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Dependence of chain conformation on degree of sulfonation and counterion dissociation of sodium poly(styrene sulfonate) in semidilute aqueous solution

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Abstract

The chain conformation of sodium poly(styrenesulfonate) (NaPSS) in the semidilute aqueous solution, estimated from the plots of reduced viscosity versus segmental concentration, was found to be dependent on the degree of sulfonation and dissociation extent of counterions. The latter, altered by the content of sodium chloride external salt, was estimated from the ionic conductivity measurements on the basis of the modified Manning's conductivity theories with consideration of the influence of chain overlapping in the semidilute regime. The results indicate that the increase of chain extension of NaPSS with counterion dissociation was further enhanced by increasing the degree of sulfonation.
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1. Introduction

In more than a half century ago, Fuoss and Strauss [1] reported that the polyelectrolyte solutions show an anomalous behavior in semidilute salt-free systems or with low salt content, in that the reduced viscosity η_{red} is abruptly increased with decreasing the segmental concentration c_{p}. They described it with an empirical equation: $\eta_{\mathrm{red}} = A/(1 + Bc_{\mathrm{p}}^{1/2})$, where A and B are constants. In 1976, de Gennes et al. [2] derived a similar expression $\eta_{\mathrm{red}} \sim c_{\mathrm{p}}^{-1/2}$, by assuming that the polyelectrolyte chains were in a rod form. However, most of the experimental data [3–5] did not support the relation $\eta_{\mathrm{red}} \sim c_{\mathrm{p}}^{-1/2}$. Recently, we have suggested the polyelectrolytes as a flexible chain with a succession of segments (or blobs) each carrying a g-number of monomers [6]. By referring to Rouse dynamics and neglecting the entanglement effects, the viscosity of the polyelectrolyte solutions, η was expressed as follows [7]

$$\eta - \eta_0 = \frac{1}{36} \rho \bar{r}_0^2 N^* f_0 \tag{1}$$

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where η_0 is the viscosity of solvent, ρ, the moles of polymer chains/volume $\approx c_{\mathrm{p}}/N$, N, the number of segments per chain, $\bar{r}_0^2 = N^* \xi^2$, the mean square end-to-end distance of a chain, $N^* = N/g$, the number of blobs per chain, $f_0 = 3\pi\eta_0\xi$, the friction coefficient for one blob (here we assume the system is undraining inside the blob) against the solvent, and $g \approx c_{\mathrm{p}}\xi^3$, indicating that each volume ξ^3 is occupied by one blob on the average. Thus, Eq. (1) was rewritten as follows [6]

$$\eta_{\mathrm{red}} = \frac{\eta - \eta_0}{\eta_0 c_{\mathrm{p}}} \approx \frac{N}{c_{\mathrm{p}}^2 \xi^3} \tag{2}$$

Based on de Gennes et al. [2], the crossover from the dilute to the semidilute regime is characterized by a critical concentration $c^* \approx N/R^3$, where R is the average end to end distance of polyelectrolyte chains. Due to the overlapping of the polymer chains and the formation of an isotropic network in the semidilute regime, all properties of the polymer solutions lose their molecular mass dependence. Thus, the behavior of the polymer solution is governed by the correlation length $\xi(c_{\mathrm{p}})$, which is molecular weight independence. We then assumed $R = N^\nu a$, in which a is the length per mer and ν is the chain conformation index in a range of $0.5 \leq \nu \leq 1$, corresponding to the chain

conformation from Gaussian flexible to rigid rod extreme. By using the formula of correlation length [2]

$$\xi = R\left(\frac{c^*}{c_p}\right)^m \qquad (c_p \gg c^*) \tag{3}$$

where m is the unknown power of the concentration, we obtained $\xi \approx N^{\nu+m-3\nu m}c_p^{-m}$. Since $\xi \approx N^0$, $m = \nu/(3\nu - 1)$. From Eq. (2) and $\eta_{red} \approx c_p^n$ expression, we obtained [6]

$$\nu = \frac{n+2}{3n+3} \tag{4}$$

It can be found that the exponent n changes from $-1/2$ for a rod-like chain conformation ($\nu = 1$) to 1 for a Gaussian flexible chain ($\nu = 0.5$). For a real free-coil chain ($\nu = 0.6$), $n = 0.25$ was obtained. A similar result was also obtained by Muthukumar [8], who give $n = 0.25$ for the polyelectrolyte solutions with high salt content.

The above new scaling relation was able to be employed to estimate the chain conformations of polyelectrolytes in the semidilute regime with and without containing external salts, simply by calculating n from the double-logarithmic plots of reduced viscosity versus concentration [6]. It is noteworthy that the conformation of polyelectrolyte chains is mainly influenced by their charge density and counterion dissociation. Although the conductivity of polyelectrolyte solution can provide some measure of counterion dissociation [9], the interpretation for the conductivity measurements of polyelectrolyte solutions has relied primarily on the Manning's conductivity theories [10,11]. However, it is still in doubt if they are able to apply to the semidilute regime because of overlapping of the polymer chains. Kuhn et al. [12] has suggested that Mannings' theory underestimates the number of condensed counterions in the semidilute regime. We have also found that the extent of aggregation of polyelectrolytes in the semidilute salt-free aqueous solution substantially affects the ionic conductivity of the solution [13].

In this study, sodium poly(styrenesulfonate) (NaPSS) with various degrees of sulfonation (or charge densities) were prepared and estimated their chain conformations in semidilute salt-free and salt-containing aqueous solutions, by using the double-logarithmic plots of reduced viscosity versus segmental concentrations. Their dissociation extent of counterion was estimated on the basis of the Manning's conductivity theories with some modification by considering the influence of chain overlapping in the semidilute regime [14,15]. Thus, the dependence of chain conformation on the degree of sulfonation and counterion dissociation of NaPSS in the semidilute aqueous solutions was established.

2. Experimental

2.1. Materials

A narrow molecular weight polystyrene (PS) sample (purchased from Aldrich Chemical Company), which had a number average molecular weight of 180,000 with a M_w/M_n ratio of 1.1, was used to prepare NaPSS with various degrees of sulfonation. The preparation procedure followed the method provided by Vink [16] with some modifications. In general, 0.25 g PS was dissolved in 70 ml cyclohexane first, and then transferred to the flask that has already been loaded with 50 ml sulfuric acid (40 and 25 ml were also used to vary the degrees of sulfonation) and 5 g P_2O_5 (98.0%, Showa Co. Japan). After stirred for 80 min at 55 °C, the reaction mixture became separated into pure cyclohexane and a faintly yellow phase containing the mineral acids and poly(styrenesulfonic acid) (PSSA). Then it was allowed to stand for 70 min before cooled to 0 °C. After that, 20 g crushed ice was slowly added to the flask with stirring. The mixture was then transferred to a separating funnel and the heavier mineral acids were separated from the PSSA/cyclohexane mixture. 120 ml water (ultrapure, 18.3 MΩ), which was purified by the Barnstead Easypure RF system, was added to the latter to dissolve PSSA. After separated from cyclohexane, the PSSA solution was filtered through a porous glass filter and dialyzed in a Sprectra/Pro regenerated cellulose membrane tube (molecular weight cutoff at 3500) against ultrapure water. The dialysis tube was cleaned by using the Sprectra/Pro sulfide removal kit. The dialysis was completed after the conductivity of the repeatedly refreshed water surrounding the dialysis tube closed to 1 μS/cm. Afterwards, the PSSA solution was freeze-dried to a solid product (~0.5 g), which retained up to 10 wt% water as measured by thermogravimetric analyzer (Du Pont model 9900-954 TGA). The obtained PSSA was dissolved in 250 ml ultrapure water and then converted to the NaPSS solution by potentiometric titration with 0.1 M NaOH. After that, it was dialyzed again to remove the excess NaOH. The degree of sulfonation (α) and average segmental equivalent weight (m_s) (molecular weight divided by number of sulfonate groups in a chain) of prepared NaPSS were determined from the amount of NaOH consumed in titration. The results were listed in Table 1. The molecular weight and molecular weight distribution of the prepared NaPSS were measured by gel permeation chromatography (Testhigh Series III RI detector with $H_2O/CH_3OH/NaNO_3/NaH_2PO_4$ buffer solution as a mobile phase). The calibration

Table 1
Data for the prepared NaPSS samples

Sample	α (%)	m_s (g mol^{-1})	M_n (g mol^{-1})	M_w/M_n
1	~100	206	350,000	1.10
2	83	227.3	330,000	1.11
3	51	305.9	270,000	1.08

curve was obtained from the monodispersed poly(ethylene oxide) standard sample.

The NaPSS aqueous solutions with various degrees of sulfonation were prepared from the volumetric dilutions for concentrations ranging from 0.015 to 0.00002 g/dl, respectively. Polymer solutions with added sodium chloride (NaCl) salts were prepared from the highest polymer concentration first and then gradually diluted with sodium chloride aqueous solutions having predetermined concentrations.

2.2. Methods

The viscosity measurements were carried out by using a capillary Ubbelohde viscometer (type 0A, Cannon co.) immersed in a thermostatic water bath (TAMSON co., model TV 2000) maintained at 30 ± 0.01 °C. A typical flow time of polymer solutions in a viscometer was measured in a range of $100–300$ s with an accuracy of ± 0.1 s, and each flow time was determined by repeating at least five time measurements. The conductivity measurements were conducted in a beaker containing 100 ml polymer solutions at 30 ± 0.01 °C under a nitrogen atmosphere, by using a conductivity cell, with platinized electrodes and a cell constant of $3.64\ cm^{-1}$. The signal was recorded on a Radiometer Copenhagen CDC-230 conductivity meter, and the data were then subtracted the conductivities of water and NaCl external salts.

3. Results and discussion

3.1. Salt-free polyelectrolyte solutions

Fig. 1 shows the double-logarithmic plots of reduced viscosity η_{red} versus segmental concentration c_p of NaPSS with various degrees of sulfonation in salt-free aqueous solutions. Two regimes separated by $c_{p,max}$, that shows the

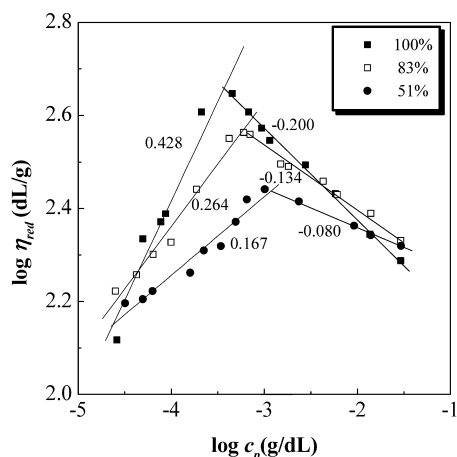Fig. 1. Double-logarithmic plots of η_{red} versus c_p of NaPSS with various degrees of sulfonation in salt-free aqueous solutions. The numbers obtained from the slops denote the exponent n in $\eta_{red} \sim c_p^n$.

highest η_{red}, were clearly seen. It is convenient to assign $c_{p,max}$ as a break point that separates the dilute and semidilute regimes. According to Muthukumar, [8] the behavior that η_{red} increases with c_p, in the dilute solution can be described by the Zimm dynamics. In this regime, the chains barely interact with each other so that their properties depend on the molecular weight of polymers. When the polyelectrolyte concentration was increased to the semidilute regime, the polymer chains began to overlap. Thus, their chains have a tendency to aggregate together and melt into an isotropic lattice, which is often pictured as a collection of uncorrelated blobs with average diameter much less than the end-to-end distance of polyelectrolyte chains.

According to our derived scaling relation, [6] the average end-to-end distance $R = N^\nu a$ of NaPSS in the semidilute regime can be estimated by Eq. (4), i.e., $\nu = (n+2)/3(n+1)$, where n in $\eta_{red} \sim c_p^n$ was obtained from the slope of Fig. 1. The obtained chain conformation indexes of NaPSS with various degrees of sulfonation were listed in Table 2. Apparently, with increasing the degree of sulfonation, the chain was more extended.

Fig. 2 shows the plots of the equivalent conductivities of NaPSS with various degrees of sulfonation in aqueous solutions versus the segmental concentration c_p in monomole/l. The equivalent conductivities barely changed with the concentration in a range of $0.0022 > c_p > 0.00015$ monomole/l, which is in the semidilute regime by referring to Fig. 1. Thus, we compared the experimental data of equivalent conductivity Λ with the theoretical prediction by the Manning's conductivity theory for salt-free polyelectrolyte solutions [10].

$$\Lambda = f_{theo}(\lambda_c^0 + \lambda_p) \tag{5}$$

where

$$f_{theo} = 0.886|z_c|^{-1}\xi_M^{-1}, \qquad \xi_M = \frac{Q}{b} = \frac{e^2}{\varepsilon KTb} > |z_c|^{-1} \tag{6}$$

λ_c^0 is the equivalent conductivity of the counterion in pure solvent, z_c is the valence of the counterion, ξ_M is the charge density parameter, $Q = e^2/\varepsilon KT$ is the Bjerrum length (e is the electronic charge and ε is the dielectric constant of water), b is the charge spacing of the polyelectrolyte chain, and λ_p the equivalent conductivity of the polyions in the

Table 2
Solution properties of NaPSS samples in the salt-free semidilute aqueous solutions

Sample	ν^a in $R = N^\nu a$	f_{theo}	f
1	0.750	0.308	0.193
2	0.718	0.371	0.214
3	0.696	0.604	0.223

[a] Chain conformation index was estimated from Fig. 1 in the semidilute regime.
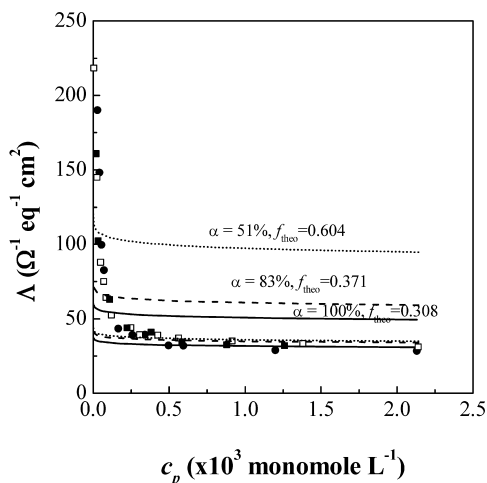
Fig. 2. Concentration dependence of equivalent conductivities for the salt-free aqueous solutions of NaPSS with following degrees of sulfonation: (■) 100%, (□) 83%, and (●) 51%. Note: The curves above the data points were drawn from Eq. (5) with f_{theo}, whereas those on the data points were drawn with adjusted f to substitute f_{theo} in Eq. (5).

solution, given by

$$\lambda_p = \frac{279A|z_c|^{-1}\ln \kappa r}{1 + 43.2(|z_c|\lambda_c^0)^{-1}A \ln \kappa r} \tag{7}$$

where

$$A = \frac{\varepsilon KT}{3\pi\eta e} \tag{8}$$

κ is the Debye–Hückel screening constant

$$\kappa^2 = \left(\frac{4\pi e^2}{\varepsilon KT}\right)\frac{c_p}{\xi_M} \tag{9}$$

and r is the radius of the polyions. Eq. (6) indicates that f_{theo} only depends on the charge densities and is not a function of the concentration, whereas Λ obtained from Eq. (5) slightly depends on the segmental concentration because of λ_p. We have used Eqs. (5)–(9) to calculate f_{theo} and Λ for the NaPSS solutions with various degrees of sulfonation, the results of which were listed in Table 2 and plotted in Fig. 2, respectively. The discrepancy between the Manning's conductivity theory and the experimental results in the semidilute regime for $c_p > 0.00015$ monomole/l is due to the fact that the former does not consider the overlapping of the polymer chains. As a result, the fraction of uncondensed counterions should be less than that predicted by Eq. (6).

If we allow the fraction of uncondensed counterions in Eq. (6) to be adjustable (i.e. f_{theo} is replaced by f in order to fit the experimental data), we found that the predicted equivalent conductivities are well matched with the experimental data in the region of $c_p > 0.00015$ monomole/l as shown in Fig. 2. The obtained f was also listed in Table 2. Obviously, the Manning's condensation theory underestimates the number of condensed counterions in the semidilute regime. Similar result was also reported for the

poly(xylylene tetrahydrothiophenium chloride) (PXT) in the semidilute aqueous solution [14]. The deviation of f from f_{theo} was considered as the influence of overlapping of polyelectrolyte chains on the counterion condensation. The results also indicate that the lower the degree of sulfonation or charge density, the counterion dissociation is greater, which is apparently attributed to the lower coulomb attractive force created by the dissociation of counterions. Briefly, it is interesting to note from Table 2 that the higher the degree of sulfonation, NaPSS chain is more extended but the dissociation extent of counterions is less.

3.2. Salt-containing polyelectrolyte solutions

When NaPSS aqueous solutions were added with NaCl salts, $c_{p,max}$ shifted to higher segmental concentration with smaller η_{red} but larger n in $\eta_{red} \sim c_p^n$ as shown in Fig. 3. With increase of NaCl concentration c_s from 2×10^{-6} to 5×10^{-4} M, $c_{p,max}$ continuously shifted to higher concentration. At $c_s = 5 \times 10^{-4}$ M, $c_{p,max}$ became indiscernible for NaPSS with the smallest degree of sulfonation $\alpha = 51\%$. With further increase of c_s to 1×10^{-3} M, $c_{p,max}$ was not observable for all three degrees of sulfonation. The increase of n in $\eta_{red} \sim c_p^n$ with c_s indicates that the conformation of polyelectrolyte chains turned to a more coiled state. The chain conformation indexes of NaPSS estimated by Eq. (4) with various degrees of sulfonation and salt contents were listed in Table 3. To correlate the chain conformation of NaPSS with the dissociation extent of counterions in the salt-containing aqueous solutions, the latter was estimated from the ionic conductivity measurements on the basis of another Manning's conductivity theory derived particularly for the polyelectrolyte solutions with external salts [11].

Fig. 4 shows that the equivalent conductivities of NaPSS in the region of $0.0022 > c_p > 0.00015$ monomole/l were decreased with c_s for all three NaPSS samples with various degrees of sulfonation. For the salt-containing polyelectrolyte solutions, Manning [11] has modified λ_p as following

$$\lambda_p = \Im U \tag{10}$$

where $\Im$ is the Faraday constant and U is the electrophoretic mobility of polyelectrolyte chains, expressed by

$$300U = (300U^*)(\alpha/\beta) \tag{11}$$

Table 3
The chain conformation index ν and dissociation extent f of counterions of NaPSS with various degrees of sulfonation in the semidilute aqueous solution containing various NaCl concentrations

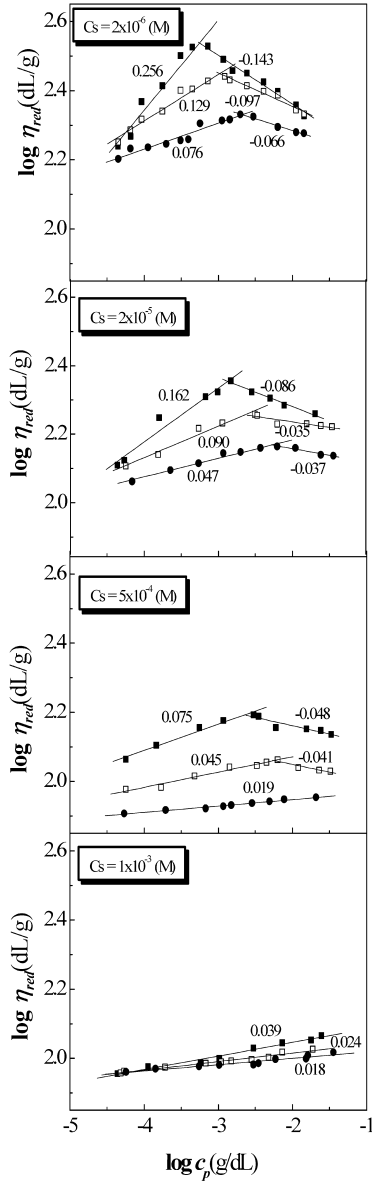| Salt contents (M)	$\alpha = 100\%$		$\alpha = 83\%$		$\alpha = 51\%$	
	ν	f	ν	f	ν	f
2×10^{-6}	0.723	0.175	0.702	0.190	0.690	0.220
2×10^{-5}	0.698	0.152	0.679	0.184	0.679	0.215
5×10^{-4}	0.684	0.115	0.681	0.136	0.661	0.155
1×10^{-3}	0.654	0.097	0.659	0.108	0.661	0.093

Fig. 3. Double-logarithmic plots of η_{red} versus c_p of NaPSS with (■) 100%, (□) 83%, and (●) 51% degrees of sulfonation in aqueous solutions with indicated concentration of NaCl. The numbers obtained from the slops denote the exponent n in $\eta_{red} \sim c_p^n$.
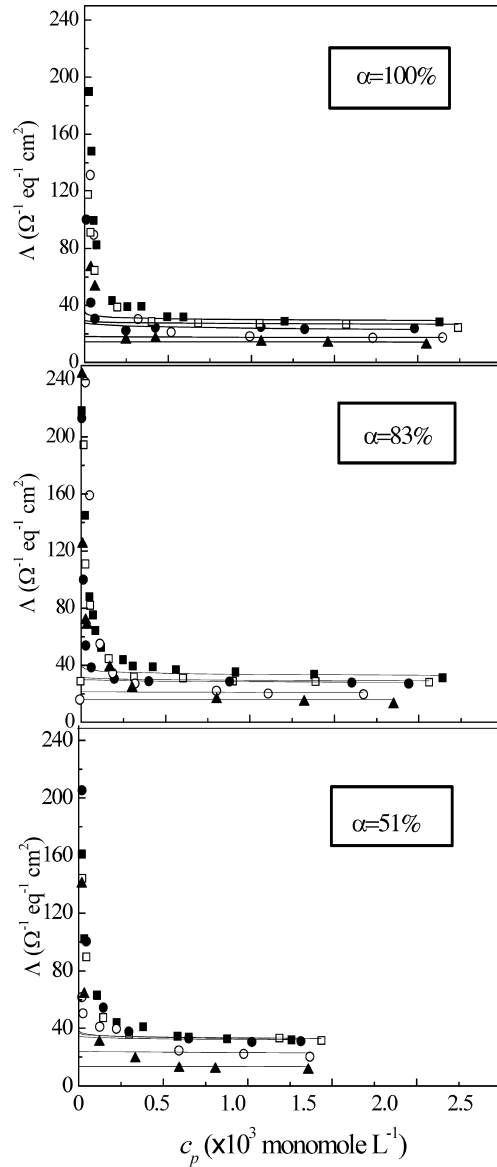

Fig. 4. Concentration dependence of equivalent conductivities of NaPSS with indicated degrees of sulfonation in aqueous solutions with following NaCl concentrations c_s : (■) salt-free, (□) 2×10^{-6} M, (●) 2×10^{-5} M, (○) 5×10^{-4} M, and (▲) 1×10^{-3} M.

where $300U^*$ contains only the charged-solvent effect and was given by

$$300U^* = |z_1|^{-1}\left[\varepsilon kT/(3\pi\eta e)\right]|\ln(kb)| \tag{12}$$

while

$$\alpha = 1 - \tfrac{1}{3}\nu_1(\nu_1 + \nu_2)^{-1}|z_1 z_2|^{-1}(z_1^2 - z_2^2) \tag{13}$$

$$\beta = 1 + 108\nu_1(\nu_1 + \nu_2)^{-1}(300U^*)\left(\frac{z_1^2}{\lambda_1^s} + \frac{z_2^2}{\lambda_2^s}\right) \tag{14}$$

where ν_i is the number of ions of species i in the formula for the small electrolyte (e.g. $\nu_1 = 1$, $\nu_2 = 1$ for NaCl); λ_i^s is the ionic conductivity of the small ions; z_i is the valence of

the small ions; and κ defined here is as follows:

$$\kappa^2 = \left(\frac{4\pi e^2}{\varepsilon KT}\right)\left(\frac{c_p}{\xi_M} + 2c_s\right) \tag{15}$$

Eqs. (10)–(15) were used to calculate λ_p of NaPSS polyions as functions of c_p and c_s for various degrees of sulfonation. f was then obtained by fitting the experimental data in Fig. 4 with calculated λ_p substituting for Eq. (5) and allowing f_{theo} replaced by the adjustable f. The results shown in Table 3 indicate that f decreased with the concentration of external salts for all three NaPSS samples. Since f is also an indication of chain conformation for NaPSS in the semidilute regime, we plotted ν obtained from Figs. 1 and 3 as a function of f obtained from Figs. 2 and 4. The results
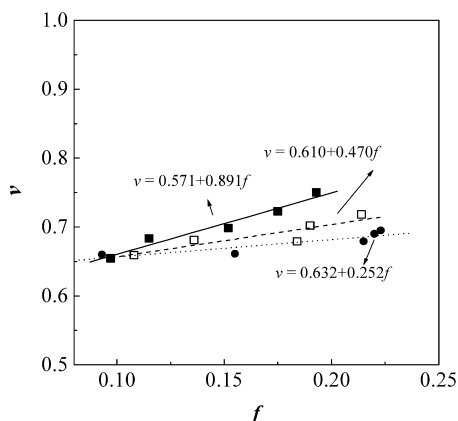
Fig. 5. Plots of the chain conformation index ν versus the dissociation extent f of counterions in salt-containing aqueous solutions of NaPSS with following degrees of sulfonation: (■) 100%, (□) 83%, and (●) 51%. The lines were obtained by fitting the data with the first-order least-square method.

shown in Fig. 5 indicate that they could be fit by the first-order least-square method with following relationship:

$$\nu = \nu_0 + Bf \qquad (16)$$

where ν_0 is the chain conformation index at $f \rightarrow 0$ and equal to 0.604 ± 0.02 averaged from the data of three NaPSS samples with various degrees of sulfonation; and B is the proposition constant between ν and f. The increase of B with the degree of sulfonation shown in Fig. 5 indicates that the trend of increasing the chain extension of polyelectrolytes with the extent of counterion dissociation was enhanced by increasing the charge density.

When NaPSS approached to a neutral chain under the condition of $f \rightarrow 0$ or $B \rightarrow 0$ (at $\alpha \rightarrow 0$), ν closed to 0.6, which is agreeable with most of the theoretical predictions [8,17]. Muthukumar [8] gave $n = 0.25$ in $\eta_{red} \sim c_p^n$ for the polyelectrolyte solutions with high salt content, which is corresponding to $\nu = 0.6$ from Eq. (4). Rubinstein et al. [17] have pointed out that, for the polyelectrolyte solutions in the semidilute regime with high salt content to screen the Coulomb interaction between charged monomers, the concentration dependence of the correlation length ξ (defined in Eq. (3)) is similar to that of the uncharged polymer $\xi \sim c_p^{-0.75}$, which is corresponding to $\nu = 0.6$ according to our scaling relation.

4. Conclusions

The relationship between the chain conformation of NaPSS with various degrees of sulfonation and the dissociation extent of counterions in the semidilute region was established in this study. For the salt-free system, to increase the degree of sulfonation increases the chain conformation index ν but decreases the dissociation extent f of counterions. For the salt-containing systems, ν increased linearly with f by decreasing the salt content and the slope was increased with the degree of sulfonation. All the estimated ν approached to the theoretical value of 0.6 for neutral chain when the dissociation extent of counterions was linearly extrapolated to zero.

Acknowledgements

References

[1] Fuoss RM, Strauss UP. J Polym Sci 1948;3(2):246–63.
[2] De Gennes PG, Pincus P, Velasco RM, Brochard F. J Phys (Paris) 1976;37:1461–73.
[3] Yamanaka J, Araie H, Matsuoka H, Kitano H, Ise N, Yamaguchi T, Saeki S, Tsubokawa M. Macromolecules 1991;24:6156–9.
[4] Roure I, Rinaudo M, Milas M. Ber Bunsen-Ges Phys Chem 1996; 100(6):703–6.
[5] Cohen J, Priel Z, Rabin Y. J Chem Phys 1988;88(11):7111–6.
[6] Lin KF, Cheng HL. Macromolecules 2000;33:4961–5.
[7] Bueche F. Physical properties of polymer. New York: Interscience; 1970. Chapter 3.
[8] Muthukumar M. J Chem Phys 1997;107:2619–35.
[9] Colby RH, Boris DC, Krause WE, Tan JS. J Polym Sci Polym Phys 1997;35:2951–60.
[10] Manning GS. J Phys Chem 1975;79(3):262–8.
[11] Manning GS. J Phys Chem 1981;85(11):1506–15.
[12] Kuhn PS, Levin Y, Barbosa MC. Macromolecules 1998;31:8347–55.
[13] Lin KF, Yang SN, Cheng HL, Cheng YH. Macromolecules 1999;32: 4602–7.
[14] Cheng HL, Lin KF. Langmuir 2002;18:7287–90.
[15] Cheng HL, Lin KF. Macromolecules 2003;36:6949–51.
[16] Vink H. Makromol Chem 1981;182:279–81.
[17] Dobrynin AV, Colby RH, Rubinstein M. Macromolecules 1995;28: 1859–71.