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NMR Investigations of Temperature-Induced Phase Transition in Aqueous Polymer Solutions

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Summary: The different dynamics of polymer segments forming phase-separated globular structures in aqueous (D_2O) solutions affects both the shape of NMR spectra and NMR relaxation times of polymer and solvent. Two types of the approach are discussed. The first one is based on the reduction of integrated intensities of polymer NMR lines in high-resolution NMR spectra in the system undergoing the coil-globule phase transition. The fraction p of phase-separated units (units with significantly reduced mobility) and subsequently, e.g., thermodynamic parameters ΔH and ΔS characterizing the coil-globule phase transition can be determined. The second approach is based on measurements of ^{1}H NMR relaxation times of water (HDO) which provide information on behaviour of water during phase transition. The power of both approaches is demonstrated on results obtained with solutions of several thermoresponsive homopolymers and copolymers.

Keywords: aqueous polymer solutions; cooperative effects; NMR; phase transition; stimuli-sensitive polymers

Introduction

It is well known that some acrylamide-based polymers and other polymers with amphiphilic character exhibit in aqueous solutions a lower critical solution temperature (LCST). These polymers are soluble at lower temperatures but heating above the LCST results in phase separation which especially at polymer concentrations $c \geq 1$ wt% makes solutions milk-white turbid.[1,2] On the molecular level, both phase separation in solutions and similar volume phase transition (collapse) in crosslinked hydrogels are assumed to be a macroscopic manifestation of a coil-globule transition followed by further aggregation and formation of so-called mesoglobules. In addition to temperature, which represents an external stimulus which is most often used, phase separation can be induced also by change of other factors such as solvent composition, pH, electric field, etc. Their ability to react on the change in various external stimuli makes these systems interesting for possible biomedical and technological applications, especially if the systems are in the form of hydrogels which can be used in the creation of ''smart'' material systems (sensors, actuators, switching devices etc). The fact that LCST of these thermoresponsive polymers can be adjusted near to human body temperature (37 °C) makes them viable as drug release polymers.[1,3] Of various methods, NMR spectroscopy was also used in investigations of these systems.[4]

The present paper provides an overview of our recent ^{1}H NMR studies dealing with phase transitions in D_2O solutions of several thermoresponsive homopolymers (poly(vinyl methyl ether) (PVME), poly(*N*-isopropylacrylamide) (PIPAAm), poly(*N*-isopropylmethacrylamide) (PIPMAm), poly(*N*-

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vinylcaprolactam (PVCL)) and thermoresponsive P(IPMAm/AAm) random copolymers. At the same time some new results are presented, especially on thermodynamic parameters of coil-globule transition and behaviour of acrylamide (AAm) component of P(IPMAm/AAm) copolymers at phase transition. From the methodical point of view, two types of the approach will be discussed. The first one is based on the changes of the shape and integrated intensities in high-resolution ^{1}H NMR spectra at the phase transition. The second approach is based on measurements of NMR relaxation times (spin-spin relaxation time T_2 and spin-lattice relaxation time T_1) of the solvent (water).

Manifestation of Phase Transition in NMR Spectra

The most significant effect of coil-globule transition on NMR spectra is illustrated in Figure 1 where high-resolution ^{1}H NMR spectra of PVME/D_2O solution ($c = 4$ wt%) measured at two slightly different temperatures 307 K and 308.5 K (LCST = 308 K) are shown.[5,6] The assignment of resonances to various types of protons of PVME is shown directly in a spectrum measured at 307 K, i.e., below the LCST transition. The strong line on the left is a signal of HDO. The most important effect observed in the spectrum measured at higher temperature (308.5 K, just above the LCST) is a marked decrease in the integrated intensity of all PVME lines. This is evidently due to the fact that at temperatures above the LCST the mobility of most PVME units is reduced to such an extent that corresponding lines become too broad to be detected in high-resolution spectra. The depicted changes of the NMR spectra, which have been observed for a number of aqueous polymer solutions or physical gels and chemically crosslinked hydrogels,[4] show that reaching LCST results in marked line broadening of a major part of polymer units, evidently due to the phase transition and formation of globular structures.

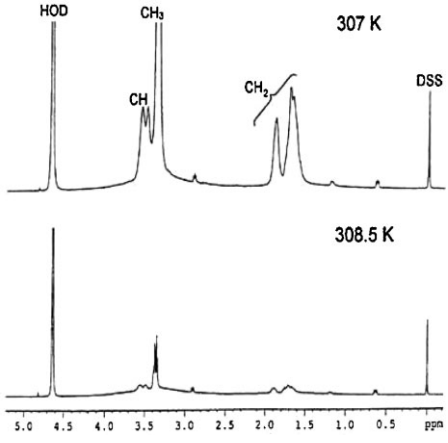

Figure 1.
500 MHz ^{1}H NMR spectra of PVME/D_2O solution ($c = 4$ wt%) measured at 307 and 308.5 K under the same instrumental conditions.[6]

Figure 2a shows the temperature dependence of the integrated intensity of the signal of CH_3 protons for PVME/D_2O solution ($c = 6$ wt%). As illustrated in this figure, in the LCST region the integrated intensity transitionally decreases with increasing temperature. Such dependence can be easily transformed in temperature dependence of the fraction p of phase-separated units (units in globular-like structures with significantly reduced mobility) by using the relation

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

where I is the integrated intensity of the given polymer line in a partly phase-separated system and I_0 is the integrated intensity of this line if no phase separation occurs. For I_0 we took values based on the integrated intensities below the phase transition, using the fact that integrated intensities should decrease with absolute temperature as $1/T$; in Figure 2a, the I_0 values at various temperatures are marked by dotted line. For illustration, Figure 2b shows temperature dependences of the phase-separated fraction p as determined from integrated intensities of the CH_3 line for PVME/D_2O solutions of various concentration.[5,6] For dilute solution of PVME ($c = 0.1$ wt%) the transition was virtually

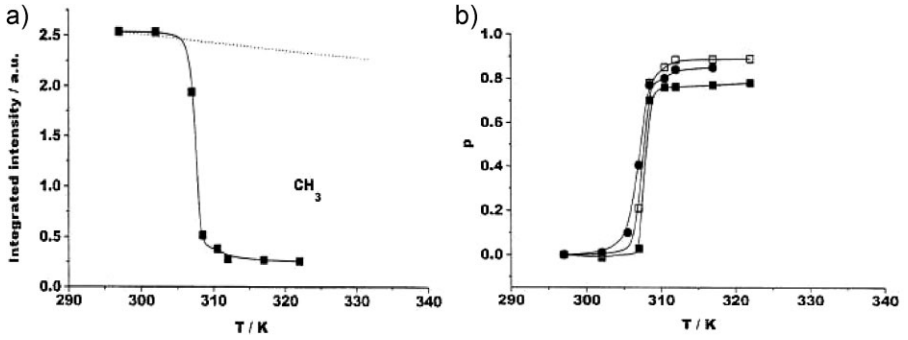

Figure 2.
(a) Temperature dependence of ^{1}H NMR integrated intensity of CH_3 band for PVME/D_2O solution ($c = 6$ wt%). Dotted line shows the $1/T$ dependence. (b) Temperature dependences of the phase-separated fraction p of CH_3 protons in PVME/D_2O solutions with $c = 0.1$ (■), 6 (□) and 30 (●) wt%.[4,6]

discontinuous while for highly concentrated solution ($c = 30$ wt%) the transition set in already at lower temperature and was 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. Similar behaviour as shown in Figure 2b for PVME/D_2O solutions was found also for D_2O solutions of poly(*N,N*-diethylacrylamide) (PDEAAm) and PIPMAm where the transition interval is $\sim$ 6 K broad and virtually independent of polymer concentration.[7,8] In contrast, there is a strong concentration dependence of the transition temperatures for PVCL/D_2O solutions; transition temperatures for $c = 30$ wt% are here 5 K lower in comparison with $c = 0.2$ wt%. For PIPMAm/D_2O solution ($c = 10$ wt%) also a pronounced thermal hysteresis was found by ^{1}H NMR spectroscopy, in accord with IR results.[9] This hysteresis is probably associated with polymer-polymer hydrogen bonding in the globular state.[10,11]

Thermodynamic Parameters of Coil-Globule Transition

For D_2O solutions of PDEAAm, PIPMAm and PVME, it was found from time dependences of ^{1}H NMR integrated intensities in the transition region that the respective change in the integrated intensity is rather fast, mostly in first $\sim$3 min (this time is necessary to reach the desired temperature in the sample) and then the integrated intensities do not change with time.[5–7,12,13] Therefore both the integrated intensities and p-values as shown for illustration in Figure 2 represent equilibrium values. We then could use the approach, applied for the first time by the author during his studies of selfaggregation in solutions of syndiotactic poly(methyl methacrylate),[14] to determine the thermodynamic parameters (ΔH, ΔS) of the coil-globule transition; a similar approach was relatively recently applied by Rice to PIPAAm hydrogel.[15] In terms of the values of the phase-separated fraction p we can write for the equilibrium constant $K(T)$ of the coil $\Leftrightarrow$ globule transition the ratio

$$K(T) = p/(1-p) \quad (2)$$

At the same time it holds

$$K(T) = \exp(-\Delta G/RT) = \exp[-(\Delta H/RT) + (\Delta S/R] \quad (3)$$

and values of the changes of the enthalpy ΔH and entropy ΔS can be determined from van't Hoff plots

$$\ln[p/(1-p)] = -(\Delta H/RT) + (\Delta S/R) \quad (4)$$

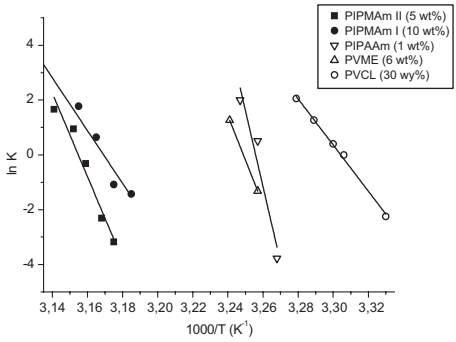

Figure 3.
Van't Hoff plots (ln *K* vs 1/*T*) as obtained by using NMR data for D_2O solutions of several thermoresponsive polymers of various concentration.

The values of the critical transition temperature T_{cr} defined so that $\Delta G(T_{cr}) = 0$ can be also calculated from the formula

$$T_{cr} = \Delta H/\Delta S \quad (5)$$

Van't Hoff plots for the phase transition in D_2O solutions of several thermoresponsive polymers are shown for illustration in Figure 3. The different slopes for PIPMAm I and II (left part of the Figure 3) are due to the different molecular weight of these polymers (cf. Table 1).

ΔH and ΔS values obtained for D_2O solutions of several thermoresponsive polymers by using the analysis described above are shown in the third and fourth columns of Table 1. From this Table it follows that both ΔH and ΔS values are positive and very large showing that also the cooperative units is very large. In accord with other authors[16] we assumed that cooperative unit is the whole macromolecule. In the last two columns of the Table 1, ΔH and ΔS values related to monomer unit (obtained by dividing the original ΔH and ΔS values by degree of polymerization (DP)) are shown. For PIPMAm II in D_2O ($c = 10$ wt%) ΔH was determined also by DSC; the obtained value $\Delta H = 4.14$ kJ/mol (monomer unit) agrees well with the value 4.3 kJ/mol (monomer unit) as determined by NMR analysis. Generally, ΔH values shown in Table 1 are in accord with values reported for PIPMAm,

PIPAAm, PVME and PVCL aqueous solutions using DSC by other authors.[16–18] There are probably two contributions to the values of the changes of enthalpy and entropy shown in Table 1. The first one is in connection with breakdown of polymer-water-hydrogen bonds.[16] The second possible contribution is in connection with disruption of local structure of water molecules surrounding hydrophobic groups of polymer units (hydrophobic hydration), which promotes hydrophobic interaction.[19] Rather small values of ΔH (around 4 kJ/mol (monomer unit), cf. Table 1) which can be rather expected for hydrophobic interactions might imply that second contribution can be more important in the LCST transition. The values of the critical

Table 1.
Thermodynamic parameters determined by using NMR data for D_2O solutions of several thermoresponsive polymers of various concentration.

Polymer	*c* (wt%)	ΔH (kJ/mol)	ΔS (J mol^{-1} K^{-1})	T_{cr} (K)	DP	ΔH (kJ/mol) monomer unit	ΔS (Jmol^{-1} K^{-1}) monomer unit
PIPMAm I	0.1	792	2513	315.4	193	4.1	13.0
	1	1092	3450	315.6		5.7	17.9
	10	799	2533	315.4		4.1	13.1
PIPMAm II	5	1266	3993	317.0	292	4.3	13.7
PIPAAm	1	2315	7542	306.9	841	2.8	9.0
PVME	0.1	1356	4390	308.9	348	3.9	12.6
	6	1346	4372	307.9		3.9	12.6
	30	870	2830	307.4		2.5	8.1
PVCL	0.2	455	1481	307.2	86	5.3	17.2
	3	675	2216	304.6		7.8	25.8
	30	700	2313	302.6		8.1	26.9

transition temperature T_{cr} are also included in Table 1. They are in accord with experimental values and well reflect the fact that for PIPMAm/D_2O solutions the transition temperatures are virtually independent of polymer concentration while there is a strong concentration dependence of transition temperatures for PVCL solutions.

Phase Transition in Solutions of P(IPMAm/AAm) Copolymers

The power of NMR spectroscopy in investigation of temperature-induced phase separation in solutions of multicomponent polymer systems such as copolymers consists in its ability to provide quantitative information on phase-separation behaviour of both monomer units in a binary copolymer separately. In this paragraph we shall discuss the phase transition in solutions of P(IPMAm/AAm) random copolymers which were prepared by radical polymerization. In contrast to PIPMAm, PAAm homopolymer is not thermoresponsive. In ^{1}H NMR spectra of D_2O solutions of P(IPMAm/AAm) copolymers the signals of IPMAm units are well resolved and therefore the temperature dependences of the fraction p of IPMAm units with reduced mobility for series of P(IPMAm/AAm) copolymers with various IPMAm/AAm molar ratio can be easily obtained;[20] they are shown in Figure 4. From this figure it follows that increasing fraction of hydrophilic AAm units in the copolymer significantly shifts the transition towards higher temperatures, broadens the transition interval and reduces the maximum value of the phase-separated fraction p_{max}; the last point is probably most interesting.

Though the analysis of the phase-separation behaviour of AAm component in P(IPMAm/AAm) copolymers is complicated by the fact that signals of AAm units overlap with the CH_2 signal of IPMAm units, desired information can be obtained via the composition of the part which is directly detected in ^{1}H NMR spectra at

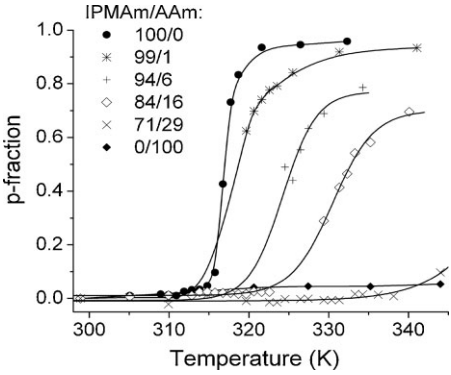

Figure 4.
Temperature dependences of the fraction p of IPMAm units with reduced mobility for D_2O solutions of P(IPMAm/AAm) random copolymers with various molar ratios of IPMAm and AAm units.[20]

temperatures above the phase transition and its comparison with overall composition of copolymer as determined by ^{1}H NMR.spectroscopy at room temperature. The respective values are markedly different as shown for several P(IPMAm/AAm) solutions in Table 2. In the last column of Table 2 the values of the molar fraction of AAm units in the part directly detected in NMR spectra above the LCST transition are shown which were obtained using the relation[20]

$$(\mathrm{AAm})_{\mathrm{above}} = (1-p_{\mathrm{IPMAm}})\,(\mathrm{IPMAm}) \times (\mathrm{AAm/IPMAm})_{\mathrm{above}} \quad (3)$$

where (IPMAm) is the molar fraction of IPMAm units in the copolymer (determined at room temperature). From Table 2 it follows that $(\mathrm{AAm})_{\mathrm{above}}$ values are either just the same or virtually the same as those of the molar fraction of AAm units in the copolymer. Therefore virtually all AAm units are visible in the ^{1}H NMR spectrum measured at the temperature above the phase transition and the fraction of phase-separated AAm units with reduced mobility, $p_{\mathrm{AAm}} = 0$. Because AAm units are incorporated in polymer chains forming phase-separated globular structures, their

Table 2.
Analysis of NMR behaviour of AAm-component of P(IPMAm/AAm) copolymers at LCST phase transition.

Solvent	Composition of the copolymer from ^{1}H NMR spectra at 300 K (LPMAm/AAm molar ratio)	P_{IPMAm}	Composition of the part of the copolymer detected in ^{1}H NMR spectra above the LCST $(IPMAm/AAm)_{above}$	Molar fraction of AAm units $(AAm)_{above}$ in the part detected in NMR spectra above the LCST
D_2O	94/6	0.77	75/25	0.07
D_2O	84/16	0.68	63/37	0.16
D_2O/EtOH (80/20)	94/6	0.69	83/17	0.06
D_2O/acctonc (80/20)	94/6	0.67	86/14	0.05

rather high mobility implies that they are hydrated. This finding also indicates that a part of IPMAm units, which retain high mobility above the phase transition (fraction $(1 - (p_{IPMAm})_{max})$ which increases with increasing content of AAm units in the copolymer) are hydrated IPMAm units surrounding AAm units (sequences). This suggests that in P(IPMAm/AAm) mesoglobules there are domains where both hydrophilic AAm sequences and surrounding IPMAm sequences are hydrated and mobile, while major part of IPMAm sequences are dehydrated and their mobility is strongly reduced. Such picture is corroborated by the fact (cf. Table 3) that there is a good correlation between fraction of mobile IPMAm units (fraction $(1 - (p_{IPMAm})_{max})$ and fraction of IPMAm-AAm diads which was calculated as 2[IPMAm] [AAm], where [IPMAm] and [AAm] are molar fractions of IPMAm and AAm units, respectively, in the copolymer. Together with the changes in the character of the transition (larger transition width), the heterogeneous structure of (PIPMAm/AAm) mesoglobules (or generally mesoglobules formed by copolymers containing hydrophilic units) might adversely affect the efficiency of these systems in some applications, such as drug delivery.

Table 3.
Correlation between values of the fraction of mobile IPMAm units $(1 - p_{IPMAm})$ and fraction of IPMAm-AAm diads for several P(IPMAm/AAm) random copolymers of various composition.

Copolymer composition (IPMAm/AAm)	$1 - P_{IPMAm}$ (in D_2O)	Fraction of IPMAm-AAm diads (= 2[IPMAm][AAm]
100/0	0.04	0
99/1	0.07	0.02
94/6	0.22	0.11
84/16	0.32	0.27

NMR Relaxation and Behaviour of Water at the Phase Transition

One possibility how to obtain information on polymer-solvent interactions (hydration) during temperature-induced phase transition in aqueous solutions of thermoresponsive polymers is an application of measurements of NMR relaxation times of the solvent. For illustration, Figure 5 shows the temperature dependences of spin-lattice relaxation time T_1 and spin-spin relaxation time T_2 of HDO molecules in D_2O solutions of PIPMAm. Both T_1 and T_2 dependences show a decrease in the LCST transition. Similar T_1 and T_2 dependences of water (HDO) were previously reported for aqueous solutions of PIPAAm, P(IPAAm-*co*-ethylene glycol), P(IPMAm-*co*-sodium methacrylate) and P(IPMAm-*co*-AAm) copolymers, and PIPMAm/PVME mixtures.[8,9,20–22] The reduced T_1 and T_2 values of HDO at temperatures above the phase transition show the existence of a portion of HDO molecules that exhibit a lower, spatially restricted mobility. Evidently, this portion corresponds to HDO bound in mesoglobules.[4] The single-exponential character of relaxation curves indicates a fast exchange between bound and free water

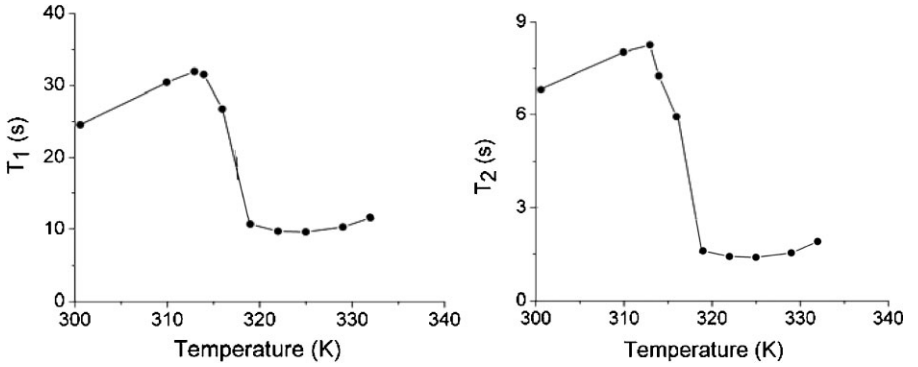

Figure 5.
Temperature dependences of ^{1}H spin-lattice relaxation time T_1 and spin-spin relaxation time T_2 of HDO in D_2O solution of PIPMAm ($c = 5$ wt%).

molecules. In such case, the observed relaxation rates at temperatures above the LCST transition are given as weighted average of the relaxation rates of bound and free HDO molecules.[8,9,13,23] At temperatures above the phase transition the shorter T_1 and T_2 of HDO in solutions of P(IPMAm/AAm) copolymers, compared with PIPMAm solution, reflect the existence of hydrated AAm and IPMAm sequences in copolymer mesoglobules, which can result in larger amounts of bound HDO.[20]

One order of magnitude shorter T_2 values of HDO at temperatures above the phase transition than those at temperatures below the phase transition were found also for D_2O solutions of PVME and PIPAAm, again showing that a certain portion of water molecules is bound in mesoglobules induced by temperature; for D_2O solutions of PVCL the difference in T_2 values of HDO at temperatures above and below the phase transition was much smaller. Interestingly enough, when the sample was kept at the temperature above the phase transition and time dependence of T_2 of HDO was measured, after some induction period T_2 values increased with time in all cases showing that originally bound water is very slowly released from globular-like structures,[13,23] in contrast to the fact that phase transition itself is rather fast (faster than 1 s in PIPAAm aqueous solutions[24]). For PVME/D_2O solution ($c = 6$ wt%) a release of water from globular-like structure is also shown by decreasing values of a short T_2 component of CH_2 protons of PVME with time when sample is kept at temperature above the LCST transition (due to the high flexibility of PVME chains it is possible to detect directly protons of PVME units in globular structures at certain instrument conditions).[23] No induction period and much faster releasing process was found from T_2 measurements of HDO for PVCL/D_2O solution ($c = 5$ wt%), indicating a different character of the releasing process in this case.

As already mentioned, a fast exchange between bound and free water was found for PVME, PIPMAm and PVCL aqueous solutions (for PVME solutions this holds only for concentrations $c = 2$-10 wt%). The exchange time ~1 ms was found for these solutions from dependences of spin-spin relaxation rate on the time interval t_d in CPMG pulse sequence 90°_x-(t_d-180°_y-t_d)$_n$-acquisition.[25,26] For highly concentrated PVME/D_2O solutions ($c = 20$–60 wt%) the existence of the separate signal of the bound HDO with ~0.74 ppm smaller chemical shift in comparison with the main HDO signal shows a slow exchange process.[27] At the same time the fractions of bound water in highly concentrated PVME/D_2O solutions were unchanged even for

70 h; from their values it follows that the polymer concentration in mesoglobules is 89 wt%. To detect a slow exchange in highly concentrated PVME/D_2O solution ($c = 50$ wt%) we applied an one-dimensional exchange ^1H NMR experiment with selective excitation of the main HDO signal and for the exchange time we obtained the value 2.1 s.[26] Assuming that exchange between free and bound water is associated with diffusion process, a three orders of magnitude slower exchange in highly concentrated PVME solutions is in accord with our optical microscopy findings that mesoglobules are here approx. 20 times larger than in PVME solutions with $c = 6$ wt%.

Conclusion

The different dynamics of polymer segments forming phase-separated globular structures in aqueous solutions affects both the shape of NMR spectra and NMR relaxation times of polymer and solvent. From the methodical point of view, two types of the approach were discussed. The first one is based on the reduction of integrated intensities of polymer NMR lines in high-resolution NMR spectra in the system undergoing the coil-globule phase transition. The fraction p of phase-separated units (units with significantly reduced mobility) and subsequently, e.g., the changes of the enthalpy ΔH and entropy ΔS characterizing the phase transition then can be determined. The second approach is based mainly on measurements of NMR relaxation times of the solvent (water) which provide information on behaviour of water during phase transition. The power of both approaches was demonstrated on results obtained with solutions of several thermoresponsive polymers. A promising class of systems for the application of NMR methods are multicomponent polymer systems as illustrated with solutions of P(IPMAm/AAm) random copolymers.

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