Polymer Vol. 38 No. 24, pp. 6083–6085, 1997
© 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/97/$17.00+0.00

PII: S0032-3861(97)00243-7

Electrostatic persistence length of NaPSS polyelectrolytes determined by a zero average contrast SANS technique

Koji Nishida[a], **Hiroshi Urakawa**[b], **Keisuke Kaji**[a,*], **Barbara Gabrys**[c] **and Julia S. Higgins**[d]
[a]*Institute for Chemical Research, Kyoto University, Uji, 611 Kyoto-fu, Japan*
[b]*Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, 606 Kyoto, Japan*
[c]*Department of Physics, Brunel University, West London, Kingston Lane, Uxbridge UB8 3PH, Middlesex, UK*
[d]*Department of Chemical Engineering, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW1 2AZ, UK*
(Revised 7 March 1997)

The electrostatic persistence lengths b_e of NaPSS polyions have been measured as a function of ionic strength I in the solutions using a small-angle neuron scattering (SANS) technique combined with a zero average contrast (ZAC) method. This ZAC method provides the optical *theta* condition distinguishing the intermolecular scattering functions $S_2(q)$, and thereby the scattering functions of a single chain $S_1(q)$ free from the intermolecular interferences were obtained. The resulting b_e values which were derived by the analysis of $S_1(q)$ are proportional to $I^{-1/2}$. This work confirms and extends an earlier SANS study where the contrast-match was used. © 1997 Elsevier Science Ltd.

(Keywords: polyelectrolytes; electrostatic persistence length; zero average contrast SANS)

Introduction

For several decades polyelectrolytes have been the subject of extensive theoretical and experimental investigation. The conformation of a single polymer chain and the interchain structure in polyelectrolyte solutions are mainly determined by the electrostatic forces except for molecular weight of the polymer chain, which in turn is dominated by the charge density on the polymer chain and ionic strength of the solution as well as polymer concentration[1–4]. Recently, some researchers have proposed a phase diagram showing the characteristics of polyelectrolyte solutions as functions of degree of polymerization and concentration[5]. The phase diagram was drawn on the basis of theory[2,3,6,7] and partly confirmed from scattering experiments[8–11]. In the construction of the phase diagram, the persistence length of the polymer chain plays an essential role, hence more extensive and reliable data for the persistence length is necessary over a wide range of concentration.

In this communication, we report on the concentration dependence of the persistence length for poly(sodium styrene sulfonate) (NaPSS) solutions obtained by using a small angle neutron scattering (SANS) technique. The rationale behind this study is to determine the dependence of the electrostatic persistence length b_e on the concentration; a subject still open for discussion among researchers[2,7,11–19]. In previous SANS studies the contrast-matching method was used[11,20] and, more recently, a technique of the zero average contrast (ZAC)[21] has been employed, which is also employed in this study.

Experimental

Sample preparation. Both deuterated and hydrogenated poly(sodium styrene sulfonate)s (NaPSS) were prepared from deuterated and hydrogenated polystyrenes (PS), respectively, using a conventional method[22]. Weight-averaged molecular weights M_w of the parent PSs were 72 000 and 66 000 for the deuterated and hydrogenated samples, respectively. Both of them had a narrow molecular weight distribution $M_w/M_n = 1.03$. Taking into account the molecular weight of the monomer, this gives nearly the same degree of polymerization $N \cong 640$ for both polymers. Subsequently a mixture of deuterated and hydrogenated NaPSS was prepared with a fraction of deuterated polymer $x = 0.2$. As the solvent, a mixture of heavy water and light water having an isotopic ratio $(D/H)_{solv} = 0.546/0.454$ was employed. The ratio was calculated to meet the optical theta condition (see below). Polymer concentration was varied from 0.183 to 1.445 mol/l.

SANS measurement. Small angle neutron scattering measurements were carried out on the LOQ diffractometer at the pulsed neutron source ISIS, Chilton, UK[23]. This instrument operates in the time-of-flight mode using a 'white beam' of neutrons[24]. The range of the length of scattering vector q accessed in this experiment was 0.01–0.2 Å^{-1}. Here, $q = 4\pi \sin(\theta/2)/\lambda$, θ being the scattering angle, and λ the neutron wavelengths which varied from 2.0 to 9.8 Å at a frequency of 25 Hz. The sample was positioned at a distance of 11.1 m from a liquid hydrogen moderator, which operated at $T = 22$ K, and the sample-to-detector distance was 4.4 m. The scattered intensity was registered with a two-dimensional^{3}He detector. Data reduction was carried out using the standard LOQ data processing program 'Colette'[25]. Further data analysis was carried out using a set of our own programs.

ZAC method-scattering function of a single chain $S_1(q)$. In principle, the observed scattered intensity $I(q,x)$ can be

---

[*] To whom correspondence should be addressed. Tel.: +81-774-38-3140; Fax: +81-774-38-3146

Table 1 Total persistence lengths b_t of NaPSS solutions as a function of polymer concentration C, calculated from q^* values using equation (2)

C (mol/l)	0.183	0.241	0.361	0.482	0.723	0.963	1.445
b_t (Å)	59.7	50.3	42.4	40.6	34.7	32.4	26.5

separated into the intrachain part $S_1(q)$ and interchain part $S_2(q)$[11,20]:

$$I(q,x) = [xb_D^2 + (1-x)b_H^2]S_1(q) + [xb_D + (1-x)b_H]^2 S_2(q) \tag{1}$$

where b_D and b_H denote the average scattering lengths for the deuterated and hydrogenated monomer with respect to the solvent, respectively. The values of b_D and b_H can be controlled by changing the $(D/H)_{solv}$ ratio. Thus, one can choose an appropriate $(d/h)_{solv}$ ratio for a given value of x in order to adjust the coefficient of $S_2(q)$ in equation (1) to zero: the intermolecular interference term $S_2(q)$ disappears. Then, only the scattering intensity $S_1(q)$ arising from the intramolecular interference remains. Note that the disappearance of the intermolecular interference has nothing to do with the existence or nonexistence of intermolecular interaction. In this sense, it is appropriate to refer to this particular case as 'optical theta condition'.

It can be argued that this ZAC method is more convenient than the contrast-matching method if only $S_1(q)$ is measured. In the former method the optical theta condition ($S_2(q) = 0$) is used, hence $S_1(q)$ can be obtained directly from one measurement, whereas the latter method requires several measurements against various x values under the contrast-match condition ($b_H = 0$) in order to extrapolate x to zero from the Zimm plot[26] for example.

Results and discussion

In general, the total persistence length b_t and the radius of gyration R_g of a single chain can be derived from $S_1(q)$. However, the molecular dimension of polyelectrolytes is usually much larger than that of nonelectrolyte polymers, which makes it difficult to access such a low q range where R_g is determined. Therefore, the only pertinent quantity which can be determined is the total persistence length b_t. We determined the value of b_t as outlined below.

Typical examples of scattering curves $S_1(q)$ experimentally obtained are shown in *Figure 1*. Solid lines show Debye functions[26] [equation (2)] for the Gaussian coil

$$S_1(q)_{\mathrm{Debye}} = \left(\frac{2}{k^2}\right)(e^{-k} - 1 + k) \tag{2}$$

where $k = (q^2 b_t L)/3$.

The dashed line represents des Cloizeaux function[27] [equation (3)] for a Kratky–Porod (KP) chain with $N = 640$ at a rigid rod limit ($b_t = \infty$), which shows q^{-1} dependence in the asymptote. Actually, this function has a dependence on b_t, however the lines representing different b_t are so close to that of $b_t = \infty$ in this q and b_t range that only a line of $b_t = \infty$ is shown in *Figure 1* for simplicity.

$$S_1(q)_{\mathrm{Cloizeaux}} = \frac{\pi}{qL} + \frac{2}{3q^2 b_t L} \tag{3}$$

The observed data were normalized to fit in with the Debye functions and the des Cloizeaux function in the low q and in the high q region, respectively. In this procedure, the contour length L was taken to be constant as $a_0 N = 1600$ Å, where a_0 is the monomer length. b_t was then taken to be an adjustable parameter to give the best fit. The b_t values obtained in that way as a function of C are shown in *Table 1*.

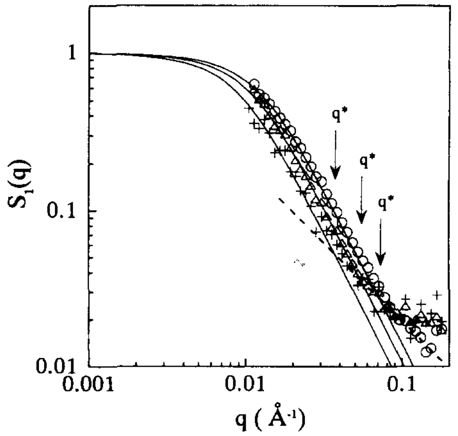

Figure 1 Logarithmic plot of intramolecular scattering function $S_1(q)$ as a function of the scattering vector q. q^* denotes the transition point (see text). (○): $C = 1.445$ mol/l; (△): $C = 0.723$ mol/l; (+): $C = 0.241$ mol/l. Solid lines: Debye functions for Gaussian coil; the values of parameter b_t are listed in *Table 1*. Dashed line: des Cloizeaux function for $N = 640$ in the rod limit

The q values at which the two characteristic regions intersect each other are marked with q^* as transition points in *Figure 1*. The values of q^* can be read to be 0.072, 0.055 and 0.038 Å^{-1} for C = 1.445, 0.723 and 0.241 mol/l, respectively. From these q^* values we calculated b_t using equation (4) [26].

$$b_t = \frac{1.91}{q^*} \tag{4}$$

The resulting values agree with those obtained by the former method. Equation (4) is usually applied in the Kratky plot[26] of $S_1(q)$. However, as shown in this communication, this relationship works well in the logarithmic plot of $S_1(q)$.

The electrostatic persistence length b_e is obtained from b_t, assuming the following relationship is valid[16]:

$$b_t = b_0 + b_e \tag{5}$$

where b_0 is the intrinsic persistence length ($\cong$ 12 Å for the polystyrene backbone[11]). In *Figure 2*, the electrostatic persistence lengths b_e obtained from this study (marked by solid circles) are shown as a function of the ionic strength I. The values obtained by other authors[11–14] for NaPSS are also shown, as detailed in the figure caption. A single master curve seems to accommodate all the data obtained by different experimental methods and for all the systems whether they are salt-free or salt-added. To plot these data, the polyelectrolyte concentration C and the added salt concentration C_s were converted to the ionic strength I according to the condensation theory of Oosawa–Manning[28,29]:

$$I = \frac{0.35}{2}C + C_s \tag{6}$$

A close inspection of *Figure 2* reveals the decrease of the electrostatic persistence length b_e with increasing ionic strength I of the solution. This confirms and extends the

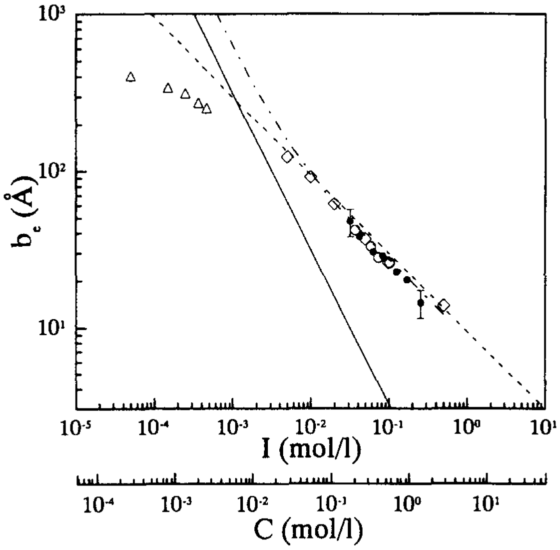

Figure 2 Electrostatic persistence lengths b_e as a function of ionic strength I. Experiments: (●) this study; (○) SANS by Nierlich *et al.*[11]; (◇) intrinsic viscosity by Tricot[13]-Takahashi *et al.*[14]; (△) transient electric birefringence by Degiorgio[12]. Theories: (—) Odijk[16]-Skolnick–Fixman[17]; (- - -) Koyama (for $f = 0.8$, see ref. [19]); (- · -) Bret[7]–Fixman[18]

results (○) of Nierlich *et al.*[11], which were obtained also by SANS, but in a narrower range of concentration with the contrast-matching method. Solid, dashed and strip-dashed lines are the theoretical curves given by Odijk[16]–Skolnick–Fixman[17], Koyama[19] and Le Bret–Fixman[18], respectively. Clearly, all experimental values of b_e agree well with the theoretical curves by Koyama and Le Bret–Fixman for $I > 10^{-2}$ mol/l, where the following universal relationship is valid:

$$b_e \propto I^{-1/2} \tag{7}$$

On the other hand, the observed values begin to level off when $I < 10^{-3}$ mol/l though the number of data is still small. Unfortunately, any theory cited here fails to explain the experimental behavior for this region, hence further theoretical and experimental investigations are required.

Acknowledgements

H. Urakawa expresses his gratitude to the British Council, Tokyo for awarding a Fellowship which enabled us to carry out the small-angle scattering measurements. K. Kaji, J. Higgins and B. Gabrys are also obliged to the British Council for the Collaborative Research Project (CRP) support. We are grateful for the use of the ISIS facility and would like to thank Dr S. M. King for his help with the experiment. B. Gabrys is grateful to the Japanese Society for the Promotion of Science for awarding a fellowship under the 'JSPS Invitation Fellowship Program for Research in Japan' which allowed us to conclude these studies. She would also like to thank Professor K. Kajiwara for his hospitality during the writing of this communication.

References

1. Oosawa, F., *Polyelectrolytes*. Marcel Dekker, New York, 1971.
2. de Gennes, P. G., Pincus, P., Velasco, R. M. and Brochard, F. J., *Phys. (France)*, 1976, **37**, 1461.
3. Odijk, T., *Macromolecules*, 1979, **12**, 688.
4. Förster, S. and Schmidt, M., *Advances in Polymer Science*, 1995, **120**, 51.
5. Kaji, K., Urakawa, H., Kanaya, T. and Kitamaru, R. J., *Phys. (France)*, 1988, **49**, 993.
6. Mandel, M., *Eur. Polym. J.*, 1983, **19**, 911.
7. Le Bret, M. J., *Chem. Phys.*, 1982, **76**, 6243.
8. Krause, R., Maier, E. E., Deggelmann, M., Hagenbüchle, M., Schulz, S. F. and Weber, R., *Physica*, 1989, **A160**, 135.
9. Johner, C., Kramer, H., Batzill, S., Graf, C., Hagenbüchle, M., Martin, C. and Weber, R., *J. Phys. II (France)*, 1994, **4**, 1571.
10. Kaji, K., Urakawa, H., Kanaya, T. and Kitamaru, R., *Macromolecules*, 1984, **17**, 1835.
11. Nierlich, M., Boue, F., Lapp, A. and Oberthür, R., *Colloid and Polymer Sci.*, 1985, **263**, 955.
12. Degiorgio, V., Mantegazza, F. and Piazza, R., *Europhys. Lett.*, 1991, **15**, 75.
13. Tricot, M., *Macromolecules*, 1984, **17**, 1698.
14. Takahashi, A., Kato, T. and Nagasawa, M., *J. Phys. Chem.*, 1967, **71**, 2001.
15. Förster, S., Schmidt, M. and Antonietti, M., *J. Phys. Chem.*, 1992, **96**, 4008.
16. Odijk, T., *J. Polymer Sci., Polymer Phys. Ed.*, 1977, **15**, 477.
17. Skolnick, J. and Fixman, M., *Macromolecules*, 1977, **10**, 944.
18. Fixman, M., *J. Chem. Phys.*, 1982, **76**, 6346.
19. Koyama, R., *J. Phys. Soc. Jpn.*, 1989, **58**, 2062.
20. Williams, C. E., Nielich, M., Cotton, P. J., Jannink, G., Boué, F., Daoud, M., Farnoux, B., Picot, C., de Gennes, P. G., Rinaudo, M., Moan, M. and Wolff, C., *J. Polym. Sci., Polym. Lett. Ed.*, 1979, **17**, 379.
21. Boué, F., Cotton, J. P., Lapp, A. and Jannink, G., *J. Chem. Phys.*, 1994, **101**, 2562.
22. Vink, H., *Makromol. Chem.*, 1982, **182**, 279.
23. ISIS User Guide — Experimental facilities, ed. B. Boland and S. Whapham. RAL, 1992.
24. Heenan, R. K. and King, S. M., Intl. Seminar on Structural Investigations at Pulsed Neutron Sources, Dubna, 1992.
25. King, S. M. and Heenan, R. K., Using Colette. RAL Report, RAL-95-005, DRAL, 1995.
26. Glatter, O. and Kratky, O., *Small Angle X-ray Scattering*. Academic Press, London, 1982.
27. des Cloizeaux, J., *Macromolecules*, 1973, **6**, 403.
28. Oosawa, F. J., *Polym. Sci.*, 1957, **23**, 421.
29. Manning, G. S., *J. Chem. Phys.*, 1969, **51**, 924.