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ORIGINAL CONTRIBUTION

Bruno Jean
Lay-Theng Lee

Effects of sodium dodecyl sulfate on poly(*N*-isopropylacrylamide) adsorption at the air–water interface above the lower critical solubility temperature

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B. Jean · L.-T. Lee (✉)
Laboratoire Léon Brillouin,
Laboratoire commun CEA-CNRS,
CEA-Saclay,
91191 Gif-sur-Yvette Cedex,
France

Abstract The behavior of poly (*N*-isopropylacrylamide) (PNIPAM) at the air–water interface above the lower critical solubility temperature and the effects of sodium dodecyl sulfate (SDS) have been studied by neutron reflectivity. In the absence of SDS, PNIPAM adsorbs at the air–water interface and forms a thick and dense multilayer which can be characterized by two regions: a first region made up of pure polymer, and a second containing the same volume fraction of polymer as in the bulk precipitate. In the presence of SDS, polymer adsorption is decreased, and the structure of the adsorbed polymer can be described as a layer of colloidal particles of collapsed PNIPAM stabilized by SDS molecules. At higher SDS concentrations where the PNIPAM is completely resolubilized into charged chains, most, but not all, of the polymer is displaced from the surface, and the remaining adsorbed polymer forms a thin and dilute layer.

Keywords Neutron reflectivity · Adsorption · Structure · Polymer–surfactant interaction

Introduction

Poly(*N*-isopropylacrylamide) (PNIPAM) is a hydrosoluble, thermosensitive polymer that exhibits lower critical solubility temperature (LCST) behavior: it phase-separates above a critical temperature of about 33 °C. Its high surface activity and strong interaction with surfactants, in particular sodium dodecyl sulfate (SDS) [1, 2] have attracted much attention in areas where polymers and surfactants are used to control rheological properties of the bulk phase, or to stabilize interfaces in colloidal systems. PNIPAM is an interesting polymer in this field of application because its thermosensitivity, which is detected within a small range of temperature near ambient, adds an easy and convenient parameter in controlling the polymer–surfactant interaction, and in tailoring the structure of the complexes formed.

In a previous article [3], we reported the effect of temperature on PNIPAM adsorption at the air–water interface below the LCST: adsorption is almost insensitive to temperature below 25 °C but increases significantly beyond 28 °C. This enhancement in adsorption is attributed to a decrease in solvent quality, the effect of which is significant even below the bulk theta temperature of around 31 °C [4], owing to the higher concentration of polymer chains confined in the surface layer. A modification of the polymer adsorption by surfactant and the close relation between the structural properties of the adsorbed layer and those in the bulk solution of the polymer–surfactant system have also been reported [5].

The next step in our investigation of PNIPAM adsorption is to see if the close relation between the structural properties of the adsorbed layer and those in the bulk solution also holds under poor solvent conditions, where aggregation problems and nonequilibrium structures be may encountered. Furthermore, few experimental studies exist on polymer adsorption under poor solvent conditions. From a practical point of view, adsorption of polymers from poor solvents has important implications in areas where a high coating of polymer onto the surface is desirable. In this article, we report the adsorption behavior of PNIPAM above the LCST and the effects of SDS under these conditions.

Materials and methods

Protonated and partially deuterated (*d*-7) PNIPAM were purchased from Polymer Science. Their molecular weights, determined by size-exclusion chromatography coupled with low-angle light scattering are $M_w = 190{,}000$ and 251,000, with polydispersity indices of 2.7 and 3.6, respectively. These measurements were carried out at Saclay by P. Lixon. The LCST of these samples was verified to be around 33 °C. Protonated and deuterated SDS were purchased from BDH (UK) and Isotec (France), respectively, and were used as received.

Polymer solutions ($cp = 1$ gl^{-1}) were prepared in the respective solvent (D_2O or Millipore water) under gentle stirring for at least 24 h. For most of the experiments in this study, protonated polymer was used, and deuterated SDS was matched out in D_2O. This isotopic composition gives a contrast term, $\Delta Nb = 4\pi(Nb_p - Nb_s) = -62.8$ Å^{-2}, where Nb_p and Nb_s are the scattering length densities of the polymer and the solvent, respectively. Deuterated polymer was used only to confirm the results in cases where the adsorption density was very low. In this case, protonated SDS and partially reflecting water (20% D_2O and 80% H_2O by volume) were used ($\Delta Nb = 49.4$); the signal from the protonated SDS is insignificant in this solvent mixture. These two isotopic compositions allow us to study the polymer adsorption behavior in the presence of surfactant.

The experimental protocol for the reflectivity measurements is as follows. The solution containing dissolved polymer (or dissolved polymer and surfactant) was introduced at room temperature into a Teflon cell (15 cm×5 cm×0.3 cm) which was completely enclosed in a thermostated aluminum cell with quartz windows to allow the neutron beam to enter and exit the cell. For better temperature control, the entire aluminum cell was further enclosed in a second aluminum container with similar quartz windows. This additional enclosure helped reduce condensation of water vapor on the inner cell windows, especially when working at higher temperatures, and enabled the temperature inside the first cell to be controlled to ±0.1 °C. The solution was then heated (or cooled) to the desired temperature. The temperature registered on the horizontal copper support on which the Teflon cell was attached was taken to be the solution temperature. For all the experiments at 40 °C, the heating process took about 45 min. After about 15 min of thermal stability, the reflectivity data acquisition was started.

Specular neutron reflectivity experiments were carried out on the time-of-flight reflectometers DESIR and EROS in the ORPHEE reactor, Saclay. The grazing incident angle used was about 1.3° with an angular resolution of about 3%. The acquisition time for each reflectivity spectrum was 2 h. In the absence of kinetic effects, several 2-h spectra were summed to obtain better statistics.

Results

Polymer alone

The normalized reflectivity, R/R_f, of protonated PNIPAM adsorbed at the free surface of D_2O at 40 °C is shown in Fig. 1. R_f is the "Fresnel" reflectivity, which in this case is the reflectivity of pure D_2O, taking into consideration angular resolution. In this representation, all the deviation of the normalized reflectivity from unity is directly attributed to the presence of polymer at the interface. Two qualitative features can be seen: a tenfold deviation indicating a significant amount of polymer at the surface and strong oscillations suggesting a thick and well-defined adsorbed layer. The periodicity, P, of these Kiessig fringes yields a characteristic layer thickness of $h = 2\pi/P = 261$ Å. These two features are not common to polymers adsorbed under good solvent conditions, where deviation from Fresnel reflectivity is smaller, and the curves tend to be monotonic in the same Q range owing to a lower adsorbed amount and the diffuse nature of the adsorbed layer. The continuous line through the experimental points is the best-fit curve using a two-layer model: the first surface layer comprises almost pure polymer about 30-Å thick and the second layer consists of about 60% (volume fraction) polymer extending to about 250 Å. This model gives a better fit than a one-layer model. The total layer thickness obtained from the fit, 280 Å, is close to that estimated from the interference fringes. The amount of polymer is 3.3 mgm^{-2} in the first layer and 17.2 mgm^{-2} in the second layer, giving a total adsorbed density of 20.5 mgm^{-2}. Compared to the adsorption density generally obtained under good solvent conditions, this represents a tenfold increase (see Fig. 2 for a comparison of the profiles). For the same polymer, the adsorption densities are 1.5 and 5.6 mgm^{-2} at 20 and 31 °C (near-theta condition), respectively.

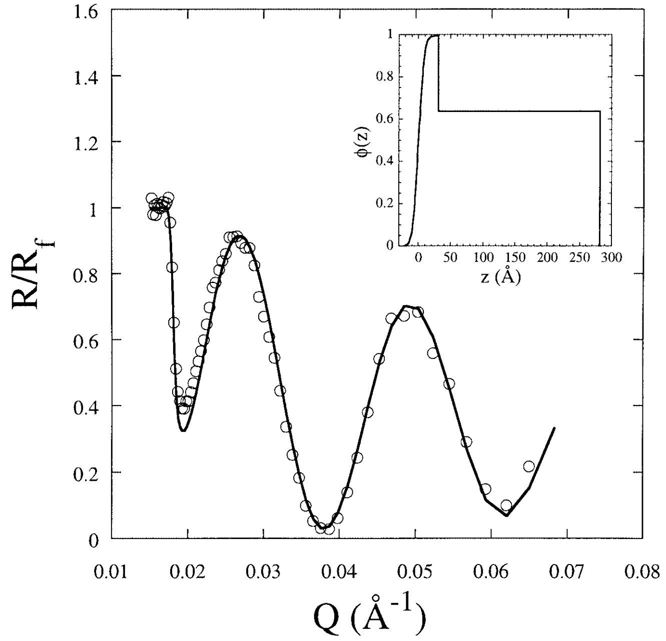

Fig. 1. Normalized reflectivity curve of protonated poly(*N*-isopropylacrylamide) (*PNIPAM*) adsorbed from D_2O at 40 °C, $c_p = 1$ gl^{-1}. The *solid line* through the data points is the best-fit curve calculated using the concentration profile shown in the *inset*

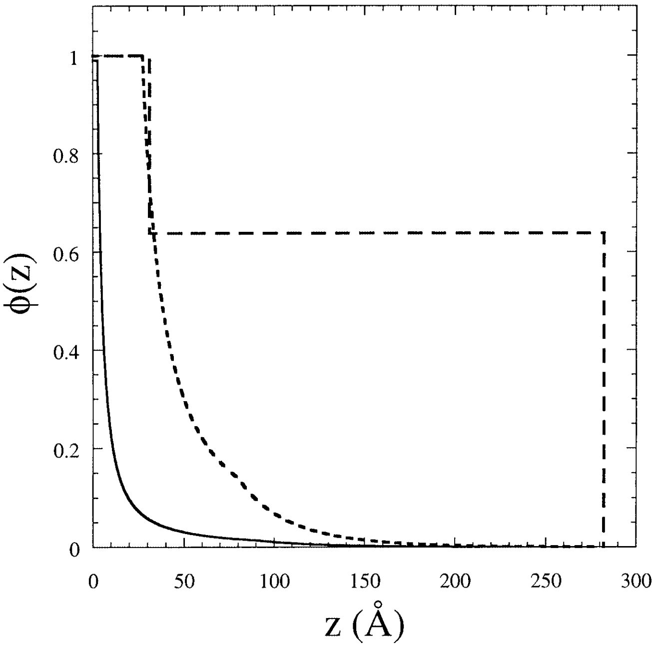

Fig. 2. Comparison of concentration profiles of adsorbed PNIPAM at 20 °C (*solid line*), 31 °C (*short dashed line*), and 40 °C (*long dashed line*) ($c_p = 1$ gl^{-1})

Presence of SDS

The normalized reflectivities of PNIPAM in the presence of SDS at different surfactant/polymer mass ratios, $S/P = 0.2$ and 0.34 are shown in Fig. 3a. The SDS is matched to the solvent and as previously, all the deviation of R/R_f from unity is due to adsorbed polymer. Two clear effects of SDS can be seen: a decrease in R/R_f and smoothing out of the oscillations. The continuous lines through the data points are the best-fit reflectivity curves using a two-layer model (Fig. 3b) which gives a better fit that a one-layer model. The concentration profiles show that in the first layer, the volume fraction of polymer is reduced almost tenfold, to a very low value of $\phi = 0.\ 12$. This means that the surface is no longer covered with a continuous layer of pure polymer. The second layer is similarly reduced in polymer. For $S/P = 0.34$, the second layer is extremely dilute and extends to about 550 Å.

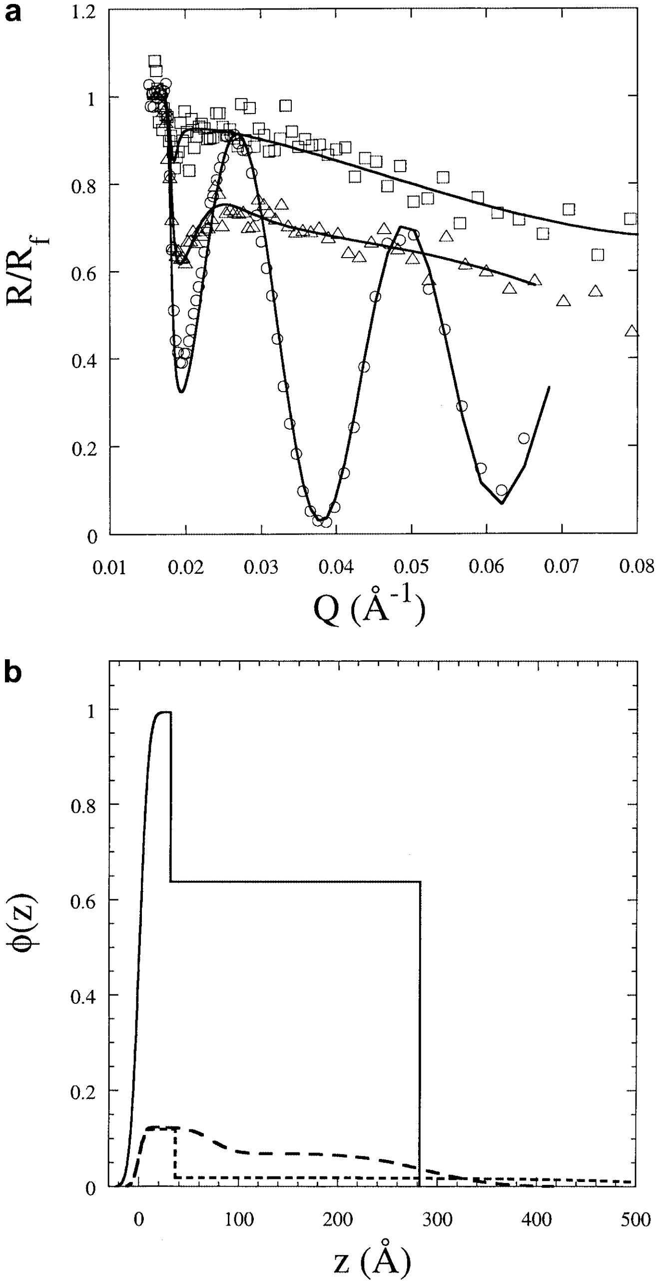

Fig. 3. **a** Normalized reflectivity curves of protonated PNIPAM adsorbed from D_2O at 40 °C, $c_p = 1$ gl^{-1}: effect of sodium dodecyl sulfate (*SDS*) at the surfactant/polymer weight ratio, S/P, 0 (*circles*), 0.2 (*triangles*), and 0.34 (*squares*). The *solid lines* through the data points are the best-fit curves calculated using the concentration profiles shown in **b**. **b** Concentration profiles of adsorbed PNIPAM at 40 °C at $S/P = 0$ (*solid line*), 0.2 (*long dashed line*), and 0.34 (*short dashed line*)

Discussion

Polymer alone

PNIPAM adsorbs spontaneously at the air–water interface owing to its partially hydrophobic nature. This adsorption reduces the interfacial tension to around 42 mNm^{-1} at 20 °C. In a past study [3], we reported the effect of temperature on the adsorption density up to the LCST of around 33 °C. It is found that adsorption remains insensitive to temperature up to about 25 °C, but increases steeply beyond 28 °C. This is attributed to a decrease in solvent quality, the effect of which is detected below the bulk solution theta temperature of around 31 °C [4] owing to confinement reasons and a higher concentration in the adsorbed layer. At 33 °C, the results are more delicate to interpret; the reflectivity curves continue to evolve over several days, suggesting a prohibitively long equilibration time.

In the present study, in order to study adsorption under poor solvent conditions, we conducted the measurements further away from the LCST, at 40 °C, and with improved thermal control. In these experiments, the polymer solution was transferred into the Teflon cell at room temperature, around 20 °C, and heated slowly to 40 °C. This heating process takes about 45 min. Therefore, the polymer layer is already preformed at room temperature and undergoes progressive thermal variation up to 40 °C, before the data acquisition is begun. The results of these experiments show that under these conditions one can obtain a very stable and extremely well defined surface layer, containing 10 times as much polymer as can be obtained at 20 °C.

Thus, under poor solvent conditions, precipitation of the polymer in the bulk phase does not extract the polymer from the surface. On the contrary, a thick and dense polymer layer is formed which is very well characterized by a two-layer structure: a first layer comprising almost pure polymer about 30 Å thick and a second layer consisting about 60% (volume fraction) polymer extending to about 250 Å. The amount of polymer in the first and second layer is 3.3 and 17.2 mgm^{-2}, respectively, giving a total adsorbed density of 20.5 mgm^{-2}. (Note that the effect of temperature on the monomer–surface interaction is small since at 20 °C a monomer-rich proximal zone of $\phi\approx1$ is obtained.) The origin of this high adsorption density can be expressed in terms of intrachain and interchain attractions as the solvent quality decreases with temperature. Since the polymer layer is preformed at 20 °C, as the temperature is slowly increased, the solvent quality decreases, and intrachain attraction of the adsorbed chains contracts the adsorbed layer in a direction perpendicular to the surface and increases the lateral packing owing to a decrease in the size of the polymer chain. These two effects result in a more compact and thinner layer, the dimension of which is expected to be of the order of the radius of gyration of the chain in the bulk. We can attribute the first layer of the concentration profile (30-Å thick, containing almost pure polymer) to these intrachain effects. Note that formation of such a dry polymer layer is possible owing to the air phase. Indeed, the dimension of this first layer is of the order of the average size of a dry globule (40 Å), and a close-packed layer of such globule would yield 3 mgm^{-2}, in agreement with the amount that is obtained from the concentration profile.

Interestingly, the first layer is already fully formed at 31 °C (Fig. 2); when the temperature is increased to 40 °C, all additional polymer is deposited beyond this region toward the water phase, forming the second layer containing about 60% (volume fraction) polymer. Interchain attractions of the collapsed molecules are clearly responsible for the buildup of this second layer, which is more hydrated and surprisingly well defined. The polymer concentration in this second layer is close to that on the concentrated branch of the bulk coexistence curve [6]. Thus, at 40 °C, collapsed chains are transported from the bulk to the surface, forming a multimolecular layer which is in equilibrium with the dense phase in the bulk.

The multilayer formed is reversible. Upon cooling the sample from 40 to 20 °C, a dilute and diffuse layer, identical to that obtained at 20 °C prior to heating, is recovered. Although the structure and reversibility of an adsorbed layer obtained under poor solvent conditions is expected to depend on the sample history, the distance from the critical temperature and the heating time, it appears that at 20 °C, the original hydrated structure of the polymer is recovered without difficulty. Indeed, it has been reported [7] that the coil-to-globule transition in the bulk is irreversible owing to intrachain bonding in the collapsed globule. As such, during the globule-to-coil transition, full expansion to the original structure is not achieved. Below 25 °C, however, the initial fully swollen coils are obtained. The authors attribute this observation to the fact that below this temperature, water becomes a good enough solvent to overcome these intrachain effects.

In the presence of SDS

From the previous discussion, we have seen that above the LCST, it is possible to form a thick and well-defined multilayer of PNIPAM at the surface. Such a property is desirable in applications where a thick coating of polymer is required. In several surface-related applications, however, other surface-active molecules are usually present in the same system. Therefore, it is important to know the effects of these coadsorbing molecules on the tenacity of the polymer layer and its structure.

It has already been shown in our previous studies that below the LCST adsorbed PNIPAM can be displaced by addition of surfactants [5]. In the presence of a nonionic surfactant which does not interact with the polymer, desorption is due solely to the competition of surface pressures exerted by each species [8]. In this case, complete desorption of polymer can be obtained. If the surfactant interacts with the polymer, as in the case of SDS, the surface properties depend strongly on the bulk behavior. For the PNIPAM–SDS system, the loss of polymer from the surface is directly related to the formation of a charged polymer–surfactant complex in the bulk phase, and the structure of the adsorbed layer is

Table 1. Adsorption of poly(*N*-isopropylacrylamide) in the presence of sodium dodecyl sulfate at 40 and 20 °C at $c_p = 1$ gl^{-1}

c_s (M)	Γ (mgm^{-2})		reduction in Γ (%)	
	40 °C	20 °C	40 °C	20 °C
0	20.5	1.2	–	–
6.0×10^{-4} ($S/P = 0.2$)	2.5	1.2	88	0
1.1×10^{-3} ($S/P = 0.34$)	1.5	0.8	93	33
5.0×10^{-3} ($S/P = 1.57$)	< 0.2	~0.2	98	83

determined by the equilibrium of this complex at the surface and in the bulk [5].

Above the LCST, the present study shows that in spite of the formation of a dense and compact multilayer, PNIPAM adsorption is also significantly reduced in the presence of SDS. In addition, the degree of reduction is higher at 40 °C than at 20 °C for the same SDS concentration (Table 1). An interesting feature of the concentration profiles obtained in the presence of SDS (Fig. 3b) is the tenfold reduction in the volume fraction of polymer in the first layer, to $\phi = 0.12$. This means that the surface is no longer completely covered with a layer of pure polymer. These concentration profiles are different from those obtained below the LCST, where at intermediate surfactant concentrations, the surface region of the adsorbed layer remains completely covered with pure polymer ($\phi \approx = 1$ in the proximal region [5]). At $S/P = 0.34$, the second layer is further diluted, with an increase in the total extension of the adsorbed layer.

These concentration profiles can be interpreted in terms of structures that are consistent with the structural properties that have been obtained using neutron scattering [9]. We have found that at 40 °C, the macroscopically phase separated PNIPAM is redispersed in the presence of SDS. Depending on the S/P ratio, two types of structures are obtained. At $S/P \leq 0.3$, a colloidal dispersion is obtained (turbid solution) where polydisperse colloidal particles of collapsed polymer are stabilized by adsorbed surfactant molecules; this prevents the particles from forming large macroscopic aggregates. At $S/P \geq 0.4$, the colloidal particles are completely solubilized (clear solution) to form charged "necklaces", each necklace comprising a polymer chain with adsorbed SDS micelles. Between these two limits, coexistence of particulate and solubilized chain structures is observed. For the polymer used in the present reflectivity studies, at $S/P = 0.2$, the average size of the particles is found to be around 100 Å. Adsorption of these polydisperse particles at the surface would give a surface layer which can be described by a two-layer structure: the first layer corresponds to the average dimension of the particles and the second layer results from the size distribution (Fig. 4). At $S/P = 0.34$, the dilute and large extension of the adsorbed layer may be explained by the formation of partially solubilized chains which coexist with colloidal particles of polymer that are not completely redissolved. At $S/P > 0.4$, the solutions become clear owing to complete solubilization of the polymer by the surfactant micelles. These charged polymer–surfactant necklaces have low affinity for the surface, and adsorption is insensitive to temperature; for $S/P = 1.57$ in the range 20–40 °C, all the reflectivity curves superpose. Although the chains are easily displaced from the surface by excess surfactant, residual adsorbed polymer is detectable, and the polymer forms a thin layer which is in equilibrium with the polymer–surfactant complex in the bulk.

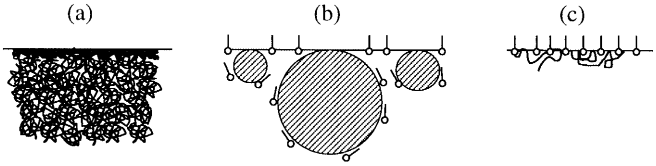

Fig. 4a–c. Schematic drawing of the structure of adsorbed PNIPAM at 40 °C. **a** $S/P = 0$: dense multilayer; **b** $S/P < 0.3$: turbid solution, colloidal particles stabilized by adsorbed SDS; **c** $S/P > 1$: clear solution, solubilized chains

Conclusions

PNIPAM adsorbs spontaneously at the air–water interface owing to its partially hydrophobic nature. The adsorbed polymer layer undergoes various structural modifications depending on the temperature and the concentration of SDS present in the system. Below the LCST, the adsorbed polymer forms a dilute layer. When the solution temperature is increased above the LCST, the dilute layer contracts and a compact multilayer of collapsed polymer molecules is formed. In the presence of SDS, the polymer adsorption is significantly decreased; depending on the surfactant concentration, the structure of the adsorbed layer varies from that of adsorbed colloidal particles to thin dilute layers. These modifications in the adsorbed layer are related directly to the changes in conformation and the state of hydration of the polymer chains in the bulk phase that are induced by temperature and by interaction with SDS. Such a variety of surface structures allows great flexibility in tailoring adsorbed polymers at interfaces to specific applications.

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