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Swelling Dynamics of Ultrathin Polymer Films

Amarjeet Singh and M. Mukherjee*

Surface Physics Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar,
Kolkata-700064, India

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ABSTRACT: Solvent uptake and swelling of ultrathin spin-coated polyacrylamide films in the presence of saturated vapor of water at room temperature was studied using gravimetric and X-ray reflectivity methods. Solvent uptake was observed to be a faster process, compared to swelling, governed by the Fickian dynamics of the diffusion of water molecules into the free volume of the polymer structure. The swelling demonstrates a slower dynamical behavior that can be modeled in terms of the swelling of a free polymer coil in the presence of a good solvent. Unlike interdiffusion of polymer chains at the interfaces, the attractive interaction of the substrate was found to have no influence on the diffusion process in the case of swelling.

1. Introduction

When a dry bulk polymer is exposed to a solvent, the solvent molecules enter into the porous structure of the polymer and diffuse into all accessible volume. This phenomenon is commonly referred as mass uptake, since the solvent molecules at this stage are physically or chemically adsorbed on the surface as well as are absorbed into the pores and the available free volume. If however the polymer is soluble in the solvent, there is a strong attractive interaction between the polymer and the solvent, and the net interaction between the polymer segments is repulsive. As a result, the coiled chains start to swell as soon as they are in contact with the solvent molecules. In other words, the polymer starts to go into the solvent as it is in the early stage of the solution process. The understanding of the mobility of polymer chains near surfaces and interfaces for ultrathin polymer films in the presence of solvent is of technological importance in many areas like emulsion, coating, and adhesion.[1] Knowledge of the bulk polymer properties is not useful in this case because the equilibrium structural and dynamical behaviors of the polymer chains close to the substrate or at some interface are quite different as observed for the thickness and film−substrate interaction dependence of glass transition temperature,[2−6] dewetting kinetics,[7−9] rheological properties,[10] or chain mobility close to the substrate.[11,12] The phenomenon of solvent absorption into the pores of a polymeric structure have been exploited by several authors to study different aspects of polymeric material such as diffusion of solvents into the pores,[13−16] pore size distribution,[17] viscoelastic properties,[18] etc. Elaborate theoretical[19−25] and experimental[26−28] studies are also available for the dynamics of polymer chains in a polymer melt or through some random medium equivalent to a cross-linked polymer gel network. However, the study on the dynamical behavior for the mass uptake and the swelling processes, particularly for ultrathin soluble polymer films, is not available in the literature. In the present work we performed X-ray reflectivity and gravimetric measurements to study the dynamical behavior of the swelling as a result of solvent uptake for ultrathin polyacrylamide films supported on silicon substrates. Spin-coated polyacrylamide films on silicon substrates were exposed to water vapor at saturated vapor pressure condition at room temperature while the mass and the thickness were monitored using gravimetric and X-ray reflectivity methods, respectively. The comparison of the results suggests that the mass uptake is a faster process governed by the capillary condensation and subsequent diffusion of water into the free volume of the polymer films whereas the swelling starting simultaneously with the mass uptake demonstrates a slower dynamical behavior.

2. Experimental Section

2.1. Sample Preparation. High molecular weight ($>5 \times 10^6$) polyacrylamide (supplied by BDH Chemicals, UK) has been used to prepare the thin films on silicon substrate by spin-coating. We have used a 2 mg/mL aqueous solution of the polymer for this purpose. The silicon substrate was chemically treated with ammonia and hydrogen peroxide solution, which makes the surface of the wafer hydrophilic by producing OH dangling bonds on to the surface, thus making it suitable for the coating of a water-soluble polymer. Different spinning speeds ranging from 400 to 600 rpm were used to prepare films of different thickness. Spin-coating with the same solution concentration at different spin speeds would cause the polymer films to be in a highly nonequilibrium configuration. At the center of the spin, the polymer chains are less perturbed compared to the edges of the films due to the elongation flow. A standard procedure to release the strain developed in the spin-coated films is to swell the films in the solvent vapor after their preparation. All the films were exposed to water vapor in a closed container for 15 min. The films were then stored in a dry desiccator before experiments were performed with them. Additionally, we have annealed the films at 80 °C in a vacuum for half an hour to remove any further residual strain in the films. To avoid the ambiguity in the thickness of the films, the X-ray reflectivity measurements were performed before the gravimetric measurements with the same set of samples.

2.2. Gravimetric Measurements. To study the mass uptake of the films, we have used a microbalance (Metler, MT5) of microgram mass resolution. A source of water was placed inside the weighing chamber, and the weight of the film was recorded as a function of time. It was observed that the clean substrate also adsorbs some amount of moisture initially. The data for clean substrate were subtracted from the film data to find the actual mass uptake of the pure polymeric films. The mass uptake behavior shows a release of mass after attaining a maximum in some of the films. We believe this is due to the fact that the capillary free volume enlarged with

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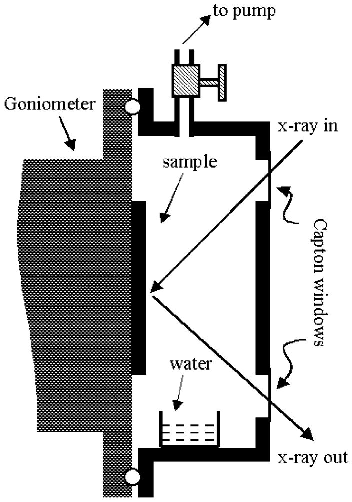

Figure 1. Schematic view of chamber for carrying out X-ray reflectivity study for ultrathin polymer films in a vacuum and saturated vapor pressure environment.

the expansion of the film to larger pores and the water that was adsorbed purely due to the surface force was released, resulting in a weight loss in these films.

2.3. X-ray Reflectivity. X-ray reflectivity data were collected on Microcontrol triple-axis goniometer, keeping the incident and the exit angles identical for maintaining specular condition as a function of momentum transfer vector q normal to the surface given by $q = (4\pi/\lambda) \sin \theta$, with θ equal to the incident and the exit angle of the X-ray. An Enraf Nonius FR591 rotating anode generator followed by a Si(111) monochromator was used to obtain Cu $K\alpha_1$ radiation. To measure the thickness and the electron density of the swelling polyacrylamide films, we have performed X-ray reflectivity measurements while the films were exposed to the saturated vapor of their solvent water. At first the films were kept under vacuum at 80 °C for 30 min in a specially designed chamber, and the X-ray reflectivity data for the dry film were collected at room temperature, in situ, allowing the X-ray beam to enter and exit the chamber through Capton windows. After breaking the vacuum, a small amount of cotton fully soaked with water in a container was placed very quickly in the chamber below the films, as shown in Figure 1. The outlet of the chamber was kept open to maintain atmospheric pressure inside during the experiment. The water vapor inside the chamber provides a saturated vapor pressure condition at room temperature, and the films expand as a result of swelling due to absorption of the vapor into the free volume. The reflectivity data for the swelling of the films were taken as a function of time. The q range for the data collection was carefully optimized to accommodate sufficient number of thickness oscillations as well as the data acquisition time. Reasonably good statistics were obtained in 7 min, during which data were collected for each thickness. The reflectivity data were analyzed using Parratt formalism[29] to obtain information about the thickness and the electron density for every thickness of all the films. In Figure 2 we have presented experimental data along with the fitted profiles for a particular film for different swelling stages; the inset of the figure shows three typical electron density profiles corresponding to the reflectivity profiles shown by the triangle symbols in the figure. It was clearly observed that the frequency of the oscillations increased on swelling, indicating increase of film thickness given by $d = 2\pi/\Delta q$ for large q, where Δq is the separation between two successive minima in the data. The data show a clear indication of changes in density in terms of the changes in the critical electron density q_c as the thickness increases. In the Parrat formalism the roughness of the polymer surface, the electron density, and the thickness of the films along with the roughness of the substrate were used as parameters for the fitting. For simplicity of the model, a single electron density was allowed for the entire polymer film for each thickness.

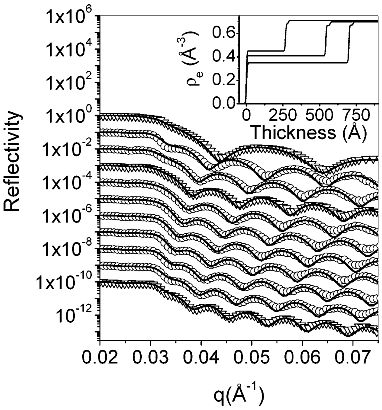

Figure 2. Reflectivity data (symbols) with fitted profiles (lines) of the swelling polymer films when exposed to solvent, from top to bottom as increasing swelling time. Inset shows three different electron density profiles (ρ_e) corresponding to the scans represented by down triangles.

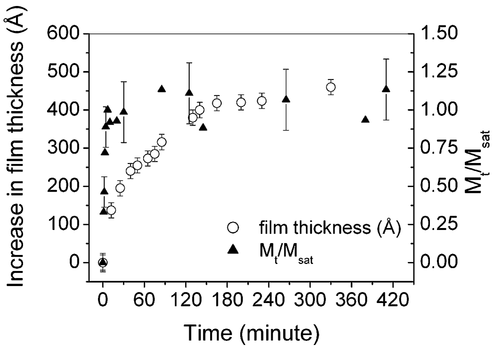

Figure 3. Normalized mass uptake and the increase in thickness as a function of time for the film of initial thickness of 240 Å.

3. Results and Discussion

3.1. Diffusion of Water. In Figure 3 we have compared the data for mass uptake and the thickness change for a particular film. It is clearly shown in Figure 3 that the slope of the mass uptake data is much higher compared to that of thickness expansion data with the former saturating much earlier, which suggests the mass uptake to be a much faster process. Considering the fact that the two time scales are widely different, one can assume the two processes to be independent. Under this approximation and the facts that (a) a plot of M_t/M_{sat} vs $t^{1/2}$ is linear in the initial phase, (b) the linearity holds for at least up to $M_t/M_{\text{sat}} = 0.6$, (c) above the linear region curves bend toward the abscissa, and (d) uptake curves obtained by plotting M_t/M_{sat} vs $t^{1/2}/l$ for different film thickness l coincides (Figure 4), the diffusion processes can be considered as Fickian.[13,30] This kind of diffusion can be described by Fick's second law of diffusion, which can be solved considering appropriate boundary conditions for diffusion into a semi infinite[31,32] film exposed to a infinite bath of penetrant for the short time (initial phase of uptake) to read $M_t/M_{\text{sat}} = (4/l)(Dt/\pi)^{1/2}$, where M_t is the mass uptake at time t defined as $M_t = (w_t - w_0)/w_0$, where w_t and w_0 are the weight of the films at time t and the initial weight, respectively. M_{sat} is the saturated mass uptake, and D is the diffusion coefficient. In Figure 4 we have plotted normalized mass uptake, M_t/M_{sat}, against square root of time scaled by the film thickness $t^{1/2}/l$ for the films, and from the slope of the curve we determine the diffusion coefficient of water, $D_w = (1.7 \pm 0.7) \times 10^{-15}$

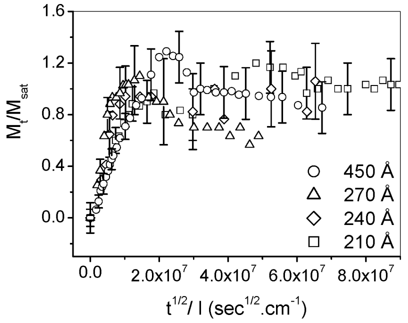

Figure 4. Normalized mass uptake against square root of time scaled with film thickness. Initial thickness of the films is shown against the symbols.

cm^2/s, for the diffusion of water into the free volume of the thin polymer films.

3.2. Dynamics of Polymer Chains. The thickness of all the films studied in the present work is less than the R_g of the polymer, which indicate that the films are constituted by the placement of the individual coils side by side in the form of pancakes as predicted by de Gennes.[33] We assume that in the presence of solvent vapor all the coiled chains swell independently. This allows us to study swelling dynamics in terms of the dissipative equation of motion for the end-to-end distance of the polymer R, combined with Flory approximation for the free energy $F(R)$ in d-dimensions as[34,35]

$$\frac{\partial R}{\partial t} = -\mu \frac{\partial F(R)}{\partial R} = -\mu k_B T \frac{\partial}{\partial R}\left(\frac{R^2}{N} + v\frac{N^2}{R^d}\right) \qquad (1)$$

The first and the second terms in the parenthese give entropic and excluded-volume contributions to the free energy, respectively. The diffusion coefficient for the polymer chains can be described in terms of chain mobility μ using Einstein relation as $D_p = \mu k_B T$.

The general solution of the above differential equation reads

$$R(t) = e^{-(2\mu k_B T/N)t}\left[R_0^{\,d+2} + \frac{vdN^3}{2}\left(e^{[2(d+2)\mu k_B T/N]t} - 1\right)\right]^{1/(d+2)} \qquad (2)$$

with initial condition $R(t{=}0) = R_0$ describing the change of the size of a polymer coil on swelling as a function of time.

In the case of thermal expansion of ultrathin polymer films, the movements of the polymer chains were observed mainly in the direction perpendicular to the film surface, other two directions being restricted by the physical boundary of the substrate size.[36] In the present swelling study of the polymer films, no spillover of the polymer was observed on swelling, indicating that in this case also the expansion of the film can be considered to be one-dimensional and occurs in the direction perpendicular to the surface similar to that of thermal expansion. For one-dimensional case, eq 2 reads

$$R(t) = e^{-(2D_p/N)t}\left[R_0^{\,3} + \frac{vN^3}{2}\left(e^{(6D_p/N)t} - 1\right)\right]^{1/3} \qquad (3)$$

where N is the degree of polymerization, the ratio of polymer to monomer molecular weight, and v is the excluded volume, a positive quantity in the case of swelling.

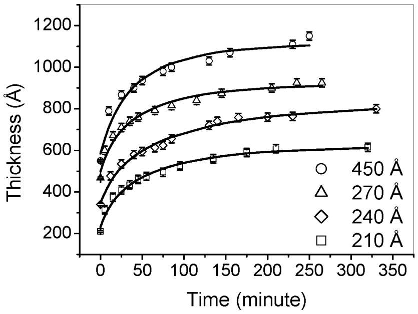

Figure 5. Swelling of the films as they are exposed to saturated solvent vapor. Symbols represent experimental data, and the lines are obtained by fitting the data using eq 3. Initial thickness of the films is shown against the corresponding symbols. The films with initial thickness 240, 270, and 450 Å are shifted upward by 100, 200, and 100 Å, respectively, for clarity.

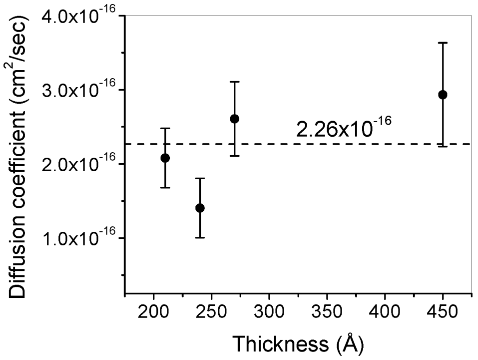

Figure 6. Diffusion coefficient of the polymer chains D_p as a function of film thickness.

In Figure 5 we have plotted the thickness of four different films obtained from X-ray reflectivity measurements as functions of swelling time along with the fitted data using eq 3. The excellent fit for all the data indicates that the swelling of the polymer films in this case can be expressed in terms of the swelling of noninteracting individual polymer coils due to entropic and excluded-volume interaction. The diffusion coefficients obtained for different films are found to be nearly the same, indicating they are independent of film thickness. In Figure 6 we have plotted the diffusion coefficients D_p observed from the analysis for the films of different thickness along with the average value as a dotted line. In the case of interdiffusion of polymer chains at the interfaces of polymer films, the chain dynamics was observed to slow down when the interface was at a distance of several R_g from the substrate due to the influence of the substrate on the dynamics of the diffusing polymer chains.[11,12] In the present case we do not observe any systematic dependence of the diffusion coefficient on the film thickness. We tend to believe that the magnitude of the interchain repulsive interaction for the swelling process is much larger compared to the attractive polymer–substrate interaction; hence, the latter contributes negligibly to the dynamics of swelling. For the completeness of the study we have also analyzed our data in terms of swelling of a free-standing cross-linked gel,[37–39] although the films are soluble and does not have chemical cross-links between the segments. Using the formalism of Li and Tanaka[38] for the swelling of a disk-shaped gel, since this geometry was closest to that of our thin film case, we find that the observed time constants do not follow the predicted proportionality to the square of the saturated thickness of the swelled films, indicating that the gel model was not suitable for the present case. The diffusion coefficients predicted by this theory were also much larger compared to those predicted by the present model of swelling of free chains.

4. Summary and Conclusion

We have studied the mass uptake and swelling of ultrathin polyacrylamide films prepared by spin-coating on silicon substrate in the presence of saturated vapor of the water at room temperature using gravimetric and X-ray reflectivity methods. We observe that water uptake is a much faster process governed by the Fickian dynamics of the diffusion of water molecules into the free volume of the polymer structure. The swelling phenomena start almost simultaneously with that of water uptake, demonstrating a slower dynamical behavior that can be modeled in terms of the swelling of a free polymer coil in the presence of good solvent. It was observed that, unlike interdiffusion in polymer interfaces, the diffusion coefficient of the polymer chains are not influenced by attractive polymer−substrate interaction.

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(31) A finite thickness can be considered as infinite for the Fickian diffusion to hold good, if the quantity of solvent which would lie outside this length in a truly infinitely thick film, is an insignificant portion of the total solvent present in the film. Considering a 1% of the total amount of the solvent as a sufficiently insignificant portion, we can solve for x in the equation $10^{-2} = (\int_x^\infty e^{-z^2/4Dt}\,dz)/(\int_0^\infty e^{-z^2/4Dt}\,dz)$ to give $x \cong 3.6\sqrt{Dt}$. For sufficiently short time and slow diffusion process any length can be considered as infinite. Considering the diffusion coefficient D equal to 1×10^{-15} cm^2/s and the time t to be 20−30 min (corresponding to $M_t/M_{sat} = 0.6$), we get x to be 395−480 Å, which is very close to the thickness of our films.

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