

THERMOTROPIC PHASE TRANSITION IN AQUEOUS POLYMER SOLUTIONS AND GELS AS STUDIED BY ^1H NMR METHODS

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SUMMARY

The paper deals with investigation of structural-dynamic changes during thermotropic phase transition in aqueous polymer solutions and gels. Poly(vinyl methyl ether) (PVME)/D₂O solutions and gels, poly(N,N-diethylacrylamide)(PDEAAm)/D₂O solutions and gels, and poly(N-isopropylmethacrylamide)/D₂O solutions were studied by combination of several ^1H NMR methods. For all systems studied, both phase separation in solutions and volume phase transition (collapse) in gels of crosslinked polymers result in a marked line broadening of a major part of polymer segments, evidently due to the formation of compact globular structures. Chemical crosslinking and especially the presence of the negative charges on polymer chain result in the shift of the transition region. In most cases (with exception of dilute PVME/D₂O solutions) the transition as observed by NMR appeared as continuous. ^1H MAS NMR spectra and $T_{2\text{eff}}$ relaxation measurements (using multiple-pulse MW4 sequences) have shown that motion of PDEAAm segments in D₂O solutions and gels above the transition region is effectively isotropic with correlation time $\tau_c=2\ \mu\text{s}$; such motion probably corresponds to isotropic Brownian motion of globules as a whole. Measurements of spin-spin relaxation time T_2 in PVME/D₂O solutions have shown that globular structures are more compact in dilute solution in comparison with semidilute or concentrated solutions where globules probably contain a certain amount of water. A certain portion of water molecules bound at elevated temperatures in (to) PVME globular structures in semidilute and concentrated solutions was revealed from measurements of spin-lattice and spin-spin relaxation times of HDO molecules.

Keywords: Thermotropic phase transition, collapse, D₂O solutions and gels, poly(vinyl methyl ether), poly(N,N-diethylacrylamide), poly(N-isopropylmethacrylamide), ^1H NMR spectroscopy, relaxation times.

1. INTRODUCTION

Polymer gels are interesting systems because they simultaneously exhibit liquid-like and solid-like properties. Their liquid-like properties are a consequence of the fact that gels contain a substantial amount of solvent; if solvent is water then we speak about hydrogels. Solid-like properties of polymer gels are a consequence of the existence of crosslinks between polymer chains which can be formed either by chemical bonds (chemically crosslinked gels) or by other physical interactions (physically crosslinked gels). It is now well established that acrylamide (AAm)-based polymer hydrogels undergo a volume phase transition (collapse) induced by a small change in external parameters like solvent composition, temperature, pH etc [1]. At the collapse, the gels volume can decrease 10-1000 times. Most experimental results were obtained with hydrogels of poly(acrylamide) (PAAm) (collapse induced by a change in solvent composition) and of poly(N-isopropylacrylamide) (PIPAAm) (collapse induced by a temperature change). Collapse was usually interpreted as a first-order phase transition, but there are also studies claiming that this is rather a second-order transition; this point is still under discussion.

It is also well known that some acrylamide-based polymers and some other polymers like poly(vinyl methyl ether) (PVME) exhibit interesting behavior

in aqueous solution, showing a lower critical solution temperature (LCST); they are soluble at low temperatures but heating above the LCST results in phase separation. 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 PIPAAm in water by light scattering [3]. The transition is probably due to competition between hydrogen bonding and hydrophobic interactions [5].

Their thermosensitivity makes these systems interesting for possible biomedical and technological applications, especially if the polymers are chemically crosslinked (in the form of hydrogels). Stimuli-responsive hydrogels that undergo abrupt changes in volume have potential applications in the creation of "intelligent" material systems, e.g. as drug delivery systems. A certain similarity of temperature induced phase separation to thermal denaturation of proteins in aqueous solutions makes these systems interesting also from an academic point of view.

To our knowledge, the number of papers dealing with phase transitions in polymer solutions and hydrogels, as studied by nuclear magnetic resonance (NMR), is rather limited (cf. references cited in [4]). In the present work, ^1H NMR results obtained on the temperature-induced phase transition of linear and crosslinked PVME, linear and crosslinked poly(N,N-diethylacrylamide) (PDEAAm) and linear poly(N-

isopropylmethacrylamide) (PIPMAAm) in D₂O are reported. For PDEAAm and PIPMAAm, the effect of ionization (1-10 mol % of negative charges on the chain) was also followed. From the methodical point of view, we combined an approach based on measurements of temperature dependences of high-resolution ¹H NMR spectra with measurements of broad-line ¹H NMR spectra, ¹H NMR spectra under magic angle spinning (MAS) and with measurements of spin-lattice (*T*₁) and spin-spin (*T*₂, *T*_{2eff}) relaxation times.

2. EXPERIMENTAL PART

2.1. Samples

PVME: 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=3) was used after drying to prepare PVME/D₂O solutions with polymer concentrations in the range *c* = 0.1-60 wt.-% [4]. Crosslinked PVME/D₂O samples were prepared by γ -irradiation of a PVME/D₂O solution (*c* = 10 wt.-%); four samples of swollen networks were prepared using various radiation doses. Mechanical measurements of the shear equilibrium modulus *G* were used to check the degree of crosslinking. All samples of PVME/D₂O 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.

PDEAAm: Polymerization initiated with ammonium peroxy sulfate and *N,N,N',N'*-tetramethylethylenediamine at 277 K, directly in 5 mm NMR tubes, was used to prepare samples of linear PDEAAm in D₂O with monomer concentrations in the range 2-50 wt.-% [7]. Samples of concentrations 0.5 and 1 wt.-% were prepared by diluting the original sample of 4 wt.-% concentration. While the PDEAAm samples with concentration below 4 wt.-% were true solutions, samples with concentrations *c* \geq 6 wt.-% were physical gels (they did not flow). Three samples of gels of crosslinked PDEAAm (total concentration of monomer and crosslinker was 10 wt.-%) of various crosslinking density were prepared by a similar procedure as given above, using various amount of *N,N'*-methylenebisacrylamide as a crosslinking agent; mechanical measurements of the shear modulus *G* were used to check the degree of crosslinking. Three samples of gels of ionized crosslinked PDEAAm (*c* = 10 wt.-%) were prepared in an analogous way, and adding 1, 3 and 6 mol % of sodium methacrylate (MNa) relative to DEAAm monomer [8]. Linear ionized PDEAAM (*c* = 10 wt.-%) containing 3 mol % of MNa was also prepared.

PIPMAAm: IPMAAm and MNa were used to prepare PIPMAAm/D₂O solutions with various polymer concentration *c* (*c* = 0.1-10 wt.-%) and

degree of ionization *i* (content of MNa, *i* = 0-10 mol %). 4,4'-azobis(4-cyanopentanoic acid) was used as initiator and polymerization was carried out in ethanol/water mixture; the volume fraction of all monomers in mixture was 0.25.

2.2. NMR measurements

Most of ¹H NMR measurements were done with a Bruker Avance 500 spectrometer operating at 500.1 MHz (PVME, PIPMAAm) and with Bruker Avance DPX 300 spectrometer operating at 300.1 MHz (PDEAAm). Some spectra of PDEAAm/D₂O solutions and gels were also measured with a Jeol PS-100 cw spectrometer at 100 MHz; broad-line (FT-FID) ¹H NMR spectra and *T*_{2eff} relaxation times of these systems were measured at 60 MHz, while ¹H MAS NMR spectra were measured at 399.9 MHz. The ¹H spin-spin relaxation times *T*₂ were measured at 500.1 MHz using the CPMG pulse sequence 90^o_x-(*t*_d-180^o_y-*t*_d)_n-acquisition. Selective and nonselective ¹H spin-lattice relaxation times *T*₁ of the solvent (residual HDO) were measured using an inversion recovery pulse sequence 180^o- τ -90^o. In selective *T*₁ measurements, the Gaussian shaped pulse was used to generate selectively the first 180^o pulse.

3. RESULTS AND DISCUSSION

3.1. Coil-globule transition and its manifestation in ¹H NMR spectra

In Fig. 1 are shown high-resolution ¹H NMR spectra of PVME in D₂O (*c* = 4 wt.-%) measured at two slightly different temperatures (307 and 308.5 K) and under identical instrument conditions. The assignment of resonances to various types of protons of PVME and to residual water (HDO) is

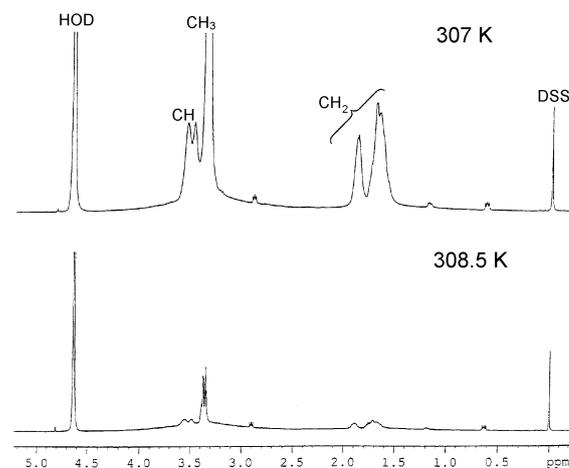


Fig. 1 500.1 MHz ¹H NMR spectra of PVME/D₂O solution (*c* = 4 wt.-%) measured at 307 and 308.5 K under the same instrument conditions [4].

shown in a spectrum measured at 307 K. The most significant effect observed at a slightly higher temperature (308.5 K) is a marked decrease in the integrated intensity of all PVME lines. 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 became too broad to be detected in high-resolution spectra. A typical two-component line-shape is shown in Fig. 2, where the

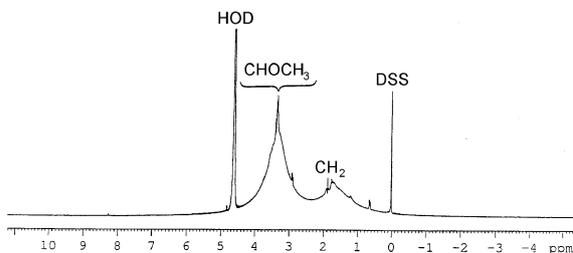


Fig. 2 500.1 MHz ^1H NMR spectrum of PVME/ D_2O solution ($c = 4$ wt.-%) measured at 312 K with spectral width 15 kHz [4].

same system was measured at 312 K with larger spectral width. Most of PVME units contribute to broad line with linewidth of 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 as shown in Figs. 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.

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 units (units in globular-like structures) can be determined using the relation [10]:

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

where I is the integrated intensity of a given resonance of polymer 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. 3. The experimental points in this figure were measured ~ 30 min after the corresponding temperature was reached (by heating). Measurements of time dependences of integrated NMR intensities in the transition region have shown that the respective change in the

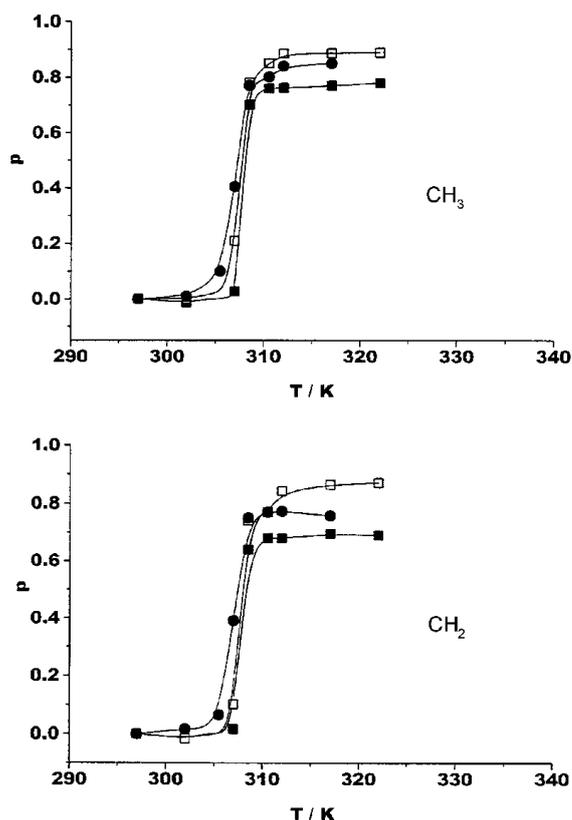


Fig. 3 Temperature dependences of the phase-separated fraction p of CH_3 and CH_2 protons in PVME/ D_2O solutions with $c = 0.1$ (■), 6 (□) and 30 (●) wt.-% [4].

integrated intensity is rather fast, mostly in first 3 min and therefore the points in Fig. 3 are the equilibrium values. From Fig. 3 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 probably a consequence of the preferred polymer-polymer contacts at higher concentrations, which allow hydrophobic interactions to predominate at a somewhat lower temperature.

In the whole range of polymer concentrations, the fraction p is virtually constant and equal to 0.85 ± 0.1 [4]. 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 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. This assumption was corroborated by GPC analysis which has shown that only low-molecular-weight part of PVME is present in aqueous solution after removing the phase-separated polymer by centrifugation at 313 K and 15000 rpm. This result shows that low-molecular-weight oligomers of PVME (molecular weight ≤ 1000) do not take part in the phase transition.

PVME/D₂O solutions were also investigated by measurements of spin-spin relaxation times T_2 . While at temperatures below the transition, the spin-spin relaxation (as measured by CPMG technique) was biexponential, with shorter and longer components assigned to polymer segments affected by polymer-polymer and polymer-solvent interactions, respectively, at temperature above the transition the T_2 relaxation was triexponential, with a predominant, very short component ($T_2 = 0.85$ ms (CHOCH₃) and $T_2 = 0.30$ - 0.72 ms (CH₂)) which is clearly visible in Fig. 4. For CH₂ protons this very short component decreases with decreasing

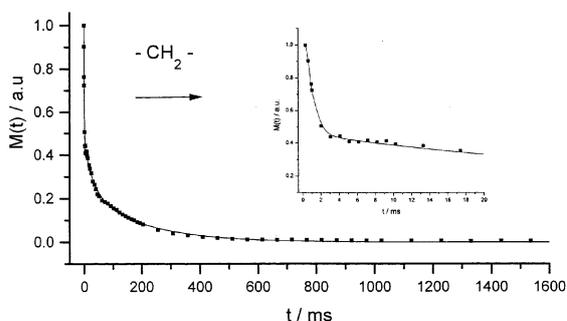


Fig. 4 T_2 relaxation curve (CH₂ protons) for PVME/D₂O solution ($c = 2$ wt.-%) at 309.5 K. Inset in the right part of the figure shows in detail the beginning of the curve.

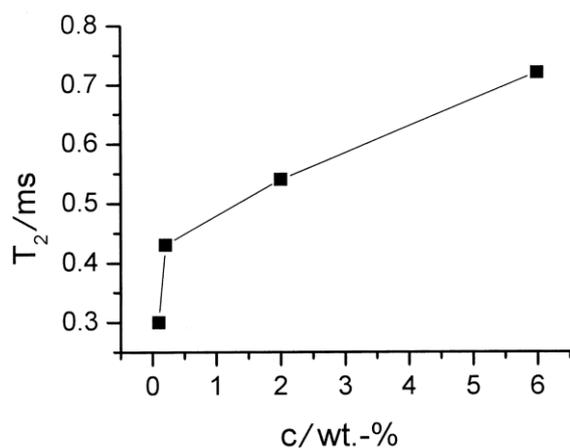


Fig. 5 Concentration dependence of very short component of spin-spin relaxation time T_2 as determined for CH₂ protons in PVME/D₂O solutions. concentration of the solution (Fig. 5), showing that globular-like structures are more compact in dilute

solution in comparison to semidilute or concentrated solutions, where globules probably contain a certain amount of water.

A similar behavior as illustrated in Figs. 1-3 on PVME/D₂O solutions was observed also for PDEAAm/D₂O [7,8] and PIPMAAm/D₂O systems with following minor departures: (i) Temperature dependences of phase-separated fraction p in PDEAAm/D₂O solutions and physical gels, as obtained for side-chain CH₃ and CH₂ protons and for main-chain CH₂ protons, have shown that here the phase transition is not discontinuous even for dilute solution ($c = 0.5$ wt.-%), but there is an interval of transition temperatures ~ 6 K broad [7]. This holds also for unionized PIPMAAm/D₂O solutions (cf. further text and Fig. 9, curve for $i = 0$ %). (ii) Marked line broadening of phase-separated segments has also been observed for PDEAAm and PIPAAm aqueous solutions and gels [7,8,12]. However, as illustrated in Fig. 6, linewidths of the broad component ($\Delta\nu = 3.8$ kHz) were in these systems significantly larger than those found for PVME (cf. Fig. 2). This difference is 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 [2], showing

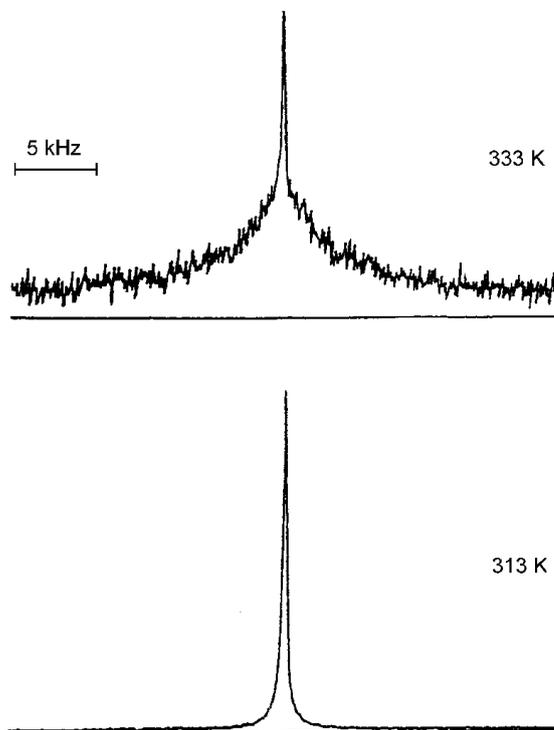


Fig. 6 60 MHz broad-line (FT-FID) ¹H NMR spectra of PDEAAm containing 3 mol % of MnA units ($c = 10$ wt.-%) in D₂O measured at 313 and 333 K [8].

that PVME chains are at temperatures above LCST (~ 308 K) highly flexible, in contrast to PDEAAm and PIPAAm, where phase separation occurs well below the respective T_g .

3.2. Effects of chemical crosslinking and ionization

The NMR behavior of the swollen PVME/D₂O and PDEAAm/D₂O networks during thermotropic phase transition is very similar to that of the respective linear polymer in D₂O solution, as discussed in previous paragraph. Nevertheless, the temperature interval where NMR integrated intensities decline is slightly different. This fact is documented in Fig. 7, where the temperature dependences of integrated intensities of PDEAAm

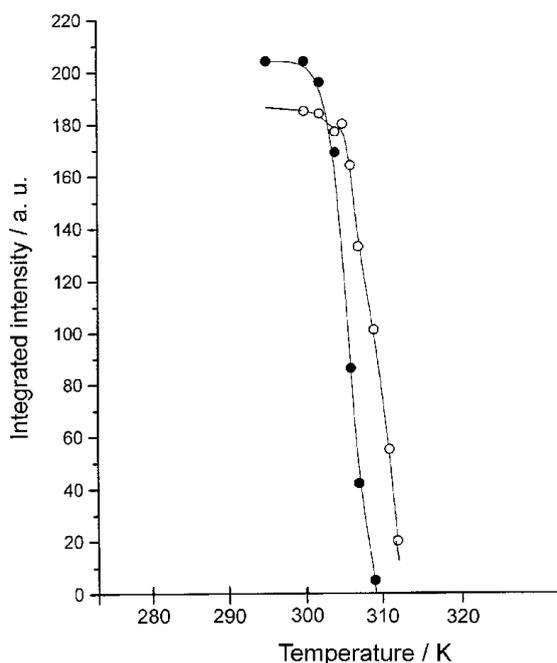


Fig. 7 Temperature dependences of integrated intensities of high-resolution ¹H NMR bands of linear PDEAAm ($c = 10$ wt.-%) (°) and chemically crosslinked PDEAAm ($c = 10$ wt.-%, $G = 20$ g/cm²) (●) in D₂O. Absolute values of integrated intensities of two samples are not directly comparable [8].

bands in high-resolution ¹H NMR spectra of linear and crosslinked PDEAAm (in both cases $c = 10$ wt.-%) in D₂O are compared. We can see that for the crosslinked PDEAAm the transition is shifted by 3–4 K towards lower temperatures. The trend of slightly lowering the temperature interval of the phase transition by chemical crosslinking is also corroborated by results obtained on PDEAAm/D₂O or PVME/D₂O swollen networks of various crosslinking density [4,8]. Somewhat lower transition temperatures obtained for crosslinked systems are a consequence of the lower mobility of polymer segments, due to crosslinks. The continuous nature of the phase transition as observed for swollen PVME/D₂O and PDEAAm/D₂O networks by ¹H NMR spectra is in contrast to swelling measurements, where the transition was virtually discontinuous. This difference might be due to the

fact that high-resolution ¹H 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. Otherwise, the NMR spectra confirm the same nature of the collapse in the hydrogels of chemically crosslinked polymers and of phase separation in solutions of the respective polymer, namely the coil-globule transition.

The effect of ionization on the thermotropic phase transition is demonstrated in Figs. 8 and 9, where the

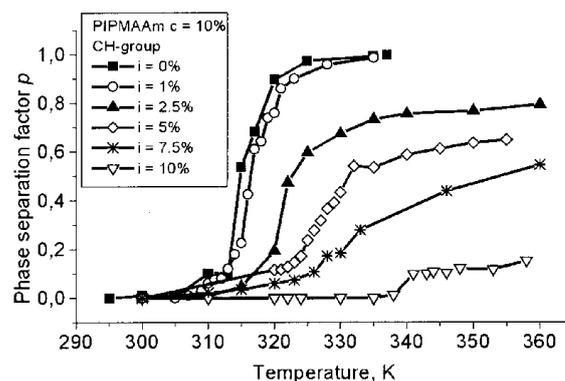


Fig. 8 Temperature dependences of phase-separated fraction p for PIPMAAm/D₂O solutions with polymer concentration $c = 10$ wt.-% and various degree of ionization i

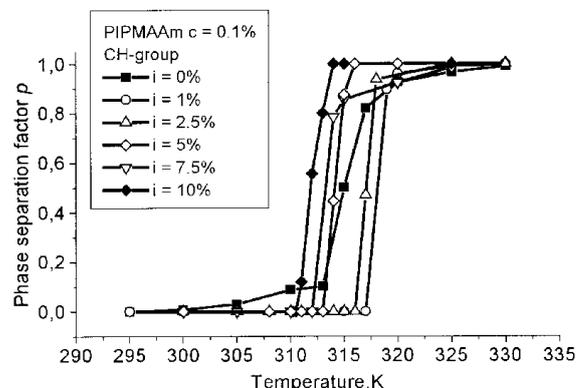


Fig. 9 Temperature dependences of phase-separated fraction p for PIPMAAm/D₂O solutions with polymer concentration $c = 0.1$ wt.-% and various degree of ionization i

temperature dependences of phase separation factor p for PIPMAAm/D₂O solutions ($c = 10$ and 0.1 wt.-%) are shown. From Fig. 8 ($c = 10$ wt.-%) it follows that the transition region shifts towards higher temperatures with increasing concentration of negative charges on the chain and simultaneously the fraction of PIPMAAm segments involved in globular structures is reduced. Very similar behavior was found also for hydrogels of chemically crosslinked PDEAAm [8]. In both cases the increasing content of hydrophilic MNa units increases the mobility of polymer segments, and higher temperature is necessary to allow

hydrophobic interactions to predominate. Interesting results were obtained for dilute PIPMAAm/D₂O solutions ($c = 0.1$ wt.-%) and various degree of ionization i (Fig. 9). In this case the transition is always relatively sharp. Interestingly enough, while for $i = 1$ % the transition is shifted towards higher temperatures in comparison with $i = 0$ %, further increasing of degree of ionization i gradually shifts the transition towards lower temperatures, even below the curve for $i = 0$ %. We assume that this complex behavior is in connection with very low polymer concentration where globular structures are formed by individual macromolecules. From Figs. 8 and 9 it follows that the temperature interval of the transition can be “tuned” by changing the polymer concentration c and the degree of ionization i .

3.3. Nature of broadening of NMR lines in PDEAAm/D₂O gels

To obtain some information about the nature of the motional restrictions resulting in a pronounced broadening of NMR lines at elevated temperatures, ¹H MAS NMR spectra of PDEAAm/D₂O physical gels were measured at variable spinning frequency [7]. 399.9 MHz ¹H MAS NMR spectrum of this system measured at 308 K with a spinning frequency of 10 kHz and with large spectral width (50 kHz) is

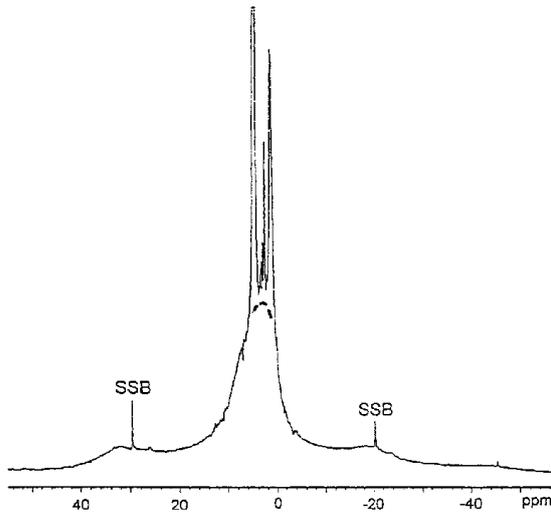


Fig. 10 399.9 MHz ¹H MAS NMR spectrum of PDEAAm/D₂O physical gel ($c = 6$ wt.-%) measured with spinning frequency 10 kHz and spectral width 50 kHz at 308 K. SSB denotes spinning sidebands [7].

shown in Fig. 10. A typical two-component lineshape is observed. Most of PDEAAm units contribute to the broad line with a linewidth of 3.6 kHz (virtually the same as the linewidth of 3.8 kHz found by broad-line NMR measurements at 60 MHz, cf. Fig. 6), on which narrow lines of PDEAAm units retaining a high mobility are superimposed. The result that the line broadening of phase-separated PDEAAm segments cannot be removed, not even

using MAS with spinning frequency significantly larger than the linewidth of the broad component, shows that the broadening to the 3.6 kHz linewidth is not due to near-static dipolar interactions, but the respective motion is effectively isotropic with motional correlation time $\tau_c \approx 1$ μ s. This is in agreement with $\tau_c = 2$ μ s as obtained from a measurement of the temperature dependence of the relaxation time $T_{2\text{eff}}$, which characterizes the magnetization decay in MW4 multiple-pulse experiments [8].

The correlation time $\tau_c = 2$ μ s could be associated with retarded segmental motion in the globular state and/or with motion of globules of phase separated PDEAAm as a whole. The relatively fast and effectively isotropic motion of PDEAAm segments in dense globular-like structures is rather improbable. For the second case, it follows from the relation

$$\tau_c = 4\pi\eta a^3/(3kT) \quad (2)$$

where η is the solvent viscosity and a the radius of globular-like particles, such that $a = 15$ nm. This value agrees well with the z-averaged radius of gyration of globular-like particles, $R_z = 18$ nm, as determined by small-angle neutron scattering [6], thus supporting the idea that correlation time $\tau_c = 2$ μ s could correspond to the Brownian tumbling of the whole globules.

3.4. Behavior of water molecules

The measurements of temperature dependences of absolute integrated intensities of the ¹H NMR line of HDO have shown that in studied systems all the solvent is detected in high-resolution spectra in the whole range of temperatures. To characterize polymer-solvent interactions in PVME/D₂O solutions, we used measurements of nonselective (NS) and selective (SE) ¹H spin-lattice relaxation times T_1 , and spin-spin relaxation times T_2 of HDO molecules. It is well known that relaxation times $T_1(\text{SE})$ and $T_1(\text{NS})$ exhibit different dependences on the motional correlation time τ_c ; explicit expressions are given e.g. in [11]. While for correlation times fulfilling the condition $\omega_0\tau_c < 1$ (ω_0 is the resonance frequency), $T_1(\text{SE})$ is somewhat longer than $T_1(\text{NS})$ (for $\omega_0\tau_c \ll 1$, $T_1(\text{SE}) = 1.5 T_1(\text{NS})$), for $\omega_0\tau_c > 1$, $T_1(\text{SE})$ is significantly shorter than $T_1(\text{NS})$. 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 (T_1) or spin-spin (T_2) relaxation time is given as [11]

$$(T_{1,2\text{obs}})^{-1} = (1-f) (T_{1,2\text{F}})^{-1} + f (T_{1,2\text{B}})^{-1} \quad (3)$$

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

We measured ^1H $T_1(\text{NS})$ and $T_1(\text{SE})$ of residual HDO molecules in PVME/D₂O solutions of various polymer concentration as function of temperature. In all cases the relaxation curves were exponential (single T_1). The results obtained for $c = 6$ wt.-% are shown in Fig. 11. Similar temperature dependences

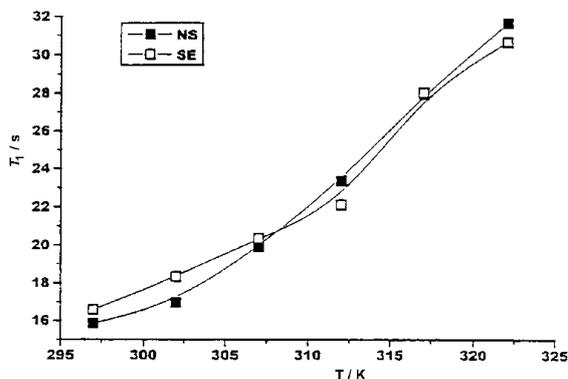


Fig. 11 Selective (open symbols) and nonselective (filled symbols) ^1H spin-lattice relaxation times T_1 (standard deviation less than 0.5 %) of HDO molecules in PVME/D₂O solution ($c = 6$ wt.-%) as function of temperature at 500.1 MHz [9].

of $T_1(\text{SE})$ and $T_1(\text{NS})$ were also found for other concentrations in semidilute or concentrated regime ($c = 4, 10, 60$ wt.-%). From Fig. 11 it follows that while at temperatures below the transition ($T \leq 307$ K) we observed somewhat lower values of $T_1(\text{NS})$ in comparison with $T_1(\text{SE})$, as expected for $\omega_0\tau_c < 1$, the reverse situation (i.e. $T_1(\text{NS}) > T_1(\text{SE})$) was found at temperatures above the LCST transition. These results evidence that at elevated temperatures, where most PVME forms globular structures, a part of HDO molecules is bound to PVME. Such HDO molecules exhibit (similarly as phase-separated PVME) a slow-motion behavior ($\omega_0\tau_c > 1$) with fast exchange between bound and free sites regarding T_1 values (~ 20 s), i.e. the lifetime of the bound HDO molecules is ≤ 2 s. For dilute PVME/D₂O solution ($c = 0.2$ wt.-%) the behavior shown in Fig. 11 was not found.

Results obtained for semidilute and concentrated PVME/D₂O solutions from $T_1(\text{SE})$ and $T_1(\text{NS})$ measurements are also corroborated by measurements of spin-spin relaxation times T_2 of HDO molecules. Also in this case the T_2 relaxation curves were exponential. While for dilute PVME/D₂O solutions ($c = 0.1$ and 0.2 wt.-%) T_2 values of HDO molecules 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 T_2 at 305 K (e.g. for $c = 6$ wt.-%, $T_2 =$

4.8 and 0.44 s at 305 and 309.5 K, respectively). Taking into account Eq. (3), these results evidence that in semidilute and concentrated solutions a certain portion of HDO molecules is bound at elevated temperatures in (to) PVME globular structures, in accord with results of T_2 measurements of PVME protons (cf. Fig. 5).

4. CONCLUSION

In this work we present results of the investigation of structural-dynamic changes during temperature-induced phase transitions in PVME/D₂O solutions and gels, PDEAAm/D₂O solutions and gels, and PIPMAAm/D₂O solutions by combination of ^1H NMR methods. For all systems studied, both phase separation in polymer solutions and volume phase transition (collapse) in gels of crosslinked polymers result in a marked line broadening of a major part of polymer segments, evidently due to the formation of compact globular-like structures. The minority mobile component, which does not participate in phase transition, is probably from low-molecular-weight fraction. Chemical crosslinking and especially the presence of negative charges on polymer chain result in the shift of the transition region. ^1H MAS NMR spectra and results of MW4 multiple-pulse experiments ($T_{2\text{eff}}$ relaxation times) have shown that motion of PDEAAm segments in D₂O solutions or gels above the transition region is effectively isotropic with correlation time $\tau_c \cong 2$ μs ; such motion can correspond to isotropic Brownian tumbling of globules as a whole. Measurements of spin-spin relaxation time T_2 in PVME/D₂O solutions have shown that globular structures are more compact in dilute solution in comparison with semidilute or concentrated solutions where globules probably contain a certain amount of water. A certain portion of water molecules bound at elevated temperatures in (to) PVME globular structures in semidilute or concentrated solutions was evidenced from measurements of nonselective and selective spin-lattice relaxation times T_1 and spin-spin relaxation times T_2 of HDO molecules.

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Jiří Spěváček was born in 1946. In 1968 he graduated (Mgr.) at the Charles University in Prague, Faculty of Mathematics and Physics. In 1974 he obtained PhD from the same university and in 1990 the scientific degree Doctor of Sciences (DSc) from Czechoslovak Academy of Sciences. The title of his DSc thesis was „Characterization of associated structures of stereoregular poly(methyl methacrylate)s and other polymers by spectroscopic methods“. Since 1968 he is working in the Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, since 1985 as Chief Research Fellow. His scientific research is focusing on studies of the structure and dynamics of polymers by NMR spectroscopy and other physical methods.