Anomalous Scattering Behavior of Poly(*N*-*n*-propylacrylamide) in 2-Propanol/Water

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Light scattering study of poly(*N*-*n*-propylacrylamide) in a mixed solvent of 2-propanol and water was carried out. At high volume fraction (80 vol%) of 2-propanol, the scattering envelopes showed anomalous upsweep inflection at low scattering angles for finite polymer concentrations. This behavior can be elucidated in terms of the long-range repulsive interaction potential, and should correlate to the complex multiple volume phase transition of the gel in a mixed solvent.

It is well known that hydrogels exhibit a volume phase transition.[1] Volume phase transition of the polymer gel is thought to be analogous to the liquid-vapor phase transition of common materials.[2] Such a phase behavior results from various interactions between polymer chains constructing macroscopic gel and between polymer chain and the solvent. Reentrant type volume phase transition has been found for poly(*N*-isopropylacrylamide) gel, PNiPAM gel, in mixed solvents,[3] e.g. alcohol/water, and it was explained by the cosolvency effect of the mixed solvent. Recently, it was observed that poly(*N*-*n*-propylacrylamide) gel, PNnPAM gel, which is a homologous one of PNiPAM gel, shows more complex phase behavior: multiple volume phase transition in similar mixed solvents.[4] Such a behavior remind us the presence of another kind of order parameters in addition to the polymer concentration. Because both PNiPAM and PNnPAM gels are nonionic ones, electrostatic interactions does not take part in the phase behavior. Degree of hydrogen bonding is one of the candidates. In a series of our light scattering studies of PNnPAM solutions, it was pointed out that crumpling of PNnPAM chains accompanied by the change of chain stiffness takes place near the region of coil-globule transition which is the essential origin of volume phase transition of the gel.[5]

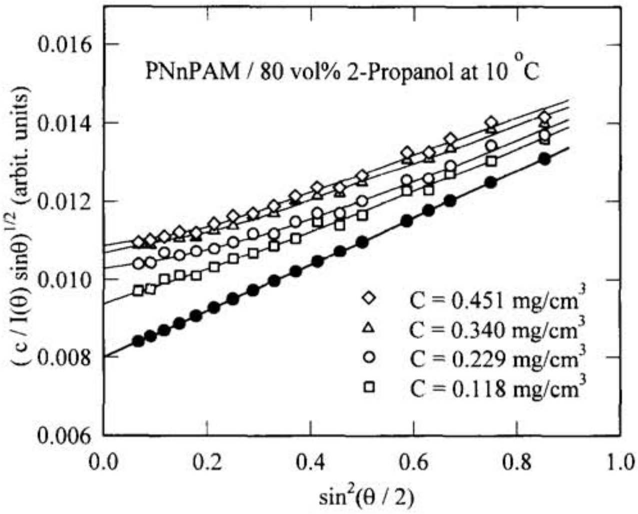

Figure 1. Scattering envelopes vs $\sin^2(\theta/2)$ plotted as a square root form for PNnPAM in 80 vol% 2-propanol at 10 °C. Solid circles denote the extrapolated results for zero concentration which corresponds to the particle scattering factor.

In order to study the solution behaviors of PNnPAM in a mixed solvent, light scattering experiments were carried out for PNnPAM in 80 vol% of 2-propanol. Homemade light scattering spectrometer was used with a wavelength of 488.0 nm as a light source. Sample is linear PNnPAM, and molecular weight is 141 x 10^4 with a sufficiently narrow molecular weight distribution.[5] Measurement was carried out at 10 °C. Before light scattering measurements, the sample solution was dialyzed sufficiently by the solvent, and the dilution was done by this solvent. PNnPAM gel is in a swollen state in the present mixed solvent at this temperature. The scattering envelope is shown in Figure 1, which is plotted as a square-root plot form to retrieve a reliable angular dependence.[6] Anomalous upsweep inflection were observed at low scattering angles for finite polymer concentrations, contrary to the cases of usual polymer solutions where the almost linear angular dependencies with positive slope are obtained. In fact, the present PNnAPM sample showed a good linear angular dependence in water as usual cases. The radius of gyration in this mixed solvent is almost the same as that in water, and this anomalous behavior is not due to the magnitude of molecular size. PNnPAM molecules have no electric charges, and the effect of electrostatic interaction is not probable. Because the molecular weight determined from the concentration dependence of the scattered intensity at zero-scattering angle coincides well with that determined in water, no aggregation or complex formation occurs. Similar upsweep inflection has been observed before for polyelectrolytes, poly(vinylcarbanilate) and copolymers.[7-9] The upsweep inflection can be explained by the decrease of scattered light intensity due to the interference from different molecules where the intermolecular interaction potential becomes very long range. Using the general equation for the scattered intensity assuming the spherically symmetric distribution of PNnPAM molecules (because the effect of depolarized scattered intensity was not observed, the contribution of molecular orientation should not affect), the reduced scattered intensity R(θ) is written as[10]

$$R(\theta)/KCM \equiv P^*(\theta,C) = P(\theta)\{1 + (N_AC/M)\int[g(r) - 1](\sin qr/qr)4\pi r^2 dr\} \quad (1)$$

where θ, K, C, M, N_A, g(r), q, and r are the scattering angle, Rayleigh constant, polymer concentration, molecular weight of polymer, Avogadro's number, radial distribution function, scattering vector, and the distance between the centers of two polymer molecules, respectively.

From a little mathematical manipulations and the approximation of g(r) by $\exp[-U(r) / k_BT]$, the equation $P(\theta) / P^*(\theta,C) - 1 = (N_AC / M)B \langle r^2\rangle^{3/2} \exp(-q^2\langle r^2\rangle / 6)$ was obtained. U(r), k_B, and T are the interaction potential, Boltzmann constant, and temperature, respectively.[8,9] B and $\langle r^2\rangle$ represent the constants characteristic to the interaction potential and the mean square distance between two polymer molecules defined by

$$B = \langle r^2 \rangle^{-3/2} \int \{1-\exp[-U(r)/k_BT]\} 4\pi r^2 dr \quad (2)$$

$$\langle r^2 \rangle = \int \{1-\exp[-U(r)/k_BT]\} 4\pi r^4 dr / \int \{1-\exp[-U(r)/k_BT]\} 4\pi r^2 dr \quad (3)$$

respectively. The resultant value $\langle r^2 \rangle_0^{1/2}$, the extrapolated value of $\langle r^2 \rangle^{1/2}$ to the infinite dilution, was 110 nm. On the other hand, the z-averaged mean square radius of gyration $\langle R_g^2 \rangle_z$ was determined from the particle scattering factor P(θ) and was 60.0 nm. (The angular dependence of P(θ) is quite normal.) The ratio is 110/60.0 = 1.83. In case of the usual polymer solutions in good solvent, this should be about $2^{1/2}$ (Guinier plot). Much larger value of $\langle r^2 \rangle_0^{1/2}/\langle R_g^2 \rangle_z^{1/2}$ than $2^{1/2}$ means that the long range repulsive intermolecular interaction works between polymer molecules. Even for the solution in pure 2-propanol, a similar upsweep inflection was observed and the interaction distance was about 1.7 times as much as the radius of gyration. 2-Propanol should be adsorbed strongly to the polymer chain and this solvation atmosphere will avoid the approach of other polymer molecules near by. That is, the observed repulsive interaction should be due to the selective adsorption of solvents to polymer molecules. According to the swelling curve of PNnPAM gel in the mixed solvent of 2-propanol and water reported by Tokita et al, a substantial histeresis in the swelling curve appears in the region of high volume fraction of 2-propanol including 80 vol%.[4] In the process of decreasing 2-propanol concentration from pure 2-propanol, the swelling curve exhibits fairly larger swelling ratio than that in the process of increasing 2-propanol concentration.[4] Moreover, multiple volume phase transition is observed in this region. In case of PNnPAM gel in the mixed solvent, subchains between crosslinking points interact with each other in the similar manner as the case of the present results, and the long range repulsive interaction should affect the swelling behavior remarkably. In our previous paper about PNnPAM in water, it has been observed that crumpling of the chain accompanied by the chain stiffening (conformational change) occurs in PNnPAM molecules near the transition point. Inhomogeneous crumpling will affect the interpolymer repulsive interaction, and plays as an extra order parameter. On the other hand, the long range repulsive interaction between subchains of the gel in mixed solvents works to resist the shrinkage and collapse. Therefore, the unique interpolymer interaction observed here must be related to such a complex phase behavior (hysteresis and multiple phase transition) of PNnPAM gel. It should be also mentioned here that the solvation behavior and the swelling behavior of PNnPAM gel in mixed solvents might be dependent on temperature substantially. It is very interesting to examine the temperature effect on the anomalous scattering behavior observed in the present study. The detailed study of linear PNnPAM solutions in the mixed solvent will give important information about the origin of the complex phase behavior of PNnPAM gel. Such a study is in progress now.

References and Notes

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