J|A|C|S
COMMUNICATIONS

Hydration and Dynamic Behavior of Poly(*N*-isopropylacrylamide)s in Aqueous Solution: A Sharp Phase Transition at the Lower Critical Solution Temperature

Yousuke Ono and Toshiyuki Shikata*
Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Received June 6, 2006; E-mail: shikata@chem.sci.osaka-u.ac.jp

Poly(*N*-isopropylacrylamide), P(NIPAm), is a well-known water soluble polymer whose aqueous solutions exhibit lower critical solution temperatures (LCSTs).[1−4] P(NIPAm) exists in an expanded conformation in water below the LCST of 32 °C in a homogeneous liquid phase. It becomes more compact above the LCST, resulting in the formation of separate liquid and solid phases. P(NIPAm), therefore, exhibits a high potential for practical applications[3] as a thermo-sensitive polymer. It is accepted (including from a theoretical point of view[4]) that this phase transition is governed by cooperative dehydration of P(NIPAm) chains. However, there have been only a few convincing reports[1,2] on the temperature dependence of the hydration number of P(NIPAm)s in aqueous solution.

Dielectric relaxation techniques are the most powerful method to detect the existence of electric dipoles in various systems and to determine precise relaxation frequencies of such dipoles. Dielectric relaxation measurements in the high-frequency range, up to 20 GHz (or 1.26×10^{11} s^{-1} in angular frequency, ω), allowed us to determine relaxation times and strengths for the P(NIPAm) solute and also for the solvent, water. These experimental results were definitely related to the number and dynamics of hydrated water molecules associated with the P(NIPAm), especially when compared to the rotational relaxation time τ_w of pure water molecules, which is 8.3 ps (1.2×10^{11} s^{-1} in ω) at 25 °C.[5,6]

In this study, the high-frequency dielectric relaxation behavior, real and imaginary parts (ϵ' and ϵ'') of complex permittivity versus ω, was investigated for aqueous P(NIPAm) solutions[7] at concentrations $c = 500$ and 1250 mM (in monomer units) over a wide ω range, up to 1.26×10^{11} s^{-1}, at various temperatures, T, from 6 to 31 °C, just below the LCST.[8] The number of hydrated water molecules per P(NIPAm) monomer unit was precisely determined as a function of T. An exchange process of hydrated water molecules associated with P(NIPAm) chains and rotational relaxation processes of P(NIPAm) side chains will be discussed.

To determine exactly the dielectric contribution of the P(NIPAm)s, $\Delta\epsilon'$ and $\Delta\epsilon''$, to the total spectra, ϵ' and ϵ'', the real and imaginary parts of complex permittivity for pure water, ϵ'_w and ϵ''_w, were subtracted as follows: $\Delta\epsilon' = \epsilon' - 1 - \Phi(\epsilon'_w - 1)$ and $\Delta\epsilon'' = \epsilon'' - \Phi\epsilon''_w$, where Φ represents the fractional dielectric contribution of pure water. Figure 1 shows typical dielectric spectra, ϵ' and ϵ'', ϵ'_w and ϵ''_w, and $\Delta\epsilon'$ and $\Delta\epsilon''$ versus ω, for an aqueous P(NIPAm) solution with $c = 1250$ mM at 25 °C. The value of Φ was evaluated to be 0.59, as the obtained $\Delta\epsilon'$ and $\Delta\epsilon''$ curves were perfectly described by the summation of Debye-type relaxation functions over the ω range examined according to standard dielectric theory (Figure 1).[5,9,10] The dependences of $\Delta\epsilon'$ and $\Delta\epsilon''$ on ω for the sample involved two major sharp and broad dielectric relaxation processes observed at 4×10^{10} and 10^8 s^{-1}, as seen in Figure 1, and similar dielectric spectra were also observed for all samples examined below the LCST.

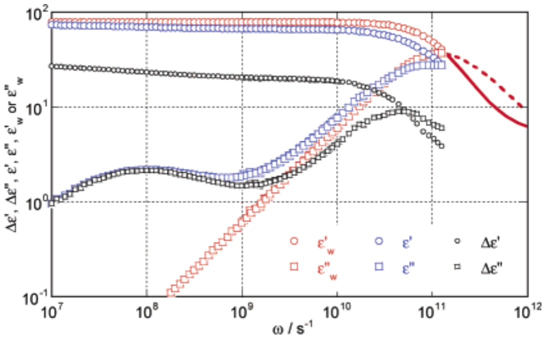


Figure 1. Angular frequency, ω, dependence of real and imaginary parts of electric permittivity, ϵ' and ϵ'', for aqueous solution of P(NIPAm) with $M_w = 3.1 \times 10^5$ at $c = 1250$ mM and 25 °C. This figure also contains the contribution of P(NIPAm), $\Delta\epsilon'$ and $\Delta\epsilon''$, and that of bulk water, ϵ'_w and ϵ''_w. Solid and broken lines represent the calculated standard ϵ'_w and ϵ''_w lines at 25 °C from the literature.[6]

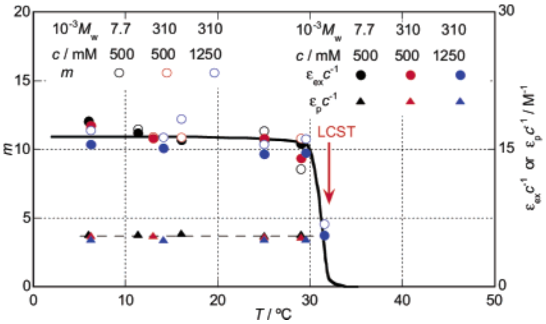


Figure 2. Temperature, T, dependences of the hydration number per P(NIPAm) monomer unit, m; concentration normalized dielectric relaxation strength of the exchange process for hydrated water molecules, $\epsilon_{ex}c^{-1}$; and that of the rotational relaxation process of isopropylamide groups, $\epsilon_p c^{-1}$, for aqueous P(NIPAm) solutions.

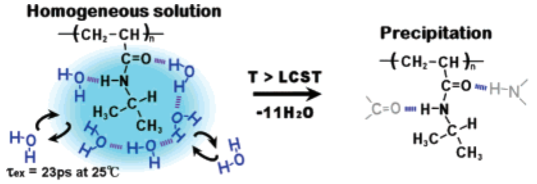
The relationship between Φ and c contains important information related to solute volume fraction and also to the number of hydrated water molecules per P(NIPAm) monomer unit, m. Φ was described accurately by eq 1 using the monomer partial molar volume of P(NIPAm), $\bar{V}_p$,[11] and the partial molar volume of water, $\bar{V}_w$, at the measured temperatures

$$\Phi = (1 - 10^{-3}\bar{V}_p c)/(1 + 10^{-3}\bar{V}_p c/2) - 10^{-3} m \bar{V}_w c \quad (1)$$

where $10^{-3}\bar{V}_p c$ gives the solute volume fraction.[5,12] The value of m is plotted as a function of T for aqueous P(NIPAm) solutions in Figure 2. This value was evaluated to be about 11 below 30 °C, irrespective of M_w (and M_w/M_n) of P(NIPAm)s and T, and decreased significantly at the LCST of 32 °C. Consequently, the number of water molecules dehydrated from each monomer unit at the LCST was 11, corresponding closely to the literature[1] value of about 13, determined for P(NIPAm) gels via a differential scanning calorimetric technique. These results suggested that the reason for the phase transition induced by increasing temperature was the complete

10.1021/ja063990i CCC: $33.50

Scheme 1



dehydration of P(NIPAm) and consequent generation of bare polymer chains at the LCST.

In the $\Delta\epsilon'$ and $\Delta\epsilon''$ spectra (Figure 1), a fast relaxation mode was found that was sharp and well-described by *one set* of Debye-type relaxation functions,[9] with a relaxation time of $\tau_{ex} = 23$ ps at 25 °C. This mode, of which relaxation time, τ_{ex}, decreased with increasing T with an activation energy, E^*_{ex}, of 25 kJ mol^{-1},[13] was assigned to the exchange or dehydration process of water molecules associated with P(NIPAm) chains. In this exchange process, the contribution of hydrated water molecules to the permittivity, in the limit of infinitely high ω, was given as $\epsilon_{ex}{}^{\infty} = 10^{-3}(\epsilon_w{}^{\infty} - 1)m\bar{V}_w c$, assuming that the hydrated water molecules had a polarizability identical to that of bulk water molecules. The m values calculated from $\epsilon_{ex}{}^{\infty}$ agreed reasonably well with those determined from Φ using eq 1.

The concentration normalized relaxation strength of the exchange process, $\epsilon_{ex}c^{-1}$, was perfectly proportional to the value of m, as seen in Figure 2.[14] This proportionality constituted strong evidence in favor of our assignment of the fast relaxation mode discussed above. Although the source dipoles belonged to water molecules in both the exchange and the rotational relaxation process of bulk water, the magnitude of the relaxation strength per unit concentration of the hydrated water molecules in the exchange process, $\epsilon_{ex}(mc)^{-1} = 1.5$ M^{-1}, was slightly greater than that of bulk water, $10^{-3}\epsilon_w\bar{V}_w$, by about 0.2 M^{-1}, below the LSCT. Such a discrepancy has been widely noted in some aqueous hydrated systems possessing τ_{ex} sufficiently longer than τ_w.[12]

Spectroscopic methods other than dielectric spectroscopy have shown that each amide group of P(NIPAm) is hydrated by two (to three) water molecules as a result of hydrogen-bond formation.[3,15] Thus, the value of $m = 11$ obtained above strongly suggested that nine (or eight) additional water molecules formed hydrogen bonds to the water molecules directly hydrating P(NIPAm), and also to each other, producing hydrogen-bond bridges between all the water molecules involved in hydration (Scheme 1).

On the other hand, the above-mentioned, slow, broad relaxation mode was well-described by the summation of *three sets* of Debye-type functions, with relaxation times of 0.8, 5.7, and 32 ns at 25 °C, irrespective of c and M_w of the P(NIPAm)s. Each relaxation time decreased with increasing T, with the same activation energy, E^*_p, as that of the rotational relaxation time for bulk water molecules, E^*_w. Because ratios of relaxation strength for each mode were kept constant in these dielectric spectra, the shape of ω dependence of spectra for the slow mode was independent of M_w, M_w/M_n, c, and T. Moreover, the concentration normalized total relaxation strength of the slow relaxation mode, $\epsilon_p c^{-1}$, appeared to be independent of T below the LCST (Figure 2). These findings suggested the assignment of the slow relaxation to the rotational relaxation of dipoles in the amide groups of P(NIPAm) in aqueous medium, a viscosity-governed process also with an activation energy identical with E^*_w. Because sample solutions exhibited significant precipitation due to the phase transition, the value of $\epsilon_p c^{-1}$ above the LCST did not describe the dielectric relaxation strength of P(NIPAm)s exactly.

Longitudinal relaxation times, T_1, of ^{13}C NMR for a D_2O solution of the P(NIPAm) with $M_w = 3.1 \times 10^5$ were measured at $c =$ 1800 mM and 25 °C to estimate the average time scale for molecular motions of P(NIPAm) monomer units, including both main chain moieties and isopropylamide groups, in aqueous (D_2O) solution below the LCST.[16] The obtained T_1 data yielded a rotational relaxation time, τ_r,[17] of about 30 ns for P(NIPAm) monomer units. This result strongly supported our assignment of the slow relaxation mode in our spectra to rotational motions of P(NIPAm) monomer units in aqueous solution below the LCST.

Acknowledgment. The authors thank Dr. S. Yusa, Hyogo University, for his kind supply of a P(NIPAm) sample. Y.O. wishes to express special thanks to the Center of Excellence (21COE) program "Creation of Integrated EcoChemistry of Osaka University".

Supporting Information Available: Results of T_1 determination from ^{13}C NMR measurements and of τ_c evaluation. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Shibayama, M.; Morimoto, M.; Nomura, S. *Macromolecules* **1994**, *27* (7), 5060−5066. (b) Shibayama, M.; Mizutani, S.; Nomura, S. *Macromolecules* **1996**, *29*, 2019−2024.
(2) (a) Fujishige, S.; Kubota, K.; Ando, I. *J. Phys. Chem.* **1989**, *93*, 3311−3313. (b) Kogure, H.; Nanami, S.; Masuda, Y.; Toyama, Y.; Kubota, K. *Colloid Polym. Sci*. **2005**, *283*, 1163−1171.
(3) Winnik, F. M. *Macromolecules* **1990**, *23*, 233−242.
(4) Okada, Y.; Tanaka, F. *Macromolecules* **2005**, *38*, 4465−4471.
(5) Pottel, R. *Water*; Franks, F., Ed.; Plenum: New York, 1973; Vol. 3, Chapter 8.
(6) Kaatze, U. *J. Chem. Eng. Data* **1989**, *34*, 371−374.
(7) Two kinds of P(NIPAm)s with different molecular weights and distributions, $M_w = 7.7 \times 10^3$ and $M_w/M_n = 1.12$, kindly supplied by Dr. S. Yusa, and $M_w = 3.1 \times 10^5$ and $M_w/M_n = 3.04$, purchased from Scientific Polymer Products, Inc. (Ontario), were employed. The M_w and M_w/M_n values for both the polymers were determined via gel permeation chromatographic experiments with tetrahydrofuran as a carrier solvent.
(8) An RF LCR meter (Agilent Technologies, 4287A), equipped with a homemade electrode cell, was used to determine dielectric relaxation spectra for sample solutions over the frequency range from 1 MHz to 3 GHz at various temperatures from 6 to 31 °C. Real and imaginary parts, ϵ' and ϵ'', of the complex permittivity were evaluated in the conventional manner: $\epsilon' = CC_0{}^{-1}$ and $\epsilon'' = (G - G_{dc})C_0{}^{-1}\omega^{-1}$, where C_0, C, G, and G_{dc} were the capacitance of the (vacant) used electrode cell; that of samples; conductivity of samples; and direct current conductivity due to ionic impurities, respectively. In the frequency range from 50 MHz to 20 GHz, ϵ' and ϵ'' were determined using a dielectric material probe system (Hewlett-Packard, 85070B) consisting of a network analyzer (Hewlett-Packard, 8720ES); details described elsewhere (Imai, S.; Shiokawa, M.; Shikata, T. *J. Phys. Chem. B* **2001**, *105*, 4495−4502).
(9) Fröhlich, H. *Theory of Dielectrics*; Clarendon Press: Oxford, U.K., 1949.
(10) According to standard dielectric theory,[9] real and imaginary parts of electric complex permittivity are completely described by the summation of Debye-type relaxation functions of a mode i; $\epsilon_i/(1 + \omega^2\tau_i{}^2) + \epsilon_i{}^{\infty}$ (real) and $\epsilon_i\omega\tau_i/(1 + \omega^2\tau_i{}^2)$ (imaginary), where τ_i, ϵ_i, and $\epsilon_i{}^{\infty}$ represent, respectively, the relaxation time, strength, and permittivity in the high ω limit for the mode i. In the case of pure water at 25 °C, the following values are well-known: $\tau_w = 8.3$ ps, $\epsilon_w = 73.3$, and $\epsilon_w{}^{\infty} = 5.1$.[6]
(11) $\bar{V}_p$ was evaluated to be between 99.0 and 99.5 cm^3 mol^{-1} for P(NIPAm)s via density measurements of aqueous P(NIPAm) solutions at 20.0 to 25.0 °C using a DMA5000 density meter (Anton Paar, Graz, Austria). The temperature dependence of $\bar{V}_p$ was described by the relationship $\bar{V}_p = 97.02 + 0.099T$ (in °C) below the LCST. $\bar{V}_w$ varied from 18.0 cm^3 mol^{-1} at 6 °C to 17.9 cm^3 mol^{-1} at 32 °C in the temperature range examined.
(12) Ono, Y.; Shikata, T. *J. Phys. Chem. B* **2006**, *110*, 9426−9433.
(13) The magnitude of the activation energy, $E^*_{ex} = 25$ kJ mol^{-1}, which was clearly greater than that of the rotational relaxation time for bulk water, i.e., $E^*_w = 19$ kJ mol^{-1},[6] was related to the energy necessary to break hydrogen bonds between hydrated water molecules to P(NIPAm) chains.
(14) Because the scale of the right-hand ordinate is 1.5 times as large as that of the left-hand one, the relationship $\epsilon_{ex}c^{-1} = 1.5m$ is obtained.
(15) Maeda, Y.; Kitano, H. *Spectrochim. Acta, Part A* **1995**, *51*, 2433−2466.
(16) Determination of T_1: ^{13}C NMR measurements were performed using JEOL EX-270 (resonance frequency for ^{13}C: $\omega_r = 67.80$ MHz) and JEOL Lambda-500 ($\omega_r = 126.7$ MHz) spectrometers at 25 °C via a conventional inversion recovery pulse sequence under the deuterium lock mode.
(17) The obtained T_1 values at different resonance frequencies provided the correlation time, τ_c (Lyerla, J. R., Jr.; Levy, G. C. *Topics in Carbon-13 NMR Spectroscopy*; Levy, G. C., Ed.; Wiley: New York, 1974; Vol. 1, pp 79−148.). This τ_c value was subsequently converted to the rotational relaxation time with the same physical meaning of dielectric relaxation times, using the expression $\tau_r = 3\tau_c$.

JA063990I