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^{1}H NMR study of thermotropic phase transition of linear and crosslinked poly(vinyl methyl ether) in D_2O

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Abstract

The changes in the dynamic structure during temperature-induced phase transition in poly(vinyl methyl ether) (PVME)/D_2O solutions and gels in a broad range of concentrations ($c = 0.1$–30 wt%) and crosslinking densities, respectively, were studied by ^{1}H NMR methods. Similar behaviour was found both for linear and crosslinked systems, indicating the formation of compact globular-like structures during the phase transition. The fraction of PVME segments in globular-like structures is ~0.85 for solutions and ~1.0 for swollen networks, independent of the polymer concentration or the crosslinking density. While for dilute PVME solutions the thermotropic transition as detected by NMR is virtually discontinuous, for semidilute and concentrated solutions, and for swollen networks, the transition sets in at lower temperatures and its width is several Kelvin broad. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(vinyl methyl ether); Thermotropic phase transition; ^{1}H NMR spectroscopy

1. Introduction

Poly(vinyl methyl ether) (PVME) is a water-soluble polymer that exhibits phase separation above 308 K as a consequence of a lower-critical-solution temperature (LCST) behaviour [1–3]. On molecular level, both phase separation in solutions and collapse transition in crosslinked hydrogels, are assumed to be a macroscopic manifestation of a coil-globule transition followed by aggregation, as shown for poly(*N*-isopropylacrylamide) (PIPAAm) and poly(*N*,*N*-diethylacrylamide) (PDEAAm) in water by light scattering and small angle neutron scattering methods [4–8]. Similarly to acrylamide-based polymers, the transition of the little studied PVME/water systems is probably due to competition between hydrogen bonding and hydrophobic interactions [9]. Swelling behaviour of radiation crosslinked PVME system has been studied and a discontinuous phase transition has been found [10]. The existence of a molecular complex between water and PVME, which is stable at least up to a temperature close to the melting point of water [11] or to the transition temperature [9], has been demonstrated by DSC, near-infrared and viscometric measurements.

So far, NMR spectroscopy has been used to study phase transitions in poly(acrylamide) hydrogels [12,13], in aqueous solutions and swollen networks of PIPAAm and its copolymers [14–20] and in swollen networks of poly(*N*-isopropylmethacrylamide) [21]. In most of these studies, the changes in NMR spectra, in ^{1}H NMR relaxation times (T_1 and T_2) and diffusion coefficients were employed to investigate the dynamics of both polymer segments and solvent molecules during the phase transition. Recently, we used ^{1}H NMR spectroscopy to characterise the temperature-induced phase transition in PDEAAm/D_2O solutions and gels [22,23]. The temperature dependences of ^{1}H NMR spectra have shown, that the significant decrease in the segmental mobility appears as a consequence of the coil-globule transition even in dilute PDEAAm/D_2O solutions. The ^{1}H magic angle spinning (MAS) NMR experiments [23] evidenced that the broadening of ^{1}H NMR lines in phase-separated PDEAAm/D_2O physical gels is not due to near-static dipolar interactions, but the respective motion is effectively isotropic and retarded (correlation time ~1 μs). To our knowledge, no NMR studies exist on phase transition in PVME aqueous solutions or gels.

In the present work, we employed ^{1}H NMR spectroscopy to study the temperature-induced phase transition of linear and crosslinked PVME in D_2O. For this purpose, PVME solutions and swollen networks were prepared in a broad range of polymer concentrations ($c = 0.1$–30 wt%) and

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network densities, respectively. From the methodical point of view, we used an approach based on measurements of temperature dependences of ^{1}H NMR spectra (lineshapes and integrated intensities), used by us in the past to study association phenomena in various polymer solutions and gels [24–26]; we also used this approach in previous studies of PDEAAm/D_2O solutions and gels [22,23].

2. Experimental

2.1. Samples

Linear PVME (purchased from Aldrich, supplied as 50 wt% aqueous solution; 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 with polymer concentrations $c = 0.1$, 0.2, 0.5, 1, 2, 4, 6, 10, and 30 wt%. Crosslinked PVME/D_2O samples were prepared by γ-irradiation of a PVME/D_2O solution (^{60}Co γ-source with a dose rate of 0.8 kGy/h, Artim Prague). NMR tubes with 10 wt% solutions were irradiated at room temperature for a required time to obtain a desired dose of γ. Using various radiation doses four samples of swollen networks with different crosslinking density were prepared. Mechanical measurements of the shear equillibrium modulus G were used to check the degree of crosslinking. The dependence of the shear modulus G on the applied radiation dose γ is summarised in Table 1. All samples of PVME/D_2O solutions and networks 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

High-resolution ^{1}H NMR spectra were recorded with a Bruker Avance 500 spectrometer operating at 500.1 MHz. Typical measurements conditions were as follows: 90° pulse width 10 μs, relaxation delay 10 s, spectral width 4735 Hz, aquisition time 1.73 s, 16 scans. To detect correctly broad lines, spectra with spectral width 15,015 Hz were also measured. The integrated intensities were determined with the spectrometer integration software with an accuracy of ±2%. The temperature was maintained constant within ±0.2 K with a BVT 3000 temperature unit.

3. Results and discussion

3.1. PVME/D_2O solutions

Table 1
Dependence of shear equilibrium modulus G on radiation dose γ for PVME/D_2O swollen networks

γ (kGy)	20	30	40	50
G (g/cm^2)	27	110	209	253

High-resolution ^{1}H NMR spectra of PVME/D_2O solution ($c = 4$ wt%) measured at two slightly different temperatures (307 and 308.5 K) are shown in Fig. 1. The assignment of resonance to various types of protons of PVME and to residual water (HOD) is shown in a spectrum measured at 307 K (Fig. 1a). Weak multiplets centered at 0.62 and 2.9 ppm arise from DSS standard. The splitting of CH, CH_3 (not shown) and CH_2 resonances of PVME is due to tacticity [27,28]. From the CH_2 region analysis it follows that the studied PVME is atactic (59% of isotactic diads). At the same time, the splitting of CH and CH_3 bands shows that the proportions of isotactic and heterotactic triads are significantly larger than that of syndiotactic triads. The most important effect observed in the spectrum measured at a slightly higher temperature (308.5 K, Fig. 1b) is a marked decrease in the integrated intensity of all PVME bands. This is a consequence of a pronounced reduction in mobility of most PVME units to such an extent that corresponding PVME lines become too broad and escape the detection in high-resolution spectra. From Fig. 2, presenting the spectrum of the same system at 312 K as measured with a larger spectral width of 15 kHz, a typical two-component line shape can be seen: An intensive broad component with linewidth of 300 and 700 Hz for $CHOCH_3$ and CH_2 protons, respectively, and a narrow component of much smaller integrated intensity corresponding to PVME units with unrestricted mobility. Similar behaviour as shown in Figs. 1 and 2 was found for all studied PVME solutions ($c =$ 0.1–30 wt%). The depicted changes of the shape and intensity of NMR lines show that reaching LCST results in marked line broadening of a major part of PVME units, evidently due to the phase separation and formation of compact globular-like structures. Marked line broadening of phase-separated segments has also been previously

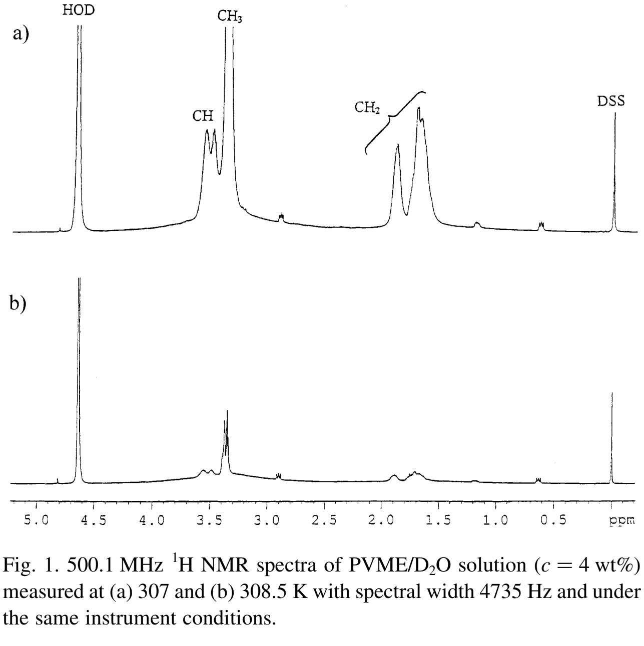

Fig. 1. 500.1 MHz ^{1}H NMR spectra of PVME/D_2O solution ($c = 4$ wt%) measured at (a) 307 and (b) 308.5 K with spectral width 4735 Hz and under the same instrument conditions.

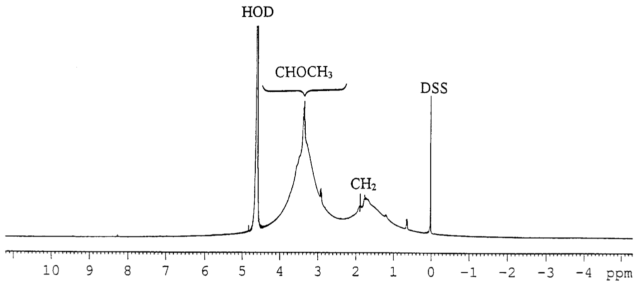

Fig. 2. 500.1 MHz ^{1}H NMR spectrum of PVME/D_2O solution ($c = 4$ wt%) measured at 312 K with spectral width 15 015 Hz.

observed for PIPAAm and PDEAAm aqueous solutions [16,22,23]; however, linewidths of the broad component ($\Delta\nu \approx 3.6$ kHz) were there significantly larger than those found for PVME. This difference is evidently in connection with the quite different flexibility of polymer chains at temperatures around LCST in both cases. Values of the T_g (glass transition temperature) for PVME are reported in the range 191–251 K [29] showing that PVME chains are at temperatures above LCST highly flexible, in contrast to PIPAAm and PDEAAm, where phase separation occurs well below the respective T_g.

Fig. 3 shows the temperature dependences of the integrated intensities of CH_3 and CH_2 bands as obtained from ^{1}H NMR spectra measured under conditions when only the narrow component is detected (cf. Fig. 1); PVME/D_2O solution ($c = 6$ wt%) was chosen for illustration. The experimental points were measured ~30 min after the corresponding temperature was reached (by heating). It is well known that integrated intensities in spectra measured at negligible saturation should decrease with the absolute temperature as $1/T$ (in Fig. 3, the $1/T$ dependence is marked by dotted lines) [23,30]. The most important feature shown for PVME protons in Fig. 3 and observed both for lower and higher concentrations is a marked decrease in the integrated intensity in the temperature range 302–308 K due to phase separation in these systems. Time dependences of integrated intensities at several temperatures in the transition region were also measured; it was found 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 ~20 min, the integrated intensities are constant and therefore the points in Fig. 3 (and in similar plots obtained for other PVME concentrations) are the equilibrium values.

From a comparison of integrated intensities (measured at negligible saturation and under conditions allowing to detect only the narrow component), the fraction p of phase-separated PVME units (units in globular-like structures) can be determined using the relation [23,30].

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

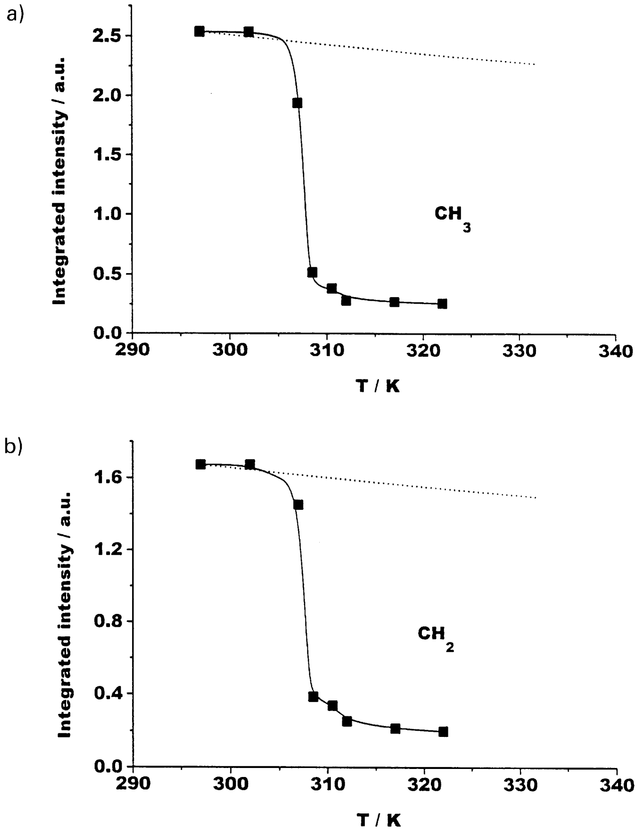

Fig. 3. Temperature dependences of ^{1}H NMR integrated intensities of (a) CH_3 and (b) CH_2 bands for PVME/D_2O solution ($c = 6$ wt%).

where I is the integrated intensity of a 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 values based on integrated intensities below the transition, using the expected $1/T$ temperature dependence. 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. 4. From Fig. 4 it follows that dependences of fraction p as obtained for side-chain CH_3 protons and for main-chain CH_2 protons are virtually the same. 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. For $c = 30$ wt%, the transition sets in already at lower temperature (305.5 K) and is 3 K broad. This is evidently a consequence of the preferred polymer–polymer contacts at higher concentrations, which allow hydrophobic interactions to predominate at a somewhat lower temperature.

From temperature dependences of the phase-separated fraction p (Fig. 4), it follows that above the transition region, the fraction p achieves constant values, p_∞. In Fig. 5, the phase-separated fraction p_∞, as obtained for $CHOCH_3$ and CH_2 protons of PVME, is plotted as function of polymer concentration c. From Fig. 5 it follows that in the whole range of polymer concentrations, the fraction p_∞ is virtually

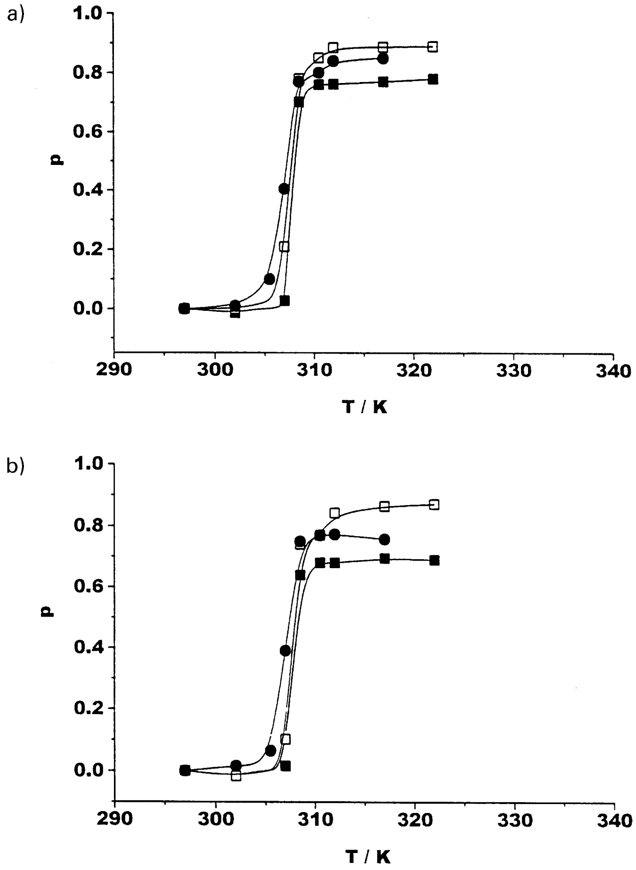

Fig. 4. Temperature dependences of the phase-separated fraction p of (a) CH_3 and (b) CH_2 protons in PVME/D_2O solutions with $c = 0.1$ (■), 6 (□) and 30 (●) wt%.

constant and equal to 0.85 ± 0.1. As the most probable explanation for the ~15% PVME segments which contribute to the minority mobile component and do not participate in phase separation, we suggest that they are from low-molecular-weight fraction which one can expect for polymer with rather large polydispersity 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. The alternative explanation that mobile PVME units are those on the surface of globular-like particles is in our opinion less probable, especially taking into account the preliminary results obtained from measurements of selective and non-selective spin-lattice relaxation times of HOD molecules [31]. These results evidence that at elevated temperatures, where most PVME forms globular-like structures, a part of solvent molecules is bonded to PVME forming a complex in which both components exhibit lower mobility.

3.2. Swollen PVME/D_2O networks

Fig. 6 shows ^1H NMR spectra of chemically crosslinked PVME/D_2O gel ($\gamma = 40$ kGy), measured at 307 (spectrum a) and 309.5 K (spectrum b). A comparison of integrated intensities of polymer bands for all studied PVME/D_2O gels, measured at 300 K, with the linear PVME/D_2O solution of the same polymer concentration ($c = 10$ wt%) has shown that the integrated intensity is practically unaffected by the presence of crosslinks and their density. From Fig. 6, it is obvious that the effect of a distinct reduction of integrated intensities at temperatures approaching the transition region appears also for swollen PVME/D_2O networks. Measurements of time dependences of ^1H NMR spectra have shown that similarly to PVME/D_2O solutions, also, here the collapse transition is rather fast (measuring the integrated intensities of PVME protons, the final state is reached within several minutes). Contrary to PVME/D_2O solutions, in gels the narrow component of PVME as observed at lower temperature (Fig. 6a) practically completely disappears from the spectrum and only the top of the broad component, which belongs to collapsed PVME

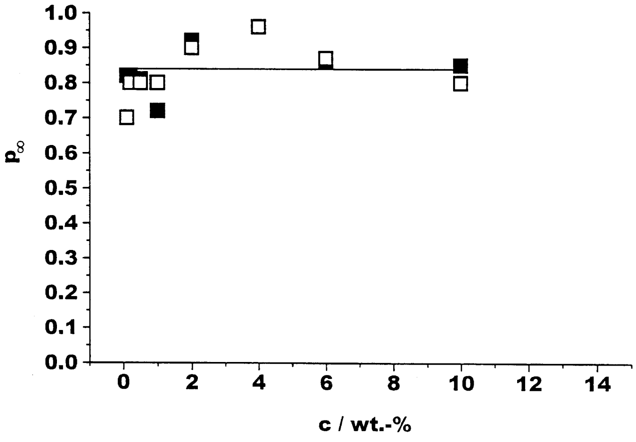

Fig. 5. Concentration dependence of the phase-separated fraction p_∞ of PVME units as determined from integrated intensities of $CHOCH_3$ (closed symbols) and CH_2 (open symbols) bands in PVME/D_2O solutions.

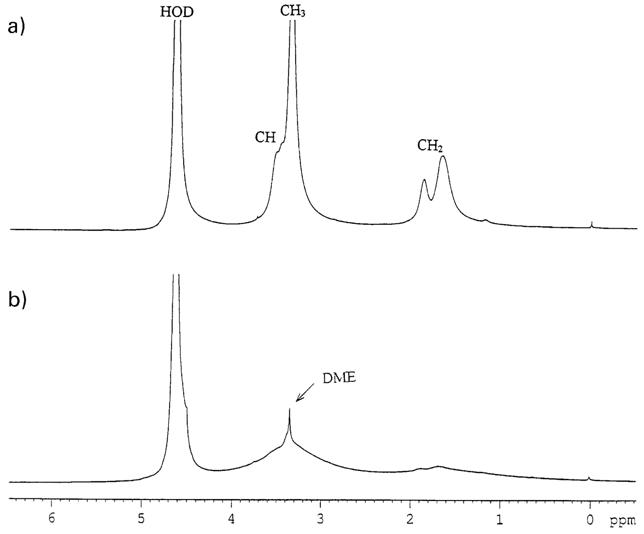

Fig. 6. 500.1 MHz ^1H NMR spectra of PVME/D_2O swollen network with $\gamma = 40$ kGy measured at (a) 307 K and (b) 309.5 K with spectral width 4735 Hz and under the same instrument conditions.

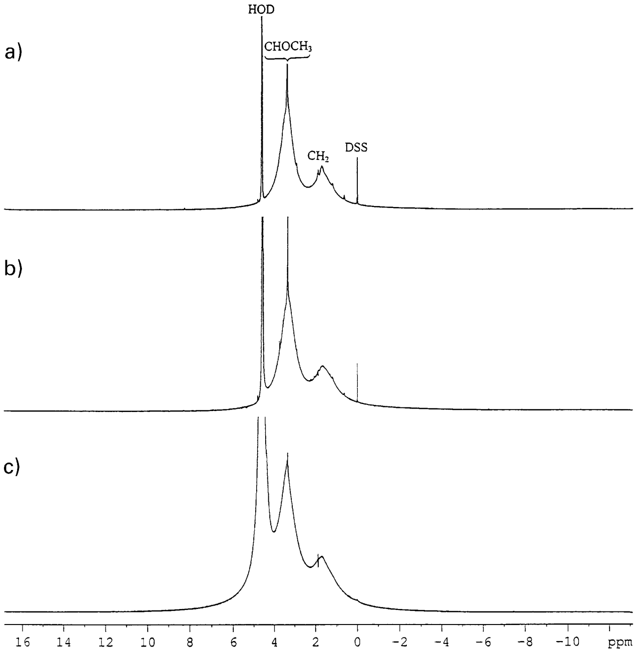

Fig. 7. 500.1 MHz ^{1}H NMR spectra of (a) PVME/D_2O solution ($c = 10$ wt%), (b) PVME/D_2O swollen networks with $\gamma = 20$ kGy and (c) $\gamma = 50$ kGy, measured at 312 K with spectral width 15 015 Hz.

segments, is shown in the spectrum at 309.5 K (Fig. 6b), especially for CH_3 protons. An additional sharp line at 3.35 ppm (cf. Fig. 6b) is due to dimethyl ether (DME) formed in the crosslinking reaction. Fig. 7 shows ^{1}H NMR spectra of swollen networks obtained with $\gamma = 20$ and 50 kGy and measured at 312 K with a large spectral width of 15 kHz, to detect correctly the shape of broad lines corresponding to collapsed PVME segments; a spectrum of PVME/D_2O solution of the same concentration ($c =$ 10 wt%) measured under identical conditions is also shown for comparison. The linewidths corresponding to the collapsed part in swollen networks are only about 100 Hz (for CH_2 line) or 150–250 Hz (for $CHOCH_3$ line) larger than those in respective solution. From Fig. 7 it, therefore, follows that the mobility in collapsed state is very similar in these three cases, thus confirming the same nature of the collapse in D_2O gels of chemically crosslinked PVME and of phase separation in PVME/D_2O solutions.

Analogously to PVME/D_2O solutions, the collapsed fraction p was determined using Eq. (1) also for PVME/D_2O networks. The temperature dependences of the fraction p for gel samples with different crosslinking densities and for PVME/D_2O solution of the same concentration ($c =$ 10 wt%) are plotted in Fig. 8. A comparison of the temperature region of the phase transition indicates that while the swollen networks with lower crosslinking density ($\gamma = 20$ and 30 kGy) and the respective solution show almost the same width of transition region, the transition region observed for the network with $\gamma = 40$ kGy is broader (≈ 7 K) and sets in at 302 K. Somewhat lower transition temperatures are here, similar to crosslinked PDEAAm [22], a consequence of a lower mobility of PVME segments, due to crosslinks. The higher crosslinking density in PVME networks, therefore, has a similar effect to the higher polymer concentration in PVME/D_2O solutions (cf. Fig. 4). The continuous nature of the phase transition as observed for swollen PVME/D_2O networks by ^{1}H NMR spectra is in contrast to swelling measurements, where the transition was virtually discontinuous [10]. This difference is probably due to the fact that high-resolution ^{1}H NMR spectra detect only the fast first stage of formation of globular-like structures, being insensitive to possible slower changes due to further removal of water from these structures [22]. Fig. 8 also shows that values of the collapsed fraction above the transition region (p_∞) do not depend on the crosslinking density. Taking into account the contribution of the dimethyl ether line to the integrated intensity I in Eq. (1) (so apparently lowering fraction p to 0.9), we assume that virtually all PVME segments in swollen networks are collapsed above the phase transition.

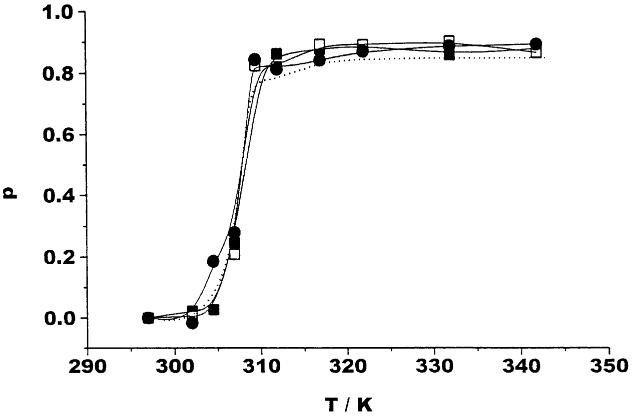

Fig. 8. Temperature dependences of the collapsed fraction p of $CHOCH_3$ protons in PVME/D_2O swollen networks with $\gamma = 20$ (■), 30 (□) and 40 (●) kGy (solid lines with symbols) and in PVME/D_2O solution ($c =$ 10 wt%) (dotted line).

The time dependence of the line of residual water (HOD), both in PVME/D_2O solutions and swollen networks, was also investigated. While the signal of HOD in all solutions and in swollen networks with $\gamma = 20$ and 30 kGy is a single line and this lineshape does not vary with time after the

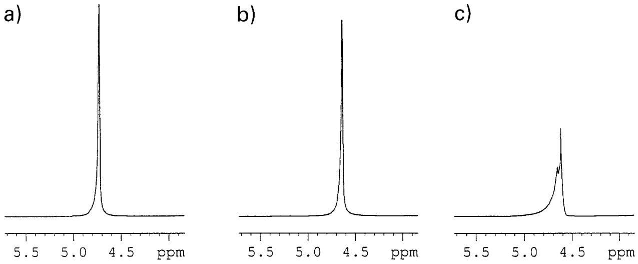

Fig. 9. ^{1}H NMR resonance of HOD molecules measured at (a) 300 K, (b) 307 K, 5 min after temperature jump, (c) 307 K, 18 h after temperature jump in swollen PVME/D_2O network with $\gamma = 40$ kGy.

temperature jump above the transition region, a pronounced change in the HOD lineshape was found for the swollen network with higher crosslinking density, $\gamma = 40$ kGy (Fig. 9). As temperature increased from 300 to 307 K, the HOD line shape significantly changed during several hours, showing partly overlapping sharp and broad components; at the same time, the total integrated intensity of the whole HOD band remained constant. In the past, similar behaviour has been found for the signal of solvent in swollen gels of highly crosslinked poly(methyl methacrylate) (PMMA) in benzene [32]. The authors explained the splitting of the solvent signal by assuming the existence of two types of benzene molecules for which interchange is not sufficiently rapid: those which rather strongly interact with polymer and those which are relatively free in macrovoids probably existing in highly crosslinked networks. For the HOD signal in swollen PVME network with high crosslinking density at temperatures above the transition, we assume similar origin of the splitting. In our opinion, this splitting indicates a slow formation of heterogeneous structure where some HOD molecules are confined in domains formed by PVME chains while the remaining HOD molecules are free. Similarly to PMMA/benzene gels, the difference between both types of HOD molecules is apparent only for swollen networks of high crosslinking density.

4. Conclusion

In this work the thermotropic phase transition in PVME/D_2O solutions and swollen gels was investigated by ^1H NMR spectroscopy. A very similar behaviour was observed for solutions of linear PVME and for swollen networks. Both the phase separation in PVME solutions and the collapse in gels of crosslinked PVME result in broadening (linewidths of several hundreds Hz) of NMR lines of a major part of PVME units, evidently due to the formation of compact globular-like structures. The fraction of PVME units in globular structures is ~0.85 for solutions and ~1.0 for swollen networks, independent of the polymer concentration or the crosslinking density. In solutions, ~15% of PVME units retain high mobility even at temperatures above the transition region; we assume that these units are from PVME chains of low-molecular-weight which do not take part in the phase transition. While for dilute PVME solutions, the phase transition is virtually discontinuous, for semidilute and concentrated solutions, and for swollen gels, the transition is several K broad and sets in at somewhat lower temperatures. The continuous character of the thermotropic transition as revealed by NMR for swollen PVME networks is probably due to the fact that high-resolution NMR spectra are sensitive only to the fast first stage of the shrinking process. Slow formation of heterogeneous structure is indicated for swollen network of relatively high crosslinking density by splitting of the resonance of residual water (HOD).

Acknowledgements

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