

# Adsorption kinetics of non-ionic polymers: an ellipsometric study

Boris A. Noskov,<sup>\*a</sup> Alexander V. Akentiev,<sup>a</sup> Alexander Yu. Bilibin,<sup>a</sup> Dmitriy O. Grigoriev,<sup>b</sup> Giuseppe Loglio,<sup>c</sup> Ivan M. Zorin<sup>a</sup> and Reinhard Miller<sup>b</sup>

<sup>a</sup> Department of Chemistry, St. Petersburg State University, 198904 St. Petersburg, Russian Federation.

Fax: +7 812 428 6939; e-mail: boris@bn1664spb.edu

<sup>b</sup> MPI für Kolloid- und Grenzflächenforschung, D-14424 Golm, Germany

<sup>c</sup> Dipartimento di Chimica Organica, Università degli Studi di Firenze, 50019 Sesto Fiorentino, Firenze, Italy

DOI: 10.1070/MC2005v015n05ABEH002040

The ellipsometric measurements of polymer adsorption and adsorbed film thickness demonstrate that the adsorption process consists of two steps corresponding to the consecutive formation of the proximal region of the surface layer and the region of tails and loops protruding into the bulk phase.

Although the surface properties of aqueous polymer solutions have been investigated for more than half a century,<sup>1</sup> most of the results correspond to equilibrium systems. The adsorption kinetics of non-ionic polymers at the air–water interface was studied by the measurements of dynamic surface tension.<sup>2</sup> The dynamic surface elasticity was measured only at high frequencies (>10 kHz) where the viscoelastic behaviour of adsorbed polymer films was similar to that of insoluble monolayers.<sup>3</sup> Recent applications of low-frequency mechanical relaxation spectrometry of liquid surface layers to solutions of various non-ionic polymers showed that their dilational dynamic properties were different from those of conventional surfactant solutions and polyelectrolyte solutions.<sup>4–7</sup> For example, if the molecular mass was sufficiently high (> 10000), the dynamic surface elasticity was low (< 5 mN/m) and almost independent of concentration in a broad range of 0.00001–0.1%. On the other hand, the kinetic dependencies of both the real and the imaginary parts of the dynamic surface elasticity proved to be non-monotonic.<sup>6,7</sup> These peculiarities were explained using a theory that did not assume non-monotonic changes of the adsorption and the adsorbed film thickness but only gradual changes of the mechanism of surface stress relaxation. The aim of this work was to examine these ideas by the direct measurements of adsorbed film parameters using time-resolved null ellipsometry for polymer solutions where the non-monotonic kinetic and concentration dependencies of the dynamic surface elasticity were observed.<sup>4,5,7</sup> Note that although ellipsometry does not allow us to determine the surface layer structure, we can use this method to examine the theoretical inferences.

The ellipsometric measurements were performed with a Multiskop instrument from Optrel, Germany. This instrument and the procedure used for calculating the thickness of surface films and adsorbed amounts were described in detail elsewhere.<sup>8</sup> This technique is based on the measurements of changes in the light polarization state at the reflection from a liquid surface. In practice, one measures two ellipsometric angles  $\Delta$  and  $\Psi$ , which are related to the film thickness  $\delta$  and the film refractive index

$n_1$  by the following equation (at the assumptions that  $\delta$  is much less than the light wavelength, and the film is non-absorbing, plane-parallel, homogeneous and isotropic):<sup>9</sup>

$$\tan \Psi e^{i\Delta} = \tan \Psi_0 e^{i\Delta_0} \left[ 1 + i \left( \frac{4\pi\delta \cos \varphi_0 \sin^2 \varphi_0 n_2^2 M}{\lambda(n_2^2 - n_0^2)(n_0^2 \sin^2 \varphi_0 - n_2^2 \cos^2 \varphi_0)} \right) \right]. \quad (1)$$

Here,  $\Delta$  and  $\Psi$  are the ellipsometric angles for the layer covering the interface;  $\Delta_0$  and  $\Psi_0$  are the corresponding parameters for the interface without this layer;  $n_0$  and  $n_2$  are the refractive indices of the ambient and substrate phases, respectively,  $\varphi_0$  is the angle of incidence (50°) and  $M = n_0^2 + n_2^2 - n_1^2 - n_0^2 n_2^2 / n_1^2$ . To calculate the refractive index and the thickness of the adsorbed layer from the measured ellipsometric angles, a numerical iteration procedure was applied.

Using the same assumptions, one can calculate the adsorbed amount from the refractive index and the layer thickness if  $n_1$  depends linearly on the solute concentration  $C$

$$n_1 = n_2 + \frac{dn}{dC}(C_1 - C_2), \quad (2)$$

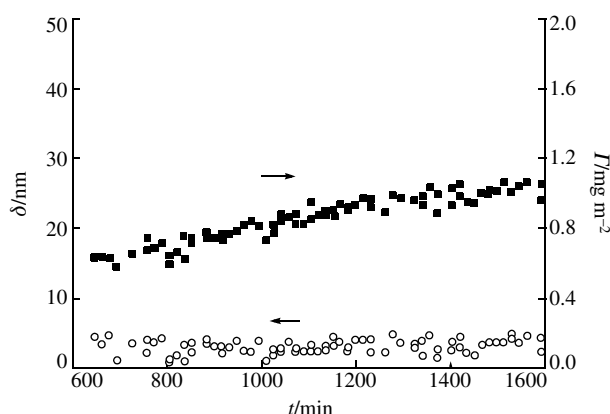
where  $C_1$  and  $C_2$  are the solute concentrations in the homogeneous layer and the substrate, respectively. This leads to the following equation for the adsorption  $\Gamma$ :<sup>10</sup>

$$\Gamma = \frac{\delta(n_1 - n_2)}{dn/dC}, \quad (3)$$

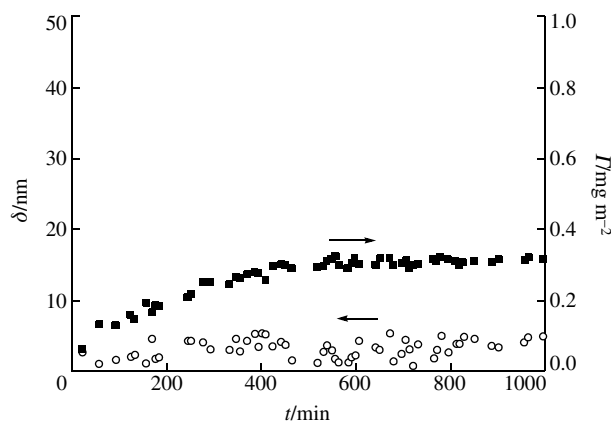
where  $dn/dC$  is the concentration increment of the refraction index, which is usually determined from the slope of the function  $n = n(C)$  in the bulk phase.

Experimental data show that equation (3) leads to reasonable results for non-ionic substances.<sup>11</sup> Note that the assumptions made at the derivation of (3) can influence the absolute value of adsorption. One can determine the relative changes of  $\Gamma$  with a higher precision.

The ellipsometric experiments were started after cleaning the surface by suction of a small amount of liquid using a Pasteur pipette and waiting for 20 s for mechanical equilibration of the



**Figure 1** Kinetic dependencies of the adsorbed amount (squares) and surface film thickness (circles) at a pNIPAM concentration of 0.00004%.

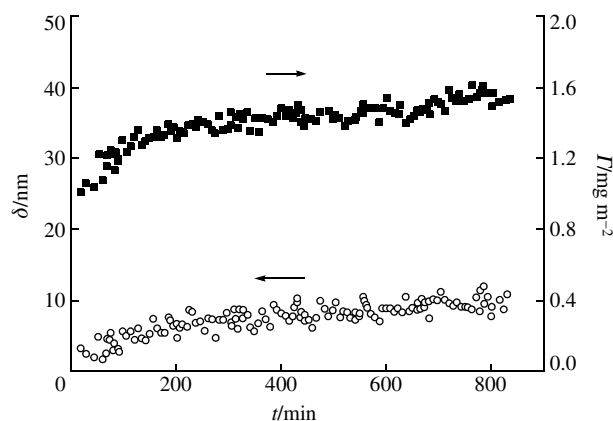


**Figure 2** Kinetic dependencies of the adsorbed amount (squares) and surface film thickness (circles) at a PEG concentration of 0.00001%.

liquid surface. Poly(*N*-isopropylacrylamide) (pNIPAM) with an average molecular mass of  $\sim 300\,000$  was prepared using the methodology of Schild and Tirrell.<sup>12</sup> Poly(ethylene glycol) (PEG) from Merck of the molecular mass of 4600 was used as received. All solutions were freshly prepared before measurements and stirred carefully for about 15 min. Fresh water deionized and purified by microfiltration was used for this purpose.

All of the determined kinetic dependencies of adsorption and film thickness can be divided into two main groups, which approximately correspond to the concentrations lower and higher than 0.0001% (ranges I and II). In range I, the adsorbed film thickness is low ( $\sim 3$  nm) and almost constant. At least the large error ( $\pm 2$  nm) does not allow observation of any variation with time. Figures 1 and 2 illustrate this behaviour of the film thickness for solutions of pNIPAM at  $C = 0.00004\%$  and PEG at  $C = 0.00001\%$ . Note that ellipsometry gives only a rather complex average of the film thickness.<sup>11</sup> The relative contributions from the proximal, central and distal regions of the surface layer to the mean value can depend on their real thicknesses and segment concentrations. According to published data,<sup>13,14</sup> the thickness of the proximal region is determined by the monomer adsorption energy and is of the order of a monomer size, while the interactions of monomers with the surface are negligible in the other two regions. For the above polymers, the film thickness is small and the scatter of the measured ellipsometric angles, especially  $\psi$ , is large. This leads to large relative errors of the thickness calculated from equation (1). Nevertheless, the large number of experimental points allows the determination of the mean film thickness with a reasonable accuracy (about 20–40% depending on the absolute value) and the main trend of the thickness variation with time. Although the determined values are a few times larger than those expected for the proximal region of the surface layer,<sup>15,16</sup> this region probably gives the main contribution to the ellipsometric signal in range I. The data in Figure 1 are close to the thickness of spread pNIPAM films,<sup>17</sup> where the formation of long loops and tails seems improbable. The results for PEG solutions (Figure 2) are close to the thickness for spread films of poly(ethylene oxide) (PEO) with a larger molecular mass,<sup>18</sup> which also supports the significant contribution of the proximal region. Moreover, ellipsometry usually gives an overestimated film thickness in comparison with more exact neutron reflectivity.<sup>16</sup> Therefore, we can consider that the kinetic dependencies in Figures 1 and 2 mainly reflect the formation of the proximal region, probably, together with a narrow region of short loops and tails.

Substitution of the determined values of  $n_1$  and  $\delta$  into equation (3) leads to the kinetic dependence of the adsorbed amount (Figures 1 and 2). The refractive index increments  $dn/dC$  of  $0.219\text{ ml g}^{-1}$  for pNIPAM solutions<sup>17</sup> and  $0.134\text{ ml g}^{-1}$  for PEG solutions<sup>19</sup> were used. Note that the relative error of the adsorption values is significantly lower than the error for  $\delta$ . This is typical of ellipsometric results because of the mutual compensation of errors for the refractive index and thickness in the calculation of the adsorbed amount.<sup>20</sup>

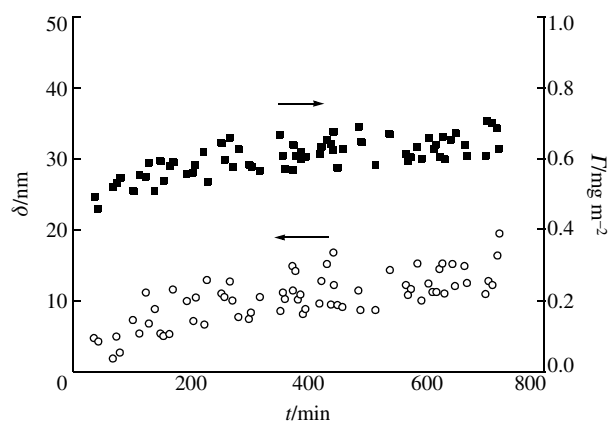


**Figure 3** Kinetic dependencies of the adsorbed amount (squares) and surface film thickness (circles) at a pNIPAM concentration of 0.001%.

For PEG solutions at  $C = 0.00001\%$ , the adsorption reaches an equilibrium in a few hours after the creation of a fresh surface (Figure 2). A comparison with calculations according to the Ward and Tordai equation shows that the adsorption kinetics of PEG is controlled by diffusion in the bulk, likely to PEO<sup>21</sup> in the range of low bulk concentrations.<sup>5–7</sup> The data for pNIPAM solutions (Figure 1) show that, in range I, the surface layer is far from equilibrium for more than one day after the creation of a fresh surface. The difference in the adsorption rates between PEG and pNIPAM solutions cannot be explained only by distinctions in the molecular mass, and we can conclude (in agreement with the results of Zhang and Pelton<sup>2</sup>) that pNIPAM adsorption is controlled by diffusion only during the initial step of the process. In general, conformational changes in the surface layer should also be taken into account. A comparison of the adsorption direct measurements (Figures 1 and 2) with the dynamic surface tension and elasticity<sup>4–7</sup> shows that the formation of the proximal region is accompanied by strong changes in the surface tension and the dynamic surface elasticity in accordance with the theory of polymer adsorption.<sup>14</sup>

In concentration range II, the kinetic dependencies of adsorption and film thickness show other features (Figures 3 and 4). For pNIPAM solutions, the film thickness appreciably increases with time from values characteristic of range I up to 6–12 nm (10 nm at  $C = 0.001\%$ , Figure 3). These values are close to those determined by Lee *et al.*<sup>15</sup> and Kawaguchi *et al.*<sup>17</sup> The corresponding kinetic dependencies of the adsorbed amount show that the equilibration process consists of two main steps. The relatively fast and strong increase in adsorption after creation of the interface for a few hours at  $C = 0.0001\%$  and less than half an hour at  $C = 0.01\%$  is followed by more gradual changes for many hours in the interval from 1.2 to  $1.6\text{ mg m}^{-2}$ . These values are close to the adsorption determined by neutron reflectivity.<sup>15,16</sup> The first step of adsorption can be approximately attributed to the formation of a relatively dense proximal region of the surface layer. A comparison with the kinetic curves of dynamic surface tension and elasticity<sup>4–7</sup> shows that almost all changes in the mechanical surface properties correspond to step I, where the surface elasticity reaches a local maximum and takes low values after that.

The second step is characterised by slight and slow changes in the adsorbed amount, and a more pronounced increase in the film thickness. It can be connected with the formation of long loops and tails protruding into the bulk phase (the central and distal regions of the surface layer). At the same time, the proximal region does not change significantly during this step. This leads to an almost constant (equilibrium) surface tension. The dynamic surface elasticity is low due to a large number of loops and tails and, consequently, to the fast relaxation of dilational surface stresses. Figure 3 shows that, in range II, an equilibrium is not reached even after more than one day. However, this does not lead to noticeable changes in the surface tension and dynamic surface elasticity. Similar kinetics with a slight increase in the adsorption layer thickness and adsorbed



**Figure 4** Kinetic dependencies of the adsorbed amount (squares) and surface film thickness (circles) at a PEG concentration of 0.1%.

amount was also determined for PEG solutions in the same concentration range (Figure 4). These slow changes can also be related to processes in the central region of the surface layer when the proximal region is almost at equilibrium. Macromolecules arrived first at the surface, occupy most of the area and form only short loops and tails, in contrast to the chains adsorbing later. Similar arguments proved to be useful in the explanation of homopolymer adsorption at the solid–liquid interface.<sup>22</sup> This can lead to a slow establishment of the equilibrium distribution of loops and tails if the segmental attraction to the surface is sufficiently strong. Note that our ellipsometric results do not allow us to propose a detailed mechanism of surface equilibration. The formation of long loops and tails can proceed, for example, by the replacement of relatively short adsorbed chains by larger macromolecules. In principle, slow changes in the film thickness can also be connected with the adsorption of trace impurities of a high surface activity. This can be the case for poly(vinylpyrrolidone) solutions of higher concentrations ( $C > 0.1\%$ ).<sup>6</sup> However, this interpretation seems improbable for the systems under consideration for two main reasons. First, a strong surfactant has to influence the surface tension and dynamic surface elasticity. Second, the adsorption of impurities usually leads to non-monotonic changes in the thickness. However, slow changes in the thickness of pNIPAM and PEG adsorption films are always monotonic and not accompanied by a decrease in other surface properties.

Although the surface activity of the test polymers differs significantly, the kinetics of adsorption and film thickness are similar. They are in accordance with the theoretical results and allow us to explain the non-monotonic kinetic dependence of the dynamic surface elasticity.<sup>4–7</sup> At the beginning of adsorption, polymer chains at the surface have mainly flat two-dimensional conformations, and the adsorbed film is characterised by a high dynamic surface elasticity. The subsequent formation of long loops and tails leads to a faster relaxation of the surface stresses and, consequently, to a decrease in the surface elasticity.

This work was supported by the Russian Foundation for Basic Research (grant no. 03-03-32366).

## References

- [doi>](#) 1 E. L. Lovell and H. Hibbert, *J. Am. Chem. Soc.*, 1940, **62**, 2144.
- [doi>](#) 2 J. Zhang and R. Pelton, *Langmuir*, 1999, **15**, 5662.
- [doi>](#) 3 Q. R. Huang and C. H. R. Wang, *Langmuir*, 1999, **15**, 634.
- [doi>](#) 4 B. A. Noskov, A. V. Akentiev, G. Loglio and R. Miller, *Mendeleev Commun.*, 1998, 190.
- [doi>](#) 5 B. A. Noskov, A. V. Akentiev, G. Loglio and R. Miller, *J. Phys. Chem. B*, 2000, **104**, 7923.
- [doi>](#) 6 B. A. Noskov, A. V. Akentiev and R. Miller, *J. Colloid Interface Sci.*, 2002, **255**, 417.
- [doi>](#) 7 B. A. Noskov, A. V. Akentiev, A. Yu. Bilibin, I. M. Zorin and R. Miller, *Adv. Colloid Interface Sci.*, 2003, **104**, 245.
- 8 R. Miller, V. B. Fainerman, A. V. Makievski, J. Krägel, D. O. Grigoriev, F. Ravera, L. Liggieri, D. Y. Kwok and A. W. Neumann, *Characterisation of Water/Oil Interfaces, Encyclopaedic Handbook of Emulsion Technology*, ed. J. Sjöblom, Marcel Dekker, New York, 2001, p. 1.
- [doi>](#) 9 D. Ducharme, A. Tessier and R. M. Leblanc, *Rev. Sci. Instr.*, 1987, **58**, 571.
- [doi>](#) 10 J. A. de Feijter, J. Benjamins and F. A. Veer, *Biopolymers*, 1978, **17**, 1759.
- 11 H. Motschmann and R. Teppner, in *Novel Methods to Study Interfacial Layers*, eds. D. Möbius and R. Miller, Elsevier, Amsterdam, 2001, vol. 11, p. 1.
- [doi>](#) 12 H. G. Schild and D. A. Tirrell, *Langmuir*, 1991, **7**, 665.
- [doi>](#) 13 P. G. de Gennes, *Adv. Colloid Interface Sci.*, 1987, **27**, 189.
- 14 G. J. Fleer, M. A. Cohen Stuart, J. M. H. M. Scheutjens, T. Cosgrove and B. Vincent, *Polymers at Interfaces*, Chapman and Hall, Cambridge, 1993.
- [doi>](#) 15 L. T. Lee, B. Jean and A. Menelle, *Langmuir*, 1999, **15**, 3267.
- [doi>](#) 16 R. M. Richardson, R. Pelton, T. Cosgrove and J. Zhang, *Macromolecules*, 2000, **33**, 6269.
- [doi>](#) 17 M. Kawaguchi, Y. Hirose and T. Kato, *Langmuir*, 1996, **12**, 3523.
- [doi>](#) 18 M. Kawaguchi, M. Tohyama, Y. Mutoh and A. Takahashi, *Langmuir*, 1988, **4**, 407.
- 19 H. Venohr, V. Fraaue H. Strunk and W. Borchard, *Eur. Polym. J.*, 1998, **34**, 723.
- [doi>](#) 20 D. O. Grigoriev, V. B. Fainerman, A. V. Makievski, J. Kraegel, R. Wuestneck and R. Miller, *J. Colloid Interface Sci.*, 2002, **253**, 257.
- [doi>](#) 21 B. B. Sauer and H. Yu, *Macromolecules*, 1989, **22**, 786.
- [doi>](#) 22 J. F. Douglas, H. M. Schneider, P. Frantz, R. Lipman and S. Granick, *J. Phys. Condens. Matter*, 1997, **9**, 7699.

Received: 15th September 2004; Com. 04/2365