Changes in the Hydration States of Poly(*N*-*n*-propylmethacrylamide) and Poly(*N*-isopropylmethacrylamide) during Their Phase Transitions in Water Observed by FTIR Spectroscopy

Yasushi Maeda,* Tomoya Nakamura, and Isao Ikeda

Department of Applied Chemistry and Biotechnology, Fukui University, Fukui 910-8507, Japan

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ABSTRACT: Phase transitions of poly(*N*-*n*-propylmethacrylamide) (PnPMA) and poly(*N*-isopropylmethacrylamide) (PiPMA) in H_2O and D_2O have been investigated by using Fourier transform infrared (FTIR) spectroscopy. IR spectra of these polymer solutions have been collected as a function of temperature in both heating and cooling processes. The positions of IR bands due to the alkyl and amide groups of these polymers critically shift at their phase transition temperatures (T_p). The amide II, C−H stretching and C−H bending bands undergo red shift, whereas the amide I band undergoes a blue shift upon the coil-to-globule transitions. The amide I bands of PnPMA and PiPMA measured below their T_p consist of three (1642, 1611, and 1586 cm^{-1}) and two (1635 and 1606 cm^{-1}) Gaussian components, respectively. The areas of the 1642 cm^{-1} component of PnPMA and the 1635 cm^{-1} component of PiPMA, which can be attributed to the carbonyl group that forms a hydrogen bond with an amide N−D group (C=O···D−N), increase with temperature while the phase transitions of the polymer solutions proceed. Molar fractions of the C=O···D−N species are estimated to be 0.40 and 0.42 in the globule states of PnPMA and PiPMA, respectively, which are much larger than those of corresponding poly(*N*-alkylacrylamide)s, i.e., poly(*N*-*n*-propylacrylamide) (PnPA) and poly(*N*-isopropylacrylamide) (PiPA). We attribute greater thermal hystereses of PnPMA and PiPMA than those of PnPA and PiPA, which are characterized by a large difference between T_p for a heating process and T_p for a cooling process, to higher degrees of the polymer−polymer hydrogen bonding in the globule states of PnPMA and PiPMA. Although T_p of each polymer solution greatly depends on polymer concentration, the molar fraction of the C=O···D−N species and the wavenumbers of C−H stretching bands at the end point of its phase transition are independent of the concentration (5−20 wt %). The result indicates that the local concentration of polymer chains in each globule is independent of the total polymer concentration as it is expected from its phase diagram.

Introduction

Poly(*N*-alkylacrylamide)s and poly(*N*-alkylmethacrylamide)s are known to exhibit phase transitions in water at critical temperatures. The phase transition of poly(*N*-isopropylacrylamide) (PiPA), in particular, has been extensively studied by using calorimetry,[1] fluorescence,[2] light scattering,[3] NMR,[4] and many other techniques.[5] The macroscopic phase separations of these polymer solutions are accompanied by large conformational changes in the polymer chains.[6] The polymer chains are dehydrated upon the phase transition and attractive interactions between hydrophobic moieties lead the polymer chains from a randomly coiled structure to a collapsed globular structure. Although most of the studies concerning the phase transitions of aqueous polymer solutions have concentrated on PiPA, several studies have also been carried out on poly(*N*-isopropylmethacrylamide) (PiPMA).[7] The presence of α-methyl groups makes the phase behavior of PiPMA to be quite different from that of PiPA in some aspects. The phase transition temperature of aqueous solution of PiPMA is about 44.0 °C, which is higher than that of PiPA by ca. 10 °C. Ito et al. reported that the trace of the turbidity change is accompanied by a significant retardation for the rate of cooling, which is attributed to the effects of a restricted free rotation because of the presence of the α-methyl groups.[8] The transition temperature of poly(*N*-*n*-propylmethacrylamide) (PnPMA)

has been reported to be 28.0 °C,[8] which is also higher than that of PnPA. However, the features of the phase behavior of PnPMA have not been studied in detail.

Recently, we have reported FTIR spectroscopic investigation on the coil−globule transition of PiPA,[9] PnPA, and poly(*N*-cyclopropylacrylamide) in water.[10] IR spectroscopy is a quite suitable method for observing changes in hydration states of individual chemical groups on the polymer chain. In particular, analysis of the amide I band, which is mainly due to the C=O stretching vibration, provides important information concerning hydrogen bonding of the C=O group. In short, the amide I band of PnPA and PiPA observed below T_p contains a single component that can be assigned to C=O···H−O (polymer−water hydrogen bond), whereas, the second component due to C=O···H−N (polymer−polymer hydrogen bond) exists above T_p. The molar fraction of the C=O···H−N species are estimated to be 0.3 and 0.13 for PnPA and PiPA in their globule states, respectively. The phase transition of PnPA shows a large thermal hysteresis, that is, the transition temperature region for a cooling process is lower than that of a heating process, and we attribute the larger hysteresis of PnPA in comparison with that of PiPA to a higher degree of polymer−polymer hydrogen bonding in its globule state. The objective of the present study is to clarify differences between phase behaviors of poly(*N*-alkylmethacrylamide)s and those of corresponding poly(*N*-alkylacrylamide)s and to reveal relationship between the natures of hydrogen bonding about the amide groups of these polymers and the features of their phase behaviors. For

* Corresponding author: Fax: +81-776-27-8747. E-mail: y_maeda@acbio.fukui-u.ac.jp.

Table 1. Observed IR Frequencies (in cm^{-1}) and Assignments of PnPMA-h and PnPMA-d

PnPMA-h				PnPMA-d		
H$_2$O solution	difference IR band in H$_2$O solution	neat	assignment	D$_2$O solution	difference IR band in D$_2$O solution	neat
2973	2983($-$), 2961($+$)	2963	antisymmetric C$-$H stretching of $-$CH$_3$	2973	2992($-$), 2962($+$)	2965
2943	2946($-$), 2927($+$)	2934	antisymmetric C$-$H stretching of $-$CH$_2-$	2943	2948($-$), 2931($+$)	2932
2882	2885($-$), 2874($+$)	2875	symmetric C$-$H stretching of $-$CH$_3$	2882	2886($-$), 2873($+$)	2874
ov[a]	ov	1633	amide I	1611	1639($+$), 1611($-$)	1637
1568	1573($-$), 1541($+$)	1550	amide II	1488	1490($-$), 1476($+$)	1524
1462	1463($-$), 1457($+$)	1459	deformation of $-$CH	1466	1470($-$), 1451($+$)	1459
1446	1447($-$), 1437($+$)	1443	deformation of $-$CH	1442	1443($-$), 1429($+$)	1424
1386	1387($-$), 1379($+$)	1383	deformation of $-$CH	1389	1392($-$), 1487($+$)	1386
1206	1208($-$), 1199($+$)	1213	skeletal vibration	ov	ov	1215

[a] ov: overlap with other band.

this purpose, we follow changes in the profiles of the amide and C$-$H stretching bands of PnPMA and PiPMA in the courses of their phase transitions in both heating and cooling processes by using IR spectroscopy and compare them to those of PnPA and PiPA.

Experimental Section

Materials. *N-n*-propylmethacrylamide (nPMA) and *N*-isopropylmethacrylamide (iPMA) were synthesized via coupling of methacryloyl chloride (Wako Pure Chemicals) and *n*-propylamine or isopropylamine (Wako) in benzene, respectively. Purification of nPMA was carried out by distillation at 82 °C (1.5 mmHg). iPMA was recrystallized from benzene/hexane before use. The chemical structures of nPMA and iPMA were confirmed by ^{1}H NMR. Poly(*N-n*-propylmethacrylamide) (PnPMA) and poly(*N*-isopropylmethacrylamide) (PiPMA) were synthesized via radical polymerization in methanol at 70 °C for 7 h using 2,2′-azobis(isobutyronitrile) as an initiator. After evaporation these polymers were precipitated from acetone-*n*-hexane. Polymers obtained were purified by dialysis (seamless cellulose tube, exclusion limit 8000), and they were recovered by freeze-drying. To prepare *N*-deuterated PnPMA ([$-$CH$_2$C(CH$_3$)(COND^{i}Pr)$-$]$_n$, PnPMA-d) and PiPMA ([$-$CH$_2$C(CH$_3$)(COND^{i}Pr)$-$]$_n$, PiPMA-d), the corresponding polymers dissolved in D$_2$O (EURIS-TOP, 99.9%) were allowed to stand more than 1 day below T_p to equilibrate H$-$D exchange and were then freeze-dried. To distinguish from PnPMA-d and PiPMA-d, the undeuterated counterparts are denoted as PnPMA-h and PiPMA-h, respectively.

Turbidimetry. The turbidity of an aqueous polymer solution was followed by the absorbance at 500 nm by using a spectrophotometer as described previously.[10]

Differential Scanning Calorimetry (DSC). DSC measurements were performed using a Micro Calorimetry System (MicroCal Inc.).[10] Polymer sample was dissolved in H$_2$O (0.5 wt %) and scanned at a rate of 0.75 °C/min.

FTIR Measurements. IR spectra were measured using a Bio-Rad FTS-3000 IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The other experimental procedure was the same as previously described.[10] The IR difference spectrum obtained by subtracting an IR absorption spectrum measured at the starting temperature (T_o) from a spectrum measured at T is designated as ΔA_{T-T_o}. The difference in the values of ΔA_{T-T_o} at the positive and negative peaks of a selected vibration mode in a difference spectrum is defined as

$$\Delta\Delta A_{T-T_o}(\nu_1, \nu_2) = \Delta A_{T-T_o}(\nu_1) - \Delta A_{T-T_o}(\nu_2) \qquad (1)$$

where ν_1 and ν_2 denote wavenumbers at the positive or negative peaks in the IR difference spectrum and ν_1 is defined to be lower than ν_2. A positive value of $\Delta\Delta A_{T-T_o}(\nu_1, \nu_2)$ indicates a red shift of the corresponding IR absorption band during the temperature change from T_o to T.

Results and Discussion

Phase Transitions and IR Spectra of PnPMA and PiPMA in Water. Figure 1a shows the IR absorp-
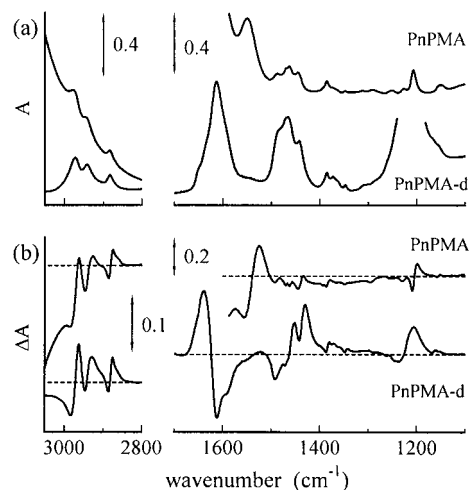

Figure 1. (a) IR absorption spectra of PnPMA-h (12.3 °C) in H$_2$O and PnPMA-d (12.4 °C) in D$_2$O. (b) IR difference spectra induced by the phase transition of PnPMA-h ($\Delta A_{35.5-12.3}$) in H$_2$O and PnPMA-d ($\Delta A_{35.1-12.4}$) in D$_2$O.

tion spectra of PnPMA-h in H$_2$O and PnPMA-d in D$_2$O measured at 12 °C. The IR frequencies and assignments of major peaks are compiled in Table 1. Because the amide II band contains contribution from an N$-$H bending vibration, it is sensitive to deuteration and shifts from 1561 cm^{-1} for PnPMA-h to 1470 cm^{-1} for PnPMA-d. Other bands are insensitive to the deuteration. For the clarity the amide bands for *N*-deuterated species ($-$COND$-$) are denoted as the amide I′ and amide II′. A major advantage of using D$_2$O as a solvent is a shift in the deformation band of water to around 1200 cm^{-1}, which prevents the band from overlapping the amide I′ band.

The IR difference spectra (ΔA_{35-12}) of PnPMA-h and PnPMA-d obtained by subtraction of the IR absorption spectra measured below T_p (12 °C) from those measured above T_p (35 °C) are shown in Figure 1b. In the IR difference spectra, negative peaks are associated with IR absorption by the polymer in the coil state and positive peaks represent IR absorption in the globule state. For example, a pair of IR difference peaks observed at 2983 (negative) and 2961 cm^{-1} (positive) in Figure 1b are due to a red shift of antisymmetric C$-$H stretching band of the methyl group during the transition. Most of the bands undergo red shifts during the transition with an exception of the amide I band, which shifts from 1605 to 1636 cm^{-1} (blue shift). The IR absorption spectra of PiPMA-h in H$_2$O and PiPMA-d in D$_2$O measured at 35 °C are shown in Figure 2a and the IR difference spectra (ΔA_{53-35}) are shown in Figure 2b. The IR frequencies and assignments are compiled in

Table 2. Observed IR Frequencies (in cm⁻¹) and Assignments of PiPMA-h and PiPMA-d

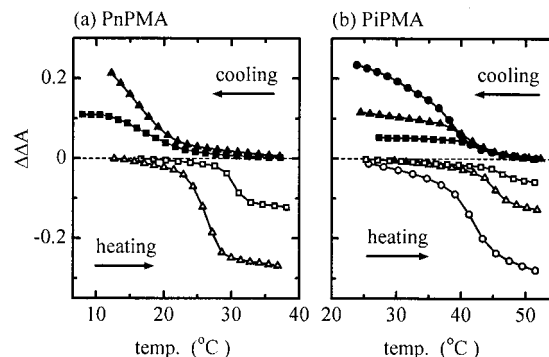| PiPMA-h				PiPMA-d		
H_2O solution	difference IR band in H_2O solution	neat	assignment	D_2O solution	difference IR band in D_2O solution	neat
2986	2992(−), 2971(+)	2972	antisymmetric C−H stretching of −C(CH₃)₂	2984	2991(−), 2971(+)	2969
2940	2949(−), 2932(+)	2933	C−H stretching of −CH₂−	2941	2947(−), 2933(+)	2923
2881	2886(−), 2873(+)	2875	symmetric C−H stretching of −C(CH₃)₂	2883	2886(−), 2874(+)	2876
ov^a	ov	1634	amide I	1606	1638(+), 1606(−)	1631
1541	1550(−), 1517(+)	1523	amide II	1486	1489(−), 1473(+)	1523
1463	1466(−), 1456(+)	1458	deformation of −CH	1464	1466(−), 1460(+)	1458
1391	1393(−), 1386(+)	1388	deformation of −CH	1392	1393(−), 1386(+)	1386
1371	1372(−), 1367(+)	1366	deformation of −CH	1371	1372(−), 1366(+)	1368
1206	1208(−), 1198(+)	1199	skeletal vibration	ov	ov	1199

^{a} ov: overlap with other band.
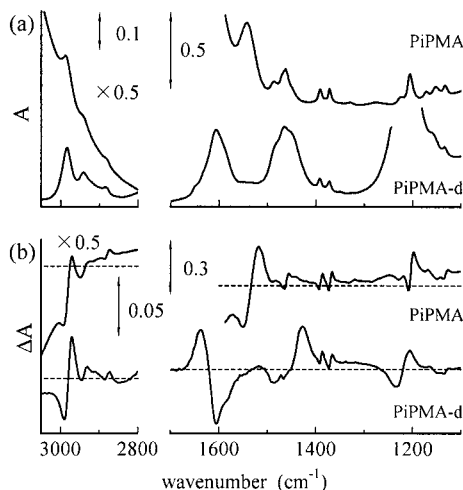
Figure 2. (a) IR absorption spectra of PiPMA-h (34.9 °C) in H_2O and PiPMA-d (35.2 °C) in D_2O. (b) IR difference spectra induced by the phase transition of PiPMA-h ($\Delta A_{52.9-34.9}$) in H_2O and PiPMA-d ($\Delta A_{52.7-35.2}$) in D_2O.
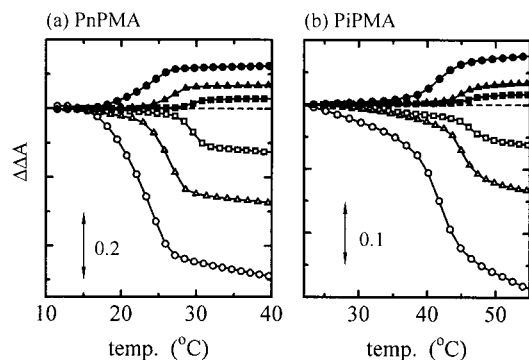
Figure 3. Values of $\Delta\Delta A_{T-T_0}(\nu_1, \nu_2)$ for the amide I′ (closed marks) and amide II′ (open marks) modes of (a) PnPMA-d and (b) PiPMA-d in D_2O at 5 (■, □), 10 (▲, △), and 20 wt % (●, ○) are plotted against temperature.

Figure 4. Values of $\Delta\Delta A_{T-T_0}(\nu_1, \nu_2)$ for the amide I′ modes of (a) PnPMA-d and (b) PiPMA-d in the heating (open marks) and the cooling (solid marks) processes plotted against temperature. The polymer concentrations are 5 wt % (■, □), 10 wt % (▲, △), and 20 wt % (●, ○).
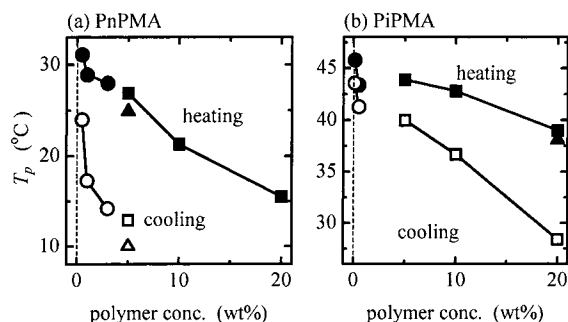
Figure 5. Phase transition temperatures, T_p, of (a) PnPMA and (b) PiPMA measured in the heating (solid marks) and cooling (open marks) processes plotted against polymer concentration: (●, ○) determined by turbidimetry in H_2O; (▲, △) determined by IR in H_2O; (■, □) determined by IR in D_2O.

Table 2. The spectral feature of PiPMA is similar to that of PnPMA.

To follow the progress of the phase transitions, the values of $\Delta\Delta A_{T-T_0}(\nu_1, \nu_2)$ for the C−H stretching and amide I′ modes of PnPMA (5, 10, 20 wt %) and PiPMA (5, 10, 20 wt %) measured in D_2O are plotted against temperature in Figure 3. Slopes of $\Delta\Delta A_{T-T_0}(\nu_1, \nu_2)$ curves for 5 wt % PnPMA solution abruptly changes at around 26 °C and are steep in the temperature range of 26−31 °C. The transition temperature (T_p) for the heating process is determined from the onset temperature where $\Delta\Delta A_{T-T_0}(\nu_1, \nu_2)$ curve departs from the linear baseline of the lower temperature side. A gradual slope of the baseline is attributed to a small shift or broadening of the IR band because of a simple temperature effect. The transition temperature, T_p, of PnPMA lowered with an increase in the polymer concentration (10 wt %, 19.9 °C; 20 wt %, 14.5 °C). The transition temperatures of PiPMA also exhibited concentration dependence, which is less significant than that of PnPMA.

To show the thermal hysteresis of the phase transition, values of $\Delta\Delta A_{T-T_0}(\nu_1, \nu_2)$ for the amide I′ modes of PnPMA and PiPMA in the heating and cooling processes are plotted as a function of temperature in Figure 4. The transition temperature T_p of PnPMA and PiPMA in the heating and cooling processes are plotted as a function of polymer concentration in Figure 5. The circles represent T_p determined by using turbidimetry in H_2O. The triangles and squares represent T_p measured by using IR spectroscopy in H_2O and D_2O, respectively. The transition temperatures of these poly-
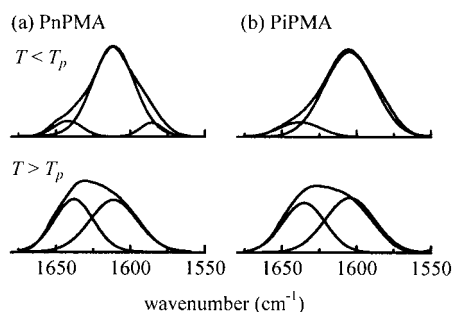
Figure 6. (a) Baseline-subtracted amide I′ bands of PnPMA-d measured at 12.4 °C ($<T_p$) and 35.1 °C ($>T_p$) and best-fitted Gaussian components (12.4 °C; center, 1642 cm^{-1}; width at half-height (W_h), 23 cm^{-1}; center, 1611 cm^{-1}; W_h, 33 cm^{-1}; and center, 1586 cm^{-1}; W_h, 19 cm^{-1}; 35.1 °C; center, 1638 cm^{-1}; W_h, 31 cm^{-1}; and center, 1611 cm^{-1}; W_h, 38 cm^{-1}). (b) Baseline-subtracted amide I′ bands of PnPMA-d measured at 35.2 °C ($<T_p$) and 52.7 °C ($>T_p$) and Gaussian components (35.2 °C; center, 1635 cm^{-1}; W_h, 33 cm^{-1}; and center, 1606 cm^{-1}; W_h, 39 cm^{-1}; 52.7 °C; center, 1635 cm^{-1}; W_h, 33 cm^{-1}; and center, 1606 cm^{-1}; W_h, 39 cm^{-1}).

mers measured in H_2O were slightly lower than those measured in D_2O, because of lower strength of hydrogen bonding of H_2O than that of D_2O. The transition temperature for the cooling process is defined as the temperature where the turbidity-vs-temperature curve or the $\Delta\Delta A_{T-T_0}$-vs-temperature curve return to the baseline after passing the transition temperature region. T_p for the cooling processes represented by open marks in the figure are lower than T_p for the heating processes (closed marks). T_p for the cooling process of 20 wt % PnPMA solution might be lower than 0 °C at the cooling rate examined. The values of T_p for both heating and cooling processes decrease and the hestereses become more significant with an increase in the polymer concentration.

Change in the Amide Bands of PnPMA-d and PiPMA-d during the Phase Transition. The amide I′ bands of these polymers in D_2O were analyzed by using a peak decomposition method in more detail. As shown in Figure 6 the amide I′ band of PnPMA and PiPMA observed below T_p consist of three (1642, 1611, and 1586 cm^{-1}) and two (1635 and 1606 cm^{-1}) Gaussian components, respectively. This is a marked contrast to PnPA and PiPA whose amide I′ bands consist of a single component below T_p.[9,10] The 1611 cm^{-1} and 1606 cm^{-1} components are the main components for PnPMA and PiPMA below T_p, respectively, and the areas of these bands decrease with increasing temperature. The 1586 cm^{-1} component of PnPMA disappears in the course of the phase transition and the amide I′ bands of both PnPMA and PiPMA measured in their globule states can be decomposed into two components.

It is known that the strength of hydrogen bond about an amide group correlates with the frequency of its amide I vibration mode. That is, the stronger the hydrogen bond involving the amide C=O, the lower the electron density along the C=O bond and the lower the amide I frequency. Analysis on the positions of the amide I′ bands of monomer analogues such as *N-n*-propylpropionamide (nPPA) and *N*-isopropylpropionamide (iPPA) is helpful for the assignments of these components of amide I′ bands of the polymers. Amide I′ bands of nPPA and iPPA shift toward higher wavenumbers while the fraction of the amide-amide hydrogen bonds (C=O···D−N) increases and that of the amide−water hydrogen bonds (C=O···D−O−D) de-

creases with an increase in their concentration in water.[10] The result indicates that the wavenumbers of the amide I′ band of the C=O···D−N species are higher than those of the C=O···D−O−D species. In a similar way, the 1611 cm^{-1} band of PnPMA and the 1606 cm^{-1} band of PiPMA can be assigned to the C=O···D−O−D species, whereas the 1642 cm^{-1} band of PnPMA and the 1635 cm^{-1} band of PiPMA are assigned to the C=O···D−N species. In the previous study we have shown that the amide I′ bands of PnPA and PiPA consist of two components (PnPA: 1630 and 1650 cm^{-1}, PiPA: 1625 and 1650 cm^{-1}) and have assigned the low-frequency components to C=O···D−O−D species and the high-frequency components to the C=O···D−N species.[9,10] The differing degrees of peak shift upon the coil-to-globule transitions (PnPA 20 cm^{-1}, PiPA 25 cm^{-1}, PnPMA 29 cm^{-1} and PiPMA 34 cm^{-1}) might be related to the differences in the strength of hydrogen bonding in each polymer.

On the other hand, the assignment of the 1586-cm^{-1} component of PnPMA is unclear at this moment. The extremely low wavenumber of the component indicate the existence of a very strong hydrogen bond about the C=O group or the formation of more than two hydrogen bonds between the C=O group with hydrogen-donors. PnPMA should have a more open chain conformation than PnPA and PiPA due to hindered rotation and should be less sterically inhibited than PiPMA. Therefore, it might not be surprising that PnPMA exclusively shows this component if it is due to the formation of multiple hydrogen bonds. Similar phenomena have been observed with several coiled-coil proteins such as tropomyosin, whose amide I band occurs at about 1630 cm^{-1} and is well below that of standard α-helical peptides (the C=O···H−N hydrogen bonds are formed). The shift to lower frequency is attributed to additional hydrogen bonding of solvent accessible C=O group to water (each C=O group forms both the C=O···H−N and C=O···H−O−H hydrogen bonds).[11]

To perform a quantitative analysis, we define molar fractions of the C=O···D−O−D and C=O···D−N species of PiPMA as f_1 and f_2. Because the amide I′ band of PiPMA consists of two components arising from these species, f_1 plus f_2 is one in the whole temperature range examined. Areas of these components (S_1 and S_2) are given by $S_1 = \epsilon_1 f_1$ and $S_2 = \epsilon_2 f_2$, respectively, where ϵ_1 and ϵ_2 are the molar absorption coefficients of the C=O···D−O−D and C=O···D−N species, respectively. Thus, S_1 is expressed as a function of S_2 as follows,

$$S_1 = \epsilon_1 f_1 = \epsilon_1(1 - f_2) = \epsilon_1 - S_2\epsilon_1/\epsilon_2 \qquad (2)$$

The ratio of the absorption coefficients, ϵ_1/ϵ_2, is calculated to be 1.1 from a slope of S_1-vs-S_2 line (data not shown). The molar fractions of the C=O···D−N species of PiPMA at various temperatures are estimated by using the ratio and are shown in Figure 7b. Figure 7b indicates that about 42% of the C=O groups of PiPMA form hydrogen bonds with the amide hydrogen in the globule state, which connect polymer chain through intrachain and/or interchain cross-linkages. The remaining ca. 60% of the C=O groups retain polymer−water hydrogen bonds even in the globule state, where the polymer chains are partially dehydrated. Moreover, the fraction of the C=O···D−N species in the globule state is independent of the polymer concentration although the transition temperature of PiPMA depended on the concentration. The result indicates that
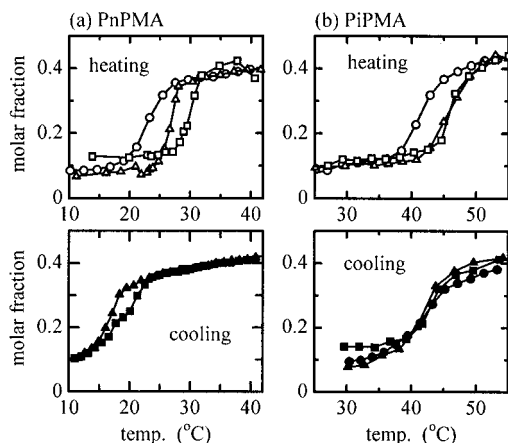
Figure 7. Molar fractions of the amide C=O groups of (a) PnPMA-d and (b) PiPMA-d that form hydrogen bond with the amide N−D group (the C=O···D−N species) in D_2O plotted against temperature. The polymer concentrations are 5 wt % (■, □), 10 wt % (▲, △), and 20 wt % (●, ○). Open and solid marks represent the heating and cooling processes, respectively.
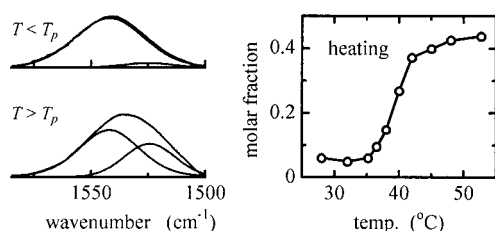

Figure 8. (a) Baseline-subtracted amide II bands of PiPMA-h measured at 35.2 °C ($< T_p$) and 52.7 °C ($> T_p$) and best-fitted Gaussian components (35.2 °C; center, 1545 cm^{-1}; W_h, 15 cm^{-1}; 52.7 °C; center, 1543 cm^{-1}; W_h, 7.7 cm^{-1}; and center, 1525 cm^{-1}; W_h, 4.4 cm^{-1}). (b) Molar fractions of the amide N−H groups of PiPMA-h (20 wt %) that forms hydrogen bond with the amide C=O group (the N−H···O=C species) in H_2O solution in the heating process plotted against temperature.

the polymer concentration and water contents within each globule of PiPMA are almost independent of the total polymer concentration of the solution in the range of the measurements (up to 20 wt %).

To confirm the result obtained via the analysis of the amide I′ band, which is mainly due to C=O stretching vibration, we also investigated the hydrogen bonding of the counterpart, i.e., the amide N−H group through an analysis of the amide II band. Because the amide II′ band of PiPMA-d overlaps with the C−H bending vibration bands, we observed the amide II band of PiPMA-h in H_2O. The amide II bands of PiPMA-h observed in the transition temperature region consist of two components centered at 1545 and 1525 cm^{-1} (Figure 8a). The 1545 and 1525 cm^{-1} components are assigned to the amide N−H group that forms a hydrogen bond with water and the amide C=O group, respectively. The molar fractions of the N−H···O=C species are plotted as a function of temperature in Figure 8b. In the globule states of PiPMA, the fraction is estimated to be 0.4, which agrees well with that of the C=O···D−N species. Thus, the analyses from both sides of the hydrogen bonding partners show that about 40% of the amide groups of PiPMA form the polymer−polymer hydrogen bonds. To be precise, the polymer−H_2O interaction is not the same as the polymer−D_2O interaction. However, the difference might not be so large that it makes the comparison meaningless.
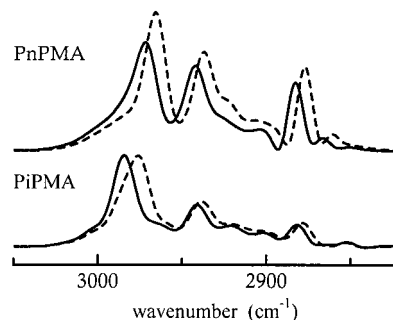

Figure 9. Fourier self-deconvoluted C−H stretching IR absorption spectra of PnPMA-d (12.4 (solid) and 35.1 °C (broken)) and PiPMA (35.2 (solid) and 52.7 °C (broken)) in D_2O.

On the other hand, precise evaluation of the fraction of the C=O···D−N species of PnPMA is rather difficult because its amide I′ band contains three components. However, the area of the third component (1586 cm^{-1}) is relatively small, especially at temperatures above T_p. If we neglect the component, we can calculate the molar fraction of the C=O···D−N species as shown in Figure 7a. About 40% of the C=O groups of PnPMA seem to form the polymer−polymer hydrogen bond, and the value is independent of the polymer concentration. Molar fractions of the C=O···D−N species in the globules of PnPA and PiPA were previously estimated to be 0.30 and 0.13, respectively.[9,10] These results indicate that a larger portion of the polymer−polymer hydrogen bonds are formed in the globules of PnPMA and PiPMA than those of PnPA and PiPA. The phase transitions of PnPMA and PiPMA show extensive thermal hystereses as shown in Figure 4, meaning that their globule-to-coil transitions contain more time-consuming processes than their coil-to-globule transitions. The cross-linkages resulted from the intrachain and interchain hydrogen bonds that are formed between the amide groups in the contracted polymer chains might be responsible for the hystereses. In addition to the relatively large number of the polymer−polymer hydrogen bonds, the presence of α-methyl groups restrict the freedom of the conformational changes, and the hystereses of PnPMA and PiPMA are more significant than those of PnPA and PiPA.

Changes in C−H Stretching Bands of PnPMA and PiPMA during Their Phase Transitions. The C−H stretching vibration region (2840−3000 cm^{-1}) of the IR spectra provides information about hydration of the alkyl groups of these polymers. Figure 9 shows Fourier deconvoluted spectra in the C−H stretching region of PnPMA and PiPMA. The IR bands undergo red shifts upon the phase transitions. As described in our previous papers, red shifts of the C−H stretching IR bands indicate dehydration of the alkyl groups.[9,10] In short, exchange force in C−H···OH$_2$ interaction, which tends to contract C−H bonds, is slightly larger than the forces pushing toward elongation (electrostatic, polarization, charge transfer, and dispersion).[12] The C−H bond contracts in the complex, and therefore, the C−H stretching frequency experiences a blue shift upon interaction with water. The positions of the major C−H stretching bands are plotted as a function of temperature in Figure 10. The position of these bands shift toward lower wavenumbers in the transition temperature region, which depend on the polymer concentration. Although the transition temperature regions are lowered with increasing concentration, the positions of the
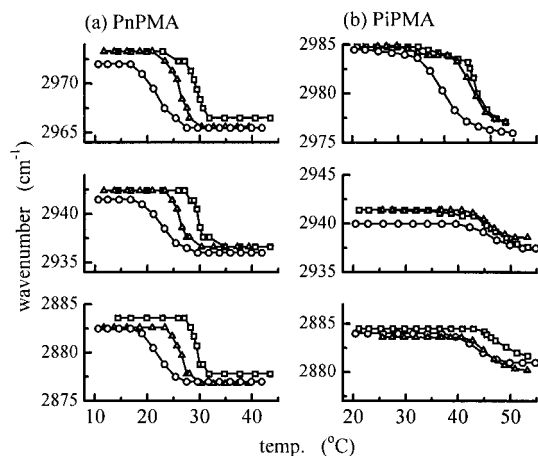
Figure 10. Positions of the C−H stretching IR bands of (a) PnPMA and (b) PiPMA measured in D$_2$O plotted against temperature. The polymer concentrations are 5 wt % (■, □), 10 wt % (▲, △), and 20 wt % (●, ○).

C−H stretching bands above and below the transition regions are almost independent of the polymer concentration. The result agrees with the concentration dependences of the hydrogen bonding of the amide groups of these polymers and indicates that the conditions of each polymer chain in the globule state are identical among solutions at different polymer concentration. This is consistent with change of polymer concentration in the polymer-rich phase during the phase transition that is expected from phase diagram. That is to say, polymer concentrations in both polymer-rich and water-rich phases depend only on temperature but they are independent of total polymer concentration.

Conclusion

The phase behaviors of poly(*N*-alkylmethacrylamide)s (PnPMA and PiPMA) are somewhat different from those of the corresponding poly(*N*-alkylacrylamide)s (PnPA and PiPA). First, PnPMA and PiPMA show a larger thermal hysteresis than PnPA and PiPA. The differences in the transition temperatures for the cooling and heating processes increase with polymer concentration. Second, poly(*N*-alkylmethacrylamide)s and poly(*N*-alkylacrylamide)s are dissimilar in hydrogen bonding about their amide C=O groups. Most of the amide C=O groups of PnPA and PiPA form hydrogen bond with water below T_p, which give rise to a single amide I′ component. In contrast, amide I′ bands of PnPMA and PiPMA consists of three and two components below T_p, respectively, which contain a component that can be attributed to amide-amide hydrogen bonding. Part of the amide−water hydrogen bonds of PnPMA and PiPMA are broken and molar fractions of the amide-amide hydrogen bonds increase during the coil-to-globule transition. The remarkable hystereses of their phase transitions might be related to the formation of the polymer−polymer hydrogen bonds within the aggregated globules to a larger extent than PnPA and PiPA.

Detailed IR spectroscopic analyses on the changes in the hydration states of polymer chains upon the phase transitions of poly(*N*-alkylacrylamide)s and poly(*N*-alkylmethacrylamide)s in water have provided important information that is useful to explain the differences in their phase in molecular term. Further systematic study on the phase behavior transition phenomena of macromolecules in water are in progress in our laboratory.

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