Preparation and Surface Properties of Poly(vinyl alcohol) Brush

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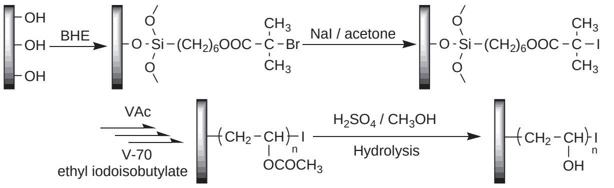
Poly(vinyl alcohol) (PVA) brush was prepared by surface-initiated iodine-transfer polymerization of vinyl acetate (VAc) from a silicon wafer and successive hydrolysis of acetyl groups. The adhesion forces of PVA and PVAc brush surfaces were measured by atomic force microscopy.

The adhesive of poly(vinyl alcohol) (PVA) is fundamentally important in many industrial processes and applications such as coating, spraying, and hot-melting methods.[1] The authors have an interest in polymer brush with regard to development of a new adhesive surface consisting of PVA. One of the most exciting expectations for the use of polymer brush is its potential for affecting a variety of different surface properties, ranging from adhesion to tribology on different substrates with high mechanical and thermal stability due to the covalent grafting of polymer chains.[2,3]

PVA is usually obtained by hydrolysis of poly(vinyl acetate) (PVAc); therefore, a controlled or living polymerization system of VAc should 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 owing to its nonconjugated nature. One successful CRP process is degenerative-transfer polymerization with alkyl iodides.[4–6] Recently, Sawamoto et al. have reported the CRP of VAc with alkyl iodide as an initiator, iron complex as a catalyst, and metal alkoxides as additives.[7] Matyjaszewski and Iovu have also used alkyl iodide in the degenerative-transfer polymerization system to produce PVAc with predictable molecular weight and narrow molecular weight distribution (MWD).[8] Very recently, Kamigaito et al. achieved stereospecific and molecular weight-controlled polymerization of VAc initiated with alkyl iodide in fluoroalcohol.[9] These reports have described that an alkyl iodide is a suitable radical initiator for VAc and that the iodide restricts the decomposition of dormant species and the possible transformation of growing radicals during the propagation reaction. The authors, therefore, expected that surface-initiated radical polymerization of VAc with alkyl iodide would afford a well-defined PVAc brush, which could be successively converted to PVA brush by hydrolysis. The surface characterization of PVAc and PVA brush was carried out by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and adhesion force measurements.



Scheme 1.

The general procedure for preparation of PVA brush is displayed in Scheme 1. The silicon (111) wafer (Ferrotec Silicon Co.) was cleaned by Piranha solution ($H_2SO_4/H_2O_2 = 70/30$, v/v) and irradiated by a vacuum ultraviolet ray ($\lambda = 172\,\text{nm}$) for 10 min under a pressure of 30 Pa. The surface initiator, (2-bromo-2-methyl)propionyloxyhexyltriethoxysilane (BHE),[10] was immobilized on the hydrophilic wafer by the chemical vapor adsorption method.[11] The BHE-immobilized silicon wafer was converted to (2-iodo-2-methyl)propionyloxyhexyltriethoxysilane-immobilized silicon wafer by immersion in sodium iodide/acetone solution at 333 K for 72 h.[12] The conversion of C–Br bond into the C–I was estimated to be 70% using an atomic ratio determined by XPS analysis. The initiator-immobilized silicon wafer, 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70), ethyl iodoisobutylate, and VAc were introduced into a glass tube, which was degassed by repeating the freeze-and-thaw process five times. The polymerization reaction was carried out at 303 K for 12 h under argon atmosphere to simultaneously generate a polymer brush on a substrate and a free polymer from ethyl iodoisobutylate. 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 using polystyrene standards. The thickness of the PVAc brush was estimated by an imaging ellipsometer (Moritex Co.). Hydrolysis of the PVAc brush was accomplished by dipping PVAc-grafted substrates into a 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. The obtained PVAc and PVA brush was annealed at 373 K under vacuum.

Free radical polymerization of VAc with V-70 in the absence of ethyl iodoisobutylate produced a PVAc with a very broad MWD ($M_w/M_n = 3$–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 ethyl iodoisobutylate and V-70 polymerized VAc, resulting in the polymer having relatively narrow polydispersity ($M_w/M_n = 1.7$–2.0). The authors suppose that the iodine-transfer polymerization with ethyl iodoisobutylate reduces the propagation rate and improves the initiator efficiency of polymerization. Surface-initiated polymerization with ethyl iodoisobutylate gave the PVAc brush with 10–30 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 polymerization system.[13] In this study, a good relationship was observed between brush thickness and the M_n of the corresponding free polymer. The grafting density calculated from the relationship

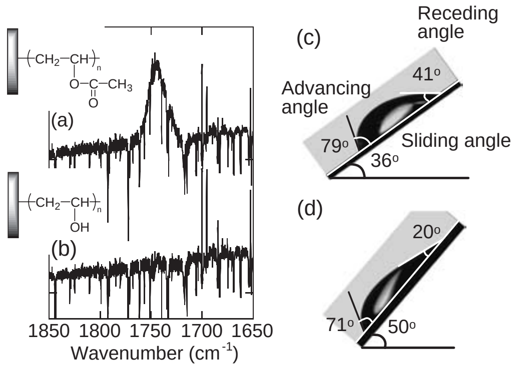


Figure 1. FT-IR spectra of PVAc brush (a) and PVA brush (b) in carbonyl region. Side view of dynamic contact angles of PVAc (c) and PVA brush (d).

between the M_n and the brush thickness was 0.09 chains/nm^2, which is not a particularly high value considering the molecular cross sectional area of VAc.

FT-IR measurements of polymer brush on double-sided polished silicon substrates were carried out using a Spectrum One (Perkin-Elmer). An incident p-polarized IR beam struck the sample at a Brewster's angle to reduce the interference fringes. Figures 1a and 1b show 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} attributed to the hydroxy group was increased. XPS spectrum of PVAc brush showed the split C_{1s} peaks at 289.0, 286.5, and 285.0 eV, corresponding 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 corresponding to the C–OH bond appeared. These IR and XPS results indicated that the PVAc brush was successfully converted to PVA brush without cleavage of grafting chains from silicon wafer. The water contact angle was also changed after the acidic hydrolysis, as shown in Figures 1c and 1d. Although similar advancing contact angles were observed for both PVAc and PVA brush surfaces, a large difference appeared in the receding contact angles of 41 and 20°. The surface free energy γ_{SV} using Owens and Wendt's equation[14] 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 surface wettability was enhanced because hydrolysis of the acetyl unit in PVAc afforded hydroxy 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 hydroxy groups at the interface of water and PVA brush.

The adhesion force of brush surface was measured by E-sweep (SII NanoTechnology Inc.) at 293 K in vacuo (10^{-6} Pa). The curvature radius of the used cantilever (Sphere Tips CONT, Nanosensors) made of SiO_2 was 1000 nm. The bending spring constant of the cantilever tip was 0.24 N/m. The cantilever approached and retracted to the brush surface at a rate of 20 nm/s. The magnitude of the adhesion force was determined from 50 individual force–distance curves. All measurements were performed using the same cantilever. As shown in Figure 2, fairly larger adhesion force was observed in PVAc brush surface compared with PVA brush. The authors suppose that the contact area of the cantilever tip on the PVAc brush surface was larger than that of PVA brush because of the low glass-transition temperature and the low modulus of PVAc. The glass-transition temperature of PVAc is 310 K, which is lower than that of PVA, 358 K. PVAc brush thin film would be compressed and deformed by the cantilever tip to give a large contact area.

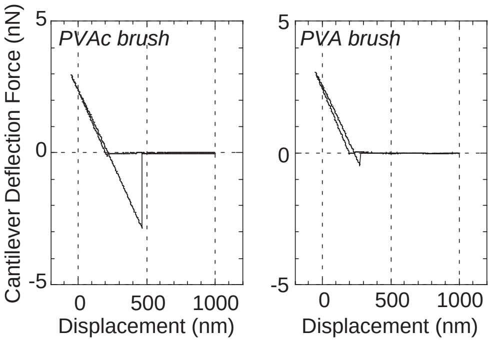


Figure 2. Force curves observed at the surface of PVAc (left) and PVA brush (right).

In conclusion, surface-initiated radical polymerization of VAc in conjunction with an iodine-transfer reaction produced PVAc brush on silicon wafer. IR, XPS, contact angle, and adhesion force measurements indicated that PVAc brush was successfully converted to PVA brush by hydrolysis.

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