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Coil–globule transition studies of sodium poly(styrene sulfonate) by dynamic light scattering

Ersin Serhatli[a], Müge Serhatli[b], Bahattin M. Baysal[c,d,*], Frank E. Karasz[e]

[a]Department of Chemistry, Istanbul Technical University, 80626 Maslak, Istanbul, Turkey
[b]TUBITAK-Institute for Genetic Engineering and Biotechnology, 41470 Gebze, Turkey
[c]Department of Chemistry, TUBITAK-Marmara Research Center, P.O. Box 21, 41470 Gebze, Kocaeli, Turkey
[d]Department of Chemical Engineering, Boğaziçi Üniversity, 80815 Bebek, Istanbul, Turkey
[e]Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA

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Abstract

The coil–globule transition behavior of sodium poly(styrene sulfonate) (NaPSS) ($M_w = 1.2 \times 10^6$ g/mol) in 4.17 M aqueous NaCl solution has been studied by dynamic light scattering. The polymer dimensions show a smooth and continuous contraction below the reference temperature (18 °C). The hydrodynamic radius ($\langle R_h \rangle$) of NaPSS in this system was reduced from 13.1 nm (18 °C) to 9.1 nm at 10 °C. At the latter temperature the polymer segment volume fraction was calculated to be 0.58. The contraction for this and other NaPSS samples investigated in this study is somewhat limited because under these high ionic strength conditions the polymer chains already contracted as a result of the screening effect of the ions. © 2002 Published by Elsevier Science Ltd.

Keywords: Dynamic light scattering; Coil–globule transition; Sodium poly(styrene sulfonate)

1. Introduction

A fundamental phenomenon in polymer science is the coil–globule transition of a single solvated macromolecular chain which occurs when a polymer is quenched from a good solvent into a poor solvent. This transition has been the subject of many investigations during the past four decades. Early contributions in this area were reviewed by Yamakawa [1], Williams et al. [2], Fujita [3], and Des Cloizeaux and Jannink [4].

Most coil–globule transition experiments have been carried out using polystyrene solutions of extremely low concentration. Various experimental methods such as static and quasi-elastic light scattering, small angle neutron scattering, ultracentrifuge and viscometric measurements have been used for the determination of linear polymer dimensions. Two sets of contradictory experimental results for the contraction of polystyrene in cyclohexane have been reported in early studies, one yielding a very sharp transition with the other indicating a gradual contraction [5,6]. The overall chain contraction reported for the polystyrene–cyclohexane system was only to 75% of the unperturbed theta state [5–9]. This small decrease in size does not satisfy criteria for a densely packed collapsed globule. Recent work which extended coil–globule studies to highly dilute solutions of macromolecules containing polar groups, such as the halogenated polystyrenes, poly(4-chlorostyrene) and poly(2-chlorostyrene), show that chain contractions can exceed those reported in earlier studies of the polystyrene/cyclohexane system. However, they are still not consistent with single globule formation [10].

The collapse from a coil to a compact globular state is now established experimentally for two flexible macromolecules: Poly(*N*-isopropylacrylamide) and poly(methyl methacrylate) (PMMA). Experimental studies of the collapse of poly(*N*-isopropylacrylamide) in water solutions have been reported in detail [11–15]. For PMMA detailed static [16,17] and dynamic [18,19] light scattering as well as viscometric [20] measurements have been carried out in various solvents. Since phase separation occurred very slowly in this system, molecular dimensions could be determined reliably even far below the phase separation temperature [16]. In each of the solvent systems investigated, a gradual contraction of PMMA chains was observed

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* Corresponding author. Address: Department of Chemistry, TUBITAK-Marmara Research Center, P.O. Box 21, 41470 Gebze, Kocaeli, Turkey.
E-mail address: bmbaysal@hotmail.com (B.M. Baysal).

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and the chain size was reduced to about 35% of its θ-state dimension. The segment volume fraction was estimated as $\phi = 0.56$, which indicates that the density in the polymer domain of the globule is relatively high [18,20].

Since the prediction of the collapse of a polymer chain from a coil to a rather dense form by Stockmayer in 1960 [21], the coil–globule transition has also been the subject to extensive theoretical research. The expansion of a random coil and the temperature dependence of the expansion factor α can be obtained from the classical Flory equation for the excluded volume [22] as

$$\alpha^5 - \alpha^3 = (2/\pi^2)BN^{1/2}\tau. \quad (1)$$

Ptitsyn et al. [23] devised a generalization of the Flory self-consistent field theory of polymer solutions. Birshtein and Pryamitsyn [24] carried out a rigorous approach to the calculation of the elastic entropy or the corresponding entropy force connected with chain deformation. For the contracted coil they derived an equation for the expansion factor α, ($\alpha^2 = \langle R_g^2\rangle/\langle R_{g(\theta)}^2\rangle$ or $\alpha_\eta^2 = \langle R_h^2\rangle/\langle R_{h(\theta)}^2\rangle$)

$$\alpha^3 - \alpha - C(\alpha^{-3} - 1) = BN^{1/2}\tau, \quad (2)$$

where in the above equations N represents the number of Kuhn segments in the chain, B and C are parameters that do not depend on both molecular weight M and temperature T but depend on chain stiffness; $\tau = (T - \theta)/\theta$ is the reduced temperature; C is related to the third virial coefficient [24].

The theory of coil–globule transition of homopolymers has now been developed with quantitative accuracy. Theoretical studies have utilized a variety of approaches in focusing on different aspects of the polymer collapse problem [25]. Theoretical progress covering the last 40 year period has been reviewed recently by Grosberg and Khokhlov [26].

Recently we have studied the kinetics of the coil–globule chain collapse of PMMA in isoamyl acetate and *n*-butyl chloride by dynamic light scattering (DLS) [27]. The coil/globule transition times for a high molecular weight PMMA chain rapidly cooled from the θ-state (61 °C for isoamyl acetate; 38 °C for *n*-butyl chloride) to the lowest possible temperatures (18.5 and 13.8 °C) attainable without complete aggregation was found to be of the order of the thermal equilibration time (about 15 s) of the solution [19, 27]. A two-stage kinetic scheme for a single chain collapse was proposed theoretically [28–30]. Since the coil–globule relaxation time for a flexible polymer (PMMA) is rather fast, the earlier reported appearance of two-stage kinetics for the contraction process are not related to single chain collapse but rather to the aggregation of the polystyrene [31] or PMMA [32,33] molecules.

The extensive theoretical studies on heteropolymers have been motivated by their perceived relation to the protein folding problem. Theoretical treatments of copolymer collapse are increasing and a first-order coil–globule transition, unlike that in the homopolymer, has been predicted [34–40]. In recent work, we have studied the coil–globule transitions of random (statistical) and alternating copolymers of styrene and methyl methacrylate in various solvents and compared these results with the contractions observed in homopolymers. It was noted that in copolymers the temperature interval from the θ-state to that in the collapsed state was rather short compared to homopolymers [41].

The logical next step in this topic is the study of the coil–globule collapse transition in polyelectrolytes. One of the first relevant experiments were on the studies of dimensional changes of linear poly(*N*-isopropylacrylamide) ionomers [42] and of ionizable derivatives of poly(*N*-isopropylacrylamide) in water [43].

Many biological macromolecules and synthetic polymers are highly charged. Cellular processes often take advantage of shape fluctuations of charged biomolecules in performing biological functions.

The second virial coefficient of polyelectrolytes can be highly nonideal because of the electrostatic interaction between ionic charges as well as the polymeric character of polyions. Most of the nonideal behavior of linear polyelectrolytes is erased by the strong electrostatic interaction between charges, but the contribution of the polymeric character of polyions cannot be neglected [44]. There is a considerable amount of theoretical work on chain expansion and virial coefficients of charged homo and copolymers. A brief review of theories of polyelectrolyte conformation has been presented by Stigter and Dill [45] recently. Most of the polyelectrolyte experiments involve added salt which provides a relationship to many biopolymer solutions.

Studies of the solution properties and chain expansion behavior of stiff (DNA) [45–47] rigid-rod [48] and flexible polyelectrolytes has also been the subject of extensive research [45,47,49]. Dimensional studies have been performed using various polyelectrolytes such as poly(styrene sulfonate) [45,47,49] and other ion-containing polymers [48,50,51].

The collapse kinetics of strongly charged polyelectrolytes in poor solvents has been investigated by Langevin simulations and scaling arguments [52]. The role of counterion, valency, solvent quality, and the shape of the counterions on the dynamics of collapse have been studied recently [52]. Simulation results show that, the rate of collapse, which is measured using the time dependence of the radius of gyration of the chain, increases sharply as the counterion charge increases from 1 to 4. The structure of the globule is controlled by the counterion charge, and a general collapse mechanism emerges [52].

Small-angle neutron scattering (SANS) experiments have been used to study fully charged poly(styrene sulfonate) (PSS) polyions. In sodium poly(styrene sulfonate) (NaPSS) solutions, at low ionic strength the conformation does not change; the chain remains wormlike. For high ionic strength NaPSS solutions progressive changes occur. With multivalent ions, the chain progressively deviates from a wormlike chain model. If multivalent ions are added, the chain appears ‘thicker’ and ionic strength is not the only parameter that controls the conformation [53].

SANS observations of the polycationic polyelectrolyte, poly(methacrylo ethyl trimethylammonium methyl sulfate) of high molecular weight in dilute solution in acetone–water mixtures displays a coil–globule transition above a certain threshold concentration of acetone. The collapsed state of this molecule consists of a short sequence of dense spheres with smooth surfaces, connected by regions of loose polymer [54].

In this work, we have studied the coil–globule transition of poly(styrene sulfonate) in a 4.17 M aqueous NaCl solutions at 16.4 °C (θ-solvent) [44,49]. The hydrodynamic radius, R_h, of the polyelectrolyte was measured by a dynamic laser spectrometer.

2. Experimental section

2.1. Materials

NaPSS samples were purchased from Scientific Polymer Products, Inc., Ontario, NY. Two samples were used with the following characteristics: for NaPSS-1, $M_w = 1.21 \times 10^6$, $M_w/M_n = 1.17$, elemental analysis for sulfur found 13.18% (85% of theoretical value); and for NaPSS-2, $M_w = 7.96 \times 10^5$, $M_w/M_n = 1.16$, elemental analysis for sulfur found 13.28% (86% of theoretical value). Molecular weights were obtained by light scattering, while polydispersities were obtained by GPC.

2.2. Dynamic light scattering measurements

The preparation of dust-free solutions for DLS measurements was as follows. A stock solution of NaPSS-1 with a concentration 7.5×10^{-5} g/g was prepared in the theta solvent 4.17 M NaCl deionized water. The stock solution was held in an oven at 25 °C for complete dissolution. This stock solution having a concentration of 8.59×10^{-5} g/ml was filtered carefully into a dust-free light scattering cell using 0.2 μm Millipore filters.

DLS measurements were conducted by using a commercial DLS spectrometer (ALV/LSE 5000) operating at $\lambda = 514.5$ nm with an Ar laser. Thin-walled cylindrical cells (0.3048 mm wall thickness, 10 mm outer diameter and 75 mm length were used to shorten the thermal equilibration time [27]. (The borosilicate flat bottom DLS cells were purchased from Wilmad Glass, Buena, NJ). The temperature of the DLS vat was controlled to ± 0.01 °C.

The polymer solution was quenched to the selected temperature from 25 °C to induce the size change which was determined by means of DLS in terms of the hydrodynamic radius (R_h).

The raw output of a DLS experiment is the autocorrelation function of the scattered light intensity, $G_2(\sigma)$, typically plotted against logarithmic time. The correlation functions were measured at a scattering angle of 33°. $G_2(\sigma)$ is related to the normalized first-order electric field correlation function $g_{(1)}(\sigma)$ by [33,34]

$$G_2(\sigma) = A[1 + \beta|g_1(\sigma)|^2] \tag{3}$$

where A is a baseline constant, β, the coherence parameter depending on the instrumental optics and σ ($\equiv \Gamma^{-1}$) the delay time. For polydisperse and concentrated systems, $g_{(1)}(\sigma)$ is expressed by the distribution function $G(\sigma)$ of the decay rate Γ as

$$g_1(\sigma) = \int G(\Gamma)\exp(-\Gamma\sigma)\mathrm{d}\Gamma \tag{4}$$

where $G(\Gamma)\mathrm{d}\Gamma = 1$. That is, $g_{(1)}(\sigma)$ is the Laplace transform of $G(\Gamma)$.

For a diffusive relaxation, Γ can be further related to the average translational diffusive coefficient D by $D = (\Gamma/q^2)_{q\to 0}$, where $q = 4\pi n/\lambda(\sin\theta/2)$, $\lambda = 514.5$ nm, $n =$ refractive index of solvent and $\theta =$ scattering angle. By using the Stokes–Einstein equation, the hydrodynamic radius, R_h, may be evaluated from the diffusion coefficient

$$\langle R_h\rangle = k_B T/6\pi\eta D \tag{5}$$

where k_B is the Boltzmann constant, η, the solvent viscosity and T is the absolute temperature. Viscosity (η) of the solvent (4.17 M aqueous NaCl) was measured by a precision capillary viscometer (Cannon-Ubbelohde 100 C-660). The viscometer constant was the same at all temperatures and is 0.01016 cS/s. The solvent viscosity, η, in centipoise (cP) was obtained by multiplying the efflux time in seconds by the viscometer constant and the density of the solvent in g/cm^3. The temperature dependence of the solvent viscosity is given by the following equation

$$\log \eta(T) = -2.8316 + 891.3/T \tag{6}$$

where η is the solvent viscosity (cP) and T is the temperature (K). Data analysis of the electric field time correlation curve were performed by using the method of cumulants [31] and the CONTIN method [55]. The data obtained by the latter method are reported in this work.

3. Results and discussion

Various comments on the distinction between the dilute and semidilute concentration regimes, and on the ionic strength dependence of the dimensions of polyelectrolytes have been reviewed recently [56,57]. Takahashi et al. [44] found from phase separation experiments that 4.17 M aqueous NaCl solution is a θ solvent at 25 °C. However, Beer et al. [58] recently claimed that NaCl solutions of their NaPSS samples did not exhibit solubility or precipitation behavior consistent with the presence of a θ state. Hirose et al. [49] in a comprehensive investigation have analyzed narrow distribution samples of NaPSS which were studied by static light scattering, sedimentation equilibrium, and intrinsic viscosity in 0.5 M aqueous NaCl at 25 °C and in 4.17 M aqueous NaCl at 16.4 °C. They reported that the light scattering second virial coefficient vanished for high M_w samples in 4.17 M aqueous NaCl solution of NaPSS at 16.4 °C (the θ point).

NaPSS has an extended chain conformation in pure aqueous solution due to the electrostatic repulsion between negative charges on the polyelectrolyte chain. If a salt is added to a dilute solution of NaPSS, the counterion condensation causes the polyelectrolyte chain to contract. The conformation of NaPSS chains in aqueous solutions is strongly dependent on both the sulfur content of the macromolecules as well as the electrolyte concentration. The different solution behaviors of NaPSS reported earlier by three research groups [44,49,58] that are mentioned above are obviously related to the variety of sulfur contents of their samples. At the θ-temperatures, the value of characteristic constant is given [49] as $\langle R_g^2\rangle/M = 3.0\times10^{-4}$ nm^2 for a completely (100%) sulfonated polyelectrolyte. This corresponds a constant value $\langle R_h^2\rangle/M = 1.3\times10^{-4}$ nm^2 if one consider the following Akcasu–Han relation [59], $(R_h/R_g) = 0.664$. The values of R_h^2/M calculated for NaPSS-1 and NaPSS-2 at 18 °C are 1.4×10^{-4} and 1.0×10^{-4} nm^2, respectively. Considering experimental errors (±5%) in R_h determinations and sulfur content differences of polymeric samples, we can say that 18 °C is a good choice to estimate the expansion factor.

Measurements of contraction in dilute water solution of NaPSS in terms of R_h by the addition of small amounts of NaCl (5 and 100 mM) has been reported earlier [60].

Fig. 1 shows the intensity autocorrelation function $G_2(\tau)$ of the dilute (8.59×10^{-5} g/ml) NaPSS-1 solution with an average decay rate, $\Gamma = 0.559$ ms^{-1} and the variance $\mu_2/\Gamma^2 = 0.115$ at the θ temperature of 16.4 °C and a scattering angle of 33°. M_z/M_w was found to be 1.44 for this sample by using the relation [61] $M_z/M_w \cong 1 + 4(\mu_2/\Gamma^2)$. The average hydrodynamic radius R_h of the polymer was calculated from CONTIN analysis [55] to be 11.6 nm at 16.4 °C (13.4 nm at 18.0 °C). In Fig. 2 the hydrodynamic radius determined from the correlation function measurements is shown as a function of temperature for dilute NaPSS-1 and NaPSS-2 solutions in 4.17 M aqueous NaCl DLS measurements at each temperature were conducted after equilibrium was reached. All experimental points represent the average values of two experiments. The contraction of the single chains can be clearly seen in Fig. 2. As we have already mentioned above there is some ambiguity in establishing the θ temperature of this system. Since a relatively large contraction was observed for each NaPSS sample below 18.0 °C, we have considered this temperature as the reference temperature in calculation of the expansion factor for the 4.17 M aqueous NaCl system. A gradual contraction was observed for both samples down to 10.0 °C, where aggregation started after 25 min. At this temperature, calculated α_h values were 0.69 and 0.74 for samples NaPSS-1 and NaPSS-2, respectively. The system was thermodynamically stable and the reported hydrodynamic radius values were independent of time. The hydrodynamic size (R_h) of the NaPSS chains at 10.0 °C was reduced to about 70% of their dimensions at 18.0 °C. The contraction for NaPSS samples observed in this work is rather limited because in this high ionic strength NaCl solution polymer chains were already highly contracted due to the screening effect [58]. After reaching a globular state at 10 °C the sample was gradually heated and R_h values were

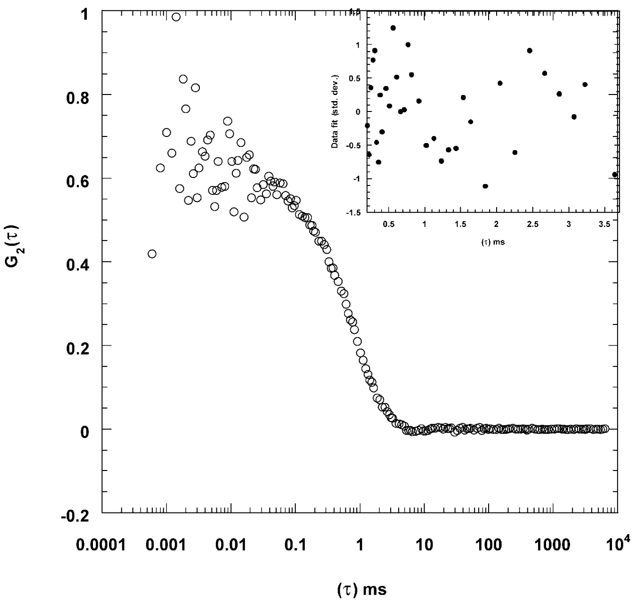

Fig. 1. The intensity autocorrelation function $G_2(\tau)$ of NaPSS-1 ($M_w = 1.21\times10^6$) in 4.17 M aqueous NaCl solution ($C = 8.59\times10^{-5}$ g/ml) at 16.4 °C. The inset shows the deviation plot based on a second-order cumulants fit.

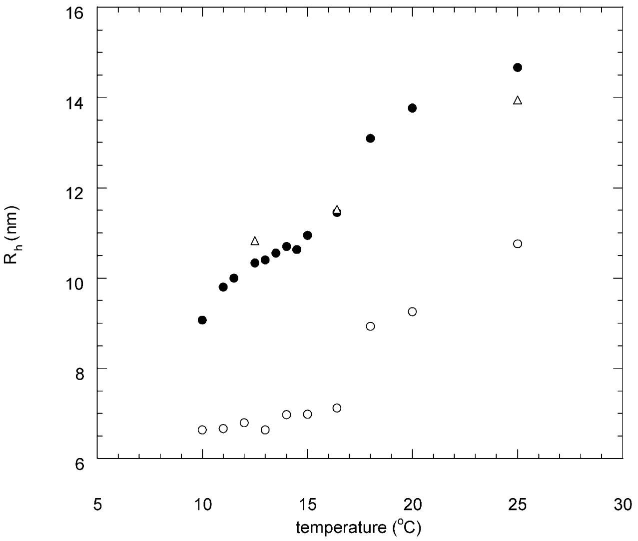

Fig. 2. Hydrodynamic radius, $\langle R_h\rangle$ vs temperature for NaPSS-1 in 4.17 M aqueous NaCl solution. Cooling (•) and heating (△). Cooling and heating runs coincide at 16.4 °C.

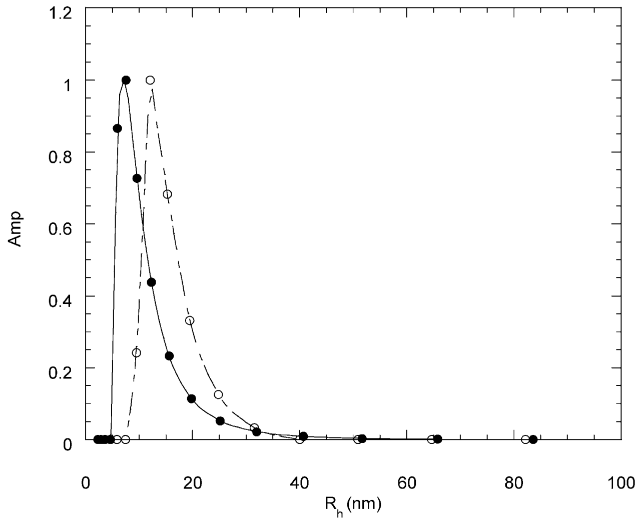

Fig. 3. Hydrodynamic size distribution of NaPSS-1 in 4.17 M aqueous NaCl solution at 18.0 °C (○: $T = 18.0$ °C, $\langle R_h \rangle = 8.93$ mm), and poor solvent conditions (•: $T = 10.0$ °C, $\langle R_h \rangle = 6.64$ nm).

obtained at elevated temperatures. These experiments are indicated in Fig. 2 by open triangles at 12.5, 16.4 and 25 °C, respectively. The collapse and expansion curves do not display significant hysteresis.

A typical hydrodynamic size distribution of NaPSS-1 in 4.17 M aqueous NaCl at 18 °C and poor solvent condition ($T = 10$ °C) are given in Fig. 3. In this figure, the data for the distribution plot was taken 10 min after the sample solution was quenched from 18 to 10 °C. Although the shape of R_h distribution still obeyed a single mode distribution, the polydispersity of R_h distribution (M_z/M_w) increased from 1.44 to 1.56 at 10 °C and the symmetry of the curve became distorted, with the upper end of the distribution curve being stretched out. This observation implies that the polymer coil was stable in the contracted state for about 10 min, and at this point DLS could not yet resolve a bimodal distribution.

In Fig. 4, the contraction of the hydrodynamic radius of NaPSS-1 in the experiment from the reference temperature (18.0 °C) to 16.4 °C and finally quenched to 10 °C is shown as a function of time. The R_h values of the globule was measured 4 min after the quench and was constant for about 25 min. After this time aggregation was observed.

Fig. 5 shows the temperature dependence of the measured linear expansion of the two NaPSS samples in 4.17 M aqueous NaCl. The experimental DLS measurements exhibit a continuous rather than a discrete transition. The temperature interval to reach the globular state from the reference state is rather narrow, about 8 °C for both samples.

Fig. 6 shows the contraction of the hydrodynamic radius of NaPSS-1 in 2.0 M aqueous NaCl solution as a function of temperature. Since the system is in a good solvent it is not possible to observe globule formation. We have observed only the expansion of the coil by increasing the temperature.

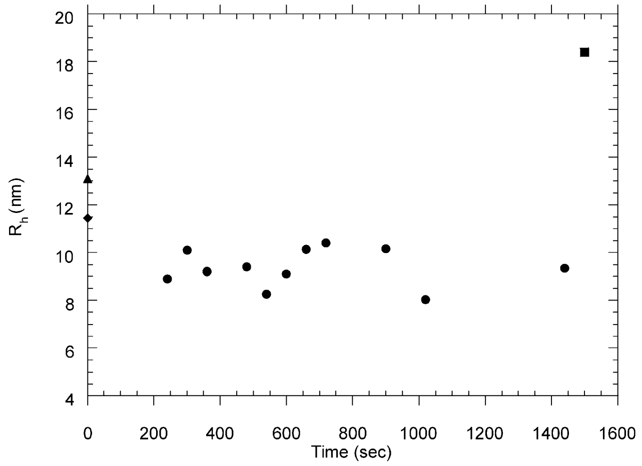

Fig. 4. $\langle R_h \rangle$ of NaPSS-1 in 4.17 M aqueous NaCl solution as a function of time. The $\langle R_h \rangle$ values measured 18.0 °C (▲) and 16.4 °C (◆). The sample was further quenched to 10.0 °C. The $\langle R_h \rangle$ values of globule were measured 4 min after quenching and were constant for about 25 min. (■) corresponds to aggregation appearing after about 1500 s.

The segment volume fraction (Φ) in the globule may be given by

$$\Phi = (M_w/\rho)/\{(4\pi/3)\langle R_h^2 \rangle^{3/2} N_A\} \tag{7}$$

where $\rho = 1.1$ g/ml is the density of NaPSS in the solid state, M_w the molecular weight of NaPSS and $N_A$is Avogadro number. (It should be noticed that, for a DLS value of radius R_h^3, $\kappa = 1$.) The calculated values of the segment volume fractions (Φ) for NaPSS samples at various temperatures are given in Table 1. It will be seen that even at 25 °C the polymer chains show considerable contraction. The segment volume fractions of the globules at 10 °C are very high. The volume fractions increase about four times by lowering the temperature from 25 to 10 °C.

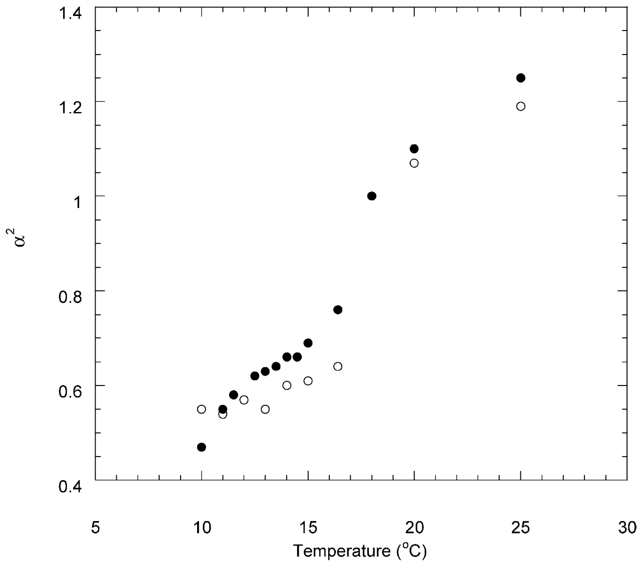

Fig. 5. Expansion factor, α_h^2, vs temperature for NaPSS in 4.17 M aqueous NaCl solution. (•) NaPSS-1, (○) NaPSS-2. A reference temperature of 18.0 °C is assumed, $\alpha_h^2 = 1$ for both samples.

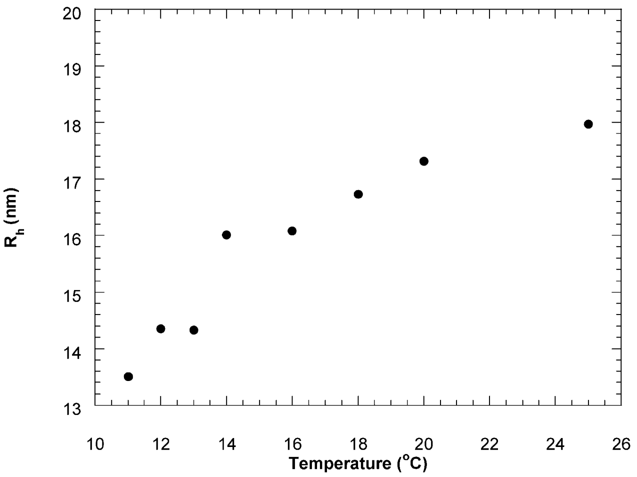

Fig. 6. Hydrodynamic radius, $\langle R_h \rangle$, vs temperature for NaPSS-1 in 2.0 M aqueous NaCl solution.

Table 1
The polymer segment volume fractions of NaPSS chains at various temperatures

Sample	M_w (× 10^6 g/mol)	Temperature (°C)	R_h (nm)	Φ
NaPSS-1	1.21	25	14.7	0.14
		18	13.1	0.19
		10	9.07	0.58
NaPSS-2	0.796	25	10.8	0.23
		18	8.93	0.40
		10	6.69	0.96

4. Conclusions

DLS experiments were performed for very dilute NaPSS solutions in 4.17 M and in 2.0 M aqueous NaCl. In high ionic strength NaCl solution, polyelectrolyte chains were already highly contracted due to the screening effect of the salt. However, a further contraction of polyelectrolyte was observed and globular forms were obtained at about 10 °C. The segment volume fractions at the globular state are estimated as 0.58 (NaPSS-1) and 0.96 (NaPSS-2) for two polyelectrolyte samples studied in this work. The value of $\Phi = 0.96$ means that the solvent molecules are expelled nearly completely from the globule of polymer chain, and it is observed the first time for a coil–globule transition of a synthetic macromolecule. The difference between these two calculated values may come from the differences of sulfur contents of the polymeric samples or because of experimental errors in R_h determinations.

Acknowledgments

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References

[1] Yamakawa H, Modern theory of polymer solutions, New York: Harper & Row; 1971.
[2] Williams C, Brochard F, Frisch CH. Annu Rev Phys Chem 1981;32:433.
[3] Fujita H. Polymer solutions. New York: Elsevier; 1990.
[4] Des Cloizeaux JJ, Jannink G. Polymer solutions: their modelling and structure. Oxford: Clarendon Press; 1990.
[5] Chu B, Wang Z. Macromolecules 1988;21:2283.
[6] Park IHo, Wang QW, Chu B. Macromolecules 1988;20:1965.
[7] Park IH, Fetters L, Chu B. Macromolecules 1988;21:1178.
[8] Chu B, Wang Z. Macromolecules 1989;22:380.
[9] Baysal BM, Uyanık N. Polymer 1992;33:4798.
[10] Hamurcu EE, Akcelrud L, Baysal BM, Karasz FE. Polymer 1998;39:3657.
[11] Kubota K, Fujishige S, Ando I. J Phys Chem 1990;94:5154.
[12] Ito D, Kubota K. Macromolecules 1997;30:7828.
[13] Wang X, Qin X, Wu C. Macromolecules 1998;31:2972.
[14] Wu C, Wang X. Phys Rev Lett 1998;80:4092.
[15] Graziano G. Int J Biol Macromol 2000;27:89.
[16] Nakata M. Phys Rev E 1995;51:5770.
[17] Nakata M, Nakagawa T. Phys Rev E 1997;56:3338.
[18] Gürel EE, Kayaman N, Baysal BM, Karasz FE. J Polym Sci, Polym Phys 1999;37:2253.
[19] Kayaman N, Gürel EE, Baysal BM, Karasz FE. Polymer 2000;41:1461.
[20] Baysal BM, Kayaman N. J Chem Phys 1998;109:8701.
[21] Stockmayer WH. Macromol Chem Phys 1960;35:54.
[22] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press; 1953.
[23] Ptitsyn OB, Krow AK, Eizner YY. J Polym Sci, Part C 1968;16:3509.
[24] Birshtein TM, Pryamitsyn VA. Macromolecules 1991;24:1554.
[25] Halperin A, Goldbart PM. Phys Rev E 2000;61:565.
[26] Grosberg AYu, Khokhlov AR. Statistical physics of macromolecules. New York: AIP; 1994.
[27] Kayaman N, Gürel EE, Baysal BM, Karasz FE. Macromolecules 1999;32:8399.
[28] de Gennes PG. J Phys Lett 1985;46:L639.
[29] Grosberg AY, Nechaev SK, Shaknovich EI. J Phys (Paris) 1988;49:2095.
[30] Grosberg AY, Kuznetzov DV. Macromolecules 1993;26:4249.
[31] Chu B, Ying Q, Grosberg AY. Macromolecules 1995;28:180.
[32] Nakata N, Nakagawa T. J Chem Phys 1999;110:2703.
[33] Nakata N, Nakagawa T. J Chem Phys 1999;110:2711.
[34] Monari H, Stella AL, Vanderzande C, Orlandini E. Phys Rev Lett 1999;83:112.
[35] Ganazzoli FJJ. Chem Phys 1998;108:9924.
[36] Olaj OF, Neubauer B, Zifferer G. Macromolecules 1998;31:4342.
[37] Timoshenko EG, Kuznetsov AY, Dawson KA. J Chem Phys 1995;102:1816.
[38] Crooks GE, Ostrovsky B, Bar-Yam Y. Phys Rev E 1999;60:4559.
[39] Noguchi H, Yoshikawa K. J Chem Phys 1998;109:5070.
[40] Kuznetsov AY, Timoshenko EG, Dawson KA. J Chem Phys 1995;103:4807.
[41] Karal-Yılmaz O, Gürel EE, Kayaman-Apohan N, Baysal BM, Karasz FE. Polymer 2001;42:9433.
[42] Qiu X, Li M, Kwon CMS, Wu C. J Polym Sci, Part B: Polym Phys 1998;36:1501.
[43] Lu T, Vesterinen E, Tenhu H. Polymer 1998;39:641.

[44] Takahashi A, Kato T, Nagasawa M. J Phys Chem 1967;71:2001.
[45] Stigter D, Dill KA. Macromolecules 1995;28:5325.
[46] Ueda M, Yoshikawa K. Phys Rev Lett 1996;77:2133.
[47] Borochov N, Eisenberg H. Macromolecules 1994;27:1440.
[48] Liu T, Rulkens R, Wegner G, Chu B. Macromolecules 1998;31:6119.
[49] Hirose E, Iwanoto Y, Norisuye T. Macromolecules 1999;32:8629.
[50] Aseyev VO, Tenhu H, Klenin SI. Macromolecules 1998;31:7717.
[51] Aseyev VO, Tenhu H, Klenin SI. Polymer 1999;40:1173.
[52] Lee N, Thirumalai D. Macromolecules 2001;34:3446.
[53] Dubois E, Boue F. Macromolecules 2001;34:3684.
[54] Aseyev VO, Klenin SI, Tenhu H, Grillo I, Geissler E. Macromolecules 2001;34:3706.
[55] Provencher SW. Macromol Chem 1979;20:180.
[56] Mandel M. In: Hara M, editor. Polyelectrolytes, science and technology. New York: Marcel Dekker; 1993. p. 1.
[57] Förster S, Schmidt M. Adv Polym Sci 1995;120:53.
[58] Beer M, Schmidt M, Muthukumar M. Macromolecules 1997;30:8375.
[59] Akcasu AZ, Han CC. Macromolecules 1979;12:276–80.
[60] Chu B, Wang Z. Prog Colloid Polym Sci 1993;91:142.
[61] Brown JC, Pusey PN. J Phys D 1974;L31:7.