

Structural Characterization of Surface-grafted Poly (Vinyl Alcohol) on Silicon Wafer

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Grafted-from poly(vinyl alcohol) (PVA) brush on inorganic surfaces is potentially applicable to various surface functional materials. In this study, the molecular aggregation states of PVA brush thin film in the dried state were analyzed by X-ray diffraction. PVA brush was prepared by surface-initiated polymerization of vinyl acetate (VAc) from alkylbromide-immobilized silicon wafer using 2,2'-azobis(isobutyronitrile), ethyl iodoacetate for 18 h at 343 K, and followed by hydrolysis in acidic solution for 12 h at 323 K. Both the IR and XPS spectra revealed that the hydrolysis of PVAc brush gave a PVA brush. The crystalline states of PVA brush were characterized by wide-angle X-ray diffraction and grazing incidence X-ray diffraction measurements. No crystalline diffraction of PVA was observed from the PVA brush surface on a silicon wafer, although the spin-cast thin film formed a crystalline structure. These differences were thought arise from the influence of a polymer-substrate interfacial interaction and the anchoring states of polymer brush to restrict the molecular reorganization for crystallization.

Key words: Polymer brush, Surface-initiated radical polymerization, GIXD, PVA, Vinyl acetate

1. INTRODUCTION

Polymer brush is a new kind of nanostructure that has recently emerged and has been extensively investigated.¹ The peculiar properties of polymer brush at the liquid interface have been examined in many studies, for example, a hydrophilic polymer and polyelectrolytes brushes have attracted much attention due to effective modifications, such as wettability², adhesion³, friction⁴, and so on. However, the crystallization behavior of crystalline polymer brush has never been studied. The authors have wondered if crystalline polymer covalently attached to the substrate at one end could form a crystalline structure. In principle, densely grafted polymer chains stretch away from the surface in a perpendicular direction to form a brush-like conformation due to the cross-over among neighboring chains. The polymer chains in low-density brush would be extended and laid on the surface because they adsorb to the surface to cover the substrate surface. Consequently, there may be a competition between the orienting action of the stretched polymer chains and the chain-folding tendency to form the crystalline structure. In addition, the anchoring effect of polymer brush might also restrict crystallization. The motivation for this research is to clarify the difference in crystalline lamella structures between polymer brush thin film and spin-cast film. In this study, the authors focused on a poly(vinyl alcohol) (PVA) as a crystalline polymer. PVA has been researched for many years and widely used in many fields such as fibers, films and adhesives.

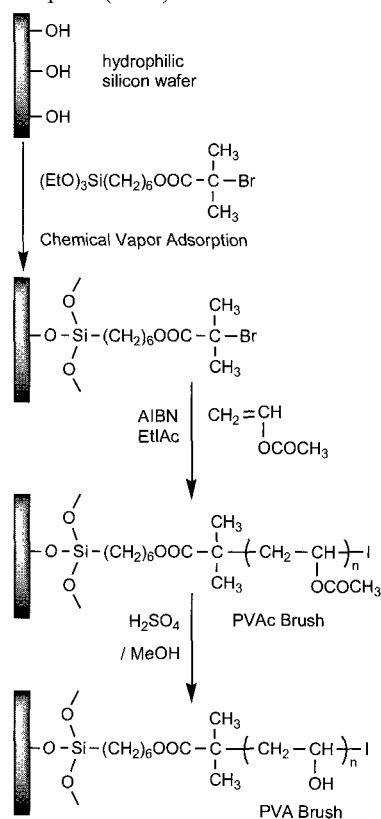
PVA is usually obtained by hydrolysis of poly(vinyl acetate) (PVAc), and a controlled or living

polymerization system of VAc should therefore be required to prepare well-defined and high-density polymer brush. However, controlled radical polymerization (CRP) of VAc has been quite difficult because the propagating radical of VAc is highly reactive due to its non conjugated nature. One successful CRP process is degenerative transfer polymerization with alkyl iodides.⁵⁻⁷ Recently, Sawamoto and his co-workers have reported the CRP of VAc with alkyl iodide as an initiator catalyzed by iron complex and metal alkoxides as additives.⁸ Matyjaszewski *et al.* also used alkyl iodide in the degenerative-transfer polymerization system to produce a PVAc with predictable molecular weight and narrow molecular weight distribution (MWD).⁹ Very recently, Kamigaito achieved stereospecific and molecular weight-controlled polymerization of VAc initiated with alkyl iodide in fluoroalcohol solvent.¹⁰ These reports have described that an alkyl iodide is suitable as a radical initiator for VAc, and the iodide restricts the decomposition of dormant species and the possible transformation of growing radicals during the propagating reaction. Therefore, the authors expected that surface-initiated radical polymerization of VAc with alkyl iodide could afford a well-defined PVAc brush, which could be successively converted to PVA brush by hydrolysis. This paper describes the characterization of the crystallinity of PVA brush thin film by wide-angle X-ray diffraction (WAXD) and grazing incidence X-ray diffraction (GIXD) measurements.

2. EXPERIMENTAL SECTION

2-1. Materials

VAc was purified by distillation over CaH_2 . Ethyl iodoacetate (EtIAc) (98 %, Aldrich) and 2,2'-azobis(isobutyronitrile) (AIBN) (Wako Pure Chemical Industries) were used as received. The synthesis and purification procedure of 6-triethoxysilylhexyl 2-bromoisobutyrate (BHE) have been reported elsewhere.^{2,11} The Silicon (111) wafer (Sumitomo Mitsubishi Silicon Co.) was cleaned by Piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 = 70/30$, v/v) and irradiated by a vacuum ultraviolet ray ($\lambda = 172$ nm) for 10 min under a pressure of 30 Pa. The obtained hydrophilic wafer was immersed in a vapor of BHE under dry nitrogen atmosphere at 428 K for 4 h to immobilize the radical initiator by using the chemical vapor adsorption (CVA) method.¹²



Scheme 1

2-2. Preparation of PVA brush by a grafting-from method

The general procedure for preparation of PVA brush is displayed in Scheme 1. The initiator-immobilized silicon wafer, AIBN, EtIAc, and VAc were introduced into a glass tube, and were degassed by repeating the freeze-and-thaw process three times. The polymerization reaction was carried out at 343 K for 18 h under argon atmosphere to simultaneously generate a polymer brush on substrate and a free polymer from EtIAc. The reaction mixture was poured into water to precipitate the free polymer, and the wafer was washed with toluene using a Soxhlet apparatus for 12 h. The number average molecular weight (M_n) and MWD of the free polymer were determined by size-exclusion chromatography (SEC) using polystyrene standards. The thickness of the

PVAc brush was estimated by an imaging ellipsometer (Moritex Corp.). Hydrolysis of the PVAc brush was employed by dipping PVAc-grafted substrates into the acidic solution consisting of methanol/sulfuric acid (95/5, v/v) for 12 h at 323 K with stirring. The wafer was washed several times with methanol and distilled water and dried under vacuum. The obtained PVA brush was annealed at 513 K and was gradually cooled to room temperature at 1 K/min under vacuum.

2-3. Preparation of cast films

The obtained free PVAc was also converted to PVA by hydrolysis under acidic condition similar to those mentioned above. The thin cast film was prepared by spin-casting the 1 wt% PVA/ H_2O solution onto silicon wafer using a spin-coater at a spinning speed of 3000 rpm for 30 s, followed by melting at 513 K and cooling to room temperature at 1 K/min *in vacuo*.

2-4. Characterization

XPS measurements were carried out on a APEX (ULVAC-PHI, Inc.) at 10^{-7} Pa using a monochromatic Al-K α X-ray source. IR spectra of the polymer brush grown on silicon substrates were measured in the transmission mode using a Spectrum One KY type (Perkin-Elmer) system coupled with a Mercury Cadmium Tellurium detector. SEC performed on a JASCO LC system equipped with a refractive index detector, which runs through three polystyrene gel columns using THF as an eluent at a flow rate of 0.6 mL/min at 313 K. The static and dynamic contact angles were measured on a DSA-10 (Krüss Co., Ltd) using water and methylene iodide (each droplet volume 1 μL). The surface free energy was calculated from Owens and Wendt's equation.¹³ The advancing, receding, and sliding contact angles of water (droplet volume 50 μL) were measured by a tilting plane.

WAXD measurements were carried out on a Rigaku RINT 2500V (Rigaku Co., Ltd) with a Cu K α X-ray source (40 kv, 200 mA). The wavelength of the incident X-ray was 0.1542 nm. The data collection time was 3.0 s per step at 0.05° intervals. GIXD measurements were performed for the films at 300 K with a six-axis diffractometer installed at a BL13XU beam line of SPring-8 (Japan Synchrotron Radiation Research Institute, Hyogo, Japan). The wavelength of monochromatized incident X-rays used in this study was 0.0997 nm. The data collection time was 3.0 s per step. The angular interval between steps was 0.05° . The incident angle was 0.08° below the critical angle of PVA. A sample cell purged with helium gas was used to prevent the specimen from oxidizing.

3. RESULTS AND DISCUSSION

3-1. Surface-initiated radical polymerization of VAc

Thin layer film of radical initiator was prepared on a flat silicon substrate by the CVA method using BHE vapor, followed by annealing and washing. The water contact angle of the substrate was 82° after immobilization of BHE, while the silicon wafer irradiated by VUV was lower than 5° , which is the typical value of hydrophilic silicon wafer. XPS spectra of initiator-immobilized silicon wafer showed the carbon signal (C_{1s}) at 285.0 eV associated with the

organic portion of the attachable initiator along with the bromide (Br_{3d}) signal at 71 eV. The signals attributed to C=O and C-O bonds were also observed at 289.0 and 286.5 eV, respectively. These results confirm the formation of densely covered thin layer of initiator on silicon wafer.

Free radical polymerization of VAc with AIBN in the absence of EtIAc produced a PVAc with a very broad MWD ($M_w/M_n = 3\sim 5$) and a larger M_n compared with the theoretical value estimated by the additive ratio of VAc and initiator. In contrast, a combination of EtIAc and AIBN polymerize VAc to afford the polymer having relatively narrow polydispersity ($M_w/M_n = 1.9\sim 2.0$). The authors suppose that the iodide transfer polymerization with EtIAc reduces the propagation rate and improves the initiator efficiency of polymerization. Surface-initiated polymerization with EtIAc gave the PVAc brush with 10 ~ 20 nm thickness on a silicon wafer. The M_n of surface-grafted PVAc cannot yet be directly determined, but, it is well known that M_n of polymer brush corresponds with that of the free polymer simultaneously formed by a controlled/living polymerization system in solution.^{14,15} In this study, a good relationship was observed between brush thickness and the M_n of the corresponding free polymer, as shown in Fig. 1. The grafting density calculated from the relationship between the M_n and the brush thickness was 0.09 chains/nm², which is not a particularly high value considering the molecular cross sectional area of PVA.

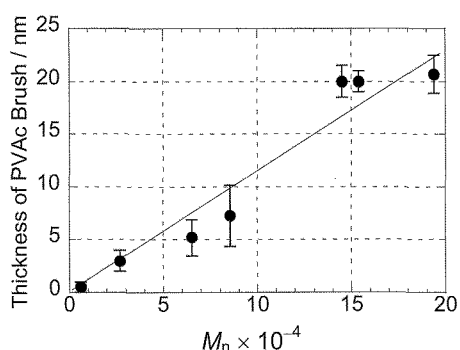


Fig. 1. Relationship of PVAc brush thickness and M_n of the corresponding free PVAc.

3-2. Hydrolysis of PVAc brush

Fig. 2 shows the IR spectra of PVAc brush before and after hydrolysis using acidic methanol. The absorption at 1750 cm⁻¹ due to the carbonyl group disappeared after the hydrolysis reaction, while the absorption at 3250 cm⁻¹ due to the hydroxyl group was increased. A similar result was obtained by XPS analysis. The split C_{1s} peaks were observed at 289.0, 286.5, and 285.0 eV attributed to the C=O, C-O, and C-C bonds of PVAc, respectively. After hydrolysis, the peaks due to C=O and C-O disappeared and a new peak at 286.5 eV for the C-OH bond appeared. These IR and XPS results were indicated that the PVAc brush was successfully converted to PVA brush. Hydrolysis of bulk PVAc also proceeded smoothly to give a PVA under the same condition. The water contact angle was also changed after the acidic hydrolysis, as shown in Fig. 2(c) and (d). Although similar advancing contact angles were obtained for both PVAc and PVA

brush surfaces, a large difference was observed in the receding contact angles of 42° and 20°. The surface free energy γ_{sv} was increased from 51 to 57 mN/m by hydrolysis. A 50- μL water droplet on the PVAc brush surface began to slide when the sample plate was tilted to 36°; in contrast, the sliding angle of the PVA brush surface was 50°. These results indicate that the wettability was enhanced because hydrolysis of the acetyl unit in PVAc afforded hydroxyl groups, which form hydrogen bonds with water molecules. The observed large sliding angle for PVA brush can be ascribed to the large contact angle hysteresis, which implies the reorientation of hydroxyl groups at the interface of water and PVA brush.

The thickness of the polymer brush also changed in response to hydrolysis. For example, the thickness of the PVAc brush decreased from 10 nm to 5 nm. As the molecular weights of VAc and the monomer unit of PVA are 86 and 44, respectively, the molecular weight of PVAc should also decrease by hydrolysis. In addition, PVA brush would shrink in response to hydrogen-bonding interaction between each hydroxyl group.

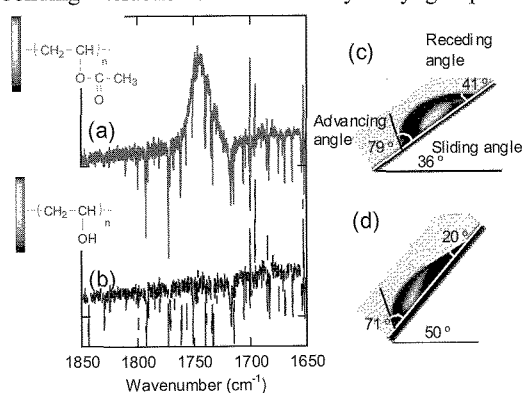


Fig. 2. FT-IR spectra of PVAc brush (a) and PVA brush (b) in carbonyl region. Side view of dynamic contact angles of PVAc brush (c) and PVA brush (d) using a 50 mL of water droplet.

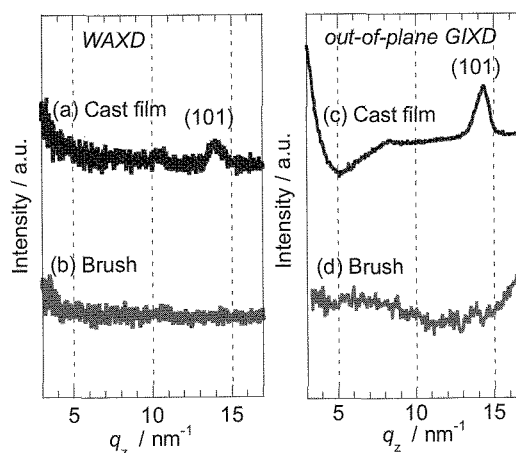


Fig. 3. WAXD and *out-of-plane* GIXD profiles of PVA cast film with 15 nm thickness (a) (c), and PVA brush with 5 nm of thickness (b) (d). The wavelength of WAXD was 0.1542 nm, and that of GIXD was 0.0997 nm. Incident angle was 0.08°.

3-3. Crystalline states of PVA brush

Fig. 3 shows the WAXD and *out-of-plane* GIXD profiles of PVA brush 5 nm in thickness and PVA cast film 15 nm in thickness. The scattering vector (q) was defined as $(4\pi/\lambda) \sin\theta$. All samples were once annealed at 513 K for 10 min, and gradually cooled to room temperature. As mentioned above, the M_n values of free polymer for spin casting and polymer brush are supposed to be same. The WAXD profile of PVA spin-cast film showed a peak around at $q_z = 14.2 \text{ nm}^{-1}$ attributed to the (101) diffraction peak of PVA, but, no diffraction peak was observed in brush film, as shown in Fig. 3(b). Therefore, a crystalline structure was formed in the bulk PVA thin film, but not in dried brush film. In order to analyze the outermost surface structure, GIXD measurements were carried out. The *out-of-plane* GIXD profile of spin-cast film in Fig. 3(c) shows a (101) diffraction peak at $q_z = 14.2 \text{ nm}^{-1}$. In contrast, GIXD profile of PVA brush film shows no peak due to a crystalline structure, as can be observed in Fig. 3(d). Additionally, an *in-plane* GIXD measurement of PVA brush was also performed, but no crystalline diffraction was observed. These results suggest that dried PVA brush film is in the amorphous state.

As a control experiment, the film thickness dependence of *in-plane* GIXD was performed for PVA thin film. The diffraction peaks at $q_{xy} = 14.2, 16.1, \text{ and } 28.8 \text{ nm}^{-1}$ attributed to (101), (200), (202) diffractions, respectively, were clearly observed by *in-plane* GIXD measurement of spin-cast film 100 nm in thickness. With a decrease in the film thickness, the diffraction peak intensities were also decreased. In the case of crystalline polymer thin films, the crystalline states and morphology might be largely influenced by a polymer-substrate interfacial interaction. Recently, Rafailovich and her coworkers analyzed an ultrathin film of polyethylene by GIXD to find the strong dependence of crystal orientation on substrate properties such as the surface free energy of the surface.¹⁶ Despite their thickness of 15 nm, the bulk PVA thin films seem to be able to form crystalline states, even though the PVA chain should strongly interact with silicon wafer by hydrogen bonding to restrict the molecular motion. On the other hand, main-chain crystalline polymer brush with similar thickness could not form any crystal structures, probably due to the anchoring effect of the chain end. The grafting density of PVA brush prepared in this work was not particularly high, so the steric hindrance effect could be ignored. The chain length of the obtained PVA brush was long enough to cover the surfaces and to form crystallite. Therefore, the authors suppose that immobilization of the chain end on the surface restricts crystallization, resulting in an amorphous PVA brush film.

4. CONCLUSIONS

Surface-initiated radical polymerization of VAc in conjunction with iodide transfer reaction produced PVAc brush on silicon wafer. IR, XPS and contact angle measurements indicated that PVAc brush is successfully converted to PVA brush by hydrolysis upon exposure to sulfuric acid/methanol solution. The crystalline states of PVA brush were characterized by WAXD and GIXD. No crystalline diffraction peak of PVA was observed from the PVA brush surface on a silicon wafer, although the

spin-cast thin film formed a crystalline structure. These differences were thought to arise from the influence of a polymer-substrate interfacial interaction and the anchoring structure of polymer brush to restrict the molecular reorganization for crystallization.

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