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Effects of thermal history on the dynamics of relaxation of poly(*N*-isopropylacrylamide) adsorbed at latex interfaces in water

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The dynamics of the relaxation of poly(*N*-isopropylacrylamide) (PNIPAM) chains absorbed from water onto the surfaces of poly(*N*-tert-butylacrylamide) latex particles has been studied. The dynamic behavior studied was induced by heating samples to 60 °C and then cooling to 6 °C. We report measurements of the effects of the thermal history on relaxation dynamics of interfacially adsorbed PNIPAM under better than θ-solvency conditions. The dynamic relaxation of the adsorbed PNIPAM chains proved to be very sluggish, displaying some features analogous to bulk glassy relaxations, especially at longer aging times. The average relaxation time, calculated from a stretched exponential function, significantly increased with increasing aging time. The extended PNIPAM layers formed under the experimental protocol adopted were found to become kinetically locked into nonequilibrium states for unexpectedly long times. The time at which the dynamic evolution of the adsorbed chains commenced depended upon the thermal history. [S1063-651X(98)09202-2]

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INTRODUCTION

Recently, interest has grown in understanding the adsorption of macromolecules at solid-liquid interfaces [1–4]. This 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. The equilibrium state of physically adsorbed polymer chains has been well understood through the application of a mean-field lattice model, scaling analysis, renormalization-group methods, and computer simulations. Some progress also has been made in understanding the adsorption of chemically adsorbed polymer chains, especially their dynamic behavior [5–10].

Morphologically speaking, adsorbed polymer may be divided into at least 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 may vary from one type to another, it is generally accepted that there is at least one 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. For example, homopolymer 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 leads to fewer contact points remaining and an additional extension of the adsorbed polymer chains normal to the surface.

On the other hand, the adsorption of polymer chains onto a surface is also considered to be a random sequential process that leads to the intrusion of kinetic phenomena. The chains that are first to arrive at a surface can participate in many segment-surface contacts and so adopt a flattened or loopy conformation. At higher polymer concentrations, the chains that arrive at longer times, however, exhibit fewer and fewer segment-surface contacts and so adsorb more loosely since they meet a nearly saturated surface. The center of mass of these later-arriving chains is expected to be located farther from the surface than those that are attached to the surface earlier. Such an interfacial architecture of polymer layers, the so-called ''hairy carpet'' model, has been confirmed experimentally [8–12]. Adsorbed polymer chains could be effectively frozen in nonequilibrium states for very long times after they adsorb onto the initial surface sites. Even if polymer chains have achieved an overall adsorption equilibrium, there still exists a steady-state exchange of polymer chains between the adsorbed state and the unadsorbed state [8–12]. Note that the diffusion of polymers at the surfaces is governed by kinetic constraints [5–7].

Like free polymer chains, adsorbed polymer chains can undergo conformational changes under different solvency conditions. However, the conformational transitions of adsorbed polymer chains apparently differ from those of free polymer chains for several reasons. First, the number of degrees of freedom of the polymer chains at surfaces are expected to be less than those in free solution. 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, adsorbed polymer chains could be trapped in a collection of nonequilibrium structures due to the topographies of the ac-

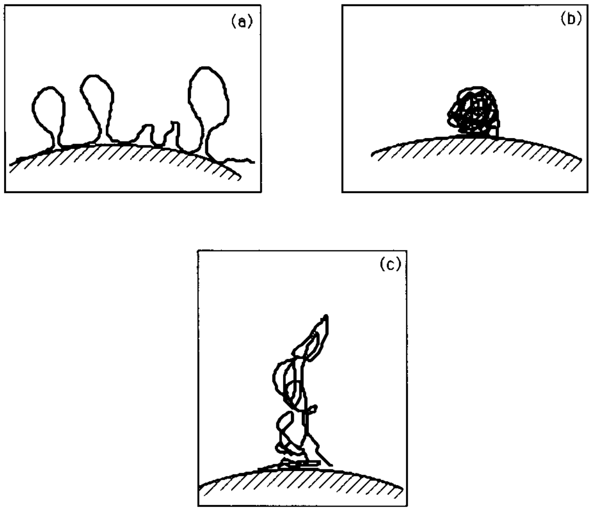

FIG. 1. Schematic representations (not to scale) of the conformational changes of adsorbed PNIPAM chains at interfaces: (a) Loopy adsorption of chains at low temperatures before heating, (b) globular conformation adopted after heating, and (c) extended brushlike conformation on cooling heated sample below the θ temperature. Note that for clarity only a single chain is displayed and so the possible overlap of neighboring chains and loosely adsorbed chains is not shown.

cessible potential energy surfaces [5–7]. Topological constraints, segment-surface interactions, and segment-segment interactions can significantly influence the dynamics of the conformational changes.

In a previous paper [13], we studied the conformational changes and corresponding relaxation dynamics for the poly (*N*-isopropylacrylamide) (PNIPAM) chains absorbed at the surfaces of poly(*N*-tert-butylacrylamide) (PNTBA) latex particles in water. As discussed above, the present system exhibits several distinctive adsorption features. First, the structural similarities between PNIPAM and PNTBA allow the adsorbed chains to interact strongly with the surfaces of particles. The system may presumably be classified as chemical adsorption of the homopolymer PNIPAM via hydrogen bonding onto the surfaces of the PNTBA particles, although other interactions may also be involved. Second, the interfacial chains may be assumed to adsorb loopily into an almost flattened conformation when they attach to the surfaces. The third feature is that at room temperature, PNIPAM chains dissolve in water to form coils that undergo a coil-to-globule transition when heated to ~31 °C–32 °C [14,15]. Finally, in contrast to the adsorption of polymer chains onto a hard surface, the surfaces of PNTBA latex particles are penetrable because PNTBA latex particles tend to swell at the temperature considered. The experimental situation of the present system necessarily is very complicated.

The observations previously reported were interpreted [13] to result from a sequence of conformational chains as a consequence of heating: transformation of the loopily adsorbed conformation to the globular conformation and then on cooling to the extended form. This series of changes are shown schematically in Fig. 1. The main factor promoting the globule-to-extended state transition was postulated to be the reduction in the number of adsorbed contact points of the PNIPAM segments with the surface when the globular conformation was adopted under bad solvency conditions induced by heating. It was recognized that the possibility of the formation of the hairy carpet structure should not be overlooked, especially at higher polymer concentrations [16].

It was also found [13] that the extended PNIPAM conformation [Fig. 1(c)] was unstable and relaxed slowly towards the lower-free-energy adsorbed state [Fig. 1(a)] under better than θ-solvency conditions. The relaxation dynamics as a function of the temperature was previously studied. In this paper, we report on the effects of thermal history on the dynamics of the relaxation of interfacially adsorbed PNIPAM chains as studied by dynamic light scattering.

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 [17]. NIPAM (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 the 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 highest weight-average molecular weight fraction 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 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.* [18] and was 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 McPhee, Tam, and Pelton [19]. 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-μm 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 5.9. The suspensions thus prepared were kept for at least ~24 h at room temperature. The nonadsorbed PNIPAM was removed by centrifugation in 10 000 rpm for 60 min at 15 °C and decantation of the supernatant. The samples were then redispersed in Millipore Milli-*Q* water at room temperature.

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 $\Theta = 90°$ and a wavelength of $\lambda = 488$ nm at a power of 50 mW. Some of the samples were also measured at a particle concentration of $\sim 1\times 10^{-4}$ (g/g) at $\Theta = 60°$. The intensity autocorrelation function $G^{(2)}(\tau)$ was measured using a Malvern 4700c correlator and has the form [20]

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

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 a single exponential

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

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 [21].

The sample temperature was controlled with an accuracy of 6.0 °C±0.1 °C during the DLS measurements. The charge introduced into the surfaces of the PNTBA latex particles by the initiator fragments was sufficient to prevent the particles from undergoing aggregation under worse than θ-solvency conditions. At each temperature, the samples were allowed to equilibrate for 30 min before the DLS experiments were performed. The relaxation dynamics of the extended PNIPAM chains were studied by transferring the samples from 60.0 °C to 6.0 °C±0.1 °C. In order to ensure the same thermal history in all experiments, the samples were first kept at 6.0 °C for ~2 h and then transferred to 60.0 °C. The time dependence of the hydrodynamic diameter was immediately followed until the original sizes obtained at 6.0 °C were attended.

RESULTS AND DISCUSSION

The temperature dependence of the hydrodynamic diameter of the PNTBA particles coated by the absorbed PNIPAM chains is shown in Fig. 2. The PNIPAM layer thickness was obtained by subtracting the PNTBA core sizes (crosses in Fig. 2) from the total measured size and dividing by 2. Note that the average radius of PNTBA particles at 6 °C was ~5 nm larger that that at 25 °C. The loopily adsorbed conformation was inferred for the present surface coverage from the observation that the layer thickness of the interfacial PNIPAM chains was ~36 nm at 25 °C, while the corresponding ''diameter'' of a single PNIPAM coil of this molecular weight would be ~120 nm. The adsorbed PNIPAM chains underwent a collapse transition with increasing temperature, which is qualitatively similar to the coil-to-globule–type transitions observed in systems in which PNIPAM chains were anchored to the particle surfaces [22,23]. When the heated latex sample was cooled from 60 °C to better than the θ-temperature range, the adsorbed layer thickness was significantly greater than that observed previously in the first heating cycle [13].

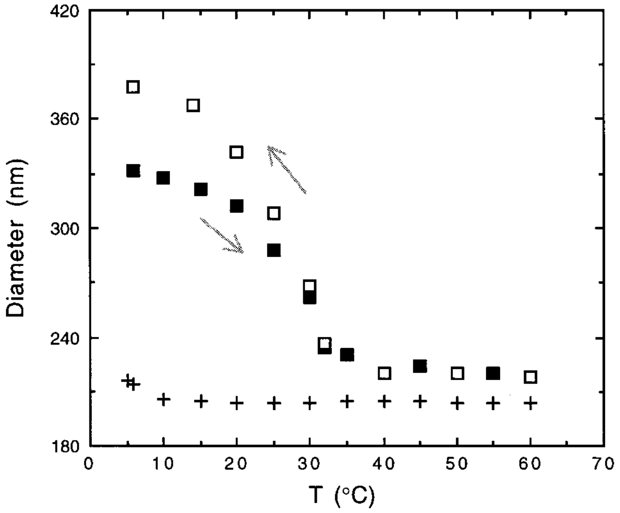

FIG. 2. DLS-measured conformational transition curves for PNIPAM chains absorbed on the surfaces of PNTBA latex particles. The filled squares are the data measured on increasing the temperature and the empty squares are those on cooling. The crosses are the data measured for uncoated PNTBA latex particles.

In Fig. 3 the time dependence of the layer thickness of adsorbed PNIPAM is presented at 6 °C in the form of semilogarithmic plots. The samples had been kept at 60 °C for 10, 240, and 960 min, respectively, before being moved to 6 °C. The data display several qualitative dynamic features. The first is that the transition processes were quite sluggish, occurring over many hours. The second is that there was a progressive slowing down of the relaxation process as the aging time increased. For example, for the aging time of 10 min the relaxed layer thickness could approach the loopily adsorbed value after the dynamic evolution of 1000 min, but was far from its equilibrium state for the aging time of 960 min over the same time scale. The third feature is that the layer thickness tended first to increase with time and reached a plateau before the onset of the decrease in chain dimensions. Apparently, after heating at 60 °C for longer times, the interfacially adsorbed chains appeared to be locked into nonequilibrium states under better than θ-solvency conditions. The times required to exit this nonequilibrium state, as estimated from Fig. 3, were about 10, 100, and 230 min after cooling, corresponding to aging times of 10, 240, and 960 min, respectively. There exit times are of the same order of magnitude as the aging times.

The existence of a plateau region presumably involves an intricate balance between the attractive and the repulsive components of the different types of interactions that govern the conformations adopted by adsorbed polymer chains. In the globular state, the intramolecular interaction in PNIPAM

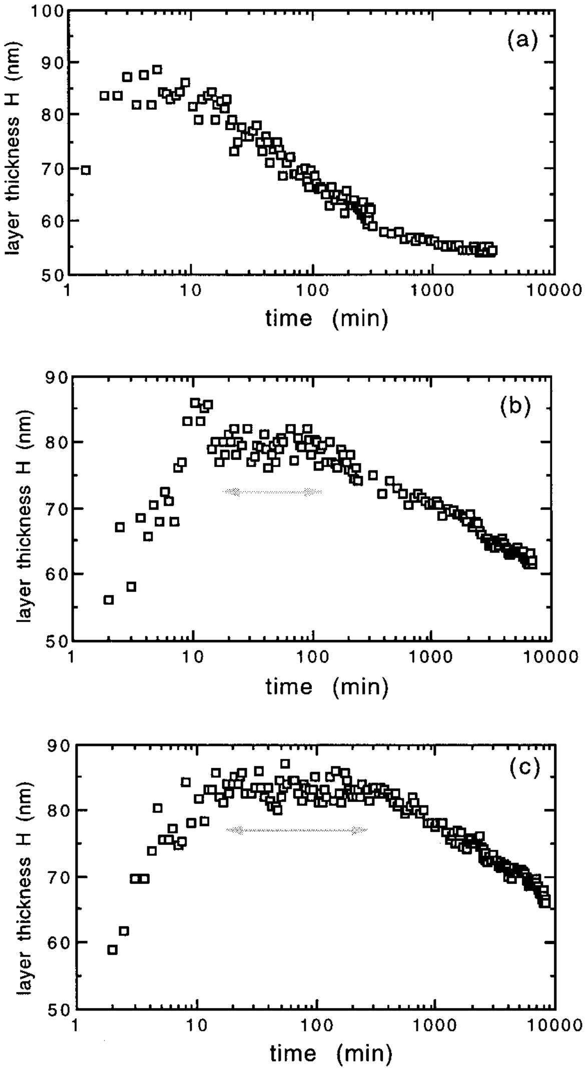

FIG. 3. Semilogarithmic plots of the time dependence of the layer thickness of the interfacial PNIPAM chains at 6 °C. The samples were first heated at 60 °C for different times (in minutes): (a) 10, (b) 240, and (c) 960, before cooled to 6 °C.

are so strong that most of the water molecules are excluded from the PNIPAM layers. When the temperature is cooled to the better than the θ-solvency range, however, the intermolecular interactions between the PNIPAM segments and the water molecules via H bonding increase dramatically, together with a progressive weakening of the hydrophobic interactions inside the PNIPAM chains as some of the hydrophobic entities become hydrated by water molecules [24–26]. Accordingly, the adsorbed PNIPAM chains were effectively extended in an overall direction normal to the surface until reaching the plateau. The average number of contacts per chain in the globule-to-extended conformational transition is significantly fewer than that in the first heating cycle, i.e., the loopily adsorbed-to-globule conformational transition [13]. The segment-surface interactions and the dynamic constraints imposed on the PNIPAM layers, on the other hand, constitute in part the overall force that balances the stretching force.

The transitions of free PNIPAM chains in solution are not the so-called *all-or-nothing* processes [27,28,31] i.e., PNIPAM chains do not undergo coil-to-globule transitions as a whole. The coil-to-globule transition of the PNIPAM chains apparently proceeds via a set of intermediates consisting of a number of the ''cooperative units'' or ''domains'' [27,28], which are randomly distributed along the chains. Neighboring small and loosely collapsed clusters aggregate to form larger and completely collapsed globules [29,30]. A similar behavior was also found in the melting of the PNIPAM globules (the globule-to-coil transition) [31]. Free PNIPAM globules are believed to undergo the transition through an intermediate state called the molten globule. The molten globule is expected to have a dense ''core'' and a molten ''shell.'' The PNIPAM chains are not fully collapsed in the molten globule state. The hydrodynamic dimensions of molten globules are larger than those of fully collapsed globules [31]. Our results for adsorbed chains imply that the formation of these intermediates is sensitive to thermal history or time. In addition to the inherent properties of PNIPAM in the transitions, the existence of segment-surface interactions in the present system can affect the intermediate states.

The dynamics of the overall relaxation of the adsorbed PNIPAM layers in this study presumably included the extended-to-loopily adsorbed state transition and, properly, the piecemeal diffusion of tenuously adsorbed chains by the incessant adjustment of their shapes, analogous to that postulated in the hairy carpet model [8–12]. The existence of such diffusion arises from the possibility that some of adsorbed PNIPAM chains may be squeezed out locally from the surfaces and incorporated into globules formed under worse than the θ temperature. Alternatively, the hairy carpet structure may form locally in the process of the preparation of the samples. These tenuously adsorbed chains may influence the layer thickness of adsorbed polymers. Fundamentally, the extended-to-loopily adsorbed conformational transition of tightly adsorbed chains and the piecemeal diffusion of tenuously adsorbed chains can be considered as a general adsorption process within the same theoretical frame [5–10].

The very sluggish relaxations of interfacially adsorbed PNIPAM chains in the present system, associated with the longer time scale, is similar in some respects to those that determine the structural relaxation of glass-forming liquids. This similarity does not mean that glassy layers were actually formed at the interfaces due to the increased segment density and is not connected to the glass transition temperature of the bulk polymer. Such considerations do not agree with the morphology of adsorbed chains and the experimental conditions studied. The reason for glassylike dynamics being observed is that, like an adsorption process from an unstable extended state to a lower-free-energy flattened adsorbed state [5–7], the strong and specific interactions of the polymer and surface, and the kinetic constraints operating within the polymer layers trap the chains and hinder their relaxations.

The likely physical origins of the kinetic constraints that trap the chains in nonequilibrium states include nearest-neighbor interactions (e.g., *n* clustering [32] and H-bonding), strong and specific segment-surface interactions, topological barriers, and the attachment to and competition for surface sites. The effects of these kinetic constraints on the dynamic processes of adsorbed chains have been explicitly discussed

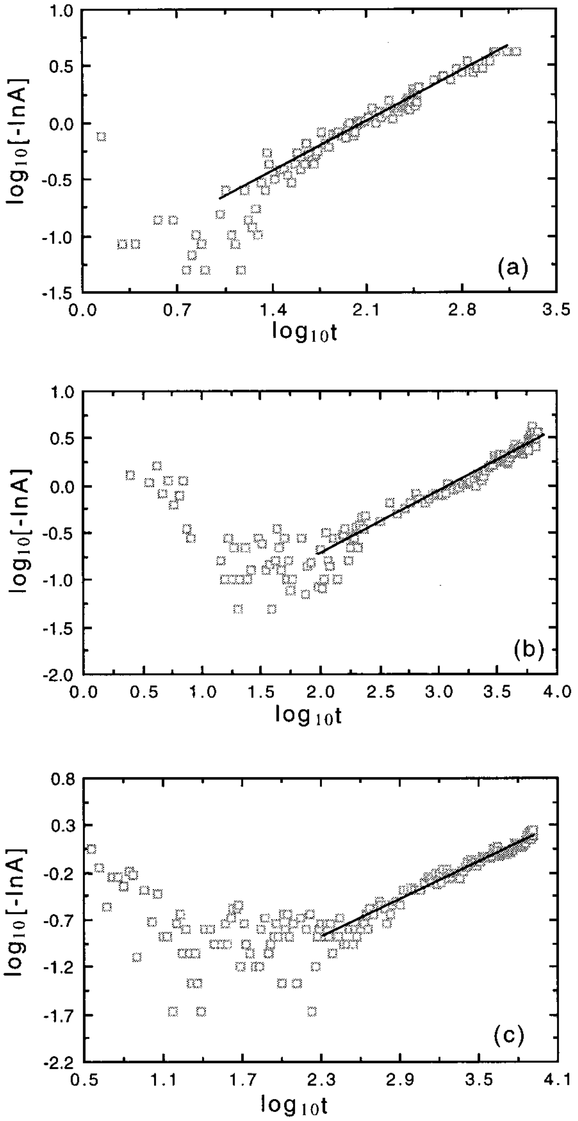

FIG. 4. Plots of the data in Fig. 3 using Eq. (3).

[5–7]. The nonequilibrium structures arise because the kinetic constraints do not allow the polymer chains to evolve rapidly to structures corresponding to the global minimum free energy. The extended-to-loopily adsorbed transition and the polymer diffusion may proceed through a number of stages. The whole process is considered to be highly cooperative. The unstable segments have to search the accessible paths in configuration space in a tortuous way to allow the dynamic evolution to occur. An additional kinetic constraint is probably induced by soft surfaces in the present system since the segments of adsorbed chains may diffuse into a certain depth of PNTBA particles under better than θ-solvency conditions [33].

The adsorbed PNIPAM chains under better than θ-solvency conditions preserve memory of their thermal history, which in turn effectively influences the kinetic constraints in the nonequilibrium structures. As the aging time increases, the kinetic constraints become more active due to the formation of more compact structures through intramolecular interactions between the PNIPAM segments. As a consequence, much longer times are needed to access the accessible paths that were kinetically blocked under worse than θ-solvency conditions. Some cooperativity over longer length scales is also likely to be required for the relaxation towards to equilibrium to be allowed to occur.

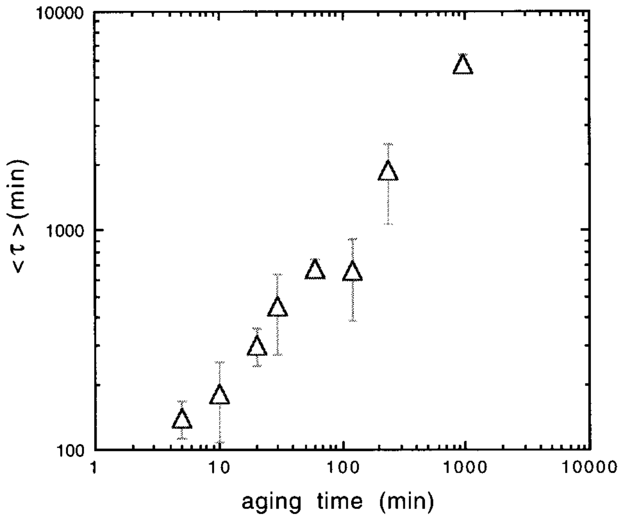

FIG. 5. Plot of the thermal history dependence of average relaxation time $\langle\tau\rangle$ obtained from Eqs. (3) and (4).

A rigorous treatment of the dynamics of the relaxation at the molecular level for the present system is difficult. The kinetic constraints or the polymer adsorption mechanisms show that the dynamics of such processes can be described by a stretched-exponential or Kohlrausch-Williams-Watts (KWW) function [34,35]. For the present system, the experimental data for the time dependence of the layer thickness were accordingly expressed by the KWW-like function

$$A=\frac{H(t)-H(\infty)}{H(0)-H(\infty)}=\exp[-(t/\tau_{\rm eff})^{\beta}], \tag{3}$$

where H is the layer thickness, $\tau_{\rm eff}$ is the effective relaxation time, and β is the stretched exponent. Microscopically, the relaxation of the interacting units is heterogeneous, corresponding to a ''distribution'' of relaxation rates of dynamic origin. The average relaxation time $\langle\tau\rangle$ can be related to the effective relaxation time $\tau_{\rm eff}$ and the stretched exponent β by [36]

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

where $\Gamma(\beta^{-1})$ is the Gamma function. The kinetic data presented in the present work were determined by plots of $\log_{10}[-\ln A]$ vs $\log_{10}(\text{time})$. Straight lines shown in Fig. 4 are representative of the use of Eq. (3). Figure 5 shows the aging time dependence of the average relaxation time. It was found that the magnitude of the average relaxation time $\langle\tau\rangle$ spanned a remarkably wide range from 140 min after 5 min of aging to 5800 min after 960 min of aging. The β values obtained were ~ 0.65, almost independent of the aging time studied.

Our time scales for the relaxation process, especially for longer aging times, are much longer than the predictions of computer simulations and the experimental results on the competitive adsorption of polymers [5–10]. It should be pointed out that the model used for the computer simulations is limited to isolated polymer chains, not to a system containing many chains. Any difference might be attributed to the additional kinetic constraints. We believe that for the present system, the kinetic constraints under consideration arise from those induced by the surface and the memory of globular conformations.

CONCLUSIONS

The effects of thermal history on the dynamics of the relaxation of poly(*N*-isopropylacrylamide) chains adsorbed at poly(*N*-tert-butylacrylamide) latex particles were studied by dynamic light scattering. The relaxation dynamics of interfacial adsorbed PNIPAM were observed by a simple experimental design: The chains were first heated to 60 °C for different times and quickly quenched to 6 °C. The time dependence of the layer thickness was then monitored. The dynamics of the relaxation of the adsorbed PNIPAM chains displayed features analogous to forms of conventional glassy dynamics. The relaxation dynamics of the adsorbed PNIPAM layers, which were found to vary from a few hundreds to several thousands minutes, were strikingly dependent on thermal history. The extended PNIPAM layers can be effectively frozen in time before relaxing. As the aging time increased, nonequilibrium states were observed from a few minutes to ~ 200 min in the range of thermal histories studied. The kinetic constraints are believed to govern the whole relaxation process.

ACKNOWLEDGMENT

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