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Polymer 42 (2001) 463–468

polymer

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^{1}H NMR study of temperature collapse of linear and crosslinked poly(*N*,*N*-diethylacrylamide) in D_2O ☆

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Received 28 February 2000; received in revised form 8 April 2000; accepted 26 April 2000

Abstract

Changes in the dynamic structure of poly(*N*,*N*-diethylacrylamide)(PDEAAm) gels in D_2O during a temperature-induced phase transition (collapse), were investigated by a combination of high-resolution, broad-line and multiple-pulse MW4 ^{1}H NMR methods. Both physical gels and solution of linear PDEAAm, and gels of chemically crosslinked PDEAAm were studied. Very similar behavior was found in both cases, indicating the formation of compact globular structures in the collapsed state. However, a lower mobility of chemically crosslinked PDEAAm results in up to 3–4°C shift of the transition region towards lower temperatures, in comparison with the linear polymer. In all cases, the transition as observed by NMR appeared as continuous, even for PDEAAm containing 1–6 mol% of sodium methacrylate units; this is probably due to the fact that high-resolution NMR spectra are sensitive only to the fast first stage of the deswelling process. The results of MW4 multiple-pulse experiments ($T_{2\mathrm{eff}}$ relaxation measurements) show that the correlation time of the motion of collapsed segments is 2 μs. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Collapse phase transition; Poly(*N*,*N*-diethylacrylamide); NMR spectroscopy

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1. Introduction

It is well known 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 [1,2]. At the collapse, the gel volume can decrease 10–1000 times. The presence of a low number of charges on the chain appeared to be a necessary condition for discontinuous phase transition; they can be formed either by spontaneous hydrolysis of AAm groups or by copolymerization with a suitable monomer, e.g. sodium methacrylate (MNa). Collapse was usually interpreted as a first-order phase transition [2], but there are also studies claiming that this is rather a second-order transition [3]; this point is still under discussion. Most experimental results were obtained with hydrogels of poly(acrylamide) (collapse induced by a change in solvent composition) and of poly(*N*-isopropylacrylamide) (collapse induced by a temperature change). Collapse induced by temperature was observed also with poly(*N*,*N*-diethylacrylamide) (PDEAAm) hydrogels and their swelling, mechanical and photoelastic behavior, as well as small-angle neutron scattering of PDEAAm hydrogels were studied previously [2,4–6]. It is also known that certain polymers including PDEAAm [7,8] exhibit a lower critical solution temperature (LCST), i.e. they are soluble at low temperatures but heating above LCST results in phase separation (precipitation). On the molecular level, both collapse in hydrogels, and phase separation in solutions are assumed to be macroscopic manifestation of a coil–globule transition [1,9,10]. This transition is probably due to the changed balance between various types of interactions (mainly the hydrogen bonds and hydrophobic interactions).

NMR spectroscopy has been used so far in several papers dealing with collapse transition in poly(acrylamide) and poly(*N*-isopropylacrylamide) hydrogels [11–14]. In most of these studies, changes in the dynamics of both polymer segments and solvent during the phase transition were investigated by nonselective ^{1}H relaxation measurements (T_1 and T_2), and measurements of diffusion coefficients. Recently, NMR spectroscopy has also been used to study phase separation in poly(*N*-isopropylacrylamide)/water solutions [15]. To our knowledge, no NMR studies exist for PDEAAm gels and solutions.

☆ Series. Phase transition in swollen gels: 28.

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PII: S0032-3861(00)00357-8

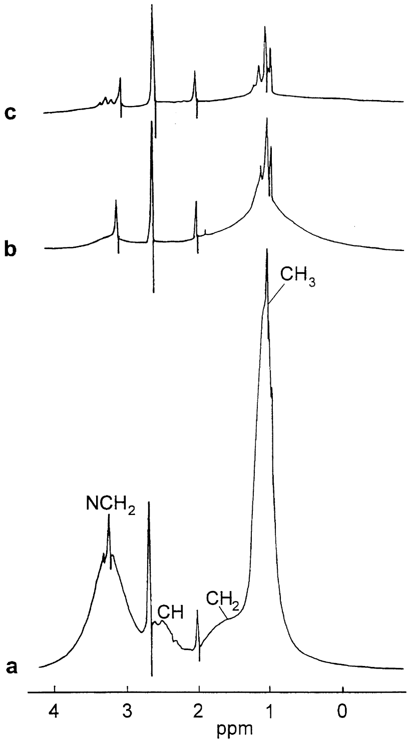

Fig. 1. ^1H NMR spectra of linear PDEAAm in D_2O ($c = 10$ wt%) measured at: (a) 32; (b) 36; and (c) 39°C under the same instrument conditions; the strong signal of HOD at 4.6–4.7 ppm is not shown.

In the present work, we used ^1H NMR methods to characterize the collapse transition and phase separation in PDEAAm/D_2O gels and solutions. For this purpose, both linear and chemically crosslinked PDEAAm samples were studied. The effect of ionization (1–6 mol% of charges on the chain) was also followed. From the methodical point of view, we combined an approach based on measurements of temperature dependences of integrated intensities in high-resolution ^1H NMR spectra (this approach was used by us in the past to study the association phenomena in various polymer solutions and gels [16–18]), with measurements of broad-line ^1H NMR spectra and effective relaxation times using multiple-pulse (MW4) sequences.

2. Experimental

2.1. Samples

Samples of linear PDEAAm in D_2O were prepared directly in NMR tubes by polymerization at 4°C, initiated by ammonium peroxysulfate and N,N,N',N'-tetramethylethylenediamine (cf. also Refs. [4,5]). Concentration of the DEAAm monomer was 3, 5.5 and 10 wt%. While the sample of lowest concentration was a true solution, samples of 5.5 and10 wt% concentrations were physical gels (they did not flow).

Samples of gels of crosslinked PDEAAm (total concentration of monomer and crosslinker was 10 wt%) were prepared by a similar procedure as given above, using N,N'-methylenebisacrylamide (MBAAm) as a crosslinking agent. Samples of various crosslinking density were prepared using 0.5, 2.5 and 5 mg of MBAAm, and 1.8 ml of D_2O solution of other components (DEAAm, ammonium peroxysulfate, N,N,N',N'-tetramethylethylenediamine). Mechanical measurements of the shear modulus G were used to check the degree of crosslinking. The values $G = 3$, 20 and 40 g/cm^2 were obtained for these three samples going from the lowest to the highest amount of MBAAm. A sample prepared with 1 mg of MBAAm and 1.8 ml D_2O solution was also studied.

Three samples of gels of ionized crosslinked PDEAAm (concentration 10 wt%) were prepared in an analogous way (using 7.2 ml D_2O, 0.8 ml DEAAm, 8 mg MBAAm), and adding 1, 3 and 6 mol% of sodium methacrylate (MNa) relative to DEAAm monomer. Linear ionized PDEAAm ($c = 10$ wt%) containing 3 mol% of MNa was also prepared.

2.2. NMR measurements

PDEAAm solution and physical and chemical gels in D_2O were measured in sealed 5-mm NMR tubes. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as an internal NMR standard in the PDEAAm solution of the lowest concentration (3 wt%). NMR lines in spectra of other samples (samples without DSS) were referenced using other lines as a reference. High-resolution ^1H NMR spectra were recorded with a JEOL PS-100 cw spectrometer at 100 MHz. The integrated intensities were measured by means of the built-in integrator with an accuracy of ±1%. The temperature was maintained constant within ±0.5°C with a JES-VT-3 unit. The absolute temperature values were calibrated using ^1H NMR. spectra of ethylene glycol [19].

Broad-line (FT-FID) ^1H NMR spectra and $T_{2\mathrm{eff}}$ relaxation times (characterizing the magnetization decay when MW4 pulse sequence is applied, cf. [20]) were measured at 60 MHz using an FT spectrometer of type FKS 178 (ZWG). The electronic assembly is characterized by a dead time of 6–7 μs and a π/2-pulse width of 1 μs. The pulse interval $2t_1$ in MW4 sequence was 24 μs.

3. Results and discussion

3.1. High-resolution ^1H NMR spectra

In Fig. 1 are shown high-resolution ^1H NMR spectra of linear PDEAAm ($c = 10$ wt%) in D_2O, measured at three temperatures and under identical instrument conditions. Strong bands centered at 1.1 and 3.3 ppm correspond to CH_3 and CH_2 protons, respectively, of ethyl groups in the side chains, while the main-chain CH_2 and CH protons resonate at 1.7 and 2.55 ppm, respectively. Sharp lines (at 1.08, 2.76 and 3.3 ppm) originate from the used D_2O and from the

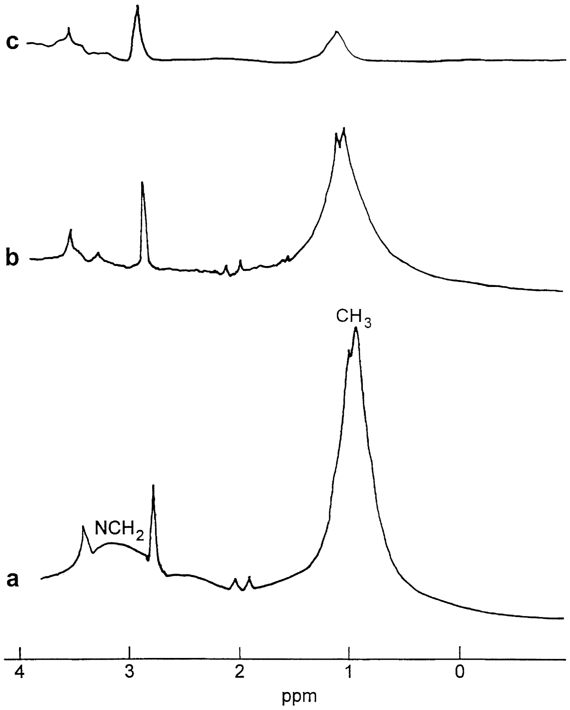

Fig. 2. ^{1}H NMR spectra of chemically crosslinked PDEAAm gel in D_2O ($c = 10$ wt%; $G = 20$ g/cm^2) measured at: (a) 29; (b) 31; and (c) 36°C under the same instrument conditions; the strong signal of HOD at 4.6–4.7 ppm is not shown.

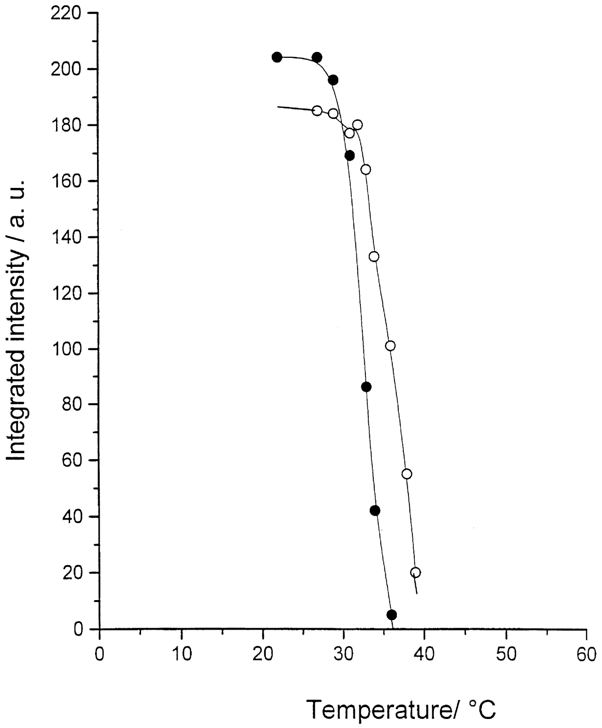

Fig. 3. Temperature dependences of integrated intensities of high-resolution ^{1}H NMR bands of linear PDEAAm ($c = 10$ wt%) (○) and chemically crosslinked PDEAAm ($c = 10$ wt%, $G = 20$ g/cm^2) (●) in D_2O. Absolute values of integrated intensities of two samples are not directly comparable.

initiator (2.05 ppm). The most important effect shown in Fig. 1 is a marked decrease in the integrated intensity of all PDEAAm bands in a rather narrow temperature interval of 32–39°C. This is due to the fact that with increasing temperature, the mobility of a major part of PDEAAm units is reduced to such an extent that they escape detection in high-resolution ^{1}H NMR. spectra (the proton linewidths of these units have to be at least ~1 kHz). Similar behavior was recently reported for poly(*N*-isopropylacrylamide)/water solutions [15]. Fig. 1 also illustrates the fact that at 39°C (and also at higher temperatures), a certain portion (~10%) of PDEAAm units with unrestricted mobility, are detected in high-resolution spectra. The same behavior, as shown in Fig. 1 for $c = 10$ wt%, was found also for lower concentrations, $c = 5.5$ and 3 wt%, i.e. the same behavior was observed regardless of whether the studied sample is physical gel ($c \geq 5.5$ wt%) or solution ($c = 3$ wt%). Evidently, the reason for the reduction in the PDEAAm segmental mobility is a phase transition resulting in the formation of compact globular structures. We assume that mobile units are those on the surface of globular particles.

High-resolution ^{1}H NMR spectra of a chemically crosslinked PDEAAm gel ($c = 10$ wt%) in D_2O are shown in Fig. 2. A comparison of integrated intensities of PDEAAm bands of linear and crosslinked samples of the same polymer concentration indicates that even at temperatures ≤30°C, i.e. below the collapse phase transition, the integrated intensity of the crosslinked sample is substantially lower amounting to 67% (for a sample with the lowest crosslinking density; $G = 3$ g/cm^2) or 50% (for a sample with the highest crosslinking density, $G = 40$ g/cm^2) of the integrated intensity of a linear sample. Fig. 2a shows that in particular, bands of CH and CH_2 main-chain protons of crosslinked PDEAAm are broadened beyond the detection limit. Evidently, mainly side groups of PDEAAm units far away from chemical crosslinks are directly revealed in high-resolution spectra. Fig. 2 shows that the behavior of these groups of crosslinked PDEAAm during phase transition is virtually the same as that of linear PDEAAm; nevertheless the temperature interval where integrated intensities decline is slightly different. This fact is even better documented in Fig. 3, where the temperature dependences of integrated intensities of PDEAAm bands in high-resolution ^{1}H NMR spectra of linear and crosslinked PDEAAm (in both cases $c = 10$ wt%) in D_2O are compared. We can see that for the crosslinked PDEAAm ($G = 20$ g/cm^2) the transition is shifted by 3–4°C towards lower temperatures. The trend of slightly lowering the temperature interval of the collapse transition by chemical crosslinking is also consistent with Fig. 4, which shows temperature dependences of integrated intensities of spectra for samples with different crosslinking densities; the transition observed for the lowest crosslinking density ($G = 3$ g/cm^2) occurs at temperatures between the transition interval for linear PDEAAm (cf. Fig. 3) and samples of higher crosslinking densities ($G = 20$ and 40 g/cm^2). Somewhat lower transition

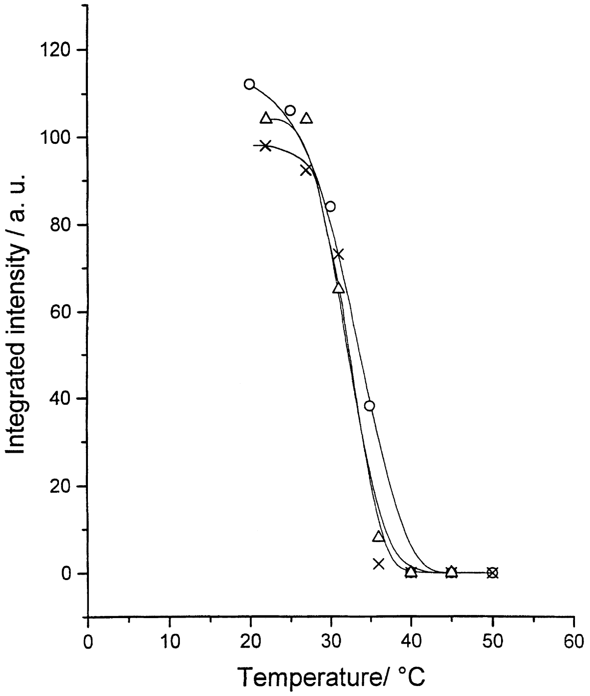

Fig. 4. Temperature dependences of integrated intensities of high-resolution ^{1}H NMR bands of chemically crosslinked PDEAAm ($c = 10$ wt%) in D_2O gels; shear modulus $G = 3$ g/cm^2 (○), 20 g/cm^2 (×) and 40 g/cm^2 (△). Absolute values of integrated intensities of different samples are not directly comparable.

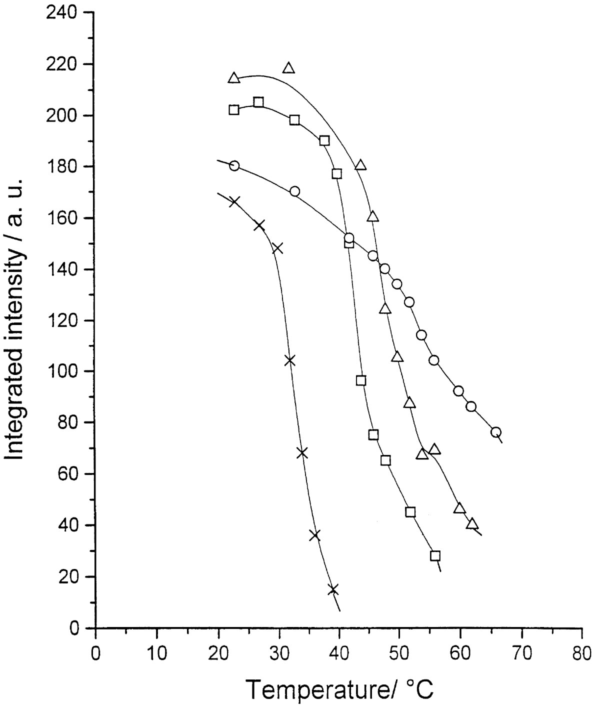

Fig. 5. Temperature dependences of integrated intensities of high-resolution ^{1}H NMR spectra of D_2O gels of chemically crosslinked PDEAAm containing 0% (x), 1 mol% (□), 3 mol% (△) and 6 mol% (○) of MNa units ($c = 10$ wt%, G ~ 20 g/cm^2). Absolute values of different samples are not directly comparable.

temperatures observed for crosslinked PDEAAm are a consequence of the lower mobility of PDEAAm segments, due to crosslinks. Otherwise, the NMR spectra confirm the same nature of the collapse in gels of chemically crosslinked PDEAAm and of phase separation in PDEAAm solutions, namely the coil–globule transition. Figs. 3 and 4 also show that both for PDEAAm physical gels (and solution) and chemically crosslinked PDEAAm gels, the observed transition is continuous, with an interval of transition temperatures ~7°C broad. In this connection, we also measured time dependences of integrated intensities at several temperatures in the transition region for several hours, both for linear and chemically crosslinked PDEAAm. We have found that integrated intensities were always time-independent, confirming that points in Figs. 3 and 4 are "equilibrium" values. These results also show that the transition as observed by NMR spectra is relatively fast; the "equilibrium" is reached in few minutes (this time is necessary to reach the desired temperature in the sample).

The effect of ionization on the collapse transition in gels of chemically crosslinked PDEAAm is demonstrated in Fig. 5, where the temperature dependences of NMR integrated intensities for systems containing various contents of MNa units are shown. In agreement with other methods, it follows from the figure that the transition region shifts towards higher temperatures with increasing concentration of negative charges bound on the chain. An increasing content of hydrophilic MNa units increases the mobility of polymer segments, and higher temperature is necessary to allow hydrophobic interactions to predominate. Interestingly enough, the transition region, as detected by ^{1}H NMR spectra, becomes broader with the increasing content of MNa (especially for 6 mol% of MNa), while swelling and mechanical measurements [4] showed that for ionized PDEAAm gels, the collapse was virtually discontinuous. This difference is probably a result of different kinetics of the collapse transition as detected by different methods. While time dependences of ^{1}H NMR spectra show collapse (coil–globule) transition as a rather fast process (the final state is reached within several minutes), measurements of the swelling ratio detect changes during 15 h [6]. From this comparison, it follows that high-resolution ^{1}H NMR spectra detect only the fast first stage of formation of globular structures, while they are insensitive to slow changes due to further removal of water from these structures.

3.2. Broad-line ^{1}H NMR spectra and T_{2eff} relaxation times in multiple-pulse MW4 measurements

In Fig. 6 are shown broad-line (FT-FID) ^{1}H NMR spectra of linear PDEAAm containing 3 mol% of MNa in D_2O ($c = 10$ wt%), measured at three temperatures. At temperatures below the collapse transition (30 and 40°C), there is a single narrow line (chemical shift is only indicated because of the broad spectral range of 33 kHz). At 60°C, i.e. above

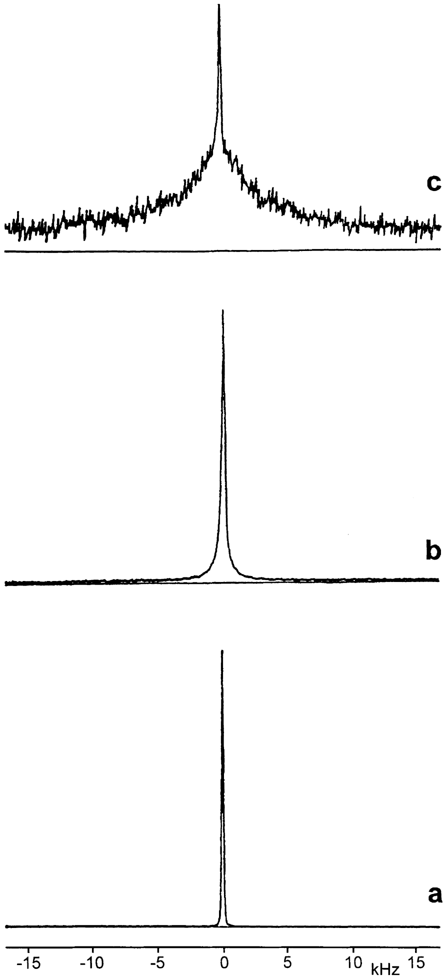

Fig. 6. Broad-line (FT-FID) ^{1}H NMR spectra of PDEAAm containing 3 mol% of MNa units ($c = 10$ wt%) in D_2O, measured at: (a) 30; (b) 40; and (c) 60°C.

the collapse transition, a typical two-component lineshape is shown. Most of PDEAAm units (~90%, as obtained by deconvolution of two components) contribute to the broad line with linewidth of 3.8 kHz, which is typical for a "solid-like" behavior combined with motional narrowing; nevertheless, a narrow component (intensity of ~10%) is also clearly visible. We can see that broad-line results are in accord with the results obtained from high-resolution spectra, as discussed in the previous section. The same behavior and similar linewidths of the broad component were found also for non-ionized systems but, in agreement with high-resolution spectra, the broad component was already detected at 40°C. A similar linewidth of ~3 kHz was previously found for the collapsed state of chemically crosslinked poly(*N*-isopropylacrylamide) [12].

In Fig. 7 are shown temperature dependences of the relaxation time $T_{2\mathrm{eff}}$, which characterizes the magnetization decay when an MW4-pulse sequence is used [20–22]. Similar to $T_{1\rho}$, the spin–lattice relaxation time in the rotating frame, $T_{2\mathrm{eff}}$, is sensitive to slow molecular motions with correlation times in the microseconds range. The temperature dependence of $T_{2\mathrm{eff}}$ is characterized in general, by a minimum at $\omega_{\mathrm{eff}}\tau_c = 1$, where τ_c is the temperature-dependent correlation time of a (slow) molecular reorientation process and ω_{eff} denotes the frequency of the effective radiofrequency field with $\omega_{\mathrm{eff}} = 2\pi/t_1$, where $2t_1$ is the pulse interval in the MW4 experiment.

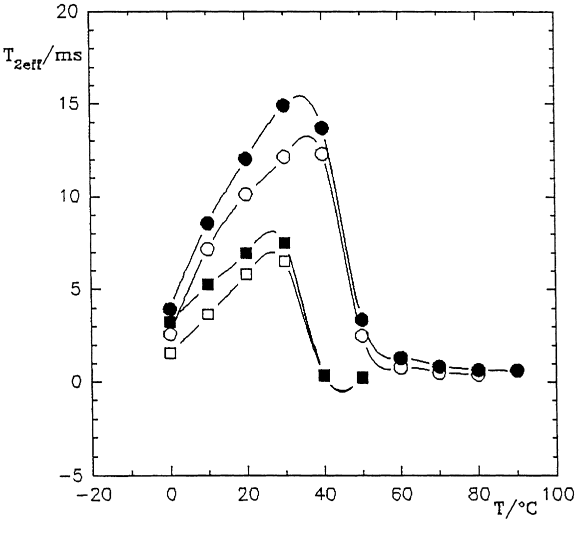

Fig. 7. Temperature dependences of the relaxation time $T_{2\mathrm{eff}}$ (measured with $t_1 = 12$ μs) for various PDEAAm gels in D_2O ($c = 10$ wt%); linear PDEAAm (■), linear PDEAAm containing 3 mol% of MNa (●), chemically crosslinked PDEAAm ($G \sim 8$ g/cm^2) (□), chemically crosslinked PDEAAm containing 3 mol% of MNa units (○).

For temperatures below 30 or 40°C (for non-ionized and ionized systems, respectively), $T_{2\mathrm{eff}}$ values increase with increasing temperature (Fig. 7). In this region, the system is in a liquid-like state with $\omega_{\mathrm{eff}}\tau_c \ll 1$, and high-resolution and broad-line spectra with relatively small linewidths correspond to this region (cf. also previous section). A sudden decrease in $T_{2\mathrm{eff}}$ in the interval 30–40°C (for linear and crosslinked PDEAAm) or 40–60°C (for linear and crosslinked samples containing 3 mol% of MNa) corresponds to the collapse coil–globule transition, in accord with the results obtained from integrated intensities of high-resolution NMR spectra (cf. Figs. 3–5). At these and higher temperatures, $T_{2\mathrm{eff}}$ values correspond virtually only to collapsed segments (contribution from the residual mobile part is negligible). The correlation time τ_c of the motion of collapsed segments can be estimated for temperatures above the transition, where $T_{2\mathrm{eff}}$ exhibits a flat minimum ($\omega_{\mathrm{eff}}\tau_c = 1$). Taking into account that $t_1 = 12$ μs, i.e. $\omega_{\mathrm{eff}} = 5 \times 10^5$, we obtain $\tau_c = 2$ μs. At higher temperatures, an increase in $T_{2\mathrm{eff}}$ can be expected.

The correlation time of the collapsed segments, $\tau_c = 2$ μs, can be associated either with retarded segmental motion in the globular state or with motion of the globules as a whole. For the latter case, it follows from the relation [23] $\tau_c = 4\pi\eta a^3/(3kT)$, where η is a solvent viscosity and a is the radius of globular particles, such that $a = 15$ nm. This value agrees well with the *z*-average radius of gyration of globular particles, $R_z = 18$ nm, as determined for PDEAAm/D_2O solution by small-angle neutron scattering [5]. Thus, not excluding the idea that correlation time $\tau_c = 2$ μs could correspond to the Brownian tumbling of the whole globules.

4. Conclusion

In this work we investigated the temperature-induced collapse phase transition in PDEAAm solution and gels in D_2O by combination of high-resolution and broad-line ^1H NMR spectra, and multiple-pulse MW4 relaxation measurements. Both PDEAAm solution (or physical gels) and chemically crosslinked PDEAAm gels were studied. In both cases, a very similar behavior was observed. Both volume phase transition (collapse) in gels of crosslinked PDEAAm and phase separation in PDEAAm solution (or physical gels) result in marked broadening (linewidth 3.8 kHz) of NMR lines of a major part of PDEAAm units, evidently due to the formation of compact globular structures. At the same time, a certain portion of PDEAAm units (~10%) with high mobility exist. The existence of chemical crosslinks lowers the mobility of PDEAAm segments, and the collapse transition is shifted up to 3–4°C towards lower temperatures in comparison with solution or physical gels of linear PDEAAm. On the other hand, the presence of hydrophilic MNa units shifts the collapse transition towards higher temperatures, evidently in connection with a higher segmental mobility. High-resolution NMR spectra are sensitive only to the fast first stage of the shrinking process; for this reason, the collapse transition as observed by NMR is continuous even for PDEAAm containing up to 6 mol% of MNa units. The coil–globule transition was also detected in temperature dependences of relaxation time $T_{2\mathrm{eff}}$, which characterizes the magnetization decay in MW4 multiple-pulse measurements. The correlation time $\tau_c = 2$ μs derived for collapsed segments from $T_{2\mathrm{eff}}$ measurements might be associated with the Brownian tumbling of globules as a whole.

Acknowledgements

This work was supported by Ministry of Education of Czech Republic—Project .no.: VS97115.

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