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^{1}H NMR Relaxation Study of Polymer-Solvent Interactions during Thermotropic Phase Transition in Aqueous Solutions

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Summary: The dynamic-structural changes and polymer - solvent interactions during the thermotropic phase transition in poly(vinyl methyl ether) (PVME)/D_2O solutions in a broad range of polymer concentrations (c = 0.1-60 wt.-%) were studied combining the measurements of ^{1}H NMR spectra, spin-spin (T_2) and spin-lattice (T_1) relaxation times. Phase separation in solutions results in a marked line broadening of a major part of polymer segments, evidently due to the formation of compact globular-like structures. The minority (~15 %) mobile component, which does not participate in the phase separation, consists of low-molecular-weight fractions of PVME, as shown by GPC. Measurements of spin-spin relaxation times T_2 of PVME methylene protons have shown that globular structures are more compact in dilute solutions in comparison with semidilute solutions where globules probably contain a certain amount of water. A certain portion of water molecules bound at elevated temperatures to (in) PVME globular structures in semidilute and concentrated solutions was revealed from measurements of spin-spin and spin-lattice relaxation times of residual HDO molecules.

Keywords: NMR; polymer-solvent interactions; poly(vinyl methyl ether)/D_2O solution; spin-spin and spin-lattice relaxation; thermotropic phase transition

Introduction

It is well known that some polymers, including poly(vinyl methyl ether) (PVME), in aqueous solutions exhibit a lower critical solution temperature (LCST) (for PVME around 308 K), i.e., they are soluble at low temperatures but their heating above the LCST results in phase separation.[1] On molecular level such phase separation is assumed to be a macroscopic manifestation of a coil - globule transition followed by aggregation, as shown, e.g., for

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poly(*N*-isopropylacrylamide) in water by light scattering.[2] The transition is probably due to competition between hydrogen bonding and hydrophobic interactions.[3,4]

Recently we studied the temperature-induced phase transition in PVME/D_2O solutions and gels by ^{1}H NMR spectra.[5,6] A similar behavior was found both for linear and crosslinked systems, indicating the formation of compact globular-like structures during the phase transition. In the present work we studied polymer - solvent interactions and dynamic-structural changes during the thermotropic phase transition in PVME/D_2O solutions in a broad range of polymer concentrations, combining the measurements of ^{1}H NMR spectra, spin-spin (T_2) and spin-lattice (T_1) relaxation times.

Experimental Part

Samples

Linear PVME (purchased from Aldrich; molecular weight determined by GPC in THF: $M_w = 60\ 500$, $M_w/M_n \cong 3$; tacticity by ^{1}H NMR: 59 % of isotactic diads) was used to prepare PVME/D_2O 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

^{1}H NMR measurements were made with a Bruker Avance 500 spectrometer operating at 500.1 MHz. The ^{1}H spin-spin relaxation times T_2 were measured using the CPMG[7] pulse sequence $90°_x$ -(t_d-$180°_y$-t_d)$_n$-acquisition, for PVME protons with $t_d = 0.5$ ms (at 305 K or at lower temperature) or 0.15 ms (0.12 ms in some cases) (at 309.5 K). Selective and nonselective ^{1}H spin-lattice relaxation times T_1 of the solvent (residual HDO) were measured using an inversion recovery pulse sequence 180°-τ-90°. In selective T_1 measurements, the Gaussian-shaped pulse[8] was used to generate selectively the first 180° pulse. In all measurements the temperature was maintained constant within ± 0.2 K using a BVT 3000 temperature unit.

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Results and Discussion

In Figure 1 are shown high-resolution ^1H NMR spectra of PVME/D_2O solution (*c* = 4 wt.-%) measured at two slightly different temperatures (307 and 308.5 K) and under identical instrumental conditions. The assignment of resonances to various types of protons of PVME and to residual water (HDO) is shown in spectrum measured at 307 K. The most significant effect observed at a slightly higher temperature (308.5 K), where the sample exhibits a milk-white opalescence, is a marked decrease in the integrated intensity of all PVME lines. This is due to the fact that at 308.5 K the mobility of most PVME units is reduced to such an extent that corresponding lines became too broad to be detected in high-resolution spectra. A typical two-component line-shape is shown in Figure 2, where the same system was measured at 312 K with a larger spectral width. Most PVME units contribute to the broad line with linewidth 420 and 730 Hz for $CHOCH_3$ and CH_2 protons, respectively; nevertheless, a narrow component of much smaller integrated intensity is also clearly visible. Similar behavior to that shown in Figures 1 and 2 was found for all studied PVME solutions (*c* = 0.1-60 wt.-%), showing that reaching LCST results in marked line broadening of a major part of PVME units, evidently due to the phase separation and formation of more compact globular-like structures.

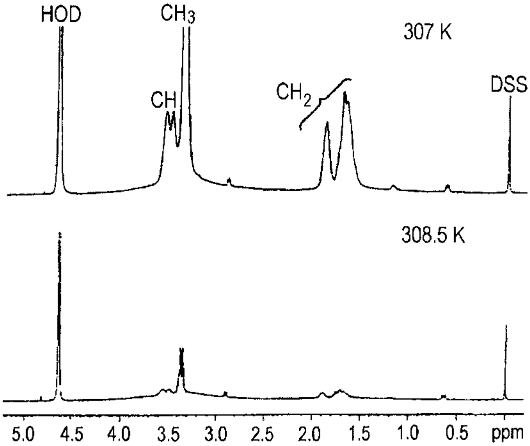

Fig. 1. 500.1 MHz ^1H NMR spectra of PVME/D_2O solution (*c* = 4 wt.-%) measured at 307 and 308.5 K under the same instrumental conditions.[6]

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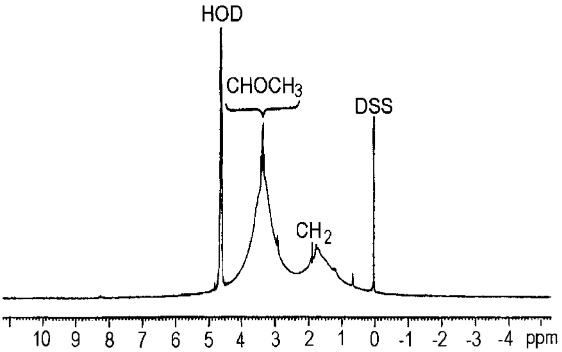

Fig. 2. 500.1 MHz ^{1}H NMR spectrum of PVME/D_2O solution (c = 4 wt.-%) measured at 312 K with spectral width 15 kHz.[6]

From a comparison of integrated intensities (measured under conditions allowing to detect only the narrow component, cf. Figure 1), one can determine the fraction p of phase-separated PVME units (units in globular-like structures).[5,6] In the range of polymer concentrations c = 0.1-10 wt.-%, the fraction p at temperatures above the phase transition is virtually constant and equal to 0.85 ± 0.1. One can speculate about the nature of ~ 15 % PVME segments which contribute to the minority mobile component and do not participate in phase separation. A possible explanation might be that these segments come from low-molecular-weight fraction which one can expect for polymer with a rather large polydispersity such as in our case ($M_w/M_n = 3$). Polymer chains in such low-molecular-weight fraction might be too short to exhibit a cooperative coil - globule transition. This assumption was corroborated by GPC analysis (in THF, calibration with polystyrene standards) which has shown that only a low-molecular-weight part of PVME is present in aqueous solution after removing the phase-separated polymer by centrifugation at 313 K and 15 000 rpm. This result shows that low-molecular-weight oligomers of PVME (molecular weight ≤ 1000) do not take part in the phase transition.

We also investigated PVME/D_2O solutions by measurements of ^{1}H spin-spin relaxation times T_2. At temperatures below the transition (298 and 305 K), the spin-spin relaxation of all proton types of PVME was biexponential, for CH and CH_2 protons with shorter and longer

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components typically in the range 20-40 ms and 120-370 ms, respectively. The biexponential ^1H spin-spin relaxation was recently observed for polyacrylamide in D_2O solution[9] and for poly(methyl methacrylate) in some organic solvents.[10] Similarly as authors of the cited papers, we assigned the shorter and longer T_2 components to polymer segments affected by polymer - polymer and polymer - solvent interactions, respectively. At temperature above the transition (309.5 K), the T_2 relaxation of PVME protons (with spectra measured in analogous way to that in Figure 2) was triexponential. In addition to two components observed below the transition, a predominant (intensity ~ 75 %), very short component (T_2 = 0.85 ms ($CHOCH_3$) and T_2 = 0.30-0.72 ms (CH_2)) was found, which is clearly visible in Figure 3. For CH_2 protons, the very short component decreases with decreasing concentration of the solution (Figure 4), showing that globular-like structures are more compact in dilute solution in comparison with semidilute solutions, where globules probably contain a certain amount of water.

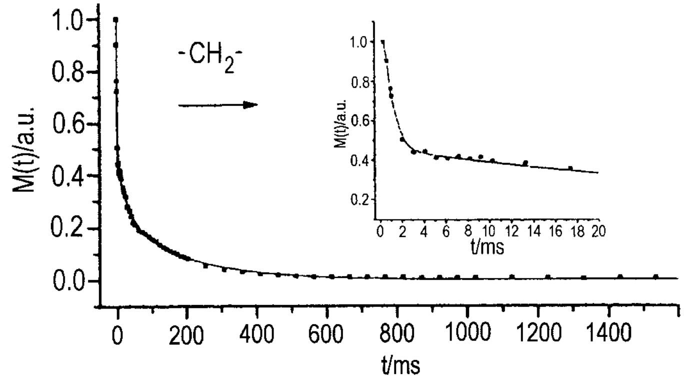

Fig. 3. T_2 relaxation curve (CH_2 protons) for PVME/D_2O solution (c = 2 wt.-%) at 309.5 K. The inset shows in detail the beginning of the curve.

To characterize polymer - solvent interactions in PVME/D_2O solutions, we used measurements of ^1H spin-spin relaxation times T_2 and nonselective (NS) and selective (SE) ^1H spin-lattice relaxation times T_1 of residual HDO molecules. In all cases the T_2 and T_1 relaxation curves were exponential. This does not exclude the possibility that a part of HDO molecules might be bound to polymer, assuming a fast exchange between bound and free water molecules. In such case the observed T_2 or T_1 relaxation time is given as[11]

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

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

The ^{1}H spin-spin relaxation times T_2 of HDO molecules in PVME/D_2O solutions of various polymer concentrations and measured at temperatures below (305 K) and above (309.5 K) the transition are shown in Table 1. 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, a significant difference was found for semidilute solutions where T_2 values at 309.5 K were one order of magnitude shorter than those at 305 K. Taking into account Eq. (1), these results evidence that in semidilute solutions a certain portion of HDO molecules is bound at elevated temperatures to (in) PVME globular structures, in accord with results of T_2 measurements of PVME protons (cf. Figure 4). The exponential character of T_2 curves (for HDO) indicates a fast exchange between bound and free sites regarding T_2 values (~1 s), i.e., the lifetime of the bound HDO molecules is $\leq$ 0.1 s.

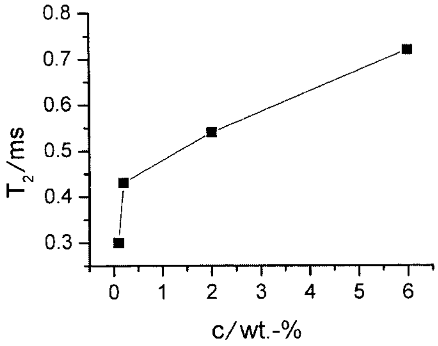

Fig. 4. Concentration dependence of a very short component of spin-spin relaxation time T_2 as determined for CH_2 protons in PVME/D_2O solutions.

Table 1. ^{1}H spin-spin relaxation times T_2 of HDO molecules in PVME/D_2O solutions at 305 K and 309.5 K.

c (wt.-%)	T_2 (s)	
	305 K	309.5 K
0.1	4.2	3.1
0.2	5.4	4.3
2	9.3	1.5
6	4.8	0.44

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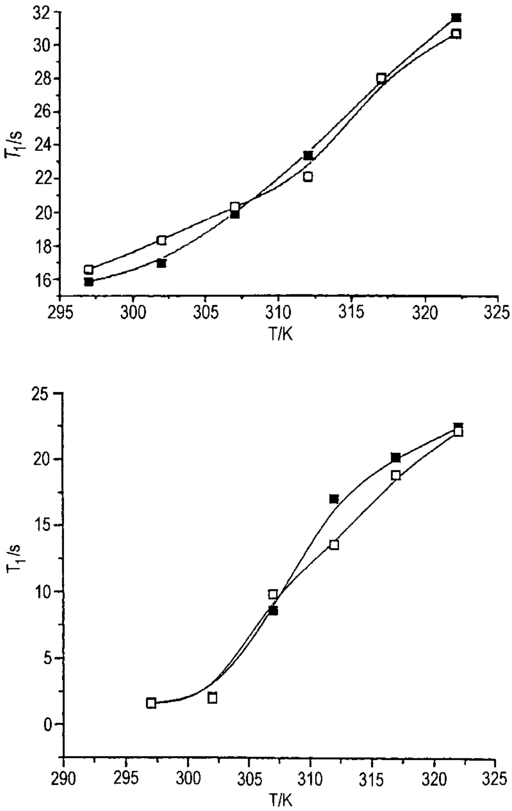

Fig. 5. Selective (open symbols) and nonselective (filled symbols) ^{1}H spin-lattice relaxation times T_1 (standard deviation less than 0.5 %) of HDO molecules in PVME/D_2O solutions as function of temperature at 500.1 MHz, c = 6 wt.-% (a) and 60 wt.-% (b).

The results obtained for PVME/D_2O solutions from T_2 measurements are also corroborated by measurements of ^{1}H T_1(NS) and T_1(SE) of residual HDO molecules in PVME/D_2O solutions of various polymer concentration as function of temperature. The results obtained for c = 6 wt.-% and 60 wt.-% are shown in Figure 5. Similar temperature dependences of T_1(SE) and T_1(NS) as shown in Figure 5a were also found for concentrations c = 4 and 10 wt.-%. 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, e.g., in ref.[11] While for correlation times fulfilling the condition $\omega_0\tau_c < 1$ (ω_0 is the resonance frequency), T_1(SE) is somewhat longer than T_1(NS) (for

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$\omega_0\tau_c << 1$, T_1(SE) = 1.5 T_1(NS)), for $\omega_0\tau_C > 1$, T_1(SE) is significantly shorter than T_1(NS). From Figure 5 it folows 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) (for c = 4, 6 and 10 wt.-%), or T_1(NS) and T_1(SE) values were virtually identical (for c = 60 wt.-%), as expected for $\omega_0\tau_c < 1$ and $\omega_0\tau_c \cong 1$, respectively, at temperatures above the LCST transition T_1(NS) > T_1(SE). For dilute PVME/D_2O solution (c = 0.2 wt.-%) the behavior shown in Figure 5 was not found. These results confirm that in semidilute and concentrated solutions at elevated temperatures, where most PVME forms globular structures, a part of HDO molecules is bound to PVME. These HDO molecules exhibit (similarly to phase-separated PVME) a slow-motion behavior ($\omega_0\tau_c > 1$) with fast exchange between bound and free sites.

Conclusion

^{1}H NMR spectral lineshapes and spin-spin relaxation times T_2 have shown that in PVME/D_2O solutions the LCST transition results in limited mobility of most PVME units, evidently in connection with formation of compact gobular-like structures. A minority (~15 %) mobile component, which does not take part in the phase transition, comes from low-molecular-weight oligomers. From concentration dependence of T_2 values of PVME methylene protons it follows that globular structures are more compact in dilute solutions in comparison with semidilute solutions where globules probably contain a certain amount of water. This is in accord with measurements of spin-spin and spin-lattice relaxation times of residual HDO molecules which have shown that in semidilute and concentrated PVME/D_2O solutions a part of HDO molecules is bound in (to) PVME globular structures.

Acknowledgment

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