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Self-assembly of Sulfonated Polystyrene Ionomers in Chloroform

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Summary: Light scattering and electric birefringence were used to determine the dimensions and extent of aggregation of dilute solutions of sodium sulfonated polystyrene ionomers with sulfonation levels of 0.5, 1.35, 2.6 and 5.8 mol% in chloroform. It was found that in solutions of ionomers with sulfonation level 1.35 and more the equilibrium between single chains and aggregates consisting of two and more chains is observed. These data were analyzed using the ''open'' association model. It was shown that an increase in the sulfonation level of ionomers results in a decrease in the hydrodynamic radius of single chain. On the other hand, it was established that an increase in sulfonation level leads to increase in the size of aggregate consisting of two chains. More pronounced expansion of ionomer chains incorporated into aggregate was found for ionomers with high sulfonation level.

Keywords: association; electric birefringence; ionomers; light scattering

Introduction

Ionomers are macromolecules containing a small number of ionic groups chemically bound to a nonpolar chain.[1–4] In polar or high dielectric constant solvents, such as dimethylsulfoxide and dimethylformamide, ionomers behave in a similar manner to polyelectrolytes.[5–8]

Ionomers with low levels of ionic groups are soluble in low - polar solvents, such as tetrahydrofuran, chloroform, p- and m-xylene.[9–17] The association of ionomers in low-polar organic solvents was studied very actively at the last years, and the lightly sulfonated polystyrene (SPS) ionomer usually was chosen as a model polymer. It was observed that in these solvents sulfonation of polystyrene results in a decrease in the intrinsic viscosity value relatively to polystyrene with the same degree of polymerisation.[2,3,11,12,16,17]. At higher concentrations the ionomers were found to be aggregated causing network formation. It was suggested that the intrachain association of ionic groups leads to compaction of the molecules. As the ionomer concentration in solution increases, the interchain association of ionic groups takes place, and the aggregates of two or more ionomer molecules are formed.[9–11,13,16,17] However at present time, there is a lack of information on the effects of varying sulfonation level on chain behavior and aggregation of ionomers in low – polar organic solvents.

In this paper, we report new results obtained from a detailed light scattering and electric birefringence studies of sulfonated polystyrene solutions in chloroform. We have investigated the effects of varying sulfonation level on single chains size of ionomers and their aggregates in solutions.

Experimental Part

Sodium sulfonated polystyrene ionomers of molecular weight $M_w = 105000$ with a polydispersity M_w/M_n less than 1.05 and sulfonation level φ of 0.5, 1.35, 2.6 and 5.8 mol%, respectively, were prepared by using anionically polymerized polystyrene as described previously.[1] The molar content

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φ of SO_3Na groups was determined by elemental analysis. The solutions of ionomers in chloroform were prepared at room temperature under continuous stirring with magnetic stirrer for 6 days. Chloroform with dielectric permittivity $\varepsilon = 4.8$, refractive index $n_0 = 1.4455$, viscosity $\eta_0 = 0.542$ cP and density $\rho_0 = 1.488$ g/cm^3 was used without further purification to dissolve the polymers.

Static (SLS) and dynamic light scattering (DLS) measurements at scattering angles θ ranging from 30 to 130° were carried out simultaneously using a ''PhotoCor Instruments'' (Russia) apparatus and a He-Ne linear polarized laser at a wavelength $\lambda_0 = 632.8$ nm. The temperature was controlled at 25 ± 0.05 °C. The normalized intensity autocorrelation functions obtained directly from the correlator have been analyzed. The constrained regulation method based on inverting Laplace transform incorporated in ''DynaLS'' program was used to obtain the distribution of relaxation times $W(\tau)$. Here $\tau = (Dq^2)^{-1}$, where D is the translation diffusion coefficient and $q = \frac{4\pi n_0}{\lambda_o} Sin\frac{\theta}{2}$ is the scattering vector.[18,19] The refractive index increment $dn/dc = 0.058$ for ionomers was measured by using IRF-23 differential refractometer. Toluene and benzene were used as standard liquids.

Electric birefringence (EB) was measured with homemade laboratory equipment in compensation mode using modulation of elliptical light polarization.[15,20,21] Rectangular electric field pulses with amplitudes up to 1 kV were applied. The relaxation time of electric field when it is switched off is equal to 0.5×10^{-6} s. A glass cell with two titanium electrodes – 2 cm long placed 0.02 cm apart from each other was used as a Kerr cell. Compensation of the measured electrical birefringence was performed by rotating a mica plate with a path difference of 6.3 nm.

Results and Discussion

As was shown earlier in solutions of SPS ionomers with sulfonation level of 1.35, 1.39 and 1.65 mol% an equilibration between single collapsed chains and aggregates of all sizes occurs in xylene.[9–13,16,17] This type of behavior was interpreted using the ''open'' association model.[9,10,13,16,22] However, it was found that in solution of ionomer with sulfonation level 0.95 single chains and aggregates consisting primarily from three chains are presented.[13] These data was interpreted using the closed association model.[13,22]

To analyze the aggregation behavior in solutions of SPS ionomers with sulfonation levels of 0.5, 1.35, 2.6 and 5.8 mol% SLS technique was used. In light scattering experiments, the apparent weight-average molecular weight is defined by [9,10,13]

$$M_{app} = \frac{R_0 N_A \lambda_0^4}{4\pi^2 n^2 c (dn/dc)^2} \tag{1}$$

Here R_0 is the Rayleigh ratio at observation angle $\theta = 0$.

When the apparent molecular weight squared M_{app}^2 is plotted against concentration a straight line is obtained almost over the whole range measured (Figure 1). The data deviate from a straight line slightly at the highest concentrations but this can be accounted for by introducing a second virial coefficient A_2. The concentration dependence of the apparent weight-average molecular weight of nonmultimerizing solutes at sufficiently low concentration c

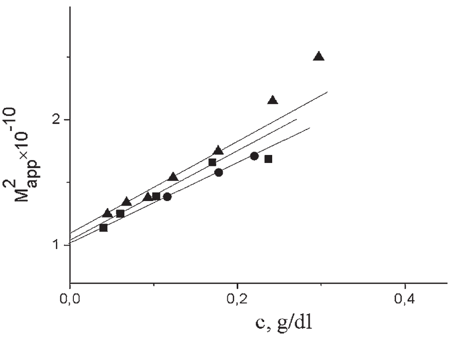

Figure 1.
Apparent molecular weight squared versus concentration c in chloroform: ■ = SPS-1.35; ▲ = SPS-2.6 and ● = SPS-5.8.

Table 1.
Molecular weight M_{W1}, equilibrium constant K_0, second virial coefficient A_2, coefficients of translation diffusion $D_{01}^{(1)}$, $D_2^{(1)}$ and $D^{(2)}$ of SPS ionomers in chloroform.

Sample	$M_{W1} \times 10^{-5}$	$K_0 \times 10^{-4}$	$A_2 \times 10^{-4}$	$D_{01}^{(1)} \times 10^7$	$D_2^{(1)} \times 10^7$	$D_0^{(2)} \times 10^7$
	g mol^{-1}	l mol^{-1}	ml mol/g^2	cm^2/s	cm^2/s	cm^2/s
SPS-0.5	1.10		—	5.03		
SPS-1.35	1.02	1.0	1.4	5.84	2.38	
SPS-2.6	1.05	1.0	−0.5	6.39	2.28	0.67
SPS-5.8	1.01	0.8	—	6.94	2.15	0.98

is expressed by[10,13]

$$\frac{1}{M_{app}} = \frac{1}{M_w} + 2A_2c \qquad (2)$$

Here M_w is the true weight-average molecular weight.

The M_{app} values for SPS-1.35 and SPS-2.6 ionomers at high concentrations of solutions were corrected using Equation (2). The second virial coefficients A_2 for these ionomers are represented in Table 1.

For ionomers with sulfonation level 1.35 and more the "open" association model appears to properly explain the data and the weight-average molecular weight is given by[10,13,22]

$$M_w^2 = M_{w1}^2 + (4 \times 10^3)K_0\frac{M_{w1}^2}{M_{n1}}c \qquad (3)$$

Here M_{n1} and M_{w1} are the number- and weight-average single chain molecular weights. The equilibrium constant, K_0, and weight-average single chain molecular weight, M_{w1}, were calculated from the gradient divided by the intercept and intercept of this plot, respectively, using Equation (3). These terms are given in Table 1. The equilibrium constant K_0 is similar in magnitude to that obtained previously for SPS ionomers with a sulfonation level of 1.39 and 1.65 in p-xylene.[10,13] An inversion in the sign of the second virial coefficient A_2 shows that the quality of the chloroform as solvent for the SPS ionomers decreases when the sulfonation level of ionomer is raised. The single chain weight-average molecular weight M_{w1} for SPS ionomers is in good agreement with molecular weight $M_{SD} = 1.17 \times 10^5$ g mol^{-1} which was calculated earlier using sedimentation and translation diffusion data for SPS-1.35 in m-xylene[16] (Table 1).

The apparent weight-average molecular weight M_{app} of SPS-0.5 ionomer calculated at the lowest solution concentration c = 0.057 g/dl coincides within experimental error with the M_{w1} value for other SPS ionomers (Table 1). It was found that an increase in solution concentration leads to a very weak decrease in M_{app} value for SPS-0.5 ionomer. Thus, the result shows that, over the concentration range studied, the apparent weight-average molecular weight M_{app} does not depend on SPS-0.5 ionomer concentration and the "open" association model is not applicable in the present system.

In order to determine hydrodynamic radius of single chain SPS ionomers and their aggregates in chloroform DLS technique was used. Figure 2 shows the

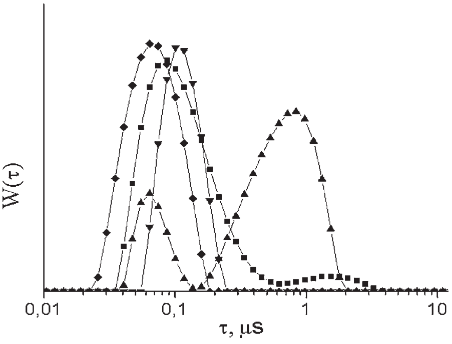

Figure 2.
Distribution function of relaxation times W(τ): ◆ = SPS-0.5; ▼ = SPS-1.35; ▲ = SPS-2.6 and ■ = SPS-5.8.

distribution of relaxation times W(τ) obtained from the "DynaLS" program. In the present concentration range we have observed one relaxation mode for SPS-0.5 and SPS-1.35 and two relaxation modes for SPS-2.6 and SPS-5.8 ionomers. To certify these modes, we have analyzed the dependence of reversal relaxation times τ^{-1} on q^2. Both sets of data can be approximated by linear dependences with a zero intercept, signifying that there are diffusive modes. From the gradient of these dependences the translation diffusion coefficients corresponding to the first $D^{(1)}$ and the second $D^{(2)}$ modes were calculated.[18,19]

The concentration dependences of $D^{(1)}$ and $D^{(2)}$ coefficients are represented in Figure 3. The results show that, over concentration range studied, the diffusion coefficient $D^{(1)}$ for SPS-0.5 ionomer as well as $D^{(2)}$ for SPS-2.6 and SPS-5.8 ionomers changes linearly with the increase in solution concentration. From these plots, the translation diffusion coefficients $D_{01}^{(1)}$ for SPS-0.5 and $D_0^{(2)}$ for SPS-2.6 and SPS-5.8 ionomers at infinite dilution were obtained.

For other SPS ionomers diffusion coefficient $D^{(1)}$ decreases nonlinearly with increasing polymer concentration (Figure 3). To analyze a concentration dependence of $D^{(1)}$ of SPS ionomers with sulfonation levels of 1.35 and more, theory of light scattering in polymer solution containing aggregates was used.[10] At low ionomer concentration where most chains exist as either single chains or aggregates consisting of two chains, the diffusion coefficient is given by

$$D_z^{(1)}\frac{M_w}{M_{w1}} = D_{01}^{(1)} + \left(2D_2^{(1)} - D_{01}^{(1)}\right)(1-\omega_1) \qquad (4)$$

Here ω_1 is the weight fraction of a single chain in solution which can be calculated by using the equation $\omega_1 = \frac{M_{w1}}{K_O c}\frac{(M_{w1}+4K_O c)^{1/2}-M_{w1}^{1/2}}{(M_{w1}+4K_O c)^{1/2}+M_{w1}^{1/2}}$[10]. Figure 4 shows the $D_z^{(1)}(M_w/M_{w1})$ dependence on ($1-\omega_1$) for the first diffusion mode of SPS ionomers in chloroform. From these plots, the single ionomer chain diffusion coefficients at infinite dilution $D_{01}^{(1)}$ as well as the diffusion coefficient of aggregates consisting of two chains $D_2^{(1)}$ were obtained and represented in Table 1. The hydrodynamic radii of single ionomer chain R_{h1} and aggregate consisting of two chains R_{h2} was calculated by using the Stokes-Einstein relationship:
$R_h = \frac{kT}{6\pi\eta_0 D}$[20]. The values of R_{h1} and R_{h2} are represented in Table 2. The hydrodynamic radius of single chain R_{h1} decreases, however the hydrodynamic radius of aggregate R_{h2} weakly increases with increase in sulfonation level φ (Table 2). Moreover, it should be noted that the hydrodynamic radius of SPS ionomers R_{h1} is smaller than

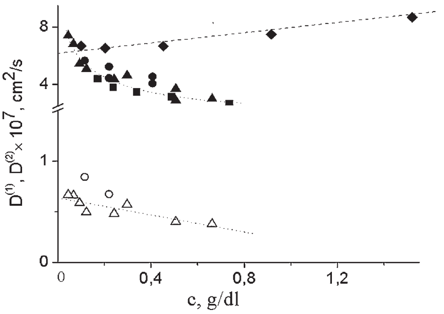

Figure 3.
Concentration dependences of translation diffusion coefficients $D^{(1)}$: ◆ = SPS-0.5; ■ = SPS-1.35; ▲ = SPS-2.6; ● = SPS-5.8 and $D^{(2)}$: Δ = SPS-2.6; ○ = SPS-5.8 in chloroform.

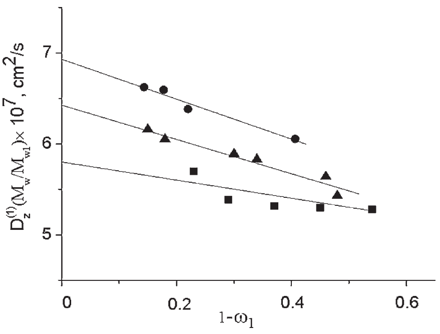

Figure 4.
Translation diffusion coefficient $D_Z^{(1)}(M_w/M_{w1})$ of ionomers versus ($1-\omega_1$): ■ = SPS-1.35; ▲ = SPS-2.6; ● = SPS-5.8.

Table 2.
Hydrodynamic radii of SPS ionomers in chloroform solutions.

Sample	Dynamic Light Scattering			Electric Birefringence	
	R_{h1}	R_{h2}	$R_h^{(2)}$	$R_\tau{}^{(1)}$	$R_\tau{}^{(2)}$
	nm	nm	nm	nm	nm
SPS-0.5	8.0			17.2	27.5
SPS-1.35	6.9	16.9		18.3	26.3
SPS-2.6	6.3	17.7	60	20.7	25.4
SPS-5.8	5.8	18.7	41	19.0	26.3

that of polystyrene molecules with the same polymerization degree $R_h^{PS} = 9.4$ nm in chloroform.

The hydrodynamic radius $R_h^{(2)}$ calculated from the diffusion coefficients $D_0^{(2)}$ is more than that of single chain R_{h1} and aggregates consisting of two chains R_{h2} (Table 2). This result shows that upon aggregation in solutions of SPS ionomers with sulfonation levels of 2.6 and 5.8 clusters consisting of more than two chains are formed.

In order to analyze the effect of sulfonation level on the size and composition of aggregates dynamics of electric birefringence in SPS ionomers solutions was studied. Figure 5 shows the rise and decay processes of electric birefringence, Δn, induced by the rectangular electric field applied across a solution. The measured electric birefringence Δn is a superposition of two relaxation processes: the initial jump of positive and a rather slow rise of negative electric birefringence approaching an ultimate steady-state value, Δn_0, when electric field is witched on. When electric field is switched off, the positive effect vanishes suddenly, and the decay of negative electric birefringence is observed. The time dependences of electric birefringence decay could not be described by the exponential function $\Delta n = \Delta n_0 \exp\{-t/\tau_d\}$ with a single relaxation time τ_d for either ionomers, indicating their polydispersity with respect to relaxation times.[15,20]

The constrained regulation procedure was used to obtain the distribution of relaxation times $W(\tau_d)$. Two relaxation modes for all investigated SPS ionomers were found (Figure 6). Figure 7 shows the concentration dependence of the relaxation times for the fast $\tau_d^{(1)}$ and slow $\tau_d^{(2)}$ modes. As can be seen from this representation relaxation times within experimental error do not change with increasing polymer concentration.

To certify these modes hydrodynamic radii of SPS ionomers corresponding to the fast $R_\tau{}^{(1)}$ and slow $R_\tau{}^{(2)}$ relaxation processes were calculated using the Stokes-Einstein equation: $R_\tau = (\frac{3\tau_d kT}{4\pi\eta_0})^{1/3}$.[20] Good agreement between hydrodynamic radii R_{h2} and $R_\tau{}^{(1)}$ obtained by using DLS and EB methods, respectively, is observed (Table 2). The value of $R_\tau{}^{(2)}$ is more than

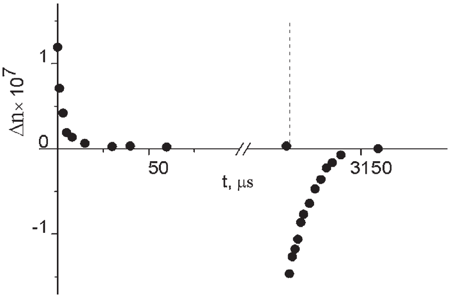

Figure 5.
Time dependence of electrical birefringence, Δn, induced by a rectangular electric field applied across solution of SPS-1.35 in chloroform. The dashed vertical line marks the moment of time when the electric field is switched off.

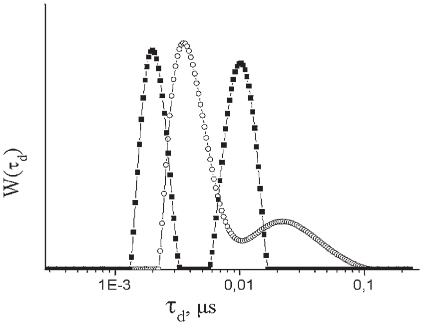

Figure 6.
Distribution function of electric birefringence relaxation times $W(\tau_d)$: ■ = SPS-1.35 and ○ = SPS-2.6.

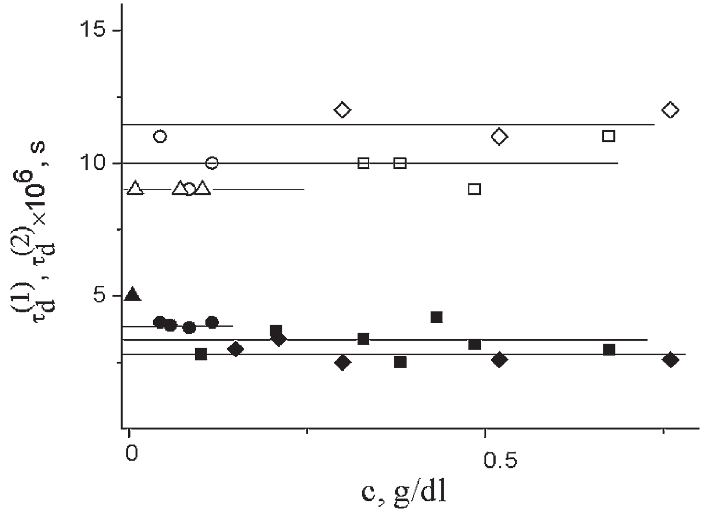

Figure 7.
Relaxation times $\tau_d^{(1)}$ and $\tau_d^{(2)}$ versus concentration c: (◆, ◇) = SPS-0.5; (■, □) = SPS-1.35; (▲, Δ) = SPS-2.6 and (●, ○) = SPS-5.8, correspondingly.

$R_\tau^{(1)}$ and does not depend on sulfonation level. We can suggest that this mode corresponds to aggregates consisting of more than two chains.

The distribution of relaxation times $W(\tau_d)$ does not contain mode corresponding to orientation of single chain. The relaxation time of electric birefringence τ_d for single SPS ionomer chain calculated by using the Stokes-Einstein equation and R_{h1} value (Table 2) does not exceed of 0.3 μs that is smaller than relaxation time (0.5 μs), which can be determined by using this laboratory equipment.

To analyze the effect of sulfonation on dimensions of single molecules and aggregates consisting of two chains the ratios of R_{h1} to R_h^{PS} and R_{h2} to R_{h1} were calculated. Figure 8 shows the dependences of R_{h1}/R_h^{PS} and R_{h2}/R_{h1} on sulfonation level φ. As can be seen from this representation as the value of φ is increased the single chain

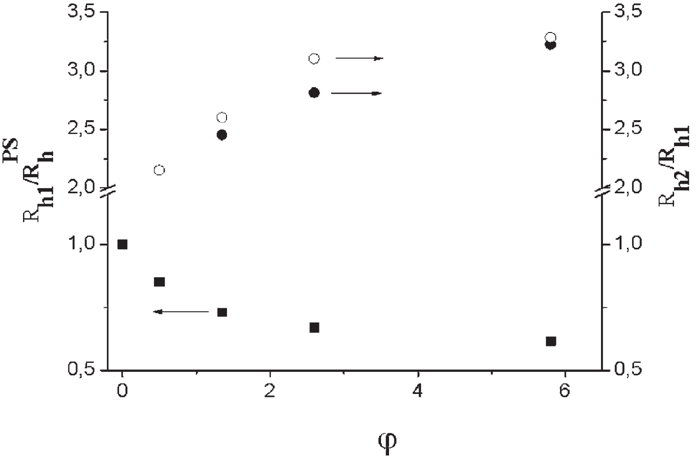

Figure 8.
Effect of sulfonation level φ on the value of R_{h1}/R_h^{PS} and R_{h2}/R_{h1}, calculated from dynamic light scattering and electric birefringence data, respectively: ■ = R_{h1}/R_h^{PS}; (●) = R_{h2}/R_{h1} and (○) = $R_\tau^{(1)}/R_{h1}$.

dimension decreases monotonically. It should be noted that in organic solvents, such as chloroform, the ionic groups are not dissociated, but exist as solvated ion-pairs, which form electric dipole. Thus, the compaction of ionomer single chains is a result of intramolecular ion pair association which is caused by the attraction between the electronic dipoles.

At the same time, a decrease in sulfonation level leads to an increase in R_{h2}/R_{h1} ratio. One can compare the obtained value of R_{h2}/R_{h1} with that estimated by using statistical theory of polymer coils.[20,23] This ratio is proportional to $2^{\nu}Z^{\nu-0.5}$, where $Z \approx 1000$ is the degree of polymerization for all samples of investigated SPS ionomers, and ν is the exponent depending on the thermodynamic quality of the solvent. Thus, if the size of the single molecule is not changed upon association and the quality of the solvent corresponds to θ – conditions (exponent $\nu = 0.5$), then $R_{h2}/R_{h1} = 1.4$. When the single molecule expands upon association, then $\nu = 0.6$ and the ratio R_{h2}/R_{h1} attains the value of 3.03, which is close to the value of this ratio obtained for SPS ionomers in chloroform (Figure 8) as well as for SPS ionomers with sulfonation levels of 1.39 and 1.69 in p- xylene.[9,10,13] Thus, the size of single chains of SPS ionomers in chloroform is increased when these chains are incorporated into aggregates.

To discuss the effect of sulfonation on the size of single chain and their aggregates mean field consideration was used.[23–25] The free energy of ionomer single chain is given by[25]

$$F = F_{el} + F_{\text{int}} + F_{ion} \tag{5}$$

The first term on the right-hand side of this equation describes the elastic energy of the chain, while the second and third terms are virial contributions to the free energy. The second term describes the interaction between nonionic units distant from each other along the chain. The third term describes the attraction of ionic groups as well as interaction between ionic and nonionic groups in the chain. It is convenient to express the equilibrium free energy of the single chain in terms of a swelling ratio, α, which gives the ratio of the chain size to that of the unperturbed Gaussian chain. In order to calculate the equilibrium average chain size as a function of the sulfonation level φ, minimization of expression (5) over α was carried out. It leads to the Flory type equation for the swelling ratio α

$$\alpha^5 - \alpha = \frac{B_{PS}N^{1/2}(1-(1+k)\varphi^2)}{A^3} + \frac{C}{A^6\alpha^3} \tag{6}$$

Here A is the Kuhn segment length, N is the number of Kuhn's segments in the chain, B_{PS} and C are the second and third virial coefficients, characterizing the interaction between nonionic groups. The coefficient $k = -B/B_{PS}$ characterizes the force of attraction between ionic groups and B is the second virial coefficient of these groups interaction. As in Ref. [25] we have accepted that the third virial coefficient C is one and the same for interactions between ionic and nonionic groups. To estimate the coefficient k in Equation 6 experimental data for A_2 in chloroform (Table 1) and in p-xylene[13] were used. It was established that the absolute value $k = 1.8 \times 10^3$ in chloroform and 4.5×10^3 in p-xylene, respectively. The distinction between obtained k values, probably, can be caused by difference in dielectric constant ε for these solvents. Earlier it was found that attraction between ionic groups of SPS ionomers is more effective for the solvents with low dielectric permittivity.[11,12]

Figure 9 shows that the increase in sulfonation level φ leads to a decrease in swelling ratio α and, consequently, in dimension of single ionomer chain. This theoretical prediction coincides with behaviour of R_{h1} value for SPS molecules in chloroform (Figure 8, Table 2).

In order to calculate the size of aggregate consisting of two ionomer molecules the mean-field approximation was used

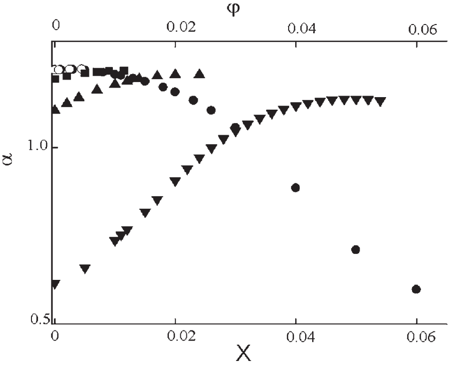

Figure 9.
Swelling ratio α versus φ and X for a single chain (●) and aggregate consisting of two chains with sulfonation level φ: 0.5 (○); 1.35 (■); 2.6 (▲) and 5.8 mol% (▼). All calculations were carried out for N = 1000, AkA = 1.8×10^3 and $B_{PS}/A^3 = 1$.

also. We can assume that formation of aggregate is caused by attraction between ionic groups belonging to different ionomer chains. Thus, the free energy of an aggregate consisting of two ionomer molecules is given by

$$F^{(2)} = F^{(1)} + F_c \tag{7}$$

The first term $F^{(1)}$ is the free energy of single ionomer molecule which is given by Equation 6. The second term F_c describes the interaction between ionomer molecules incorporated into aggregate. The dependence of equilibrium swelling ratio α on the number of ionic groups taking part in formation of intermolecular multiplets X, is found by minimization of the free energy $F^{(2)}$ over α. It leads to the next equation for the swelling ratio α

$$\begin{aligned}\alpha^5 - \alpha = {} & \frac{B_{PS}N^{1/2}}{A^3}\{1 + 2(k+1)X\varphi \\ & - (k+1)(1.176X^2 + \varphi^2)\} + \frac{C}{A^6\alpha^3}\end{aligned} \tag{8}$$

The dependences of the swelling ratio α on X for SPS ionomers with different sulfonation level φ are represented in Figure 9. As can be seen from this representation, an increase in the number of ionic groups X, incorporated into interchain multiplets, leads to increase in the value of swelling ratio α. Note that more pronounced changes of swelling ratio are observed for ionomers with high sulfonation level φ, that corresponds to the experimental dependence of R_{h2}/R_{h1} ratio on φ (Figure 8).

Conclusion

The equilibrium dimensions of single ionomer chains and their aggregates were determined using dynamic light and electric birefringence techniques. The aggregation behavior of SPS ionomers with sulfonation level of 1.35 mol% and more can be described by the "open" association model. As the sulfonation level is increased from 0.5 to 5.8 mol% the single chain dimension decreases from 8 to 5.8 nm. In contrast, the average size of aggregates consisting of two chains is increased weakly. It is caused by the expansion of ionomer chains incorporated into aggregate, because of association of ionic groups belonging to different ionomer molecules. The single ionomer chains incorporated into aggregate tend to increase their entropy due to replacements of the intra – on intermolecular contacts between ionic groups. Good agreement between our results and experimental observations for SPS ionomers with sulfonation levels of 1,25, 1.39 and 1.65 mol% in p-xylene using small angle neutron scattering method is observed.[9,10,13]

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