

Conformational Transitions of Poly(*N*-isopropylacrylamide) Chains Loopily Adsorbed at the Surfaces of Poly(*N*-*tert*-butylacrylamide) Latex Particles in Water

Peng Wei Zhu and Donald H. Napper*

School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia

Received: October 31, 1996; In Final Form: January 28, 1997[®]

Results are presented for a light-scattering study of the conformational transitions and corresponding dynamics of poly(*N*-isopropylacrylamide) (PNIPAM) chains adsorbed from water onto the surfaces of poly(*N*-*tert*-butylacrylamide) (PNTBA) latex particles. Similarities between the structures of PNIPAM and PNTBA meant that the PNIPAM chains were strongly adsorbed at the PNTBA surfaces. As the temperature was increased to the θ -temperature and above, the loopily adsorbed-to-globule conformational transition was observed. This was followed on cooling by the observation of an unexpected transition, the globule-to-extended chain conformation, that occurred under better than θ -solvency conditions. The latter transition was explained as resulting from a reduction in the number of contacts between the polymer chains and the latex particle surfaces as the globular conformation was adopted. An additional finding was that these extended conformations were unstable and subsequently relaxed toward the original loopily adsorbed conformation. The relaxation process for the extended-to-loopily adsorbed conformational transition was found to occur slowly and to depend on the temperature. It is proposed that kinetic constraints played an important role in this transition. The transition kinetics were analyzed with the aid of a stretched exponential function. The relaxation time thus calculated was found to increase with increasing temperature and obeyed an Arrhenius law over the temperature range studied. The apparent activation energy of the extended-to-loopily adsorbed conformational transition was estimated to be ~ 80 kJ mol⁻¹.

Introduction

Polymer adsorption from a solution onto a solid substrate has attracted much attention both for its intrinsic scientific interest and for its technological importance.^{1–4} Interest derives partly from the fact that adsorbed polymer layers can modify the physical properties of the surfaces and partly from the fact that the physical properties of constrained polymers differ from those of polymers free in solution. Polymer–solid surface interactions can be classified according to whether there is physical or chemical adsorption. In physical adsorption, the polymer segments interact with the surface through van der Waals interactions, whereas in chemical adsorption, specific functional groups of the polymer segments chemisorb onto the surface, through, e.g., the much stronger H-bonds. Chemical adsorption is highly specific and is much stronger than physical adsorption. From an enthalpic viewpoint, only particular functional groups of an organic polymer prefer to chemisorb on the substrate. Molecular binding energies may be as large as 200–300 $k_B T$ for chemical adsorption but only 5–20 $k_B T$ for physical adsorption (here k_B is the Boltzmann constant and T is the temperature). For polymers that are adsorbed solely by van der Waals forces, the binding energy per contact is only a very small fraction of $k_B T$. The equilibrium state of physically adsorbed polymer chains has been well-understood through the application of the mean-field lattice model, scaling analysis, renormalization group methods, and computer simulations. Some progress has also been made in understanding the nature of chemically adsorbed polymer chains.

Morphologically speaking, the polymer chains adsorbed from a solution onto a solid substrate can be divided into three categories: homopolymer layers, end-adsorbed polymer brushes, and associative polymers in which both chain ends and the main

backbone have a strong affinity for the surface. Although the mechanisms underlying the absorption process are complicated and vary from one type to another, it is generally accepted that there is a feature common to these three groups: The adsorbed polymers are predicted to extend further away from the surfaces with increasing surface coverage when the bathing medium is a good solvent. Stated differently, the hydrodynamic thickness of adsorbed polymer chains increases with increasing polymer concentration. For example, associative polymer chains could adsorb as loops and trains on the surfaces with many points of contact between the polymer chains and surfaces at low concentrations. As the polymer concentration increases, however, the polymer chains begin to overlap on the surfaces and the crowding that results forces some of the main backbone segments off the surfaces. This results in fewer contact points remaining and an additional extension of the adsorbed polymer chains normal to the surface. Such conformational transitions, so-called pancake-to-brush transitions, were initially predicted to be a first-order phenomenon for end-adsorbed polymer brushes.⁵ It has been experimentally confirmed now that associative polymer chains exhibit a sharp transition on surfaces as the surface coverage increases.⁶

Like free polymer chains, adsorbed polymer chains can undergo conformational changes under different solvency conditions. In a good solvent, the segmental pair interactions of a free polymer are repulsive and tend to swell the coil conformation. In contrast, when a polymer is in a poor solvent below the θ -temperature, the mean force acting between segments becomes attractive. This attraction under worse than θ -conditions can ultimately lead to the shrinkage of individual polymer coils so as to adopt the space-filling globular conformation. Generally speaking, the degree of shrinkage, and therefore the segment density, changes with temperature. If the temperature is changed to the worse than θ -temperature solvency domain, a polymer chain may undergo a coil-to-globule transition. The

* To whom correspondence should be addressed.

[®] Abstract published in *Advance ACS Abstracts*, March 15, 1997.

conformational transitions of adsorbed chains apparently differ from those of free polymer chains for several reasons. First, the degrees of freedom of the polymer chains at surfaces are expected to be less than those in free solution. Adsorbed polymer chains exhibit some restricted orientations, depending on the adsorption type. It has been shown that chemical adsorption strongly perturbs the conformational statistics from those observed in free solution.^{7,8} Second, morphologically, the collapse transition of the adsorbed chains may be more complex phenomenologically than implied by the simple description of a coil-to-globule transition. Third, it has been found both theoretically and experimentally that the adsorbed chains are trapped in a collection of nonequilibrium structures due to the topographies of the accessible potential energy surfaces.⁷⁻¹¹ There may be many local minima in the potential energy surface. The relaxation process from nonequilibrium states displays a nonexponential behavior and may be described by a stretched exponential of the Kohlrausch-Williams-Watts (KWW) type.⁹⁻¹¹ The relaxation time of adsorbed chains is predicted to range from milliseconds to hours, or even longer.

In this paper we report on a comprehensive study of conformational transitions of poly(*N*-isopropylacrylamide) (PNIPAM) chains adsorbed at the surfaces of insoluble poly-(*N*-*tert*-butylacrylamide) (PNTBA) latex particles in water. Some characteristics of PNIPAM chains must necessarily be considered in order to understand the rationale behind the present system. Water-soluble PNIPAM contains strongly hydrophilic components (the amide groups) and significant hydrophobic moieties (the isopropyl substituent attached to the nitrogen atom). At room temperature, PNIPAM chains dissolve in water to form coils that undergo a coil-to-globule transition when heated to $\sim 31-32$ °C, which is close to the θ -temperature.^{12,13} This transition results from changes in the balance between the various types of interactions (but especially the H-bonding between the amide groups and the water, as well as the hydrophobic interactions) that occur between the PNIPAM segments and the water molecules. It has been shown,^{14,15} on the basis of an analysis of the results of scanning microcalorimetry, that when the molecular weight of the PNIPAM chains is sufficiently large (greater than $\sim 1.0 \times 10^4$), the coil-to-globule transition of the PNIPAM chains is not a so-called *all-or-nothing* process, i.e., single PNIPAM chains do not undergo coil-to-globule transitions as a whole. The collapse transition of the PNIPAM chains proceeds through a set of intermediates consisting of a number of "cooperative units" or "domains".

Recently, the coil-to-globule type transitions of PNIPAM anchored onto the surfaces of polystyrene latex particles have been studied.^{16,17} It was found that the dimensions of the interfacial PNIPAM chains decreased continuously with increasing temperature below the θ -temperature (i.e., in better than θ -solvents). It should be noted that the transitions that occur in temperature sensitive PNIPAM chains are considered to be similar to those operative in many biological systems. These have been used to develop novel methods for preparing biomaterials, such as protein conjugates, that may serve as devices to provide the controlled release of drugs and to act as immobilized enzyme reactors.

It is apparent that structural similarities between PNIPAM and PNTBA should allow the adsorbed PNIPAM chains to interact strongly with the surfaces of PNTBA latex particles. On the basis of the above discussion, the present system is presumably classified as a chemical adsorption of the homopolymer PNIPAM via hydrogen bonding onto the surfaces of the PNTBA latex particles, although other interactions may presumably also be involved. The experimental protocol followed was quite straightforward: The sample was first heated

slowly from a low temperature to temperatures as high as 60 °C, and then the temperature was decreased slowly. Two types of conformational transition and one nonequilibrium conformation were observed. The existence of a nonequilibrium conformation of the interfacially adsorbed chains led to a study of how the dynamics of chain relaxation change as a function of both time and temperature. The dynamic behavior was investigated at several temperatures under better than θ -solvent conditions. The kinetic results were interpreted in terms of the KWW model of relaxation processes. In the present study, interest was focused primarily on the transition that appeared unexpectedly on decreasing the temperature from above the θ -temperature and on the dynamics of the relaxation of the nonequilibrium conformation.

Experimental Details

N-isopropylacrylamide and *N*-*tert*-butylacrylamide (Monomer-Polymer) were purified by recrystallization from a 65/35 mixture of hexane and benzene. Azobisisobutyronitrile (AIBN) (Fluka) was recrystallized from methanol. Potassium peroxydisulfate (KPS) (BDH Chemicals) and *N,N'*-methylenebisacrylamide (BIS, cross-linker agent) (Aldrich) were used as received. Water was Millipore Milli-Q grade.

The PNIPAM was prepared following the procedure described by Schild and Tirrell.¹⁸ PNIPAM (5 g) was polymerized for ~ 20 h at 65 °C in a 70/30 benzene/acetone mixture (100 mL) using AIBN (0.5%) as the initiator under a positive nitrogen pressure. The solvents were then evaporated in a vacuum at room temperature. The PNIPAM that was obtained was fractionated by dissolution of the dried solid in dry acetone, followed by the careful addition of dry *n*-hexane. The samples were recovered by freeze-drying. The maximum weight-average molecular weight was used for the present study. The weight-average molecular weight and radius of gyration were determined by static light scattering at 25 °C, using the Zimm plot procedure, to be 1.6×10^6 and 58 nm, respectively. The refractive index increment of PNIPAM in water was $0.164 \text{ cm}^3/\text{g}$.¹⁹ The polydispersity ratio of the PNIPAM was estimated from the dynamic light scattering measurement in the sodium dodecyl sulfate solution of 120 mg/L, following the procedure of Meewes et al.¹⁹ and found to be 1.4.

PNTBA latex particles were prepared by a free radical copolymerization of NTBA and the cross-linking agent (BIS) in water at 70 °C, following the procedure described by Pelton et al.²⁰ The purified NTBA (1.5 g) and BIS (0.3 g) were dissolved in water (~ 200 g), and KPS was added (0.017 g) as an initiator under a positive nitrogen pressure. The PNTBA latex particles generated were expected to be negatively charged as a consequence of using KPS as an initiator in the polymerization. After ~ 5 h, the particles were filtered and any residual small molecules removed by centrifugation of the latex, followed by decantation of the supernatant. The particles were then dialyzed for a further ~ 3 days with repeated changes of freshly prepared Millipore Milli-Q water. The latex particles were filtered again through a $0.45 \mu\text{m}$ filter.

The PNTBA latex particles were added to the PNIPAM solution under stirred condition at room temperature. The weight ratio of PNIPAM to PNTBA particles was 4.0. The suspension thus prepared was kept for ~ 24 h at room temperature. The nonadsorbed PNIPAM was removed by centrifugation in 10 000 rpm for 60 min at 17 °C and decantation of the supernatant. The samples were then redispersed in Millipore Milli-Q water.

Dynamic light scattering (DLS) measurements of the average latex size were performed at a particle concentration of $\sim 3 \times 10^{-4}$ (g/g) with an argon ion laser operating at a scattering angle

of $\theta = 90^\circ$ and a wavelength of $\lambda = 488$ nm at a power of 50 mW. The intensity autocorrelation function $G^{(2)}(\tau)$ was measured using a Malvern 4700c correlator and has the form²¹

$$G^{(2)}(\tau) = A[1 + B|g^{(1)}(\tau)|^2] \quad (1)$$

where A is the experimental base line, B is a spatial coherence factor, and $g^{(1)}(\tau)$ is the electric field autocorrelation function. For a polydisperse system, $g^{(1)}(\tau)$ consists of a sum of single exponential

$$g^{(1)}(\tau) = \int_0^\infty G(\Gamma) \exp(-\Gamma\tau) d\Gamma \quad (2)$$

where $G(\Gamma)$ is the normalized distribution function of the decay rates and $\Gamma = D_z q^2$ at a very dilute solution concentration. Here D_z is the z -average translational diffusion coefficient and $q = (4\pi n/\lambda) \sin(\theta/2)$ the magnitude of the scattering vector. The analysis of the electric field autocorrelation function was made using the method of cumulants. Hydrodynamic diameters d_h were calculated from the translational diffusion coefficients using the Stokes-Einstein equation, $d_h = k_B T / (3\pi\eta D_z)$, where η is the solvent viscosity. The viscosity and refractive index of water at different temperatures were taken from the literature.²²

The sample temperature was controlled with an accuracy of $\pm 0.1^\circ\text{C}$ during the DLS measurements. At each temperature, the samples were allowed to equilibrate for 30 min before the DLS experiments were performed, even though the time required for the samples to reach the designated temperature was found to be only ~ 120 s. This time was estimated by inserting a thermocouple into the sample cell filled with water.

The intrinsic stability of the very dilute suspension was checked over a period of few days by repeated measurements of the average hydrodynamic diameter at scattering angles of 90° at 25 and 50°C . The average sizes were found to be constant, implying that no aggregation was occurring in the samples studied. This indicates that, for the present sample, the charge introduced into the surfaces of the PNTBA latex particles by the initiator fragments was sufficient to prevent the particles from undergoing aggregation.

Results and Discussion

Figure 1a shows the temperature dependencies of the hydrodynamic diameter of the PNTBA particles coated by the adsorbed PNIPAM chains. Since the size of the PNTBA latex particles (crosses in Figure 1a) studied was found to be almost independent of temperature over the range studied, the PNIPAM layer thickness could be obtained by subtracting the PNTBA core sizes from the total measured size and dividing by 2. Such plots are shown in Figure 1b. The loopily adsorbed conformation was inferred for the present surface coverage from the observation that the layer thickness of the interfacial PNIPAM chains was ~ 35 nm at 25°C while the corresponding "diameter" of a single PNIPAM coil of this molecular weight would be ~ 120 nm.

It can be seen that the loopily adsorbed PNIPAM chains in pure water underwent a major continuous collapse (~ 40 nm decrease in layer thickness) with increasing temperature under better than θ -solvency conditions and then approached a constant thickness when the temperature was raised above $\sim 34^\circ\text{C}$. There was a transitional region of limited extent near ~ 31 – 32°C where the adsorbed PNIPAM chains collapsed to their minimum size; this is close the θ -temperature of the PNIPAM involved. This result is qualitatively similar to the coil-to-globule type transitions observed in systems in which PNIPAM chains were anchored to the particle surfaces.^{16,17}

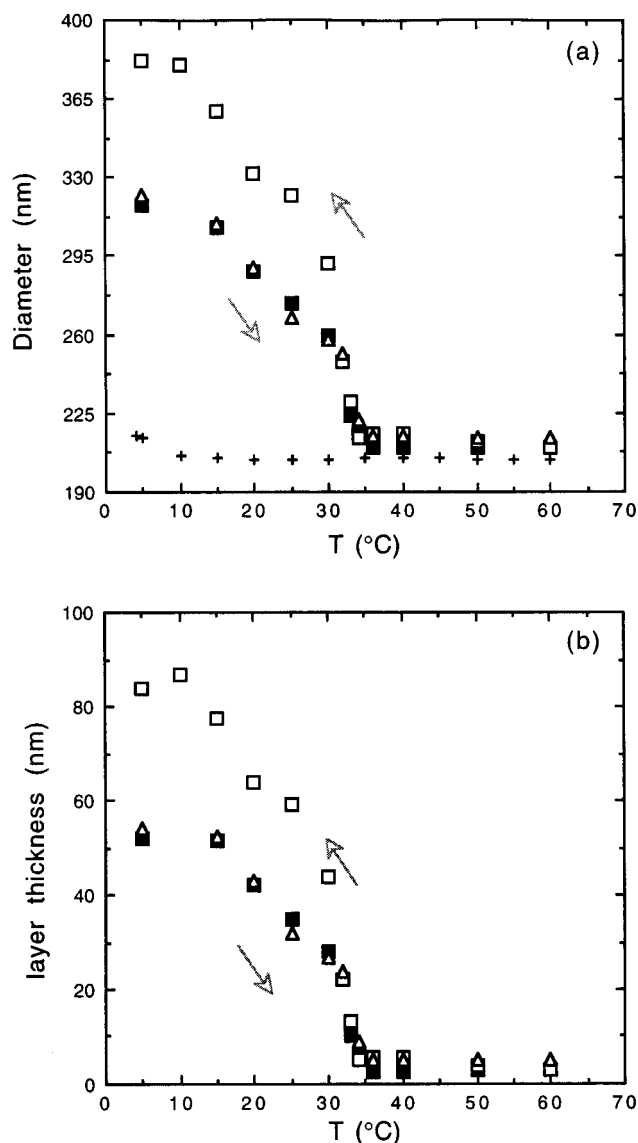


Figure 1. DLS-measured conformational transition curves for PNIPAM chains adsorbed on the surfaces of PNTBA latex particles. The filled squares are the data measured on increasing the temperature and the empty squares are those on cooling. The empty triangles are the data measured for the sample heated first from a low to a high temperature and then kept at room temperature for about two months. The crosses are the data measured for uncoated PNTBA latex particles. (a) Temperature dependence of the diameter for the PNTBA latex particles coated by adsorbed PNIPAM chains. (b) Temperature dependence of the layer thickness of the interfacial PNIPAM chains.

When the heated latex sample was cooled from 60°C , the adsorbed layer thickness was found not to change in the bad solvency region (i.e., on cooling down to 34°C). However, on further cooling, an unanticipated hysteresis was observed under better than θ -solvency conditions because the adsorbed layer thickness was found to be significantly greater than that observed previously in the first heating cycle (see Figures 1 and 2). The increase in the layer thickness was as large as ~ 30 nm, comparable in magnitude to the original thickness. This unexpected conformational transition was not observed in the chemically anchored system studied previously^{16,17} in which the interfacial globular state returned to the initial coil state with decreasing temperature within an experimental time scale of say ~ 15 min. Also, no such transition has been reported either for free PNIPAM chains or for its gels in solution. It is apparent that there is an additional type of conformational transition for the adsorbed PNIPAM chains at interfaces under the better than θ -temperature range. We designate here such a transition as a

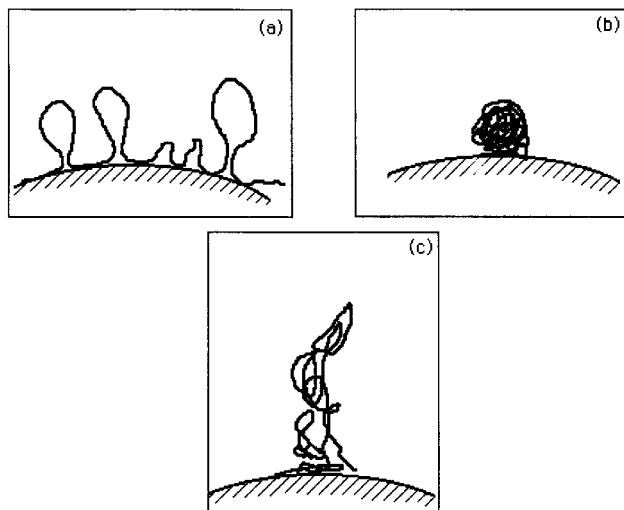


Figure 2. Schematic representations not to scale of the conformational changes of adsorbed PNIPAM chains at interfaces. (a) Loopy adsorption of chains at low temperatures before heating; (b) Globular conformational adopted on heating; and (c) extended brushlike conformation on cooling heated sample below the θ -temperature. Note that for clarity only a single chain is displayed, and so the possible overlap of neighboring chains is not shown.

globule-to-extended conformation transition of interfacially adsorbed chains. The extended conformation may be postulated to incorporate conformations with some brushlike character since it is significantly more extended than a loopily adsorbed chain, but the polymer chains are far from being fully extended. The conformational changes observed for the interfacially adsorbed PNIPAM chains are summarized schematically in Figure 2.

The globule-to-extended state transition involves an intricate balance between the attractive and the repulsive components of the different types of forces that govern the conformations adopted by adsorbed polymer chains. In the globular state, the intramolecular interactions in PNIPAM chains are so strong that most of the water molecules are excluded from the chains. As the temperature is cooled to the better than θ -solvency range however, the intermolecular interactions between the PNIPAM segments and the water molecules via H-bonding increase dramatically, together with a weakening of the hydrophobic interactions inside the PNIPAM chains as some of the hydrophobic entities become hydrated by water molecules.^{23–25} Accordingly, the PNIPAM chains are extended in a direction normal to the surface. The topological constraints imposed on the PNIPAM chains by the segmental attachment to the surface would constitute in part the overall force that balances the stretching force.

The most important factor promoting the globule-to-extended conformation transition may be postulated to be the reduction in the number of adsorbed contact points of the PNIPAM segments with the surface. It is apparent that the average number of contacts per chain is likely to be much less in the globular conformation than in the loopily adsorbed conformation. This configuration of the PNIPAM is totally different from that in the previous study^{16,17} where the PNIPAM chains were anchored to the surfaces so that the numbers of contact points were unchanging, irrespective of the temperature. The continuous decrease in the layer thickness in the present system implies that the number of contact points may be continuously reduced under better than θ -solvency conditions. The coil-to-globule transition in the chemically grafted system, however, was found to exhibit relatively sharp features.¹⁷ The dimensional changes under better than θ -solvency conditions for the chemically grafted sample was not due to a decrease in the number of contacts between the polymer chains and the surfaces and must

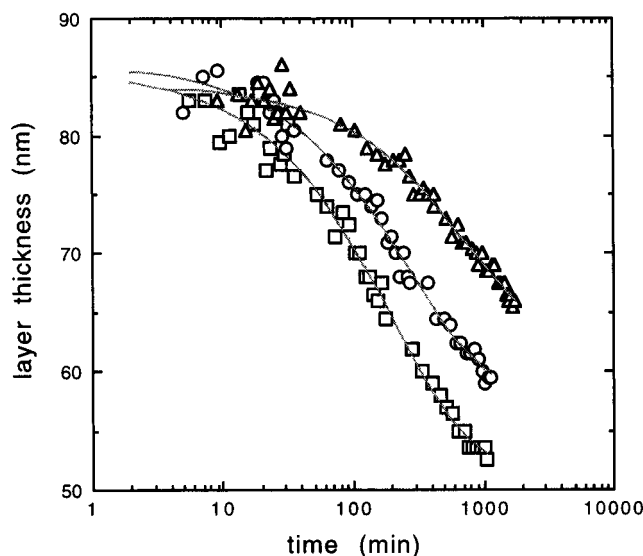


Figure 3. Semilogarithmic plots of the time dependence of the layer thickness of the interfacial PNIPAM chains for the sample which was heated at 58 °C for 30 min and then cooled and held at different temperatures (from bottom to top): 3.6, 5, and 10 °C. The solid curves are the fitting data using eq 3.

have had a different physical origin. The formation of n -clusters^{26,27} in the PNIPAM layers at interfaces may be postulated to be the driving force that induces the conformational transition under better than θ -solvency conditions.^{16,17}

Note that when considered theoretically the adsorbed-to-stretched conformation transition is found to be an unusual transition in which some features of both the first- and the second-order type transitions simultaneously appear.²⁸ The model used for these theoretical considerations is a very simple one: an adsorbed chain at an interface with a stretching force acting on the chain end. It is not yet possible to set forth such an explanation for the globule-to-extended conformation transition in the present study, but it is suggested that there would be some similarities in the thermodynamic limit.

A further interesting observation arising from this study is that the conformation of the extended chains at the latex surfaces was kinetically unstable. This is signified by the fact that the thickness of the adsorbed PNIPAM layer was found to relax to its original loopily adsorbed size at the corresponding temperature after ~ 100 days. Such results are shown in Figure 1a,b (open triangles). The sample, heated to 60 °C and cooled to room temperature (~ 20 °C), was then measured by DLS starting at the lowest temperature (3.6 °C). The nature of the interactions between the PNIPAM chains and the surfaces would thus appear to be an important determinant in this relaxational process.

The existence of a nonequilibrium conformation for the interfacially adsorbed chains has been predicted by a number of theoretical studies.^{7–11} Experimental studies, however, seem to have lagged behind the theoretical developments. Johnson and Granick²⁹ have studied the kinetics of the displacement of polystyrene on the surface of oxidized silicon by poly(methyl methacrylate) (PMMA). Although the experimental situation of competitive adsorption is somewhat different from the extended-to-loopily adsorbed conformation transition in the present work, their results suggested that the kinetics of an adsorption process may evolve through glasslike motions.

In Figure 3, the time dependence of the extended state-to-loopily adsorbed conformation transition of interfacially adsorbed PNIPAM is presented at three temperatures of 3.6, 5.0, and 10.0 °C in the form of semilogarithmic plots, where the points represent the experimental data. The samples were first heated to 58 °C for 30 min and then transferred respectively to

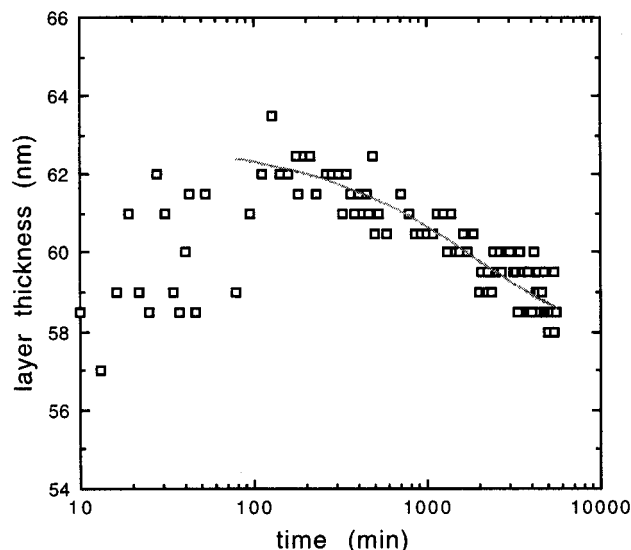


Figure 4. Semilogarithmic plot of the time dependence of the layer thickness of the interfacially adsorbed PNIPAM chains for the sample heated at 58 °C for 30 min and then measured at 20 °C. The solid curves are the fitting data using eq 3.

the requisite temperatures for DLS measurements. The data display qualitatively several important dynamic features. The first is that the transition processes were quite sluggish at the temperatures studied, occurring over many hours. The second is that there was a progressive slowing down of the relaxation process as the temperature increased (i.e., as the goodness of the solvency decreased). It is apparent that the relaxed layer thickness could approach the loopily adsorbed value at 3.6 °C but was far from its equilibrium state at 10 °C over the experimental time scale used. The third feature, which was also unexpected, is that at higher temperatures the layer thickness tended first to increase marginally with time before the onset of the decrease in chain dimensions at longer times. A typical result for 20 °C is shown in Figure 4. It can also be seen from Figures 3 and 4 that the interfacially adsorbed chains appeared to be locked into nonequilibrium conformations for relatively long times (e.g., ~20–100 min) before relaxing.

These results reveal that the extended-to-loopily adsorbed conformation transition processes, associated with the longer time scale, may be similar in some respects to those that determine the structural relaxation of glass-forming liquids. It should be pointed out that this similarity does not imply that glassy layers were actually formed at the interfaces due to an increased segment density, as proposed by Kremer.³⁰ Such considerations do not agree with the morphology of the adsorbed chains studied. If the segment density were sufficiently high, the extended conformation should be maintained by the repulsive neighboring interactions. It is the low surface coverage in the present system that provided the possibility of the observed transition. We have here considered the extended-to-loopily adsorbed conformational transition as an adsorption process from an unstable extended state to a lower free energy loopily adsorbed state. Besides the interactions between the polymer segments and the surfaces, the kinetic constraints operating within the polymer chains could play crucial roles in the dynamics of the transition.

The likely physical origins of the kinetic constraints that trap the chains in the nonequilibrium state include nearest-neighbor interactions (e.g., *n*-clustering, H-bonding), topological barriers, and competition for surface sites. The effects of these kinetic constraints on the strong adsorption processes of polymer chains are complex at the molecular level. The general reason why the nonequilibrium structures arise is that the kinetic constraints

do not allow the polymer chains to evolve rapidly to structures corresponding to the global minimum free energy.^{7–11} The extended-to-loopily adsorbed transition may proceed through four stages. First, the number of attachment points of the extended chains decreases marginally thus allowing the extension of the chains to increase marginally. Second, some extended PNIPAM segments in preferential positions may then relax into the adsorbed state. The third stage could be associated with the formation of loops as the incoming segments absorb onto empty surface sites, the adsorption rate of a PNIPAM segment being greatly affected by its nearest neighbors. In the final stage, any remnants of extended loops relax, together with the possible rearrangement of the loopily adsorbed conformation. The whole process is considered to be highly cooperative. The unstable segments have to search the accessible paths in the configuration space in a tortuous way during the transition.

The PNIPAM chains are sensitive to the temperature under better than θ -solvency conditions, which in turn effectively influences the kinetic constraints in the nonequilibrium structures. This is evidenced in Figures 3 and 4. The kinetic constraints become more active as the temperature increases and, consequently, many available paths could be kinetically blocked at higher temperatures due to the stronger intramolecular interactions between the PNIPAM segments. Much longer times are thus needed for the transition, due to greater cooperativity being required. At 20 °C, the kinetic constraints are so strong that ~100 min is taken for the PNIPAM chains to extend to the maximum layer thickness, as seen in Figure 4. The results here also support the previous observation^{16,17} that the interactions between PNIPAM and water are continuously weakened with increasing temperature under better than θ -solvency conditions.

The kinetic constraint mechanism predicts that the dynamics of such processes can be described by the KWW expression.^{31,32} The experimental data for the time dependence of the layer thickness were accordingly fitted by the following KWW-like function

$$\frac{H(t) - H(\infty)}{H(0) - H(\infty)} = \exp[-(t/\tau_{\text{eff}})^\beta] \quad (3)$$

where H = the layer thickness, τ_{eff} = the effective relaxation time, and β = the stretched exponent. Microscopically, the relaxation of the interacting units is heterogeneous, corresponding to a “distribution” of relaxation rates of dynamical origin. In the theory of entangled polymer systems, the stretched exponent β can be interpreted as a measure of the effects of heterogeneity.³³ The mean relaxation time $\langle\tau\rangle$ can be related to the effective relaxation time τ_{eff} and the stretched exponent β by³⁴

$$\langle\tau\rangle \equiv \int_0^\infty \exp[-(t/\tau_{\text{eff}})^\beta] dt = (\tau_{\text{eff}}/\beta)\Gamma(\beta^{-1}) \quad (4)$$

where $\Gamma(\beta^{-1})$ is the gamma function. The kinetic data presented in the present work were well-fitted by eq 3. The continuous solid curves shown in Figures 3 and 4 are representative of the use of this fitting function, and close correspondence was obtained with experiment. Figure 5 shows the temperature dependence of the average relaxation time. The β values obtained are ~0.74–0.79, almost independent of the temperature studied. The kinetics of the displacement of polystyrene on the surface by PMMA was also reported to obey the KWW expression with $\beta = 0.5$ –0.6.²⁹

If it is assumed that the temperature dependence of the mean relaxation time $\langle\tau\rangle$ (which is inversely related to the corresponding rate coefficient) can be represented by an Arrhenius-like equation, then we have

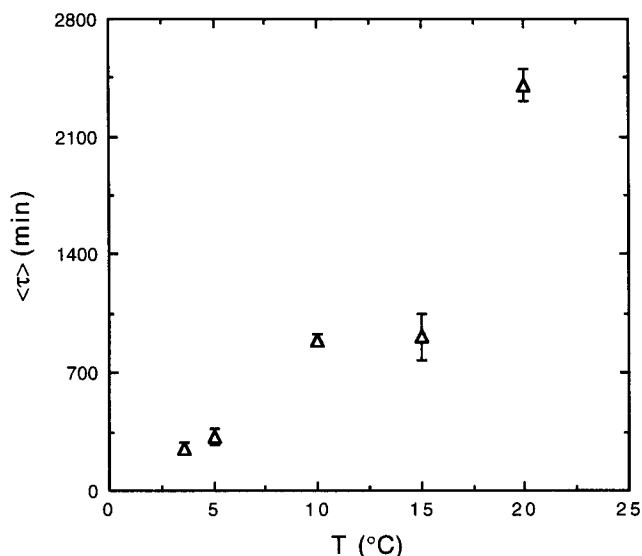


Figure 5. Plot of the temperature dependence of the average relaxation time $\langle \tau \rangle$ obtained from eqs 3 and 4.

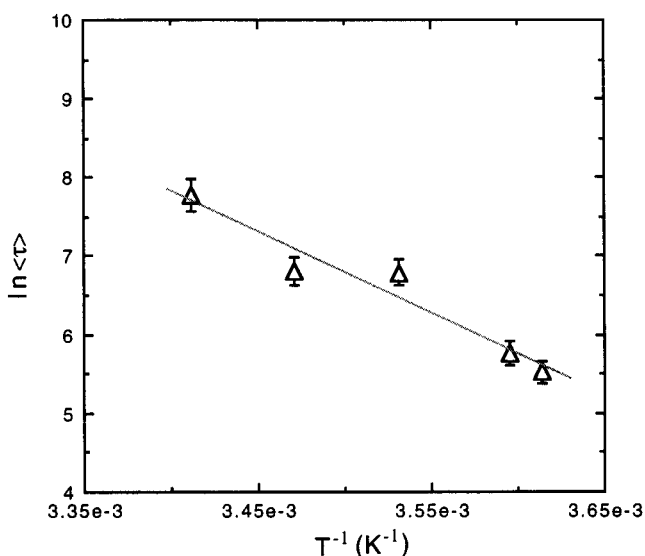


Figure 6. Arrhenius-type plot for the data shown in Figure 5.

$$\langle \tau \rangle(T) = A \exp(E/RT) \quad (5)$$

where A = a constant, R = the gas constant, and E = the apparent activation energy. From the foregoing discussion, the apparent activation energy E can be associated with the extended-to-loopily adsorbed conformational transition. The absolute magnitude of E may be obtained by plotting $\ln \langle \tau \rangle$ versus T^{-1} . Such a plot is shown in Figure 6. Over the temperature range studied, the plot exhibits a linear relation, which is in good agreement with the theoretical prediction under certain conditions.¹⁰ The slope obtained from Figure 6 yields a value of $\sim 80 \text{ kJ mol}^{-1}$ as the apparent activation energy. Note that a value of $E = 67 \text{ kJ mol}^{-1}$ was theoretically estimated for the kinetics of the adsorption of syndiotactic PMMA chains onto aluminum surfaces.¹⁰

Conclusions

The poly(*N*-isopropylacrylamide) chains were absorbed from water onto the surfaces of poly(*N*-*tert*-butylacrylamide) latex particles. The PNIPAM chains exhibited the loopily adsorbed morphology at the latex interfaces under the surface coverage

studied. As the temperature was increased to above the θ -temperature and then cooled, the interfacial chains changed their conformations sequentially from the loopily adsorbed to the globular and then to the extended form. The globule-to-extended conformational transition observed in the present system was found neither in PNIPAM gels nor in systems in which the PNIPAM chains were chemically grafted onto surfaces. The significant reduction in the average number of contacts between the polymer chains and the surfaces on globule formation was postulated to be the reason for this transition. The extended conformation was found to be unstable and to relax slowly toward the lower free energy loopily adsorbed state under better than θ -solvent conditions. The relatively low surface coverage provided the possibility for this transition. The relaxation rate of the extended-to-loopily adsorbed state transition was strongly dependent upon the temperature. Kinetic constraints were postulated to play an important role in controlling the extended-to-loopily adsorbed state transition. The relaxation times that were calculated from the KWW-like model were found to increase with increasing temperature. The apparent activation energy of this transition was estimated to be $\sim 80 \text{ kJ mol}^{-1}$ over the temperature range studied.

Acknowledgment. The Australian Research Council is thanked for its financial support of this study.

References and Notes

- (1) Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: New York, 1983.
- (2) Fleer, G. J.; Cohen-Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. V. *Polymers at Interfaces*; Chapman & Hall: New York, 1993.
- (3) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31.
- (4) Sperry, P. R.; Thibault, J.; Kostansek, E. *Adv. Org. Coat. Sci. Technol. Ser.* **1985**, *9*, 1.
- (5) Alexander, S. J. *Phys. (Paris)* **1977**, *38*, 1069.
- (6) Rodgers, S. D.; Santore, M. M. *Macromolecules* **1996**, *29*, 3579.
- (7) Shaffer, J. S.; Chakraborty, A. K.; Tirrell, M.; Davis, H. T. *J. Chem. Phys.* **1991**, *95*, 8616.
- (8) Chakraborty, A. K.; Shaffer, J. S.; Adriani, P. M. *Macromolecules* **1991**, *24*, 5226.
- (9) Adriani, P. M.; Chakraborty, A. K. *J. Chem. Phys.* **1993**, *98*, 4263.
- (10) Shaffer, J. S.; Chakraborty, A. K. *Macromolecules* **1993**, *26*, 1120.
- (11) Chakraborty, A. K.; Adriani, P. M. *Macromolecules* **1992**, *25*, 2470.
- (12) Shibayama, M.; Tanaka, T. *Adv. Polym. Sci.* **1993**, *109*, 1.
- (13) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163.
- (14) Tiktopulo, E. I.; Bychkova, V. E.; Ricka, J.; Ptitsyn, O. B. *Macromolecules* **1995**, *28*, 2879.
- (15) Tiktopulo, E. I.; Uversky, V. N.; Lushchik, V. B.; Klenin, S. I.; Bychkova, V. E.; Ptitsyn, O. B. *Macromolecules* **1995**, *28*, 7519.
- (16) Zhu, P. W.; Napper, D. H. *J. Colloid Interface Sci.* **1994**, *164*, 489.
- (17) Zhu, P. W.; Napper, D. H. *Colloids Surf.* **1996**, *113*, 145.
- (18) Schild, H. G.; Tirrell, D. A. *J. Phys. Chem.* **1990**, *94*, 4352.
- (19) Meewes, M.; Ricka, J.; de Silva, M.; Nyffenegger, R.; Binkert, T. *Macromolecules* **1991**, *24*, 5811.
- (20) McPhee, W.; Tam, K. C.; Pelton, R. J. *Colloid Interface Sci.* **1993**, *156*, 24.
- (21) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
- (22) *Handbook of Chemistry and Physics*, Weast, R. C., Ed.; CRC Press: Cleveland, OH, 1974–1975.
- (23) Skipper, N. T. *Chem. Phys. Lett.* **1993**, *207*, 424.
- (24) Guillot, B.; Guissani, Y.; Bratos, S. *J. Chem. Phys.* **1991**, *95*, 3643.
- (25) Soper, A. K.; Finney, J. L. *Phys. Rev. Lett.* **1993**, *71*, 4346.
- (26) de Gennes, P.-G., *C. R. Acad. Sci., Ser. II* **1991**, *313*, 1117.
- (27) Wanger, P.; Brochard-Wyart, F.; Hervet, H.; de Gennes, P.-G. *Colloid Polym. Sci.* **1993**, *271*, 621.
- (28) Gorbunov, A. A.; Skvortsov, A. M. *J. Chem. Phys.* **1993**, *98*, 5961.
- (29) Johnson, H. E.; Granick, S. *Science* **1992**, *255*, 966.
- (30) Kremer, K. *J. Phys. (Paris)* **1986**, *47*, 1269.
- (31) Kohlrausch, R. *Poggendorff's Ann. Phys.* **1847**, *12*, 393.
- (32) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1971**, *66*, 80.
- (33) Douglas, J. F.; Hubbard, J. B. *Macromolecules* **1991**, *24*, 3163.
- (34) Fytas, D.; Wang, C. H.; Lilje, D.; Dorfmueller, T. *J. Chem. Phys.* **1981**, *75*, 4247.