Solution Properties of Poly(N-isopropylacrylamide) in Water

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ABSTRACT: Various molecular parameters characterizing the solution properties of poly(N-isopropylacrylamide) (in the range of molecular weight from 13.8 to 910×10^4) in water at 20°C and the temperature dependence of them in the range of 20°C to 30.6°C were determined with static and dynamic light scattering technique. (Modified) Flory's fifth power law of excluded volume effect predicts well the temperature dependence of the chain dimension. It is shown that this polymer molecule behaves as a flexible coil from the molecular weight dependence of these parameters and the relation between the interpenetration function and expansion coefficients. The unique thermal behavior of this solution, temperature of phase change being independent of molecular weights and concentrations at least in the range of 1 wt%, should be mainly attributed to the hydrated structure.
KEY WORDS   Poly(N-isopropylacrylamide) / Light Scattering / Solution Properties / Hydration /

It is well-known that non-ionic water soluble polymers exhibit unusual behavior. That is, the solution property often differs significantly from that of other polymers in nonpolar organic solvents.[1] The reasons for this are still not well understood. Of course the hydrophobic interaction may play an important role. Aqueous solutions of relatively simple synthetic polymers which undergo phase transition around at 31°C on heating have attracted particular attention due to similarity with the denaturation of proteins in aqueous systems.

Previously, Heskins and Guillet[2] studied the solution properties of poly(N-isopropylacrylamide) (PNiPAM) in water which shows the phase transition on heating the solution. Although the qualitative features of their results were acceptable, they only studied one unfractionated polymer sample, the polydispersity of which was quite broad. Moreover, they reported nonproportional relation between intrinsic viscosity and partial specific volume. On the other hand, Chiantore et al.[3] reported quite unacceptable results of viscosity massurements using unfractionated samples. These peculiar results are considered due to the use of unfractionated samples. Recently, one of the authors established an effective procedure for molecular weight fractionation of this polymer.[4] As reported in our previous papers,[5,6] the phase transition of aqueous PNiPAM solution is quite sensitive, reversible and reproducible to the thermal stimulation. The phase transition takes place as the temperature reaches about 31°C, contrary to Heskins, almost independently of molecular weight and concentration in the experimental range. This newly observed behavior is quite different from that of the usual polymer solution, where the temperature of the phase change significantly depends on molecular weight and concentrations. Such a phase diagram suggests that the main reason for the phase

transition is intrinsic to single polymer chain.

Another interesting behavior is seen in the comparison of the intrinsic viscosity of PNiPAM in water with that in THF, reported in the previous work.[4] As shown there in aqueous solution at 20°C, the exponent of Mark–Houwink–Sakurada (MHS) equation is 0.50 but in THF at 27°C, 0.65. As far as the exponents are concerned, THF seems a better solvent than water, but in fact, the intrinsic viscosity obtained in THF was considerably lower than those obtained in aqueous solution. This suggests that in water strong interaction and hydration may occur between the polymer chain and solvent water resulting in increase in effective viscosity of the solution.

These situations may be characteristic of aqueous polymer solution, for a similar relation is also observed in other aqueous polymer systems. For example, poly(vinylpyrrolidone) shows that water is a theta solvent from radius of gyration measurements but seems to be a good solvent from the results of intrinsic viscosity.[7] The characteristic ratio, C_∞, of poly(oxyethylene) is 7.5 in water but is 4.9 in 0.45 M K_2SO_4. C_∞ is defined as

$$C_\infty = (\langle R^2 \rangle_0 \times nl^2)_{n \to \infty} \quad (1)$$

where $\langle R^2 \rangle_0$ is the unperturbed mean-square end-to-end distance of polymer chain linked by n repeating units with each length of l. The electrolyte should change the structure of water strongly, and the conformation of polymer chain in water should be modified by the possible structuring of water in the vicinity of the polymer chain. Therefore, investigation of chain conformation and characterization of PNiPAM is important for understanding the above behavior. Here we report the solution properties of PNiPAM in water determined mainly by light scattering.

EXPERIMENTAL

Materials

PNiPAM was polymerized from N-iso-propylacrylamide (Eastman Kodak Co.) in benzene/acetone mixture with azobisisobutyronitrile as an initiator at 60°C. The details of polymerization are described elsewhere.[4] The fractionation of this product was carried out by the phase separation technique in a carefully water-freed acetone/n-hexane mixture at room temperature. The essential condition for the effective fractionation is removal of water from the solvent. Thus, several fractions were obtained and eight fractions used in this work. Distilled water of liquid chromatography grade, was purchased from Wako Chemicals, and was used as supplied. Tetrahydrofuran (THF) for comparative check was also purchased from Wako Chemicals, Dotite Spectrosol grade THF, and was used without further purification.

Light Scattering

The details of our own light scattering apparatus have been described elsewhere.[9] A vertically polarized 488.0 nm line of Ar-ion laser was used as the incident beam, and vertically polarized scattered light was detected by a photomultiplier tube using the photon-counting method. A cylindrical cell with polished inner and outer cell surfaces with 10 mm outer diameter is placed in a thermostated silicon oil bath controlled to 20.00 ± 0.01°C. Optical purification of sample solutions was achieved by direct filtration through a membrane filter of pore size a few times larger than the radius of gyration of polymer fractions in solution (Nucleopore filter). The specific refractive index increment dn/dc of PNiPAM in water at 20°C was measured using a Brice type differential refractometer with an Ar-ion laser, as 0.162 cm^3/g. Weight averaged molecular weight, $\bar{M}_w$, second virial coefficients, A_2, and radius of gyration, R_g, were obtained by the usual method with Zimm plot, also with Berry's plot.[10]

The autocorrelation functions of the intensity of quasielastically scattered light from the sample solution were measured in the

homodyne mode and our 240 channels correlator.[11] The obtained correlation functions were analyzed by the third cumulant method to retrieve a reliable average decay rate or the first cumulant, $\bar{\Gamma}$.[12] The normalized field correlation function, $g^{(1)}(\tau)$, is expressed by

$$g^{(1)}(\tau) = \exp[-\bar{\Gamma}\tau + (\mu_2/2!)\tau^2 - (\mu_3/3!)\tau^3] \quad (2)$$

where μ_i is the i-th cumulant and $\mu_2/\bar{\Gamma}^2$ gives the normalized dispersion of decay rate distribution, which coreponds to the molecular weight distribution at a low enough scattering angle. The values of $\bar{\Gamma}/K^2$ thus obtained, K being the momentum transfer vector, are extrapolated to zero scattering angle to get the translational diffusion coefficient. Then with the Stokes–Einstein equation, the hydrodynamic radius, R_h, was calculated

Viscometry and Osmometry

A modified Ubbelohde type viscometer was used to measure the viscosity.[4] A high speed membrane osmometer, Model 501 of Hewlett Packard was used to determine the number averaged molecular weight, $\bar{M}_n$.

Phase Transition

The phase transition was traced by monitoring the transmittance at 500 nm light beam on a specially constructed spectrophotometer.[13] The rates of heating and cooling of the sample cell were each adjusted to $1\,^\circ C\,min^{-1}$.

RESULTS AND DISCUSSION

In Table I, the values of $\bar{M}_w$, A_2, R_g, R_h, D_0, and k_D measured by light scattering as well as $\bar{M}_n$ and $[\eta]$ are summarized. The ratio of weight averaged molecular weight to number averaged one is about 1.3 indicating that our PNiPAM samples have fairly narrow molecular weight distribution. $k_{f,0}$ is calculated from the equation of

$$k_f = 2A_2 M_w - k_D - v \quad (3)$$

$$k_{f,0} = k_f M_w / N_A (4\pi R_h^3/3) \quad (4)$$

where v is the partial specific volume of the polymer, and N_A is the Avogadro number. According to Pyun and Fixman, $k_{f,0}$ is a measure of coil interpenetration for flexible chain ($k_{f,0}$ should be large of about 7 in case of low interpenetration, and is 2.23 for fully interpenetrating coils).[14] Figure 1 shows the results of light scattering measurements. R_g, R_h, and $[\eta]$ are plotted as a function of weight averaged molecular weight of PNiPAM in water at 20°C. The results for THF solution of

**Table I.** Molecular parameters of poly(N-isopropylacrylamide) in water and tetrahydrofuran at 20°C

Sample code	$\bar{M}_w$ ($\times 10^4$)	$\bar{M}_n$ ($\times 10^4$)	A_2 ($\times 10^{-4}$) cm³ mol g⁻²	R_g nm	R_h nm	D_0 ($\times 10^{-8}$) cm³ s⁻¹	$[\eta]$ cm³ g⁻¹	k_D cm³ g⁻¹	$k_{f,0}$	R_g/R_h	$\bar{M}_w/\bar{M}_n$
A	910		0.79	127	96.0	2.23		213	5.0	1.32	
			(0.33)	(112)	(80.0)	(4.87)		(220)	(3.2)	(1.40)	
B	420	310[a]	0.95	88.0	66.0	3.25	256	140	3.8	1.33	1.4
C	320	270[a]	1.1	71.0	51.3	4.18	238	113	5.6	1.38	1.2
			(0.63)	(62.0)	(43.8)	(8.90)		(185)	(3.1)	(1.42)	
D	163	130	1.5	51.0	36.0	5.96	167	76	5.7	1.42	1.3
E	65.2	52	2.6	30.0	21.0	10.2	106	44	8.2	1.43	1.3
F	49.5		1.8	24.5	18.0	11.9		25	5.0	1.36	
G	25.2		2.8	18.5	13.0	16.5		15.4	5.7	1.42	
H	13.8	9.8	3.2	13.0	9.5	22.6	44	9.5	4.7	1.34	1.4

The data in the parenthese are results in tetrahydrofuran.

[a] The value of $\bar{M}_n$ is calculated from the relation between the molecular weight and intrinsic viscosity.
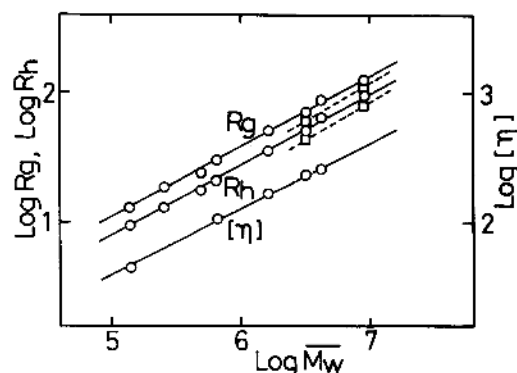
Figure 1. Radius of gyration, R_g, hydrodynamic radius, R_h, and intrinsic viscosity, [η], of PNiPAM in aqueous solution at 20°C plotted as a function of molecular weight (double logarithmic plot). The squares denote the results of THF solution at 20°C. The unit of R_g and R_h is nm and that of [η] is $cm^3 g^{-1}$.
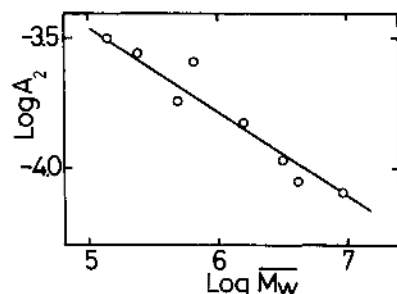
Figure 2. Molecular weight dependence of the second virial coefficient of PNiPAM aqueous solution at 20°C. The slope of the solid line is −0.34. The unit of A_2 is $cm^3 mol g^{-2}$.

two samples at 20°C are shown for comparison and in water, are expressed by the power law relation with the exponent of 0.54 for R_g, 0.54 for R_h, and 0.51 for [η] as

$$R_g = 0.022_4 \times \bar{M}_w^{0.54} \text{ (nm)} \qquad (5)$$

$$R_h = 0.016_0 \times \bar{M}_w^{0.54} \text{ (nm)} \qquad (6)$$

$$[\eta] = 0.11_2 \times \bar{M}_w^{0.51} \text{ (cm}^3/\text{g)} \qquad (7)$$

The exponents of R_g and R_h are intermediate between the values for a good solvent limit and theta solvent for the flexible coil, and the exponent 0.51 of [η] is in fairly good agreement with the MHS relation for the number averaged molecular weight in the preliminary
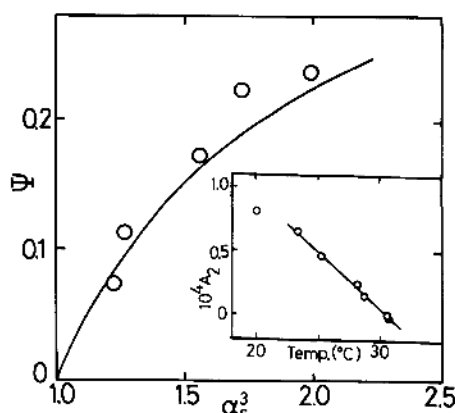
Figure 3. Relationship of the interpenetration function with the expansion factor determined for sample A. Ψ denotes the interpenetration function and α_s the expansion factor of the radius of gyration at T to that at theta temperature, $R_g(T)/R_g(\Theta)$. The solid curve denotes the theoretical prediction of modified Flory Krigbaum Orofino's fifth power law.

(inset) The second virial coefficient of PNiPAM (sample A, moleclar weight $= 910 \times 10^4$) plotted as a function of temperature. The solid circle denotes the result of sample B. From interpolation, theta temperature was determined as $(30.59 \pm 0.05)°C$. The unit of A_2 is $cm^3 mol g^{-2}$.

study.[4] Similarly, the molecular weight dependence of the second virial coefficients is shown in Figure 2, and the slope of it is approximately −0.34. Considering the magnitude of A_2, this PNiPAM aqueous solution at 20°C should be in a relatively good solvent state and this is in accordance with the exponents of R_g and R_h, and with the results of phase transition.[5]

In Figure 3, temperature dependence of the second virial coefficient measured for the sample A is shown. A_2 decreses with increasing temperature, that is LCST-like temperature dependence is observed. This temperature dependence corresponds to exothermic heat of mixing observed in the calorimetric measurement.[2] From the interpolation to $A_2 = 0$, the theta temperature was determined to be $30.59 \pm 0.05°C$. However, Heskins et al.[2] reported a positive second virial coefficient at 33°C. Their positive value of A_2 at 33°C is quite inconsistent with their phase diagram

18

which shows $T_c \sim 31.0^\circ$C, because in the case of the LCST type phase diagram the solvent must be poor above T_c. This temperature dependence is often a characteristic of aqueous solution due to the effect of hydration and hydrogen bonding.[15] Further, the relation between the second virial coefficient and radius of gyration was studied with the excluded volume theory in the range of 20°C to theta temperature. Results are shown in Figure 3 for sample A. The interpenetration function, Ψ, is defined by

$$\Psi = A_2 M_w{}^2 / 4\pi^{3/2} N_A R_g{}^3 \qquad (8)$$

The theoretical curve is the modified Flory Krigbaum Orofino (FKO) theory as,

$$\Psi = \ln(1 + 5.73 Z/\alpha_s{}^3)/5.73 \qquad (9)$$

$$\alpha_s{}^5 - \alpha_s{}^3 = 1.276 Z \qquad (10)$$

where Z is the excluded volume function and α_s is the expansion factor of the radius of gyration. Considering the uncertainty accumulated in the estimation of the interpenetration function, the agreement is fairly good. The behavior of the chain dimension with temperature is expressed by the excluded volume effect. This indicates that the PNiPAM molecule in water at 20°C behaves as an expanded flexible coil. In THF, R_g and R_h are smaller than those in water, and A_2 is positive but smaller than that in water, suggesting that water at 20°C should be a better solvent than THF from the viewpoint of A_2.

In order to examine the chain flexibility and compare with the results of viscosity measurements, the unperturbed chain dimension. $R_{g,0}$ was estimated from R_g using FKO theory. The averaged value of $R_{g,0}{}^2/M_w$ is about 9.8×10^{-18} cm^2 mol g^{-1}. Assuming the mean length of monomer unit to be 0.25 nm and from the molecular weight of monomer unit of 113, the characteristic ratio, C_∞, is estimated to be 10.6. This value is not so different from the value for common vinyl polymers, for example polystyrene.[16] This means that

PNiPAM molecules in water are fairly flexible coils like polystyrene.

On the other hand, $R_{g,0}$ for THF solution estimated by the same procedure is 98.7 nm fo sample A and 51.0 nm for sample C. The corresponding values for aqueous solution are 98.9 nm and 55.6 nm, respectively. (Measured $R_{g,0}$ of sample A is 101 nm and shows good agreement.) These values are quite acceptable if we consider the uncertainty introduced in this estimation and mean that the unperturbed chain dimension is not so different between those obtained in aqueous and THF solution. Then, the characteristic ratio and chain flexibility of PNiPAM in THF solution should be almost the same as that in aqueous solution.

Another important point is that there is a clear difference in the magnitude of $k_{f,0}$ between water and THF solutions. Comparing the magnitude of $k_{f,0}$ of both solutions, it is seen that coil interpenetration is fairly less in water than in THF, according to the theory of Pyun et al.[14] This suggests a possible effect of pronounced hydration of PNiPAM molecule in aqueous solution. Indeed, $k_{f,0}$ of nonpolar polymer in organic solvent, for example polystyrene in methyl acetate,[17] is obtained to be about 3 and close to the value obtained in THF solution, and for aqueous polymer solution, for example Pullulan in water, is obtained to be about 4—5.[18]

Therefore, it could be explained that the unique viscometric behavior observed in aqueous solution as compared with those obtained in THF solution is a result of the hydration effect and another unique thermal behavior, the phase transition taking place on heating the aqueous solution, might be attributed to the balanced interaction between the PNiPAM molecule and solvent water, for example, hydration, dehydration, and hydrophobic interaction. Indeed, it is observed in NMR measurement in deuterated water as the solvent that a remarkable restriction of the molecular motion of the solvent water occurs at the phase transition temperature, while the

relaxation time of the side chain protons increased and that of the main chain protons of PNiPAM molecule decreases drastically at the critical temperature.[19,20] This change of motion with temperature suggests that the qualitative change in the interaction between PNiPAM molecule and solvent water occurs around this temperature.

In conclusion, the molecular parameters characterizing the solution properties of PNiPAM in water at 20°C are obtained and analyzed in terms of polymer solution theory. PNiPAM molecules in water at 20°C behave as expanded flexible coils and the temperature dependence of the chain dimension in the region of good to theta state (20°C to 30.6°C) is well represented by the usual excluded volume theory. Various behaviors of this polymer in water might be strongly affected by hydration and this interaction should play an important role in the phase transition process.

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