Power law in swelling of ultra-thin polymer films

M. Mukherjee [a],[*], M. Souheib Chebil [b], Nicolas Delorme [b], Alain Gibaud [b]

[a] Surface Physics Division, Saha Institute of Nuclear Physics, 1/AF, Bidhannagar, Kolkata 700064, India
[b] LUNAM Universite, IMMM, Faculté de Sciences, Universite du Maine, UMR 6283 CNRS, Le Mans Cedex 9 72000, France

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ABSTRACT

Steady state and dynamic behaviour of swelling of spin coated polyacrylamide films have been studied at room temperature in a precisely controlled environment of 12—99% relative humidity (RH). Swelling of the films was monitored by measuring the thickness of the films using X-ray reflectivity and Atomic Force Microscopy. Swellibility of the films was observed to be independent of thickness of the films indicating no significant influence of substrate polymer interaction or confinement effect in swelling. The water content of the films swelled at different humidity conditions was calculated comparing the electron density of the dry and the swelled films. The volume fraction of water in the swelled films and their swellibility were found to follow double power law behaviour as a function of relative humidity and the transition from one regime to the other was observed around 75% RH value. The behaviour was explained in terms of transition from short to long diffusing channels in the films. Comparison of time evolution of relative humidity of the experimental chamber with that of the dynamics of swellings of the films shows that diffusion of water into the environment was several orders of magnitude faster than the swelling dynamics. The observed values of the diffusion coefficients for the films at different humidity were same whereas the excluded volume parameter, that determine the saturated thickness of the films, was found to have dependence on relative humidity and film thickness.

1. Introduction

In recent years ultra-thin polymeric films have drawn tremendous application in the fields of coating, membrane, sensors etc. Confinement of the polymer leads to the changes in the equilibrium structural and dynamical behaviours of the polymer chains close to the substrate [1—5] due to energetic interactions between polymer chains and the substrate. When a dry polymer is exposed to a solvent, the solvent molecules enter through the porous structure of the polymer. If the solvent is a good solvent for the polymer 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 polymer molecule starts to swell. The understanding of the mobility of the polymer chains and their equilibrium structure close to the substrate or interfaces in presence of solvent vapour are of technological importance in many areas like emulsion, coating and adhesion [6]. The phenomenon of solvent absorption into the pores of polymer has been exploited by several authors to study the diffusion of solvent into the pores [7,8], pore size distribution [9,10], viscoelastic properties [11,12] etc.

In our previous studies [13—17] we have presented the swelling dynamics of water soluble polymer films where the effect of various interactions on swelling dynamics have been studied extensively. Those results in general show that swelling dynamics is sensitive to the minute changes in polymeric system or on polymer solvent interaction. It may be noted that all our previous investigations were performed with uncontrolled humidity with an assumption that the saturated humidity condition was achieved very quickly in the chamber thus the process of saturation does not affect the swelling dynamics.

The present investigation was performed under variable humidity condition. Here the relative humidity (RH) of the chamber can be stabilize at a desired value with the application of saturated solution of different inorganic salts and simultaneous control of dry nitrogen flow in the sample chamber. The relative humidity and the temperature of the swelling environment can be monitored while the x-reflectivity measurements can be performed with the samples. As the temperature of the environment strongly influence the humidity, the temperature was always recorded along with humidity and the actual humidity was calculated using the calibration equation supplied with the humidity sensor (HIH-3610, Honeywell). The schematic diagram of the experimental setup is shown in Fig. 1. Here we study the swelling behaviour of polyacrylamide thin films at large number of stable humidity conditions leading to the novel result that are not available in the existing literature.

* Corresponding author.
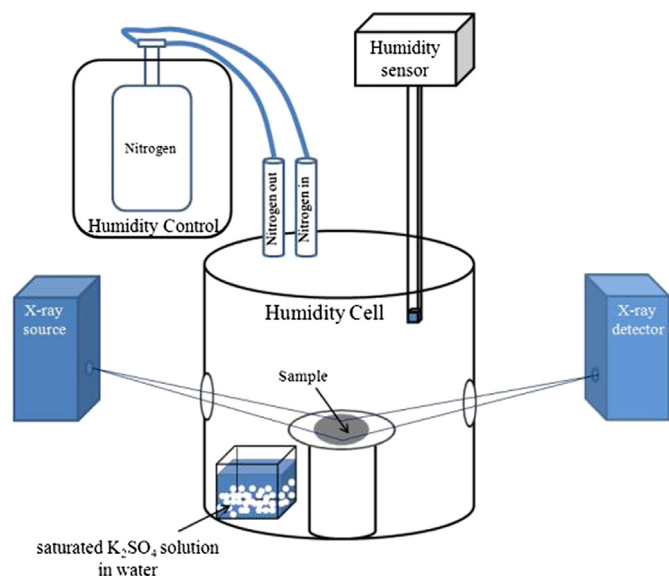E-mail addresses: manabendra.mukherjee@saha.ac.in, manabsinp@gmail.com (M. Mukherjee).

Fig. 1. Schematic representation of the humidity cell and the X-ray reflectometer. Saturated solution of K_2SO_4 was used as the source of humidity.

2. Experimental details

2.1. Sample preparation

A powder of high molecular weight polyacrylamide (Molecular weight $5-6 \times 10^6$, supplied by Polysciences, USA) was taken as starting material for the experiment. Three aqueous solutions with concentration 2, 4 and 6 mg/ml were prepared from the powder source. Films from the three solutions were prepared on silicon substrates by spin coating method. Before coating, silicon wafers were cleaned by RCA cleaning method, where the wafers were boiled at 100 °C for about 15 min in a solution of H_2O, NH_4OH and H_2O_2 (volume ratio, 2:1:1). The wafers were then rinsed with Millipore water. Apart from cleaning, this treatment enhances the hydrophilicity of the silicon surface by introducing −OH dangling bonds on the surface which helps better attachment of the water soluble polymers. Films of different thicknesses were prepared applying different spinning speeds ranging from 1000 to 3000 r.p.m.

2.2. X-ray reflectivity (XRR)

X-ray reflectivity is one of the best nondestructive methods to measure the structural aspects of thin polymeric films; here we have used this technique to study the thickness and electron density of polyacrylamide films prepared from the three solutions. X-ray reflectivity data were collected in horizontal geometry with our laboratory setup (Empyrean, PANalytical) with CuKα radiation obtained from copper sealed tube anode (1.2 kW), followed by a mirror for focussing. The samples were placed in a chamber as described in the introduction section. Specular scans with identical incoming and outgoing angles for X-rays were taken as a function of momentum transfer vector q normal to the surface ($q = (4\pi/\lambda)\sin\theta$, with θ the incident and the reflected angles of the X-ray and $\lambda = 1.54$ Å, the wavelength of the radiation). By using a Pixcel detector which has a very high dynamical range, it was possible to collect full XRR curves in about 3 min. This is a major breakthrough in such measurements which allows us to carry out kinetics studies of materials within this time scale.

To obtain information about the thickness and electron density of the films, the reflectivity data were analyzed using the matrix technique [18] including interfacial roughness. For the analysis of the XRR data, the input electron density profiles were divided into several boxes of thickness equal or more than $2\pi/q_{max}$ and the interfacial roughness were kept within 2−8 Å. During the analysis, the roughness of the polymer surface, the electron density, the thickness of the films and the roughness of the substrate were used as fitting parameters.

2.3. Atomic force microscopy (AFM)

Room temperature AFM topographic images were obtained in intermittent-contact mode (Nanosensor PPP-NCHR-W tip) with an Agilent 5500 AFM equipped with an integrated environmental chamber. Similar to XRR measurements, relative humidity was controlled by the use of a saturated aqueous K_2SO_4 solution and circulation of dry N_2. For film thickness determination, we measured the difference between the two maxima of the height distribution data across a scratch made on the polymer film [19]. Height distribution and roughness calculations were performed using Gwyddion freeware.

2.4. Steady state measurements

A set of four films in the thickness range of 60−322 Å have been investigated in the present study. X-ray reflectivity experiments were performed at room temperature (~ 25 °C) at different stable humidity conditions in the range of 13−99% relative humidity. As we have noticed that films can de-swell almost instantaneously, whereas, swelling takes several hours to stabilize, we first took the data at highest humidity ($\sim 99\%$) and then stepwise reduced the humidity of the chamber for taking the data at other RH values. For attaining highest humidity we used K_2SO_4 saturated solution as the source of water vapour in the closed chamber keeping the dry nitrogen flow at off condition. After humidity in the chamber attained its highest value ($\sim 99\%$) in about 2 h, XRR measurements were carried out. For attaining lower humidity we flew dry nitrogen in a controlled manner to attain a desired value. Adding nitrogen at an optimum rate did not disturb the experimental condition by turbulence or vibration and RH = 12−13% as minimum was achieved.

Fig. 2 shows the XRR data for a typical sample at different humidity. At stable humidity conditions, the data could be collected for a long acquisition time. Therefore these data can be used for detailed analysis of the electron density profiles of the films in
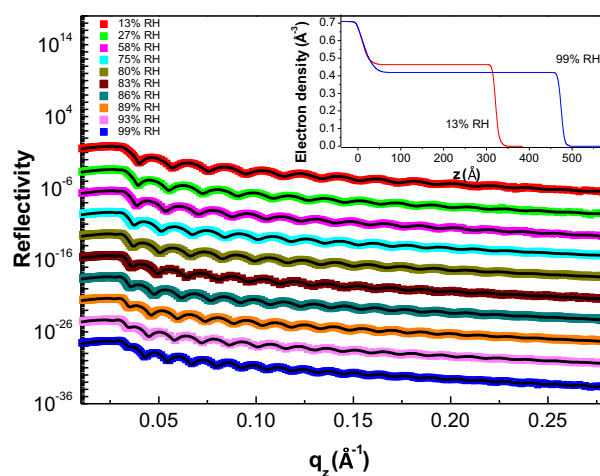

Fig. 2. Measured (symbol) and calculated (line) X-ray reflectivity curves of a film with initial thickness 322 Å at different RH. The inset shows the electron density profiles at low and high RH of 13% and 99% respectively.