Coil-to-Globule Transition of PNIPAM Graft Copolymers with Charged Side Chains: A ^{1}H and ^{2}H NMR and Spin Relaxation Study

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ABSTRACT: Graft copolymers of poly(2-vinylpyridine), P2VP, grafted to a backbone of poly(*N*-isopropyl acrylamide), PNIPAM, are investigated concerning their thermosensitive behavior in aqueous solution. ^{1}H NMR monitors the coil-to-globule transition by quantifying the fraction of mobile segments in the liquid state. Field gradient NMR diffusion studies reveal a decrease of the hydrodynamic radius with temperature as the lower critical solution temperature (LCST) is approached. The LCST and the width of the transition of PNIPAM are increasing with grafting density and decreasing upon salt addition, which is attributed to electrostatic forces. The grafted segments become partially immobilized only for low grafting density. For high grafting density a fraction of the backbone segments remains mobile even above the LCST. ^{2}H spin relaxation rates of the hydration water indicate the presence of water molecules with very slow dynamics in the transition regime, whereas above and below the transition only fast water dynamics is found.

Introduction

Thermosensitive polymers exhibit a coil-to-globule transition, which is of large interest for a number of applications that require the switching of material properties with temperature. Application areas are for example drug delivery, bioseparation, or microfluidics. Examples are the separation of DNA by capillary electrophoresis,[1] enzyme isolation, where a specific technique is used to separate antigens and enzymes,[2] or the buildup of temperature-switchable valves for microscopic fluid devices.[3] Furthermore, thermosensitive polymers are considered as a model to elucidate the role of water molecules in thermal denaturation of natural polymers such as proteins.[4−6] For several applications a hydrophilic/hydrophobic balance of thermosensitive polymers shifting the phase transition to values around room temperature or body temperature is desirable.

One of the most intensively studied polymers in this field is poly(*N*-isopropylacrylamide), PNIPAM, which exhibits a sharp coil-to-globule transition in water at an LCST of 32 °C. Raising the temperature above the lower critical solution temperature (LCST), PNIPAM chains in solution undergo a structural transition to insoluble globular particles. The phase transition is accompanied by a release of bound water molecules from the polymer chain, which is an endothermic process.

To create functional materials from molecular constituents, modern methods of self-assembly are advantageous; however, they require the introduction of interacting groups, for example, charged segments for the electrostatic layer-by-layer approach.[7−10] Previous investigations of PNIPAM statistical copolymers containing various charged comonomers, however, showed a major influence of charged groups on the phase transition properties: While at low charge density the transition is comparable with that of the homopolymer, the transition vanishes with increasing charge density.[4,11] To minimize the effect of charged comonomers on the LCST, the comonomer structure should resemble that of the NIPAM monomer. Thus, a charged co-PNIPAM, containing 10 mol % acrylamide, bearing carboxyl groups, was analyzed in solution. DSC, turbidimetry, ^{1}H NMR, and PFG-NMR diffusion showed a phase transition, which was equally sharp as for the homopolymer.[12−14]

Adsorbed at interfaces and subject to geometric restrictions, however, the transition of the same copolymer was very sensitive to the presence of the charged comonomers.[15] In conclusion, statistical copolymers cannot be considered ideal structures for the formation of thermosensitive layers on the basis of electrostatic buildup principles.

A novel idea of minimizing the charge effects on the transition is based on a spatial separation of the electrostatic function from the thermosensitive function. To achieve this, thermosensitive graft copolymers have been synthesized.[16,17] The new types of copolymers combine the thermosensitive PNIPAM with a pH-sensitive component such as poly(2-vinylpyridine) (P2VP). The idea is to achieve a high flexibility of the main chain even in a stratified 2-dimensional layer arrangement since electrostatic binding can occur via the grafted chains, if they are dissociated. First DSC curves of such copolymers in solution showed a shift of the LCST to higher temperatures with increasing grafting density and in addition a broadening of the transition.[16] Successful formation of multilayers by alternating deposition with a polyanion has already been demonstrated.[18]

Similar graft copolymers have also become of interest in studies of the phase transition behavior in solution. A series of recent papers deal with the effect of poly(ethylene oxide) graft chains on the coil-to-globule transition of PNIPAM[19−22] or with hydrophobic modification.[23]

In the present work, two thermosensitive graft copolymers with low and high grafting density of P2VP are investigated

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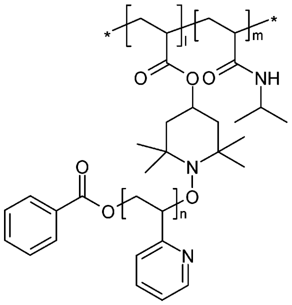
Scheme 1. Molecular Structure of Thermosensitive Copolymers



by NMR methods. The phase transition of such copolymers is determined far below the overlap concentration by ^{1}H liquid NMR. Since the presence of salt in a polymer solution induces modifications of the polymer conformation, the transition of thermosensitive copolymers was also studied in salt solution. To establish the conformational changes of thermosensitive graft copolymers monitored as a function of temperature, ^{1}H liquid-state NMR is employed. Here, the motion of the grafted segments in comparison with that of the main chain is investigated by a method simply based on a distinction of "liquid" and "solid" spins: "Solid spins" of restricted dynamics are subject to strong dipolar coupling, which leads to a fast relaxation and, therefore, to a substantial broadening of the signal which cannot be detected in a liquid-type experiment. "Liquid" spins show a fast isotropic motion with a very slow relaxation. The selective detection of "liquid" spins thus offers a simple possibility to monitor molecular dynamics. Further investigations concern the dynamics of the hydration water as a function of temperature using ^{2}H solvent relaxation measurements.

Materials and Methods

Chemicals. Two different thermosensitive copolymers with high and low grafting density are investigated. They consist of a thermoreversible main chain of poly(*N*-isopropylacrylamide) (PNIPAM) and weak polyelectrolyte chains of poly(2-vinylpyridine) (P2VP) grafted to the main chain (see Scheme 1). The synthesis is performed by radical copolymerization of chains of poly(2-vinylpyridine) (P2VP) as macromonomer with poly(*N*-isopropylacrylamide) (PNIPAM), as described previously.[16] The P2VP macromonomer is synthesized using nitroxyl-mediated radical polymerization of 2-vinylpyridine with a following transformation step of the terminated hydroxy-functionalized controlling agent to an acrylic ester, leading to a controlled block length.

Two different copolymers are synthesized from identical graft chain lengths: PNIPY-H ($M_w = 178\,000$) and PNIPY-L ($M_w = 90\,500$) have a molar monomer ratio between the main chain and charged grafted side chains of 1.42:1 and 6.33:1, respectively. Because of vinylpyridine groups, the PNIPY polymers are soluble in aqueous solutions only at low pH.

Sodium chloride (NaCl) (AR grade) and hydrochloric acid (fuming 37%) are obtained from Merck. For all experiments, either ultrapure water (H_2O, three-stage purification system (Seradest), resistivity > 18 MΩ/cm) or D_2O (99.98% isotopic purity, purchased from Chemicals and Trading) is used.

Solutions. If not indicated otherwise, polymer solutions are prepared in D_2O:H_2O (1:1, molar ratio) as the aqueous solvent and adjusted with HCl to a pH value of 2. Polymer solutions of 8 mg/mL are prepared salt-free or in 0.015 M NaCl. NMR tubes are filled with 270 μL of polymer solution, and a plastic stopper is placed about 2−3 mm above the solution surface in order to avoid water evaporation.

NMR Experiments. Temperature-dependent NMR experiments are performed either on freshly prepared samples or on samples equilibrated at least 1 week at room temperature. No difference is observed between these cases. For each temperature, the equilibration time is then 20 min. NMR investigations are performed on a 400 MHz Avance spectrometer (DMX 400, Bruker). ^{1}H spectra of the polymers are taken with a liquid-state probe head by acquisition after a 90° pulse. These conditions allow the detection of "liquid" spins only, i.e., spins with a sufficiently slow T_2 relaxation time ($T_2 >$ dead time) and a narrow liquid spectrum. For temperature-dependent signals, the resonance at 1 ppm, arising from the $-CH_3$ groups, is evaluated.

^{2}H spin relaxation rates of water are determined in a broadband liquid-state probe head. To obtain the relaxation time T_2, the Carr−Purcell−Meiboom−Gill (CPMG) sequence, described as $d_1-90_x°-(d_2-180_x°-)_n$ is applied. For the determination of the relaxation time T_1, the inversion recovery sequence $[d_1-(180-\tau-90)_n]$ is used with a relaxation delay $d_1 = 15$ s. In both methods, the echo decay is evaluated by a monoexponential fit function, resulting in the corresponding relaxation rate.

Self-diffusion coefficients of thermosensitive polymers in solution are determined by pulsed field gradient (PFG) NMR employing a probe head with gradient coils (Bruker DIFF 30). A stimulated echo sequence with gradient pulses of a length of $\delta = 1$ ms and a maximum gradient strength of 300 G/cm is employed. The diffusion time is $\Delta = 210$ ms. A known problem for nonviscous solutions, in particular at high temperatures, is convective flow arising from small temperature gradients in the sample, which leads to an apparent enhancement of the diffusion coefficient. To avoid convection, we apply a sample geometry according to Hedin and Furo:[24] The NMR tube (diameter 5 mm) is inserted into a large NMR tube (diameter 10 mm) and centered with a Teflon holder. The space between the two tubes is filled with a proton-free chemical of high viscosity (CCl_4). This geometry ensures a homogeneous temperature. Test experiments under variation of the diffusion time proved the absence of convective flow under these conditions. A temperature sensor with a precision of ±0.1 °C is immersed into the CCl_4 to determine the sample temperature. Polymer diffusion coefficients are determined from the ^{1}H resonance of the $-CH_3$ groups.

Theory of Solvent Spin Relaxation

For mobile small molecules, such as solvent molecules, typically, fast motion ensures an isotropic averaging of all interactions. Provided that the correlation time τ_c of this isotropic motion (for example, rotational diffusion) is $\tau_c \ll 1/\omega_0$ (ω_0: Larmor frequency), then the spin−spin and the spin−lattice relaxation rates are equal, a regime termed "extreme narrowing". For ^{2}H with quadrupolar interaction as the dominant relaxation mechanism, and the spectral density $J(\omega)$ given by isotropic rotation with $J(\omega) = \tau_c/(1 + \omega^2\tau_c^2)$, the relaxation rates can be expressed as[25]

$$R_1 = R_2 = \frac{3\pi^2}{4}\chi^2\tau_c \tag{1}$$

where χ is the quadrupole coupling constant and R_1 and R_2 are the relaxation rates for spin−lattice and spin−spin relaxation, respectively.

The simplest description of water in a heterogeneous system is a two-site model, where water molecules can occupy two different sites, which we describe as "free" and "bound" sites.[26−28] "Free" water molecules exhibit the same dynamics as in pure water. For colloidal dispersions, the bound site consists of all water molecules adsorbed to or incorporated into the colloidal particle and thus exhibiting reduced dynamics. In the regime of fast exchange, typically valid for small solvent molecules, the exchange time (τ_{ex}) between the two sites is fast compared to the time scale of the NMR experiment (τ_{NMR}). Then, the investigated NMR parameters such as relaxation rates

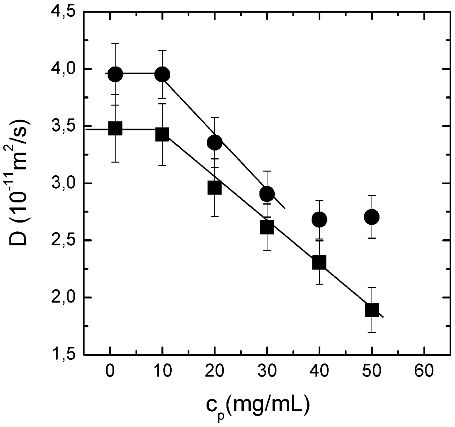


Figure 1. Variation of diffusion coefficient with the polymer concentration: (■) PNIPY-H and (●) PNIPY-L in 0.015 M NaCl at pH 2 (adjusted by HCl). The lines are guides to the eye.

(R_1, R_2), chemical shifts, etc., are weighted averages over both sites:

$$R_i = f_b R_{ib} + f_f R_{if} \tag{2}$$

where f_f and f_b are the fractions of solvent molecules in the free and bound site, respectively.

To facilitate the evaluation of the relaxation rate in heterogeneous systems, a specific relaxation rate R_{isp} normalized to that of the solvent in free sites ($R_i^0 = R_{if}$) is introduced:[26]

$$R_{isp} = \frac{R_i}{R_i^0} - 1 \tag{3}$$

such that it is

$$R_{isp} = f_b R_{ib,sp} \tag{4}$$

with $R_{ib,sp} = (R_{ib} - R_i^0)/R_i^0$. R_{2sp} monitors the relative changes of the relaxation rate due to an increase of either f_b or $R_{2b,sp}$. It thus monitors the net water immobilization in the system, which can be increased by an increase of the fraction of bound water immobilized at the colloid, f_b, or by a reduction of the dynamics of this fraction, leading to an increase of τ_c and thus an increase of $R_{2b,sp}$ (see eq 1). Thus, specific spin−lattice relaxation rates (R_{1sp}) and specific spin−spin relaxation rates (R_{2sp}) serve as parameters, which describe the average immobilization of water molecules in a colloidal dispersion.

Results and Discussion

1. Polymer Diffusion. *Concentration Dependence.* ^{1}H NMR self-diffusion coefficients of thermosensitive copolymers are evaluated on one hand to determine the overlap concentration and on the other hand to investigate changes of the polymer conformation as the LCST is approached. The overlap concentration is an important parameter since above this concentration the LCST behavior might be altered due to interchain interactions.

Figure 1 shows polymer diffusion coefficients in dependence on the polymer concentration c_P. At low concentrations below $c_0 = 10$ mg/mL, the diffusion coefficient is constant, representing the free diffusion of single chains. An estimate of the hydrodynamic radius R_H from the diffusion coefficients at low concentrations employing the Stokes−Einstein equation

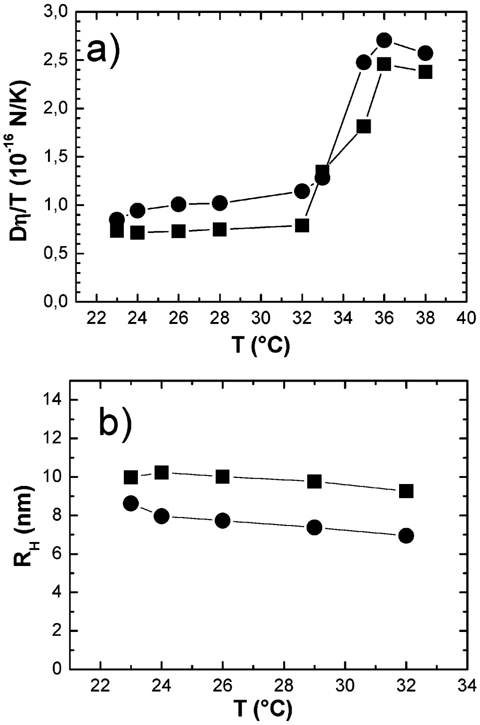


Figure 2. (a) Diffusion coefficient scaled on water viscosity and temperature as a function of temperature and (b) variation of R_H with temperature. Polymer concentration: 5 mg/mL in 0.015 M NaCl at pH 2. ■, PNIPY-H; ●, PNIPY-L. The lines are simply connecting the data points.

$$D = \frac{k_B T}{6\pi\eta R_H} \tag{5}$$

where η is the solvent viscosity, results in about 10 and 8 nm for PNIPY-H and PNIPY-L, respectively. The difference between diffusion coefficients of PNIPY-H and PNIPY-L can be attributed to different molecular weight and different structure: In PNIPY-H the higher grafting density leads to a larger extension of the chain due to self-repulsion.

For both copolymers, there is a limiting concentration of 10 mg/mL, above which the diffusion coefficient is decreasing with the polymer concentration. The decrease can be attributed to entanglement of the chains of neighboring coils.

From the values of R_H another estimate of an overlap concentration can be obtained with the help of a space-filling model of densely packed spheres: It is assumed that coils with R_H corresponding to that of the polymer coil in dilute solution are arranged in a hexagonal close packing. The concentration c_{hp} then results in about 50 mg/mL for both polymers. This value is a factor of 5 larger than the onset of the decrease of the diffusion coefficients at about 10 mg/mL. The onset of the decrease of the diffusion coefficient in Figure 1 can thus be attributed to restricted diffusion of a chain in a solution of other chains.

Temperature Dependence. The temperature dependence of the diffusion coefficient at low polymer concentrations ($c_p < c_0$) can monitor conformational changes of single chains as the phase transition temperature is approached. Diffusion experiments at low concentration ($c_p = 5$ mg/mL) show an increase of the diffusion coefficient with temperature. However, according to eq 5, this is partially due to the temperature itself and the decrease of water viscosity with temperature. In Figure 2a,

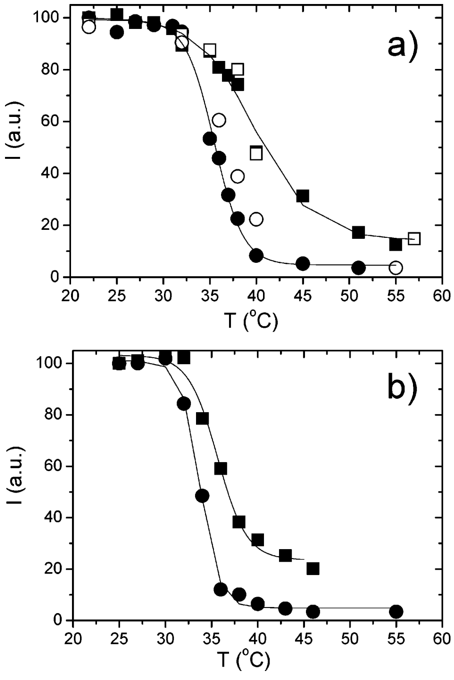


Figure 3. Normalized ^{1}H NMR signal intensities of $-CH_3$ groups in PNIPAM solution ($c_P = 5$ mg/mL, pH = 2) in dependence of temperature: (a) salt-free solution; (b) in 0.015 M NaCl. Solid symbols: heating; open symbols: cooling. ■, PNIPY-H; ●, PNIPY-L. Lines represent fits according to eq 6.

the diffusion coefficients are therefore normalized on solvent viscosity and temperature.

Below the critical temperature, the normalized diffusion coefficient $D\eta/T$ is slightly increasing with temperature, which can be interpreted as a continuous shrinkage of the coils; see also the hydration radius represented in Figure 2b. This structural reorganization might probably be similar to the "crumpled coils" of an individual PNIPAM chain in solution as assumed by Wu and Wang.[29] A similar pre-transition shrinkage had been found in diffusion experiments of the homopolymer PNIPAM.[14] The shrinking is less pronounced in the case of PNIPY-H due to the higher density of charged arms than in the case of PNIPY-L.

Above a critical temperature, which is close to the transition temperature of the homopolymer (32 °C), a steeper increase of the normalized diffusion coefficient is detected until a plateau is reached. Here, the phase transition is expected to lead to a collapse and possibly aggregation of the chains. However, in this region the results are difficult to interpret in terms of a structural model since the signal detected in a diffusion experiment arises from the "liquid" spins only, and as Figure 3 shows, the "liquid" signal is decreasing. Therefore, the diffusion coefficients might be dominated by a fraction of chains, which does not represent an average size of the structures. Therefore, the data in this region are not converted into R_H values. Nevertheless, from the diffusion coefficients the size of the globules is estimated to about 3 nm, which might correspond to particles formed by single chains or by aggregates.

2. Phase Transition Determined by ^{1}H Liquid NMR. With increasing temperature, the thermosensitive solutions become more turbid, as insoluble globules are formed. NMR spectra of the thermosensitive copolymers in aqueous acidic solution (pH = 2) are measured in dependence of temperature to monitor the phase transition. The signal at the resonance frequency of the $-CH_3$ groups dominates the spectrum, and its intensity at maximum is evaluated on both heating and cooling. A reduction of liquid signal reflects the decrease of the relaxation time T_2 due to the formation of "solid" spins and thus the presence of globular particles. Normalized ^{1}H signal intensities of both copolymers are shown for salt-free and 0.015 M NaCl solution in parts a and b of Figure 3, respectively. The ionic strength of 0.015 M NaCl is chosen below the limiting concentration, above which precipitation instead of the formation of dispersed globules occurs.[30]

Table 1. Fit Parameters Describing the Coil-to-Globule Transition

	salt-free			0.015 M NaCl		
	T_c (°C)	width (K)	b	T_c (°C)	width (K)	b
PNIPY-H	39.8 ± 0.4	3.3	0.14	36 ± 0.3	1.7	0.20
PNIPY-L	35.5 ± 0.2	1.7	0.05	34 ± 0.1	1.0	0.07
PNIPAM[a]	32.0± 0.2	<1	0.0			

[a] Data for the homopolymer PNIPAM are taken from refs 14 and 15.

The decrease of the liquid signal reflects the presence of solid segments owing to the globule formation; therefore, this signal is taken as a parameter that monitors the remaining amount of the mobile polymer segments.

For both thermosensitive copolymers ^{1}H NMR intensities are constant up to about 30 °C. Above this temperature, the ^{1}H NMR signal of PNIPY-L decreases more steeply than that of PNIPY-H. Far above the LCST the ^{1}H intensities of PNIPY-H and PNIPY-L converge toward constant positive values. As shown in Figure 3a by the open symbols, the phase transition is reversible with almost no hysteresis. The transition of the graft copolymers is significantly broadened in comparison to the transition of the homopolymer PNIPAM, which occurs very sharply at 32 °C.[14] In salt-containing solution (see Figure 3b), both thermosensitive copolymers show qualitatively the same behavior; however, the transition is less broadened as compared to the salt-free polymer solution. Another interesting feature of the graft copolymers is that above the transition temperature T_c neither in salt-free nor in salt-containing solution the ^{1}H NMR signal approaches zero as it does for the homopolymer.[14]

For a quantitative description of these features, the ^{1}H NMR intensities are fitted with a phenomenological equation

$$I = \frac{a}{1 + \exp(-k(T_c - T))} + b \qquad (6)$$

where T_c, a, b, and k are free parameters. The resulting fit parameters are given in Table 1.

As the results show, the introduction of charged side chains leads to a shift of the transition toward higher T_c; this shift increases with the grafting density. This result is consistent with DSC measurements of a series of similar PNIPAM-*g*-P2VP graft copolymers, where the transition temperature increases with the number of graft arms.[16]

The addition of NaCl leads to a partial screening of the charges on the side chain, facilitating the collapse of the polymer. Shifts of the LCST toward lower temperatures due to salt addition were observed for statistical pH- and temperature-sensitive copolymers.[31] For the graft copolymer investigated here, it can be speculated whether the electrostatic repulsion leads to an arrangement of the graft chains in an outer corona around the globule. This is investigated in the next section.

In addition to T_c, the width of the transition is increasing with grafting density (see Table 1). The statistics of attachment positions of the side chains on the main chain might be responsible for this, as it introduces a microscopic heterogeneity, i.e., heterogeneity of the main chain length between two charged side chains.

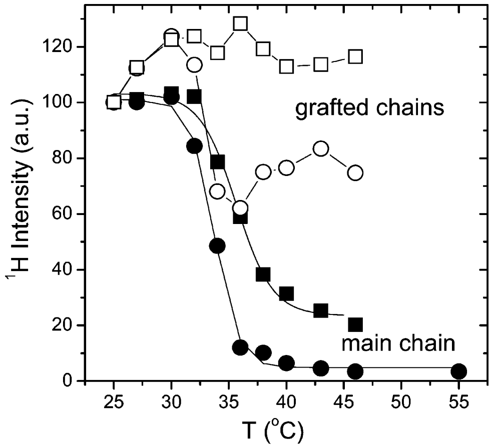


Figure 4. ^{1}H NMR signal of the backbone (solid symbols) and side chains (open symbols) in 0.015 M NaCl solution: squares, PNIPY-H; circles, PNIPY-L. The lines are fits (solid symbols) or guides to the eye (open symbols). The curves are normalized such that the intensity at 25 °C is 100.

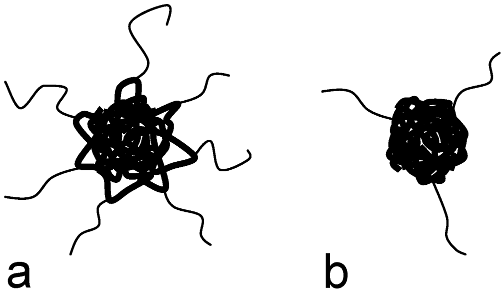


Figure 5. Sketch of possible structures of collapsed graft copolymers: (a) high grafting density; (b) low grafting density. Thick lines: main chain; thin lines: charged graft chains.

Such rearrangements of separating the charged side chains are more relevant with increasing grafting density.

3. Dynamics of Graft Chains. The ^{1}H NMR signal of the graft chains at the resonance frequency of vinylpyridine rings ($\delta \sim 7$ ppm) is well distinguishable from the main-chain signal. It is employed here to detect motional restrictions in the side chains arising due to the phase transition of the main chain. Normalized side-chain and main-chain signals are compared in Figure 4.

The signal-to-noise ratio of the ^{1}H signal of the side chains is rather poor; however, it can be clearly seen that the side chains of PNIPY-H are not strongly immobilized in the transition: The ^{1}H signal of the poly(vinylpyridine) chain of PNIPY-L decreases by about 30%; thus, here the side chains are partially immobilized, while no decrease of the ^{1}H signal and thus no immobilization is observed for the side chains of PNIPY-H.

The poly(vinylpyridine) chains remain rather mobile even when the PNIPAM main chain is forming the globular particle. Repulsive electrostatic forces between the charged side chains can explain these results. At high grafting density the repulsion is strong enough, so that the side chains are well separated and do not entangle with uncharged segments in the globule. This is consistent with the finding of a high fraction of mobile main chain segments at high T (see b value in Table 1): The side chain repulsion apparently prevents a fraction of the NIPAM segments from collapsing. This case is represented in the sketch in Figure 5a.

In contrast to this, at a lower grafting density the electrostatic repulsion of the side chains is not strong enough to prevent a significant fraction of PNIPAM segments from collapsing, the fraction b is smaller. As the main chains almost completely collapse, the side chains attached to them are immobilized with them. Thus, the lower charge density facilitates the formation of a solidlike core in which a fraction of grafted arms might be immobilized in the PNIPAM core or is immobilized due to its covalent attachment to the solid core.

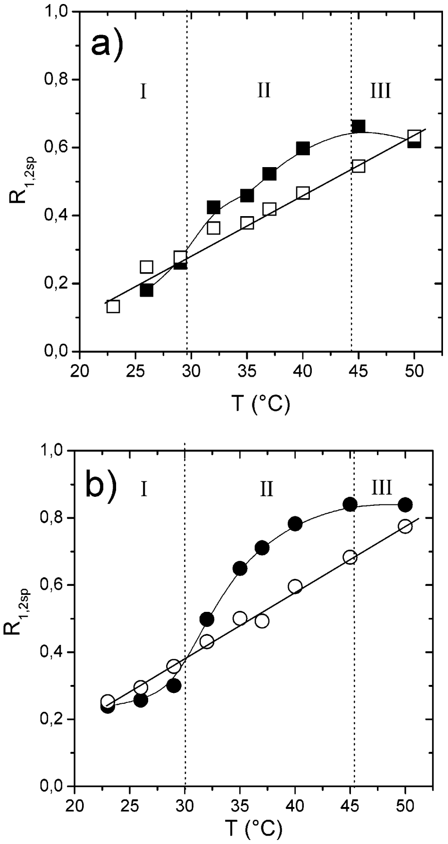


Figure 6. Variation of R_{1sp} and R_{2sp} with temperature for PNIPY-H (a) and for PNIPY-L (b). Solid symbols: R_{2sp}; open symbols: R_{1sp}. The lines are guides to the eye.

4. Hydration Water Dynamics. Complementary to the above studies of the polymer dynamics, the water dynamics in thermosensitive copolymer solutions is investigated by solvent spin relaxation. Relaxation rates R_i for spin−lattice ($i = 1$) and spin−spin ($i = 2$) relaxation are normalized on the relaxation rate of pure water according to eq 3 and are given in Figure 6. Since R_i^0 of free water is temperature-dependent, the values of R_i at each temperature are normalized on R_i^0 at the respective temperature.

For both copolymers R_{1sp} increases linearly with temperature, whereas R_{2sp} shows a steeper increase in the transition region until it approaches R_{1sp} again. Three regions, which describe the molecular dynamics of water, can be identified:

In region I below the coil-to-globule transition it is $R_{2sp} = R_{1sp}$. The water dynamics is in the extreme narrowing regime. The second region (II) between about 30 and 45 °C shows a deviation, where it is $R_{2sp} > R_{1sp}$. Here, the R_{2sp} values contain a contribution arising from the hydration water of the polymers. This is evidence of a substantial increase of the motional correlation time τ_c of the bound water, such that $\tau_c > 1/\omega_0$ and $R_{2b} > R_{1b}$.

In this region the copolymers undergo the transition to the globular state. The increase of the deviation $\Delta R_{sp} = R_{2sp} - R_{1sp}$ monitors a continuous increase of the average rotational correlation time of water molecules.

In region III, R_{2sp} and R_{1sp} coincide again and ΔR_{sp} becomes zero, indicating motional narrowing. This implies that in this region again the water molecules undergo fast isotropic rotational diffusion.

One can now discuss the mechanisms which underlie the observed water dynamics in the transition: In region I, water is present as free water and as hydration water of the chains. In dilute solutions, the hydration water is only loosely bound to the chains. It was shown that for several polyelectrolytes the motional restrictions due to binding to the chain only lead to minor increases of the relaxation rates.[27] Therefore, in region I specific relaxation rates only slightly above zero (the value of pure water) are found.

In the transition region, II, the fact that $\Delta R_{sp} > 0$ proves the presence of a fraction of the water with very slow dynamics. Since a noncompact globule structure with incorporated water molecules was found for PNIPAM above LCST,[29] the contribution of very slow water can be attributed to confined water in the globule. When the globule is further collapsing, water is leaving the confined sites, and the globule is further compacting. Finally, in region III, only water that is slightly motionally restricted due to binding on the outer part of the globule and on the charged grafted chains of the corona contributes to the signal. The values of R_{1sp} and R_{2sp} being larger than zero indicate that the water contributing to the signal is in the extreme narrowing regime, even though it is immobilized on the polymer chain.

In addition, there might be water confined in the globule, which is in the solid state and therefore does not contribute to the liquid water signal. The amount of water incorporated in solid PNIPAM globules above LCST was estimated to be about 66% with respect to polymer weight.[29]

The R_{isp} values of PNIPY-L are generally somewhat larger than those of PNIPY-H, and also the difference ΔR_{sp} is larger. This can be attributed to the different grafting densities of the thermosensitive copolymers. The smaller the grafting density, the more compact the globule and the more immobilized the water molecules. This leads to higher R_{isp} values.

Conclusions

Several NMR parameters (diffusion coefficient,^{1}H liquid signal, ^{2}H relaxation rates) elucidate the conformational changes of thermosensitive graft copolymers with charged side chains in salt-free and salt solution. The conformational changes upon approaching the LCST are already evident several degrees below the LCST, as seen by a slight enhancement of the diffusion coefficient with temperature. The phase transition of thermosensitive graft copolymers and the influence of ionic strength on their phase transition are monitored by ^{1}H-liquid NMR. An increase of grafting density shifts the LCST to higher temperatures and leads to a broadening. In the presence of salt the phase transition of either polymer occurs at smaller temperatures and with a reduced width. ^{1}H NMR as a function of temperature further monitors the dynamics of grafted chains. The coil-to-globule transition can be considered in terms of hydrophobic interactions of the PNIPAM segments, which become attractive at high T, and repulsive electrostatic interactions of the side chains: In the case of low grafting density the hydrophobic attraction dominates, such that the main chain almost completely collapses, and the side chains become partially immobilized. In contrast, at high grafting density the electrostatic forces prevent a complete collapse of the main chain, and the side chains remain fully mobile. Studies of specific ^{2}H relaxation rates (R_{1sp}, R_{2sp}) of water molecules at different temperatures reveal three regimes of the hydration water dynamics. Well below and well above the transition region the hydration water remains fairly mobile with $\tau_c < 1/\omega_0$. Only in the transition region a regime of strongly immobilized liquid water is found.

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