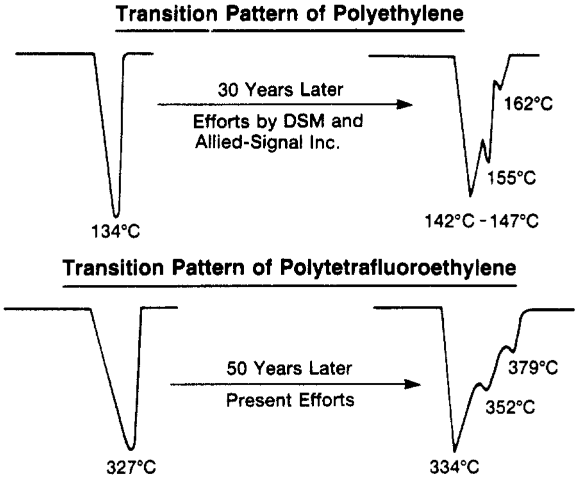
polyethylene and PTFE where processing developments over the decades have led to unusually high temperature transitions. This implies that other common polymers may also yield new morphologies representing novel properties.



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Thermodynamics of the Aggregation Phenomenon in Associating Polymer Solutions[†]

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ABSTRACT: The effect of temperature on the extent of aggregation, in dilute solution, of sodium sulfonated polystyrene ionomers in xylene has been determined by using small-angle neutron scattering (SANS). The data are described by using the open association model in which it is assumed that an equilibrium is eventually formed between single chains and aggregates of all sizes. The extent of aggregation was found to be temperature independent which suggests that there is no change in enthalpy on forming aggregates. It was therefore suggested that on aggregation intramolecular ion pair associations are broken and the same number of intermolecular associations formed. Intramolecular ion pair associations in the ionomer solutions were shown to collapse the single-chain radius of gyration (R_g) at infinite dilution to a value less than half the single chain dimension of normal polystyrene in this solvent and also smaller than for polystyrene in Θ solvents. The temperature dependence of the second virial coefficient for the ionomers was determined and compared with values for polystyrene. It was also found that 2% by volume of methanol was enough to almost completely solvate all the ionic groups and prevent both inter- and intramolecular ion pair associations in dilute solution.

Introduction

Ionomers are macromolecules containing a small number (typically less than 10 mol %) of ionic groups chemically attached to a nonpolar backbone. These materials have been commercially available for many years as modified thermoplastics and elastomers. Until very recently relatively little work had been published on their dilute solution behavior. It was suggested that one reason for this lack was due to the limited solubility of these commercially available ionomer polymers.[1] Within the last few years, however, the properties of sulfonated polystyrene ionomers in the polar solvents dimethyl sulfoxide[2] and dimethylformamide[2-4] and the nonpolar solvents xylene[5,6] and tetrahydrofuran (THF)[7,8] have been studied. It was shown that in polar solvents the iono-

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[†] This paper is dedicated in honor of the 60th birthday of Professor Walther Burchard of the Institut für Makromolekulare Chemie, Freiburg. We have many happy memories of discussion with Professor Burchard and hope for many more in the future.

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mers behaved like polyelectrolytes showing a large upturn in reduced viscosity at low concentrations.[2-4] This is due to single-chain expansion initially thought to be caused by solvation of the ionic groups by the polar solvent, resulting in negative charges along the chain and intramolecular repulsions. It was recently suggested, however, that intermolecular interactions may also be important in determining chain expansion in these solvents.[9] In xylene and THF the intrinsic viscosities are found to decrease as the sulfonation level is raised.[5-8] It was initially suggested that this was due to single chain collapse via intramolecular ion pair associations; however, no single-chain collapse was observed in either light[7] or neutron scattering[8] measurements in THF. The ionomers instead were found to be aggregated via intermolecular ion pair associations. It was suggested that the density within the aggregates must be greater than with normal polystyrene in order to cause the reduction in reduced viscosity via a reduced volume fraction. In THF it has been shown that sulfonation decreases the solubility and second virial coefficient (A_2). It was suggested that this virial term is composed of two parts[10]

$$A_2 = A_2' + A_2'' \tag{1}$$

The first part is negative due to an increase in the extent of aggregation (and therefore also in the weight-average molecular weight) via intermolecular ion pair associations on increasing the polymer concentration. The second part is due to the excluded volume of the polymer. As the sulfonation level is raised, A_2' is expected to decrease due to an increase in the extent of intermolecular ion pair associations. However, A_2'' should also become smaller since at higher sulfonation levels the polymer will also form more intramolecular ion pair associations. This results in single-chain collapse and a decrease in the polymer excluded volume.

We have recently shown by light scattering[11] that the dilute solution behavior of an ionomer (sulfonation level of 1.39 mol % and molecular weight of 105 300 g mol^{-1}) in xylene can be described and the change in molecular weight with concentration (A_2') accounted for by using the "open association" model detailed in ref 12. The term A_2'' in this system is very small due to intramolecular ion pair associations causing single chain collapse and the formation of dense aggregates. In this model it is assumed that the extent of aggregation is controlled by an equilibrium between single collapsed chains (with a hydrodynamic radius that is about 25% smaller than polystyrene in the same solvent) and aggregates of all sizes. At low concentrations aggregates consisting of two or three chains only are present. Using small-angle neutron scattering measurements, we have continued this study by determining the single chain and aggregate radii of gyration in this system. As the ionomer concentration increases, the number of intermolecular ion pair associations and average size of the aggregates increase. Close to the aggregate overlap concentration physically associated networks and very high viscosity solutions are formed. Lundberg and Makowski[13] have shown that as the temperature is raised, these networks are broken down as a large decrease in the viscosity is observed. Network formation is also prevented by the addition of a small volume of methanol. In this study we therefore also determined the effect of temperature and the addition of methanol on the extent of aggregation in dilute solution of this particular system.

Experimental Section

(A) Sample Preparation. Sodium sulfonated polystyrene ionomers S-PS were prepared by sulfonation of polystyrene of molecular weight of 105 300 g mol^{-1} and $M_w/M_n < 1.05$ as described in ref 6 and 14. Solutions of these ionomers with a sulfonation level of 1.39 mol % in deuterated xylene were prepared and agitated for 1 week before measurements were obtained. Measurements at elevated temperatures were made after the samples had been heated at the desired temperature for a least 8 h. After these measurements had been made, 2 wt % of deuterated methanol was added to the ionomer/xylene solutions and further measurements were made to determine the effect of methanol on the ion pair interactions.

(B) Small-Angle Neutron Scattering. Small-angle neutron scattering experiments were performed by using the D17 spectrometer at the Institut Laue Langevin, Grenoble, France, with a sample to detector distance of 3.4 m and a wavelength of $\lambda = 15$ Å. The data were collected on a 64 × 64 cm detector. Since the intensity of scattering was isotropic, it was radially averaged to give intensity versus scattering vector q (see later). This gave a range of q between 0.006 and 0.08 Å^{-1}. The samples were measured in 5-mm path length quartz cells held in a rack heated by water from a temperature-controlled bath. The use of a large beam, thick samples, and a high flux neutron source allowed measurements to be made on unusually dilute solutions (down to 0.04 g/dL). The temperature inside the cell was measured at the beginning and end of each experiment and found to be stable to ±1 °C. After radial averaging, the data were corrected for cell background and incoherent scattering of the solvent by subtracting the intensity of scatter from deuterated xylene at the same temperature as the solution. The data were normalized for detector efficiency and converted to absolute units by using the scattering from water in a 1-mm cell and the scattering cross section of water. The resulting intensity as a function of scattering vector q represents the scattered intensity of the polymer molecules that is mainly coherent but with a very small (and in this case negligible) flat incoherent component.

(C) Theory for Dilute Nonassociating Polymer Solutions. The apparent molecular weight is given by

$$1/M_{w_{app}} = Kc/I(0) \tag{2}$$

where, in small-angle neutron scattering

$$K = (N_a/m_o^2)[b_p - (V_p/V_s)b_s]^2 \tag{3}$$

$I(0)$ is the normalized intensity extrapolated to zero scattering angle, c is the polymer concentration, b_p and m_o are the the monomer scattering length and molecular weight, and $(V_p/V_s)b_s$ is the scattering length of the solvent corrected for the differences in molar volumes of polymer and solvent.

For $qR_g < 1$ the apparent z-average radius of gyration ($R_{g_{app}}$) and weight-average molecular weight ($M_{w_{app}}$) can be obtained from the intercept and gradient of a plot of $1/I(q)$ versus q^2 at any concentration c by using the Zimm expression

$$Kc/I(q) = [1/M_w(1 + q^2R_g^2/3)] + 2A_2c \tag{4}$$

With eq 2 this gives

$$1/M_{w_{app}} = 1/M_w + 2A_2c \tag{5}$$

Defining

$$R_{g_{app}}^2 = 3\{d[1/I(q)]/d(q^2)\}I(0) \tag{6}$$

gives

$$R_{g_{app}}^2 = R_g^2(M_{w_{app}}/M_w) \tag{7}$$

where $q = (4\pi/\lambda)\sin\theta$, M_w and R_g are the true weight-average molecular weight and z-average radius of gyration, 2θ is the angle of scatter, and A_2 is the second virial coefficient which for $c \ll 1$ is independent of both concentration and q. For the results reported here, many of the data are at $qR_g > 1$. The results obtained from the Zimm plot, however, can be corrected for this extended q range by using the correction factors calculated by Ullman et al.[15] Unfortunately even with the Ullman corrections only a small percentage of the measured q range could be used resulting in large errors in values obtained for $I(0)$ and R_g. Alternatively, a structure factor for the chains can be assumed and then the whole measured range used. The coherent intensity for polymer solutions over the whole q range can be decomposed into two parts

$$I(q) = I_s(q) + I_p(q)$$

where $I_s(q)$ is due to intramolecular and $I_p(q)$ due to intermolecular correlations. At very low concentrations $I_p(q) \ll I_s(q)$. Using the Debye model[16] for Gaussian chains gives

$$I_s(q) = K_c M_w (2/u^2)[\exp(-u) - 1 + u] \tag{8}$$

with

$$u = q^2 R_g^2 \tag{9}$$

This model can be used to describe the scattering from polymers in Θ solvents where $I_p(q)$ is small. It has also been used successfully to describe the scattering from contrast matched solutions of polymers in good solvents[17] and has been shown theoretically[18,19] to give a reasonable description of the scattering from high molecular weight polymers extended in good solvents.

(D) Theory for Aggregating Polymers. For nonassociating polymers where M_w is concentration independent it is possible to obtain the true molecular weight and A_2 from a plot of $Kc/I(0)$ versus concentration using eq 5. It is then a straightforward matter to use eqs 6 and 7 to obtain R_g. For associating polymers, however, where M_w is concentration-dependent, only the apparent molecular weight and apparent radii of gyration can be obtained. To estimate the true value, a model for the concentration dependence of M_w or a value for A_2 is required.

It has previously been shown that the "open association" model discussed in detail by Elias[12] describes well the change in molecular weight and average hydrodynamic radius of these ionomers in xylene with concentration. This model assumes that an equilibrium is formed between aggregates of all sizes and single chains, i.e.

$$\begin{aligned} M_1 + M_1 &\rightleftharpoons M_2 \quad K_1 \\ M_1 + M_2 &\rightleftharpoons M_3 \quad K_2 \end{aligned} \tag{10}$$

and

$$M_1 + M_{i-1} \rightleftharpoons M_i \quad K_{i-1}$$

where M_i represents an aggregate consisting of i chains. If the interacting groups on the ionomer chain are far apart, then the equilibrium constants, K_i, are independent of the aggregate size and the open association constant, K_0, is

$$K_0 = K_1 = K_2 \text{ etc.}$$

Then the concentration of aggregates consisting of i chains (in mol L^{-1} units) is given by

$$[M_i] = K_0^{i-1}[M_1]^i \tag{11}$$

The concentration of single chains can be shown to be

$$[M_1] = (1/K_0)[(M_w - (M_1)_w)/(M_w + (M_1)_w)] \tag{12}$$

and the weight-average molecular weight expressed in terms of the equilibrium constant K_0 and the total polymer concentration c (in g/dL units)

$$M_w^2 = (M_1)_w^2 + (4 \times 10^3 K_0 (M_1^2)_w/(M_1)_n)c \tag{13}$$

$(M_1)_w$ and $(M_1)_n$ [$(M_1)_n$ = 105 000 g mol^{-1}] are the single-chain weight and number-average molecular weight, respectively (for the complete mathematical details of this model see Elias[12]). In this system at low concentration the term $2A_2c$ in eq 5 (where $A_2 = A_2'$ in eq 1) is small since it is a measure of the excluded volume of the ionomer chains that have been shown to be collapsed single chains or compact aggregates.[11] At low concentrations, therefore, $M_{w_{app}}$ is approximately equal to M_w and a plot of $(M_w)_{app}^2$ against polymer concentration is linear (see eq 13). From the initial gradient of this plot and using eq 13, it is possible to obtain the equilibrium constant K_0. The largest error in obtaining the apparent molecular weight is in determining the value of the contrast factor K in eq 2 and its temperature dependence. It is possible, however, to obtain a value for K_0 independent of the value of K by using the gradient divided by the intercept of the plot of $M_{w_{app}}{}^2$ against concentration.

$$\begin{aligned} [\mathrm{d}I^2(0)/\mathrm{d}c]/[(I^2(0))_{c=0}] &= [\mathrm{d}M_{w_{app}}{}^2/\mathrm{d}c]/[(M_{w_{app}}{}^2)_{c=0}] \\ &= 4 \times 10^3 K_0/(M_1)_n \end{aligned} \tag{14}$$

Once K_0 is known, it is possible to determine the concentration of single chains and aggregates at any concentration using eqs 11–13.

(E) Effect of Temperature on the Extent of Aggregation. From the definition of the Gibbs function the change in the Gibbs free energy in a chemical reaction at constant temperature is given by[20]

$$\Delta G = \Delta H - T\Delta S \tag{15}$$

For standard thermodynamics it can be shown that in an ideal solution[20]

$$\Delta G = -RT \ln K_0 \tag{16}$$

Assuming that the change in enthalpy, ΔH, and the change in entropy, ΔS, on aggregation are both temperature-independent, then by determining K_0 at different temperatures these thermodynamic quantities can be calculated by using

$$\Delta H = -\mathrm{d}(R \ln K_0)/\mathrm{d}(1/T)$$

and

$$\Delta S = (R \ln K_0) + \Delta H/T$$

Forsman[21] detailed the factors affecting the extent of aggregation and attempted to predict values for ΔH and ΔS on forming an aggregate from chains where the dipole–dipole interactions are suddenly "turned on". This theory is based on the theory of rubber elasticity. In these measurements, the values obtained consist of all energy and entropy terms due to such factors as chain expansion and intermolecular ion pair formation on aggregation (as described by Forsman). In addition, however, these values also contain contributions from the entropy and enthalpy changes on "opening" a collapsed chain through breaking intramolecular ion pair associations. The change in enthalpy depends mainly on the change in the number of ion pair interactions on breaking intramolecular associations with the subsequent formation of intermolecular associations. Witten[22] has suggested that the enthalpy for ion pair association in this type of solvent is of the order of 10–20 kT. If an increase in the number of interactions occurs on aggregation, then the change in enthalpy will be negative and should result in a measurable decrease in average molecular weight on increasing the temperature.

(F) Temperature Dependence of A_2. M_w^2 versus concentration should (according to eq 13) remain linear over the entire concentration range measured. However, it was found that $(M_w)_{app}$ was smaller than the expected M_w at the highest concentration measured. This suggests that the term $2A_2c$ in eq 5 is negligible at low concentrations but has a small measurable effect at higher concentrations. By calculating the expected molecular weight (using eq 13 and the values for K_0 and $(M_1)_w$ calculated from measurements at lower concentrations), the virial term A_2 in eq 5 can be obtained from the apparent molecular weight. For better estimates for A_2 eqs 5 and 13 should be combined and fitted to data over a wide range of concentrations. At present, however, results where $2A_2c$ is nonnegligible have only been obtained at one concentration (1 g/dL). The virial term consists of two parts[23]

$$A_2 = A_{2,h} + A_{2,s} \tag{17}$$

$$A_{2,h} = -\Delta H_1/RTc^2V \tag{18}$$

$$A_{2,s} = \Delta S_1/Rc^2V \tag{19}$$

where ΔH_1 and ΔS_1 are the excess enthalpy and entropy[23] of the solvent on dilution and V the partial molar volume of the solvent. By determining the temperature dependence of the

Table I
Polystyrene and S-PS in Xylene at 24 °C (Zimm Model)

system	$10^{-5}M_w$, g/mol	10^4A_2, (g² cm⁻³ mol⁻¹)⁻¹	R_g, Å
PS	1.20 ± 0.05	7.0 ± 1	130 ± 5
S-PS + 2% methanol	1.10 ± 0.1	3.7 ± 1	115 ± 5

virial term, these two parts can be separated by using

$$A_{2,h} = T\alpha A_2 - T(\partial A_2/\partial T) \tag{20}$$

and

$$A_{2,s} = A_2(1 - \alpha T) + T(\partial A_2/\partial T) \tag{21}$$

where α denotes the coefficient of thermal expansion of the solvent. By comparison of these terms with values for polystyrene in different solvents, the reduction in A_2 on increasing the sulfonation level and its temperature dependence can, to some extent, be explained.

(G) Dimensions of Single Chains and Aggregates. Fitting the Zimm or Deybe models to the intensity of scattering from the ionomer solutions will give values for R_g averaged over all the different size aggregates in solution if A_2 and $I_p(q)$ are small. The z-average radius of gyration is given by

$$R_g = \sum w_i M_i R_{g_i} / \sum w_i M_i$$

For a solution containing particles of molecular weight M_1, $2M_1$, $3M_1$, etc. and weight fractions w_1, w_2, w_3, etc., this becomes

$$R_g = M_1/M_w[w_1R_{g_1} + 2w_2R_{g_2} + 3w_3R_{g_3} + ...]$$

At low concentrations where $w_1 + w_2 \simeq 1$

$$R_g = M_1/M_w[R_{g_1} + (1 - w_1)(2R_{g_2} - R_{g_1})] \tag{22}$$

Therefore from a plot of $R_g(M_w)/M_1$ against $(1 - w_1)$ (where w_1 is the weight fraction of single chains and can be calculated at any concentration once K_0 is measured), the single chain radius of gyration (R_g) can be obtained from the intercept. The radius for an aggregate consisting of two chains (R_{g_2}) can be estimated from the initial gradient.

Results

(A) Apparent Molecular Weight. Polystyrene in xylene behaves in a similar way to nonassociating polymers in a good solvent. For example, a straight line is obtained with the intercept giving the single-chain molecular weight and the gradient a positive second virial coefficient in dilute solution when $Kc/I(0)$ is plotted against concentration. In this experiment the molecular weight and second virial coefficient shown in Table I were obtained by using measurements at only two concentrations (1.0 and 0.4 g/dL) and eq 5. However, they still gave a single-chain molecular weight in reasonable agreement with our previous light scattering and GPC measurements.[11] The second virial term, although slightly larger than obtained by light scattering, is also within experimental error in agreement with other values for polystyrene in similar solvents such as benzene and toluene.[24] The Debye model could not be used to analyze this polystyrene data due to the intermolecular scattering ($I_p(q)$).

With the scattering from the ionomers in xylene it was found that the Debye model (eq 8) fitted the data well (see for example Figure 1). The apparent molecular weights and radii of gyration obtained from using both the Debye and Zimm models are tabulated in Table II. When $M_{w_{app}}{}^2$ (obtained from extrapolated values for $I(0)^2$) was plotted against concentration below 0.4 g/dL, straight lines were obtained at all temperatures for values obtained from both the Zimm (eq 4) and Debye models. These results suggest that $M_{w_{app}} = M_w$ and that both $I_p(q)$ and A_2 are negligible over this temperature (24–75 °C) and concentration (<0.4 g/dL) range. From these straight lines the single-chain molecular weights and values for K_0 obtained by using eq 13 and 14 were calculated (Table III). Within the experimental error for K in eq 2 the single-chain molecular weights are in good agreement. In Figure 2 the apparent molecular weights squared obtained from the Debye model and from static light scattering measurements[11] are shown normalized by the average single-chain molecular weights. The light scattering results were obtained by using similar expressions to those in eqs 2 to 7 except that the contrast factor K in eq 2 is different. The q values in these light scattering experiments were also much smaller ($(1 - 4) \times 10^{-3}$ Å⁻¹) but still gave values for $I(0)$ in good agreement with the neutron experiments. It can be seen from Figure 2 and from the values of K_0 in Table III that, within experimental error, the extent of aggregation is independent of the temperature. Using eqs 15 and 16 this gives

$$\Delta H(\text{aggregation}) = 0 \pm 3 \text{ kJ mol}^{-1}$$

and therefore

$$\Delta S(\text{aggregation}) = R \ln K_0 = +77 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$$

Within error, ΔH is considerably smaller than the esti-

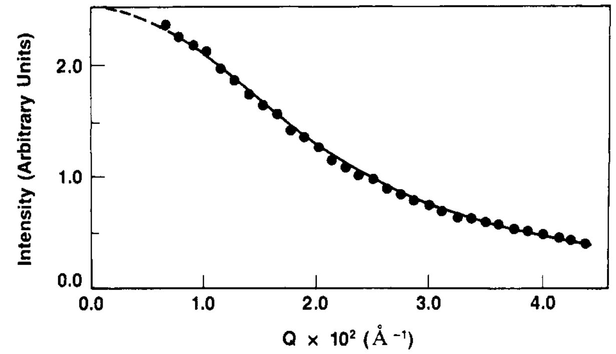

Figure 1. Intensity versus q with fit of Debye function for S-PS in xylene (0.08 g/dL) at 46 °C.

Table II
Dimensions and Molecular Weights of S-PS in Xylene

concn, g/dL[b]	$R_{g_{app}}$, Å			$10^{-5}M_{w_{app}}$, g mol⁻¹			model[a]
	24 °C	46 °C	75 °C	24 °C	46 °C	75 °C	
0.04	73	72		1.34	1.29		Zimm
	67	67		1.29	1.25		Debye
0.06	84	80	75	1.37	1.27	1.23	Zimm
	75	73	72	1.28	1.21	1.21	Debye
0.08	81	81		1.37	1.29		Zimm
	75	77		1.31	1.25		Debye
0.10	87	86	85	1.40	1.37	1.34	Zimm
	79	80	80	1.32	1.30	1.30	Debye
0.20	98	97	100	1.60	1.48	1.48	Zimm
	91	92	92	1.53	1.44	1.46	Debye
0.40	125	123	122	2.04	1.90	1.84	Zimm
	108	107	107	1.83	1.73	1.73	Debye
1.0[c]	165	157	153	2.75	2.43	2.32	Zimm
	133	130	126	2.34	2.16	2.06	Debye

[a] Zimm results corrected for the extended qR_g range by using ref 15. [b] At room temperature. [c] Radii of gyration corrected for the small virial term at this concentration are shown in Table IV.

Table III
Single-Chain Molecular Weights and Equilibrium Constants at Different Temperatures for S-PS

temp, °C	$10^{-5}(M_1)_w$, g mol⁻¹		$10^{-4}K_0$, mol L⁻¹	
	Zimm	Debye	Zimm	Debye
24	1.19 ± 0.05	1.15 ± 0.03	1.2 ± 0.2	1.02 ± 0.05
46	1.12 ± 0.05	1.11 ± 0.03	1.1 ± 0.2	0.96 ± 0.05
75	1.11 ± 0.05	1.12 ± 0.03	1.1 ± 0.2	0.95 ± 0.05

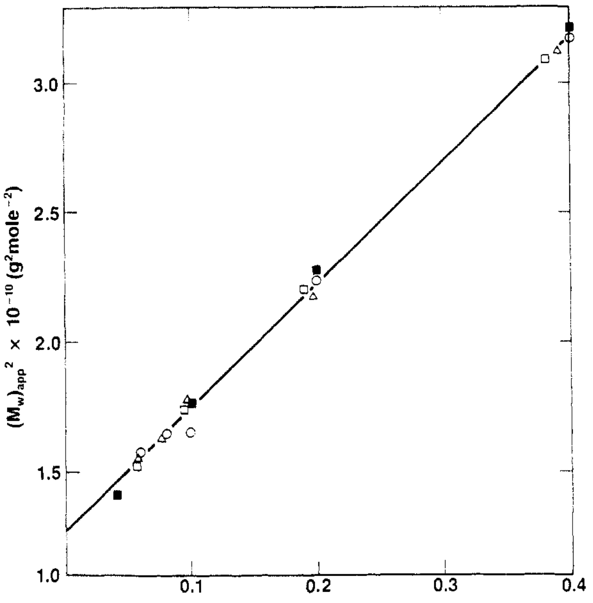

Figure 2. Normalized apparent molecular weight squared as a function of polymer concentration in xylene at 25 °C (○), 46 °C (△), and 75 °C (□) from neutron scattering and 20 °C (■) by light scattering.

Table IV
Apparent Molecular Weights and Radii of Gyration at 1.0 g/dL and Corresponding Second Virial Coefficients

temp, °C	$M_{w_{app}}/M_w$ Zimm	$M_{w_{app}}/M_w$ Debye	$10^4 A_{2,x}$, (g^2 cm^{-3} mol^{-1})$^{-1}$ $A_{2,h}$	$10^4 A_{2,x}$, (g^2 cm^{-3} mol^{-1})$^{-1}$ $A_{2,s}$	R_g, Å (Zimm)
24	1.00	0.94	-1.5 ± 0.3	1.5 ± 0.3	167
46	0.95	0.90	-1.6 ± 0.3	1.7 ± 0.3	161
75	0.92	0.85	-1.6 ± 0.3	1.9 ± 0.3	165

mated change on forming ion pair associations as suggested by Witten ($\simeq$40 kJ mol^{-1}).[22] Witten also noted that exclusion of solvent on aggregation may cost substantial energy. However, in this case changing from a collapsed chain to a compact aggregate will probably not result in substantial changes (and certainly not of the order of 40 kJ mol^{-1}) in solvation energy. It therefore appears that upon aggregation the same number of intermolecular associations are formed as intramolecular linkages are broken.

A positive change in entropy on aggregation suggests that in a multichain aggregate a single chain has more configurational freedom than in the collapsed state. It has previously been observed that within an aggregate the single chains can become expanded to a size similar to that of polystyrene in the same solvent[6] which may also suggest that there is more configurational freedom in an aggregate compared with a collapsed chain. There is of course small loss of combinatorial entropy within the solution on aggregation. However, this is very much smaller than the gain in configurational entropy when chains expand.

In Table IV $M_{w_{app}}/M_w$ (at 1 g/dL) is shown with M_w calculated by assuming that M_w is independent of temperature and using eq 13 with an average value for K_0 and the weight-average single-chain molecular weights (in Table III). From these values, estimates of A_2 were calculated by using eq 5 and are shown in Figure 3. The apparent molecular weights obtained from the Debye model at this concentration are slightly smaller than those obtained from the Zimm model. This results in larger values for A_2. These differences are probably due to errors caused by using the Zimm model at $qR_g > 1$, and problems caused by increased polydispersity at higher concentrations. In addition $I_p(q)$ also is becoming more important at this concentration which appears to result in errors particularly in R_g when using the Debye model. These results suggest that xylene is a Θ solvent for these ionomers at 10.0 ± 10 °C. The values obtained for A_2 are small enough (10 times smaller than typically observed for polystyrene in good solvents) to have negligible effect on the apparent molecular weights at concentrations below 0.4 g/dL at all the temperatures measured in this study.

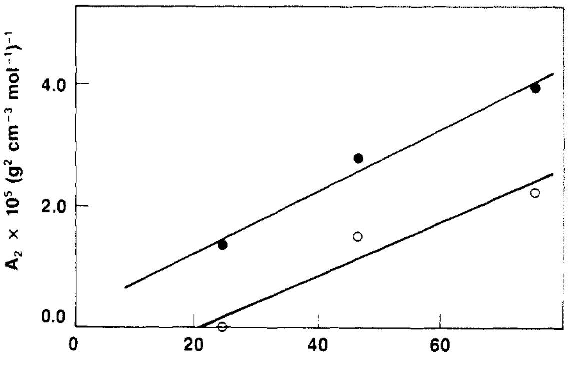

Figure 3. Second virial coefficient versus temperature for S-PS in xylene: ○, Zimm model; ●, Debye model.

$\partial A_2/\partial T$ was found to be similar in magnitude to that for polystyrene in toluene. Estimates for $A_{2,h}$ and $A_{2,s}$ obtained by using eq 20 and 21 are shown in Table IV. The value for $A_{2,s}$ is slightly smaller than for polystyrene of this molecular weight in toluene (a very similar solvent to xylene) and very much smaller than in Θ solvents. $A_{2,h}$ for this molecular weight polystyrene in toluene is approximately zero. Its value for an ionomer solution is presumably slightly negative because of a smaller enthalpy of solvation due to the ionic groups.

(B) Radii of Gyration. The average radius of gyration for polystyrene in xylene shown in Table I was obtained by using eqs 6 and 7 (Zimm model) at concentrations of 0.4 and 1.0 g/dL. Within experimental error the radius obtained is in reasonable agreement with other values for polystyrene in similar solvents such as toluene.[17]

For the ionomers, since the virial terms ($2A_2c$) are small, below 0.4 g/dL, the apparent radii of gyration can be obtained directly from a fit of eq 6 (Zimm model) or eq 8 (Debye expression) should equal the true radii of gyration. At 1 g/dL the values for R_g obtained by using eq 6 were corrected for the virial term (by using eq 7 and $M_{w_{app}}/M_w$) and are shown in Table IV. The radii of gyration for the ionomers were found to be within experimental error independent of temperature at all concentrations (see Tables II and IV). The average values for R_g plotted against $(1 - w_1)$ are shown in Figure 4. The radii of gyration obtained by using eq 8 were about 5–10% smaller than the values obtained from the Zimm model (corrected for the appropriate q range dependence using Ullman correction factors for Gaussian chains). Values obtained for the single chains and double-chain aggregates by using equation 22 are shown in Table V. In comparison with dynamic light scattering results (obtained on this ionomer in xylene simultaneously with the static results shown in Figure 1) $R_h/R_g \simeq 1.1$ for both the single chains and double-chain aggregates. The blob theory predicts that the ratio R_h/R_g varies from 0.664 at the Θ temperature to 0.848 in the poor solvent limit. If attractive interactions are sufficiently strong to contract the polymer chain to a collapsed globule whose density

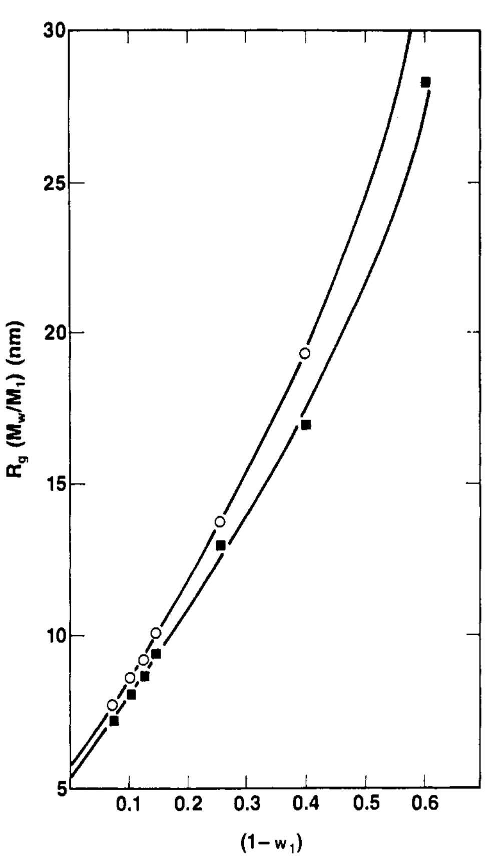

Figure 4. Plot of $R_g(M_w)/M_1$ versus $(1 - w_1)$ (where w_1 is the weight fraction of single chains (calculated by using eq 13): ■, Debye model; ○, Zimm fit.

Table V
Dimensions of Ionomers in Xylene

single-chain dimensn, Å		double-chain aggregate dimensn, Å	
Zimm	Debye	Zimm	Debye
57 ± 3	54 ● 3	175 ± 25	160 ± 20

is similar to that of a solid ball (the limit of solvent impermeability) $R_h/R_g = 1.29$.[25] A value of 1.1 for the ionomers suggests that both the single chains and aggregates at low concentrations are dense and almost solvent impermeable.

(C) Effect of Methanol on the Inter- and Intramolecular Ion Pair Associations. When 2 wt % methanol is added to the ionomer/xylene solutions, a plot of inverse intensity versus concentration becomes linear. From this plot the value of the single-chain molecular weight and second virial term shown in Table I were obtained. It is noteworthy that A_2 has a positive value. The z-average radii of gyration determined by using eqs 6 and 7 also become approximately concentration-independent at low concentrations. The average value at concentrations of 0.05, 0.2, and 0.4 g/dL is shown in Table I. This suggests that 2 wt % methanol at these polymer concentrations is sufficient to almost completely eliminate all inter- and intramolecular ion pair associations. At 1 g/dL the observed R_g is slightly larger probably due to incomplete removal of the ionic interactions.

Conclusions

From small-angle neutron scattering measurements we have shown that the extent of aggregation of sulfonated polystyrene ionomers of molecular weight 105 300 g mol^{-1} and with a sulfonation level of 1.39 mol % in xylene is controlled by equilibria between single collapsed chains and multichain aggregates of all sizes. The equilibrium constants were found to be independent of the size of the aggregates in dilute solution where only small aggregates are formed. The equilibrium constants were also found to be temperature independent. This suggests that there is no change in the number of ion pair interactions on forming aggregates from collapsed chains but that there is an increase in entropy. On forming an aggregate the same number of intramolecular ion pair associations must be broken as intermolecular linkages are formed. On increasing the temperature no change in the aggregate or single-chain dimensions could be observed, suggesting that the ion pair interactions are strong and that the increase in enthalpy on forming these interactions must be substantially larger than the loss of entropy on forming the aggregates or collapsed chains.

The reduced viscosity at low concentrations is proportional to the volume occupied by a single chain.[25,26]

$$[\eta] \propto R^3/M$$

Since the single-chain dimensions of the ionomers are very much smaller than the dimensions of polystyrene, this explains why the intrinsic viscosity of the ionomers is lower than for the unfunctionalized polymer. The volume occupied per single chain in an aggregate consisting of two chains is very much larger than in a single collapsed chain, i.e. $(R_{g_2})^3/2 > (R_{g_1})^3$. Therefore as the ionomer concentration and weight fraction of aggregates increases, the reduced viscosity rises. Below 0.4 g/dL, however, the large weight fraction of collapsed single chains results in the viscosity of the ionomer solutions still remaining lower than for the polystyrene solutions.

Values obtained for R_h/R_g for both single chains and aggregates consisting of two chains suggest that the ionomer chains are very compact in this solvent. Since according to Flory[27] A_2 is a measure of the excluded volume of a polymer molecule, this would suggest that A_2 should be small as is indeed observed. Also on increasing the temperature there is no observable change in dimensions suggesting that $\partial A_2/\partial T$ should be small. The latter value was found to be 10 times smaller than for polystyrene in other Θ solvents resulting in smaller values for $A_{2,s}$ and less negative values for $A_{2,h}$.

The addition of a small volume of methanol prevents the formation of both inter- and intramolecular ion pair associations in agreement with the viscosity measurements of Makowski and Lundberg.[13] On addition of this solvent there is also an increase in the virial term presumably due to an increase in the enthalpy of solvation of the ionomer. Presently, measurements determining the extent of aggregation have only been performed at very low concentrations. Further measurements will be required to explain why at higher concentrations the viscosity properties can become temperature,[13] time, and shear rate dependent.[6]

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Static Light Scattering of Polyelectrolyte–Micelle Complexes

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ABSTRACT: Soluble complexes are formed between poly(dimethyldiallylammonium chloride) and anionic/nonionic mixed micelles of sodium dodecyl sulfate and Triton X-100, at certain well-defined micelle compositions and ionic strengths. Static light scattering has been used to characterize the complexes generated from a 2×10^5 MW sample of this polycation and mixed micelles with 0.35 mol fraction anionic surfactant, at an ionic strength of 0.40 M. Measurements were carried out for polyion–micelle complexes at polymer concentrations ranging from 0.0025 g L^{-1} to 0.8 g L^{-1}, for surfactant-free polymer solutions, and for polymer-free micelle solutions. In the low polymer concentration range (<ca. 0.1 g L^{-1}) the results are consistent with intrapolyion complexes, with dimensions comparable to those of the free polymer, in which 10–20 micelles are bound. At higher polymer concentrations, higher order aggregates form. For a polymer sample with nominal MW of 2×10^6, such higher order aggregates appear to be present even at very low concentrations. The results suggest an equilibrium between intrapolymer and multipolymer complexes, that depends, inter alia, on polymer–micelle stoichiometry and on polymer chain length.

Introduction

Polymer–surfactant complexes have proved to be of enduring interest,[1-10] largely because the self-organization of macromolecules and low molecular weight amphiphiles into higher order structures offers some intriguing similarities to biological assemblies. For ionic surfactants above the critical micelle concentration (cmc) in the presence of oppositely charged polyelectrolytes, complex formation results from the Coulombic interaction of the polyion and the charged micelle.[11-18] Usually the interaction is very strong and a highly ion-paired amorphous precipitate forms at once. Attenuation of the interaction by reduction of the micelle surface charge density or by increase in ionic strength can totally suppress complex formation or, at intermediate micelle surface charge density or ionic strength, may lead to coacervation (liquid–liquid phase separation) in place of precipitation.[12,13] In one particular system, comprised of mixed anionic/nonionic micelles of SDS and Triton X-100, along with the strong polycation, poly(dimethyldiallylammonium chloride) (PDMDAAC), soluble complexes are formed over a reasonably wide range of conditions.[12,14,16]

We have studied these soluble complexes of SDS/TX-100/PDMDAAC by turbidimetry,[11-16] viscometry,[11] dynamic light scattering (QELS),[12,14,16] ultrafiltration,[16] and dye solubilization.[19] At an ionic strength of $I = 0.40$ M, such complexes are formed when the mole fraction of SDS in the mixed micelle, Y, is between 0.23 and 0.45. At $Y < 0.23$ the reduced specific viscosity of the mixture is the same as that of the surfactant-free solution, while the turbidity and the mean apparent diffusion coefficient by QELS are both equal to that of the polymer-free solution. From these findings, we may conclude that interactions at $Y < 0.23$ are too transient to detect by these methods. At $Y > 0.45$, i.e. at higher micelle surface charge densities, bulk phase separation takes place. At intermediate values of Y, complexation is reversible. Under such conditions, the mean apparent diffusion coefficient obtained by cumulants analysis[20] of the QELS autocorrelation function suggests that the hydrodynamic radius

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