1H NMR of thermoreversible polymers in solution and at interfaces: the influence of charged groups on the phase transition

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Abstract

The phase transition of thermoreversible polymers occurring at the lower critical solution temperature (LCST) is investigated by 1H NMR. Poly-*N*-isopropylacrylamide (PNIPAM) shows such a coil to globule transition at 32°C in aqueous solution. To study the effect of charged polymer segments on the phase transition, the temperature dependent properties of PNIPAM and of a charged PNIPAM-copolymer, containing 10% carboxylic groups, are investigated in solution. Experiments are performed by 1H spectra and PFG-NMR diffusion measurements at different polymer concentrations. The 1H liquid signal is sharply decreasing at the phase transition temperature. The transition is found to be equally sharp for the copolymer as for the homopolymer at concentrations below and around the overlap concentration, whereas the transition is broadened at higher concentrations. Diffusion measurements prove that the conformation of the polymer coils is maintained with increasing temperature until close to the phase transition, apart from a minor decrease of the hydrodynamic radius at about 2°C below the LCST. All data indicate identical phase transition properties of the copolymer as compared with the homopolymer. The introduction of charged groups (3% of monomers dissociated) has thus not altered the transition. Therefore, the copolymer is a suitable candidate for exhibiting a phase transition under electrostatic coupling conditions in layers. Both polymers are adsorbed to colloidal silica (Cab-O-Sil) and investigated by 1H NMR in order to monitor the phase transition in the restricted geometry of an adsorption layer. The liquid 1H intensities of both polymers are decreasing with temperature, this is interpreted as a phase transition of the loops and tails. The transition is substantially broader than in solution, especially at low surface coverage. Significant differences between the copolymer and the homopolymer are observed, since above the transition temperature a liquid signal from loops and tails of the copolymer is still observed. This is interpreted as a comparatively mobile arrangement of the copolymer layer, arising from electrostatic repulsion from the surface and between polymer segments, which is partly hindering globule formation. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thermoreversible polymers exhibit reversible conformational changes in solution, which make them interesting candidates for any applications with a demand to switch material properties by external conditions. In the past years, especially the phase transition of poly-*N*-isopropylacrylamide (PNIPAM) has been studied in great detail. PNIPAM forms random coils in water at low temperatures, which collapse to solid globules in a sharp transition around 32°C, since the solubility is decreasing. The temperature dependent behaviour at this lower critical solution temperature (LCST) has been studied in solution, in gels, under the influence of various additives and solvents, and in adsorption layers, as has been reviewed by Schild [1]. Substantial interest in the LCST properties is evoked by the possibility that such drastic structural changes can in principle allow switching and control of material properties by temperature. Our particular interest lies in the phase transition properties in ultrathin organic films. Here, electrostatic coupling is a recently established mechanism for layer-by-layer build-up of composite systems by self-assembly, e.g. of polyelectrolytes [2]. An interesting goal is to introduce thermosensitive polymers into such composite systems, which requires to combine temperature sensitive properties with polyelectrolyte behaviour to enable electrostatically coupled layer-build-up.

In this work we are investigating the effect of charged segments on the phase transition in solution, and furthermore in adsorption layers on colloidal silica.

By different authors, copolymers of PNIPAM containing various charged co-monomers have been synthesised and analysed concerning the LCST behaviour in solution [e.g. [3–5]]. Generally, at low charge contents the transition is maintained, while at higher charge content the LCST disappears. An especially promising compound which exhibits an LCST even at comparatively high charge content [6,7] is chosen here.

Furthermore, the phase transition of uncharged PNIPAM has been studied on latex particles in grafted chains [8,9], in cross-linked gels [10–12]

and in physisorbed polymers [13]. In these studies light scattering is employed, where the total thickness of the adsorption layer is determined. It is found that, during a heating cycle of PNIPAM grafted to latex particles, the coil to globule transition region is broadened to about 20°C compared with the single chain transition of about 1–2°C [9]. During a subsequent cooling cycle a hysteresis is observed due to an additional structure called extended brushlike conformation. This conformation is kinetically unstable and collapses to an adsorbed chain consisting of loops, which is kinetically stable [14].

With NMR methods, dynamic information about local segmental mobility can be obtained, which is complementary to structural data. Here, we apply 1H NMR spectra measured under liquid NMR conditions, which lead to a straightforward distinction of liquid and solid spins in the sample; 'Solid' spins are restricted in mobility, so that the heterogeneity on the molecular level will, due to dipolar interactions, lead to fast relaxation and a substantial broadening of the signal, such that it can not be detected in a liquid type experiment. Liquid spins, however, show fast isotropic motion, which is averaging the dipolar interaction and leads to narrow Lorentzian spectra and slow relaxation. The selective detection of liquid spins thus offers a simple possibility to probe the mobility of polymer solutions or adsorption layers as a function of concentration and temperature. The task of this work is thus to investigate the phase transition of PNIPAM by 1H NMR, (i) under the influence of charged groups and (ii) in adsorption layers as compared with the transition of free coils in solution.

2. Materials and methods

Poly(*N*-isopropylacrylamide) homopolymers (**1**) ($M_w = 10^5$ g mol^{-1}, and 3.5×10^5 g mol^{-1}) are used as obtained from Polymer Source Inc. A copolymer (**2**) of *N*-isopropylacrylamide and a carboxylic acid containing acrylamide co-monomer, see Fig. 1, is synthesised by radical polymerisation as described earlier [7]. The co-monomer content is 10 mol%, in agreement with

the feed composition, and the molecular weight (M_w) is 1.3×10^5 g mol^{-1}.

For NMR measurements the polymers are dissolved in D_2O (isotopic purity 99.98%, CD Chemicals) at appropriate concentrations. Colloidal silica 'Cab-O-Sil' (Fluka), consisting of aggregated structures of spherical particles with a surface area of 200 m^2 g^{-1}, is used as obtained. The advantage of this silica material over larger monodisperse particles is the fact that it provides a large surface area and thus high sensitivity for NMR experiments, while at the same time being easy to centrifuge due to the existence of large fused structures. For adsorption samples, silica particles and polymers are first dispersed in D_2O separately, and mixed at room temperature after 24 h. The initial silica concentration is 6 mg ml^{-1}. After equilibrating for another 24 h, the sample is centrifuged at 4000 rpm and the supernatant is removed. Centrifugation is done directly in NMR tubes in order to avoid changes in the water content, which would follow subsequent material transfer. The tubes are flame sealed to prevent water evaporation.

NMR spectra are taken either on fresh samples or on samples equilibrated at least for 1 week at room temperature after the last heating cycle. No differences between these two cases are observed. A Bruker 400 MHz Avance spectrometer is used for all NMR investigations. Solution spectra are measured in a liquid type probehead by acquisition after a 90° pulse. The pulse length is 12 μs, and the number of scans is 16. The prescan delay is 10 s, and the dead time before acquisition is 40 μs. Spectra of polymers adsorbed to silica are obtained with a solid probehead by a 90° pulse of 1.5 μs and subsequent acquisition. Dead time and pre-scan delay is set identical to the experiments in solution. These experiments allow the detection of 'liquid' spins only, i. e. spins with a sufficiently slow T_2 relaxation time ($T_2 > $ dead time).

Diffusion experiments of the polymers in solution are performed in a pulsed field gradient probe head (Bruker DIFF 30) using a stimulated echo sequence with gradient pulses of a length of $\delta = 1$ ms and variable gradient strength, separated by $\Delta = 100$ ms. To avoid convection effects possibly induced by small temperature gradients in the sample, a homogeneous temperature distribution is achieved by controlling the sample temperature by the gradient cooling system.

3. Results and discussion

3.1. Phase Transition of PNIPAM Polymers in solution

Fig. 2 shows 1H spectra of the copolymer (**2**), (a) below and (b) above the phase transition temperature. The assignment of the 1H lines of backbone, sidechain and co-monomer protons refer to the indices in Fig. 1. The spectrum of the homopolymer (**1**) is similar with the corresponding copolymer lines missing (data not shown). The proton on the amino group could not be identified, which is probably due to fast exchange with the water deuterons, so that the signal is buried in the HDO resonance. The same holds for the carboxylic acid proton. As titration of the copolymer in solution with NaOH shows, a fraction of about 30% of the carboxylic groups are dissociated.

Above the phase transition temperature no liquid 1H signal of the polymer is observed. The loss of liquid signal is reflecting the decrease of the relaxation time T_2 with the formation of solid structures. As soon as T_2 becomes smaller than the dead time before acquisition, 40 μs, the signal is decaying too fast to be detected in a liquid type experiment. The decrease of the 1H signal with increasing temperature is taken as a parameter characterising the phase transition, since it moni-
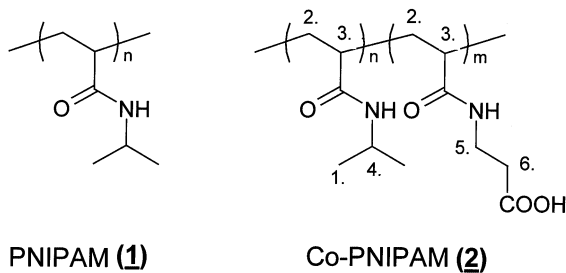

Fig. 1. Chemical structure of PNIPAM (**1**) and copolymer (**2**). The numbers refer to the 1H NMR resonance assignment in Fig. 2.
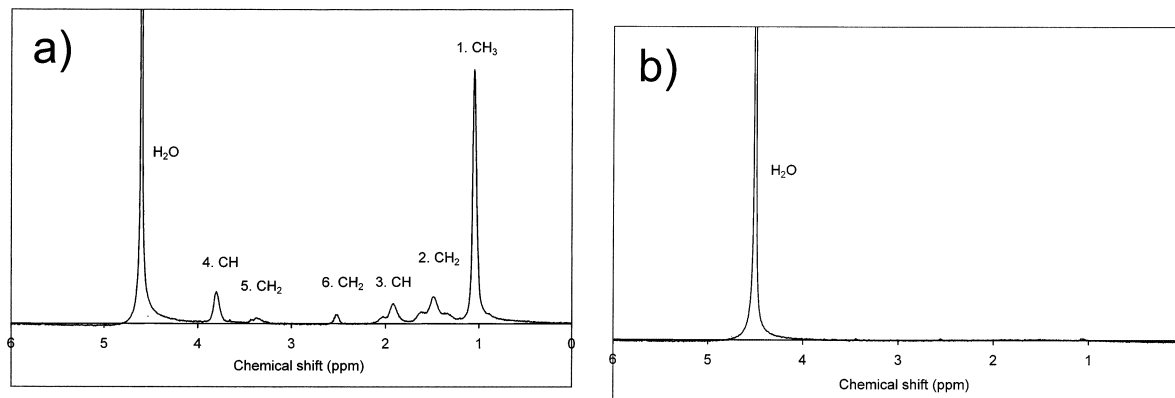
Fig. 2. 1H spectrum of the copolymer in D_2O solution at 10 mg ml^{-1} at temperatures, (a) below and (b) above the phase transition.

tors the amount of mobile polymer segments, i.e. spins which have a sufficiently long relaxation time to be detected. Fig. 3 shows the 1H signal in dependence of temperature. In all cases, the integrated area of the strongest resonance, the methyl protons of the NIPAM group, is evaluated. The results from other 1H resonances show exactly the same decrease of signal with temperature. The spectra are scaled to compensate for differences in the acquisition conditions, thus the signal level is proportional to the polymer concentration. In Fig. 3(a) the signal decrease with temperature is shown for both polymers at low concentrations. Consistent with earlier structural investigations of PNIPAM with other methods [1], the NMR signal indicates a sharp transition at 32°C. The transition of the copolymer reveals exactly the same properties, proving that the introduction of the co-monomer with weakly charged groups at this co-monomer content does not influence the LCST behaviour. This is consistent with turbidity and DSC measurements of this polymer at low pH values [7]. At the highest concentration investigated (Fig. 3(b)), a decrease of the 1H liquid signal is occurring already below the phase transition. The concentration of 115 mg ml^{-1} is higher than the overlap concentration (which is in the range around 40 mg ml^{-1}, as estimated from the hydrodynamic radius determined in diffusion experiments, see below). The onset of the transition at temperatures below the LCST is similar to results obtained for crosslinked gels [15]. Again,

the phase transition properties of the copolymer at these conditions are identical to those of the homopolymer.

1H-NMR self- diffusion coefficients of the polymers are determined to investigate the structure of the polymers at temperatures below the LCST. Echo decay data are fitted with stretched exponential functions [16], since simple monoexponentials do not represent the data well. The width of the distribution of diffusion coefficients does not depend on concentration or temperature and thus can be attributed to the polydispersity of the polymers. The mean diffusion coefficients increase with temperature, which is mainly attributed to the decrease of the viscosity of water. As compensation for such indirect effects of the temperature, the diffusion coefficients shown in Fig. 4 are normalised on the D_2O viscosity and temperature, since it is $D = kT/(6\pi\eta R_H)$. With increasing concentration, the diffusion coefficient is generally decreasing. This decrease is expected due to the increasing hindrance by surrounding coils. An estimate of the hydrodynamic radius from the diffusion coefficient data at 3 mg ml^{-1}, where the effect of restricted diffusion is negligible, results in R_H for (**1**) and (**2**) of 9 and 11 nm, and further in an overlap concentration of $c^* \approx$ 50 and 35 mg ml^{-1}, respectively. No significant change of the normalised diffusion coefficient $D \times \eta/T$ is observed with increasing temperature below the phase transition, only a slight increase occurs around 30°C. There is thus no evidence of
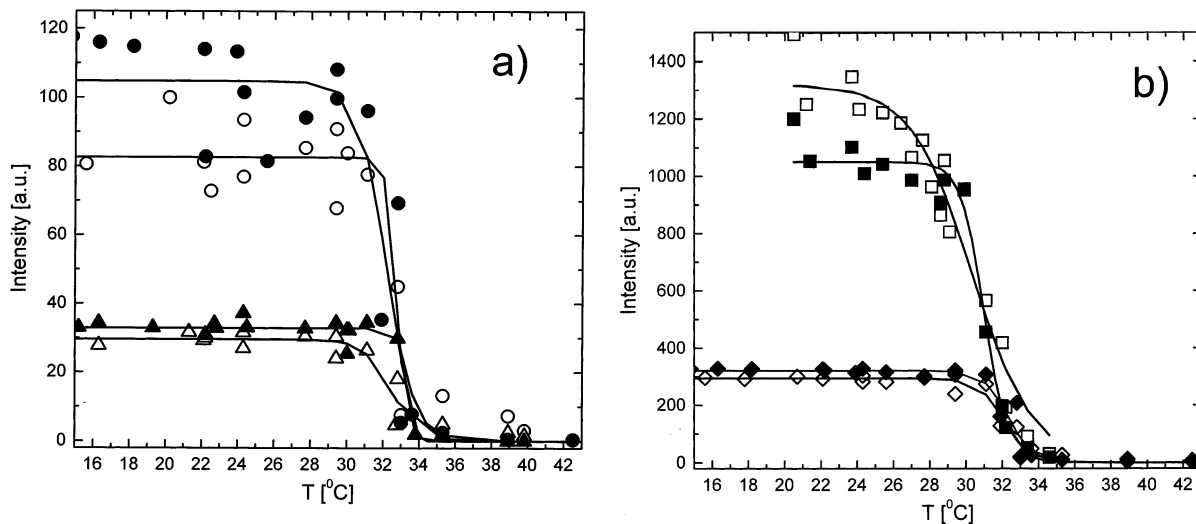
Fig. 3. Liquid state 1H signal (integral of the methyl proton resonance) in dependence of temperature for (**1**) (open symbols) and (**2**) (solid symbols) in D_2O; (a) low c; $\triangle$, $\blacktriangle$; 3 mg ml^{-1}; $\bigcirc$, $\bullet$; 10 mg ml^{-1}; (b) high c; $\diamondsuit$, $\blacklozenge$; 30 mg ml^{-1}; $\square$, $\blacksquare$; 115 mg ml^{-1}. The lines are fits with a plateau function according to Eq. (1).

a substantial rearrangement or aggregation of the coils in solution below the phase transition.

The data points at the phase transition, i.e. at 32°C, which show drastically increased values of $D \times \eta/T$ are difficult to interpret in terms of a structural model, since at the phase transition the signal arises from only part of the spins. The diffusion coefficients, therefore, might be dominated by mobile segments attached to already partly collapsed polymer chains. They might alternatively reflect the polydispersity, assuming that shorter chains would collapse at a slightly higher temperature. The width of the stretched exponential distribution, β, indicates a much lower polydispersity for the copolymer than for the homopolymer. This might possibly support the latter interpretation since the decrease of R_H at the phase transition is less pronounced for the copolymer. At higher polymer concentration ($c > c^*$), the echo decay in the diffusion experiment shows biexponential behaviour due to an additional slowly diffusing component, so that the analysis by a stretched exponential function does not lead to satisfying results.

The concentration effect of the coil-to-globule transition has been discussed in earlier work; at extremely dilute polymer concentrations, individ-

ual chains undergo a transition to a globule [17], while in the region of $c \approx$ mg ml^{-1} the globule size depends on the PNIPAM concentration [18], and at high concentrations above the overlap it is discussed that the transition occurs via chain aggregation and subsequent collapse [7].
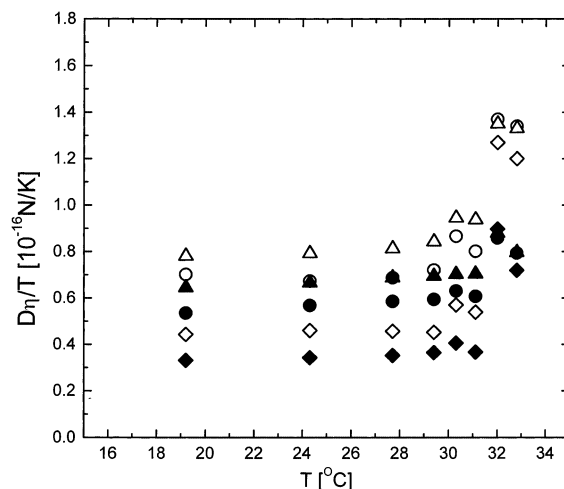

Fig. 4. $D \times \eta/T$; diffusion coefficients normalised on water viscosity and temperature for (**1**) (open symbols) and (**2**) (solid symbols) in D_2O at different polymer concentrations; $\triangle$, $\blacktriangle$; 3 mg ml^{-1}; $\bigcirc$, $\bullet$; 10 mg ml^{-1}; $\diamondsuit$, $\blacklozenge$; 30 mg ml^{-1}.

Our diffusion results prove that at concentrations $c < c^*$, neither drastic changes of the coil conformation nor aggregation of the chains are occurring below the phase transition temperature. Only a slight increase of the diffusion coefficient is found about 2°C below the LCST, which points at a minor rearrangement of the chains, probably similar to the formation of 'crumpled coils', as discussed by Wu and Wang [17] for the extremely dilute regime. This holds for the PNIPAM homopolymer as well as for the copolymer, though the increase of the diffusion coefficient is less pronounced for the copolymer, possibly the formation of 'crumpled coils' is slightly hindered by electrostatic repulsion. In all experiments performed in solution, the copolymer reveals an LCST behaviour similar to PNIPAM. With about 3% dissociated charges when dissolved in water, (**2**) can thus be considered as an appropriate compound combining the phase transition properties of the homopolymer with the existence of charged groups for electrostatic coupling.

3.2. Phase transition of PNIPAM polymers in adsorption layers

The CH_3 group dominates the polymer signal from adsorbed PNIPAM. The resonance is substantially broadened as compared with the polymer in solution. The increased spectral width can be attributed to homogeneous broadening arising from an increased relaxation rate and thus a reduced mobility of the segments observed.

The polymer signal decreases in magnitude with increasing temperature. Fig. 5 shows the signal of the compounds (**1**) and (**2**) in dependence of temperature for samples of different mixing ratio of polymer and silica. Similar to the solution data, the signal is decreasing with T, indicating a phase transition. The data are fitted with an empirical function

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

where T_C, a and b are fit parameters. The transition is significantly broadened compared with that of free polymers in solution. At low polymer amount a very broad transition with a smooth
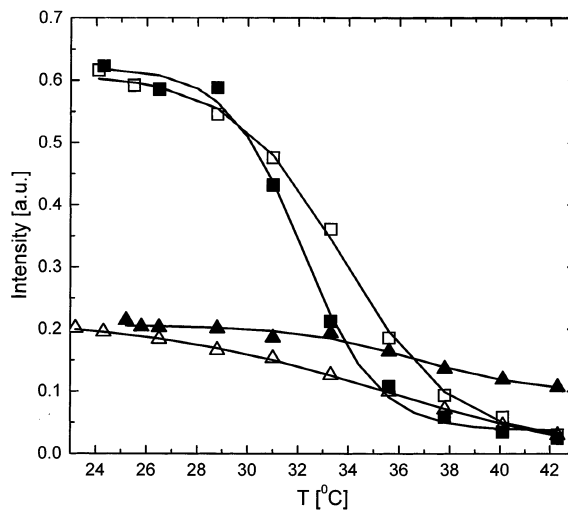

Fig. 5. Liquid state 1H signal (integral of the methyl proton resonance) of polymers adsorbed to colloidal silica in dependence of temperature; open symbols; (**1**), and solid symbols (**2**) at different polymer/silica initial weight ratios; $\square$, $\blacksquare$; 0.85; $\triangle$, $\blacktriangle$; 0.25. The lines are fits according to Eq. (1).

decrease of signal is observed, while at high polymer amount the transition is sharper, but still broadened as compared with polymer in solution. It can be assumed that the broad transition is arising from polymer segments, which are located very close to the silica surface, since these probably exhibit a very low mobility. At higher initial concentrations of polymer the transition is dominated by a fraction of polymer segments further away from the interface, which can be assumed to be more mobile. These segments exhibit a sharper transition. The data thus support a picture of the width of the phase transition depending on the distance of the segments from the surface.

In Fig. 5, it also becomes obvious that the signal level at low temperatures depends on the mixing ratio of polymer to silica. On the other hand, measurements of the polymer amount adsorbed to the silica at low concentrations (data not shown) suggest that saturation of the surface is achieved at 0.25 weight ratio. For NMR measurements, a higher initial concentration of silica had to be used in order to achieve a sufficiently large sample volume after centrifugation in NMR tubes. This obviously causes the presence of poly-

mer chains, which are entangled between the silica particles and can be considered as not directly adsorbed but restricted in mobility as compared with free chains in solution.

Since in adsorption samples with an even lower polymer/silica ratio (< 0.2) no liquid signal is observed, it can be concluded that the transition at low coverage in Fig. 5 reflects the behaviour of tails and loops in the adsorbed layer, while polymer segments directly interacting with the surface ('trains'), are too rigidly bound to show a liquid signal. In T_2 experiments performed with a solid echo, indeed a biexponential decay with a fast component of $T_2 \sim 40\text{--}50$ µs is found, which is decaying too fast to be detected in a liquid type experiment. This corresponds to the general picture of a 'solid' type dynamics of trains, and 'liquid' type dynamics of tails and loops in swollen adsorption layers of polymers [19]. Interestingly, Zhu and Napper have performed a similar experiment by 13C NMR of PNIPAM grafted to latex particles [20]. In addition to the phase transition, they find a signal increase with T at lower temperatures, which does not occur in our data of adsorption samples of (**1**).

Though the phase transition properties of the copolymer in solution are the same as those of (**1**), distinct differences are observed in adsorption samples; while the spectra are similar (data not shown), and the phase transition is clearly visualised by a decrease of the liquid signal with temperature, the difference between the transition types of nonadsorbed and adsorbed chains is even more pronounced for (**2**) as for (**1**); at low polymer amount the phase transition is substantially broadened. Furthermore, the liquid signal seems to reach a plateau value at high temperatures, which is larger than zero. This indicates that not all polymer segments are taking part in the phase transition, but retain a liquid-like mobility even at high temperature. The fit results of the curves in Fig. 5 confirm the finding of a decrease of the width of the phase transition with increasing polymer coverage for both polymers, and a nonzero plateau at high T for (**2**) only, which is largest at low coverage.

This behaviour is quite striking, since on the one hand the substantially broadened phase tran-

sition is an indication for strongly immobilised polymer chains close to the surface. On the other hand, the presence of a liquid signal proves the existence of rather mobile segments at high temperatures. This apparent contradiction can, however, be understood by considering the electrostatic repulsion of the copolymer from the interface, and the implications for the mobility on different length scales. Since the copolymer has the same sign of charge as the surface, it is probably directly adsorbed with NIPAM monomers only, while the carboxylic groups are arranged in a distance from the surface. Such a repulsion might immobilise the polymer configuration on the scale of several segments and thus hinder the rearrangements necessary for a collapse, so that a certain mobility is preserved on the segmental scale, resulting in a liquid signal. This effect occurs predominantly at low coverage. At high coverage, obviously segments, which are repelled from the surface, can collapse, since they have access to a sufficient number of polymer segments in the vicinity, due to the presence of excess polymer. Only at low coverage, these rearrangements can not take place, so that a larger absolute number of segments stays mobile above the phase transition.

4. Conclusions

1H spectra can in a qualitative way monitor the mobility of polymer segments and thus the coil-to-globule transition. The charged copolymer, which has about 3% active charges in this study, shows a sharp phase transition in dilute solution at about 32°C, identical to the homopolymer of PNIPAM. Results from 1H spectra and PFG-NMR diffusion agree in the finding that there is no conformational change of either polymer below the phase transition in solutions below and around the overlap concentration. A slight increase of the diffusion coefficient is evident some degrees below the LCST. At higher concentrations the transition is broadened. The copolymer is a promising candidate for studies at the interface, combining intact phase transition properties with electrostatic binding capacity.

Both polymers bind to the silica particles. With 1H NMR, segments not directly bound to the surface (tails, loops) are monitored. The phase transitions at the interface are much broader than in solution, the width probably reflecting the polymer mobility gradient in dependence of the distance from the surface. Polymer close to the surface shows a broader phase transition than polymers at a larger distance from the surface. While PNIPAM undergoes a complete transition to a solid state, the phase transition of the copolymer is hindered by electrostatic repulsion from the surface. This effect is most pronounced at low coverage.

Acknowledgements

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