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Study of structural evolution during controlled degradation of ultrathin polymer films

Mojammel H. Mondal, M. Mukherjee*

Surface Physics Division, Saha Institute of Nuclear Physics, 1/AF, Bidhannagar, Kolkata-64, India

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ABSTRACT

The structural aspects of polyacrylamide thin films annealed at degradation threshold temperature have been studied as a function of annealing time using in situ X-ray reflectivity technique in vacuum. We observe significant decrease of thickness and increase of density with annealing time for all the films. The dynamical behavior of the changes was modeled in terms of two distinct exponential decay functions, following our earlier observation of two different time scales for the chemical modification pathways, and was found to be in excellent agreement with the data. The diffusion coefficients of the polymer chains corresponding to the two modes are found to be different by an order of magnitude. It was found that the two dynamical modes correspond to the formation of two degradation products at two different rates. The larger time constants for both the modes in case of thickness reduction compare to the chemical changes was explained in terms of inter-chain entanglement and attachment of the polymer with the substrate.

1. Introduction

Polymers are widely used in modern industrial societies in a wide range of products such as disposable food service wares, product cases or as structural components in industrially important materials ranging from children's toys to aircraft manufacturing. Environmental factors such as heat, sunlight and chemicals may alter physical and chemical properties of polymer. From both academic and industrial viewpoints it is crucial to understand the mechanism of polymer degradation in terms of their chemical and structural changes. Much research has been devoted to the causes and effects of degradation in polymers [1–13] since the development of the plastic industry. Moreover, a detail understanding of polymers breakdown on heating is important in order to design materials with improved properties and to relate stability and breakdown mechanisms to their chemical structures. In recent years, nanometer scale polymer thin films have drawn tremendous interest due to their technological importance particularly in areas like microelectronics, coatings, biomaterials, membranes, lubricants, adhesives and paints [14–17]. Thin polymer films are interesting because they often exhibit properties that are different from the corresponding bulk polymers therefore the knowledge of the bulk properties is not sufficient in this case. The equilibrium structural and dynamical behaviors of the polymer chains close to the substrate or at interfaces are quite different due to entropic effects and energetic interactions arising at the interfaces. These interfacial effects lead to changes in chain conformation and mobility that affect the properties of the entire polymer film. Response of the long chain polymer molecules at surface and interfaces on annealing at elevated temperature and understanding of related structural changes are therefore of fundamental importance. From a practical point of view it is important to study thermal degradation [18–22] of polymers at the degradation threshold temperature as this temperature determines the upper limit for fabrication when polymers are processed and for their use in applications. It is also important to know the volatile products of degradation in order to guarantee the safety of the workers. Recently we have studied the kinetics of controlled thermal degradation of polyacrylamide ultrathin films by annealing them at the degradation onset temperature (220 °C) using X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and X-ray reflectivity (XRR) techniques [1]. We observed that the chemical modification of the polymer follows two distinct dynamical modes for the two different final products. It was also observed that despite of chemical modification the interfacial morphology of the film stays almost unmodified indicating that the films retain their polymeric property. However, a study of detail morphological/structural evolution of these ultrathin films during annealing is not available in the literature. This motivates us to perform the present investigation.

* Corresponding author.
E-mail address: manabendra.mukherjee@saha.ac.in (M. Mukherjee).

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In the present article we discuss the structural changes of thin polymer films on controlled annealing at degradation onset temperature (220 °C). To understand how thermal degradation affects the structural aspects or if there is any influence of the two different degradation modes on the structure modification dynamics of the films during annealing, we have performed X-ray reflectivity measurements with time at this temperature in situ in vacuum. During annealing at 220 °C chemical modification of the films occurs and as a result the structures of the films are also changed. It was observed that with annealing time thickness of the films decrease along with increase in their density and reach a saturated value. It was found that thickness reduction with time at 220 °C consists of two dynamical modes, much slower compared to their chemical counterpart.

2. Experimental

2.1. Sample preparation

In order to understand whether there was any effect of initial polymer concentration or chain morphology, three sets of polymer films were prepared from three different solutions. A powder and an aqueous solution (1%, 10 mg/ml) of high molecular weight polyacrylamide (Supplied by Polysciences, USA) were taken as starting materials for the experiment. Two solutions of concentrations 2 mg/ml and 4 mg/ml were prepared from the powder source (molecular weight $5–6 \times 10^6$). A third solution of concentration 4 mg/ml was prepared from the partially entangled [23] solution source (molecular weight 5×10^6). The solutions are denoted as solutions A, B and C respectively. Three sets of films from the three solutions were prepared on silicon substrate by spin coating method. The films prepared from the solutions A, B and C were designated as films A, B and C respectively. During the spinning, clean and warm (60 °C) air was flown gently over the sol using a homemade arrangement to facilitate faster evaporation of water [24]. 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 500 to 4000 r.p.m.

2.2. X-ray reflectivity

X-ray reflectivity is one of the best nondestructive methods to measure the thickness, electron density and roughness of ultrathin polymer films. We have used this technique here to study the structural aspects of thermally annealed polyacrylamide films prepared from the three solutions. X-ray reflectivity data were collected in our laboratory setup with CuKα radiation obtained from copper sealed tube anode (2.2 kW, Bruker AXS, D8 Discover). 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 equal to the incident and the reflected angles of the X-ray and $\lambda = 1.54$ Å, the wavelength of the radiation). Spin coated polyacrylamide films remain at strained configuration in the as deposited condition. All the films were swelled in saturated water vapor condition in a closed chamber at room temperature for 12 h to release the strain before they were dried and stored in a desiccator. As the films of water soluble polymer are hygroscopic in nature, it was important to remove absorbed water molecules from the films in order to study their actual structure. At first, data for all the films were collected at room temperature in a chamber continuously evacuated by a rotary pump. The corresponding thicknesses of the films were considered as initial film thickness. The films were subsequently heated at 105 °C for 45 min in vacuum and the reflectivity data at this temperature were collected in situ in vacuum. The total time at 105 °C including that of data acquisition was about 3 h for all the films. From X-ray photoemission spectroscopy studies we found that the films heated above 100 °C under vacuum for 1 h contains nearly no water and can be considered as practically dry for our study. The structural aspects of the dry films were derived from the X-ray reflectivity data taken at 105 °C. Corresponding thickness and density of the films were considered as dry thickness and density of the films.

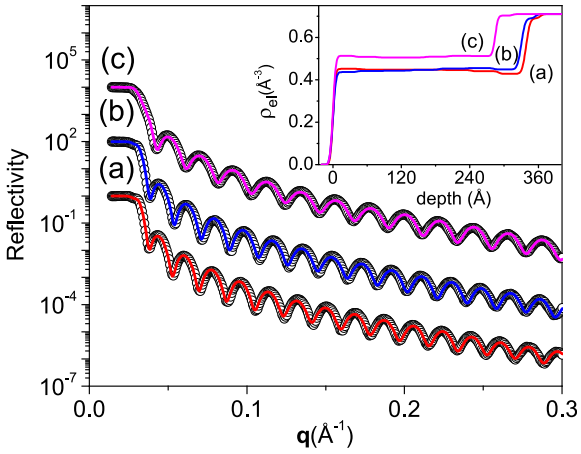

Fig. 1. X-ray reflectivity data (symbols) with fitted profiles (lines) of as grown film (a), annealed at 105 °C (b) and annealed at 220 °C (c) of a particular film of initial thickness 338 Å. Inset shows corresponding electron density profiles. The values 0.0 and 0.7 Å^{-3} in electron density corresponds to air and silicon substrate respectively.

To study the dynamics of change in film thickness it is important to understand the response of the films as a function of annealing at various temperature and time. In order to investigate the change in film thickness with temperature, we have performed X-ray reflectivity study of a particular film as a function of temperature. The film was dried at 105 °C under vacuum for about 1 h before the study. The film was then annealed in vacuum at various higher temperatures between 110 and 230 °C. After the sample was

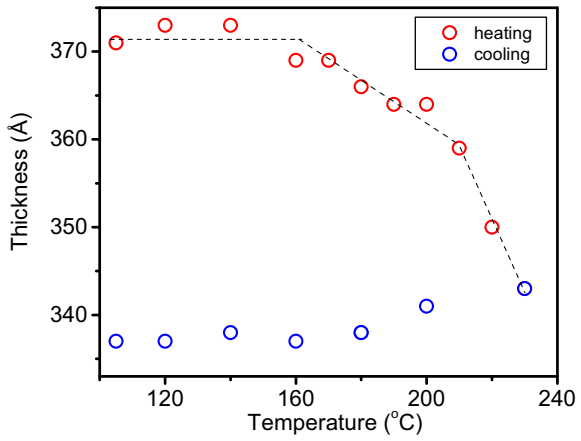

Fig. 2. Change of film thickness with temperature. Heating and cooling cycles are shown against the corresponding symbols. The dashed lines are guide to the eyes to show the thickness change behavior at different ranges of temperature.