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^{1}H NMR Study on the Hydration during Temperature-Induced Phase Separation in Concentrated Poly(vinyl methyl ether)/D_2O Solutions

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ABSTRACT: A certain portion of spatially restricted bound water (HDO) was established for concentrated PVME/D_2O solutions at temperature above the LCST transition from the measurements of ^{1}H NMR spectra and ^{1}H spin−spin relaxation times T_2 of HDO. The fast and slow exchange regime between bound and free water was revealed for polymer concentrations $c = 2-10$ wt % and $c = 20-60$ wt %, respectively. For the latter case, the residence time of bound HDO $\tau \gg 2.7$ ms and relatively weak hydrogen bonding follow from the position of the separate NMR signal of bound HDO. For polymer concentrations $c = 20-60$ wt %, the spin−spin relaxation time T_2 of bound HDO and the molar ratio [PVME monomeric unit]/[bound D_2O] remain virtually constant and equal to $T_2 \cong 40$ ms and [PVME]/[bound D_2O] $\cong 2.7$ on average, thus indicating a direct connection of the fraction of bound water with the conformational structure of phase-separated PVME.

Introduction

Poly(vinyl methyl ether) (PVME) is a water-soluble polymer that similarly to some acrylamide-based polymers in aqueous solution exhibits a lower critical solution temperature (LCST); i.e., it is soluble at low temperatures, but heating above the LCST results in phase separation. For PVME aqueous solutions the LCST is around 308 K,[1,2] i.e., at least 60 K above the temperature of the glass transition of PVME in bulk.[3] This is in contrast to acrylamide-based polymers in aqueous solutions where the LCST is well below the respective T_g.[4] On the molecular level, both phase separation in solutions and collapse transition in cross-linked hydrogels are assumed to be a macroscopic manifestation of a coil−globule transition followed by aggregation, as shown for acrylamide-based polymers in water by light scattering and small-angle neutron scattering.[5−9] The phase transition in PVME/water solutions was studied by cloud point, calorimetric, viscometric, viscoelastic, infrared, and Raman measurements.[1,2,10−16] It was found that aqueous PVME solutions exhibit a flat and wide bimodal LCST miscibility gap.[2] Similarly to acrylamide-based polymers, the transition in PVME/water systems is probably associated with competition between hydrogen-bonding and hydrophobic interactions.[11,14] Viscoelastic measurements indicate that formation of physical network accompanies the phase separation in PVME/water solutions.[14] From infrared spectra it follows that most of methyl groups of PVME are dehydrated above the LCST, whereas there is only partial dehydration of the ether groups above the LCST.[13]

Recently, we used ^{1}H NMR spectroscopy to investigate changes in the structure and dynamics during temperature-induced phase transition in PVME/D_2O solutions and gels.[4,17−20] We also applied ^{1}H NMR to investigate phase transitions in D_2O solutions of PVME/poly(*N*-isopropylmethacrylamide) (PIPMAAm) mixtures.[20,21] Both for linear and cross-linked systems, the phase transition is manifested by line broadening for a major part of PVME units, indicating the formation of more compact globular-like structures. The minority mobile component, which does not take part in the phase transition, mostly consists of low-molecular-weight fraction of PVME.[20] Measurements of spin−spin relaxation times T_2 of both PVME and water (HDO) protons evidenced that for polymer concentrations in the range 1−10 wt % a portion of water molecules is bound in PVME globular structures. With time this originally bound water is slowly released from globular-like structures. On the contrary, from T_2 measurements it follows that dehydration of PVME chains is rapid in dilute solutions.[20]

In the present study we extended our ^{1}H NMR investigations on concentrated PVME/D_2O solutions (polymer concentrations > 10 wt %). Some results for concentrations ≤ 10 wt % are also reported for comparison. We were mainly interested in behavior of water during temperature-induced phase separation in these systems. From methodical point of view we mostly combined the measurements of ^{1}H NMR spectra and spin−spin relaxation times T_2 of residual HDO to this purpose.

Experimental Section

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[18]) was used after drying to prepare PVME/D_2O (99.9% of deuterium) solutions of desired concentration in the range $c = 0.1-60$ wt %. All PVME/D_2O samples 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.

NMR Measurements. High-resolution ^{1}H NMR spectra were recorded with a Bruker Avance 500 spectrometer operating at 500.1 MHz. Typical measurement conditions were as follows: 90° pulse width 12 μs, relaxation delay 10 s, spectral

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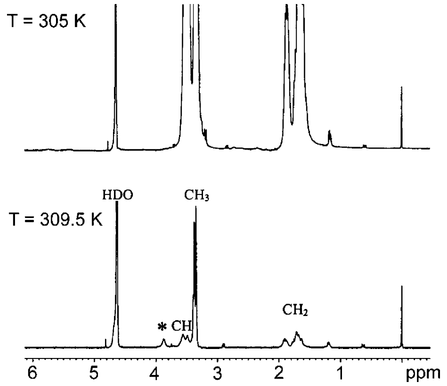

Figure 1. ^{1}H NMR spectra of PVME/D_2O solution (c = 20 wt %) at 305 and 309.5 K. Line of the bound HDO is marked by asterisk. The spectra were obtained using spin-echo pulse sequence $90°_x{-}t_d{-}180°_y{-}t_d$−acquisition with t_d = 5 ms to suppress the broad lines from protons of phase-separated PVME that exist at 309.5 K.

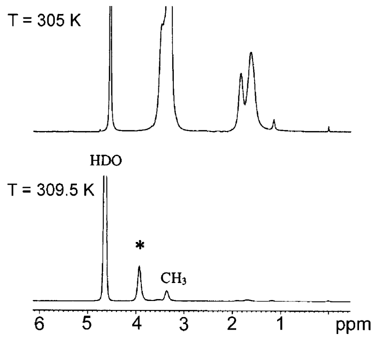

Figure 2. ^{1}H NMR spectra of PVME/D_2O solution (c = 60 wt %) at 305 and 309.5 K. Line of the bound HDO is marked by asterisk. The spectra were obtained using spin-echo pulse sequence $90°_x{-}t_d{-}180°_y{-}t_d$−acquisition with t_d = 5 ms to suppress the broad lines from protons of phase-separated PVME that exist at 309.5 K.

width 4735 Hz, acquisition time 1.73 s, 8 or 16 scans. ^{1}H NMR spectra were also obtained using the spin-echo[22] pulse sequence $90°_x{-}t_d{-}180°_y{-}t_d$−acquisition with t_d = 5 ms and relaxation delay 80 s. The ^{1}H spin−spin relaxation times T_2 of the solvent (residual HDO) were measured using the same instrument and the CPMG[22] pulse sequence $90°_x{-}(t_d{-}180°_y{-}t_d)_n$−acquisition with t_d = 5 ms, relaxation delay 80−100 s, and 8 scans. The total time for T_2 relaxation was an array of ~30 values. The relative error for T_2 values did not exceed ±5%. Spin−lattice relaxation times T_1 of HDO were measured using an inversion recovery pulse sequence $180°{-}\tau_D{-}90°$ with 8 scans separated by a relaxation delay of 80−200 s; 15−20 τ_D values were used. In all measurements the temperature was maintained constant within ±0.2 K with a BVT 3000 temperature unit.

Results and Discussion

While for PVME/D_2O solutions with $c \leq 10$ wt % there was only one signal of HDO in ^{1}H NMR spectrum at all temperatures (cf. Figure 1 in refs 18 and 20), for higher concentrations and temperature above the LCST transition a new signal of HDO appears with ~0.74 ppm smaller chemical shift in comparison with the main HDO signal (Figure 1). The relative intensity of this signal increases with increasing concentration of the solution, as shown in Figure 2 and Table 1. The spectra in Figures 1 and 2 were obtained using spin-echo pulse sequence $90°_x{-}t_d{-}180°_y{-}t_d$−acquisition with t_d = 5 ms to suppress the broad lines from fast relaxing protons of phase-separated PVME with $T_2 \leq 1$ ms[20,23] that exist at 309.5 K. From Figures 1 and 2 one can also see that at 309.5 K due to the formation of rather compact globular-like structures all intensities of PVME lines are markedly reduced because they correspond only to mobile PVME segments which do not take part in the phase separation, as mentioned in the Introduction. When the measurement of ^{1}H NMR spectra was repeated at 305 K after previous heating to 309.5 K, the new HDO signal completely disappeared and appeared again after reheating to 309.5 K back, so excluding the hypothetical possibility that this signal might correspond to some additional chemical species formed in studied solutions. The new HDO signal at ~3.88 ppm that appears only at the temperature above the phase transition and does not exist at temperatures below the phase transition evidently corresponds to HDO bound in globular-like structures. After adding a small amount (~3 μL) of H_2O into PVME/D_2O solution (c = 30 wt %), integrated intensities of both HDO lines increased ~3.6 times relative to intensities of PVME lines while the ratio of integrated intensities of both HDO lines remained unchanged; this again evidences that the new HDO line at ~3.88 ppm corresponds to bound HDO. In highly concentrated PVME/D_2O solutions therefore the condition for the slow exchange between bound and "free" water (HDO) is fulfilled. From the condition[24] $1/\tau \ll \Delta\upsilon_p$, where τ is the residence time and $\Delta\upsilon_p$ is the difference of the respective chemical shifts in hertz, it follows that for the residence time of bound HDO molecules it holds $\tau \gg 2.7$ ms. It is well-known that hydrogen bonding leads to larger chemical shifts in ^{1}H NMR spectra.[24,25] The fact that the chemical shift of the bound HDO does not depend on the polymer concentration and is ~0.74 ppm smaller in comparison with the main HDO signal indicates that for the bound HDO the hydrogen bonding is substantially weaker in comparison with that existing in neat water (D_2O). Recent study[26] of interaction of water and model compound of PVME shows that the strength of the hydrogen bond between water and ether oxygen of PVME is even larger than that between water. Therefore, an arrangement of water molecules involved in hydrogen bonding with PVME unit is changed for the bound water and/or a weaker so-called quasi-hydrogen bond between the water and the methyl group of PVME might be effective for the water bound in phase-separated structures; the latter possibility, however, contradicts the results obtained from NMR T_2 measurements of PVME protons[20] and from infrared measurements[13] that at temperatures above the LCST most methyl groups of PVME are dehydrated.

Table 1. Fractions of the Bound Water (HDO) and Spin−Spin Relaxation Times T_2 of HDO (Free and Bound) in Concentrated PVME/D_2O Solutions at 309.5 K

c (wt %)	fraction of bound HDO[a]	[PVME]/[bound D_2O]	T_2 (s) free HDO	T_2 (ms) bound HDO
20	0.035	2.5	5.9	40
30	0.057	2.6	4.7	42
40	0.089	2.6	4.1	39
50	0.116	3.0	2.6	43
60	0.199	2.6	0.9	39

[a] Estimated relative error ±5%.

The ^{1}H spin−spin relaxation times T_2 of HDO molecules in PVME/D_2O solutions measured at temperatures below (305 K) and above (309.5 K) the LCST phase transition are plotted as a function of polymer concen-

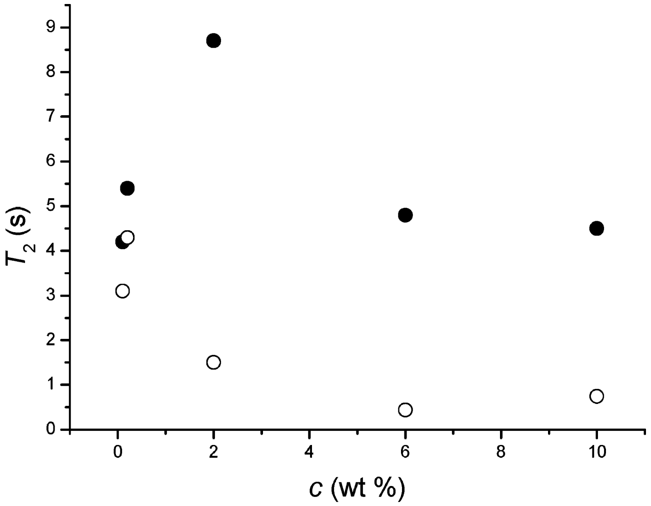

Figure 3. ^1H spin–spin relaxation times T_2 of HDO in PVME/D_2O solutions of various concentration (c = 0.1–10 wt %) measured at 305 K (●) and 309.5 K (○).

tration in the range $c = 0.1{-}10$ wt % in Figure 3. While for dilute solutions (c = 0.1 and 0.2 wt %) T_2 values measured at 305 and 309.5 K did not differ too much, for $c \geq 2$ wt % T_2 values at 309.5 K are 1 order of magnitude shorter than those at 305 K. This shows that for polymer concentrations $c \geq 2$ wt % at temperature above the transition there is a portion of HDO molecules that exhibit a restricted mobility; evidently, this portion corresponds to bound HDO molecules.[20] There was a single line of HDO in ^1H NMR spectrum in all cases in the concentration range $c = 2{-}10$ wt % and the T_2 relaxation curves were exponential, indicating a fast exchange between bound and free sites regarding T_2 values (~0.5 s); i.e., the residence time of bound HDO molecules has to be ≤50 ms. In such case the observed relaxation time $T_{2\mathrm{obs}}$ is given as

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

where subscripts F and B correspond to free and bound states, respectively, and f is the fraction of bound HDO molecules. A drop in T_2 values of water or HDO after reaching the temperature of the phase transition (by heating) was also observed for aqueous solutions of poly(N-isopropylacrylamide) (PIPAAm) (c = 1–10 wt %)[27] and PVME/PIPMAAm mixtures (c = 5 wt %)[21] as well as for cross-linked PIPAAm hydrogel.[28]

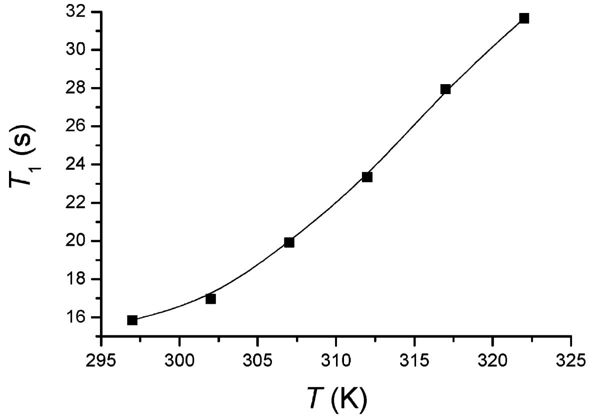

Figure 4. Temperature dependence of ^1H spin–lattice relaxation time T_1 of HDO in PVME/D_2O solution (c = 6 wt %).

In contrast to T_2 relaxation times and in contrast to solutions of PIPAAm/water,[27] PIPMAAm/D_2O, [29] and PIPAAm–poly(ethylene glycol) copolymer hydrogel,[30] where also a decrease of T_1 values of water protons was found at the transition region, in PVME/D_2O solutions spin–lattice relaxation times T_1 of HDO molecules are virtually insensitive to the phase transition as demonstrated in Figure 4, where the temperature dependence of T_1 values of HDO is shown for PVME/D_2O solution with c = 6 wt %. Figure 4 shows that T_1 values monotonically increase with increasing temperature as usual, and nothing indicates the existence of the portion of bound water from these measurements. The reason for different behavior of T_2 and T_1 relaxation times of HDO during the phase transition lies in the different sensitivity of both relaxation times to various motional modes. Assuming the magnetic dipolar interactions of a proton–deuteron pair, the proton relaxation times are given by the following expressions[22]

$$(T_1)^{-1} = (2\gamma_{\mathrm{H}}^2\gamma_{\mathrm{D}}^2\hbar^2)[(1/12)J_0(\omega_{\mathrm{H}} - \omega_{\mathrm{D}}) + (3/2)J_1(\omega_{\mathrm{H}}) + (3/4)J_2(\omega_{\mathrm{H}} + \omega_{\mathrm{D}})] \tag{2}$$

$$(T_2)^{-1} = (2\gamma_{\mathrm{H}}^2\gamma_{\mathrm{D}}^2\hbar^2)[(1/6)J_0(0) + (1/24)J_0(\omega_{\mathrm{H}} - \omega_{\mathrm{D}}) + (3/4)J_1(\omega_{\mathrm{H}}) + (3/2)J_1(\omega_{\mathrm{D}}) + (3/8)\,J_2(\omega_{\mathrm{H}} + \omega_{\mathrm{D}})] \tag{3}$$

where $J_i(\omega)$, i = 0, 1, 2, are the so-called spectral densities at frequency ω, ω_{H} and ω_{D} are the resonance frequencies of protons and deuterons, respectively, and other constants have their usual meanings. For isotropic motion of a proton–deuteron pair with correlation time τ_c, the $J_i(\omega)$ are of the form

$$J_i(\omega) = K_i\tau_c/[1 + (\omega\tau_c)^2] \tag{4}$$

where K_i are constants. It follows from eqs 2–4 that while T_1 relaxation is most sensitive to relatively rapid motions with correlation times $\tau_c \sim \omega_{\mathrm{H}}^{-1}$, T_2 relaxation is much more sensitive to slow-motional modes, as a consequence of the existence of the term with $J_0(0)$ in eq 3. The fact that spin–lattice relaxation times T_1 of HDO in PVME/D_2O solutions are not affected by the phase transition shows that the rates of the motion of bound and free HDO molecules are virtually the same. However, the motion of bound HDO is spatially restricted and anisotropic; the internuclear vector cannot reach all orientations and this fact results in the existence of near-static dipolar interactions that contribute to the term with $J_0(0)$ in eq 3 and consequently markedly shorten T_2 values.

The values of ^1H spin–spin relaxation times T_2 of HDO molecules in highly concentrated PVME/D_2O solutions (c = 20–60 wt %), again measured at temperatures below (305 K) and above (309.5 K) the phase transition, are shown in Figure 5. In contrast to solutions with $c = 2{-}10$ wt % (cf. Figure 3) where T_2 values at the temperature above the transition were 1 order of magnitude shorter in comparison with values at the temperature below the transition, here for the main HDO signal situation is opposite (cf. Figure 5a), and the T_2 values obtained at 309.5 K are substantially longer than T_2 values at 305 K; at the same time also here for concentrations c = 40–60 wt % the difference between both values amounts more than 1 order of magnitude.

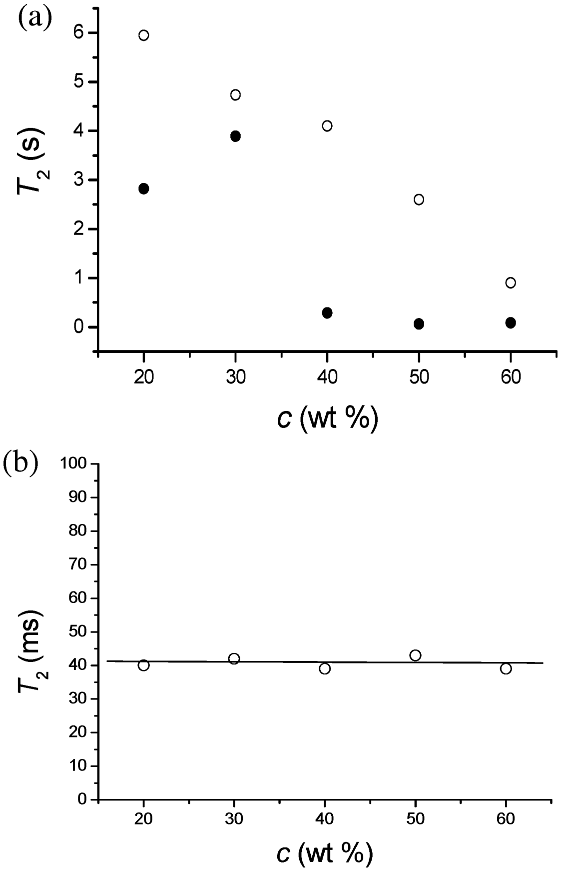

Figure 5. ^{1}H spin−spin relaxation times T_2 as determined for the main line of HDO (a) and for the line of bound HDO at ~3.88 ppm (b) in PVME/D$_2$O solutions of various concentration (c = 20−60 wt %) at 305 K (●) and 309.5 K (○).

The explanation of this different behavior is the following. The existence of the separate signal for the molecules of the bound HDO in concentrated PVME/D$_2$O solutions means that T_2 values plotted in Figure 5a correspond to "free HDO" only, because they were obtained for the main HDO peak at ~4.62 ppm. Significantly longer T_2 values as obtained at 309.5 K in comparison with values measured at 305 K are evidently due to the fact that at higher temperature the respective HDO molecules do not interact with PVME chains, and therefore they are really free while at temperature 305 K a significant part of HDO molecules interact with polymer forming; e.g., hydrogen bonds and their motion are consequently somewhat restricted. Spin−spin relaxation times T_2 of the HDO bound in PVME phase-separated structures as determined from the signal at ~3.88 ppm at 309.5 K are shown as a function of polymer concentration in Figure 5b and in Table 1. These values virtually do not depend on the concentration of the solution and are around $T_{2B} \cong 40$ ms. Being 50 times longer than T_2 values of phase-separated PVME segments,[20,23] T_2 values of bound HDO are 2 orders of magnitude shorter in comparison with those for free HDO (cf. Table 1), while the respective spin−lattice relaxation times T_1 differ much less as indicated by T_1 values for c = 60 wt % at 307 K[31] where T_1 = 2.5 and 8.3 s for bound and free HDO, respectively. Knowing the T_2 value of the bound HDO, we tried to estimate the magnitude of the spatial restrictions resulting in substantial reduction of the spin−spin relaxation time. We followed the approach of McCall and Anderson,[32] who have shown that assuming arbitrarily rapid motion subject to the restriction that $\theta > \theta_0$, where θ is the angle between the internuclear vector and static magnetic field, then for the respective NMR line width $\Delta\upsilon$ it holds

$$(\Delta\upsilon/\Delta\upsilon_{\mathrm{rig}}) \cong \cos\theta_0 \sin^2\theta_0 \qquad (5)$$

where $\Delta\upsilon_{\mathrm{rig}}$ is the line width for the rigid lattice. Assuming a Lorentzian line shape and taking into account that there is a simple relation between line width $\Delta\upsilon$ and spin−spin relaxation time T_2, $\Delta\upsilon = (\pi T_2)^{-1}$, it is possible to rewrite eq 5 in the form

$$(T_{2,\mathrm{rig}}/T_2) \cong \cos\theta_0 \sin^2\theta_0 \qquad (6)$$

Using the T_2 value for the bound HDO, $T_{2B} \cong 40$ ms, and assuming that $T_{2,\mathrm{rig}} = 127$ μs (assuming that relaxation is due to proton−deuteron dipolar interactions, cf. eq 3), then it follows from eq 6 that $\theta_0 \cong 3.2°$. In the case that contribution from dipolar interactions between HDO and PVME protons to total relaxation rate is not negligible, then the resulting value of the angle θ_0 would be even smaller. This simple calculation shows that a rather small spatial restriction of the motion of HDO molecules bound in phase-separated structures can be responsible for 2 orders of magnitude shorter T_2 values in comparison with those for free HDO.

From integrated intensities of the line of bound HDO at ~3.88 ppm and the main HDO signal at ~4.62 ppm (cf. Figures 1 and 2), the relative amount of the bound HDO in highly concentrated PVME/D$_2$O solutions can be determined. At the same time the integrated intensity of the line of bound HDO as determined from spectra recorded using spin-echo pulse sequence $90°_x$−t_d−$180°_y$−t_d−acquisition with t_d = 5 ms is somewhat lowered by T_2 relaxation; the true equilibrium integrated intensity requires to multiply the measured intensity by the correction factor $e^{(10/T_2)}$, where the respective T_2 is given in milliseconds. The values of the fraction of the bound water (HDO) obtained in this way are shown in Table 1. As already mentioned, the fraction of bound HDO increases with increasing polymer concentration. The values of the molar ratio of PVME monomeric unit and bound D$_2$O molecules (we assume that the fraction of bound D$_2$O is the same as the fraction of bound HDO) are for various concentrations of the solution also shown in Table 1. Interestingly enough, the values of the molar ratio [PVME]/[bound D$_2$O] are virtually constant and equal ~2.7 on average, thus indicating that there is a direct connection of the fraction of bound water with the structure of phase-separated PVME. The fact that in concentrated PVME/D$_2$O solutions there is a slow exchange between bound and free water (residence time of bound HDO $\gg$ 2.7 ms), as well as our former finding that the rate of the dehydration process (when the originally bound water is released) significantly differs when polymer segments forming phase-separated structures are rigid (in the glassy state, the case of PIPMAAm) or flexible (in rubbery state, the case of PVME),[20] suggests that most of the bound HDO is rather inside phase-separated structures than that they are only on the surface of globular particles forming a some kind of shell. From X-ray diffraction data on crystalline samples of isotactic PVME as well as from conformational energy calculations, it follows that the most stable conformation of

PVME chains is close to 3/1 helix.[33-35] On the basis of the finding that the molar ratio [PVME]/[bound D_2O] is also near to 3/1, one can speculate that conformation of PVME chains close to 3/1 helix might exist locally in phase-separated structures and that there is a direct relation between the bound water and this helical structure, e.g., that the bound water might be accommodated between side chains in such short-range helix (one bound water molecule per turn). Nevertheless, further experiments are necessary to support this assumption.

Conclusion

A certain portion of spatially restricted bound water (HDO) was established for concentrated PVME/D_2O solutions at temperature above the LCST transition from ^{1}H NMR spectra (polymer concentrations $c = 20-60$ wt %) and from the measurements of ^{1}H spin−spin relaxation times T_2 of HDO. The insensitivity of ^{1}H spin−lattice relaxation times T_1 of HDO to the existence of the bound water in solution with $c = 6$ wt % shows that in this case the rate of the motion of bound and free HDO molecules is virtually the same. The fast and slow exchange regime between bound and free water was revealed for polymer concentrations $c = 2-10$ wt % and $c = 20-60$ wt %, respectively. For the latter case, the residence time of bound HDO $\tau \gg 2.7$ ms and relatively weak hydrogen bonding follow from the position of the separate NMR signal of bound HDO that exists only at temperatures above the phase transition. Spin−spin relaxation times T_2 as obtained for the separate signal of bound HDO ($T_2 \cong 40$ ms) are 2 orders of magnitude shorter in comparison with “free” HDO; nevertheless, a rather small spatial restriction of the motion of bound HDO can be responsible for this difference. The fraction of bound HDO increases with increasing polymer concentration of PVME/D_2O solution. At the same time, the molar ratio of PVME monomeric unit and bound D_2O remains virtually constant and equals around 2.7 on average, thus indicating a direct connection of the fraction of bound water with the conformational structure of phase-separated PVME chains.

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(23) For PVME/D_2O solutions with $c = 30$ and 50 wt % the following T_2 values (a dominating very short component) were found for PVME protons in phase-separated structures at 309.5 K; $c = 30$ wt %: $T_2 = 0.93$ and 0.72 ms; $c = 50$ wt %: $T_2 = 0.97$ and 0.78 ms. In both cases these values are for $CHOCH_3$ and CH_2 protons, respectively. The obtained values are virtually the same as those previously reported for $c = 6$ wt %.[20]
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