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Effect of time on the hydration and temperature-induced phase separation in aqueous polymer solutions. ^{1}H NMR study

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Abstract

Dehydration during temperature-induced phase separation in D_2O solutions of poly(vinyl methyl ether) (PVME), poly(*N*-isopropylmethacrylamide) (PIPMAm) and poly(*N*-isopropylacrylamide) (PIPAAm) was followed from time dependences of NMR spin–spin relaxation times T_2 of HDO. Both the time characterizing the exclusion of the water from mesoglobules (manifested by the increase in T_2 values) and the induction period which precedes the increase in T_2 values, increased in the order PVME < PIPMAm < PIPAAm. For D_2O solutions of PIPMAm/PVME (or PIPMAm/PIPAAm) mixtures a direct connection between the state of the mesoglobules (hydrated or dehydrated) formed by the component with lower LCST (PVME, PIPAAm) and the temperatures of the phase transition of the PIPMAm component was established by NMR spectroscopy.

Keywords: Thermosensitive polymers; Hydration; ^{1}H NMR spectroscopy

1. Introduction

It is well known that some acrylamide-based polymers, including poly(*N*-isopropylacrylamide) (PIPAAm) and poly(*N*-isopropylmethacrylamide) (PIPMAm), and some other polymers like poly(vinyl methyl ether) (PVME), in aqueous solutions exhibit a lower critical solution temperature (LCST). They are soluble at low temperatures, but heating above the LCST results in phase separation which is especially at higher polymer concentrations macroscopically manifested by milk-white turbidity of the solution [1,2]. For PVME aqueous solutions the LCST is around 308 K, i.e., well above the temperature of the glass transition of PVME in bulk where values in the range $T_g = 191–251$ K are reported [3]. This is in contrast to acrylamide-based polymers in aqueous solutions where the LCST is well below the respective T_g; for PIPAAm ($T_g = 403$ K) [3] and PIPMAm ($T_g = 449$ K) [4] the LCSTs are around 307 and 315 K, respectively. On the molecular level, both phase separation in solutions and similar volume phase transition (collapse) in crosslinked hydrogels are assumed to be a macroscopic manifestation of a coil–globule transition, as was shown for PIPAAm in water, e.g., by light scattering [2,5], followed by further aggregation and formation of colloidally stable mesoglobules defined as equally sized multichain aggregates containing more than one and less than all polymer chains [2,6]. The phase transition is probably associated with the changed balance between various types of interactions, mainly hydrogen bonds and hydrophobic interactions [2]. Their thermosensitivity makes these systems interesting for possible biomedical and technological applications, e.g., as drug release systems [7,8]. Though phase transitions in aqueous solutions of PIPAAm and PVME were extensively studied by various methods (cloud point, viscometric, calorimetric, diffusion, viscoelastic, infrared and Raman measurements) and the results obtained were recently reviewed [2], the application of NMR spectroscopy in the investigations of the phase separation in aqueous solutions of thermoresponsive polymers was rather seldom [9–13]. Together with cited

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papers, more recently we have also shown that ^{1}H NMR spectroscopy can be a suitable method in the investigations of temperature-induced phase separation on molecular level and applied this method to D_2O solutions and gels of poly(*N*,*N*-diethylacrylamide) (PDEAAm) [14,15], PIPMAm (including P(IPMAm-sodium methacrylate copolymers) [16,17], PIPAAm [18], PVME [19–23], as well as PIPMAm/PVME mixtures [17] and PIPMAm/PIPAAm mixtures and random copolymers [18]. A similar NMR behaviour was found for linear and crosslinked systems, indicating the formation of compact globular-like structures (mesoglobules) during the phase transition. Two phase transitions were detected for PIPMAm/PVME and PIPMAm/PIPAAm mixtures. While the phase transition temperatures of PVME or PIPAAm component (appears at lower temperatures) are not affected by the presence of PIPMAm in the mixtures, the temperatures of the phase transition of PIPMAm component (appears at higher temperatures) are affected by the phase separation of PVME or PIPAAm component [17,18]. For D_2O solutions of PVME and PIPMAm/PVME mixtures, ^{1}H NMR relaxation measurements revealed that a certain portion of water molecules is bound at elevated temperatures in phase-separated mesoglobules in semidilute and concentrated solutions [17,19,21,22]; with time this bound water is slowly released from globular-like structures. On the contrary, dehydration of PVME chains is rapid in dilute solutions [22]. A slow exchange and relatively weak hydrogen bonding were found from the position of the separate NMR signal for bound HDO in highly concentrated PVME/D_2O solutions (polymer concentrations $c = 20$–60 wt%) [23]. At the same time, the molar ratio [PVME monomeric unit]/[bound D_2O] $\cong 2.7$ is constant in the range of concentrations $c = 20$–60 wt%, i.e., the polymer concentration in the polymer-rich phase (mesoglobules) is 89 wt%, in accord with the recently published phase diagram [24]. From phase diagrams of PIPAAm aqueous solutions it follows that also in these systems the polymer concentration in the polymer-rich phase is around 80 wt% [2,25]. According to the phenomenological classification, while PIPAAm belongs to type II polymers where the molecular weight does not affect the position of the minimum in the demixing curves, PVME is a type III polymer where phase diagram presents two critical points at low and high polymer concentrations [2,24,25].

In the present work, we concentrated on the dehydration process during the temperature-induced phase separation in D_2O solutions of several thermoresponsive polymers. We tried to compare the dehydration behaviour in PVME, PIPAAm and PIPMAm aqueous solutions. Moreover, a connection between the state of the globular-like structures (hydrated or dehydrated) of the component with lower LCST (PVME, PIPAAm) and the phase separation of the component with higher LCST (PIPMAm) in D_2O solutions of PIPMAm/PVME and PIPMAm/PIPAAm mixtures was also studied. From the methodical point of view, we combined the measurements of time dependences of spin–spin relaxation times T_2 of HDO molecules and temperature dependences of absolute integrated intensities of polymer signals in high-resolution ^{1}H NMR spectra, that make it possible to determine the temperature dependences of the phase-separated fraction [15–20].

2. Experimental

2.1. Samples

PVME (purchased from Aldrich, supplied as 50 wt% aqueous solution; molecular weight determined by SEC in THF: $M_w = 60\,500$, $M_w/M_n \cong 3$; tacticity by ^{1}H NMR: 59% of isotactic diads [20]) was used after drying to prepare PVME/D_2O (99.9% of deuterium) solutions. Polymerization of IPMAm was initiated by 4,4′-azobis(4-cyanopentanoic acid) and carried out in ethanol/water mixture (94/4 by volume); the volume fraction of the monomer in the mixture was 0.2 [16–18]. PIPAAm was prepared with photo-initiator Darocur ($\sim$2 wt% on monomer) and by UV polymerization ($\lambda = 254$ nm) in ethanol at 278 K for 1 h (volume fraction of monomer was 0.15) [18]. All samples of D_2O solutions of desired polymer concentration (mainly $c = 1$, 5 and 10 wt%) 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

^{1}H 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 $\pm 1\%$. The ^{1}H spin–spin relaxation times T_2 of HDO were measured using the CPMG [26] pulse sequence $90°_x$–(t_d–$180°_y$–t_d)-acquisition with $t_d = 5$ ms and relaxation delay 40–60 s. In all measurements the temperature was maintained constant within ± 0.2 K using a BVT 3000 temperature unit.

3. Results and discussion

Fig. 1 shows an example high-resolution ^{1}H NMR spectra of PIPAAm/D_2O solution ($c = 5$ wt%) measured at two slightly different temperatures (300 and 310 K). Moreover, spectra at elevated temperature were measured both immediately after this temperature was reached and after keeping the sample for 125 h at 310 K. The assignment of resonances to various types of protons of PIPAAm is shown directly in a spectrum measured at 300 K, i.e., below the LCST transition. The strong line on the left is a signal of HDO. The most important effect observed in the spectrum measured at higher temperature (310 K) is a marked decrease in the integrated intensity of all PIPAAm lines; with the exception of the CH_3 protons, other signals of PIPAAm almost disappeared from the spectrum. This is due to the fact that at temperatures above the LCST the mobility of most PIPAAm units is reduced to such an extent that corresponding lines become too broad to be detected in high-resolution spectra. A narrow component with unrestricted mobility (with much smaller integrated intensity) that is directly detected in high-resolution NMR

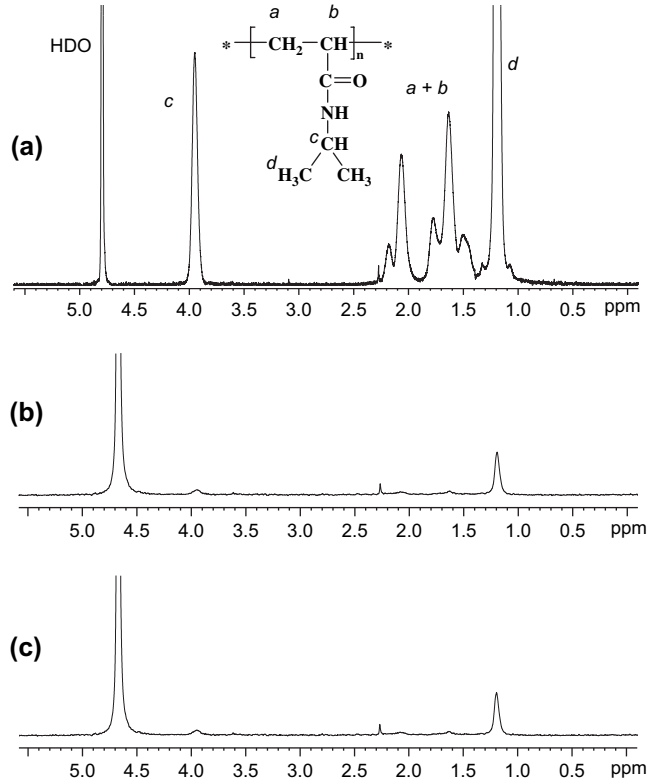

Fig. 1. High-resolution ^{1}H NMR spectra of PIPAAm in D_2O ($c = 5$ wt%) measured at 300 K (a) and 310 K (b, c). Spectra at 310 K were recorded under the same instrumental conditions immediately after reaching this temperature (b) and after keeping the sample for 125 h in magnet at 310 K (c).

spectra corresponds to PIPAAm units in the dilute (polymer-pure) phase. The depicted changes of the NMR spectra have been previously observed for D_2O solutions of acrylamide-based polymers [14–16], PVME [19–23] and mixtures PIPMAm/PVME and PIPMAm/PIPAAm [17,18]. They confirm that reaching LCST results in marked line broadening of a major part of polymer units, evidently due to phase separation and formation of rather compact mesoglobules. From Fig. 1, it also follows that no reduction of integrated intensities above LCST was observed for HDO signal. The integrated intensities of HDO monotonously decrease with absolute temperature, as expected, so confirming that all HDO molecules are directly detected in ^{1}H NMR spectra in the whole range of temperatures. Fig. 1 also shows that spectra measured at 310 K immediately after the transition and after keeping the sample at this temperature for 125 h are the same. 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); then the integrated intensities are constant [15,19,20].

Fig. 2 shows the results of the measurements of spin–spin relaxation times T_2 of HDO molecules in D_2O solutions of PVME (a), PIPMAm (b) and PIPAAm (c) (polymer concentration $c = 5$ wt%). Similarly, as we previously reported for

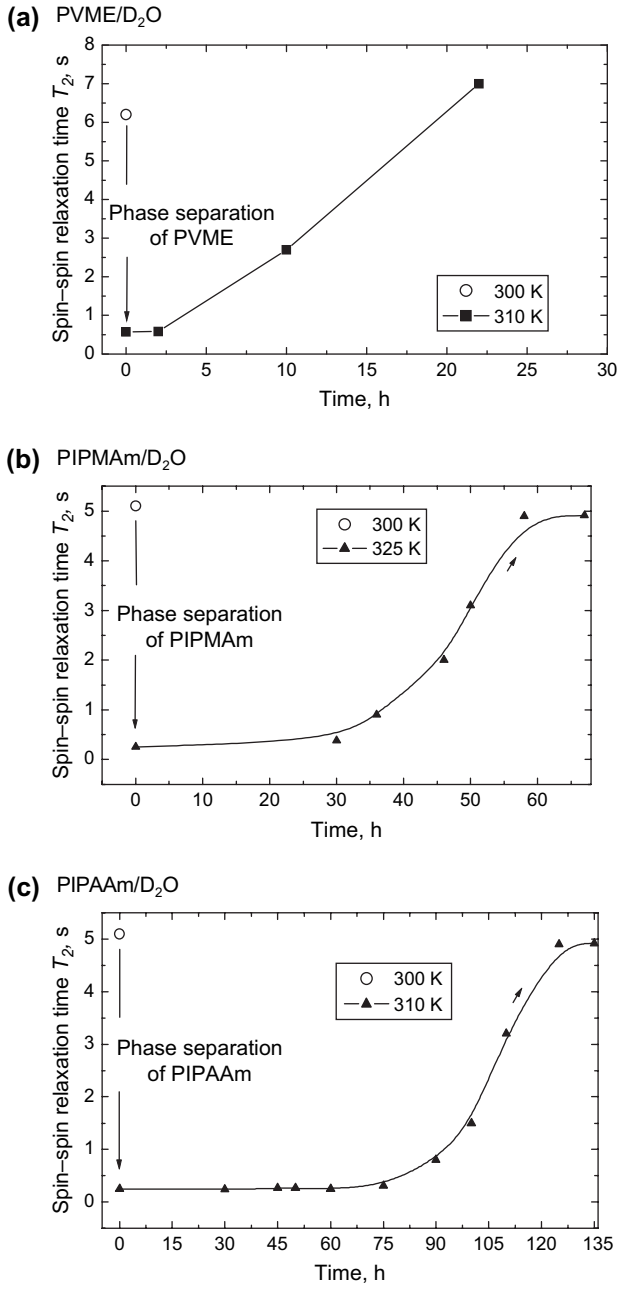

Fig. 2. Time dependences of spin–spin relaxation time T_2 of HDO in D_2O solutions ($c = 5$ wt%) of PVME (a), PIPMAm (b) and PIPAAm (c) measured at 310 K (a, c) and 325 K (b).

PVME/D_2O solutions [22], also for D_2O solutions of PIPMAm and PIPAAm the T_2 values at temperatures above the phase transition (in our case 325 and 310 K for PIPMAm and PIPAAm solutions, respectively) were 1 order of magnitude shorter than those at 300 K, i.e., at temperatures below the transition. This shows that also in D_2O solutions of PIPMAm and PIPAAm there is a portion of HDO molecules that exhibits a lower, spatially restricted mobility, similarly as reported for PVME/D_2O solutions. A contribution from the chemical exchange might be also important [27]. Evidently, this portion corresponds to HDO molecules bound in phase-separated

globular-like structures. Single-exponential character of T_2 relaxation curves indicates a fast exchange between bound and free sites regarding T_2 values ($\sim$0.5 s), i.e., the residence time of the bound HDO has to be $\leq$50 ms. In such case, the observed relaxation time $T_{2,obs}$ is given as [22,23] follows:

$$(T_{2,obs})^{-1} = (1-f)(T_{2F})^{-1} + f(T_{2B})^{-1} \quad (1)$$

where subscripts F and B correspond to "free" and bound states, respectively, and f is the fraction of bound HDO.

When the investigated sample was kept for all the time in the magnet of NMR spectrometer at elevated temperature and the time dependence of T_2 values was measured, then, as again previously reported for PVME/D_2O solutions [22], T_2 values of HDO very slowly increased with time, reaching after some time a similar value as observed at temperature below the transition. All studied solutions were cloudy at temperatures above the LCST and we did not observe visually any precipitation (sedimentation) of the phase-separated part even after a very long time ($\sim$days). This means that studied systems were colloidally stable solutions, where this term refers to solutions containing particles that do not aggregate at a significant rate in a thermodynamically unfavourable medium [2]. Therefore, the obtained results evidence that similar to PVME/D_2O solutions, also in D_2O solutions of PIPMAm or PIPAAm, the water originally bound in mesoglobules is with time very slowly released (squeezed out) from these structures. In all these systems, the mesoglobules probably exhibit a sponge-like character where molecules of water can be accommodated. Though the water releasing process is in principle similar for all three investigated systems, from Fig. 2 it follows that there are significant differences especially for PVME on the one hand, and PIPMAm and PIPAAm on the other hand. In all cases, the water releasing process can be characterized by two different time parameters. The first parameter characterizes directly the process of expelling water molecules from mesoglobules. During this time the T_2 values increase until the similar value is reached as at temperatures below the transition. This time parameter is probably mainly connected with the disruption of hydrogen bonds between water molecules and hydrophilic polymer groups. This time is approx. 20, 30 and 50 h for D_2O solutions of PVME, PIPMAm and PIPAAm, respectively (cf. Fig. 2). Even much larger differences exist in the second time parameter which characterizes the "plateau" in the time dependence of spin–spin relaxation time T_2, i.e., during this time T_2 values do not change. While for PVME/D_2O solution this "plateau" exists only for approx. 2 h, for PIPMAm/D_2O solution T_2 values do not change for 30 h and for PIPAAm/D_2O solution do not change even for 75 h. Some rearrangements of polymer segments in mesoglobules probably occur during this induction period before they reach the state when the water bound in mesoglobules can be released. The main reason for the large difference in this induction period (and also in the time parameter characterizing the process of expelling water from mesoglobules) as found for PVME on the one hand and for PIPMAm and PIPAAm on the other hand is evidently much higher mobility of PVME segments that exists in rubbery state in mesoglobules, in comparison with PIPMAm or PIPAAm segments that are in glassy state in mesoglobules. Nevertheless, large differences in the induction period exist also between PIPMAm and PIPAAm where the induction time for PIPAAm is 2.5 times longer than that for PIPMAm, though the temperature of the glass transition T_g of PIPMAm is higher by 46 K in comparison with PIPAAm [3,4]. We assume that this difference is due to the more effective packing of PIPAAm segments in globular-like structures while for PIPMAm the hydrophobic groups cannot interact in the most favourable manner due to the sterical hindrance induced by α-methyl groups. The same argument has been previously used to explain that despite the fact that PIPMAm is more hydrophobic than PIPAAm, its phase transition appears at higher temperatures (by 8 K) [28].

In addition to our former NMR relaxation study [22], DSC measurements also revealed a slow process in PIPAAm and PVME aqueous solutions of various polymer concentrations where time dependence of apparent specific heat capacity was observed during $\sim$20 h [24,29]. Authors attributed this behaviour to morphological changes and/or interphase development. At the same time, for PIPAAm aqueous solutions the time dependence of heat capacity was detected in the time interval where T_2 values of HDO are reduced and are constant (cf. Fig. 2c), so indicating that globular-like structures still contain bound water.

As mentioned in Section 1, a slow exchange regime follows from the existence of two well-resolved NMR signals of bound and "free" HDOs as detected for highly concentrated ($c \geq 20$ wt%) PVME/D_2O solutions [23]. In this case the spin–spin relaxation times T_2 of bound HDO are 2 orders of magnitude shorter in comparison with those for "free" HDO. At the same time in these PVME/D_2O solutions the spin–spin relaxation time T_2, as determined for the main HDO signal corresponding to "free" HDO, was at temperatures above the phase transition substantially longer than the respective value at temperatures below the phase transition. This is due to the fact that at higher temperature the respective HDO molecules do not interact with PVME chains while at lower temperature a significant portion of HDO molecules interact with polymer forming, e.g., hydrogen bonds and their motions are consequently somewhat restricted [23]. In ^{1}H NMR spectra of highly concentrated PIPMAm/D_2O solution ($c = 30$ wt%) there is only one signal of HDO; we did not detect any separate signal for "bound" HDO. Moreover, T_2 value determined for HDO at the temperature above the phase transition (325 K, $T_2 = 1.0$ s) was significantly shorter in comparison with the temperature below the phase transition (300 K, $T_2 = 3.3$ s). These values indicate that contrary to PVME/D_2O systems, in highly concentrated PIPMAm/D_2O solution ($c = 30$ wt%) there is still a fast exchange between bound and "free" HDO molecules, similarly as it holds for lower concentrations.

Fig. 3 shows the results obtained for D_2O solutions of PIPMAm/PVME mixtures (molar ratio of both components 1/1) related to the connection between the state of the PVME

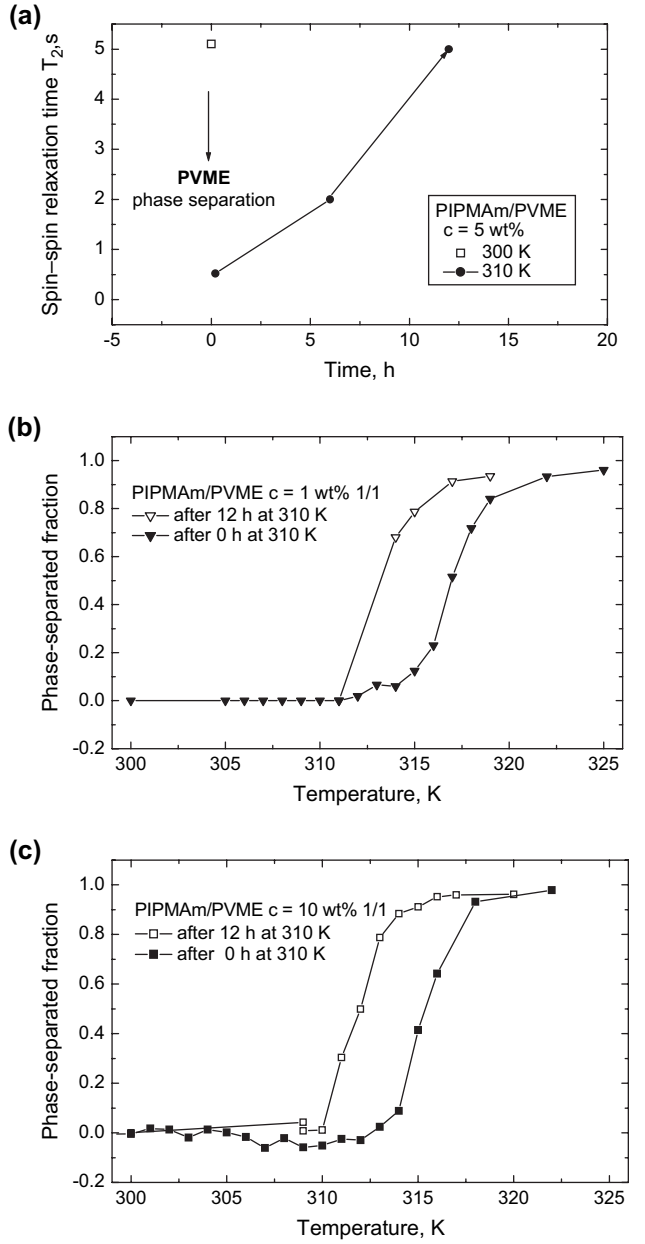

Fig. 3. Time dependence of spin–spin relaxation time T_2 of HDO at 310 K (after phase separation of PVME component) (a) and temperature dependences of the phase-separated fraction p of PIPMAm (b, c) in D_2O solutions of PIPMAm/PVME mixtures (molar ratio of monomeric units 1/1, $c = 5$ wt% (a), 1 wt% (▼, ▽) (b), and 10 wt% (■, □) (c)). Temperature dependences in the parts (b) and (c) were measured immediately after phase separation of PVME component (filled symbols) or after keeping the samples for 12 h at 310 K (open symbols).

globular-like structures (hydrated or dehydrated) and temperatures of the phase transition of the PIPMAm (component with higher LCST). From Fig. 3a, it follows that after increasing the temperature to 310 K and keeping the sample for 12 h at this temperature, after initial drop, the T_2 values slowly increased with time similarly as reported for neat PVME/D_2O solution (cf. Fig. 2a), indicating a slow release of originally bound water (HDO) from PVME mesoglobules. Fig. 3b, c shows temperature dependences of the phase-separated fraction p of PIPMAm component as determined from absolute integrated intensities of PIPMAm signals in high-resolution ^{1}H NMR spectra. In accord with our previous publications [15–20] we define the phase-separated PIPMAm fraction as fraction of PIPMAm units in concentrated, polymer-rich phase; the mobility of these PIPMAm units is significantly lower in comparison with that at temperatures below the LCST transition. We determined the values of fraction p of phase-separated PIPMAm units (units in mesoglobules) from the following relation:

$$p = 1 - (I/I_0) \tag{2}$$

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 [15–20]. In Fig. 3b, c, the temperature dependences of the fraction p are shown for two concentrations of the solutions, $c = 1$ wt% (b) and 10 wt% (c). The fact that for $c = 10$ wt% the transitions appear always at lower temperatures (by ~2 K) in comparison with $c = 1$ wt% is probably a consequence of the preferred polymer–polymer contacts at higher concentrations, allowing hydrophobic interactions to predominate at lower temperatures [17]. From Fig. 3b, c, it further follows even more interesting finding that in both cases the transition temperatures of PIPMAm component as obtained after previously keeping the sample for 12 h at 310 K, i.e., when virtually all water originally bound in PVME mesoglobules was released, were lower by ~4 K in comparison with the case when the temperature dependences were measured immediately after phase transition of PVME component, i.e., under conditions when a certain amount of water was bound in PVME globular-like structures. At the same time the transition temperatures of PIPMAm component, as obtained after keeping the samples for 12 h at 310 K, were somewhat lower in comparison with the neat PIPMAm/D_2O solutions where the transition temperatures do not depend on concentration of the solution [17]. We observed similar behaviour, as shown in Fig. 3 for PIPMAm/PVME mixtures, also for PIPMAm/PIPAAm mixtures in D_2O. Also in this case the partial release of originally bound water from PIPAAm globular-like structures as manifested by the increase of spin–spin relaxation times T_2 of HDO resulted in the shift of the transition temperatures of PIPMAm component towards lower temperatures. However, in comparison with PIPMAm/PVME mixtures the temperature shift was smaller for PIPMAm/PIPAAm mixtures. This might be at least partly due to the fact that PIPMAm/PIPAAm sample was kept in the magnet of NMR spectrometer only for 90 h at 310 K and probably only part of originally bound HDO was released (a complete release of bound HDO would require to keep the sample for 125 h at 310 K, cf. Fig. 2c). The obtained results corroborate that the temperatures of the phase separation (transition) are affected by the arrangement and by the order of water molecules. For D_2O solutions of PIPMAm/PVME or PIPMAm/PIPAAm mixtures the arrangement of water molecules is affected by the phase separation of polymeric component that occurs at lower temperatures (PVME or PIPAAm)

because a part of water molecules is bound in PVME (or PIPAAm) mesoglobules. With time this bound water is slowly released from these mesoglobules, arrangement of water molecules is changed and subsequently the phase transition of PIPMAm component appears at lower temperatures. We assume that this behaviour might be important for potential practical applications.

4. Conclusions

The dehydration behaviour during temperature-induced phase separation in D_2O solutions of PVME, PIPMAm and PIPAAm was compared on the basis of time dependences of NMR spin–spin relaxation times T_2 of HDO. A slow release of originally bound water from the respective mesoglobules was observed in all cases. Both the time characterizing the exclusion of the water from mesoglobules (it is manifested by the increase in T_2 values of HDO), and especially the induction period which precedes the increase in T_2 values, increased in the order PVME < PIPMAm < PIPAAm. The large differences in the induction period as found for PVME on the one hand and for PIPMAm and PIPAAm on the other hand are evidently in connection with the fact that while PVME segments exist in rubbery state in mesoglobules, PIPMAm or PIPAAm segments in mesoglobules are in glassy state. More effective packing of PIPAAm segments in globular-like structures in comparison with PIPMAm is probably the reason that the induction time for PIPAAm is 2.5 times longer than for PIPMAm.

For D_2O solutions of PIPMAm/PVME (or PIPMAm/PIPAAm) mixtures a direct connection between the state of the globular-like structures (hydrated or dehydrated) formed by the component with lower LCST (PVME, PIPAAm) and the temperature of the phase transition of the PIPMAm component was established by NMR spectroscopy. Transition temperatures of PIPMAm component as obtained after previously keeping the sample for 12 h at 310 K, i.e., until PVME mesoglobules were almost completely dehydrated, were lower by $\sim$4 K in comparison with the case when the temperature dependences were measured immediately after phase transition of PVME component, i.e., when PVME mesoglobules contained a certain amount of bound water. The obtained results show that the temperatures of the phase transition are affected by arrangement of water molecules in the investigated system.

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