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Temperature-Induced Phase Separation and Hydration in Aqueous Polymer Solutions Studied by NMR and IR Spectroscopy: Comparison of Poly(*N*-vinylcaprolactam) and Acrylamide-Based Polymers

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Summary: Using NMR and IR spectroscopy we compared the LCST behaviour of two types of thermoresponsive polymer systems, poly(*N*-vinylcaprolactam) (PVCL) and acrylamide-based polymers in aqueous solutions. We confirmed that during phase separation both PVCL and poly(*N*-isopropylmethacrylamide) (PNIPMAm) chains undergo coil-globule transition. At the same time some important differences were found for PVCL in comparison with PNIPMAm and poly(*N*-isopropylacrylamide) (PNIPAm), especially a much lower level of dehydration of PVCL segments at temperatures above the phase transition. We assume that the origin of these differences can be in different structure of respective monomer units. From time dependences of ATR FTIR spectra it follows that the low degree of dehydration of PVCL segments is not changed with time. Small increase in the wavenumbers of the Amide I components of the hydrated PVCL carbonyl groups with time indicates that water released from PVCL mesoglobules with time, as revealed from NMR T_2 measurements, might be mainly indirectly bound water.

Keywords: aqueous polymer solutions; FT-IR; NMR; phase separation; stimuli-sensitive polymers

Introduction

It is well known that some acrylamide-based polymers and other polymers with amphiphilic character exhibit in aqueous solutions a lower critical solution temperature (LCST). These polymers are soluble at lower temperatures but heating above the LCST results in phase separation which especially at polymer concentrations $c \geq 1$ wt% makes solutions milk-white turbid.[1–3] On the molecular level, temperature-induced phase separation is assumed to be a macroscopic manifestation of a coil-globule transition, as was shown for dilute aqueous solution of poly(*N*-isopropylacrylamide) (PNIPAm) by light scattering,[4] followed by further aggregation and formation of so-called mesoglobules.[2] Their thermosensitivity makes these polymers interesting for miscellaneous biomedical and technological applications. Thermoresponsive hydrogels that undergo abrupt changes in volume have potential applications as actuators, sensors, switching devices etc. They are also promising in assisting in wastewater treatment and enhanced oil recovery. The fact that transition temperature can be adjusted by copolymerization or using additives near to human body temperature (310 K) makes these polymers viable as drug release polymers.[2,5]

While PNIPAm was widely studied, another polymer which shows a thermoresponsive behaviour, poly(*N*-vinylcaprolactam) (PVCL), was studied less often. This polymer is biocompatible and shows a temperature-induced phase transition near physiological temperature.[2] Of various

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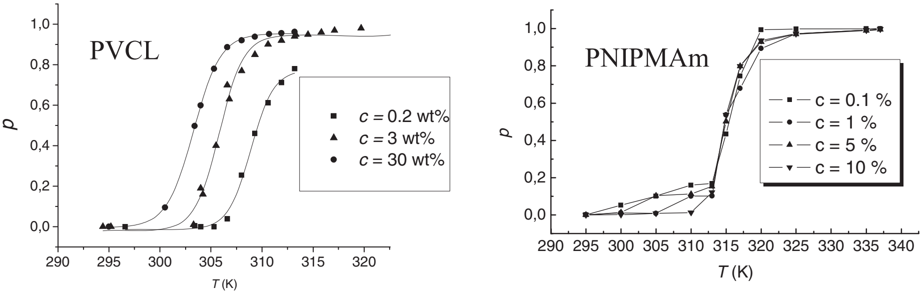

Figure 1.
Temperature dependences of phase-separated fraction p for D_2O solutions of PVCL and PNIPMAm of various polymer concentrations during gradual heating.[11,12] Reproduced by permission of The Royal Society of Chemistry (RSC) and Elsevier.

methods used in investigations of phase-separation behaviour, both NMR and infrared (IR) spectroscopy provide important information on phase-separated globular structures and interactions (hydration) in these systems.[6–10] In the present paper we discuss our recent results as obtained by NMR and IR spectroscopy on temperature-induced phase separation in PVCL/D_2O solutions[11] from the point of view of the comparison with LCST behaviour of acrylamide-based polymers, PNIPAm and poly(*N*-isopropylmethacrylamide) (PNIPMAm). At the same time some new results are presented.

Results and Discussion

It is now well established that reaching the LCST transition results in a marked reduction of integrated intensities of polymer signals in high-resolution NMR spectra due to the pronounced reduction in mobility and subsequent line broadening of polymer segments included in mesoglobules.[6] From the temperature dependent integral intensities of NMR signals it is possible to calculate the values of fraction of phase separated polymer units of significantly reduced mobility, p, using equation

$$p(T) = 1 - (I/I_0) \tag{1}$$

where I is the integrated intensity of the given polymer line in a partly phase-separated system and I_0 is the integrated intensity of this line if no phase separation occurs. In Figure 1, the temperature dependences of the phase-separated fraction p are shown for PVCL and PNIPMAm solutions in D_2O with various polymer concentration. The strong dependence of the transition region on polymer concentration is obvious for PVCL solutions; for $c = 30\,\text{wt}\%$ the transition appears at $\sim 7\,\text{K}$ lower temperatures in comparison with $c = 0.2\,\text{wt}\%$. In contrast, for PNIPMAm solutions and similarly also for poly(*N*,*N*-diethylacrylamide) solutions in D_2O the transition temperatures are virtually independent of polymer concentration.[6,12,13] Thermoresponsive polymers can be divided into three types according to the phenomenological analysis of their critical miscibility with water.[2] PVCL is of type I where the LCST decreases with increasing molecular weight while acrylamide-based polymers are of type II where the LCST is independent of molecular weight. Moreover, PVCL chains exhibit a strong tendency to aggregation[2] and larger associates (with larger molecular weight) can be formed predominantly at higher polymer concentrations. We assume that combination of these two points can be the reason for the dependence of the LCST transition region on polymer concentration as detected for PVCL/D_2O solutions.[11]

Taking into account the fact that in the transition region the p-values in Figure 1 represent equilibrium values,[6] it is then possible to use the temperature dependences of the phase-separated fraction p to determine the thermodynamic parameters (ΔH and ΔS) of the phase transition by using the approach originally suggested for the self-aggregation in solutions of syndiotactic poly(methyl methacrylate).[14] A similar approach was relatively recently applied to aqueous solutions and hydrogels of thermoresponsive polymers.[11,15,16] For the equilibrium constant $K(T)$ of the phase transition we can write the ratio

$$K(T) = p/(1-p) \qquad (2)$$

and values of the changes of the enthalpy ΔH and entropy ΔS can be determined from van't Hoff plots

$$\ln[p/(1-p)] = -(\Delta H/RT) + (\Delta S/R) \qquad (3)$$

ΔH and ΔS values obtained in this way for D_2O solutions of PVCL (the average degree of polymerization (DP) = 86) of various concentrations are shown in the 2nd and 3rd columns of Table 1. ΔH and ΔS values obtained by using the same approach for D_2O solutions of two PNIPMAm samples with different DP are shown in the 3rd and 4th columns of Table 2.

In both cases the ΔH and ΔS values are positive and very large showing that also the cooperative unit is very large. Assuming that cooperative unit is the whole macromolecule, ΔH and ΔS values related to monomer unit were obtained by dividing the original ΔH and ΔS values by the respective degree of polymerization (last two columns in Tables 1 and 2). For dilute PVCL solution ($c = 0.2$ wt%) the obtained value $\Delta H = 4.7$ kJ/mol (monomer unit) agrees well with the value 4.4 kJ/mol (monomer unit) as determined by DSC for aqueous PVCL solution of similar concentration ($c = 0.1$ wt%).[17] Very good agreement between ΔH values determined by NMR analysis (using van't Hoff plot) and DSC was established also on identical PNIPMAm/D_2O ($c = 5$ wt%) sample where values $\Delta H = 4.3$ kJ/mol (cf. Table 2) and 4.14 kJ/mol (monomer unit), respectively, were found.[11,16] These results confirm that in these systems cooperative unit is the whole macromolecule and that during phase separation both PVCL and PNIPMAm chains undergo a coil-globule transition.

Information on behaviour of water during temperature-induced phase separation in D_2O solutions of thermoresponsive polymers can be obtained from measurements of ^{1}H spin-spin relaxation times T_2 of HDO molecules. Both in D_2O solutions of

Table 1.
Thermodynamic parameters determined by using NMR data for PVCL/D_2O solutions of various concentrations.[11]

c (wt%)	ΔH (kJ/mol)	ΔS (J mol^{-1} K^{-1})	ΔH (kJ/mol) monomer unit	ΔS (J mol^{-1} K^{-1}) monomer unit
0.2	400.3	1291.9	4.7	15.0
3	519.1	1695.4	6.0	19.7
30	542.6	1787.8	6.3	20.8

Table 2.
Thermodynamic parameters determined by using NMR data for PNIPMAm/D_2O solutions of various concentrations; DP means average degree of polymerization.

DP	c (wt%)	ΔH (kJ/mol)	ΔS (J mol^{-1}K^{-1})	ΔH (kJ/mol) monomer unit	ΔS (J mol^{-1} K^{-1}) monomer unit
193	0.1	792	2513	4.1	13.0
	10	799	2533	4.1	13.1
292	5	1266	3993	4.3	13.7

acrylamide-based polymers (PNIPAm, PNIPMAm) and PVCL the reduced T_2 values at temperatures above the transition show that in these systems there is a portion of HDO bound in globular-like structures and that there is a fast exchange between bound and free water molecules (exchange time $\sim$ 1 ms).[6,11,18,19] Figure 2 shows the time dependences of the T_2 values of HDO molecules for D_2O solutions of PNIPAm, PNIPMAm and PVCL ($c = 5$ wt%); the studied samples were kept for all the time at temperature above the phase transition. An increase of T_2 with time shows that water originally bound in mesoglobules is with time released from globular-like structures. While for PNIPAm and PNIPMAm solutions the releasing process started after very long induction period (75 and 30 h, respectively), no induction period and faster releasing process were found for D_2O solution of PVCL, indicating a different character of the released water in this case.[11]

The existence of water bound in globular-like structures was revealed also by ATR FTIR spectra. Figure 3 shows the region of the C=O stretching vibrations (Amide I band) in ATR FTIR spectra of water solutions of PNIPAm, PNIPMAm and PVCL ($c = 10$ wt%) measured always at 293 K and at temperature above the phase transition (333 or 327 K). A Nicolet Nexus 870 FTIR spectrometer purged with dry air and equipped with a cooled mercury-cadmium-telluride (MCT) detector was used for the acquisition of these ATR FTIR spectra. Samples were measured on a horizontal micro-ATR Golden Gate unit (SPECAC), having a control-heated top

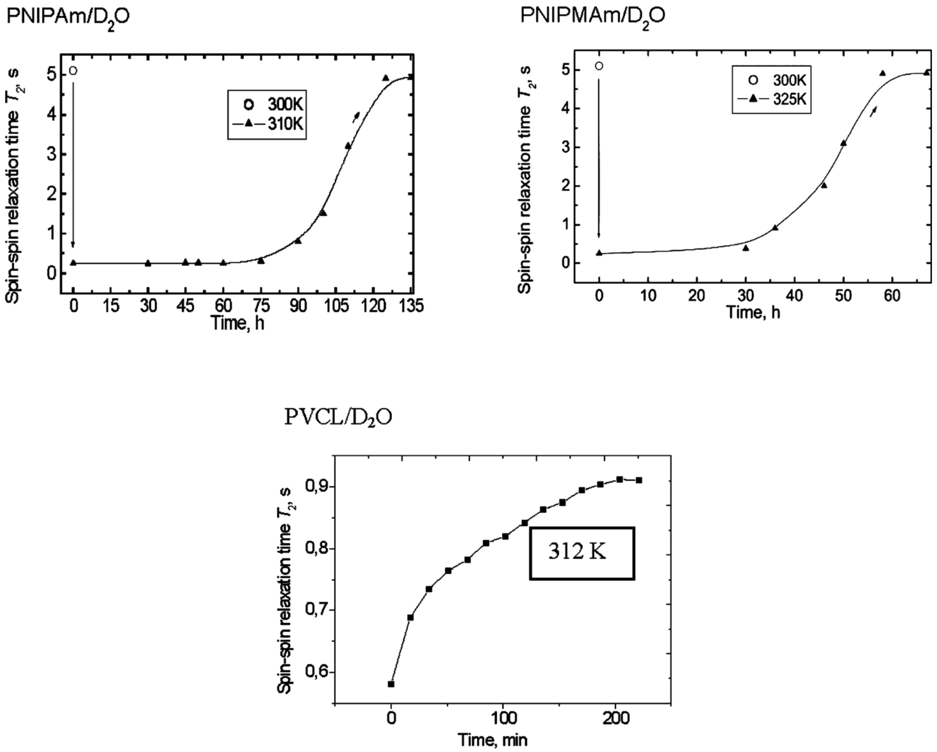

Figure 2.
Time dependences of ^{1}H spin-spin relaxation time T_2 of HDO in D_2O solutions of PNIPAm, PNIPMAm and PVCL ($c = 5$ wt%) measured always at temperature above the phase transition and 500.1 MHz (PNIPAm and PNIPMAm) and 600.2 MHz (PVCL).[11,18]

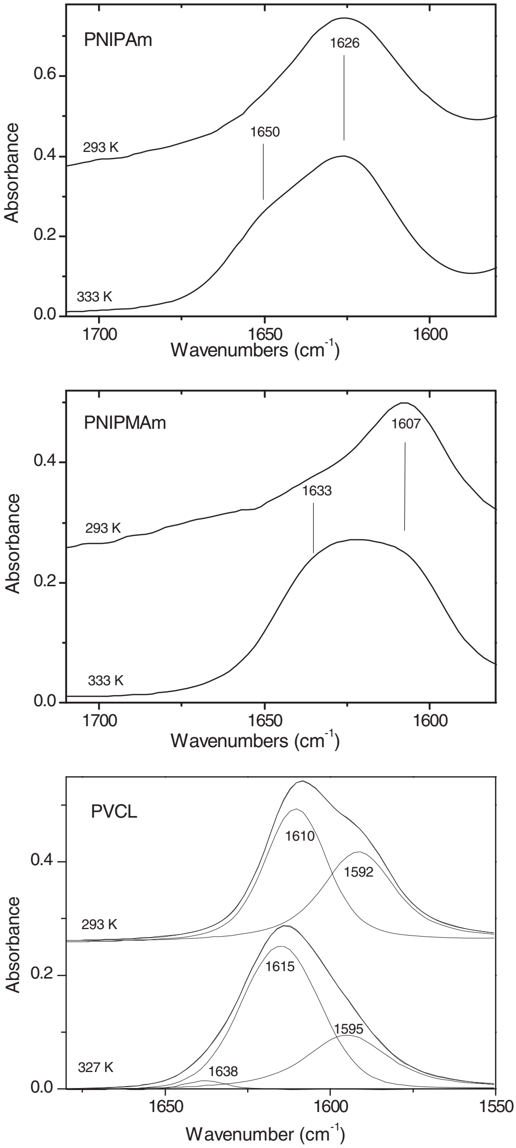

Figure 3.

ATR FTIR spectra (Amide I region) of the solutions of PNIPAm and PNIPMAm in H_2O (spectra of water subtracted) and PVCL solution in D_2O; polymer concentration was always 10 wt%.[11,20]

plate with a diamond prism. All the spectra were processed by the advanced ATR correction using OMNIC™ software. Two components can be identified in Amide I at temperature above the phase transition for PNIPAm and PNIPMAm solutions. For PNIPMAm the ratio of intensities of both components is approx. 1:1; at the same time the wavenumber 1633 cm^{-1} is the same as for the solid PNIPMAm[20] showing that this component corresponds to fully dehydrated carbonyl groups. Also component of fully dehydrated carbonyls shown as a shoulder at 1650 cm^{-1} in the spectrum of the PNIPAm suspension at 333 K is significant. Analysis of the spectra of the PVCL/D_2O solution revealed that three components can be identified in Amide I at temperature above the phase transition (327 K) that correspond to C=O groups situated in three significantly different distinguishable environments (cf. Figure 3). For the interpretation of these components quantum-chemical DFT calculation on model hydrogen bonded complexes of the PVCL segments with water molecules were helpful.[11] On the basis of these calculations and the fact that wavenumber 1638 cm^{-1} of the weak component is the same as the wavenumber of the Amide I band in solid PVCL it was possible to assign this component to fully dehydrated C=O groups. Component at 1615 cm^{-1} corresponds to structures where water molecules are hydrogen-bonded to two lactam groups either from neighbouring monomer units or from two different segments/chains. Component at lowest wavenumber 1595 cm^{-1} then corresponds to the C=O groups hydrogen bonded to two water molecules. The same assignment was recently published for hydrogels of chemically-crosslinked PVCL.[21] In contrast to mesoglobules of PNIPMAm and PNIPAm where the shape of Amide I band suggests that amount of dehydrated carbonyls is rather large, ATR FTIR spectra show that amount of fully dehydrated carbonyl groups in PVCL globular-like structures is very small. Dehydration in PVCL solutions at temperatures above the phase transition mainly consists in transformation of structures where PVCL carbonyl is hydrogen bonded to two water molecules to structures with single hydrogen bonded water molecule and in breaking away indirectly bound water molecules, i.e., molecules interacting with water molecules directly hydrogen bonded to PVCL units.[11]

For PVCL/D_2O solution also a time dependence of ATR FTIR spectra was measured at 327 K, i.e., at temperature above the phase transition. Figure 4 shows time dependences of the intensities of the three Amide I components (cf. Figure 3). Figure 5 then shows time dependences of the wavenumbers of the middle- and low-wavenumber Amide I components corresponding to carbonyl groups with single and double hydrogen-bonds to water molecules, respectively. For the weak

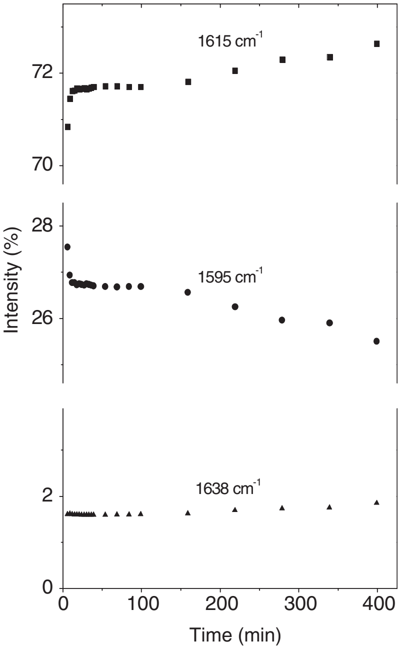

Figure 4.
Time dependences of intensities of the three Amide I components in FTIR spectra of the PVCL/D_2O solution ($c = 10$ wt%) measured at 327 K.

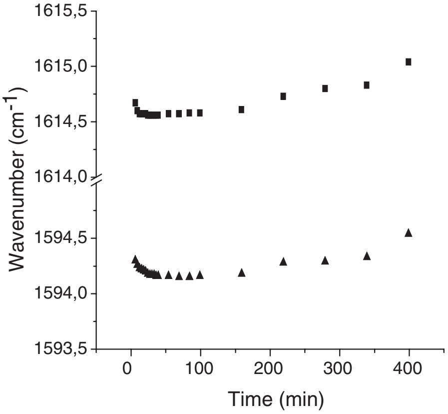

Figure 5.
Time dependences of wavenumbers of the middle (■) and low-wavenumber (▲) Amide I components in FTIR spectra of the PVCL/D_2O solution ($c = 10$ wt%) measured at 327 K.

high-wavenumber Amide I component corresponding to dehydrated carbonyl groups we assumed that its wavenumber does not change with time and from Figure 4 it follows that also the intensity of this component is constant. Figure 4 shows that intensities of the components corresponding to hydrated carbonyl groups change with time very little, by 1–1.5% (we assume that small changes at beginning of time dependences can be in connection with the fact that temperature was not equilibrated in the sample). At the same time the intensity of the component at 1595 cm^{-1} slightly decreases and intensity of the component at 1615 cm^{-1} slightly increases with time showing that main dehydration process during phase transition in PVCL solution (cf. Figure 3), i.e. transformation of structures where PVCL carbonyl is hydrogen bonded to two water molecules to structures with single hydrogen bonded water molecule, very slowly decays with time. Small changes we revealed also in the wavenumbers of the components corresponding to hydrated carbonyl groups; their values slightly increase with time (Figure 5). DFT quantum-chemical calculations on model hydrogen bonded complexes of the PVCL segments with water molecules have shown that presence of the indirectly bound water molecules, i.e., molecules interacting with water molecules directly hydrogen bonded to PVCL units, results in reduced wavenumbers of the Amide I components of hydrated carbonyl groups.[11] Therefore a small increase of the wavenumbers of these components with time is in accord with the assumption that water molecules released from PVCL mesoglobules with time without any induction period (cf. Figure 2) might be mainly indirectly bound water molecules.

Supramolecular structure of PVCL mesoglobules was characterized by small-angle X-ray scattering (SAXS) and optical microscopy. SAXS results have shown that “primary” globular-like structures of the 50 nm size (diameter) are formed at temperatures above the phase transition for all investigated concentrations of PVCL/D_2O solutions 0.5–10 wt%.[11] These “primary” mesoglobules further aggregate and in semidilute or concentrated solutions form large agglomerates in the μm scale as documented by optical microscopy. Formation of agglomerates with the mean size ~2 μm was shown by optical microscopy also for PNIPMAm aqueous solutions.[22]

Conclusion

We discussed here two types of thermoresponsive polymer systems, PVCL and acrylamide-based polymers, and their behaviour during temperature-induced phase separation in aqueous solutions from the point of view of methods of molecular spectroscopy. We have confirmed that during phase separation both PVCL and PNIPMAm chains undergo coil-globule transition and we have shown that always a certain amount of water is bound in globular-like structures. On the other hand some important differences were found for PVCL solutions in comparison with solutions of acrylamide-based polymers, namely strong dependence of transition temperatures on PVCL concentration, different character of water released from mesoglobules with time and especially a much lower level of dehydration of PVCL segments at temperatures above the phase transition. We assume that the origin of these differences can be in different structure of respective monomer units; in contrast to acrylamide-based polymers, due to the absence of hydrogen in the amide group PVCL cannot form polymer-polymer hydrogen bonds in the globular state and therefore in PVCL mesoglobules hydrogen bonded water molecules can serve as intermediaries of interactions between polymer segments.[11] From time dependences of ATR FTIR spectra it follows that the low degree of dehydration of PVCL segments is not changed with time. Small increase in the wavenumbers of the Amide I components corresponding to hydrated PVCL carbonyl groups with time indicates that water released from PVCL mesoglobules with time without any induction period, as revealed from NMR T_2 measurements, might be mainly indirectly bound water.

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