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Polymer-Solvent Interactions during Phase Transition in Poly(vinyl methyl ether)/D_2O Solutions as Studied by NMR Methods

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SUMMARY: The structural-dynamic changes and polymer-solvent interactions during temperature-induced phase transition in poly(vinyl methyl ether) (PVME)/D_2O solutions in a broad range of concentrations (0.1–30 wt.-%) were studied by ^1H NMR methods. In the whole concentration range the phase transition is manifested by line broadening (linewidth 350–500 Hz) of a major part of PVME units, evidently due to the formation of globular-like structures. Above the LCST transition, the fraction of phase-separated PVME segments is equal to 0.8 ± 0.1, independent of polymer concentration. While at low concentrations the transition is virtually discontinuous, at high concentrations the transition region is ~ 3 K broad. Measurements of nonselective and selective ^1H spin-lattice relaxation times T_1 of solvent (HDO) molecules evidenced that at elevated temperatures, where most PVME forms globular structures, a part of solvent molecules is bound to PVME forming a complex; the lifetime of the bound water (HDO) molecules is ≤ 2 s.

Introduction

Poly(vinyl methyl ether) (PVME) in aqueous solution is known to exhibit a lower critical solution temperature (LCST) around 308 K, i.e., it is soluble at low temperatures but heating above the LCST results in phase separation[1-5]. On molecular level, such phase separation is assumed to be macroscopic manifestation of a coil-globule transition. The transition is probably associated with competition between hydrogen bonding and hydrophobic interactions[4]. The existence of molecular complex between water and PVME, which is stable at least up to a temperature close to the melting point of water[5] or to transition temperature[4], has been shown by DSC, near-infrared and viscometric measurements. To our knowledge, no NMR studies exist on phase transition in PVME/water solutions.

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In the present work we applied ^{1}H NMR spectroscopy to characterize phase separation and polymer-solvent interactions in PVME/D_2O solutions in the broad range of polymer concentrations (0.1–30 wt.-%). From the methodical point of view, we combined the approach based on measurements of temperature dependences of high-resolution ^{1}H NMR spectra, used by us in the past to study association phenomena in various polymer solutions and gels[6,7] with measurements of nonselective and selective ^{1}H spin-lattice relaxation times T_1 of the solvent (residual HDO)[8,9].

Experimental part

Samples: PVME from Aldrich (supplied as 50 wt.-% solution in water; molecular weight determined by GPC in THF: M_w = 60 500, $M_w/M_n \cong 3$) was used after drying to prepare PVME/D_2O solutions (concentrations c = 0.1, 0.2, 0.5, 1, 2, 4, 6, 10 and 30 wt.-%). Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as an internal NMR standard. Five-mm NMR tubes with samples were then degassed and sealed under argon.

NMR measurements: High-resolution ^{1}H NMR spectra were measured with a Bruker Avance 500 spectrometer at 500.1 MHz. Typical measurement conditions were as follows: pulse width 11.5 μs (90° pulse), relaxation delay 10 s, spectral width 4735 Hz, acquisition time 1.73 s, 16 scans. To correctly detect broad lines, spectra with spectral width 15015 Hz were also measured. The integrated intensities were determined using the spectrometer integration software. ^{1}H spin-lattice relaxation times T_1 of the solvent (residual HDO) were measured by using an inversion recovery pulse sequence (180°-τ-90°) with 8 scans separated by a relaxation delay of 80–200 s; 12–16 τ values in the range 0.1 ms - 300 s were used. In selective T_1 measurements, the Gaussian shaped pulse[10] was used to generate selectively the first 180° pulse.

Results and discussion

In Fig. 1A are shown high-resolution ^{1}H NMR spectra of PVME in D_2O (c = 6 wt.-%), measured at two slightly different temperatures (307 and 308.5 K) and under identical instrument conditions. The assignment of resonances is shown in a spectrum measured at 307 K. From this spectrum it also follows[11] that the studied PVME is atactic; at the same time, the fractions of isotactic and heterotactic triads are significantly larger than that of syndiotactic triads. The most significant effect observed at a slightly higher temperature (308.5 K, cf. Fig. 1A) is a marked decrease in the integrated intensity of all PVME bands. This is evidently due to the fact that at 308.5 K, the mobility of most PVME units is reduced to such an extent that corresponding lines become too broad to be detected in high-resolution spectra. For OCH_3 (and CH) protons, the top of this broad line can be seen in spectrum at 308.5 K in Fig. 1A. A typical two-component line shape is shown in Fig. 1B, where the same system was measured at 312 K with larger spectral width. Most of PVME units contribute to broad line with linewidth of 350 and 500 Hz for $CHOCH_3$ and CH_2 protons, respectively; nevertheless, a narrow component of much smaller integrated intensity is also clearly visible. The same behaviour as depicted for illustration in Fig. 1 for PVME/D_2O (c = 6 wt.-%) was found both for lower and higher concentrations, showing that reaching the LCST results in marked line broadening of a major part of PVME units, evidently due to the phase separation in studied systems and formation of more compact globular-like structures.

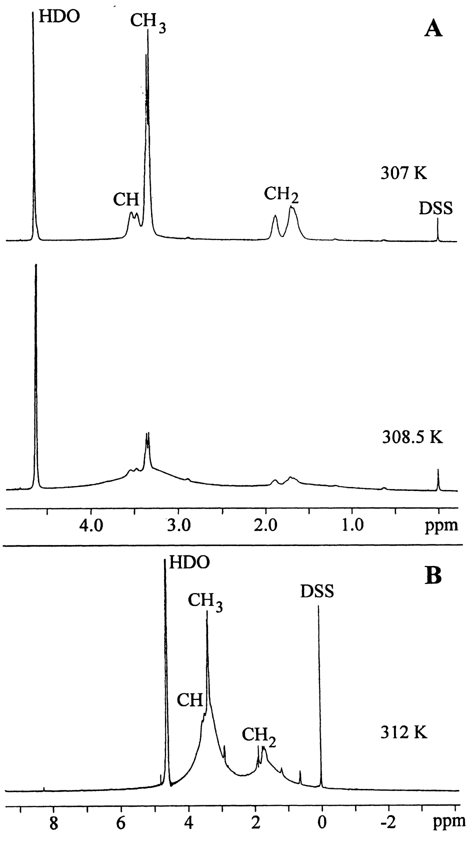

Fig. 1: 500.1 MHz ^1H NMR spectra of PVME/D_2O solution (c = 6 wt.-%) measured at several temperatures: (A) spectra at 307 and 308.5 K measured with spectral width 4735 Hz and under the same instrument conditions; (B) spectrum at 312 K measured with spectral width 15015 Hz.

From a comparison of absolute integrated intensities of the narrow component, the fraction p of phase-separated PVME units (units in globular-like structures) can be determined using the relation

$$p = 1 - (I/I_0) \qquad (1)$$

where I is the integrated intensity of given resonance of PVME measured in (partly) phase-separated system and I_0 is the integrated intensity of this resonance if no phase separation occurs. For I_0, we took the values based on integrated intensities below the LCST, using the expected $1/T$ temperature dependence[6,12)]. Temperature dependences of the fraction p of phase-separated units of PVME as obtained from integrated intensities of CH_3 and CH_2 protons are shown for three concentrations (c = 0.1, 6 and 30 wt.-%) in Fig. 2. From this figure it follows that dependences of fraction p as obtained for side-chain CH_3 protons (A) and for main-chain CH_2 protons (B) are virtually the same. The experimental points in Fig. 2 were measured ~ 30 min after the corresponding temperature was reached (by heating). 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). After 30 min, the integrated intensities are constant; therefore, the points in Fig. 2 are the equilibrium values. Figure 2 shows that for c = 0.1 wt.-%, the transition is virtually discontinuous. Also for c = 6 wt.-%, the transition of most phase-separated PVME is rather sharp, but a small portion of PVME exhibits a lower mobility already at lower or only at higher temperatures (pretransition and posttransition). For c = 30 wt.-%, the transition region sets in already at 305.5 K and is about 3 K broad. In the range of concentrations c = 0.1-10 wt.-%, the phase-separated fraction p at temperatures above the transition is virtually constant and equal to 0.8 ± 0.1. One can speculate about the nature of ~20% PVME segments which contribute to the minority mobile component. We assume that these mobile units might be those on the surface of globular particles and/or from low-molecular-weight PVME oligomers.

The measurements of temperature dependences of absolute integrated intensity of the ^1H NMR band of HDO have shown that in the studied PVME solutions, all the solvent is

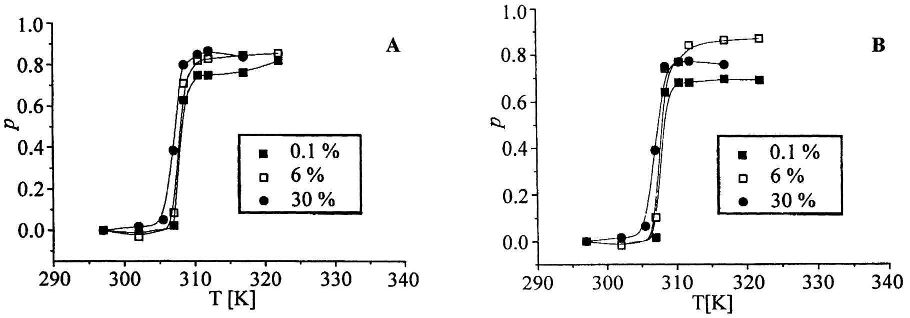

Fig. 2: Temperature dependences of the phase-separated fraction p of CH_3 (A) and CH_2 (B) protons in PVME/D_2O systems with c = 0.1, 6 and 30 wt.-%.

detected in high-resolution spectra in the temperature range 297–352 K. To characterize polymer-solvent interactions in solutions of PVME in D_2O, we used the approach based on measurements of nonselective (NS) and selective (SE) ^{1}H spin-lattice relaxation times T_1 of solvent (HDO) molecules. It is well known that relaxation times T_1(SE) and T_1(NS) exhibit different dependences on the motional correlation time τ_c; explicit expressions are given in refs.8,9). While for correlation times fulfilling the condition $\omega_0\tau_c<1$ (ω_0 is the resonance frequency), T_1(SE) and T_1(NS) do not differ much, T_1(SE) being somewhat longer than T_1(NS) (for $\omega_0\tau_c \ll 1$, $T_1(\mathrm{SE}) = 1.5\ T_1(\mathrm{NS})$), a marked difference exists for $\omega_0\tau_c > 1$ where T_1(SE) is significantly shorter than T_1(NS). If we assume that a part of solvent molecules is bound to polymer, while the other part of solvent is free, and if we assume a fast exchange between bound and free solvent molecules, then the observed spin-lattice relaxation time is given as9)

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

where subscripts F and B correspond to free and bound states, respectively, and f is the fraction of bound solvent molecules. If bound solvent molecules show slow motions ($\omega_0\tau_c>1$), then, on the basis of Eq. (2), one can expect somewhat reduced T_1(SE) values.

We measured ^{1}H T_1(NS) and T_1(SE) relaxation times of residual HDO protons in PVME/D_2O solutions as function of temperature in the range 297–322 K. In all cases the relaxation curves were exponential (single T_1). In Fig. 3, a series of partially selectively relaxed ^{1}H NMR spectra of PVME/D_2O solution is shown to demonstrate T_1(SE) measurements. The results obtained for c = 6 wt.-% are shown in Fig. 4. Similar temperature dependences of T_1(SE) and T_1(NS) were also found for c = 4 wt.-%, while for c = 30 wt.-%, the differences between T_1(SE) and T_1(NS) were less significant. From Fig. 4 it follows that while at temperatures below the transition ($T \leq 307$ K), we observed somewhat lower values of T_1(NS) in comparison with T_1(SE) as expected

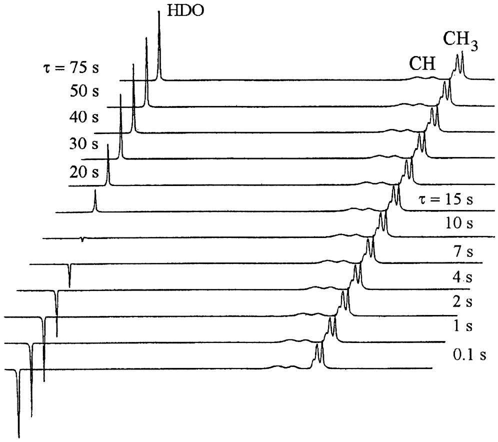

Fig. 3: Selective partially relaxed ^{1}H NMR spectra of PVME/D_2O (c = 6 wt.-%, 297 K) (upfield resonance of CH_2 protons is not shown).

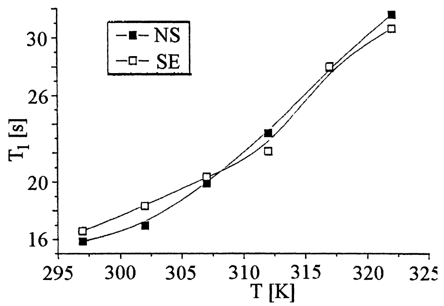

Fig. 4: Selective (open symbols) and nonselective (filled symbols) ^{1}H spin-lattice relaxation times (standard deviation less than 0.5 %) of HDO molecules in PVME/D_2O solution (c = 6 wt.-%) as a function of temperature at 500.1 MHz.

for $\omega_0\tau_c < 1$, the reverse situation (i.e., T_1(NS) > T_1(SE)) was found at temperatures above the LCST transition. At the same time, T_1(NS) increases with increasing temperature, confirming that the reduction in T_1(SE) values at temperatures above the LCST is not simply due to a changed motional behaviour of the bulk solvent. These results evidence that at elevated temperatures, where most PVME forms globular structures, a part of solvent molecules is bound to PVME forming a complex. Such HDO molecules exhibit (similarly as phase-separated PVME) a slow-motion behaviour ($\omega_0\tau_c > 1$) with fast exchange between bound and free sites regarding T_1 values (~ 20 s), i.e., the lifetime of the bound solvent molecules is ≤ 2 s.

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References

1. P. Molyneux, *Water-Soluble Synthetic Polymers: Properties and Behavior, Vol. I,* CRC Press, Inc., Boca Raton (Florida) 1983, p. 58
2. R.A. Horne, J.P. Almeida, A.F. Day, N-T. Yu, *J. Colloid Interface Sci.* **35**, 77 (1971)
3. H. Maeda, *J. Polym. Sci.: Part B: Polym. Phys.* **32**, 91 (1994)
4. H. Schafer-Soenen, R. Moerkerke, H. Berghmans, R. Koningsveld, K. Dušek, K. Šolc, *Macromolecules* **30**, 410 (1997)
5. F. Meeussen, Y. Bauwens, R. Moerkerke, E. Nies, H. Berghmans, *Polymer* **41,** 3737 (2000)
6. J. Spěváček, B. Schneider, *Adv. Colloid Interface Sci.* **27**, 81 (1987)
7. J. Spěváček, M. Suchopárek, C. Mijangos, D. López, *Macromol. Chem. Phys.* **199**, 1233 (1998)
8. G. Valensin, T. Kushnir, G. Navon, *J. Magn. Reson.* **46**, 23 (1982)
9. J. Spěváček, M. Suchopárek, *Macromolecules* **30**, 2178 (1997)
10. C. Bauer, R. Freeman, T. Frenkel, J. Keeler, A.J. Shaka, *J. Magn. Reson.* **58**, 442 (1984)
11. K.C. Ramey, N.D. Field, I. Hasegawa, *J. Polym. Sci., Part B: Polym. Lett.* **2**, 865 (1964)
12. J. Spěváček, L. Hanyková, M. Ilavský, *Macromol. Chem. Phys.,* submitted