Change in Solvation of Poly(*N*,*N*-diethylacrylamide) during Phase Transition in Aqueous Solutions As Observed by IR 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*-dimethylacrylamide) (PdEA) in water and methanol/water mixture were investigated by Fourier transform infrared (FTIR) spectroscopy. IR spectra of the solutions measured as a function of temperature exhibited critical changes upon the phase transition. The amide I band of PdEA consists of three components centered at 1638, 1619, and 1599 cm^{-1}, which can be assigned to free carbonyl groups and those connected to one and two water molecules through hydrogen bonds, respectively. The relative areas of the 1619 and 1599 cm^{-1} components decrease and that of the 1638 cm^{-1} component increases above the phase transition temperature (T_p), but the change is relatively small and most of the amide C═O groups remain hydrated even above T_p. The C−H stretching bands shift toward lower wavenumbers that are close to those measured in the neat solid state, indicating that the alkyl groups are almost fully dehydrated above T_p. In the methanol/water mixture, T_p is almost independent of methanol concentration up to ca. 20% and increases steeply above ca. 30%. The heat of transition (ΔH) decreased linearly with an increase of methanol concentration up to 30% and is nearly zero above 40%. The areas of the 1599 and 1638 cm^{-1} bands decrease with an increase in methanol concentration with a slight change in the 1619 cm^{-1} band. The result suggests that methanol replaces parts of the C═O···H−O−H hydrogen bonds to form a C═O···H−O−CH_3 hydrogen bond, and its bulky methyl group prevents the carbonyl group to form the second hydrogen bond that is responsible for the 1599 cm^{-1} band.

Introduction

It is well-known that aqueous solutions of some poly(*N*-alkylacrylamide)s and poly(*N*-alkylmethacrylamide)s exhibit a phase separation above their own lower critical solution temperatures (LCST). Poly(*N*-isopropylamide) (PiPA) has been extensively studied from both basic and technological points of view by using a variety of techniques such as turbidimetry,[1] calorimetry,[2,3] NMR,[4,5] fluorescence,[6,7] light scattering,[8,9] and neutron scattering.[10] Our recent study of PiPA has shown that IR spectroscopy is a suitable method to observe changes in the hydration states of individual chemical groups upon the phase transition.[11] Especially, analysis of the amide I band, which is mainly due to C═O stretching vibration, provides important information on hydrogen bonding of the C═O group. The amide I band of PiPA observed below the LCST consists of a single component (1625 cm^{-1}) due to the C═O groups that form a hydrogen bond with water. The second component (1650 cm^{-1}) due to the C═O···H−N hydrogen bonds appears at the LCST, and its molar fraction becomes 0.13 at the end of the transition. It is reasonable to expect that the macroscopic phase behavior of PiPA is related to the C═O···H−N hydrogen bonds. For example, a sharp temperature responsiveness (the phase transition is completed in a narrow temperature range) might be related to a cooperative formation of the C═O···H−N hydrogen bonds upon the phase transition. A retardation of the globule-to-coil transition in comparison with the coil-to-globule transition can be ascribed to the inter- and intrachain C═O···H−N hydrogen bonds. Hence, the presence of the amide proton in the poly(*N*-monoalkylacrylamide) as a hydrogen bond donor is an important determinant of its phase behavior. Because poly(*N*,*N*-dialkylacrylamide)s do not contain the amide protons, their segmental interactions may be weaker than those of poly(*N*-alkyl(meth)acrylamide)s. It is probable that the phase behavior of the former polymers is different from that of the latter. Therefore, a detailed study of the phase behavior, hydration, and inter- and intrachain interactions of poly(*N*,*N*-dialkylacrylamide)s is desirable. Several researchers have reported on the phase transition of poly(*N*,*N*-diethylacrylamide) (PdEA). Idziak et al.[12] and Lessard et al.[13] have observed the phase transition of PdEA by DSC and turbidimetry. Baltes et al.[14] prepared PdEA by radical, group transfer, and anionic polymerization to investigate the phase transition as a function of molecular size and tacticity. The LCST of PdEA synthesized by anionic polymerization is about 10 °C higher than those synthesized by radical and group transfer polymerization. Nakahama et al.[15] also prepared highly isotactic PdEA by anionic polymerization and found that the phase behavior of PdEA is dependent on tacticity. Spěváček et al.[16,17] applied ^1H NMR to observe changes in the dynamics of polymer segments during the transition. Itakura et al.[18] have studied the aggregation behavior of PdEA in dilute aqueous solution by using static and dynamic light scattering. However, changes in the hydration states of PdEA during the phase transition have not yet been studied. Therefore, in the present study we investigate hydrogen bonding of the amide groups of poly(*N*,*N*-diethylacrylamide)s by IR spectroscopy and compare its phase behavior with those of poly(*N*-alkyl(meth)acrylamide)s.

Experimental Section

Materials. *N*,*N*-Diethylacrylamide (dEA) was kindly donated by Kohjin (Tokyo, Japan) and purified by distillation before use. Poly(*N*,*N*-diethylacrylamide) (PdEA) was synthe-

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

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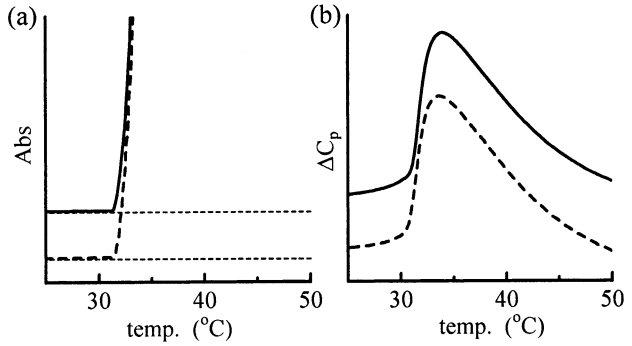


Figure 1. (a) Turbidity at 500 nm of 0.5 wt % PdEA measured at heating (solid line) and cooling (broken line) processes in H_2O. (b) DSC thermograms of 0.5 wt % PdEA measured at heating (solid line) and cooling (broken line) processes in H_2O.

sized with radical polymerization in methanol at 70 °C for 7 h using 2,2′-azobis(isobutyronitrile) as an initiator. After evaporation the polymers were precipitated from acetone−*n*-hexane. Polymers obtained were purified by dialysis, and they were lyophilized. Roughly estimated molecular weight of the polymer determined by gel permeation chromatography was 19 000. D_2O (Aldrich) and methanol-d_4 (Aldrich) was used to prepare sample solutions for IR measurements.

Measurements. Methods of turbidity, differential scanning calorimetry (DSC), and FTIR measurements have been described previously.[19] IR spectra were measured by using a Bio-Rad Excalibur FTS-3000 spectrometer at a resolution of 2 cm^{-1}. The IR difference spectrum obtained by subtracting IR spectrum at the starting temperature (T_0) from a spectrum measured at a temperature (T) is designated as ΔA_{T-T_0}. The difference in the values of ΔA_{T-T_0} at the positive and negative peaks of a selected vibration mode in a difference spectrum is defined as

$$\Delta\Delta A_{T-T_0}(\nu_1,\nu_2) = \Delta A_{T-T_0}(\nu_1) - \Delta A_{T-T_0}(\nu_2)$$

where ν_1 and ν_2 denote wavenumbers at the positive or negative peaks in the IR difference spectrum. DSC measurements were performed using a Micro Calorimetry System (MicroCal Inc.) at a scanning rate of 0.75 °C/min.

Results

Changes in IR Spectra of Aqueous Solutions of PdEA on the Phase Transition. Figure 1 shows the phase transition of aqueous solution of PdEA observed by turbidimetry and DSC. The phase transition temperature (T_p) that is defined as the onset temperature of turbidity change or the endothermic peak of the DSC thermogram is 33.4 °C. As observed in DSC curves, the transition temperature region of PdEA (>15 °C) is much wider than that of PiPA (ca. 1 °C). Thermal hysteresis was not observed; i.e., the thermogram and the turbidity change are the same during cooling and heating. This behavior is different from that of PiPA, where the transition temperature is lower during cooling than during heating.[11]

Figure 2 shows IR absorption spectra of PdEA measured in H_2O (top) and D_2O (bottom) around 25 °C. Frequencies of IR bands of PdEA measured in H_2O, D_2O, and chloroform as well as in the neat solid state are compiled in Table 1. Prominent IR bands of PdEA are C−H stretching (ν(C−H), 2800−3000 cm^{-1}), amide I (1615 cm^{-1}), C−N stretching (ν(C−N), 1486 cm^{-1}), and C−H deformation bands ((δ(C−H), 1350−1500 cm^{-1}). Because PdEA contains no dissociable protons, the positions of IR bands of PdEA measured in D_2O were essentially the same as those measured in H_2O. D_2O was mainly used instead of H_2O for IR measurements because the bending mode of D_2O moves to around 1200 cm^{-1} from 1640 cm^{-1} (H_2O) and does not overlap the amide I band of PdEA (1615 cm^{-1}).

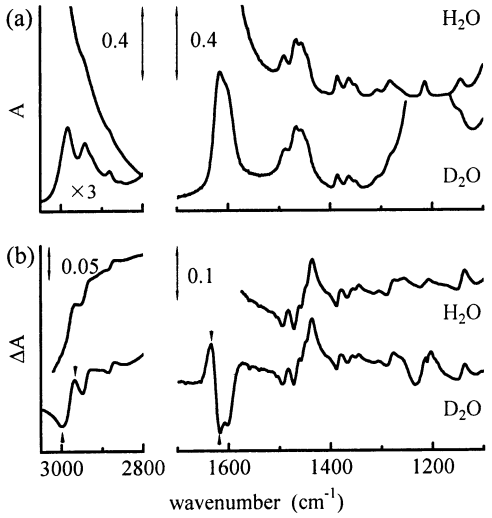


Figure 2. (a) IR absorbance spectrum of 10 wt % PdEA measured in H_2O (top) and D_2O (bottom) at 25 °C. (b) Temperature-induced difference IR spectra (ΔA_{39-25}) of PdEA measured in H_2O (top) and D_2O (bottom). The IR absorbance spectrum measured at 25 °C was subtracted from the IR absorbance spectrum measured at 39 °C. Short arrows indicate the negative and positive peaks that are used to calculate the values of $\Delta\Delta A$ (a).

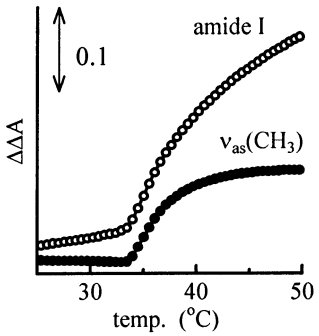


Figure 3. Values of $\Delta\Delta A$ for the amide I (○) and $\nu_{as}(CH_3)$ (●) modes of 10 wt % PdEA/D_2O are plotted against temperature.

Difference IR spectra that are obtained by subtracting the spectrum measured above T_p from the spectrum measured below T_p are shown in Figure 2b. The temperature-induced difference spectra of PdEA measured in H_2O (top) and D_2O (bottom) are quite similar, indicating high reproducibility and accuracy of the IR measurements. Most of the IR bands have a positive peak at a higher wavenumber side and a negative peak at a lower wavenumber side, indicating a red shift of the corresponding IR band upon the phase transition. There are one positive (1634 cm^{-1}) and two negative (1616 and 1602 cm^{-1}) peaks in the amide I region, indicating that the amide I band contains at least three components.

To follow the growth of the difference peaks in the course of the phase transition, the values of $\Delta\Delta A_{T-T_0}$ for the amide I mode and the antisymmetric C−H stretching vibration mode of methyl group ($\nu_{as}(CH_3)$) of PdEA are plotted against temperature in Figure 3. The onset temperature where each $\Delta\Delta A_{T-T_0}$ curve departs from a linear baseline (33.3 °C) is defined as T_p from IR measurement. The temperature is close to the values

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

H_2O solution	difference IR band in H_2O solution	D_2O solution	difference IR band in D_2O solution	neat	$CHCl_3$ solution	assignment
2984	2988(−), 2966(+)	2984	2994(−), 2965(+)	2972	2976	antisymmetric C−H stretching of $-CH_3$
2941	2947(−), 2930(+)	2940	2946(−), 2930(+)	2933	2934	antisymmetric C−H stretching of $-CH_2-$
2880	2884(−), 2870(+)	2880	2884(−), 2870(+)	2874	2874	symmetric C−H stretching of $-CH_3$
ov[a]	ov	1615	1634(+), 1616(−), 1602(−)	1635	1628	amide I
1490	1493(−), 1482(+)	1489	1493(−), 1482(+)	1482	1482	deformation of −CH
1466	1469(−), 1463(+)	1467	1470(−), 1463(+)	1463	1463	deformation of −CH
1455	1455(−), 1438(+)	1455	1455(−), 1438(+)	1449	1450	deformation of −CH
1385	1388(−), 1380(+)	1385	1388(−), 1380(+)	1382	1382	deformation of −CH
1362	136(−), 1356(+)	1363	1366(−), 1356(+)	1362	1363	deformation of −CH
1282	1286(−), 1278(+)	ov	1286(−), 1279(+)	1277	1277	
1215	1219(−), 1207(+)	ov	ov	1219	1216	
1144	1149(−), 1134(+)	1147	1150(−), 1136(+)	1136	1137	

[a] ov: overlap with solvent peak.

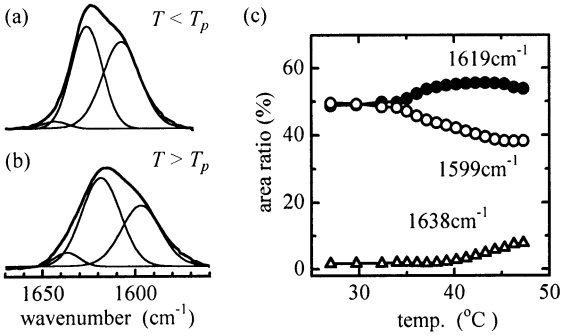


Figure 4. Baseline-subtracted amide I bands of 10 wt % PdEA measured at (a) 25 and (b) 39 °C (thick lines) in D_2O and Gaussian components (thin lines). (c) Temperature dependences of the relative areas of the three components (1599, 1619, and 1638 cm^{-1}) of the amide I band of PdEA.

of T_p determined by DSC and turbidimetry, indicating that the shifts of IR bands are related to the phase transition of the PdEA solution.

To investigate the hydrogen bonding of the amide C═O group, the amide I bands of PdEA measured both below and above the transition temperature region are shown in Figure 4. Judging from the intensity of O−H stretching IR band of water, H_2O as a contamination was so small that the O−H bending IR band did not influence the amide I band of PdEA. To determine the number and the positions of components of the amide I band, Fourier self-deconvolution of these spectra was carried out (data not shown). The result showed that the amide I band consists of three components centered at 1638, 1619, and 1599 cm^{-1} both below and above T_p. We analyzed the profiles of the amide I band by using a curve-fitting method. Results of the peak separation are shown by broken lines in Figure 3a,b, and relative areas of the three components are plotted against temperature in Figure 4c. The areas of the 1619 and 1599 cm^{-1} components decrease, and that of the 1638 cm^{-1} component increases with increasing temperature above T_p. To assign these three amide I components, the relationship between the amide I frequency and the hydrogen bond strength of amide C═O group will be considered. In general, the stronger the hydrogen bond involving the amide C═O group, the lower the electron density along the C═O bond and the lower the amide I frequency. Because PdEA does not have any amide hydrogen as a hydrogen bond donor, it cannot form C═O···H−N hydrogen bonds. Since the 1638 cm^{-1} component is close to the position of the amide I band of neat solid PdEA (1635 cm^{-1}), it can be assigned to the C═O groups that form no hydrogen bonds. The 1619 and 1599 cm^{-1} components can be assigned to the C═O groups that are bound to one and two water molecules through a hydrogen bond, respectively. The amide I band of poly(*N*-vinyl-2-pyrrolidone) has also been reported to consist of three components (free, 1680 cm^{-1}; singly hydrated, 1660 cm^{-1}; doubly hydrated, 1641.3 cm^{-1}).[20,21] The area of the amide I component due to the free C═O groups is relatively small even at the end of phase transition, indicating that a large part of the C═O groups are hydrated in a separated polymer-rich phase.

Changes in the hydration of the ethyl side groups and the main chain of PdEA can be observed in the IR spectra at the C−H stretching vibration region (2800−3050 cm^{-1}). Fourier self-deconvoluted spectra of PdEA in the region measured at 25 and 39 °C are shown in Figure 5a. Major peaks are due to the ethyl side chain and located at 2984, 2941, and 2881 cm^{-1} below T_p, which are assigned to the antisymmetric stretching of methyl ($\nu_{as}(CH_3)$) and methylene ($\nu_{as}(CH_2)$) groups and the symmetric stretching of methyl group ($\nu_s(CH_3)$), respectively. Shifts of these peaks in the course of the phase transition are shown in Figure 5b. Every peak undergoes a red shift upon the phase transition. The positions of these peaks at the end of the transition are close to those for a neat solid PdEA and PdEA dissolved in chloroform shown with solid circles in the figure. This result suggests that the ethyl groups are mostly dehydrated at the end of the phase transition and that they exist in an apolar environment. Many experimental[22] and theoretical[23] studies have shown that the ν(C−H) bands exhibit blue shifts upon interaction of alkyl groups with water. The interaction results in shortening and strengthening of the C−H bonds and a concomitant increase of the C−H stretch vibration frequency (a blue shift) compared to the noninteracting species.[24] On the other hand, the C−H stretching bands due to the main chain located at 2923 and 2905 cm^{-1} are assigned to the vibrations of the methylene and methine groups, respectively. The positions of these bands are almost insensitive to the phase transition. It is not clear whether these bands are essentially insensitive to environmental changes or the environment does not change upon the phase transition.

Effects of Polymer Concentration on T_p and IR Spectra of PdEA. To investigate the effect of concentration of PdEA on the hydration states of both alkyl group and amide group, IR measurements were carried out at different solution concentrations (5−90 wt %). The values of T_p as a function of PdEA concentration give a phase diagram of a PdEA/water mixture as shown

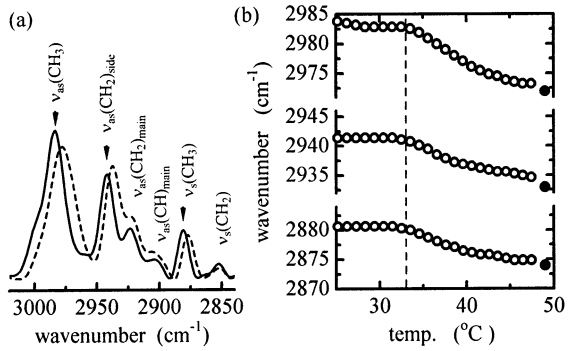


Figure 5. (a) Fourier self-deconvoluted C−H stretching IR absorption spectra of PdEA measured at 25 (solid line) and 39 °C (broken line) in D_2O. The half-width used for the calculation was 30 cm^{-1}. (b) The positions of three major ν(C−H) bands are plotted against temperature. Closed circles indicate the positions of each band observed in a cast film of PdEA.

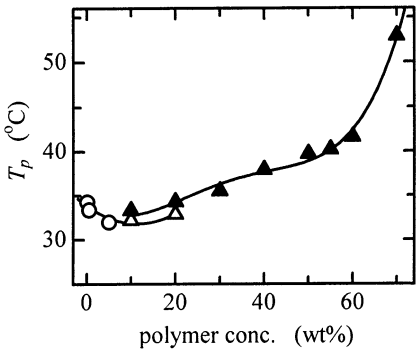


Figure 6. Phase transition temperatures (T_p) of PdEA measured by using turbidimetry (○) and IR spectroscopy (△, ▲) in H_2O (△, ○) and D_2O (▲) are plotted against polymer concentration.

in Figure 6. The values of T_p determined by turbidity (in H_2O) and IR measurements (in H_2O and D_2O) are designated by circles and triangles, respectively. The transition temperature in D_2O is slightly higher than in H_2O at the same polymer concentration probably because hydrogen bonds of D_2O are slightly stronger than those of H_2O. The phase diagram has a lower critical solution temperature (LCST) of 32 °C and a critical concentration of 5−10 wt %.

Profiles of the amide I bands of PdEA measured below and above T_p at different concentrations are shown in a superimposed form in Figure 7a,b. The relative area of the 1619 and 1599 cm^{-1} components decreased and that of the 1638 cm^{-1} increased with an increase in polymer concentration below T_p, whereas the profiles of the amide I band is almost independent of the concentration above T_p. The relative areas of the three components are plotted against polymer concentration in Figure 7c. Above 70% the intensity of the amide I band is so strong that we cannot measure it without spectral saturation. The molar ratio of water to the monomer unit of PdEA (*W*/*M*) is also shown on the top of these figures. Because the amount of water is not sufficient to hydrate all amide groups below some critical *W*/*M* value, they are partially dehydrated, and the area of the 1599 cm^{-1} component, which is assigned to the C═O groups connected to two water molecules, gradually decreases with an increase in polymer concentration. The change in the areas of the amide I components below T_p is similar to that observed during

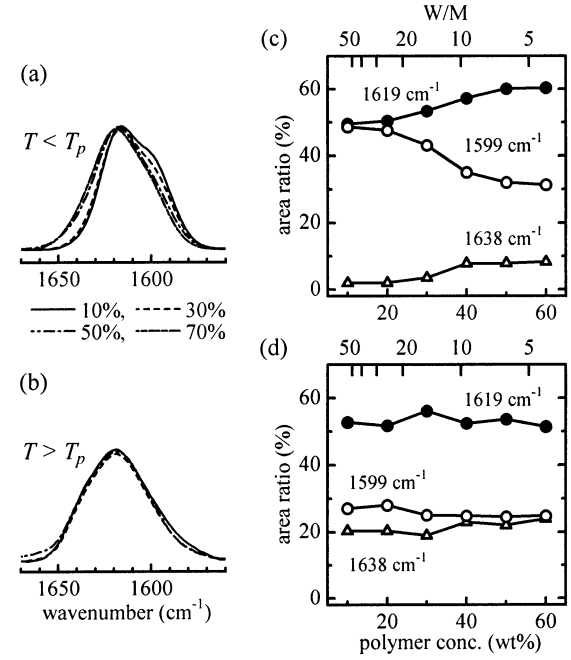


Figure 7. Profiles of amide I band of PdEA measured at different polymer concentrations (a) below (10, 30, 50, and 70 wt %) and (b) above T_p (10, 30, and 50 wt %) are shown in a superimposed form. The relative areas of the three components (1599, 1619, and 1638 cm^{-1}) of the amide I band of PdEA (c) below and (d) above T_p are plotted against polymer concentration.

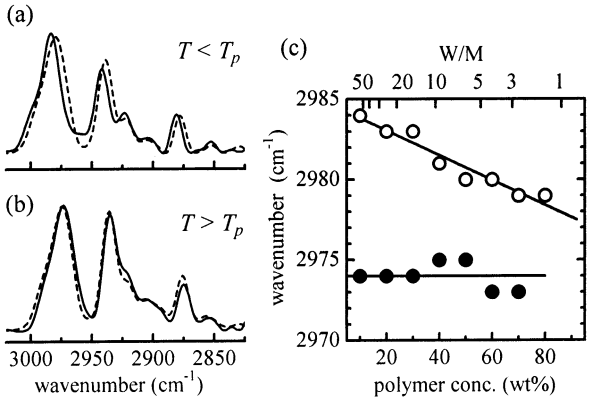


Figure 8. Profiles of the ν(C−H) bands of PdEA measured at different polymer concentration (a) below (10 and 50 wt %) and (b) above T_p (10 and 50 wt %) are shown in a superimposed form. (c) The positions of the $\nu_{as}(CH_3)$ bands of PdEA measured below (○) and above (●) T_p are plotted against polymer concentration.

the phase transition, indicating that polymer concentration in polymer-rich phase increases with temperature during the phase transition.

Profiles of the IR spectra in the ν(C−H) region measured below and above T_p at different polymer concentrations are shown in a superimposed form, and the position of the $\nu_{as}(CH_3)$ band is plotted against polymer concentration in Figure 8. Closed and open circles in the figure show the peak positions measured below and above T_p, respectively. The wavenumber of the $\nu_{as}(CH_3)$ band decreases linearly with an increase in the concentration, indicating a gradual dehydration of the methyl groups, whereas the position of the $\nu_{as}(CH_3)$ band was almost independent of the polymer concentration and centered around 2974 cm^{-1} above T_p. This suggests that microenvironment around the methyl

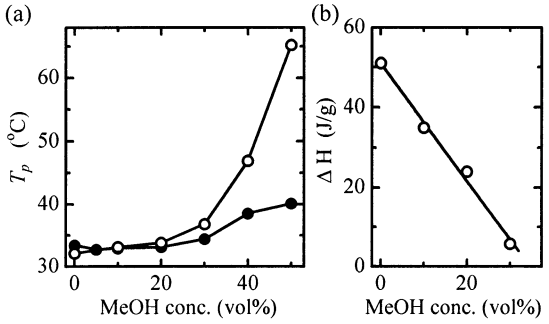


Figure 9. (a) Phase transition temperatures (T_p) of PdEA measured in methanol/water mixture by using turbidimetry (0.5 wt % in methanol/H_2O, ○) and IR spectroscopy (20 wt %, in methanol-d_4/D_2O, ●) are plotted against methanol concentration (vol %). (b) The heat of phase transition (ΔH) of 0.5 wt % PdEA measured in methanol/H_2O mixture is plotted against methanol concentration (vol %).

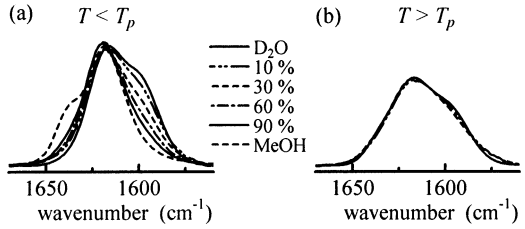


Figure 10. Baseline-subtracted amide I band of 10 wt % PdEA measured above and below T_p in methanol-d_4/D_2O at different methanol concentration (0, 10, 30, 60, 90, and 100%).

group is identical. This is consistent with the finding that the profiles of the amide I band measured above T_p do not depend on the polymer concentration. These results are reasonable if the composition of the condensed phase is independent of the total polymer concentration. In that case, the fraction of the condensed phase in the total volume depends on the total polymer concentration.

Effects of Methanol on T_p and IR Spectra of PdEA. Next, effects of methanol on T_p and the profiles of the difference IR spectra of PdEA were investigated. The values of T_p determined by IR (20 wt %) and turbidity (0.5 wt %) measurements are plotted against methanol concentration in Figure 9a. T_p is almost independent of methanol concentration up to ca. 20% and increases steeply above ca. 30%. This behavior is similar to that of poly(*N*-vinylcaprolactam) and is different from that of PiPA, whose T_p in methanol/water mixture passes through a minimum around 55%.[25,26] The heat of transition (ΔH) of PdEA decreases linearly with an increase of methanol concentration up to 30% although T_p is independent of it (Figure 8c). The endothermic peak is so small that we can determine neither T_p nor ΔH above 40%.

The amide I band of PdEA measured both below and above T_p at different methanol concentration is shown in Figure 10. Addition of methanol alters the amide I band of PdEA, because methanol replaces water and forms a hydrogen bond with the C═O group of PdEA. The area of the 1619 and 1599 cm^{-1} components decrease and that of the 1638 cm^{-1} component increases at $T < T_p$ with an increase of methanol concentration, whereas the profiles of the amide I band do not change at $T < T_p$. The position of the main component of the amide I band of PdEA measured in methanol is 1618 cm^{-1} and is close to that measured in water, suggesting that the strength of the hydrogen bond between a

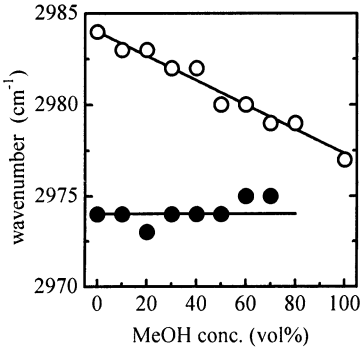


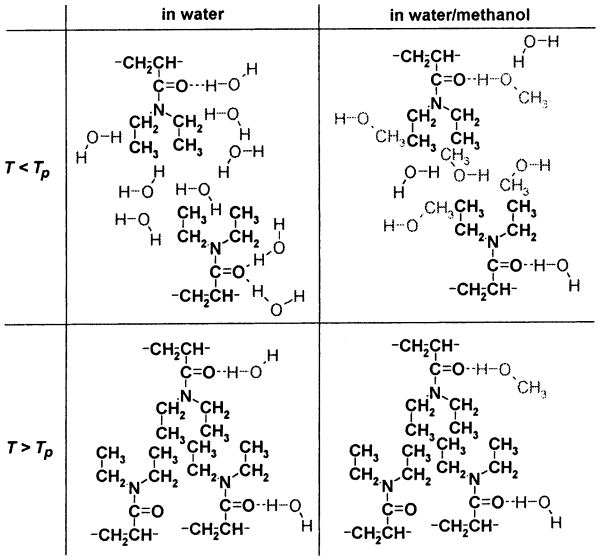
Figure 11. Positions of the $\nu_{as}(CH_3)$ bands of PdEA (10 wt %) measured below (○) and above (○) T_p in methanol-d_4/D_2O mixture are plotted against methanol concentration.

hydroxyl group of methanol and the C═O group of PdEA is close to that of the C═O···H−O−H hydrogen bond. However, the 1599 cm^{-1} component is not observed in methanol, indicating that the C═O group cannot form the double hydrogen bond with two methanol molecules probably because of the bulkiness of the methyl group. In addition, a larger area of the 1638 cm^{-1} component in methanol than in water suggests that the ratio of free C═O group is higher in methanol than in water. The 1599, 1619, and 1638 cm^{-1} components of amide I band of PdEA in methanol/water mixtures can be assigned to the C═O groups that form two hydrogen bonds with two water molecules, one hydrogen bond with either methanol or water, and no hydrogen bonds, respectively. The assignments are further supported by the facts that the 1619 cm^{-1} component is the main component in ethanol and 2-propanol and that the 1638 cm^{-1} component is the main component in tetrahydrofuran and dioxane, which do not contain any hydrogen bond donors.

The dependence of the position of $\nu_{as}(CH_3)$ band of PdEA on the methanol concentration is also similar to that on polymer concentration. The band shifts toward a lower wavenumber with increasing methanol concentration at $T < T_p$, and it is independent of methanol concentration at $T > T_p$ (Figure 11).

The amide I and $\nu_{as}(CH_3)$ bands of PdEA show that methanol interacts directly with both amide and alkyl groups. Replacement of the C═O···H−O−H hydrogen bonds by methanol may slightly destabilize the polymer solution and cause a decrease in T_p, whereas the interaction between the alkyl groups of PdEA and the methyl group of methanol stabilizes the polymer solution and raises T_p by preventing an unfavorable decrease in entropy due to a stabilization of the hydrogen-bonding water structure around the hydrophobic alkyl groups. A balance between two opposite effects may determine T_p of PdEA in methanol/water mixtures. In the case of PiPA, because the N−H···OH_2 hydrogen bonds are also replaced by methanol, the effects that reduce T_p are stronger than those that raise T_p, so that T_p decreases with an increase in methanol concentration up to 55%. On the other hand, the heat of transition (ΔH) mainly reflects the breaking of hydrogen bonds between water molecules that surround the alkyl groups, and therefore, the replacement of water in the first hydration shell by methanol reduces it. Thus, the effects of methanol on the macroscopic phase behavior can be explained by the microscopic solvation of the polymer chain.

Scheme 1



Conclusions

The change in solvation of PdEA during the phase transition in water and water/methanol mixture is summarized in Scheme 1. In water at $T < T_p$, most of the C═O groups of PdEA are associated with one or two water molecules through hydrogen bonds, which are represented by the amide I band at 1619 and 1599 cm^{-1}, respectively. The ethyl groups of PdEA are also hydrated, and the ν(C−H) bands are observed at relatively higher wavenumbers. Upon phase transition, most of the ethyl groups are dehydrated and associate through hydrophobic interaction, whereas the C═O groups are only partially dehydrated and most of them form hydrogen bonds with water even at $T > T_p$. The heat of transition (ΔH) reflects mainly the breaking of hydrogen bonds between the molecules of the structured water surrounding the ethyl groups.

In water/methanol mixture at $T < T_p$, a large part of the C═O groups are bound to water or methanol through a hydrogen bond, both of which provide the amide I band at 1619 cm^{-1}. The ethyl groups are also solvated by water or methanol at $T < T_p$. The water is stripped from the ethyl groups which then associate through hydrophobic interaction. Because the structure of water is disturbed by methanol, ΔH decreases with an increase of methanol concentration and is nearly zero above ca. 40%. Though some part of water and methanol are removed upon the phase transition, most of the C═O groups form hydrogen bonds with water or methanol even at $T > T_p$.

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