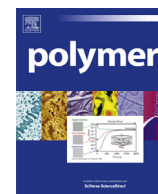




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## Observation of constraint surface dynamics of polystyrene thin films by functionalization of a silsesquioxane cage

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### ABSTRACT

The surface dynamics of polyhedral oligomeric silsesquioxane (POSS)-functionalized polystyrene (PS-POSS) thin films above the glass transition temperature were studied by grazing-incidence X-ray photon correlation spectroscopy in order to elucidate the effects of POSS at the end of the polystyrene chains. Much slower fluctuations were observed in the surface of PS-POSS thin films than in the polystyrene thin films, despite the negligible difference in their bulk viscosity. Quantitative analysis based on fluctuation-dissipation theorem indicated that there is a high-viscosity layer at the surface of the PS-POSS films, and that the substrate interface originated from POSS segregation.

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### 1. Introduction

The stability of polymer thin films is important in applications such as coatings and dielectric layers. Various methods of inhibiting dewetting of the layers have been developed, such as modifying the substrate, adding a nanofiller, and cross-linking the polymer [1–4]. Adding polyhedral oligomeric silsesquioxanes (POSS) to thin films is an efficient way to prevent them from dewetting. For example, Hosaka et al. stabilized polystyrene (PS) thin films by inhibiting dewetting with dispersed phenethyl-POSS and octacyclopentyl-POSS [5,6]. Miyamoto et al. also observed the inhibition of dewetting using octacyclopentyl-POSS-terminated PS thin films (PS-POSS) [7]. Miyamoto et al. found that the low molecular weight PS-POSS ( $M_n \approx 2000$ ) produced a large difference in the dewetting behavior, whereas the high molecular weight analog ( $M_n \approx 40,000$ ) produced a small difference [7]. They investigated the structures of

thin films by neutron reflectivity measurements, and discussed the suppression of dewetting in terms of the segregation of POSS at the surface and at the substrate interface. However, the question of how the segregation of POSS affects the inhibition of dewetting remains unsettled. To answer this fundamental question, the physical properties, such as viscosity and surface tension, of PS-POSS thin films rather than bulk PS-POSS should be examined.

Above the glass transition temperature, thermally agitated capillary waves are generated and damped continually at the surface of polymer thin films. The capillary wave spectra for homogeneous liquids have been studied by fluctuation-dissipation theorem, and they were described by using the viscosity, surface tension, and density in the thin films [8,9]. The dynamics of capillary waves have been experimentally studied by coherent scattering techniques, such as surface dynamic light scattering [10,11] and grazing-incidence X-ray photon correlation spectroscopy (GI-XPCS) [12–17]. Kim et al. performed GI-XPCS for linear PS thin films, and observed the capillary waves as predicted by the hydrodynamic theory for homogeneous thin films with bulk viscosity [18]. The unique properties of the thin films can be determined by

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the dynamical behavior of capillary waves on the films. Wang et al. measured the surface fluctuations of branched-polymer thin films and found that the viscosities calculated from the capillary wave spectra of thin films were 100 times higher than in the bulk [16]. Jiang et al. considered the dynamics of bilayer as a representative example of inhomogeneous thin films, and calculated the surface and interfacial dynamics of polymeric liquid bilayer films based on fluctuation-dissipation theorem [19].

The dynamics of the capillary waves reflects the physical properties of thin films in thin film conditions, and thus the inhomogeneity of thin films can be discussed by investigating the dynamics of capillary waves. In this study, we investigated the capillary waves on PS and PS-POSS thin films with different molecular weights ( $M_n = 40k, 25k, \text{ and } 2.3k$ ) by using GI-XPCS. For high molecular weight polymers ( $M_n = 40k$  and  $25k$ ), no major difference was observed between the PS and PS-POSS thin films, and the dynamics of the capillary waves were described by uniform viscosity and their viscosities were same as the bulk viscosity throughout the films. However, for low molecular weight polymers ( $M_n = 2.3k$ ), unique behavior was observed for the PS-POSS thin films. The difference between the PS and PS-POSS films may originate from the non-uniform structure of the PS-POSS thin films. We quantitatively discuss the capillary wave dynamics of PS-POSS thin films based on the fluctuation-dissipation theorem and discuss the physical properties of the films.

## 2. Experimental

PS and PS-POSS were prepared via living anionic polymerization. Tetrahydrofuran was transferred to a flask and cooled to  $-78^\circ\text{C}$ . After 5 min, *sec*-BuLi was added until the solution turned yellow. The flask was removed from the cooling bath and allowed to reach room temperature, upon which the solution became colorless. The solution was cooled to  $-78^\circ\text{C}$  again, and 1.07 M *sec*-BuLi solution in hexane/cyclohexane was added. Styrene was added, turning the mixture orange. After polymerization, half of the reaction mixture was poured into a large amount of methanol to prepare proton-terminated PS (Fig. 1(a)). The other half was quenched with  $\text{CO}_2$  to obtain carbonyl-terminated PS (PS-COOH), and precipitated in a large amount of methanol/HCl. The polymers were filtered and dried under vacuum at  $100^\circ\text{C}$  for 24 h. PS-POSS (Fig. 1(b)) was obtained by adding 1-(3-amino)propyl-3,5,7,9,11,13,15-isooctylpentacyclo [9.5.1.1<sup>3,9</sup>.1<sup>5,15</sup>.1<sup>7,13</sup>]octasiloxane (POSS(isooctyl)) (Hybrid Plastics) and 1,4-dioxane, *N,N'*-dicyclohexylcarbodiimide to a 20 wt % solution of PS-COOH in 1,4-dioxane. The mixture was stirred at  $50^\circ\text{C}$  for 12 h, filtered, and then poured into a large amount of hexane. The residue was filtered and dried under vacuum at  $100^\circ\text{C}$  for 24 h. The molecular weight and POSS content of the PS and PS-POSS are summarized in Table 1. The molecular weight of the PS moieties of PS-POSS40k, PS-POSS25k, and PS-POSS2.3k were the same as for PS40k, PS25k, and PS2.3k, respectively, because they were obtained from the same mixture.

We investigated the dynamics of the surface fluctuation of PS and PS-POSS thin films with  $M_n = 40k, 25k, \text{ and } 2.3k$  spin-coated on silicon wafer substrates using cyclopentanone as a solvent. Prior to the film coating, the silicon wafer substrates were cleaned by piranha solution ( $\text{H}_2\text{O}_2$  (30%)/ $\text{H}_2\text{SO}_4$  (70%) (v/v)) for 2 h, and rinsed with deionized water. Before the GI-XPCS measurements the thin films were annealed above the glass transition temperature for 24 h at 423 K for molecular weights of 25k and 40k, and for 12 h at 383 K for the molecular weight of 2.3k. No dewetting of thin films was observed after annealing and the GI-XPCS measurements.

The GI-XPCS measurements were performed on the BL19LXU beamline of SPring-8 with a 27-m-long undulator [20]. The

undulator source and Si(111) monochromator were tuned to an energy of 7.30 keV. The incident X-rays with transverse coherence of  $16 \times 125 \mu\text{m}$  ( $H \times V$ ) at the sample position were cut by slits with dimensions of  $20 \times 20 \mu\text{m}$ . The parasitic scattering was shielded by the other slits. The experimental geometry is illustrated schematically in Fig. 2. The sample was irradiated with partially coherent X-rays in a vacuum with an incident angle of  $0.14^\circ$ , which was below the critical angle for total external reflection. Direct and specular beam were hidden by beam-stop, and the off-specular diffuse scattering, in which exit angles  $\sim 0.25\text{--}0.6^\circ$ , from the polymer surface was recorded. The surface fluctuations in the irradiated area of polymer thin films were measured through the scattered X-rays. The scattered X-rays were detected by a two-dimensional hybrid pixel array detector (PILATUS 100K, DECTRIS) with a grid mask resolution enhancer (the effective detected area of each pixel is  $\sim 45 \mu\text{m}$  in diameter) mounted  $\sim 3.5$  m downstream of the sample [21–23]. For the measurements, 5000–20,000 images were taken with an exposure time of 10–300 ms and a readout time of 3 ms. During the GI-XPCS measurements, the thin films with  $M_n = 25k$  and  $40k$  were kept at 413 K, and the thin films with  $M_n = 2.3k$  were kept at 393 K. For investigating the thickness dependence, three different thickness of each polymer were measured: 50, 81, and 146 nm for PS40k; 50, 84, and 142 nm for PS-POSS40k; 44, 89, and 155 nm for PS25k; 44, 79, and 144 nm for PS-POSS25k; 47, 58, and 76 nm for PS2.3k; and 35, 52, and 61 nm for PS-POSS2.3k. The thicknesses were measured by an ellipsometer (MASS-103FH, Five lab.) or interferometer (Optical NanoGauge C11627, Hamamatsu Photonics).

During GI-XPCS measurements, the fluctuation of the scattering intensity,  $I(\mathbf{q}, t)$ , at a scattering vector  $\mathbf{q}$ , is obtained in a time series,  $t$ , and the intensity time-autocorrelation function  $g_2(\mathbf{q}, t)$  is evaluated as

$$g_2(\mathbf{q}, t) = \langle I(\mathbf{q}, t')I(\mathbf{q}, t' + t) \rangle / \langle I(\mathbf{q}, t') \rangle^2, \quad (1)$$

where the angle brackets indicate time-averaging. In the evaluation,  $g_2(\mathbf{q}, t)$  is averaged over all pixels within area belonging to  $|\delta\mathbf{q}_{\parallel}| = 0.5 \times 10^{-3} \text{ nm}^{-1}$  where the vector  $\mathbf{q}_{\parallel}$  indicates the in-plane component of  $\mathbf{q}$ ,  $q_{\parallel} = |\mathbf{q}_{\parallel}| = \sqrt{q_x^2 + q_y^2}$ . To check the radiation damage, all the  $g_2(q_{\parallel}, t)$  for last 1000 frames were compared to that for first 1000 frames. In the present study, the deviations were small enough compared to error bars shown in figures later.

The glass transition temperature,  $T_g$ , was measured by differential scanning calorimetry with a colorimeter (EXSTRA DSC-6000, Seiko Instruments Inc.). The viscosities,  $\eta$ , of bulk polymers were measured by using a rotational rheometer (Physica MCR101, Anton Paar). To determine the surface tension,  $\gamma$ , the contact angles,  $\theta$ , of four from the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide [ $C_n\text{mim}$ ][ $\text{Ntf}_2$ ] ( $n = 2, 4, 6, 10$ ) ionic liquids were measured on thin films of PS25k, PS40k, PS-POSS25k, and PS-POSS40k at 413 K and PS2.3k and PS-POSS2.3k at 393 K  $\gamma$  was determined by linear extrapolation of the surface tension data of the ionic liquids [24] to  $\cos\theta = 1$ . The measured values of  $T_g$ ,  $\eta$ , and  $\gamma$  are summarized in Tables 2 and 3.

X-ray photoelectron spectroscopy (XPS) depth profiles (PHI 5000 VersaProbe, ULVAC-PHI) were obtained with an Ar gas cluster ion beam gun (GCIB) with a monochromatic Al-K $\alpha$  X-ray source (1486.6 eV) [25,26]. The Ar GCIB gun was operated at a 2.5 kV accelerating voltage and a 5 nA beam current. The photoelectron take-off angle was maintained at  $45^\circ$ . High-resolution C 1s, Si 2p and O 1s spectra were acquired at 0.1 eV steps for PS-POSS2.3k (44-nm-thick), PS-POSS25k (105-nm-thick) and PS-POSS40k (120-nm-thick) thin films.

Grazing incidence small angle scattering (GI-SAXS) measurements were performed at BL45XU beamline in SPring-8 [27]. The

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