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^{1}H NMR Study of Phase Transition of Uncharged and Negatively Charged Poly(*N*-isopropylmethacrylamide) in D_2O Solutions

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Summary: ^{1}H NMR spectroscopy has been applied to the analysis of dynamic-structural changes during temperature-induced phase transition of non-ionized poly(*N*-isopropylmethacrylamide) (PIPMAm) and ionized copolymers of *N*-isopropylmethacrylamide with sodium methacrylate, all in D_2O solutions with various polymer concentrations (c = 0.1-10 wt.-%) and ionic comonomer mole fractions (i = 0-10 mole %). It was found that the formation of compact globular-like structures during the phase transition is independent of polymer concentration for non-ionized samples; the presence of negative charges on the polymer chains leads to a dependence of the phase transition temperature on c and i. Virtually all PIPMAm segments are in globular-like structures for low polymer concentrations; for $c \geq 1$ wt.-%, this holds only for low content i of the ionic comonomer. An increase in c and i leads to a decrease in the fraction of polymer segments in globular-like structures; for samples with highest values of c and i, the phase transition was not observed.

Keywords: effect of ionization; lower critical solution temperature; NMR; phase separation; poly(*N*-isopropylmethacrylamide)

Introduction

Poly(*N*-isopropylmethacrylamide) (PIPMAm) solutions in water undergo the phase transition at a lower critical solution temperature (LCST).[1,2] While below the LCST polymer chains are flexible and exhibit coil structure, heating of polymer solutions above the LCST results in the phase separation due to the changed balance between various polar and non-polar interactions. In such a way, with increasing temperature, attractive interactions between hydrophobic groups of PIPMAm units in water lead to the change of polymer chain conformations from a randomly

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coiled structure to a collapsed globular structure.[3] In our previous work we have studied temperature-induced phase transition in negatively charged PIPMAm hydrogels.[4]

In this paper we have used ^1H NMR spectroscopy to study the temperature-induced phase transition of uncharged PIPMAm and negatively charged PIPMAm copolymers in D_2O solutions in a broad range of polymer concentrations and ionic comonomer mole fractions, and to investigate the dynamic-structural changes during the transition; sodium methacrylate was used as an ionic comonomer.

Experimental Part

Samples: *N*-isopropylmethacrylamide (IPMAm, Fluka) and sodium methacrylate (MNa) were used to prepare PIPMAm/D_2O solutions of various polymer concentrations c (c = 0.1-10 wt.-%) and ionic comonomer mole fractions i (i = 0-10 mole %). 4,4'-azobis(4-cyanopentanoic acid) was used as initiator and polymerization was carried out in an ethanol/water mixture (94/6 by vol.); the volume fraction of the sum of the monomers in the mixture was 0.2. After polymerization and subsequent drying of polymers to constant weight, the PIPMAm/D_2O solutions were prepared, degassed and sealed under argon in 5-mm NMR tubes; sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as an internal NMR standard.

NMR measurements: High-resolution ^1H NMR spectra were recorded with a Bruker Avance 500 spectrometer operating at 500.1 MHz. Typical measurement conditions were as follows: 90° pulse width 10 μs, relaxation delay 10 s, spectral width 5 kHz, acquisition time 3.28 s, 16 scans. The integrated intensities were determined using the spectrometer integration software with accuracy of ±1 %. The temperature was maintained constant within ±0.2 K with a BVT 3000 temperature unit.

Results and Discussion

High-resolution ^1H NMR spectra of D_2O solution of uncharged PIPMAm with polymer concentration c = 10 wt.-% measured at the temperatures 314 and 317 K under the same instrumental conditions are shown in Figure 1. The absorption peaks centered at 3.9, 1.85, 1.1 and 0.95 ppm correspond to PIPMAm groups CH, CH_2, CH_3 (isopropyl), and CH_3 (methacryloyl), respectively. Sharp line at 4.55 ppm originates from the residual HDO in the used D_2O. Weak multiplets centered at 0.62, 1.75 and 2.9 ppm belong to the DSS standard. The temperature 314 K (the first spectrum) corresponds to the homogeneous state before the phase transition; the other spectrum was measured at 317 K, i.e. just above the phase separation temperature (the sample is turbid). The most important effect shown in Figure 1 is a pronounced decrease in the integrated intensity of all PIPMAm bands in a rather narrow temperature interval of 314-317 K. This is due to the fact that with increasing temperature, the mobility of a major part of PIPMAm segments is reduced to such an extent that they escape detection in high-resolution ^1H NMR spectra. Unusually large linewidths of PIPMAm indicate the existence of certain aggregated structures, which are stable in solution. This is evidently due to the phase separation and formation of compact globular structures in the studied system.[5–10] For further analysis, we have used the value of the phase-separated fraction $p = 1 - I/I_0$, where I is the integrated intensity of a given band of PIPMAm in a partly phase- separated system and I_0 is the integrated intensity of this band if no phase separation occurs.[7-10] As it is shown in Figure 2, the temperature dependences of integrated intensities obtained for side-chain (CH) and main-chain (CH_2) groups are virtually the same. The phase transition of all uncharged

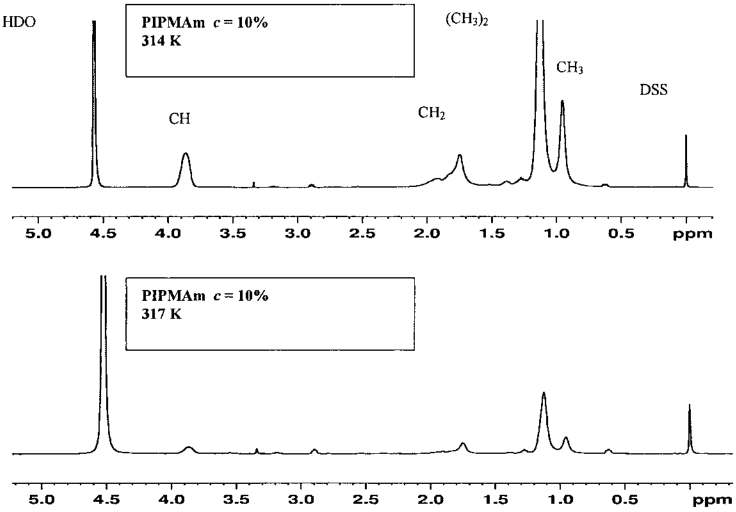

Fig. 1. High resolution ^1H NMR spectra of uncharged PIPMAm in D_2O (c = 10 wt.-%) at two temperatures.

samples was found in the temperature range 314–320 K. The maximum value of the phase-separated fraction above the transition region, p_{max} is practically constant and equal ~1; from this result we can assume that virtually all segments in the uncharged polymer are involved in globular structures.

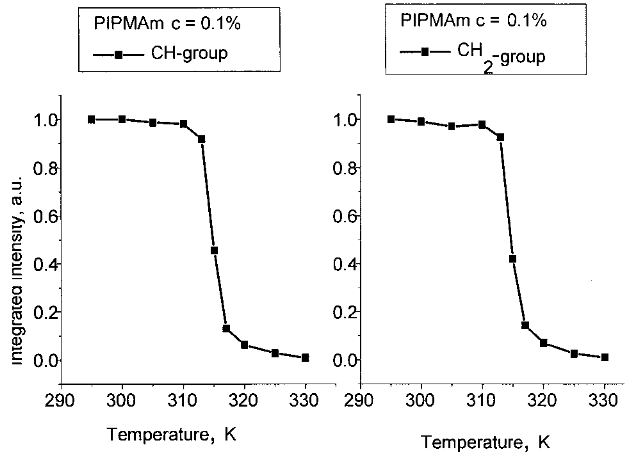

Fig. 2. Temperature dependences of integrated intensity for side-chain (CH) and main-chain (CH_2) groups of PIPMAm in D_2O (c = 0.1 wt.-%).

The effect of ionization on the phase transition in PIPMAm copolymer solutions is demonstrated in Figures 3 and 4. For the ionic comonomer mole fraction i = 1 % and polymer concentrations $c \leq 1$ wt.-%, we can observe a virtually discontinuous phase transition (Figure 3). The maximum value of the phase-separated fraction p_{max} above the transition is roughly constant and equal to 1 independent of c; similar results were found also for uncharged PIPMAm solutions (Figure 2). As it follows from Figure 4, for polymer with the highest MNa mole fraction i = 10 %, the transition region becomes broader with increasing polymer concentration. As the concentration of charges increased, the transition region is shifted towards higher temperatures (Figure 4, c = 1 and 10 wt.-%); similar results were found for charged PIPMAm hydrogels.[4] When increasing the content of hydrophilic MNa units in the polymer, the solubility and therefore also the mobility of polymer chains increases, and due to this fact, a higher temperature is necessary for hydrogen bonds to break and hydrophobic interactions to predominate. At the same time, for *i* = 10 %, we can observe a pronounced decrease in the maximum value of the phase-separated fraction $p_{\max}$ with polymer concentration. This means that with higher polymer concentration, the number of segments involved in globular structures, decreases and number of mobile units above the transition temperature increases. Samples with c > 1 wt.-% and with two highest values of ionic comonomer mole fraction (*i* = 7.5 % and 10 %) have a very broad transition region and remain transparent even at 360 K. The maximum value of the phase-separated fraction is lower than 0.3, i.e. approximately 70 % of polymer segments are mobile, being involved in the interaction with water.

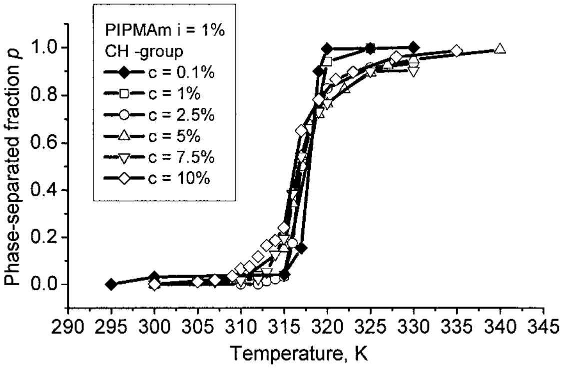

Fig. 3. Temperature dependences of fraction *p* for PIPMAm copolymers in D_2O with ionic comonomer content *i* = 1 mole % and various polymer concentration *c*.

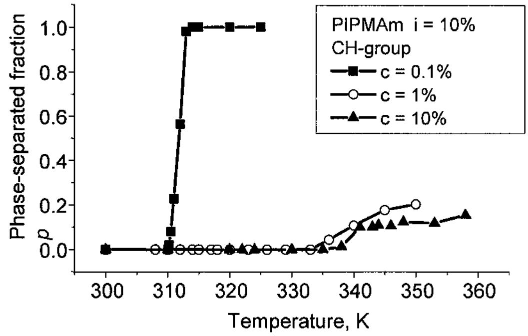

Fig. 4. Temperature dependences of fraction *p* for PIPMAm copolymers in D_2O with ionic comonomer content *i* = 10 mole % and various polymer concentration *c*.

As it is shown in Figures 5 and 6, the temperature dependences of the phase-separated fraction p for polymer concentrations $c = 1$ and 10 wt.-% and various mole fractions of the ionic comonomer have a similar character. As expected, increasing ionization leads to a shift of the transition region toward higher temperatures and, at the same time, to the reduction in the number of polymer segments involved in globular structures. These observations are in agreement with previous results obtained on poly(*N*,*N*-diethylacrylamide)/D_2O gels.[6]

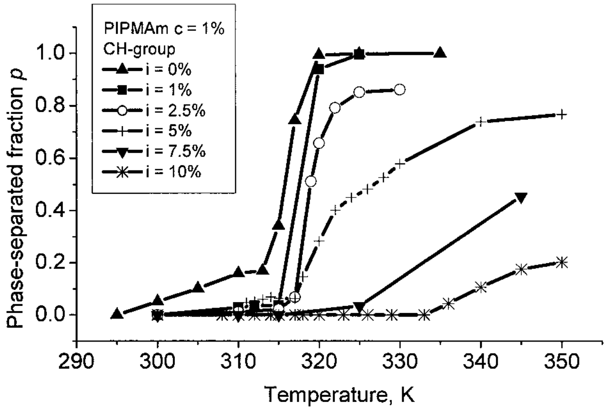

Fig. 5. Temperature dependences of fraction p for PIPMAm copolymers in D_2O with polymer concentration $c = 1$ wt.-% and various content of ionic comonomer i.

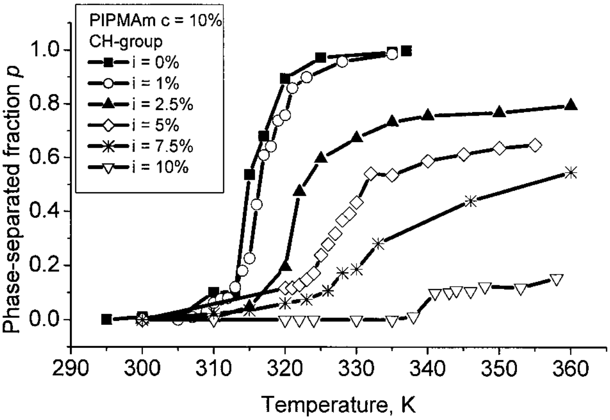

Fig. 6. Temperature dependences of fraction p for PIPMAm copolymers in D_2O with polymer concentration $c = 10$ wt.-% and various content of ionic comonomer i.

Interesting results were obtained for solutions with polymer concentration c = 0.1 wt.-% and with various fraction of the ionic comonomer i (Figure 7); in this case we observed relatively sharp transition with p_{max} ~ 1, independent of c. Surprisingly enough, while the transition for I = 1 % occurs at higher temperature in comparison to i = 0 %, further increasing the MNa content in the PIPMAm copolymer shifts the transition gradually towards lower temperatures, even below the curve for i = 0 %. This unexpected behaviour is probably associated with a very low polymer concentration at which no intermolecular interactions between various polymer chains occur, and globular structures are formed by individual molecules.

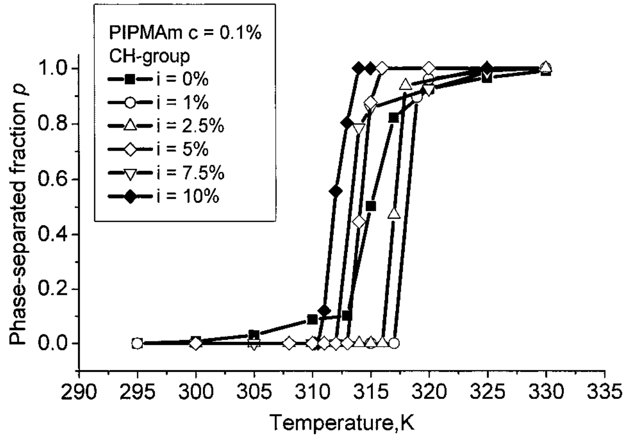

Fig. 7. Temperature dependences of fraction p for PIPMAm copolymers in D_2O with polymer concentration c = 0.1 wt.-% and various content of ionic comonomer i.

Conclusions

It was found that ^{1}H NMR spectroscopy provides evidence about conformational changes of PIPMAm molecules from random coil to globular structure during the temperature-induced phase transition in D_2O solutions. In all solutions of the uncharged homopolymer, the transition was found to occur in the temperature region 314-320 K; above the transition region (at higher temperatures), virtually all polymer units are involved in globular structures. Introduction of negative charges into polymer chains leads to a shift of the transition region to higher temperatures and, at the same time, to a decrease in the fraction of polymer segments involved in globular structures. The exception was found for very dilute solutions ($c = 0.1$ wt.-%), where an increase in concentration of negative charges on the chain results in the shift of the transition region to lower temperatures. This unexpected behaviour is probably in connection with a very low polymer concentration where globular structures are formed by individual macromolecules.

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