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Thermoreversible Polymers Adsorbed to Colloidal Silica: A ^{1}H NMR and DSC Study of the Phase Transition in Confined Geometry

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The phase transition of the thermoreversible polymer PNIPAM, which shows a coil-to-globule transition due to the lower critical solution temperature (LCST) behavior in aqueous solution, is investigated in the restricted geometry of an adsorption layer. Furthermore, a charged copolymer is studied to investigate the influence of charges on the phase transition. Both polymers are adsorbed to colloidal silica and studied by ^{1}H NMR and differential scanning calorimetric (DSC) experiments. In solid state ^{1}H NMR relaxation experiments the signals of solid spins in trains and of liquid spins in tails and loops can be identified. [1]H liquid state spectra detect the phase transition of the loops and tails into immobile segments with increasing temperature. The transition is broadened as compared to the polymer in solution, especially at low surface coverage. For the copolymer, the transition is incomplete, since mobile segments remain even at high temperature. They are attributed to electrostatic repulsion from the surface, leading to a mobile arrangement of the copolymer layer. Micro-DSC experiments confirm the finding of an increased width of the transition at the interface, which depends on the surface coverage. Furthermore, an increase of the transition temperature with decreasing polymer amount is observed, which is most pronounced for the copolymer, and is a further indication of an electrostatically hindered phase transition. In conclusion, despite a negligible influence of a low fraction of charges on the phase transition in solution, the phase transition in adsorption layers is very sensitive to charged segments. Combining NMR and DSC methods, local information on the transition behavior of different polymer segments at the interface, such as loops and tails, or charged monomers, can be obtained.

Introduction

The thermoreversible polymer poly(*N*-isopropylacrylamide) (PNIPAM) shows a reversible coil-to-globule transition in aqueous solution, which is denoted the lower critical solution temperature (LCST) behavior. Raising the temperature above the transition temperature, water bound to the polymer chain is released and soluble polymer coils start to form solid globular particles. Since for PNIPAM the LCST transition is very sharp and occurs at 32 °C, it offers opportunities for temperature controllable applications in a convenient temperature range. In solution and in gels, the phase transition has been studied in great detail, for example under the influence of various additives and solvents, as has been reviewed by Schild.[1]

In solution, also a number of statistical PNIPAM copolymers have been studied. The LCST behavior depends on the balance of the enthalpy and entropy of mixing of the polymer with water, and is thus strongly influenced by the nature and molar concentration of the co-monomer. In general, hydrophobic compounds lower the LCST and hydrophilic compounds raise it.[2−6] Concerning charged components, several PNIPAM copolymers containing different charged groups have been synthesized and analyzed in solution.[2,5−7] The LCST behavior remains unchanged only at extremely low co-monomer con-

centrations, while the transition can disappear at co-monomer contents of only several mol %.[7] These properties depend again strongly on the nature of the co-monomer. A suitable charged co-monomer should thus resemble the chemical structure of the NIPAM monomer. Charged PNIPAM-copolymers, containing acrylamide derivatives bearing carboxylic groups attached to spacers were recently synthesized and investigated in solution.[4,8] Most promising is the compound with a C_2 spacer, where the phase transition was found to persist up to a co-monomer content of 10 mol %. ^{1}H NMR and PFG-NMR diffusion showed a transition, which was equally sharp as for the homopolymer.[9]

Adsorbed to interfaces, polymers can exhibit very different dynamic properties as compared to volume systems. A few investigations of the interfacial phase transition of PNIPAM have been published. Light scattering was employed, where the total thickness of the adsorption layer was determined in dependence of temperature. Grafted interfacial PNIPAM has been studied on silica particles[10] and on latex particles,[11,12] the latter system with detailed investigations of the kinetics of the coil-to-globule transition.[13,14] In grafted layers, the coil-to-globule transition region was divided into two types of transition, a broad one occurring below 31 °C at better than θ-solvency conditions, and a narrow one at higher temperature. The transition of physisorbed PNIPAM on latex particles was similarly broadened as in grafted layers, as detected by changes of the layer thickness. In a heating−cooling cycle a hysteresis was observed and attributed to an "extended brushlike conformation", which was formed after cooling. This conformation was kinetically unstable and relaxed to loopily adsorbed chains

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Phase Transition in Adsorption Layers

J. Phys. Chem. B, Vol. 106, No. 32, 2002 **7801**

which were kinetically stable.[15,16] The LCST transition was furthermore not reversible with respect to the adsorbed amount, since if excess polymer was present, the adsorbed amount changed in the transition.[17] At very low surface coverage on silica, no transition was detected.[18] PNIPAM copolymers have, according to our knowledge, not yet been studied at interfaces.

In the future, thermoreversible polymers can have interesting applications in building functionalized interfaces with temperature-controllable properties. A long-term goal is the incorporation of thermosensitive polymers into polyelectrolyte multilayers formed by self-assembly.[19] Another interesting perspective are potential applications of temperature controllable polymer layers with respect to protein binding. Inducing conformational changes in the polymer layer by temperature variation could be employed to change the nature of chemical groups present at the surface, leading to controlled release of selectively binding proteins. Both potential applications require fundamental knowledge of the conformational and dynamic changes of the polymers induced by the interfacial transition. In particular the influence of charges on the transition is of interest, since the task is to combine temperature sensitive properties with polyelectrolyte behavior to enable electrostatically coupled layer-build-up. This is the motivation for the present work, where we investigate charged PNIPAM copolymers at interfaces in comparison to the uncharged homopolymer.

The methods employed in this work, namely NMR and DSC, are sensitive to dynamic properties in the phase transition: NMR methods have only in the past decade become feasible in the investigation of organic adsorption layers and provide a wealth of dynamic information, as has recently been reviewed.[20] For example, employing a separation of two dynamic states, "solid" and "liquid", polymer conformations at interfaces can be studied, where one possibility is the separation of the signal from solid and liquid spins in a so-called solid−liquid echo.[21] The generally established model of adsorbed polymers consists of directly bound "trains", which interact with the surface and can be considered rigid, and of "tails" and "loops", which are not directly interacting with the interface, but exhibit a reduced mobility which is determined by the covalent bonds to immobilized trains. An NMR experiment can thus distinguish between trains with a solid-like mobility and tails and loops with a liquid-like mobility. Here, we apply ^{1}H NMR spectra measured under liquid NMR conditions, which lead to a straightforward distinction of liquid and solid spins in the sample.

DSC is a well-established method to investigate the phase transition of PNIPAM and PNIPAM copolymers in solution.[3,8,22,23] Heskin and Guillet[24] were the first to report that an endotherm can be observed at the transition temperature upon heating aqueous solutions of PNIPAM. The endothermic heat of the phase transition is related to the breaking of hydrogen bonds between water molecules and the polymer. The heat of transition of PNIPAM copolymers is strongly influenced by the nature of the co-monomer. A higher transition temperature is generally accompanied by a reduced heat of transition, which was described by a linear relationship.[3,4] In the present study of adsorption layers, DSC data reveal broadening of the transition and shifts of the LCST due to adsorption. Since in adsorption samples the amounts of polymer are rather low, high sensitivity DSC (micro-DSC) was employed, which allows to detect heat flow signals of rather low intensity.

Materials and Methods

Materials. Poly(*N*-isopropylacrylamide) homopolymer (**1**) ($M_w = 3.5 \cdot 10^5$ g/mol) was used as obtained from Polymer
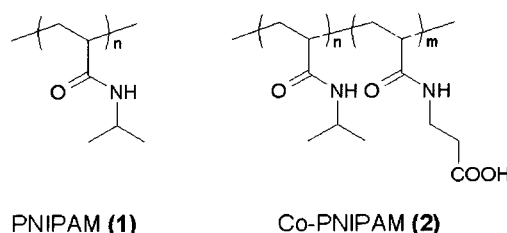
Figure 1. Chemical structure of PNIPAM (**1**) and copolymer (**2**).

Source Inc. A statistical copolymer (**2**) of *N*-isopropylacrylamide and a carboxylic acid containing acrylamide co-monomer, see Figure 1, was synthesized by radical polymerization as described previously.[8] The co-monomer content was 10 mol-% in agreement with the feed composition, and the molecular weight (M_w) was $1.3 \cdot 10^5$ g/mol.

Colloidal silica Cab-O-Sil (Fluka), consisting of aggregated structures of spherical particles with a surface area of 200 m[2]/g, was 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 a high sensitivity for NMR experiments, while at the same time it is easy to centrifuge due to the existence of large fused structures. For all experiments, either ultrapure water (H_2O, Seradest, resistivity > 18 MΩcm) or D_2O (Chemicals and Trading, 99.98% isotopic purity) was used.

For adsorption samples, silica and polymers were dispersed or dissolved, respectively, in water and stirred for 24 h. For NMR experiments D_2O was used, for DSC experiments, H_2O. Polymer solutions were diluted to achieve the appropriate concentrations, then added to the silica dispersion under stirring and finally equilibrated for another 24 h at room temperature. The initial silica concentration in the mixed samples was 6 mg/mL and the maximum polymer/silica ratio was 1 by weight. Dispersions in NMR tubes were centrifuged at 4000 rpm (corresponding to 2950 *g* in a Sigma 6K15 centrifuge) at room temperature. For DSC studies and adsorption isotherms the dispersions were centrifuged in Eppendorf tubes at 10000 rpm (corresponding to 2950 *g*; Sigma 3K30 centrifuge). The supernatant was subsequently removed. For the adsorption isotherm ^{1}H NMR spectra of the supernatant were taken, and the concentration was determined by calibration on samples of known concentrations.

NMR. To prevent possible drying of the centrifugation pellets, which might occur with the transfer to NMR tubes, samples for NMR experiments were centrifuged in NMR tubes. The tubes were flame sealed after removal of the supernatant to prevent water evaporation. NMR spectra were taken either on newly prepared samples or on samples equilibrated at least for one week at room temperature after the last heating cycle. No differences between these two cases were observed.

NMR investigations were performed in a 400 MHz Avance spectrometer (DMX 400, Bruker). Spectra of polymers adsorbed to silica were obtained with a static ^{1}H probe head (Bruker) by a 90° pulse of 1.5 μs and subsequent acquisition. The prescan delay was 10 s, and the dead time before acquisition was 40 μs. These conditions allowed 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 relaxation measurements a solid echo sequence with water suppression (180-*d*2-90$_x$-τ-90$_y$-τ-acqu) was applied under variation of τ. The first pulse served to invert the magnetization and to suppress the signal of residual water protons, since *d*2 was set to *d*2 = T_1^{HDO} ln2. The delay *d*2 was manually adjusted to minimize
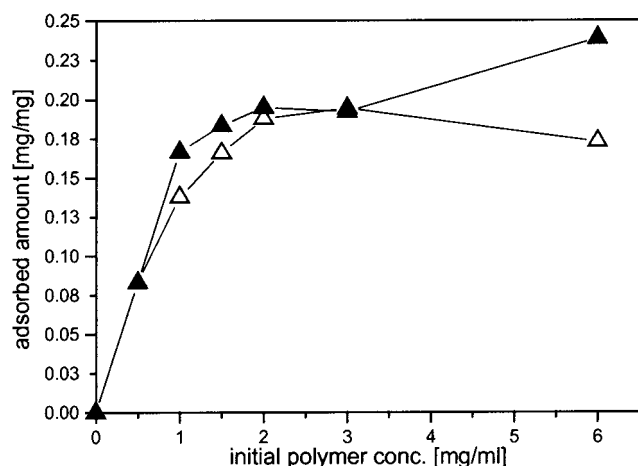
Figure 2. Adsorption isotherms of PNIPAM (**1**) (open symbols) and copolymer (**2**) (solid symbols) on colloidal silica. Lines are guides to the eye only.

the water signal. The signal intensity was extracted directly from the echo intensity in the time domain, without Fourier transform. Under these conditions the signal corresponding to the total number of polymer spins was detected.

DSC. For calorimetric analysis adsorption samples were prepared in the same way as the samples for NMR measurements: the initial silica concentration was thus 6 mg/mL in H_2O. After centrifugation and removal of the supernatant, the polymer−silica pellet was transferred to a 1 mL measurement batch vessel (Hastelloy C) and 0.4 mL water was added to prevent changes in the water content of the pellet during the heating process.

Differential scanning calorimetry was performed using a Setaram micro DSC III heat conduction scanning microcalorimeter (Setaram, France). Absorbed or released heat was recorded relative to the 1 mL reference vessel filled with an appropriate blank sample (silica dispersion in water: 6 mg/mL). The vessels were allowed to stabilize at 3 °C for 60 min prior to the initiation of the scanning experiment over the temperature range of 3 °C to 80 °C. The heating rate was 0.5 K min^{-1} for all experiments. Cooling of the vessel to the initial conditions and rescanning of the sample were done in order to check whether the polymer transitions were reversible. The silica material itself produced no evidence of endothermic or exothermic transitions over the temperature range examined. For comparison, the polymer transitions were also studied in aqueous solution (0.5−1 wt %) under the same experimental conditions. An appropriate amount of pure water was used as blank sample in these cases.

Results

Adsorption Isotherm. The adsorption isotherms of both polymers on colloidal silica are given in Figure 2 for an initial concentration of 6 mg/mL silica. PNIPAM (**1**) and the copolymer (**2**) show a similar behavior with a strong affinity to the surface. This results in a sharp increase of the adsorbed amount until a plateau is reached at about 0.2 mg/mg, corresponding to a monolayer coverage of uncharged PNIPAM on silica of about 1 mg/m². This coverage is on the same order as those determined for the homopolymer on other polydisperse silica materials (0.1 g/g, corresponding to 0.8 mg/m²).[25]

NMR Spectra. Figure 3 shows ¹H spectra of the homopolymer (**1**) (a) in solution below the LCST, and adsorbed to silica (b) below and (c) above the phase transition temperature. In
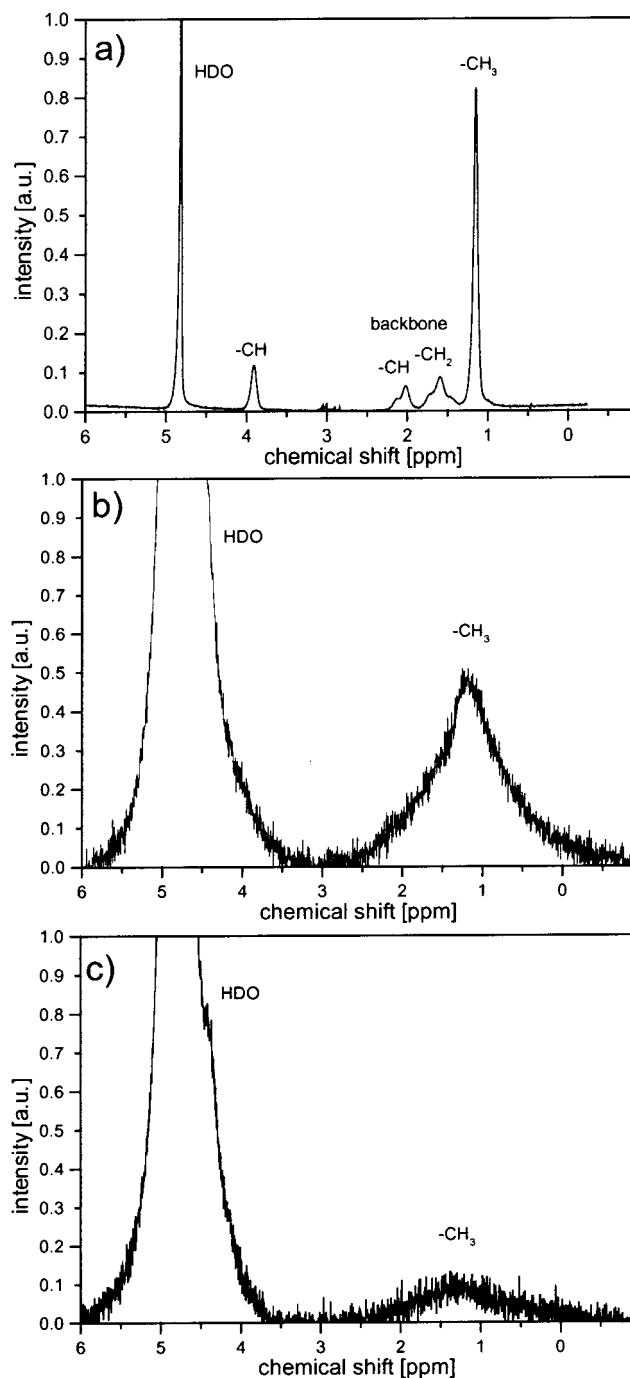

Figure 3. ¹H liquid spectra of (**1**) in solution and on silica: (a) in D_2O solution (30 mg/mL) below the phase transition ($T = 22$ °C); (b) adsorbed to silica at a polymer/silica ratio of 0.25 below the phase transition ($T = 23$ °C); and (c) adsorbed to silica at a polymer/silica ratio of 0.25 above the phase transition ($T = 40$ °C). To compensate for changes of the chemical shift with temperature, spectra are calibrated with the water resonance set to 4.8 ppm.

the solution spectrum, the ¹H resonances are identified as indicated. The spectrum of adsorption samples is dominated by the signal of the CH_3 group (see Figure 3b). In comparison to the polymer in solution, this resonance is broadened, so that further ¹H resonances cannot be identified in adsorption layer spectra. As will be discussed below, the increased spectral width can be attributed to homogeneous broadening arising from an increased relaxation rate of the adsorbed polymer, and thus reflects a reduced mobility of the segments observed. The spectra of (**2**) are similar, the solution spectrum additionally showing the corresponding copolymer resonances in the liquid
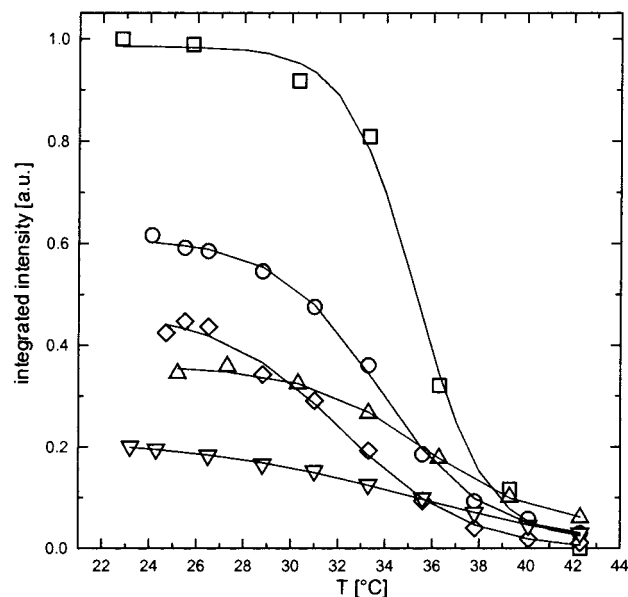
Phase Transition in Adsorption Layers

J. Phys. Chem. B, Vol. 106, No. 32, 2002 **7803**

Figure 4. Liquid state ^{1}H signal (integrated intensity) of PNIPAM **(1)** adsorbed to colloidal silica in dependence of temperature at varying polymer/silica initial weight ratio: □, 1; ○, 0.85; ◇, 0.65; △, 0.5; ▽, 0.25. The integral intensities are normalized on the maximum value at weight ratio 1. The solid lines are fits according to eq 1.

Figure 5. Liquid state ^{1}H signal (integrated intensity) of the copolymer **(2)** adsorbed to colloidal silica in dependence of temperature at varying polymer/silica initial weight ratio: ■, 1; ●, 0.85; ▲, 0.5; ▼, 0.25. The integral intensities are normalized on the maximum value at weight ratio 1 of the polymer **(1)**. The lines are fits according to eq 1.

state.[9] The adsorption samples of the copolymer are also dominated by the broadened −CH$_3$ resonance (data not shown).

At temperatures above the phase transition, the polymer signal is reduced, see Figure 3c. This reduction is arising from a further decrease of the relaxation time T$_2$ with the decrease of segmental mobility. For a number of segments thus the resonance becomes broadened beyond detectability. The remaining signal in spectra taken under liquid-state NMR conditions can be employed as a measure of the fraction of spins remaining in a liquid state.

Information about segmental mobility of the polymers can in principle also be obtained from the shape of the spectrum. The line width (FWHM) of the liquid spectrum is clearly increasing with increasing temperature, indicating immobilization. A detailed deconvolution of the CH$_3$ resonance employing Lorentzian lines resulted in several dynamic components, which exhibit different line widths, and an unambiguous deconvolution is difficult to achieve. The resonances obviously are affected by a strong dynamic heterogeneity, which is also proven by the relaxation data described below. The most reproducible parameter evaluated from the ^{1}H spectra is thus the integrated intensity, which is used for further analysis. The integral of the methyl proton signal and its decrease with temperature is taken as a parameter to characterize the phase transition.

^{1}H Signal Decrease. Figure 4 gives the integrated PNIPAM **(1)** CH$_3$ signal in dependence of temperature for samples of different mixing ratio of polymer and silica, i.e., different initial polymer amounts. With increasing temperature, the signal is decreasing, indicating a transition, which causes a decrease of the amount of mobile polymer segments. Applying the same method to PNIPAM solutions, a sharp transition (width < 2K) had been observed for both compounds **(1)** and **(2)** in D$_2$O.[9] In contrast to free polymer in solution, the transition of surface bound PNIPAM is significantly broadened.

Adsorption samples of **(2)** show similar temperature-dependent behavior in ^{1}H spectra as **(1)**. The phase transition is again clearly visualized by a decrease of the liquid signal with temperature, which shows a transition broadened as compared to the phase transition in solution, see Figure 5. However, in comparison to the transition of the homopolymer, pronounced
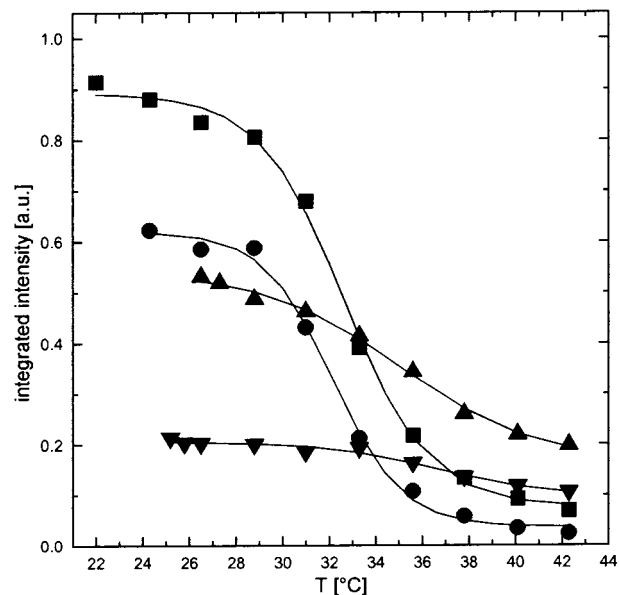
differences occur. At a low polymer coverage the liquid signal at high temperatures approaches a plateau value, which is larger than zero. It can thus be concluded that the presence of the charges, though their concentration is low, has a large influence on the phase transition properties. For the copolymer, electrostatic repulsion of the charged segments from the surface charge, which has the same sign, can be expected. This appears to hinder the phase transition. The plateau in Figure 5 forms thus evidence that not all polymer segments are taking part in the transition, but a liquid-like mobility is retained for a fraction of segments even at high temperature.

The solid curves in Figures 4 and 5 are fits of the data with the phenomenaological function

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

where T_c, a, b, and k are fit parameters. This function gives a very good description of all transitions and allows a quantitative analysis of the width, the plateau value, and the transition temperature. The fit results are discussed further below in comparison with the DSC experiments.

^{1}H Relaxation. As argued above, the liquid state spectra monitor mobile loops and tails only. In contrast to this, a solid echo experiment detects spins of solid as well as of liquid-type mobility. Here, solid echo relaxation experiments are performed on adsorption samples. In all cases the echo decays can be described by biexponential fit functions, clearly indicating the presence of at least two fractions of spins that exhibit different mobility. Figure 6 gives an example of echo decay data, together with biexponential fit functions. Below the LCST the relaxation time T$_{21}$ of the fast component is 70 μs, it is thus on the order of the dead time in the liquid-type (90°− acqu) experiment. This proves that there are solid spins present in the sample, which are not taken into account in the evaluation of the area in Figures 4 and 5. The relaxation experiments thus demonstrate that the liquid signal can be interpreted as the mobile fraction of segments consisting of loops and tails. It should be noted that, though the data are in all cases well described by
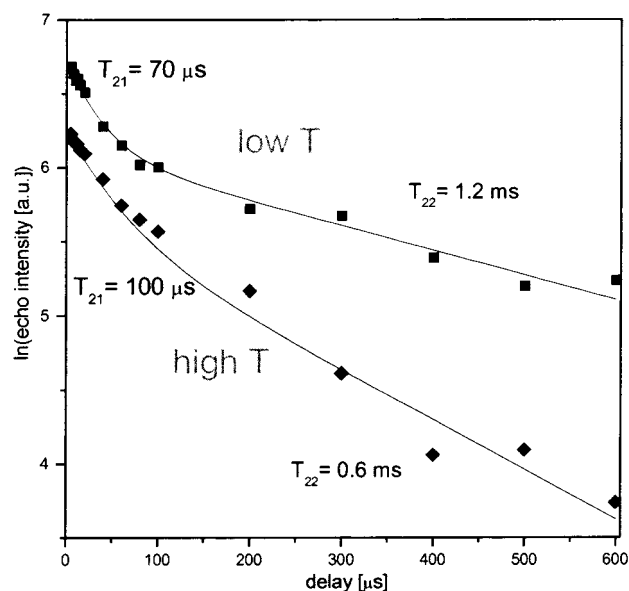
Figure 6. Relaxation experiments showing the echo decay of an adsorption sample of (**2**) with a polymer/silica initial weight ratio of 0.25. Squares: below LCST (*T* = 21.3 °C), diamonds: above LCST (*T* = 45.6 °C).

biexponential fits, this model is a strong simplification. In reality a rather continuous distribution of T_2 can be expected. We will here interpret trends obtained from the fit parameters of the two components, though the T_2 values and the relative amplitudes I_1 and I_2 of the fast and slow component, respectively, scatter somewhat due to fit errors (data not shown). Typical T_2 values for the fast component are in the range of $70-100 \mu s$, while T_2 for the slow component is on the order of 0.6 to 2.6 ms. The following trends can be extracted:

(1) With increasing temperature the relaxation time of the slow component, T_{22}, and I_2 both decrease. Both are due to the solidification of segments, which causes the corresponding spins to disappear from this component.

(2) At low temperature, T_{22} and I_2 both increase with increasing polymer coverage. Thus the slow component represents a larger fraction of mobile segments, if the polymer coverage is higher.

(3) At high temperature, T_{22} is independent of polymer coverage. Considering that T_{22} represents the most mobile fraction, the conclusion is that the outermost segments of the layer collapse to a state of mobility, which is independent of the thickness of the layer.

(4) Differences between the fit parameters comparing both polymers are too small to be considered relevant.

(5) Interestingly, for the fast component no systematic dependencies of T_{12} and I_1 on surface coverage or temperature could be identified. Assuming that the fast component would represent the spins in train segments, an increase of the intensity with temperature would be expected.

The latter result can, however, be explained by the assumption that the fast component does not represent trains, but rather segments of intermediate mobility, while the ^{1}H spins in trains relax even faster and are not detected even in the solid echo experiment. Then, above the phase transition, liquid spins of the component T_{22} become immobilized and contribute to T_{21}, while spins from the intermediate component with T_{21} immobilize further and are not detected any more. In such a three-fraction model the parameters of the component with intermediate mobility can remain constant, while the slow relaxing component decreases.
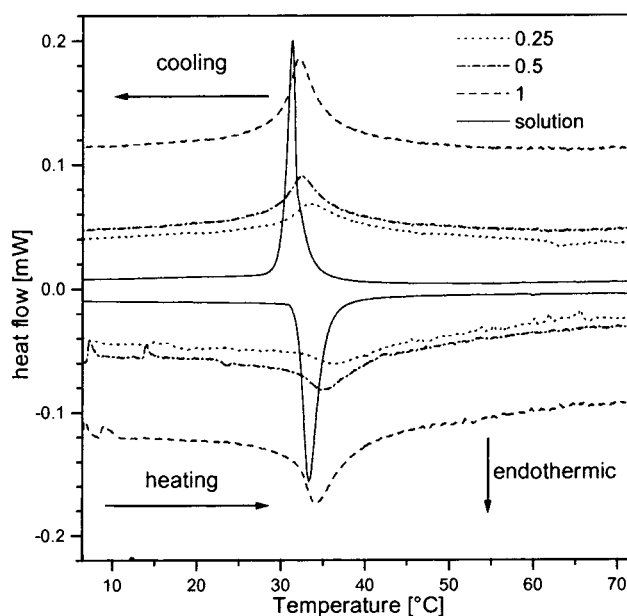

Figure 7. DSC curves of the second heating and cooling cycle of (**1**) adsorbed to silica at varying polymer/silica weight ratio as indicated, and compared to aqueous solution. The upper curves are taken during cooling of the sample, and the lower curves are taken on heating of the sample (endothermic transition). The solution curves are reduced by a factor of 10 in this figure.

DSC Thermograms. For aqueous PNIPAM solutions a single sharp endothermic peak was obtained; the coil-to-globule transition occurs at $T_{onset} = 32$ °C in agreement with data reported by other authors.[1] Solutions of PNIPAM copolymer (**2**) show the phase transition at $T_{onset} = 33$ °C, in agreement with data reported earlier.[4] As may be seen from the cooling of the sample to the initial conditions and rescanning, the phase transition is reversible for both polymers.

For the adsorbed polymers an endothermic transition peak was detected upon heating, irrespective of the adsorbed amount (see Figure 7). As for the case of polymer in solution, the transitions are reversible. For the homopolymer the first heating curves of samples with a low polymer content, however, show very broad peaks that are difficult to detect due to a very low heat flow. The transition peaks reproducibly become more pronounced in the first cooling and in subsequent heating—cooling cycles. We attribute this to a rearrangement of the polymer at the interface, leading to an equilibration after the first heating cycle. This might correspond to rearrangements observed by Zhu and Napper for PNIPAM adsorbed to dispersed latex particles, which were interpreted as the formation of an extended brushlike conformation.[16] For the copolymer, the peaks obtained at the first heating do not deviate significantly from that of the following heating procedures. The peaks detected during the cooling cycle are slightly broadened and in addition asymmetric for the adsorbed samples of high polymer content, and also for the polymer in solution. In the analysis of the thermograms averages of several heating or cooling cycles and several samples of identical composition are taken, since despite the peak shapes, the temperatures were generally not dependent on the history of the sample.

Since the total sample amounts were not always reproducible, and furthermore difficulties in determining the baseline (start and end temperature of the peak) occurred especially for broad peaks, a quantitative evaluation of the transition enthalpies for the adsorbed polymer samples is not performed. For both polymers a dependence of the transition temperature on the

Phase Transition in Adsorption Layers

J. Phys. Chem. B, Vol. 106, No. 32, 2002 **7805**

polymer surface coverage is observed, which becomes obvious in Figure 7 and will be analyzed in further detail below.

Analysis and Discussion of the Phase Transition

In view of the motional heterogeneity of adsorbed polymer segments, as for example manifested in the relaxation data, it is interesting to discuss the origin of the NMR signals in relation to the position and conformation of the corresponding polymer segments at the interface. In Figures 4 and 5, it is observed that not only the transition but also the liquid signal at low temperatures depend on the mixing ratio of polymer to silica. Furthermore, the integrals of the DSC curves similarly increase with the polymer initial weight fraction. Both effects suggest an increase of the adsorbed amount with polymer concentration up to the mixing ratio of 1. On the other hand, the adsorption isotherm shows saturation of the surface already around a mixing ratio of 0.3 (2 mg/mL polymer). However, the adsorption isotherms were found to be strongly dependent on the initial silica concentration, and reproducibility was poor, especially at high silica concentrations. Investigating two different mixing ratios in a previous publication, we had argued that the high concentration of silica used for the preparation of NMR samples could lead to polymer chains becoming entangled between the particles in the centrifugation process,[9] which could then lead to samples which contain adsorbed chains and an additional fraction of not directly adsorbed chains. Though the adsorption isotherm in Figure 2 was prepared using the same initial silica concentration as for NMR and DSC samples, it is still possible that entangled chains could affect the integrated signals.

Alternatively, it should be noted that neither the integrals of the NMR resonances nor the integrals of the DSC raw data peaks are proportional to the adsorbed amount. In DSC only the segments undergoing a transition are detected, and the liquid NMR signal arises from mobile segments only. Assuming that the solid trains do not contribute to the heat of transition, the signal intensity in both methods can roughly be identified with the loop and tail fraction. A dependence of this fraction on the initial polymer concentration could occur even at full surface coverage, if the conformation at the surface is dependent on the initial polymer concentration. With the current data it is difficult to decide which of these two explanations holds. For the further discussion we will interpret the DSC and NMR signal in terms of the transition of the loops and tails with the understanding that additional entangled polymers might contribute as well.

Transition Temperatures. In the literature, the calorimetrically determined transition temperature of PNIPAM or PNIPAM copolymers has been defined either as the onset of the DSC transition endotherm, T_{onset}, (i.e., the intersection of the baseline and the leading edge of the endotherm),[3,26] as the temperature at the peak of the thermogram T_{peak},[22] or as the temperature corresponding to the maximum of the first derivative of the observed thermogram.[23] Usually, for characterizing a transition it is recommended to use the extrapolated start temperature T_{onset}, as it is not so much dependent on experimental parameters compared to other characteristic points (T_{peak} or end temperature of the peak T_{end}) of the DSC thermogram.[27]

For sharp peaks as they are obtained for the polymer in solution in the present study, it is possible to determine T_{onset} very precisely (see above). If peaks are broadened or if the signal-to-noise ratio is poor, a reliable determination of T_{onset} is made more difficult, e.g., due to inaccuracy in fixing the baseline. In such cases it may be more reliable to determine
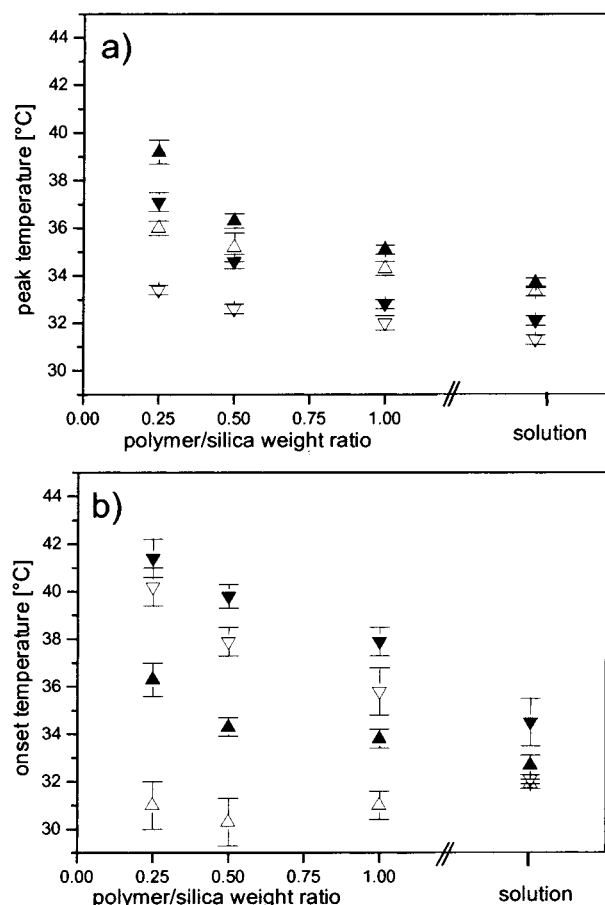

Figure 8. Phase transition temperatures evaluated from DSC curves: (a) peak temperatures, (b) onset temperatures. Up triangles are evaluated from heating curves, down triangles from cooling curves. (**1**): open symbols, (**2**): solid symbols. The data points are averages over samples of identical composition and several heating cycles. The error bars represent the statistical error.

the peak maximum T_{peak}. This is sufficient for comparative studies as in the present work, if all experiments have been done under the same experimental conditions.

Thus, here the temperature at the respective maximum or minimum, T_{peak}, from the DSC heating and cooling curves is evaluated and shown in Figure 8a. The difference between the heating and cooling values is a constant for fixed experimental conditions. Compared to the polymers in solution the adsorbed polymer samples show an increased transition temperature, which is increasing further with decreasing polymer content. The surface thus has the effect of hindering the phase transition, so that a collapse of the chains cannot occur as easily as for free chains in solution. The effect is more pronounced for the copolymer, indicating that the presence of charges drives the equilibrium further to high temperatures. These results are discussed below in more detail in context of the conformation and the entropy-energy balance.

The onset temperatures are plotted in Figure 8b for comparison. Due to the uncertainties mentioned above the data points have larger errors than the T_{peak} data, but they confirm the same trend of an increased transition temperature T_c with decreasing surface coverage. Transition temperatures obtained from the NMR data by fits of the signal decays, Figures 4 and 5, with eq 1 show too large errors, so that no trends of the T_c can be identified (data not shown).

As seen from Figure 8b, for the homopolymer in solution the difference between the onset temperatures for the heating
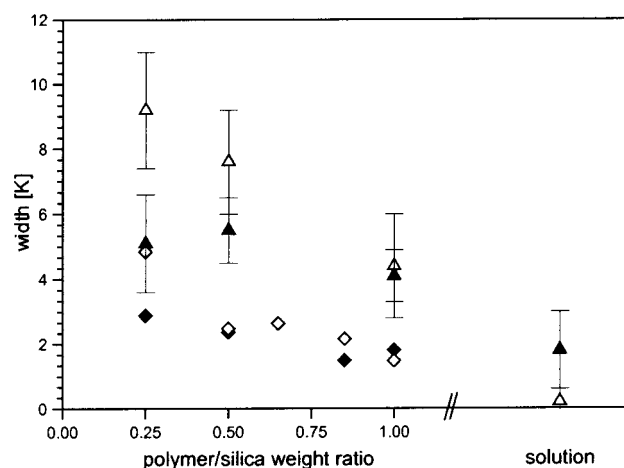
Figure 9. Width of the phase transition as determined from DSC onset temperatures (triangles) and from fits of the NMR signal decrease (diamonds), respectively. **(1)**: open symbols, **(2)**: solid symbols. Error bars of the DSC data represent the statistical error of several samples and heating cycles.

Figure 10. Fraction f of liquid spins not undergoing a phase transition as determined from the fit parameters of the curves in Figures 5 and 6 by $f = b/(a + b)$. **(1)**: open symbols, **(2)**: solid symbols. Lines are guides to the eye.

and cooling peak is negligibly small, while the difference is rather large for the adsorbed polymer samples. While the determination of onset temperatures compensates for the potential influence of experimental parameters (e.g., the heating rate) on the thermogram, differences of T_{onset} of the heating and cooling peak are merely due to the width of the peaks themselves. For example, for the homopolymer the fact that T_{onset} for heating is constant while T_{peak} for heating is increasing with decreasing polymer amount is merely due to the width of the transition increasing with decreasing polymer amount.

Width of the Transition. The difference between the onset temperatures for the heating and cooling thermogram may therefore be considered as a measure for the increase in transition width. Figure 9 gives the transition widths, which were evaluated as the difference of the onset temperatures of heating and cooling thermograms, respectively. Width data obtained from the fits of the NMR data in Figures 4 and 5 are included for comparison. The widths obtained from both methods do not agree quantitatively. This cannot be expected either, since the parameters determined in both methods are conceptually different. Especially in view of the large motional heterogeneity within the layer, the latent heat and the mobile fraction of segments, respectively, can be affected in a different way. The trends however, agree very well, since in both methods the transition width is increased at a lower polymer amount.

The dependence of the width of the transition on polymer amount can be understood in a model assuming that the motional heterogeneity is caused by a gradient of mobility in dependence on the distance from the surface. Such models were employed to describe the distribution of mobility in other polymer adsorption layers, where the motional correlation time is generally assumed to decrease with distance from the surface.[28,29] If polymer segments, which are located close to the silica surface, exhibit a broader transition due to their stronger immobilization, then the width of the phase transition can be considered dependent on the distance of the segments from the surface. The transition width in our experiments thus appears to scale with the motional correlation time of the segments, since at low coverage the layer is dominated by immobile segments close to the surface, while at higher coverage more mobile segments with a smaller broadening of the transition contribute to the signal.

Furthermore, NMR and DSC data both result in an increased width of the transition for the homopolymer as compared to
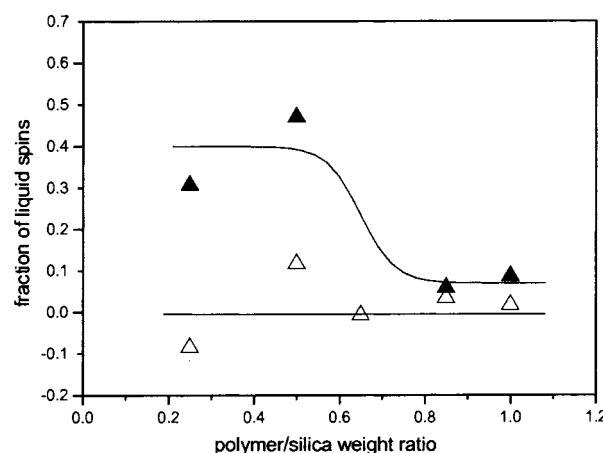
the copolymer at low coverage. This point is rather interesting. Employing the model discussed in the previous paragraph, a gradient of mobility along the surface normal causes a gradient of the transition width. This argument is implying that segmental immobilization causes a homogeneous broadening of the transition. If now the transition of the copolymer is less broadened at low coverage as compared to the homopolymer, it follows that the copolymer segments are *less* immobilized in the layer. Indeed, this is the effect of the electrostatic repulsion from the surface, which is supported by the data presented in the next paragraph.

Liquid Fraction at High Temperature. As discussed before, the transition observed in the DSC and NMR measurements can be attributed to those liquid segments (i.e., loops and tails), which undergo a transition and become solid. Information about the fraction of segments, which are liquid below the transition and still mobile at high temperature, can be extracted in form of the parameter b from the fits of the data in Figures 4 and 5. Figure 10 gives the fraction f of liquid spins not undergoing a transition $f = b/(a + b)$. For the homopolymer no change of f with coverage is observed, and the data scatter around zero. This implies that the transition of the homopolymer at the interface is complete, i.e., it involves all liquid segments. For the copolymer, however, increased values of f are found at low coverage. On the other hand, particularly at low coverage the polymer dynamics have in general been found slower, as seen, e.g., from the larger train fraction or the faster relaxation of the slow component in the solid echo. This slower dynamics is now accompanied by a liquid signal and thus mobile segments remaining at higher temperatures. This apparent contrast of liquid segments present only in a layer that is rather rigid below the T_c can be understood by taking the electrostatic repulsion of the copolymer from the silica surface into account. Since the carboxylic co-monomer has the same sign of charge as the surface, **(2)** is probably directly adsorbed with NIPAM monomers only, while the carboxylic groups are arranged in loops in a distance from the surface (see sketch in Figure 11). The electrostatic repulsion in this arrangement could have different implications for the mobility of the chains on different length scales. The long-range repulsive Coulomb interaction can freeze the polymer configuration on the scale of several segments, which might prevent the long scale rearrangements necessary for a collapse. This would keep the charged segments fixed at a distance from the surface in a configuration, where mobility
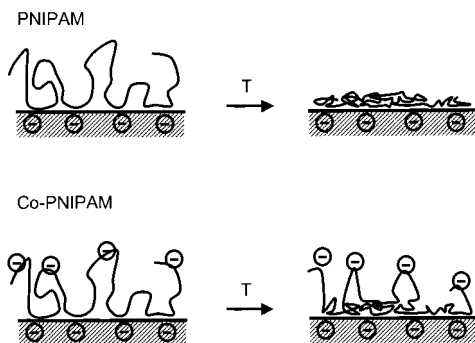
Phase Transition in Adsorption Layers

J. Phys. Chem. B, Vol. 106, No. 32, 2002 **7807**

PNIPAM

Co-PNIPAM

Figure 11. Proposed model of the polymer configuration in a charged and uncharged adsorption layer, leading to the differences observed in the phase transition properties.

is preserved on the scale of the local bond motions, resulting in a liquid signal.

An interesting observation is that this effect occurs predominantly at low coverage. The explanation is that at high coverage the repelled segments find a sufficient number of other segments to interact with, so that they can collapse and become solid. Thus apparently for the charged polymer, a critical surface density of loops is required to allow collapse.

Discussion of the Effect of Surface Constraints on the Transition. The effect of certain mobility constraints on the phase transition has already been discussed in a number of different systems: Mobility constraints were also found in the phase transition of a charged PNIPAM network, which formed the shell of core−shell latex particles. While the volume phase transition of the same gel material is discontinuous, i.e., sharp, the spatial constraint in the shell film causes a broad continuous transition.[30,31] Here, the transition was also incomplete, which was explained by a merely one-dimensional shrinking of the network along the surface normal.

Furthermore, in PNIPAM volume networks a slight increase of the transition temperature with increasing cross-linking density was found for highly cross-linked gels.[32] This can be interpreted as a consequence of the length of the free chains in the network, where a higher transition temperature is required for shorter chains. In a similar picture the increase of the transition temperature with decreasing polymer coverage in adsorption layers can be understood. At high polymer content only a low fraction of segments is bound to the surface as trains, leading to long loops and tails, which have a phase transition temperature and width similar to free chains in solution. At lower polymer coverage the fraction of segments bound as trains is larger, thus the loops and tails are shorter. These shorter chains require a higher transition temperature.

For long grafted PNIPAM chains on latex particles a similar NMR experiment employing 13C was performed.[12] A sharp decrease of the intensity, similar to the solution transition was found for these chains. Due to their length, the transition of grafted chains is not strongly affected by the presence of the surface.

Discussion of the Effect of Charges on the Interfacial Transition. It is reasonable to assume that the chain conformation at the surface at low temperatures is similar for charged or uncharged PNIPAM, since no experimental data obtained below the T_c indicated otherwise. For (**2**) it can be expected, though, that charged segments are less likely to be bound in trains than uncharged ones, due to the electrostatic repulsion from the surface (see Figure 11). Differences in the phase transition behavior can now be interpreted in terms of the properties of these charged segments.

Though the transition temperatures of both polymers are approximately the same in solution and are thus unaffected by the presence of the charged monomers, the charges appear to have a strong influence on the phase transition in adsorption layers. This is most probably due to the particular charge density used here. In aqueous solution at the dissociation equilibrium, about 30% of co-monomers are charged. The influence of the charges on the water behavior and on the entropy−energy balance determining the T_c is compensated by the alkyl C_2 spacer, which is hydrophobic and causes the opposite effect, i.e., a decrease of the T_c.[4] The direct interaction of charged segments, on the other hand, is apparently negligible in solution. Hence, even in the transition, where an increase of the local segment density takes place, the charge density is small enough for the repulsive Coulomb interactions not to affect the T_c.

At the surface, however, a high surface charge density leads to a higher overall repulsive Coulomb interaction in the layer, which reaches values that obviously do affect the phase transition. Therefore, even more pronounced effects could be expected for the case of an attractive interaction between the polymer segments and a surface (or a charged precoated layer), since the motional restraints for the charged segments are stronger in an attractive potential. Our results thus imply that for the aim of the formation of multilayered temperature-sensitive structures, statistic copolymers in adsorption layers are probably too much influenced by the immobilization of the charged segments and might not be suitable candidates. Charged polymers should rather be designed in a way which maximizes the surface density of the uncharged loops within a layer and separates them spatially from the charged segments necessary for layer build-up. Current work is going on to investigate copolymers specifically designed for this purpose in adsorption layers.

Conclusions

^{1}H NMR and DSC experiments provide insight into the molecular level of the phase transition behavior of charged and uncharged thermoreversible polymer chains at interfaces. In general, the effect of the solid surface on the phase transition is an increased transition temperature and an increased width of the transition, which both are more pronounced at lower surface coverage. The temperature increase is attributed to motional constraints in the layer, since the presence of rigidly bound train segments hinders the phase transition. The increase of the width is explained by the assumption of motional heterogeneity in the film.

The effects of charges in the polymer chain on the phase transition are an even further increased transition temperature, a smaller width of the transition, and the presence of a mobile fraction of segments above the transition temperature for low polymer amounts. All these findings are interpreted in a model of the adsorption layer being trapped in a conformation with charged segments at a distance from the surface. Despite a negligible influence of charges at this co-monomer content on the LCST of free chains, the confined configuration in an interfacial layer makes the chains far more susceptible to electrostatic interactions.

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