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M. Shibayama, T. Tanaka, C. Han. Small-angle neutron scattering study on poly(N-isopropyl acrylamide-co-acrylic acid) copolymer solutions. Journal de Physique IV Proceedings, 1993, 03 (C8), pp.C8-25-C8-28. 10.1051/jp4:1993805 . jpa-00252224

HAL Id: jpa-00252224

<https://hal.science/jpa-00252224>

Submitted on 1 Jan 1993

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Small-angle neutron scattering study on poly(N-isopropyl acrylamide-co-acrylic acid) copolymer solutions

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Abstract. - The structure factor (scattered intensity), $I(q)$, for weakly charged polymer solutions of a poly(N-isopropyl acrylamide-co-acrylic acid) copolymer (NIPA/AAc) was obtained by means of small-angle neutron scattering (SANS) as a function of temperature, where q is the magnitude of the scattering vector. It was found that $I(q)$ was well described with a Lorentz-type scattered intensity function when the temperature was lower than the so-called Θ temperature, which is about 34.6°C. Above this temperature, $I(q)$ started to have a peak around $q = 0.02 \text{ \AA}^{-1}$, which increased with temperature. In addition, an upturn in $I(q)$ appeared by approaching $q = 0$, indicating a macroscopic inhomogeneity. The structure factor was analyzed on the basis of the theory of Borue and Erukhimovich for polyelectrolytes in a poor solvent [*Macromolecules*, 1988, **21**, 3240].

Introduction.

In our previous papers, we studied the structure factors for temperature sensitive polymer gels consisting of poly(N-isopropyl acrylamide) (NIPA) [1] and of poly(N-isopropyl acrylamide-co-acrylic acid) (NIPA-AAc) polyelectrolyte gels [2]. The former exhibited a critical phenomenon and divergence of the correlation length. On the other hand, the polyelectrolyte gels underwent a first-order volume transition at about 50.2°C and no divergence in the correlation length was detected. Instead, a scattering maximum appeared above the so-called Θ temperature of NIPA. The structure factors for these gels were successfully analyzed with the Borue-Erukhimovich (BE) theory [3]. Upon utilizing the theory, however, we ignored the effect of the presence of crosslinks on the structure factor, which might be fatal in the analysis of the structure factor particularly at low q region. In this work, we study the structure factor for weakly charged polyelectrolyte solutions, examine the BE theory, and compare the structure factors with those for the corresponding gels.

Experimental.

A copolymer solution of NIPA/AAc was prepared by polymerizing 7.462g of N-isopropyl acrylamide (NIPA) and 217 μl of acrylic acid (AAc), initiated by 43 mg of ammonium persulfate, in 100 ml of deuterated water. 480 μl of N,N,N',N'-tetramethylethylenediamine (TEMED) was added as a catalyst. The polymerization was conducted in a temperature controlled water bath at 20°C for 20 hrs. The details of the gel preparation are described elsewhere [3]. The polymer volume fraction, ϕ , of the solution (S3) was 0.118.

The small-angle neutron scattering (SANS) experiments were conducted on the 8m-SANS facility at the National Institute of Standards and Technology. Neutron beams were monochromated with a velocity selector to a 9Å-beam and then collimated with a focusing

collimation system. The details of the optical setup and the detection system were described by Glinka et al [4].

Results and discussions.

Fig. 1 shows the temperature dependence of the structure factors of NIPA/AAc solutions. At temperatures lower than 40°C, $I(q)$ is a monotonously decreasing function with q . However, above this temperature, a scattering maximum appears around $q = 0.02 \text{ \AA}^{-1}$. This peak is buried at higher temperatures due to the domination of the strong scattering at low q region. These behaviors are very different from those for gels [2].

According to Borue and Erukhimovich, $I(q)$ for polyelectrolytes in a poor solvent is given by

$$I(q) \sim S(x) \approx C_1 \frac{(x^2 + s)}{(x^2 + t)(x^2 + s) + 1} \quad (1)$$

(C_1 ; constant)

where $S(x)$, x , t , and s are the reduced structure factor, the reduced variables of the scattering vector, temperature and charge concentration, respectively. x is given by using the characteristic scale of screening of Coulombic interaction by ideal Gaussian chains, r_0 , as follows,

$$x = r_0 q \quad (2)$$

$$r_0 = a \left\{ 1 + \left[\frac{1}{2\phi} (1 - 2\chi) \right]^{1/2} \right\}^{1/8} \left(\frac{48\pi l_B}{a} \phi \alpha^2 \right)^{-1/4} \quad \text{for } \chi < \frac{1}{2} \quad (3)$$

$$r_0 = a \left(\frac{48\pi l_B}{a} \phi \alpha^2 \right)^{-1/4} \quad \text{for } \chi \geq \frac{1}{2}$$

where a , χ , and ϕ are the segment length, the Flory's interaction parameter, and the polymer volume fraction, respectively. α and l_B are the degree of ionization and the Bjerrum length, respectively. The reduced charge concentration s is defined with the Debye length, κ^{-1} as follows,

$$s = \kappa^2 r_0^2 = 4\pi \frac{l_B}{a^3} \sum_i (z_i \phi_{s,i} + \alpha \phi) r_0^2 \quad (4)$$

where $\phi_{s,i}$ is the salt concentration of kind i having the valency z_i . The reduced temperature stands for the solvent quality. For a larger t value, the solvent is good for the solute, and the solvent becomes a poor solvent by decreasing t . t is defined by

$$t = 12 \left(\frac{r_0}{a} \right)^2 \left[(1 - 2\chi) + \frac{3B_3}{a^3} \phi \right] \quad (5)$$

where B_3 is the third virial coefficient.

We now calculate the theoretical structure factors by employing Eq.(1). Before the calculation, we need to examine the parameters t and s or χ and κ^{-1} . χ is given by

$$\chi = \frac{\Delta h - T \Delta s}{k_B} = \frac{1}{2} + A \left(1 - \frac{\Theta}{T} \right) \quad (6)$$

Fig. 1 Temperature dependence of the structure factor, $I(q)$, of NIPA/AA polyelectrolyte solutions at several temperatures.

where Δh and Δs are the enthalpy and entropy parameters for NIPA, respectively. According to Ohtake et al.[5], Δh is -5.5×10^{-21} J. Since $\Theta = 306.5$ K, we get $\Delta s = -2.8$ J/K, and $A = -1.535$. The degree of ionization for the NIPA/AAC copolymer solution, α , is estimated to be 0.475, i.e., the molar ratio of AAC to NIPA monomers. Thus r_0 and t are calculated. For the value of s , we have to take into account the presence of salt ions. Since the catalyst, TEMED, is still present in the solution and it has an ionization equilibrium, we need to add the contribution of OH $^-$. Thus Eq.(4) has to be modified to

$$s = \kappa^2 r_0^2 = 4\pi \frac{l_B r_0^2}{a^3} (2\alpha_{\text{TEMED}} + \alpha) \phi \quad (7)$$

where α_{TEMED} is the molar ratio of TEMED to the polymer networks.

In order to remove the contribution of the low angle scattering, we subtract the contribution of the low angle component by introducing a Guinier function,

$$I_G(q) = C_G \exp[-R_g^2 q^2/3] \quad (C_G; \text{constant}) \quad (8)$$

$I_G(q)$ indicates the presence of a solid-like inhomogeneity at low q region with the radius of gyration of R_g [6]. The corrected structure factor $I_{\text{corr}}(q)$ is then obtained by subtracting $I_G(q)$, as follows,

$$I_{\text{corr}}(q) = I_{\text{obsd}}(q) - I_G(q) \quad (9)$$

Then a curve fitting was conducted on $I_{\text{corr}}(q)$ based on Eq.(1). Fig. 2 shows the result of the curve fitting for S3 at 45°C. The open circles, closed circles, and the dotted curve, denote $I_{\text{obsd}}(q)$, $I_{\text{corr}}(q)$, and $I_G(q)$, respectively. The theoretical, $I_{\text{th}}(q)$, and fitted curves, $I_{\text{fit}}(q)$, were shown with the dashed and solid curves, respectively. It is clear that $I_{\text{th}}(q)$ does not reproduce the corrected structure factor. On the other hand, $I_{\text{fit}}(q)$, where all the parameters except r_0 were floated, well recovers $I_{\text{corr}}(q)$. Fig. 3 shows the observed (symbols) and curve fitted (solid curves) structure factors for S3 at several temperatures. The fitted structure factors seem to reproduce well the observed ones except for the low angle region.

Fig. 2 SANS curve decomposition and curve fitting for S3 at 45°C. Open and closed circles denote the observed intensity, $I_{\text{obsd}}(q)$, and corrected intensity, $I_{\text{corr}}(q)$. The other symbols are shown in the Figure.

Fig. 3 Observed (symbols) and fitted (solid curves) structure factors for S3 at several temperatures.

We now discuss the parameter t . Fig. 4 shows temperature dependence of the calculated and fitted t . The calculated t is given by Eqs.(5) and (6), where $B_3 = 0$. The fitted t has a stronger temperature dependence and crosses the zero line at a higher temperature than the calculated t . These facts indicate that the temperature dependence of t , which we assumed to be identical to that for pure NIPA, is not appropriate to the NIPA/AAC copolymers. The NIPA/AAC copolymer aqueous solution has a stronger temperature dependence of χ and a higher Θ temperature than pure NIPA. This is due to the presence of ionic groups, which pushes the Θ temperature upward. As a matter of fact, the cloud point of S3 was visually observed around 36°C, which is higher than that of NIPA homopolymers in heavy water (around 34°C).

Moussaid et al.[7] reported that a good agreement between the observed and the fitted structure factors was obtained for partially ionized poly(acrylic acid) aqueous solutions with respect to temperature, salt concentration, and ionization degree. The fitting parameters were the segment length, a , the solvent quality parameter, t , and the contrast factor C_1 . In their case, no steep upturn in the structure factor at low q region was observed, which allowed them a direct application of the theory. The appearance of the steep upturn in the structure factor at low q region, which we observed, might be due to the occurrence of microphase separation due to a strong hydrophobic interaction of NIPA at temperatures above the LCST. Further investigations are currently under way, which will be reported elsewhere [8].

Concluding remarks.

The SANS study for NIPA/AAC copolymer solutions disclosed the following facts: (1) The structure factor of the solution is well represented with a Lorentz type scattering function at temperatures lower than the Θ temperature, but has a scattering maximum at higher temperatures. The physical meaning of the scattering maximum is well explained with a theory of Borue and Erukhimovich. (2) At high temperatures, however, a non-trivial difference between the observed and theoretical structure factors, which is due to the ignorance of long-range concentration fluctuations (macrophase separation) in the theory. (3) In order to circumvent this discrepancy, a method to subtract this contribution is proposed. The result was rather successful and the observed structure factor was re-constructed with the theory.

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Fig. 4 Temperature dependence of the calculated and fitted t values.