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Hydration and Phase Behavior of Poly(*N*-vinylcaprolactam) and Poly(*N*-vinylpyrrolidone) in Water

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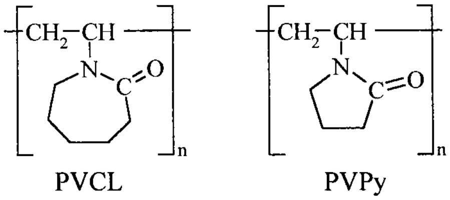
ABSTRACT: Phase transitions of poly(*N*-vinylcaprolactam) (PVCL) and poly(*N*-vinylpyrrolidone) (PVPy) in H_2O and D_2O were investigated by turbidimetry, differential scanning calorimetry (DSC), and Fourier transform infrared (FTIR) spectroscopy. The phase diagram of PVCL solution is binodal with a lower critical solution temperature (LCST) of 32.5 °C and a critical concentration of about 5 wt %. PVPy also undergoes a phase separation around 30 °C in aqueous 1.5 M KF solution. The IR spectra of PVCL and PVPy in water critically change at the phase transition temperature (T_p). Above T_p the C−H stretching and the C−H bending bands shift to lower wavenumbers. The amide I band of PVCL is divided into four components, and the intensities of the 1565, 1588, and 1625 cm^{-1} components increase and that of the 1610 cm^{-1} component decreases while the phase transition proceeds. Addition of KCl and KF lower T_p of PVCL, whereas KI and KBr raise T_p. Addition of methanol gradually raises T_p up to ca. 40 vol % and steeply raises T_p at > 40 vol %. Although these salts do not alter the profiles of IR spectra of PVCL, methanol induces a change in the amide I band.

Introduction

Recently, three different types of LCST behavior of aqueous polymer solutions have been discussed.[1−4] Type I represents the Flory−Huggins miscibility behavior. The position of the critical point shifts toward lower polymer concentration with increasing length of the polymer chain. In the limit of infinite chain length, the critical concentration is zero at the θ-temperature. In type II systems, the critical point is almost independent of the polymer chain length. A typical example of such a polymer is poly(*N*-isopropylacrylamide) (PiPA).[5−10] Type III is characterized by one zero limiting critical concentration and two off-zero limiting critical concentrations.[4] Poly(vinyl methyl ether) (PVME) belongs to this type.[4] Gels of polymers belonging to type I show continuous deswelling upon heating; in contrast, gels belonging to type II and III exhibit discontinuous volume phase transition. These behaviors are highly related to the differences in the interaction between the polymer chain and water, and they can be modeled by the introduction of a polymer−solvent interaction function in the expression of the Flory−Huggins theory.[1] The polymer−solvent interaction can be observed by using IR spectroscopy as we reported in previous papers, which dealt with the phase transitions of PiPA,[11] poly(*N*-alkylacrylamide)s,[12] poly(*N*-alkylmethacrylamide)s,[13] and PVME[14] in water. IR spectroscopy has provided detailed information on the hydration states of individual groups in these polymers both below and above their LCST.

Poly(*N*-vinylpyrrolidone) (PVPy) and poly(*N*-vinylcaprolactam) (PVCL) contain five- and seven-membered lactam rings, respectively. Aqueous solutions of PVCL exhibit a phase separation, and PVCL hydrogels exhibit a continuous swelling−deswelling near the room temperature. PVCL has attracted much attention due to its thermosensitivity and its biocompatibility. Because hydrolysis of the amide group of PVCL will not produce small amide compounds, PVCL is suitable for biomedical applications. Up to now, several studies have been reported on the phase behavior of PVCL in water.[15−22] Kirsh et al. have investigated the relationship between the complexation with small molecules such as 1-anilinonaphthalene-8-sulfonate and the phase transition behavior of PVCL in dilute solutions.[17] Tager et al. reported phase diagrams of PVCL with different molecular weights and thermodynamic parameters for the mixing of water and the polymer.[18] Meessen et al.[1] have carried out cloud point measurements and theoretical calculations. They concluded that the phase behavior of the system PVCL/H_2O corresponds to Flory−Huggins miscibility behavior (type I).[1] Mikheeva et al. have carried out a microcalorimetric study of PVCL hydrogels and found that the gel system undergoes two successive cooperative transitions.[19] They assigned the low-temperature transition to the microsegregation in the gel and the high-temperature transition to the gel volume collapse. Wu et al. have measured static and dynamic light scattering of PVCL and PVCL gels.[20−22] Since PVPy is less hydrophobic than PVCL, it exhibits a phase separation phenomenon only in solutions containing a considerable amount of salt. Therefore, its phase behavior has scarcely been studied.



In the present study, we have carried out an IR spectroscopic study of the phase transitions of PVCL and PVPy in water. Changes in hydrogen bonding of the amide groups and the hydration states of the alkyl groups during their phase transitions were observed. Effects of the addition of salts and methanol on the phase transition temperature and the IR spectra were also investigated in order to reveal the interaction between these additives and the polymer chain.

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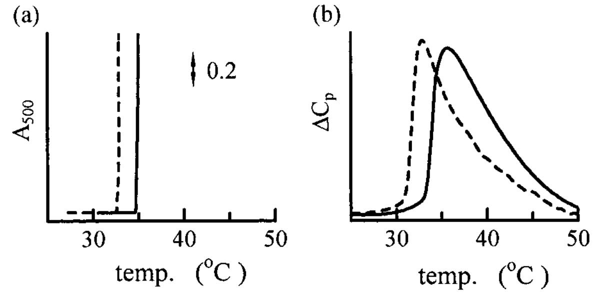

Figure 1. (a) Temperature-induced turbidity changes for the heating processes of PVCL-M solution (solid line) and PVCL-H solution (broken line) observed at 500 nm. (b) DSC thermograms of PVCL-M solution (solid line) and PVCL-H solution (broken line) measured in the heating processes.

Experimental Section

Materials. *N*-Vinylcaprolactam was purchased from Aldrich. PVCL with weight-average molecular weights (M_w) of 13 000 (PVCL-M) and 150 000 (PVCL-H) were synthesized via radical polymerization in methanol at 70 °C for 7 h using 2,2′-azobis(isobutyronitrile) as an initiator. After evaporation the polymer was precipitated from acetone−*n*-hexane, purified by dialysis (seamless cellulose tube), and lyophilized. The molecular weights of the polymers were determined by gel permeation chromatography [Toso HLC-803D; column, Toso G3000PW (30 cm) + G5000PWXL (30 cm); mobile phase, water (1.0 mL min^{-1}); poly(ethylene glycol)s used as standard samples]. PVCL is dissolved in deionized and distilled water, D_2O (99.9%, Aldrich), or a D_2O/methanol-d_4 (Aldrich) mixture, and the solutions were incubated for several hours below T_p to equilibrate before measurement. PVPy (M_w = 50 000) was purchased from Wako Pure Chemicals and was used without further purification.

Measurements. Details of the method of IR, DSC, and turbidity measurements were described elsewhere.[12] For IR measurement a sample solution was placed between two CaF_2 windows at a typical path length of approximately 10 μm. The background spectrum for one cycle of the measurement was obtained with a sample solution in the IR cell equilibrated at starting temperature. IR spectra were continuously collected at a resolution of 2 cm^{-1}. An IR difference spectrum that was obtained by subtracting the IR absorption spectrum measured at a lower temperature (T_0) from that measured at a higher 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 denoted by $\Delta\Delta A_{T-T_0}$.

Results and Discussion

Phase Transitions of PVCL in Water. First, we investigated general features of the phase behavior of PVCL by means of DSC and turbidimetry. Figure 1 shows turbidity-vs-temperature curves and DSC thermograms of 0.5 wt % PVCL-M and PVCL-H in H_2O. The phase transition temperatures (T_p) determined from onsets of the turbidity-vs-temperature curves were 34.6 and 33.3 °C for PVCL-M and PVCL-H, respectively. T_p decreased with increasing molecular weight as expected by the Flory−Huggins theory. The value of T_p of PVCL-M is comparable to the value that has been reported in a literature (33.5 °C) for PVCL with molecular weight of 11 700.[18] The onset temperature and the temperature at a maximum of the endothermic peak in the DSC thermogram of PVCL-M were 33.0 and 35.8 °C, respectively. Each DSC peak of PVCL exhibits a sharp increase followed by a gradual decrease toward an end point. The DSC peak of PVCL is broader than that of PiPA and is comparable to that of poly(*N*,*N*-diethylacrylamide) (PdEA), whose transition temperatures are close to that of PVCL. It has been shown that the width of a DSC peak for a phase separation of a polymer solution depends on the shape of the coexistence curve and polymer concetration.[3,23] A polymer whose demixing temperature exhibits a more significant concentration dependence has a broader DSC peak.

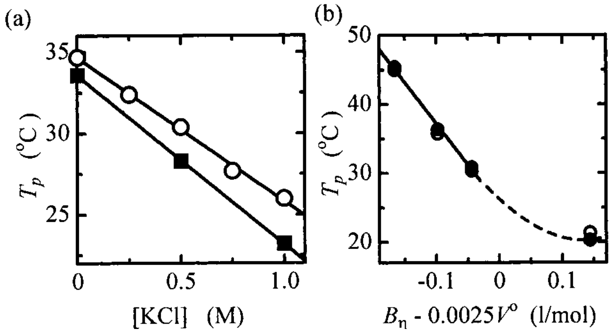

Figure 2. (a) KCl concentration dependence of the phase transition temperatures (T_p) of PVCL-M solutions determined by turbidimetry (○: 0.5 wt % in H_2O) and IR spectroscopy (■: 20 wt % in D_2O). (b) Phase transition temperatures (T_p) of PVCL-M solutions containing a salt (0.5 mol/L solvent) are plotted against values of (B_η − 0.0025V^0) of the anions (F^-, Cl^-, Br^-, I^-) resulting from the salts. ○, sodium salts; ●, potassium salts.

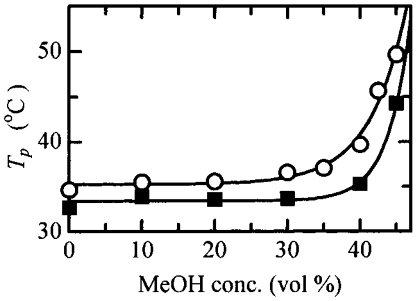

Figure 3. (a) Methanol concentration dependence of the phase transition temperature (T_p) of PVCL-M determined by turbidimetry (○, 0.5 wt % in methanol/H_2O) and IR spectroscopy (■, 20 wt % in methanol-d_4/D_2O).

The values of T_p of PVCL decreased linearly with increasing concentration of KCl as shown in Figure 2a. The values of T_p of PVCL solutions containing potassium halides or sodium halides (0.5 M) are plotted against B_η − 0.0025V^0 of anions resulting from the salts in Figure 2b, which represent the strength of interaction between the ions and water.[24] B_η and V^0 are the viscosity B coefficient and partial molal volume of the anions, respectively.[25,26] I^- and Br^- raise T_p of PVCL, whereas Cl^- and F^- lower T_p. Na^+ and K^+ has almost the same effect on T_p of PVCL. It is noteworthy that KBr and NaBr raise T_p of PVCL, because those salts are known to lower T_p of PiPA, poly(*N*-*n*-propylacrylamide), poly(vinyl methyl ether), and so forth.[11,12,14] On the other hand, addition of methanol gradually raises T_p up to ca. 40 vol %, and above the concentration T_p increases steeply (Figure 3). Two different responses of the phase transition temperatures of polymer solutions upon the addition of methanol have been reported. That is, T_p of PVME[27] and PdEA increases monotonically with increasing methanol concentration in a similar way as PVCL. In contrast, the transition temperature of poly(*N*-isopropylacrylamide) in methanol/water mixture passes through a minimum around 55 vol % methanol.[28] Differences in the interactions between these polymers and methanol are suggested.

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

H_2O soln		D_2O soln				
abs	difference	abs	difference	neat	$CHCl_3$ soln	assignment
2944	2950(−), 2910(+)	2940	2947(−), 2908(+)	2928	2935	C−H stretching
2864	2867(−), 2846(+)	2863	2867(−), 2845(+)	2855	2858	C−H stretching
ov[a]	ov	1610	1632(+), 1611(−), 1574(+)	1621	1626	amide I
1487	1490(−), 1478(+)	1486	1490(−), 1478(+)	1481	1480	C−N stretching
1461	1464(−), 1457(+)	1462	1465(−), 1457(+)	1456	1458	deformation of $-CH_2$
1448	1451(−), 1441(+)	1449	1451(−), 1441(+)	1443	1445	
1430	1433(−), 1422(+)	1430	1432(−), 1423(+)	1425	1425	(twisting, rocking,
1266	1268(−), 1260(+)	ov	ov	1262	1263	
1201	1205(−), 1194(+)	ov	ov	1196	1199	scissoring, waging)
1154	1157(−), 1149(+)	ov	ov	1152	1152	

[a] ov: overlap with absorption by solvents.

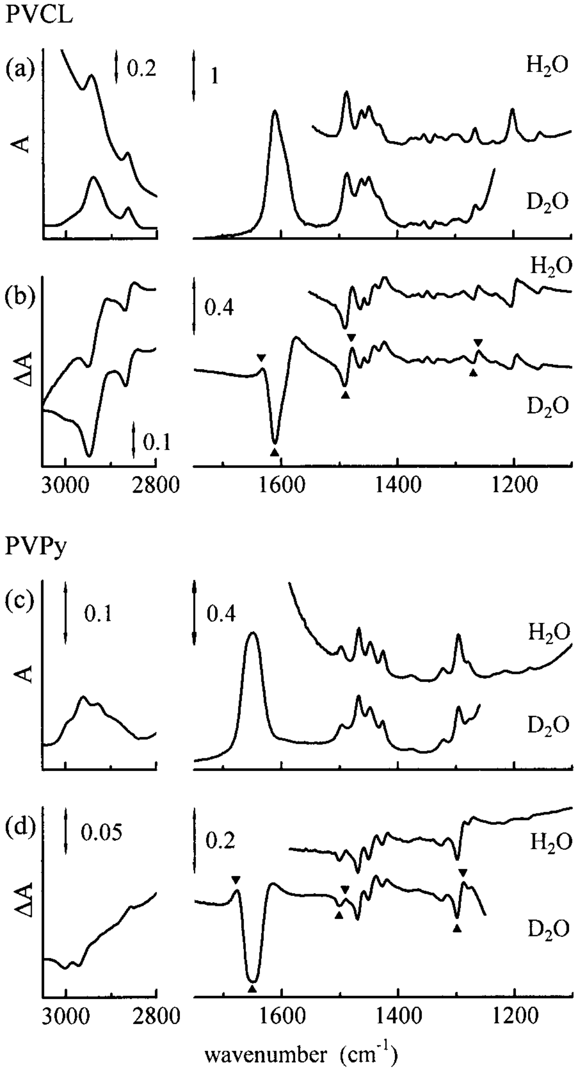

Figure 4. (a) IR absorption spectra of 20 wt % PVCL-M measured at 26.0 °C in H_2O (top) and in D_2O (bottom). (b) IR difference spectra ($\Delta A_{41.2-26.0}$) of PVCL-M measured in H_2O (top) and in D_2O (bottom). (c) IR absorption spectra of PVPy measured at 20.0 °C in 1.5 M KF/H_2O (top) and in 1.5 M KF/D_2O (bottom). (d) IR difference spectra ($\Delta A_{44.9-20.0}$) of 20 wt % PVPy in 1.5 M KF/H_2O (top) and in 1.5 M KF/D_2O (bottom). Triangles in (b) and (d) indicate peaks that are used to calculate the values of $\Delta\Delta A_{T-T_0}$ shown in Figure 5.

IR Spectra of PVCL and PVPy in Water. Figure 4a shows IR absorption spectra of PVCL measured in H_2O and D_2O around 26 °C. The IR frequencies and assignments of observed IR bands are compiled in Table 1. Prominent IR bands of PVCL are C−H stretching bands (ν(C−H), 2800−3000 cm^{-1}), amide I band (1610 cm^{-1}), C−N stretching (ν(C−N), 1486 cm^{-1}), and C−H deformation bands ((δ(C−H), 1350−1500 cm^{-1}). Because PVCL contains no dissociable protons, the positions of IR bands of PVCL measured in D_2O were essentially identical with those measured in H_2O. Only IR bands due to solvent water (O−H stretching ca. 3400 cm^{-1}, O−H bending ca. 1640 cm^{-1}, O−D stretching ca. 2800 cm^{-1}, O−D bending ca. 1200 cm^{-1}) are shifted. D_2O was mainly used instead of H_2O in order to prevent the bending mode of water (1640 cm^{-1}) from overlapping the amide I band of PVCL (1610 cm^{-1}).

Changes in positions and intensities of IR bands upon the phase transition can be visually presented by an IR difference spectrum. An IR difference spectrum can enhance small spectral changes in structurally altered parts.[29−31] The IR difference spectra (ΔA_{41-26}) of PVCL obtained by subtraction of the IR absorption spectra measured below T_p (26 °C) from those measured above T_p (41 °C) are shown in Figure 4b. The difference spectra of PVCL measured in H_2O and D_2O were quite similar, indicating high reproducibility and accuracy of the IR measurements. Each difference spectrum represents difference in IR absorption by a single sample solution in two different states. A negative peak associates with IR absorption by the polymer in the one-phase state and a positive peak represents absorption in the two-phase state. Appearance of both positive and negative peaks for one vibration mode of PVCL indicates a shift of the IR band induced by changes in hydration and/or conformation of corresponding chemical group upon the phase transition. For example, a negative peak at 2867 cm^{-1} and a positive peak at 2846 cm^{-1} are due to a red shift of the antisymmetric C−H stretching band of the methylene group upon the transition. Most of the bands showed red shifts upon the phase transition with the exception of the amide I band, which have positive peaks at both sides of the negative peak observed at 1611 cm^{-1} (see below). The wavenumbers of IR bands due to ν(C−H) and δ(C−H) modes are higher in water than in both neat solid state and in chloroform, whereas the wavenumber of the amide I band is lower in water.

Although PVPy dissolved in pure water does not exhibit phase transition, it does in the presence of 1.5 M KF at around 30 °C. The IR absorption and difference spectra of PVPy in 1.5 M KF/D_2O are shown in Figure 4c,d, and IR frequencies and assignments are compiled in Table 2. The wavenumber of the amide I band of PVPy is 1650 cm^{-1} and is higher than that of PVCL by 40 cm^{-1}. Directions of peak shits of PVPy during the phase transition are the same as those of corresponding peaks of PVCL.

The phase transition can be followed by measuring growth in the intensities of positive and negative peaks

Table 2. Observed IR Frequencies (in cm^{-1}) and Assignments of PVPy

H_2O soln		D_2O soln				
abs	difference	abs	difference	neat	$CHCl_3$ soln	assignment
–^{a}	–	2996	3002(–), 2984(+)	2984	2984^c	C–H stretching
–	–	2964	2970(–), 2948(+)	2956	2957	C–H stretching
–	–	2922	–	2922	2924	C–H stretching
ov^b	ov	1649	1676(+), 1650(–), 1615(+)	1674	1673	amide I
1498	1500(–), 1490(+)	1497	1500(–), 1489(+)	1494	1494	C–N stretching
1467	1469(–), 1458(+)	1467	1469(–), 1459(+)	1461	1461	CH_2 scissoring
1449	1450(–), 1437(+)	1448	1450(–), 1438(+)	1437	1437	CH_2 scissoring
1425	1426(–), 1419(+)	1426	1426(–), 1419(+)	1423	1423	CH_2 scissoring
1322	1325(–), 1314(+)	1322	1325(–), 1315(+)	1318	1319	CH_2 wagging
1295	1298(–), 1287(+)	1296	1298(–), 1287(+)	1290	1289	CH_2 wagging

^{a} –: unclear. ^{b} ov: overlap with absorption by solvents. ^{c} In $CDCl_3$.

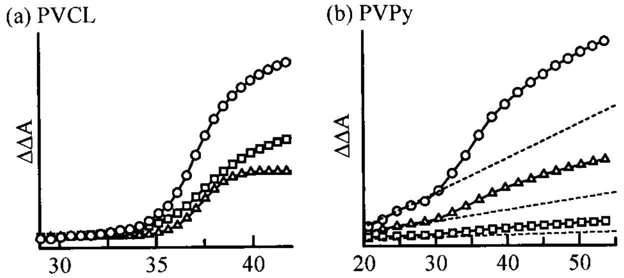

Figure 5. Values of $\Delta\Delta A_{T-T_0}$ of selected vibration modes of (a) PVCL-M (20 wt %) in D_2O and (b) PVPy (20 wt %) in 1.5 M KF/D_2O are plotted against temperature. ○, $\Delta\Delta A_{T-T_0}$ for the amide I mode; □, $\Delta\Delta A_{T-T_0}$ for the ν(C–N) mode; △, $\Delta\Delta A_{T-T_0}$ for the δ(C–H) mode.

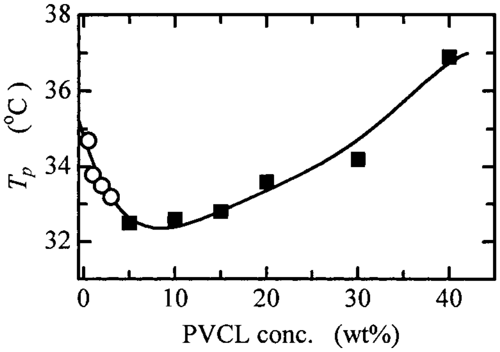

Figure 6. Phase transition temperatures (T_p) of PVCL-M in water are plotted against polymer concentration (wt %). Open circles and solid squares represent the values determined by turbidimetry and IR measurements, respectively.

observed in the IR difference spectra. Values of $\Delta\Delta A_{T-T_0}$ for the amide I, ν(C–N), and δ(C–H) modes of PVCL and PVPy are plotted against temperature in Figure 5. By using $\Delta\Delta A_{T-T_0}$ instead of ΔA_{T-T_0}, errors caused by baseline drifts can be canceled. Onset temperatures for the three $\Delta\Delta A_{T-T_0}$ curves for PVCL and PVPy, which are defined as the phase transition temperatures (T_p) from IR measurements, are ca. 37 and 30 °C, respectively. The values of T_p as a function of PVCL concentration give a phase diagram of PVCL/water mixture as shown in Figure 6. The values of T_p determined by turbidity and IR measurements are plotted with open circles and filled squares, respectively. The phase diagram is binodal with a lower critical solution temperature (LCST) of 32.5 °C and critical concentration about 5 wt %.

We analyzed the amide I band of PVCL measured in D_2O by using a curve-fitting method. To determine the number and the positions of the amide I components, we performed Fourier self-deconvolution of the spectra, which enhance the positions of individual components.

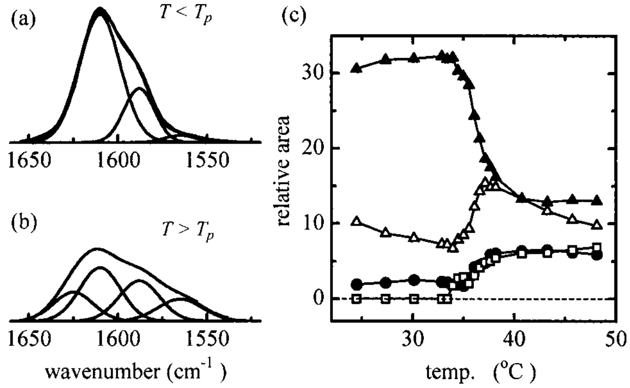

Figure 7. (a) Amide I band of PVCL-M at 26.0 °C (solid line) and Gaussian components (center: 1565 cm^{-1}; width at half-height (W_h): 21 cm^{-1}, center: 1588 cm^{-1}; W_h: 20 cm^{-1}, center: 1610 cm^{-1}; W_h: 27 cm^{-1}). (b) Amide I band at 41.2 °C (solid line) and four Gaussian components (center: 1565 cm^{-1}; W_h: 30 cm^{-1}, center: 1588 cm^{-1}; W_h: 27 cm^{-1}, center: 1610 cm^{-1}; W_h: 27 cm^{-1}, center: 1625 cm^{-1}; W_h: 24 cm^{-1}). (c) Integrated areas of the amide I components of PVCL-M are plotted against temperature. ●, 1565; △, 1588; ▲, 1610; □, 1625 cm^{-1}.

The amide I band consists of three Gaussian components centered at 1565, 1588, and 1610 cm^{-1} below T_p (Figure 7a) and four components (1565, 1588, 1610, and 1625 cm^{-1}) above T_p (Figure 7b). Relative areas of these four components of the amide I band of PVCL are plotted against temperature in Figure 7c. The areas of the 1625, 1588, and 1565 cm^{-1} components increase with increasing temperature above T_p, whereas the 1610 cm^{-1} band, which is dominant below T_p, becomes weaker with increasing temperature. In general, the amide I frequency correlates with the hydrogen bond strength and electron density on the C=O bond. 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. The amide I band of PVCL contains larger number of components than poly(*N*-monoalkyl acrylamide)s such as PiPA and PnPA, whose amide I band consists of one and two components below and above T_p, respectively.[11,12] There are several possible reasons for the multiple components of the amide I band of PVCL. The amide I vibration mode of a lactam as a cyclic cis-amide group is less localized to the C=O stretching vibration than the amide I mode of a trans-amide group and contains a considerable contribution from the C–N stretching vibration.[32] Thus, hydrogen bonding of lone pair electrons on both of the nitrogen and oxygen atom of the lactam affects the frequency of the amide I band. Indeed, formation of hydrogen bond between the nitrogen of

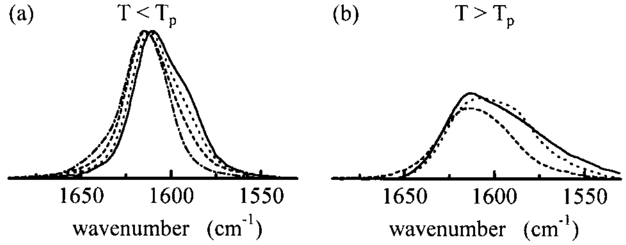

Figure 8. Amide I band of PVCL-M in D_2O/methanol-d_4 mixtures measured (a) below T_p and (b) above T_p. Methanol-d_4: 0 vol % (—), 20 vol % (• • •), 45 vol % (- - -), and 100 vol % (- • -).

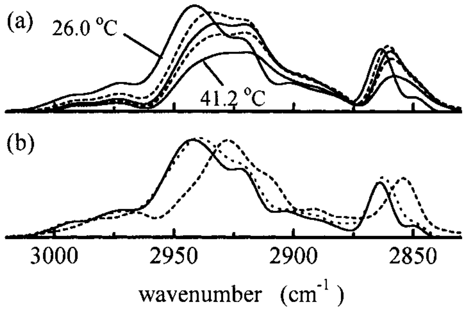

Figure 9. (a) Fourier self-deconvoluted ν(C−H) band of 20 wt % PVCL measured at 26.0 (solid line), 36.1 (broken line), 37.0 (solid), 38.4 (broken), and 41.2 °C (solid) in D_2O. (b) Fourier self-deconvoluted ν(C−H) band of 5 wt % (solid line) and 50 wt % (dotted line) of PVCL in D_2O and neat solid PVCL (broken line) measured at 30 °C.

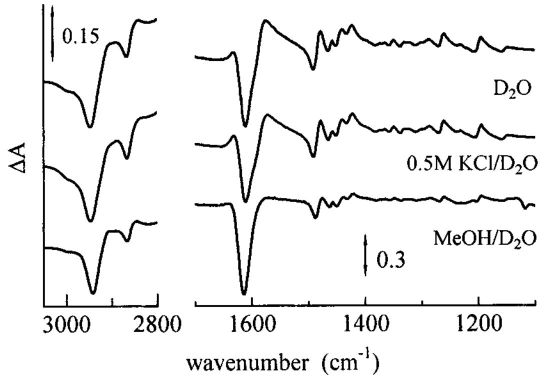

Figure 10. IR difference spectra (ΔA_{T-T_0}) of PVCL-M in pure D_2O (top, T_p = 33.7 °C), 0.5 M KCl/D_2O (middle, T_p = 29.3 °C), and 45 vol % methanol-d_4/D_2O (bottom, T_p = 44.4 °C). To obtain these difference spectra, the IR absorption spectrum measured at T_p of each polymer solution is subtracted from the IR absorption spectrum measured at T_p + 5 °C.

1-methyl-2-pyrrolidinone and water has been shown to induce a shift of the amide I band.[33] In contrast, hydrogen bond formation of the N−H group of the trans-amide does not influence the frequency of the amide I mode. At present, precise assignment of the four amide I components of PVCL is not possible. However, we can guess the hydrogen-bonding situation of the amide group which gives rise to each component. Because the maxima of the amide I band of neat solid PVCL and PVCL dissolved in chloroform is located at 1621 and 1626 cm^{-1}, respectively, the 1625 cm^{-1} component can be assigned to the amide group whose C=O group and nitrogen atom do not form hydrogen bond with water. Because addition of methanol reduces the intensity of the 1588 cm^{-1} band (Figure 8), it relates to the amide group that forms at least one hydrogen bond with water. The 1610 cm^{-1} component may also relate to the amide group which forms hydrogen bonds with water.

Fourier self-deconvoluted spectra in the C−H stretching vibration region (2800−3050 cm^{-1}) are shown in Figure 9. The ν(C−H) bands of 20 wt % PVCL measured during the phase transition (Figure 9a), and those measured at different PVCL concentrations (5, 50, and 100 wt %) at 30 °C (below T_p, Figure 9b) are presented. Despite of a small difference among the IR spectra of homogeneous PVCL solutions up to 50 wt %, the difference between the IR spectra of the demixed PVCL solution and those of the single-phase solutions is relatively large. This indicates that the phase separation of PVCL solution is accompanied by changes in the hydration states and/or conformation of the polymer chains. Major components of the ν(C−H) band are located at 2941, 2922, and 2864 cm^{-1} below T_p. The former two components can be assigned to the antisymmetric C−H stretching vibration of methylene groups, and the last component is due to the symmetric C−H stretching vibration. All components undergo red shifts, a reduction of intensities, and peak broadening upon the phase transition. The wavenumbers of these components of PVCL observed in neat solid and in chloroform are lower than those observed in water, suggesting that the ν(C−H) bands exhibit blue shifts upon interaction with water. In fact, interaction between the C−H proton and water pushes electron on the hydrogen toward the C−H bond and increases electron density on the C−H bond. As a result, the strength of the C−H bond increases, which causes a blue shift of the ν(C−H) band.[34] The red shift of the ν(C−H) bands of PVCL, therefore, indicates the dehydration of the methylene and methyne groups upon the phase separation.

Effects of Salts and Methanol on the IR Spectra of PVCL. The values of T_p determined by IR measurement are plotted against KCl and methanol concentration in Figure 2a and Figure 3, respectively, with solid squares. Because the concentration of PVCL was 20 wt % in the IR measurements, these values are slightly lower than the corresponding values of T_p determined by turbidimetry using 0.5 wt % PVCL solutions. The features of dependencies of T_p determined by different methods at two different polymer concentrations are similar. The values of T_p exhibit a linear decrease with increasing concentration of KCl and a gradual increase with increasing concentration of methanol up to ca. 40% followed by a steep increase at >40%.

The IR difference spectra of PVCL in the presence and absence of KCl and methanol are shown in Figure 10. Here, the IR absorption spectrum measured at T_p of each polymer solution was subtracted from the spectrum measured near T_p + 5 °C. The presence of KCl did not influence the profiles of the IR spectra of PVCL solution although it affects T_p. The ineffectiveness of some metal halides on the profiles of the IR spectra of PiPA was also shown in previous papers.[11,12] Ions may interact with water and induce changes in the interaction between polymer and water. The indirect effect of the ions might alter the transition temperatures of polymer solutions, and therefore, ions do not alter the IR spectra of polymers. In contrast, addition of methanol alters the IR spectrum of PVCL at the amide I band, probably because methanol forms weaker hydrogen bonds with the C=O group of PVCL than water. Other IR bands are insensitive to the addition of methanol. Thus, the mechanism of the effect of methanol on T_p is different from that of salts.

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References and Notes

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