ACS APPLIED MATERIALS & INTERFACES
Research Article
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Scaffold for Growing Dense Polymer Brushes from a Versatile Substrate

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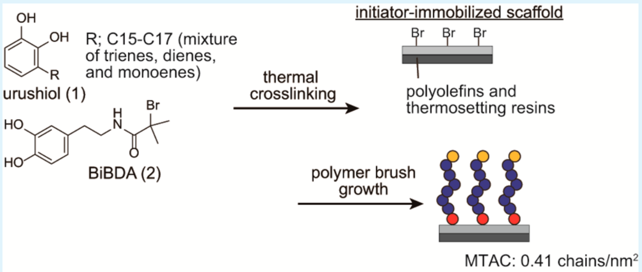
Ⓢ *Supporting Information*



ABSTRACT: We have demonstrated a universal approach to growing polymer brushes from various substrates. Urushiol was mixed with initiator-containing catechol, and it was spin-coated or cast on various substrates. Because urushiol is strongly adhered to various substrates, the thin film can serve as a general scaffold for grafting polymer brushes from various substrates. Note that the film was formed even onto the surface of polyolefins and thermosetting resins that are known as chemically inert materials to functionalize the surface. Moreover, the initiator-immobilized scaffold showed mechanical robustness and chemical inertness because of the flexible long unsaturated hydrocarbon side chain of urushiol. After the grafting of polyelectrolyte PMTAC polymer brushes, the material obtained exhibited hydrophilicity, typical of PMTAC. The concept shown here could provide a general approach for grafting practical polymer brushes from various substrates.

KEYWORDS: *urushi, urushiol, polymer brushes, catechol derivatives, scaffold, surface modification*

1. INTRODUCTION

Surfaces and interfaces have a strong influence on material properties such as adhesion, friction, electrical properties, and biocompatibilities.[1] Therefore, precise control of surfaces and interfaces is indispensable for the promotion of innovation in future science and technology. Polymer brushes are layers of ultrathin polymers in which chain ends are covalently tethered to a substrate surface.[2−4] Because the surface properties can be tunable by chemical structure of surface-grafted polymers, surface modification with polymer brushes is useful for functionalizing material surfaces. In particular, the preparation of polymer brushes by the "grafting from" method has extensively been researched because such a method provides high-density polymer brushes with extended morphology.[5−7] Because the method involves the anchoring of initiator on substrate surfaces, various anchoring method are well designed depending on the substrates.[8−16] However, they are subject to certain restrictions in a variety of substrates. For example, initiator-bearing silane coupling agents that are often used to immobilize initiators on silicone and glass substrates are useless for other substrates such as plastics. Accordingly, the immobilization of initiating species independent of the physical and chemical characteristics of the substrate is strongly desired. Especially, surface modification of chemically inert materials such as polyolefin and thermosetting resins is meaningful.

The use of scaffold layer is a universal approach to growing polymer brushes from a versatile substrate. Gopalan and coworkers reported a method using initiator-containing epoxy resin.[17] In that approach, thermal cross-linking of an epoxide moiety creates a scaffold layer (which they called a "mat") on a substrate. Polymer was then grafted from the immobilized initiators. The use of initiator-containing catechol derivatives is also proposed.[18−21] It is known that catechol derivatives is useful for the surface modification of various artificial materials.[22−24] Catechol derivatives were directly reacted with substrate surfaces through the coordination of the two OH groups of catechol, and a thin scaffold layer with several nanometers thick was formed through the oxidative reaction. Here, we report a permanent surface modification method using catechol derivative urushiol. Urushiol is the main component of the natural resin urushi (oriental lacquer), and a highly cross-linked structure is formed by either oxidative polymerization or thermal treatment.[25−28] The main difference between urushiol and other catechol derivatives is the presence of a long $C_{15}-C_{17}$ hydrocarbon side chain in the 3-position (Figure 1a). Note that the flexible urushiol side chain imparts robustness to the material.[29] Therefore, urushiol thin film can serve as a tough scaffold layer to immobilize the initiating species onto a substrate. Toughness of the scaffold is indispensable for practical applications, for example, in friction control and antibiofouling materials. The concept shown here could provide a general method for grafting practical polymer brushes from various substrates such as plastics, metals,and

Received: December 25, 2013
Accepted: February 4, 2014
Published: February 4, 2014

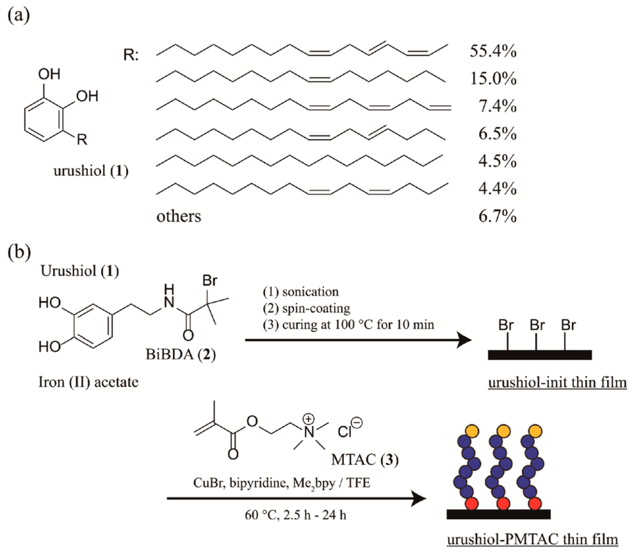


Figure 1. (a) Chemical structure of urushiol and (b) preparation procedure for initiator-immobilized urushiol thin film and the following PMTAC-grafted urushiol thin film.

ceramics, as well as of natural materials such as cellulose because of its superior adhesion characteristics.

2. EXPERIMENTAL SECTION

2.1. Materials. The raw urushi (***Caution***: *uncured urushiol can cause an allergic skin rash on contact and should be handled carefully!*) used in this study was purchased from Kanwa-do Urushi Club Co. Ltd., Shiga, Japan. The material was prepared from sap collected from *Rhus vernicifera* in Japan. Urushiol was extracted from the sap according to the literature.[27] CuBr (Wako Pure Chemicals, 98%) was purified by washing it with acetic acid and ethanol, and was dried under vacuum prior to use. 2-(Methacryloyloxy)ethyltrimethylammonium chloride) (MTAC) was prepared as previously reported.[30] Other chemicals were used as received without further purification.

2.2. Synthetic Procedure of Catechol-Containing Surface Initiator. (*N*-{2′-(3′,4′-Dihydroxyphenyl)ethyl} 2-bromopropionamide (BiBDA) was synthesized as an initiator-bearing catechol derivative as follows: Dopamine hydrochloride (2.0 g, 10.5 mmol) was poured into 20 mL of methanol. The white suspension turned transparent after the addition of 1.46 mL of triethylamine (10.5 mmol). The solution was continuously stirred at 0 °C, and 2-bromoisobutyryl bromide (1.3 mL; 10.5 mmol) in 2 mL of tetrahydrofuran (THF) and triethylamine (2.19 mL; 15.8 mmol) in 2 mL of methanol were alternately added to the solution. The solution was kept at pH 9 during the process. It was then warmed to room temperature and continuously stirred for 1 h. Then its liquid component was removed by evaporation. The remaining crude products were again dissolved in 50 mL of chloroform and purified by sequentially washing the resulting solution with 1 N HCl, water, and brine. The solution was dried over anhydrous Na_2SO_4 overnight, and the final products were obtained after evaporating all volatiles in vacuo (yield: 1.32 g, 41.6%). The characterization of BiBDA was done by ^1H NMR and Fourier transform infrared (FT-IR) spectroscopic measurements.[18,31]

2.3. Preparation of Initiator-Immobilized Urushiol (urushiol-init) Thin Films. Initiator-immobilized urushiol thin films were prepared similarly to our previous work.[29,32] Urushiol was first dissolved in ethanol. Iron(II) acetate was then added to the solution to initiate the oxidative reaction of urushiol to form oligomers. Next, BiBDA was added to the solution. The molar ratio of urushiol to BiBDA was varied from 100/0 to 0/100. The iron(II) acetate concentration was fixed at 0.5 mol equiv relative to the total amount of urushiol and BiBDA. The solution was then homogenized using a Branson Sonifier ultrasonic cell disruptor. After diluting the solution with ethanol as necessary, it was spin-coated or cast on various substrates to obtain urushiol-init thin films. The substrates were typically 2.0 × 2.5 cm^2. The thickness of the films was adjusted to be in the range of several tens of nanometers to several micrometers by changing the coating method or the concentration of the solution. After air exposure for 5 min, the samples were cured at 100 °C for 10 min while pressing them with a flat Si wafer to obtain flat, dense thin films. The pressing was performed using a nanoimprinter (NM-0501-T, Meisho Kiko) with a static pressing force of 2.5 kN.

2.4. PMTAC Brush Grafting. The surface-initiated atom transfer radical polymerization (ATRP) of MTAC was performed as follows to prepare grafted poly(MTAC) (PMTAC):[30] An urushiol-init thin film on a certain substrate (typically 2.0 × 2.5 cm^2), copper(I) bromide [CuBr] (0.1 mmol), and 4,4-dimethyl-2,2-bipyridine (0.2 mmol) were placed in a flask fitted with a stopcock and dried by repeated degassing and purging with argon. A Si substrate modified with [((2-bromo-2-methylpropionyl)oxy)hexyl]triethoxysilane (BHE) was also placed in a flask for the reference.[33] Moreover, ethyl 2-bromoisobutyrate was introduced to obtain free polymers. Then, 1.01 M MTAC in 2,2,2-trifluoroethanol (TFE, 20.0 mL, 20.2 mmol) was added to the solution. After oxygen elimination through several freeze−pump−thaw cycles, the polymerization reaction was conducted at 60 °C for 24 h in argon atmosphere. The reaction was stopped by opening the glass vessel to air, and the sample was washed with methanol to remove any free polymer adsorbed on the surface. Then, the sample was dried under reduced pressure at 80 °C for 1 h.

2.5. Measurements. X-ray photoelectron spectroscopy (XPS) was performed using an XPS-APEX instrument (Physical Electronics Co., Ltd.) with a monochromatic Al−Kα X-ray source at a power of 150 W and a pressure of 1×10^{-6} Pa. The takeoff angle of X-rays was fixed as 45° for the measurement. Ultraviolet−visible (UV−vis) absorption and FT-IR reflection absorption spectra were recorded on a Shimadzu UV-3500PC and a Bruker Optics VERTEX70 spectrophotometer equipped with a Seagull system (Harrick Scientific), respectively. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were performed using a Keyence VE7800 and an Agilent 5500 microscope equipped with a standard cantilever (Olympus: OMCL-AC160TS-W2) in noncontact AC mode, respectively. Young's modulus of the material was determined by strain-induced elastic buckling instability for mechanical measurement (SIEBIMM) experiment. Ultimate tensile strength (σ) and ultimate elongation (ε) were determined by bulge test. Details of the bulge test and SIEBIMM experiment are given in our previous papers.[34,35] Static water contact angle (CA) measurement was performed using a DSA10 Krüss contact angle measurement system equipped with an automatic liquid dispenser and a monochromatic CCD camera. During the CA measurement, temperature and humidity were controlled at 23.5 °C and 60%, respectively. QCM measurements were conducted by Affinix QN using 27 MHz QCM gold electrodes (initium Inc., Japan).

3. RESULTS AND DISCUSSION

3.1. Fabrication of Urushiol-init Thin Film. Urushiol-init thin film was fabricated by either spin-coating or casting a mixture of urushiol, BiBDA and iron(II) acetate in ethanol, followed by baking at 100 °C for 10 min (Figure 1b) (see the Experimental Section). Hard solid films were obtained regardless of BiBDA concentration, as confirmed by a pencil test (see Supporting Information). A 2.3-μm thick urushiol thin film showed a level of 3H hardness on a Si substrate. The FT-IR reflection absorption measurement of a sample containing 20 mol % BiBDA revealed that thermal Diels−Alder cycloaddition and/or addition to double bonds occurred during curing (see Figure S1 in the Supporting Information).[29] Absorption peaks at 3015 and 945 cm^{-1}, which respectively are originated from the stretching vibration and out-of-plane bending mode of double bonds in the urushiol side chain, mostly disappeared upon baking at 100 °C for 10 min. In contrast, the stretching vibration of alkyl bromide were observed at 668 cm^{-1} even after baking, indicating that the bromide end group of BiBDA remained intact during baking. XPS measurements were also conducted to determine the chemical species presenting at the surface (see Figure S2 in the Supporting Inforamtion). The measurement was done after soaking the sample in TFE at 60 °C for 6 h. The C/N/O/Fe atomic ratio of the scaffold was calculated to be 79.2/0.78/18.0/2.0. The value was in good agreement with that of the calculated value in seed (81.2/0.77/16.1/1.92) (see the Supporting Information in detail). Small difference of oxygen may be attributed from the slight oxidation. The deconvolution of C_{1s} peak revealed that 18% of hydroxyl group of urushiol was changed to quinone structure through the air oxidation. It also indicated that acetoxy group of iron(II) acetate was remained intact in the cured film.

3.2. Characteristics of Urushiol-init Thin Films. From the UV−vis absorption measurement, 100 nm thick urushiol-init thin films on a quartz plate showed a broad absorption peak at around 350−900 nm (λ_{max} = 586 nm) because of a typical metal-complex absorption band, called the ligand-to-metal charge-transfer (LMCT) band (see Figure S3 in the Supporting Information).[29] However, the transmittance at 450 nm was over 80% and the film was apparently colorless. The LMCT absorption was monotonically increased with the increase of film thickness. The color of a cast film with ∼4−5 μm thickness was black (which are called "piano black"), and the transmittance at 450 nm was almost 0 as confirmed by the spectroscopic measurement. Although the absorption spectra were nearly independent of the molar ratio of BiBDA, small increase of the LMCT absorption was observed with the increase of BiBDA ratio. It may be attributed to the difference of the coordination interaction of these catechol derivatives with different substituents.

To evaluate the mechanical properties of urushiol-init films, SIEBIMM and bulging experiments were conducted (see the Supporting Information for the procedure). Figure 2a shows the relationship between the molar ratio of BiBDA and the Young's modulus of the films determined by SIEBIMM. Young's modulus of the urushiol-init films increased as the molar ratio of BiBDA was increased. However, the film with several tens of nanometer thickness easily fragmented into small pieces when its molar ratio of BiBDA exceeded 50 mol %. Figure 2b shows the ultimate tensile strength (σ) and ultimate elongation (ε) of the films determined by bulge test. As shown in Figure 2b, σ and ε decreased as the amount of BiBDA was increased, suggesting that the urushiol-init thin film became hard but brittle. Such brittleness was also found in oxidative polymerized 2-(3,4-dihydroxyphenyl)ethylamine and 3,4-dihydroxy-L-phenylalanine (DOPA) thin films that have a highly cross-linked but inflexible structure.[29] It is clear that the long hydrocarbon side chain of urushiol imparts flexibility to the material.

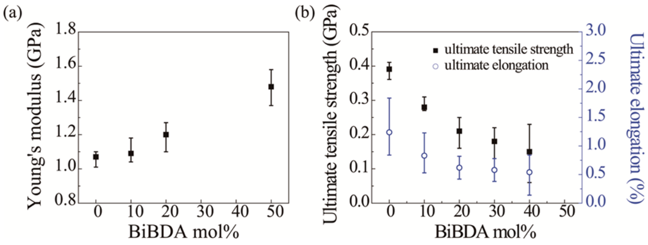


Figure 2. Mechanical properties of urushiol-init thin films as functions of molar ratio of BiBDA: (a) Young's modulus (GPa) of films determined by SIEBIMM experiment, and (b) ultimate tensile stress (σ) and ultimate elongation (ε) of films determined by bulge test.

To evaluate their solvent tolerance, we immersed 80 nm thick urushiol-init films on a Si substrate in various solvents, namely, water, methanol, ethanol, THF, N,N-dimethylformamide, dimethyl sulfoxide, toluene, chloroform, acetone, and TFE. When the BiBDA concentration was less than 50 mol %, no change in surface morphology was observed by atomic force microscopy (AFM) even after immersion at 60 °C for 24 h. The films remained intact even in TFE, the solvent for the following PMTAC grafting. The films showed a smooth surface with an ∼0.8 nm root-mean-square (RMS) roughness within a 5 × 5 μm^2 area (see Figure S4 in the Supporting Information). BiBDA molecules remained intact against solvent treatment, as confirmed by FT-IR measurement. Moreover, no mass loss was found in QCM measurements before and after the immersion. Because both urushiol and BiBDA have a catechol structure, BiBDA molecules were covalently immobilized in the urushiol matrix by curing. When the BiBDA concentration was more than 50 mol %, the thin films were damaged by the immersion in TFE. The film with 100 mol % BiBDA dissolved completely. This may be due to the less degree of cross-linking in the side chain of urushiol at high BiBDA concentrations. The high mechanical strength and the high chemical resistance are major advantages of urushiol-init thin films over conventional catechol thin films as a scaffold for growing polymer brushes.

Subsequently, the adhesiveness of urushiol-init films to various substrates was evaluated by standard tape test methods (ASTMD3359: see Supporting Information for details). Urushiol thin films were fabricated on various substrates by either spin coating (∼80 nm thickness) or casting (∼4−5 μm thickness), and the adhesiveness was evaluated from 0B (poor) to 5B (good). The BiBDA concentration was fixed at 20 mol %. Interestingly, both spin-coated and cast films strongly adhered onto various substrates such as a Si wafer, glass, polymers, and metals (Table 1). Note that the urushiol-init thin films adhered onto the surface of polyolefins and thermosetting resins. Unfortunately, urushiol-init thin films cannot form on a poly(tetrafluoroethylene) surface because of the dewetting of the material during the procedure.

Table 1. Adhesiveness of Urushiol-init Thin Films to Various Substrates.[a]

substrate	spin-coating[b]	casting[c]
vacuum UV-treated Si	5B	5B
glass	5B	5B
polytetrafluoroethylene (PTFE)	–[d]	0B
polyethylene (PE)	5B	4B
polypropylene (PP)	5B	4B
polyethylene terephthalate (PET)	5B	4B
polystyrene (PS)	5B	5B
acrylic resin	5B	5B
cupper plate	5B	5B
SUS304	5B	4B
ceramics	5B	5B
melamine resin	4B	4B
phenolic resin	5B	4B

[a] Evaluated from 0B (poor) to 5B (good). [b] 80 nm thickness. [c] 4−5 μm thickness. [d] Dewetting during the coating.

3.3. PMTAC Grafting on Urushiol-init Thin Film.

To demonstrate the usability of urushi-init thin films as a scaffold, the surface-initiated ATRP reaction of MTAC was conducted from the surface (Figure 1b) (see Experimental Section for details). PMTAC was chosen because the surface of polyelectrolyte polymer brushes exhibits superior surface properties such as hydrophilicity and antifouling property.[36] The results of the FT-IR reflection absorption measurement (Figure S1) confirmed that a polymer brush layer formed on the surface through the reaction at 60 °C for 24 h. The PMTAC-grafted urushiol ("urushiol-PMTAC", hereafter) thin film showed new absorption peaks at 3054 and 2170 cm^{-1}, which correspond to the stretching and combination vibrations of the quarternized amine group, respectively. Subsequently, XPS measurements were conducted on MTAC-grafted urushiol thin films (see Figure S2 in the Supporting Information). After the grafting, new characteristic peaks at 197 and 270 eV, which were assigned to Cl_{2p} and Cl_{2s} of PMTAC, were observed. No peaks originating from iron(II) acetate was found, indicating that the surface was fully covered with PMTAC. In contrast, no peaks originating from PMTAC were found when the reaction was performed on an urushiol thin film without BiBDA molecules. These results indicate that PMTAC was grafted from BiBDA initiator immobilized in the scaffold matrix.

AFM observation was performed on the urushiol-PMTAC thin films to evaluate the surface morphology and density of PMTAC polymer brush layers. The films showed a smooth surface with a roughness of about 3.0 nm in RMS roughness within 5 × 5 μm^2 area (see Figure S5 in the Supporting Information). This means that PMTAC polymer brushes were homogeneously grown from the surface of the urushiol-init film. The thickness of the grafted PMTAC polymer brushes was determined by measuring the thickness difference between the urushiol-PMTAC and urushiol-init thin films. The thickness of the PMTAC layer that was determined by AFM observation in dried state was about 120 nm, which was comparable to that of the polymer brush layer directly grafted from a Si wafer (134 nm thickness). Molecular weight (M_n) and molecular weight distribution (M_w/M_n) of PMTAC were 195,000 and 1.23 which were separately determined by size-exclusion chromatography using unbond (free) polymer. Then, grafting densitiy (σ) was calculated from the thickness of the polymer brush (see the Supporting Information). The calculated σ was 0.41 chains·nm^{-2}, which is considerably higher than those of other "very dense" brushes of PMTAC that was grafted from the Si wafer (0.20 chains·nm^{-2}).[30] We have reported the same tendency when surface-initiated ATRP was performed on bromo-functionalized polyolefins in order to grow poly(methyl methacrylate) polymer brushes.[37] This may be due to the grafting of polymers from the inner layer of the scaffold matrix. Similar surface roughness and the grafting density was obtained when PMTAC was grafted from a urushiol-initi thin film on a polyethylene (PE) sheet.

Subsequently, static contact angle was measured to evaluate the wettability of the samples. When PMTAC was grafted from an urushiol-init thin film on a Si substrate with 20 mol % BiBDA, static water contact angle changed from 62 ± 2° to 12 ± 3° after the grafting. When air bubbles and *n*-hexadecane droplets attached to the surface in water, the contact angles of urushiol-PMTAC were 148 ± 2° and 144 ± 3°, respectively. It is clear that the surface became hydrophilic, which is characteristic of PMTAC. These values are slightly different from that of the directly grown PMTAC polymer brushes from the Si substrate (see Table S1 in the Supporting Information). The difference may arise from the higher surface roughness of urushiol-PMTAC film in comparison with the smooth Si substrate. The static water contact angle of the sample was 13 ± 3° when the urushiol-PMTAC film was fabricated on a PE film. Figure 3 shows the static water contact angles on Si with different molar ratios of BiBDA. Interestingly, the water contact angle saturated at a molar ratio of BiBDA of over 10 mol %, indicating that the change in wettability was accomplished with a small number of polymer brushes. Moreover, the thickness of polymer brushes was almost independent from the BiBDA ratio. These results indicate that the surface wettability of the substrate could be simply controlled independently of the characteristics of substrates.

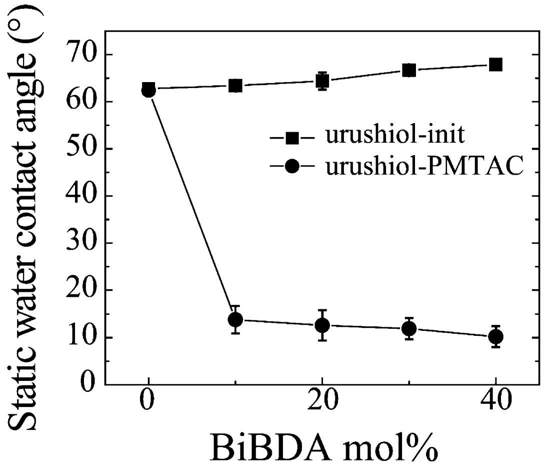


Figure 3. Static water contact angles of thin films with different molar ratios of BiBDA; (a) urushiol-init (square) and (b) urushiol-PMTAC (circle) on Si substrate.

4. IMPLICATION AND PROSPECTS

We demonstrated that urushiol thin films can serve as a general scaffold for grafting polymer brushes from various substrates. In this study, polyelectrolyte PMTAC polymer brushes were grafted as an example. The material obtained exhibited hydrophilicity, typical of PMTAC. For the general use of scaffolds for polymer brush growth, they should satisfy the following three criteria. The first is strong adhesion to various substrates. Note that the scaffold adhered phenol resin because of their good affinity as a result of their similar chemical structures. The surface modification of phenol resin with preservation of its excellent bulk properties is difficult. For example, oxidization by corona discharge treatment or plasma treatment to improve the hydrophilicity of a material is useless because the material surface gradually becomes hydrophobic in air.[38] Our method may overcome this problem to eliminate the disadvantages of phenol resin, such as poor wettability, chemical inertness, and low adhesion properties. The second criterion is covalent linkage with initiating species that enables strong immobilization of the initiating species within the scaffold matrix. This prevents the exfoliation of polymer brushes from the matrix. Because both urushiol and BiBDA have a catechol structure, covalent linkage was formed between them during curing. Halogen-bearing silane coupling agents such as BHE may also be useful as initiating species because organic functional silane forms covalent linkage with urushiol.[39]

Although BHE themselves are useful for only Si and glass substrates, the variety of applicable substrates is expanded by using urushiol.

Urushiol thin films satisfy the above two criteria, but these are the linked to the catechol structure. As confirmed by the evaluation of mechanical properties and the solvent tolerance, urushiol side chain imparts the robustness and the chemical resistance to the material. These two are the advantages of urushiol-init thin films over conventional catechol thin films, and these properties are necessary for some applications, e.g., as friction and bioantifouling materials. Moreover, the chemical inertness widens the variety of applicable grafting polymers with various polymerization techniques. Toughness including chemical inertness and robustness is the third criterion and is only accomplished by the use of urushiol. Because urushiol satisfies the three criteria mentioned above, urushiol thin films are a promising material for use as a scaffold for the grafting of various polymer brushes from various substrates. Moreover, their combination with "substitutable" polymer brushes in which the polymer structure can be changed after polymer brush growth will find breakthrough applications in industry.[40] Precise control of the surface properties of urushiol films such as wettability, friction property, adhesion property, and biocompatibility is possible through the choice of polymer structure.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Pencil hardness test procedure; FT-IR, XPS, and UV−vis absorption spectra of samples; AFM images of samples; evaluation procedure of physical properties of samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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H.W. and A.T. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Prof. Dr. Hiroshi Jinnai (JST, ERATO) for helpful discussion.

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