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^1H NMR study of temperature-induced phase transitions in D_2O solutions of poly(*N*-isopropylmethacrylamide)/poly(*N*-isopropylacrylamide) mixtures and random copolymers

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Abstract

^1H NMR spectroscopy was used to investigate temperature-induced phase transitions in D_2O solutions of poly(*N*-isopropylmethacrylamide) (PIPMAm)/poly(*N*-isopropylacrylamide) (PIPAAm) mixtures and P(IPMAm/IPAAm) random copolymers of various composition on molecular level. While two phase transitions were detected for PIPMAm/PIPAAm mixtures, only single phase transition was found for P(IPMAm/IPAAm) copolymers. The phase transition temperatures of PIPAAm component (appears at lower temperatures) are not affected by the presence of PIPMAm in the mixtures; on the other hand, the temperatures of the phase transition of PIPMAm component (appears at higher temperatures) are affected by the phase separation of the PIPAAm component and depend on concentration of the solution. For P(IPMAm/IPAAm) random copolymers, a departure from the linear dependence of the transition temperatures on the copolymer composition was found for a sample with 75 mol% of IPMAm monomeric units.

Keywords: Poly(*N*-isopropylmethacrylamide)/poly(*N*-isopropylacrylamide) mixtures and random copolymers; Temperature-induced phase transition; ^1H NMR spectroscopy

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1. Introduction

It is well known that some acrylamide-based polymers, including poly(*N*-isopropylacrylamide) (PIPAAm) and poly(*N*-isopropylmethacrylamide) (PIPMAm) exhibit interesting behavior in aqueous solutions, showing a lower critical solution temperature (LCST) [1,2]. They are soluble at low temperatures but heating above the LCST results in phase separation. On the molecular level, phase separation is a macroscopic manifestation of a coil-globule transition followed often by aggregation, as was shown for PIPAAm in water, e.g., by light scattering [1]. The phase transition is probably associated with the changed balance between various types of interactions (mainly hydrogen bonds and hydrophobic interactions). Their thermosensitivity makes these systems interesting for possible biomedical and technological applications, especially if the polymers are chemically crossliked (in the form of hydrogels) [3]. Though phase transitions especially in PIPAAm aqueous solutions were extensively studied by various methods (cloud point, viscometric, calorimetric, diffusion, viscoelastic, infrared and Raman measurements), the application of NMR spectroscopy to investigations of the phase separation in aqueous solutions of PIPAAm and its copolymers was rather seldom [4–8]. Together with cited papers, we have also shown that ^1H NMR spectroscopy can be a suitable method to follow the temperature-induced phase separation on molecular level and applied this method to D_2O solutions and gels of poly(*N*,*N*-diethylacrylamide), poly(vinyl methyl ether) (PVME) and PIPMAm [9–15], as well as to PIPMAm/PVME mixtures [16].

Recently Djokpé and Vogt published a study on LCST behaviour of aqueous solutions of PIPMAm/PIPAAm mixtures and random copolymers P(IPMAm/IPAAm) based on the measurements of the cloud points [17]. In

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the present work we studied the same type of the systems, i.e. D_2O solutions of PIPMAm/PIPAAm mixtures and statistical copolymers P(IPMAm/IPAAm) by using ^1H NMR spectroscopy. We assumed to take an advantage of this method, to follow the LCST behaviour for at least one component in the mixture or copolymer separately. For this purpose, D_2O solutions (polymer concentration $c = 0.1$, 1 and 5 wt%) of PIPMAm/PIPAAm mixtures and statistical copolymers P(IPMAm/IPAAm) ($c = 1$ wt%) of various composition (molar ratio of monomeric units was 3/1, 1/1 and 1/3 both for mixtures and copolymers) were prepared. In comparison with recently studied PIPMAm/PVME mixtures in D_2O solutions [16] there is important difference for systems investigated in the present study: while LCST is for PVME at least 60 K above the temperature of the glass transition T_g of PVME in bulk, for PIPAAm the LCST is well below the respective $T_g = 403$ K [18]. From the methodical point of view, we used an approach based on measurements of temperature dependences of ^1H NMR spectra (integrated intensities), used by us already in the past [10–16], that makes it possible to determine the temperature dependences of the phase separated fraction.

2. Experimental

2.1. Samples

N-isopropylmethacrylamide (IPMAm, Fluka) was used to prepare PIPMAm. Polymerization was initiated by 4,4′-azobis(4-cyanopentanoic acid) and carried out in ethanol/water mixture (94/6 by volume); the volume fraction of the monomer in the mixture was 0.2. *N*-isopropylacrylamide (IPAAm, Aldrich) was used to prepare PIPAAm. Above mentioned IPMAm and IPAAm monomers were used also for preparation of random copolymers P(IPMAm/IPAAm); samples with the molar ratios of IPMAm/IPAAm monomers equal to 3/1, 1/1 and 1/3 were prepared. Experimental conditions for preparation of PIPAAm and P(IPMAm/IPAAm) copolymers were the same: photo-initiator Darocur (~2 wt% on monomer(s)) was used and UV polymerization ($\lambda = 254$ nm) was carried out in ethanol at 278 K for 1 h (volume fraction of monomer(s) was 0.15) After polymerization the samples were precipitated to hexane and subsequently precipitated twice from methanol to diethylether. After subsequent drying of all samples to constant weight under low pressure, the D_2O solutions ($c = 0.1$, 1 and 5 wt%) of PIPMAm/PIPAAm mixtures and P(IPMAm/IPAAm) copolymers ($c = 1$ wt%) were prepared with molar ratio of monomeric units 3/1, 1/1 and 1/3 in both cases, together with D_2O solutions of the neat PIPMAm and PIPAAm. In accord with ref. [17], ^1H NMR analysis has shown that the proportions of IPMAm and IPAAm monomeric units in P(IPMAm/IPAAm) copolymers correspond to feed compositions of the respective monomers. All samples of D_2O solutions in 5 mm NMR tubes were degassed and sealed under argon; sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as an internal NMR standard.

2.2. NMR measurements

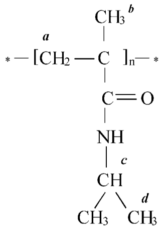
^1H NMR measurements were made with a Bruker Avance 500 spectrometer operating at 500.1 MHz. The integrated intensities were determined with the spectrometer integration software with an accuracy of ±1%. In all measurements the temperature was maintained constant within ±0.2 K using a BVT 3000 temperature unit.

3. Results and discussion

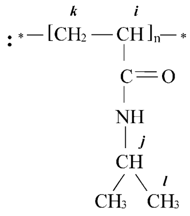
3.1. PIPMAm/PIPAAm mixtures

High-resolution ^1H NMR spectra of D_2O solution ($c = 1$ wt%) of PIPMAm/PIPAAm (polymer structures shown below) mixture (mixing ratio, i.e. the molar ratio of the respective monomeric units, 1/1) measured at temperatures 305, 308 and 325 K under the same instrumental conditions are shown in Fig. 1.

PIPMAm :



PIPAAm :



The assignments of resonances to various types of protons of PIPMAm and PIPAAm are shown directly in Fig. 1. Sharp line in the left part of the spectra (above 4.5 ppm)

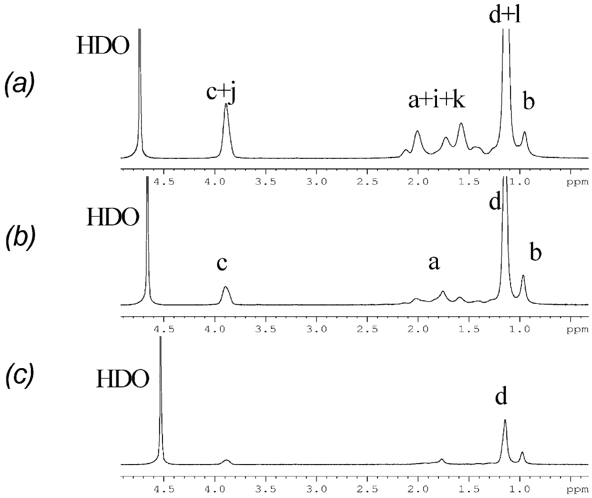


Fig. 1. High-resolution ^1H NMR spectra of PIPMAm/PIPAAm mixture in D_2O ($c = 1$ wt%, mixing ratio 1/1) measured at 305 K (a), 308 K (b), 325 K (c).

originates from the residual HDO in the used D_2O. The temperature 305 K (Fig. 1(a)) is just below LCST of both polymeric components (cf. e.g. [15,17]) and corresponds to the homogeneous solution. We can see that resonances of PIPMAm and PIPAAm overlap, with exception of the resonance *b* which corresponds only to α-CH_3 protons of PIPMAm. The next spectra were measured at 308 K, i.e. above the LCST of PIPAAm but below the LCST of PIPMAm (Fig. 1(b)) and at 325 K, i.e. above the LCST for both individual polymers in the mixture (Fig. 1(c)). The most important effect shown in Fig. 1(b) and (c) is a pronounced decrease in the integrated intensity of all PIPAAm and PIPMAm lines, respectively. This is a consequence of a marked reduction in mobility of most polymer units (forming compact globular-like structures) to such extent that corresponding lines became too broad and escape from detection in high-resolution spectra. Above the respective LCST, only small part of the respective polymer units (with unrestricted mobility) remains detectable in high-resolution spectra as seen in Fig. 1(c). Similar behaviour as shown in Fig. 1 was found for all studied polymer concentrations and compositions of PIPMAm/PIPAAm mixtures. The depicted changes of the shape and intensity of NMR lines have been also observed for D_2O solutions of neat PIPAAm or PIPMAm.

For further analysis, we have used the values of the phase-separated fraction *p* obtained as

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

where *I* is the integrated intensity of the certain polymer line in the spectrum of partly-separated system and I_0 is the integrated intensity of this line if no phase separation occurs [10–16]. For I_0 we took values based on integrated intensities below the phase-transition, using the expected $1/T$ temperature dependence. For solutions with $c \geq 1$ wt%, the estimated error in the values of the phase-separated fraction *p* is $\pm 2\%$, especially for cases where the integrated intensities of rather isolated resonance were used for the analysis (e.g. side-chain CH resonance in spectra shown in Fig. 1). For dilute solutions ($c = 0.1$ wt%), the estimated error in *p* values is approx. twice larger.

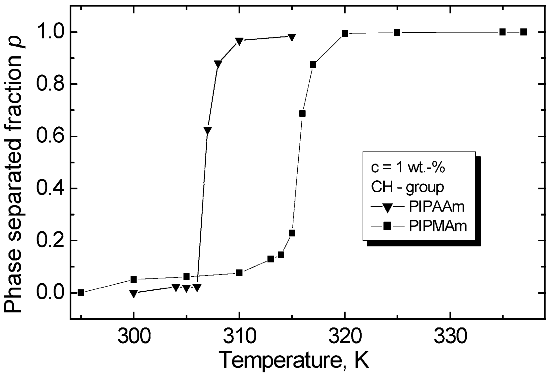


Fig. 2. Temperature dependences of the phase-separated fraction *p* as determined for side-chain CH protons of PIPAAm (▼) and PIPMAm (■) in D_2O solutions ($c = 1$ wt%).

In Fig. 2, the phase-separated fraction *p* (as determined from side-chain CH band) is plotted as function of temperature for D_2O solutions ($c = 1$ wt%) of neat PIPAAm and PIPMAm. Virtually the same temperature dependences of the fraction *p* were obtained using spectral bands of other proton groups. Despite the fact that PIPMAAm is more hydrophobic than PIPAAm, its phase transition appears at higher temperatures. This paradox behaviour was attributed to sterical hindrance induced by α-methyl groups so that the hydrophobic groups cannot interact in the most favourable manner [17]. Fig. 3 shows the temperature dependences of the phase-separated fraction *p* for D_2O solutions of PIPMAm/PIPAAm mixtures, again as determined from side-chain CH band (both PIPMAm and PIPAAm CH protons contribute to this band). The experimental points in Figs. 2 and 3 (and similarly, in all subsequent figures showing temperature dependences of the phase-separated fraction *p*) were measured ~20–30 min after the corresponding temperature was reached by heating. Our previous measurements of time dependences of integrated NMR intensities after jump heating (or cooling) of the sample above (or below) the transition region have shown that the respective change in the integrated intensity is rather fast, mostly in first 3 min (this time is necessary to reach the desired temperature in the sample) [10–13]. After 20–30 min, the integrated intensities are constant and experimental points in Fig. 2 (and similar figures) are the 'equilibrium' values. In accord with Ref. [17], two transitions are clearly visible in Fig. 3, the first one at 305–308 K, the second one at 316–321 K. From comparison with Fig. 2 and from the values of the fraction *p* after the first transition as function of the composition of the mixture it follows that the transition at lower temperatures is associated with PIPAAm while the transition at higher temperatures is associated with PIPMAm. Two distinct phase transitions at temperatures roughly corresponding to LCST of separate components were also found by us from

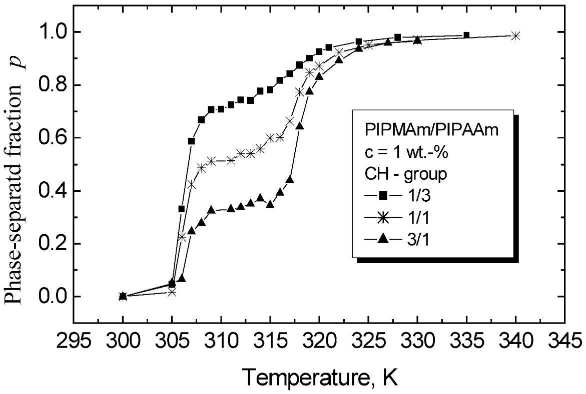


Fig. 3. Temperature dependences of the phase-separated fraction *p* as determined from side-chain CH band in D_2O solutions ($c = 1$ wt%) of PIPMAm/PIPAAm mixtures with various mixing ratios.

^{1}H NMR measurements for PIPMAm/PVME mixtures [16]. The character and temperatures of the first transition (PIPAAm) are virtually the same for the neat PIPAAm and all PIPMAm/PIPAAm mixtures (all concentrations and compositions), showing that the behaviour of PIPAAm during the phase separation is not affected by the presence of PIPMAm molecules in the solution. The situation is the same as in D_2O solutions of PIPMAm/PVME mixtures [16] where also the phase separation behaviour of PVME component, that occurs at lower temperatures, is not affected by the presence of PIPMAm molecules in the solution. Evidently, the presence of the second dissolved polymeric component in the mixture, without forming globular-like structures, has no effect on phase separation behaviour of the given polymeric component. On the other hand, the second transition (PIPMAm) is for PIPMAm/PIPAAm mixtures in comparison with the neat PIPMAm somewhat broader and shifted to higher temperatures (cf. Figs. 2 and 3). Even more clear is the situation from Fig. 4, where temperature dependences of the phase-separated fraction p of the PIPMAm component alone were determined for the neat PIPMAm and PIPMAm/PIPAAm mixtures ($c=1$ wt%) from integrated intensities of the α-CH_3 band of PIPMAm (resonance b in Fig. 1). This figure shows that transition of PIPMAm component in PIPMAm/PIPAAm mixtures is shifted to higher temperatures in comparison with the neat PIPMAm, that its transition is broader for mixtures and finally that the phase-separated fraction p of PIPMAm in mixtures at temperatures above the transition is not equal to 1 but somewhat smaller ($p\approx 0.9$), indicating that in PIPMAm/PIPAAm mixtures there is a small portion of PIPMAm units that remain mobile even at elevated temperatures and do not participate in phase separation (small portion of PIPMAm units that are not phase separated at elevated temperatures was found previously also in PIPMAm/PVME mixtures [16]). All these features are evidently in connection with the influence of the phase separated PIPAAm component that somewhat hinders the phase separation of PIPMAm component, and therefore its phase transition is shifted towards higher temperatures. From Fig. 4 it also follows that PIPMAm transition only slightly depends on the composition of the mixture and this holds also for higher ($c=5$ wt%) and lower ($c=0.1$ wt%) polymer concentrations.

On the other hand, the temperatures of the PIPMAm transition in PIPMAm/PIPAAm mixtures strongly depend on polymer concentration (Fig. 5), while there is no concentration dependence of the transition temperatures in D_2O solutions of neat PIPMAm [16]. From Fig. 5 it follows that increasing concentration leads to the shift of the transition region toward lower temperatures. Similar behaviour we observed also for PIPMAm/PVME mixtures [16] and attributed to more frequent PIPMAm-PVME contacts at higher concentrations where some PIPMAm segments might be catched in PVME globular structures. Concentration dependence of PIPMAm transition in D_2O solutions of PIPMAm/PIPAAm mixtures by itself, as shown in Fig. 5, could be explained in analogous way. However, from comparison of Figs. 4 and 5 (including similar concentration dependences as in Fig. 5 found for other compositions of the mixtures), and taking into account the fact that the transition temperatures of the neat PIPMAm do not depend on the concentration of D_2O solutions, it follows that the difference in the transition temperatures of PIPMAm in PIPMAm/PIPAAm mixtures in comparison with the neat PIPMAm increases with decreasing concentration of the solution. While for $c=5$ wt% transition temperatures of PIPMAm in PIPMAm/PIPAAm mixtures and in neat PIPMAm are virtually the same, for $c=0.1$ wt% the PIPMAm transition in PIPMAm/PIPAAm mixtures is shifted by 5 K towards higher temperatures in comparison with D_2O solution of the neat PIPMAm. Similar trend was previously found also for PIPMAm/PVME mixtures, though the differences in transition temperatures of PIPMAm in the mixture in comparison with the neat PIPMAm were in this case smaller in comparison with PIPMAm/PIPAAm mixtures [16]. We assume that in dilute D_2O solutions

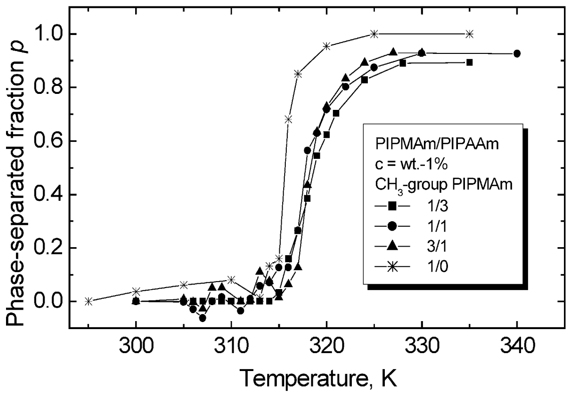


Fig. 4. Temperature dependences of the phase-separated fraction for PIPMAm component (as determined from α-CH_3 band of PIPMAm) in D_2O solutions ($c=1$ wt%) of PIPMAm/PIPAAm mixtures and various mixing ratios.

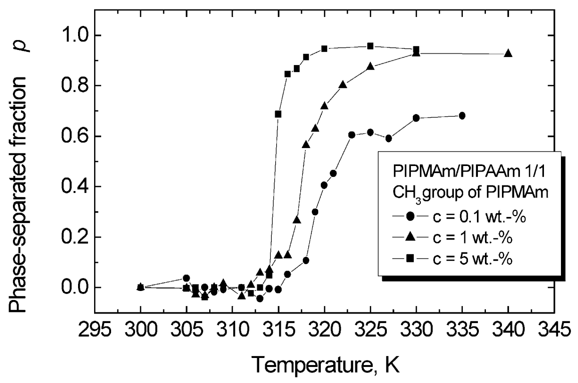


Fig. 5. Temperature dependences of the phase-separated fraction p for PIPMAm component (as determined from α-CH_3 band of PIPMAm) in D_2O solutions of mixtures PIPMAm/PIPAAm $=1/1$ and various concentrations.

($c = 0.1$ wt%) and at temperatures below its transition region, PIPMAm exists as extended nonoverlapping coils; the transition is in this case mainly of intramolecular origin. Presence of phase-separated globular structures of PIPAAm or PVME might result in the changes of the order and structures of water molecules in the surroundings of PIPMAm chains that interfere in the phase separation of the PIPMAm component.

Recently we have shown that in semidilute and concentrated solutions of PIPMAm/PVME mixtures a certain amount of water molecules is bound in globular structures of both polymeric components and that with time this bound water is very slowly released from these globular structures [16,19]. Release of water molecules from globular structures of PVME takes about 12 h at 310 K. Moreover, very recently we have found that transition temperatures of PIPMAm in D_2O solution ($c = 1$ wt%) of PIPMAm/PVME = 1/1 mixture as obtained immediately after phase transition of PVME component (occurs at 308 K), where a certain amount of water was bound in PVME globular structures, and after keeping the sample for 12 h at 310 K, i.e. when all water bound in PVME globular structures was released, differed by 4 K. At the same time the transition of PIPMAm in PIPMAm/PVME mixture thas was kept for 12 h at 310 K was shifted toward lower temperature and the respective transition temperature was almost the same as the transition temperature of the neat PIPMAm [20]. This result corroborates the idea that the state of water molecules, that is influenced by the phase separation of polymeric component that occurs at lower temperatures (PIPAAm or PVME), might affect the temperatures of the phase transition of PIPMAm component in the mixture. Similar behaviour as described above for the PIPMAm/PVME mixture we expect also for PIPMAm/PIPAAm mixtures, but taking into account that PIPAAm transition is well below the T_g of PIPAAm in bulk, one can expect that a complete release of water from PIPAAm globular structures will take a much longer time in comparison with globular structures formed by flexible PVME (the release of bound water from globular structures of the PIPMAm, with T_g of the polymer in bulk equal to 449 K [21], took ca. 50 h [19]). Nevertheless, the cited result [20] on PIPMAm/PVME mixtures shows a direction for the further study that is necessary for better understanding of the phase transition phenomena in polymer mixtures on molecular level.

3.2. P(IPMAm/IPAAm) random copolymers

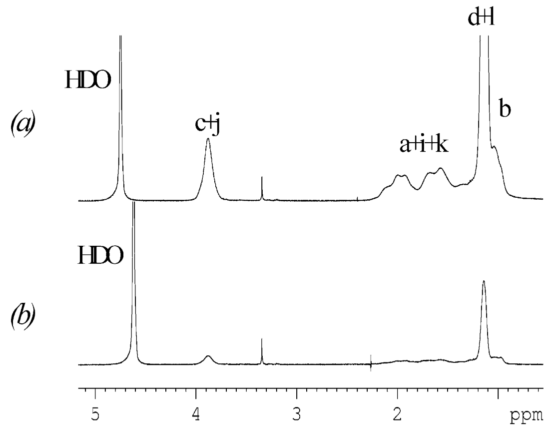


Fig. 6. High-resolution ^1H NMR spectra of P(IPMAm/IPAAm = 1/1) random copolymer in D_2O ($c = 1$ wt%) measured at 300 K (a), 311 K (b).

^1H NMR spectra of D_2O solutions of P(IPMAm/IPAAm) copolymers, measured at temperatures below the respective phase transition, resemble the spectra of PIPMAm/PIPAAm mixtures with the same molar ratio of both components (cf. Figs. 1(a) and 6(a)). The main difference, i.e. that for copolymers some lines are apparently broader (this holds mainly for main-chain CH_2 and CH resonances—lines $a+i+k$ in Figs. 1 and 6, and for α-CH_3 resonance—line b) is due to the fact that chemical shifts of these groups in various sequences of IPMAm and IPAAm units in the copolymer can be slightly different and a distribution of such overlapping resonances results in the observed broadening. Similarly as with PIPMAm/PIPAAm mixtures, also with P(IPMAm/IPAAm) copolymers the phase separation at elevated temperatures results in the reduction of integrated intensities of all copolymer lines (Fig. 6(b)). The temperature dependences of the phase-separated fraction as determined from integrated intensities of side-chain CH band (both IPMAm and IPAAm monomeric units contribute to this band) for P(IPMAm/IPAAm) copolymers of various composition, are shown in Fig. 7. Contrary to PIPMAm/PIPAAm mixtures (cf. Fig. 3) and in accord with Ref. [17], only single phase transition was found for P(IPMAm/IPAAm) random copolymers. At the same time, it follows from Fig. 7 that phase-transition temperatures strongly depend on the composition of the copolymer; increasing amount of PIPMAm component in the copolymer gradually shifts the transition region to higher temperatures. Interestingly enough, while the transition temperatures for the neat

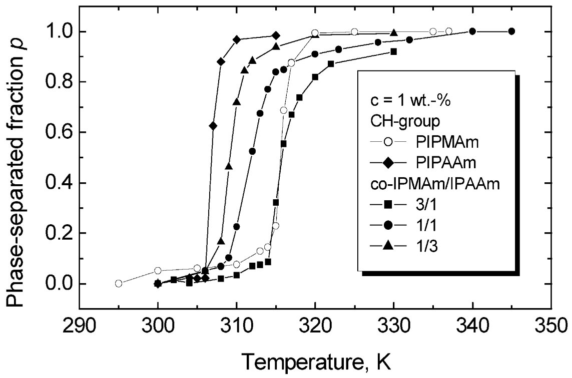


Fig. 7. Temperature dependences of the phase-separated fraction p as determined from side-chain CH band in D_2O solutions ($c = 1$ wt%) of P(IPMAm/IPAAm) copolymers of various composition.as well as for neat PIPAAm and PIPMAm.

PIPAAm and for the copolymer P(IPMAm/IPAAm = 1/3) differ by approx. 3 K, the transition temperatures for the neat PIPMAm and the copolymer P(IPMAm/IPAAm = 3/1) are virtually the same. This is documented also in Fig. 8, where the phase-separated fraction of IPMAm monomeric units alone, as determined from integrated intensities of α-CH_3 band of IPMAm units, is plotted as function of temperature for copolymer P(IPMAm/IPAAm = 3/1) and for the neat PIPMAm. The fact that the dependence of the transition temperatures on the molar composition of the copolymers is not linear in the whole range of compositions follows from Fig. 9 where the temperatures in the middle of the transition interval (corresponding to $p = 0.5$ in Fig. 7) are plotted as function of the molar fraction of IPMAm in the copolymer. For copolymer P(IPMAm/IPAAm = 3/1) a distinct departure from the linear dependence is visible. The phase separation behaviour of the copolymer P(IPMAm/IPAAm = 3/1) is probably determined by relatively large portion of sequences containing IPMAm units of sufficient length that show phase transition at similar temperatures as PIPMAm homopolymer.

A brief comparison of our results as obtained on random copolymers P(IPMAm/IPAAm) and recently published results based on cloud point measurements [17] seems to be desirable. For neat PIPAAm, as well as for all compositions of P(IPMAm/IPAAm) copolymers in our study, the temperatures shown in Fig. 9 (corresponding to $p = 0.5$) agree well with temperatures based on cloud points; in all cases the differences do not exceed 1 K. For neat PIPMAm the difference is significantly larger; the transition temperature shown by cloud point measurements is by 3 K higher than the respective temperature in Fig. 9. This discrepancy can be attributed to the cloud point behaviour found for PIPMAm solutions in water by Netopilík et al. [22] who have shown that in this case there is a rather long induction time (~30 min for $c \cong 1$ wt%) before any turbidity is detected. Taking into account the heating rate 0.1 K/min used in Ref. [17] and induction time mentioned above, this can point out why the transition temperature detected in cloud point measurements is by 3 K higher. In contrast to PIPMAm, for PIPAAm in aqueous solutions the induction time seems to be negligibly small [1,22].

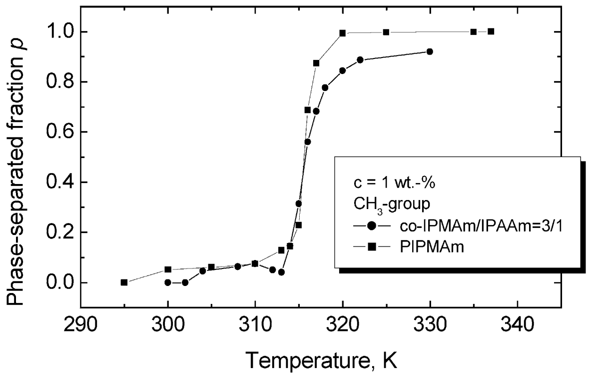


Fig. 8. Temperature dependences of the phase-separated fraction for PIPMAm component (as determined from α-CH_3 band of PIPMAm) in D_2O solutions of P(IPMAm/IPAAm = 3/1) copolymer and neat PIPMAm.

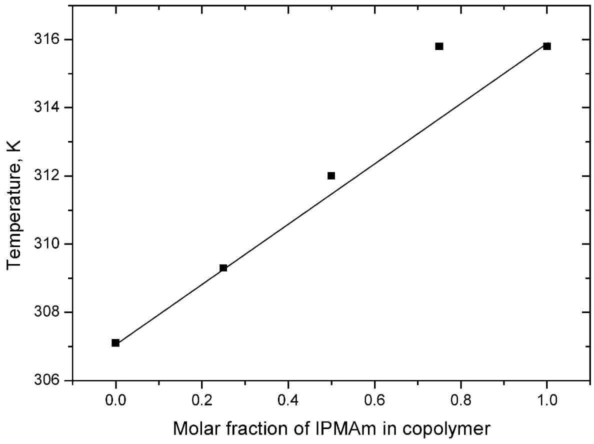


Fig. 9. The temperatures in the middle of the transition interval (corresponding to $p = 0.5$ in Fig. 7) as function of the molar fraction of IPMAm in the P(IPMAm/IPAAm) copolymers.

4. Conclusions

Phase separation transitions in D_2O solutions of PIPMAm/PIPAAm mixtures and corresponding P(IPMAm/IPAAm) random copolymers were studied using ^1H NMR spectroscopy; this method allowed us to follow the phase separation for one component (PIPMAm component in our case) in the mixture or copolymer separately. In accord with results of cloud point measurements [17], two distinct transitions were detected for PIPMAm/PIPAAm mixtures, while only single transition was found for P(IPMAm/IPAAm) copolymers. In mixtures, the LCST behaviour of the PIPAAm component (appears at lower temperatures) is not affected by the presence of PIPMAm molecules in the solution, but the phase transition of the PIPMAm in the mixture (appears at higher temperatures) is affected by the presence of the phase-separated PIPAAm component and depends on the concentration of the solution. Similar behaviour was previously found for PIPMAm/PVME mixtures [16] where our recent results indicate that the effect of the phase-separated PVME component on the transition temperatures of the PIPMAm component might be associated with the changed order of water molecules. For P(IPMAm/IPAAm) random copolymers a distinct departure from the linear dependence of the transition temperatures on the copolymer composition was found for a sample with predominating IPMAm monomeric units (P(IPMAm/IPAAm = 3/1)).

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