Polymer 53 (2012) 1028–1033

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Anisotropy and densification of polymer ultrathin films as seen by multi-angle ellipsometry and X-ray reflectometry

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ARTICLE INFO

Article history:
Received 3 May 2011
Received in revised form
23 December 2011
Accepted 8 January 2012
Available online 12 January 2012

Keywords:
Polymer thin film
Densification
Optical anisotropy

ABSTRACT

The chain conformations of cyclo-olefin polymer (COP) and polystyrene (PS) in less than 200-nm thick films on silicon wafers were investigated on the basis of the refractive index measured by multi-angle spectroscopic ellipsometry (MASE), and density measured by X-ray reflectometry (XRR). For both COP and PS, the density measured by XRR increases by decreasing the film thickness to below 50 nm. Densification may be caused by close packing of unentangled polymer chains in ultrathin films spincast from dilute solutions with polymer concentrations less than the overlap concentration (C*). For COP films, the refractive indices at incident angles of 45° and 70° measured by MASE agree well with those calculated by the Lorentz–Lorenz equation, indicating that densification of COP ultrathin films enhances their refractive indices. For PS films thinner than 50 nm, although the refractive index at an incident angle of 45° agrees with a calculation based on the Lorentz–Lorenz equation, one at 70° significantly deviates downward. A comparison of them with the results of quantum chemical calculation (QCC) suggested a plane-arrangement of benzene rings in PS ultrathin films, which was likely brought about by stacking of benzene rings and attractive interaction between π-electrons in the benzene rings and the substrate surface.

1. Introduction

The physical properties of polymer thin films on substrates have been investigated by X-ray and neutron reflectometry (XRR and NR) [1–4], ellipsometry [5–9], Brillouin scattering [10–12] etc. Theoretically, two dimensionally confined polymer chains maintain the ideal Gaussian condition in the in-plane direction [13], so that the physical properties of ultrathin films are the same as bulk polymers. However, as revealed by a number of previous studies, the glass transition temperature (T_g) [5–7,14–16], coefficient of thermal expansion (CTE) [17–20], diffusion coefficient [21,22], modulus [23,24] and viscosity [25] of polymer films thinner than approximately 50 nm on substrates are much different from those of bulk polymers. These thermodynamic, transport and mechanical properties, being governed by chain conformation and dynamics, play an important role not only in fabrication but also in the functionalization of numerous polymeric nano-structured materials. A peculiar form of chain dynamics was previously observed on spincast polymer thin films [26,27], and a distinct difference in the chain conformation between spincast films and bulk polymers was suggested.

The refractive index (n) of ultrathin polymer films measured by ellipsometry considerably differs from that of bulk polymers, which has not been satisfactorily discussed in previous studies. Through the Lorentz–Lorenz equation, n can be related to the polarizability and density of a polymer, both of which are influenced by chain conformation. One can expect that information on the chain conformation resulting from the orientation and arrangement of chain segments in polymer thin films is obtainable from the refractive index measured by ellipsometry.

In this study, we discuss the chain conformations of cyclo-olefin polymer (COP) and polystyrene (PS) in spincast thin films based on the refractive indices measured by multi-angle spectroscopic ellipsometry (MASE) and the film densities evaluated by XRR. Furthermore, the possible optical anisotropy of the ultrathin films is investigated with the help of quantum chemical calculation (QCC).

2. Experimental and quantum chemical calculation

2.1. Sample preparation

COP from JSR (ARTON, M_w = 73 000 g/mol, M_w/M_n = 3.20, T_g = 145 °C) and PS from Aldrich (M_w = 980 000 g/mol, M_w/M_n = 1.05, T_g = 100 °C) were used for this investigation. The

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doi:10.1016/j.polymer.2012.01.013

chemical structures of these polymers are shown in Fig. 1. COP is known as a polymer with extremely low-birefringence and excellent transparency. Thin films of COP and PS with thicknesses 25–200 nm were prepared on silicon wafers using spin-casting from toluene solutions with concentrations ranging from 0.10 to 5.0 % (wt/wt); thinner films were prepared from more dilute solutions. Overlap concentrations of COP and PS in toluene solutions were determined from concentration dependence of absolute viscosities (Table 1). Prior to spin coating, all silicon wafers had been cleaned using 1 wt% hydrofluoric acid to remove the native oxide layer and rinsed with deionized water. Polymer solutions on silicon wafers were spun in a range of from 1000 to 5000 rpm for 1 min and dried under vacuum for more than 24 h at a drying temperature of 15 °C above the T_g of each polymer to remove solvent and allow sufficient structural relaxation.

2.2. Ellipsometry

The thickness (d) and n of COP and PS thin films were measured by MASE (Otsuka Electronics, FE-5000s). The measurements were carried out in the PSC$_R$A arrangement: polarizer (P) – sample (S) – rotating compensator (C$_R$) – analyzer (A). The Brewster angle (θ_B) of a silicon wafer is about 73°, so the accuracy of measurements considerably deteriorated at around θ_B due to a decrease in intensity of the reflected p-polarized light. In the present study linearly polarized light with a polarization direction of 45° to the sample surface was incident on a sample with angles (θ) ranging from 45° to 70°. The spectra of the amplitude ratio (Ψ) and phase difference (Δ) between p- and s-polarized reflected light were measured over a wavelength range of from 380 to 800 nm. The data was analyzed by least-squares optimization using the isotropic n-Cauchy model to deduce the n spectrum and d. Hereafter the refractive index at $\lambda = 630$ nm measured at θ is denoted by $n^{(\theta)}$. The film thicknesses obtained by analysis of Ψ and Δ spectra at different incident angles were essentially the same over the range of from 45° to 70°, demonstrating the validity of our measurements and data analysis.

2.3. X-ray reflectometry

Out-of-plane X-ray reflectometry (XRR) was performed for the polymer thin films on a SmartLab (Rigaku). A beam of Cu-K$_\alpha$ radiation, $\lambda = 0.154$ nm, was directed with a focusing mirror onto a four-bounce Ge (220) crystal monochromator. XRR profiles were collected by scanning a small grazing angle (β) of X-rays from the monochromator and a detection angle (β) of reflected X-rays ($0° < 2\beta < 2.0°$). A typical XRR profile is shown for 22-nm PS thin film in Fig. 2, where the Kiessig fringe pattern above $2\beta = 0.5°$ shows that the film is uniformly formed on the silicon substrate. The angles, where the XRR intensity shows sudden drops, correspond to the critical grazing angles (β_c) for total reflection.

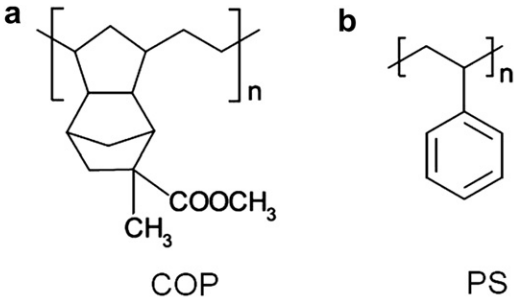

Fig. 1. Chemical structures of (a) COP and (b) PS.

Table 1
Glass transition temperatures of COP and PS determined by DSC, their unperturbed radii of gyration and overlap concentrations in toluene solutions.

	M_w	M_w/M_n	T_g (°C)	Unperturbed radius of gyration (nm)	Overlap concentration (wt%)
COP	73 000	3.20	145.3	16.4	0.75
Polystyrene	980 000	1.05	100.2	26.5	0.42

2.4. Quantum chemical calculation (QCC)

The Lorentz–Lorenz equation [28,29] describes the relation between the average refractive index and average polarizability of a molecule. To take account of the anisotropy of the refractive index, Vuks extended the Lorentz–Lorenz equation to the following form [30]:

$$\frac{n_i^2 - 1}{n_{av}^2 + 2} = \frac{4\pi}{3}\frac{\rho N_A}{M}\alpha_i. \quad (1)$$

Here M is the molecular weight, N_A is Avogadro's number, n_{av} is the average refractive index, n_i and α_i are the principal values of the refractive index and polarizability, respectively, and subscript "i" refers to the direction of the principal axis. We estimated the anisotropic refractive indices of COP and PS based on equation (1) from the calculated values of anisotropic polarizability for monomer units by QCC and the experimentally measured values of film density.

The principal values of polarizability were calculated by density functional theory (DFT) at the B3LYP level using the Gaussian 09 package [31]. Each chemical structure of a monomer unit of COP and PS was optimized with the 6-311G(d) basis set, and the principal values of polarizability at a wavelength of 630 nm were calculated with the 6-311++G(2p,d) basis set. The average polarizability, estimated by DFT, is denoted as α_{av}^{DFT}. As DFT overestimates the polarizability of a π-conjugated system, we corrected the calculated polarizability by the following procedure:

1. The experimentally estimated value of the average polarizability (α_{av}) was obtained by using both the Lorentz–Lorenz equation and measured values of the refractive index and density, 1.08 g/cm^3 for bulk COP and 1.05 g/cm^3 for bulk PS.

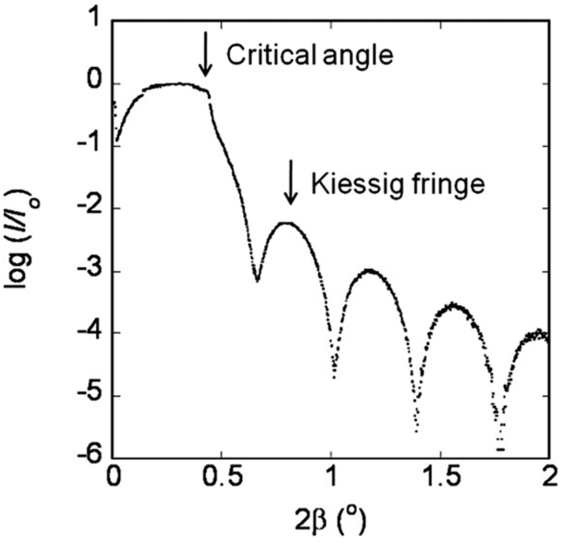

Fig. 2. XRR profile of 22-nm thick PS film on a Si wafer.