$ with molecular weight for both polymers is essentially identical. (The Mark–Houwink a is the same.) Therefore, we conclude that our estimate of M_{eff} is a lower bound on the actual M_{eff} and the variations we observe with pressure will likely be unaffected by the nonlinear nature of the chains surrounding the associating units.

Equation 14 is used to generate a plot of M_{eff} vs pressure as given in Figure 7. The M_{eff} for the associating polymer changes primarily as the degree of association between ZnSPS and PSVP changes. The zero-pressure 0.5 g/dL AP has M_{eff} = 1 320 000 indicating the onset of associations over the hypothetical NAP which has a molecular weight of 840 000. The 0.5 g/dL AP decreases ca. 13% from 0 to 3 kbar and remains virtually unaffected by pressure thereafter. The 1 g/dL AP, however, shows a marked dependence on M_{eff}. At zero pressure, the M_{eff} is 2 220 000, which decreases to around 1 700 000 at 10 kbar. Superimposed upon this overall downward trend is a spike in

M_{eff} between 1 and 3 kbar; this corresponds to the previously discussed abrupt viscosity rise.

Conclusions

Pressure is seen to be capable of influencing the degree of association in an associating polymer. The overall trend is for pressure to diminish the degree of association as can be seen in the decline of M_{eff} with increased pressure (Figure 7). However, even at the highest pressures the M_{eff} does not equal M_{v} for a hypothetical nonassociated (NAP) system, implying that some degree of association is retained. At the highest concentration studied (1.0 g/dL), there is a second effect of pressure. An abrupt viscosity rise, centered at 1.50 kbar, results in a corresponding rise in M_{eff}. We speculate that this may be some sort of association transition in which a particular geometric packing is favored. A light or neutron scattering experiment to investigate the microscopic behavior would certainly be of interest. It seems clear from this first study that high pressures can provide intriguing new data on associating polymer solutions, and we are currently pursuing studies on additional systems.

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