



Chain dynamics in spin-coated films of poly(methyl methacrylate) in a solvent annealing process

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Abstract

The dynamics of poly(methyl methacrylate) chains in spin-coating films during solvent annealing was studied. The neutron reflectometry (NR) measurement revealed that the absorbed solvent molecules homogeneously distributed in the spin-coated film and the solvent fraction increased to 0.35 in toluene vapor. From the real-time NR measurement for a stacked film of deuterated and hydrogenated PMMA in thermal annealing, the diffusion dynamics of the PMMA chain was strongly dependent on the distance from the surface: the polymer chain at the substrate was restricted. On the other hand, the depth dependence of the chain dynamics was weak in the spin-coated film in the solvent annealing process. Whereas the ratio of the diffusion constants of the PMMA chain at the surface and substrate was 50 in thermal annealing, the ratio in toluene vapor was as small as 2. Therefore, the solvent annealing provides sufficient mobility to the polymer chain near the substrate. This result indicates that the solvent annealing method enables the equilibration of a spin-coated polymer film from the surface to the substrate interface.

Introduction

Spin-coating techniques have been widely used to form polymer thin films for various purposes. The properties of polymer spin-coated films have been reported to be different from the properties of the bulk materials [1–6]. In a spin-coating process, a polymer chain is elongated in a flow by a centrifugal force on a spinning substrate and is frozen through the rapid evaporation of the solvent [7, 8], indicating that an as-prepared spin-coated film is in an un-equilibrium state. Therefore, an annealing treatment is applied to reach the equilibrium. A thermal annealing treatment above the glass transition temperature is the most common way to relax a polymer film to an

equilibrium state. The segmental and entire motion of a polymer chain at a high temperature allows the rearrangement of the chain conformation to an energetically stable state. Another method to reach equilibrium in a polymer film is a solvent annealing technique, which is performed in the vapor of a good solvent. The solvent molecules adsorbed from the gas phase provide the mobility for the relaxation of the polymer chains. The relaxation behavior in the solvent annealing is dependent on various factors such as the vapor pressure of the solvent in the atmosphere and the solubility of the polymer component; therefore, the solvent annealing techniques have been widely used to control the structures, properties, and functions of thin films [9–13]. However, the fundamental knowledge about the dynamics of polymer chains in solvent annealing has been limited in spite of its variety of applications, while the chain dynamics during thermal annealing have been extensively studied. This paper reports the motion of the poly(methyl methacrylate) (PMMA) chain in a spin-coated film during a solvent annealing process studied by the real-time measurement of neutron reflectometry (NR) [14, 15]. Toluene is a good solvent for PMMA and a most common solvent used in solvent annealing treatments. In the solvent annealing with toluene, the adsorption of solvent molecules into the PMMA film from the vapor

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phase and the diffusional motion of the polymer chain are discussed.

Experiments

Thin films of PMMA were prepared by a spin-coating method. Deuterated PMMA (dPMMA, $M_w = 9.94 \times 10^4$, $M_w/M_n = 1.08$, purchased from Polymer Source, Inc) was spin-coated on a Si wafer to form thin films with a thickness of ca. 100 nm. In order to discuss the depth dependence of the chain dynamics, stacked films of dPMMA and hydrogenated PMMA (hPMMA) were also prepared. A spin-coated 20-nm film of hPMMA ($M_w = 9.90 \times 10^4$, $M_w/M_n = 1.09$, Polymer Standards Service, GmbH) was floated on water and scooped onto a 20-nm dPMMA film on a Si wafer. A 5-layered stacked film with a total thickness of 100 nm was prepared by the repeated deposition of the 20-nm-thick dPMMA and hPMMA films as shown in Figure S1.

The NR measurements were carried out using neutron reflectometers, SHARAKU and SOFIA, at the Materials and Life Science Experiment Facility (MLF) at the Japan Particle Accelerator Research Complex (J-PARC). The static measurement in a scattering vector (q) range of $0.05\text{--}1.4\text{ nm}^{-1}$ before the solvent annealing was conducted at incidence angles of 0.3 , 0.6 , and 1.2° with a neutron beam with a wavelength range of $0.22\text{--}0.88\text{ nm}$. The in situ NR measurement was performed in a sealed aluminum chamber. The data acquisition began immediately after a sample film was sealed in the chamber with a liquid reservoir containing 0.5 mL of toluene. The in situ measurement over a q range of $0.15\text{--}1.4\text{ nm}^{-1}$ was carried out immediately after sealing the sample cell. The neutron beam at a wavelength range of $0.24\text{--}1.76\text{ nm}$ at an accelerator operation power of 400 kW was input to the sample at a constant incident angle of 1.2° . The measurement temperature was 296 K . The spatial distribution of the dPMMA and hPMMA in the thickness direction was evaluated by fitting the experimental data to a theoretical NR spectrum using MOTOFIT.

Results and Discussion

Figure 1a shows the NR spectra of a 90-nm-thick dPMMA film annealed in toluene vapor at annealing times of 0, 24, 48, 72, and 96 min. The gap of the fringe pattern due to the interference of the reflected neutron decreased during the annealing process, indicating an increase in the total thickness of the dPMMA film. The NR spectrum is dependent on the depth profile of the neutron scattering length density (SLD) in the thin film, which is directly

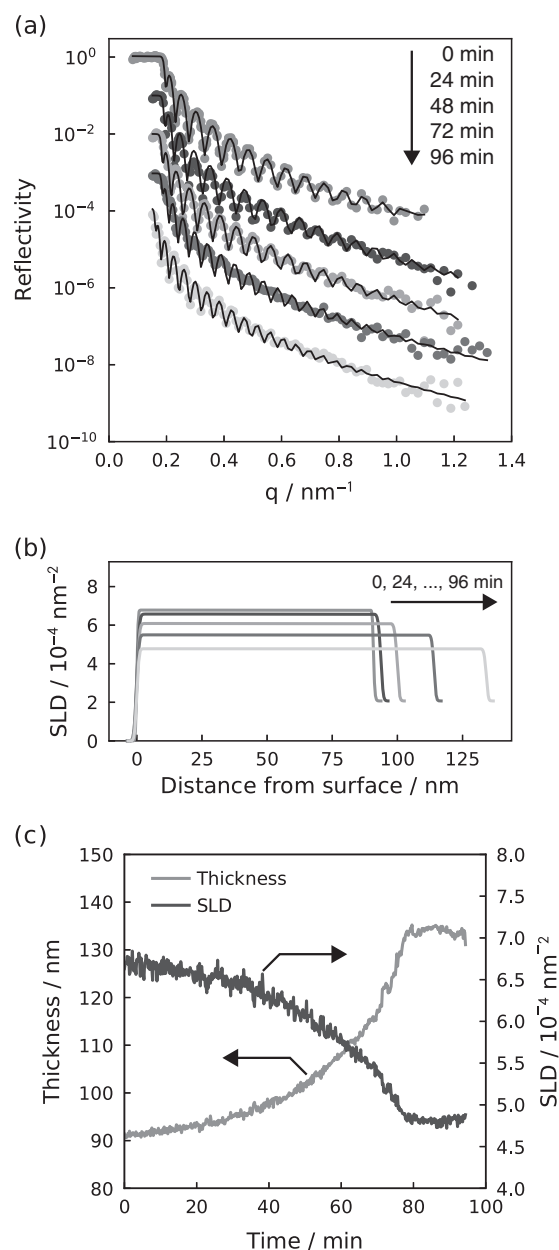


Fig. 1 Neutron reflectivity (a), scattering length density profile (b), and time evolution of them (c) for a deuterated poly(methyl methacrylate) film during a solvent annealing process in toluene vapor. The circles and black curves in a indicate the experimental data and theoretical profile, respectively. Each neutron reflectometric data is obtained in an acquisition time of 60 s

related to the chemical composition and mass density of the material. Therefore, the spatial distribution of dPMMA and toluene can be evaluated from the SLD profile to give the best-fitted theoretical NR spectrum to the experimental data. Figure 1b shows the SLD profiles in the depth direction in the dPMMA film, which are related to the theoretical curves in Fig. 1a. This indicates that the thickness of the PMMA film increased from 91 to 134 nm by the solvent annealing for 96 min and the SLD decreased from 6.75×10^{-4} down to

$4.82 \times 10^{-4} \text{ nm}^{-2}$. The values of the SLD for dPMMA and toluene in bulk states are 6.97×10^{-4} and $0.941 \times 10^{-4} \text{ nm}^{-2}$, respectively. Therefore, the decrease in the SLD in the solvent annealing process indicates the absorption of toluene molecules from the gas phase into the dPMMA film. The experimental NR spectra can be fitted to the theoretical curves for a structure with a constant SLD in the PMMA layer, which assumes the homogeneous distribution of the solvent molecule in the film. This indicates that the solvent molecule adsorbed at the surface of the PMMA film diffused into the inside of the sample film within the timescale of the data acquisition for each spectrum (60 s). This result is consistent with the diffusion constant of a solvent molecule in bulk PMMA, which is on the order of 10^{-12} – $10^{-11} \text{ cm}^2 \text{ s}^{-1}$ [16, 17]. Figure 1c shows the time evolution of the thickness and the SLD of the dPMMA film during the solvent annealing. The thickness increased and the SLD decreased by swelling with the toluene molecules absorbed from the atmosphere until the annealing time of 80 min. After this swelling period, the PMMA film reached at an equilibrium state. Considering the SLD of dPMMA and toluene, the fractions of PMMA and toluene are estimated to be 0.65 and 0.35, respectively; therefore, the volume expansion ratio of the dPMMA film in the solvent annealing in toluene vapor is 1.5. This is in good agreement with the expansion ratio of the thickness. This indicates that the spin-coated PMMA film in solvent annealing is not deformed laterally but expanded in the thickness direction.

The dynamics of the PMMA chain can be examined by the NR measurement of a 5-layered thin film of dPMMA and hPMMA. The translational diffusion of the polymer chain at the interface of the dPMMA and hPMMA results in an increase in the interface width between the dPMMA and hPMMA layers. Therefore, the diffusion dynamics of the PMMA chain is examined by the time dependence of the interface width between the dPMMA and hPMMA layers [18–20].

Figure 2a, b show the NR spectra and SLD profiles before and during the solvent annealing with toluene. Before the annealing, besides the interference fringe corresponding to the total thickness, the Bragg peaks due to the correlation of the 20-nm layers of dPMMA and hPMMA were observed at q of 0.45 and 0.72 nm^{-1} in Fig. 2a. By the solvent annealing, the peak position shifted to the low q region, indicating the increase in the thickness of each PMMA layer due to swelling. Moreover, the decrease of the intensity of the second Bragg peak indicates the blurring of the dPMMA/hPMMA interface. As shown in the SLD profile in Fig. 2b, it can be seen that the thickness of each layer and the interfacial width of the dPMMA and hPMMA layers increased by the solvent annealing in toluene vapor. Thus the solvent annealing induced the relaxation of the layered structure of a stacked spin-coated film. Figure 2c

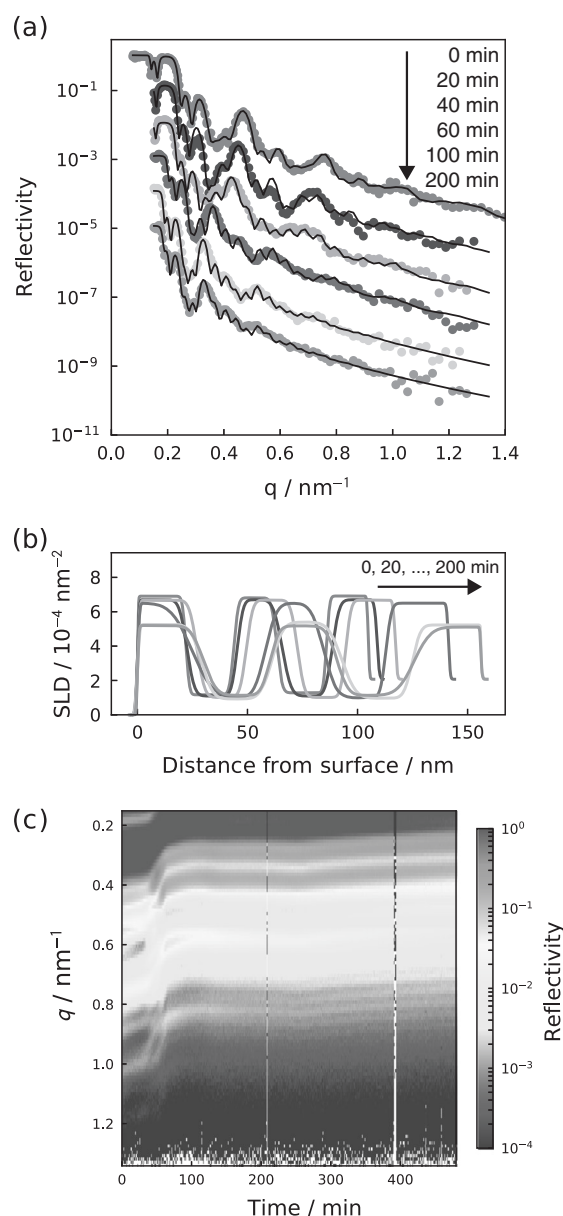


Fig. 2 Neutron reflectivity (a), scattering length density profile (b), and time evolution of reflection spectrum (c) for a 5-layered film of deuterated poly(methyl methacrylate) (PMMA) and hydrogenated PMMA in toluene vapor. The circles and black curves in a indicate the experimental data and theoretical profile, respectively. Each neutron reflectometric data is obtained in an acquisition time of 60 s

shows the time evolution of the NR spectrum for the 5-layered dPMMA/hPMMA film. Before the annealing time of 70 min, the interference peaks shifted to the low q region, and then the intensity of the second Bragg peak decreased gradually. This implies that the increase of the thickness by the absorption of toluene was followed by an increase in the interfacial width of the dPMMA and hPMMA layers.

The time evolution of the thickness, SLD, and interfacial width is shown in Fig. 3. This indicates that the increase of the thickness and the decrease of the SLD for the dPMMA

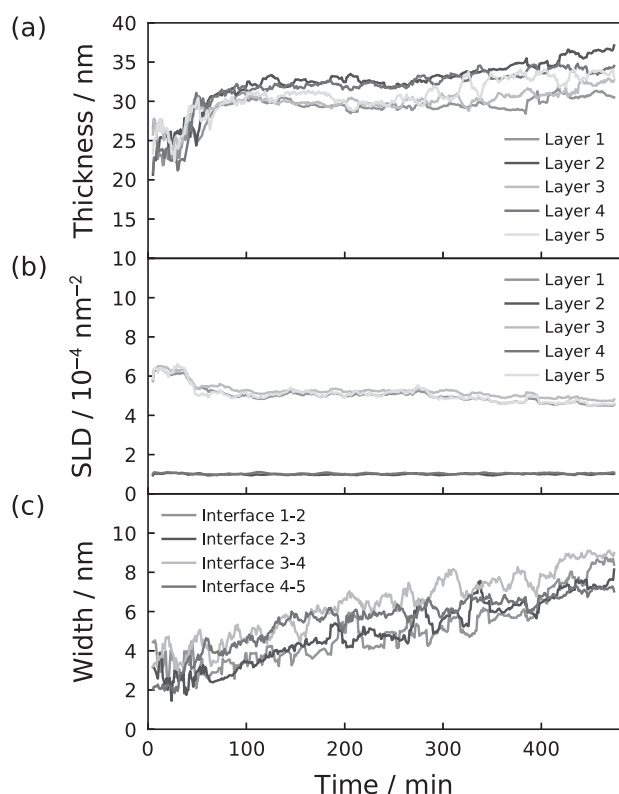


Fig. 3 Time evolution of the thickness (a), scattering length density (b), and interfacial width (c) of the 5-layered thin film in toluene vapor. The layer number is referred to Figure S1

and hPMMA layers occurred in the time region of 70 min. This time region corresponds to the swelling period observed for the dPMMA film. On the other hand, the interfacial width of the dPMMA and hPMMA layers increased after the swelling period as shown in Fig. 3c. This is due to the difference in the timescale of the toluene absorption and the relaxation time of the diffusion of the PMMA chain. The rate of the increase in the interfacial thickness is almost the same regardless of the distance from the surface, indicating that the solvent annealing method enables the equilibration of a polymer thin film almost homogeneously from the surface to the substrate interface.

The relaxation dynamics of the PMMA chain is compared with that in a thermal annealing process. Figure 4 shows the NR spectra and SLD profiles of the 5-layered PMMA film during thermal annealing at 413 K, which is 30 K greater than the glass transition temperature of spin-coated films of dPMMA and hPMMA with a thickness of 100 nm (Figure S2). This clearly indicates that the interfacial width near the surface increased with the annealing time while the width near the substrate remained almost constant. Figure 5 shows the time evolution of the thickness, SLD, and interfacial width for the 5-layered dPMMA/hPMMA film. The thickness and the SLD were constant because nothing was

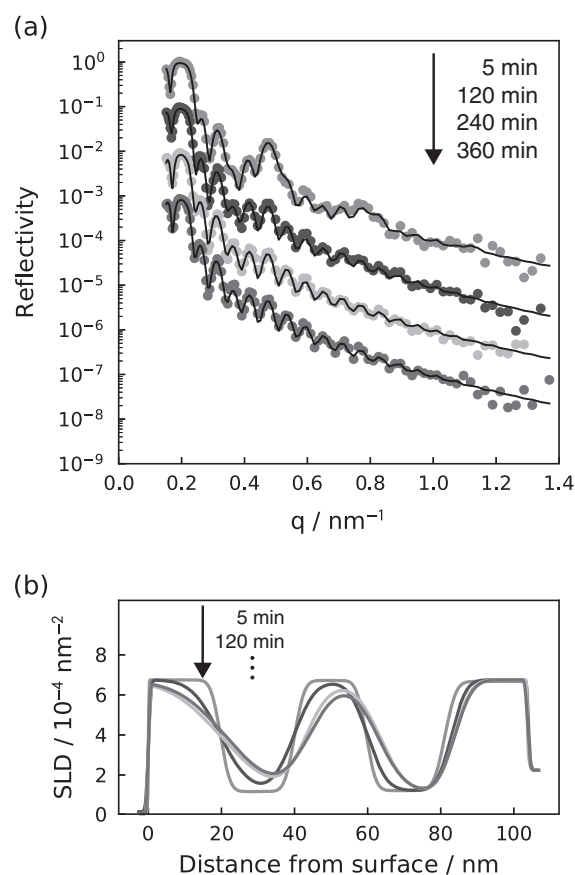


Fig. 4 Neutron reflectivity (a) and scattering length density profile (b) for a 5-layered poly(methyl methacrylate) film in a thermal annealing process at 413 K. The gray circles and black curves in a indicate the experimental data and theoretical profile, respectively. (color figure online)

absorbed from the atmosphere during thermal annealing. On the other hand, the interfacial width increased with the increase in the annealing time due to the inter-diffusion of the dPMMA and hPMMA chains. The remarkable difference from the chain dynamics in the solvent annealing is the depth dependence. The diffusion rate of the PMMA chain in the solvent annealing is almost independent of the depth in the sample film. On the other hand, the interfacial width close to the surface rapidly increased (the red curve in Fig. 5c), whereas the width near the substrate remained almost constant (the purple curve). From the time evolution of the interfacial thickness, the diffusion constant of the polymer chain was evaluated as the slope of the relationship between the squared interfacial width and the annealing time [18]. Table 1 summarizes the values of the diffusion coefficients in the solvent and thermal annealing processes (D_s and D_t , respectively) for the PMMA chain at the interfaces of the dPMMA and hPMMA layers. The diffusion constant at the interface of the layers 4 and 5 (at 20 nm from the substrate) is 50 times smaller than that at the interface of the layers 1 and 2 (at 20 nm from the surface), indicating that the

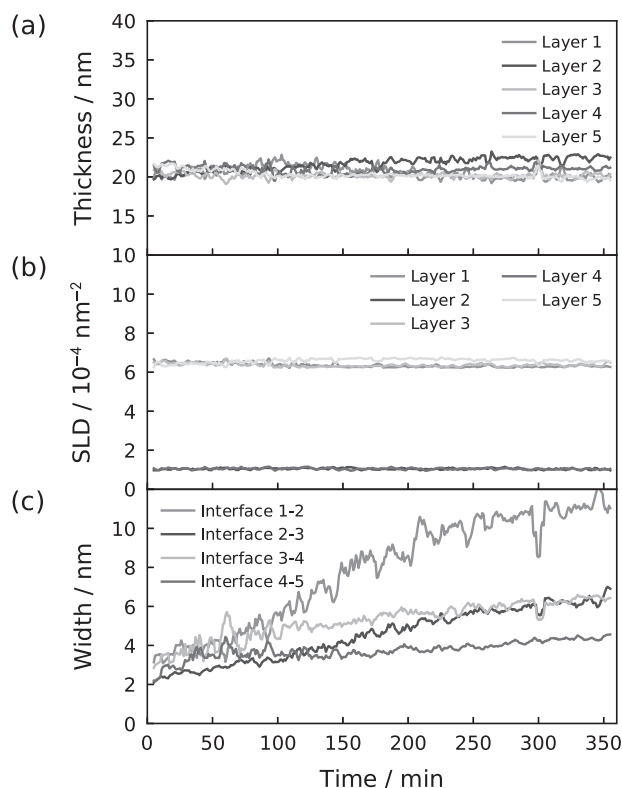


Fig. 5 Time evolution of the thickness (a), scattering length density (b), and interfacial width (c) of the 5-layered thin film in a thermal annealing process at 413 K. The layer number is referred to Figure S1

Table 1 Diffusion coefficients in solvent and thermal annealing processes

Interface	$D_s/10^{-17} \text{ cm}^2 \text{ s}^{-1}$	$D_t/10^{-17} \text{ cm}^2 \text{ s}^{-1}$
1–2	5.28	5.65
2–3	5.57	1.38
3–4	4.01	0.87
4–5	2.48	0.12

chain dynamics is constrained at the substrate. Such depth-dependent dynamics and the restricted mobility at a solid interface have been reported previously [7, 8, 21]. The mobility of the PMMA near the substrate appears more restricted compared to that of polystyrene [21]. This is due to the strong interaction between the polar side chain of PMMA and the hydrophilic native oxide layer formed on the Si substrate. Therefore, this result indicates that the thermal annealing of a polymer thin film results in an inhomogeneous relaxation. Whereas the polymer chain near the surface can be reached at an equilibrium state, it takes a long time to achieve the relaxation of the polymer chain near the substrate by a thermal treatment. On the other hand, the diffusion constant in solvent annealing is not strongly dependent on the distance from the surface. The diffusion

constant for the PMMA chain near the substrate in the solvent annealing at 296 K was greater than that at the middle of the PMMA film in the thermal annealing at 413 K, indicating that the solvent annealing equilibrated the polymer chain near the substrate interface under moderate conditions. A thermal annealing process has been reported to be unable to achieve the conformational relaxation of a segmental orientation at the substrate interface, whereas the equilibrium orientational state can be achieved using a solvent annealing method. [7] A solvent annealing treatment swells a polymer film from the surface to the substrate interface homogeneously; therefore, the polymer chain near the substrate gains enough mobility to overcome the interaction between the chain segment and the substrate. Thus the solvent annealing enables the equilibration of a polymer spin-coated film from the surface to the substrate interface.

Summary

The dynamics of PMMA chains in spin-coated films in solvent annealing processes in toluene vapor was studied. The neutron reflection measurement revealed that the spin-coated film was swelled by the toluene molecules absorbed from the atmosphere. The solvent molecule homogeneously distributed in the sample film and the fraction of the solvent in the PMMA film increased to 0.35. The depth dependence of the chain dynamics was examined using a stacked spin-coated film of dPMMA and hPMMA. Whereas a thermal annealing treatment cannot achieve an equilibrium state near the substrate of a spin-coated polymer thin film, an annealing method in solvent vapor induces the relaxation of the polymer film from the surface to the substrate interface at a room temperature. A detailed investigation of the relaxation behavior dependent on the annealing conditions, such as the solvent quality and the interaction with the substrate, would provide the further insight into the solvent annealing, and it would be useful for the precise control of the structures/properties of polymer thin films.

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Compliance with ethical standards

Conflict of interest The author declares that he has no conflict of interest.

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