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A Versatile Method of Initiator Fixation for Surface-Initiated Living Radical Polymerization on Polymeric Substrates

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ABSTRACT: A facile yet robust approach to chemically fix an initiating group for atom transfer radical polymerization (ATRP) on various polymeric substrates is described. Conventional free radical copolymerization was conducted with methyl methacrylate (MMA), 2-(2-bromoisobutyryloxy)ethyl methacrylate (an ATRP initiator-carrying monomer, BIEM), and 2-((4-azidobenzoyl)oxy)ethyl methacrylate (a photoreactive phenylazide-carrying monomer, ABEM) in *N*,*N*-dimethylformamide at 75 °C, giving a random (statistical) copolymer. Thin films of the obtained copolymer were fabricated on poly(ethylene terephthalate) (PET) film surface by spin-casting a toluene solution of the terpolymer and were immobilized on the PET substrate via UV-irradiation using the photoreactivity of the phenylazido units. The surface-initiated ATRP (SI-ATRP) of poly(ethylene glycol) methacrylate (PEGMA) mediated by a copper complex was carried out in water at 30 °C in the presence of a sacrificial (free) initiator and the initiator-immobilized PET film as the solid substrate. The polymerization proceeded in a living fashion. The molecular weight of free polymer increased with polymerization time while retaining low-polydispersity index, and more importantly, the thickness of the poly(PEGMA) graft layer increased as a function of polymerization time with a reduced graft density (surface occupancy) as high as 0.5 in all examined time. This initiator immobilization technique was applied to various polymeric substrates including polystyrene, polypropylene, polyethylene, and polylactide. The fabrication of micropatterned polymer-brush surfaces was also demonstrated by photopatterning the initiator layer followed by SI-ATRP.

Introduction

Grafting polymers on solid surfaces has long been of great importance for science and technology not only to control surface properties, e.g., wettability, friction, and adhesion, but also to fabricate intelligent materials and devices, e.g., sensors, membranes, and batteries.[1−12] Among the grafting techniques developed so far, surface-initiated living radical polymerization (SI-LRP) is one of the most promising approaches. It features the robustness and versatility inherent to LRP techniques, providing excellent control over molecular weight and polydispersity of graft polymers and affording high graft density.[13−17] It has been applied to solid surfaces of different shapes including flat substrates, fine particles, and porous or tubelike structures, and of different materials including metal, metal oxide, carbon, and organic polymers.[18]

Achieving SI-LRP on organic polymeric substrates requires the introduction of polymerization initiating sites on their surface. Several strategies based on different techniques have been attempted. Ulbricht et al. functionalized a poly(ethylene terephthalate) (PET) film, which was carboxylated by oxidative hydrolysis beforehand, with atom transfer radical polymerization (ATRP)-initiating groups via a two-step chemical reaction.[19] Yamamoto et al. modified a polyethylene (PE) film with tribromomethyl ATRP initiator via a three-step chemical reaction, and alternatively they also irradiated a similar film by UV and γ-rays to generate radical sources such as peroxides on the surface which was used as a radical initiator for reverse ATRP.[20−22] Matyjaszewski et al. irradiated a polypropylene (PP) film by UV in the presence of a benzophenone derivative carrying a 2-bromoisobutyrate ATRP initiator to produce initiating sites on the film surface.[23] Wilén et al. irradiated a poly(vinylidene fluoride) film by electron beam to produce radicals on the film surface, and these radicals were immediately reacted with vinylbenzyl chloride to surface modify with benzyl chloride ATRP initiators.[24] Huck et al. modified PET and poly(ethylene naphthalate) films by plasma oxidation to create hydroxyl groups on their surface, followed by the reaction with an ATRP initiator-carrying trichlorosilane.[25] We also used O_2-plasma treatment to produce peroxides as initiating moieties on a polymeric substrate and carried out reversible addition−fragmentation chain transfer (RAFT) polymerization on the polymeric surface.[26]

In this paper we present an alternative approach to introduce ATRP-initiating sites on polymeric substrates by utilizing an azido group which can be, upon UV irradiation, converted to nitrene highly reactive to various organic groups.[27] This feature of azide groups was used to modify the surface of many organic substrates such as polystyrene (PS),[28] polylactide (PLA),[29] polyurethane,[30] PET[31] films, or even fiber[32] and leather.[33] Matsuda et al. reported that a thin film of vinyl polymer containing phenyl azide group could be chemically immobilized on an organic polymeric substrate by UV irradiation, and they claimed that this technique can be carried out on any given polymeric substrate and at a given area if applied a photomask during UV irradiation.[34−36] We here have applied this chemistry to the immobilization of initiating sites for ATRP on a number of polymeric substrates.

Our strategy consists mainly of four steps, as shown in Figure 1. The first step is the synthesis of a random (statistical) copolymer containing both phenyl azide groups and ATRP-initiating sites as side chains. We will refer to this copolymer to be AIP hereafter, and its chemical structure is given in Figure 1. The second step consists in making a film of AIP of several tens of nanometers in

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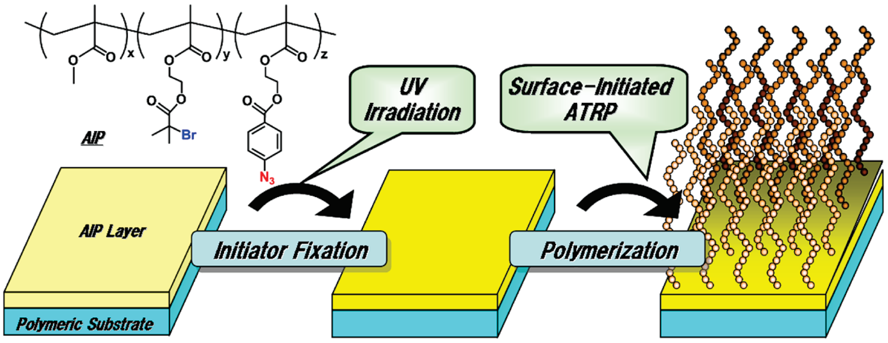

Figure 1. Chemical structure of phenyl azide and atom transfer radical polymerization (ATRP) initiator-carrying random copolymer (AIP) and schematic representation for the immobilization of AIP on polymeric substrate followed by surface-initiated ATRP.

thickness by spin-casting on a polymeric substrate. The third step is to irradiate the AIP-coated film by UV light in order to chemically immobilize the AIP layer on the polymeric substrate using the photochemical reaction of azide groups. This irradiation will lead to the formation of covalent bonds between AIP and the polymeric substrate as well as cross-links throughout AIP itself. The fourth step is the surface-initiated atom transfer radical polymerization (SI-ATRP) on the initiator-immobilized polymeric substrate so as to produce a polymer brush. It will be described below that this strategy provides a polymeric substrate grafted with well-defined polymer chains with a high surface density and, moreover, that it is easily applicable to various substrates made of many types of organic polymers.

Experimental Section

Materials. A water-soluble ATRP initiator (PEGBr) was synthesized by the reaction of poly(ethylene glycol) methyl ether (Aldrich, molecular weight ~550) and 2-bromoisobutyryl bromide (Tokyo Chemical Industries, Co., Ltd., TCI, Tokyo, Japan, 97%) in the presence of triethylamine (Wako Pure Chemicals, Osaka, Japan, 99%), following previously described procedures.[37,38] 2,2′-Bipyridine (bipy, 99%) was purchased from Nacalai Tesque Inc., Osaka, Japan. Copper(I) chloride (CuCl, 99.9%) and copper(II) dichloride ($CuCl_2$, 98%) were purchased from Wako Pure Chemicals. Methyl methacrylate (MMA, 99%) was obtained from Nacalai Tesque, Inc., and purified by passing through a column of activated basic alumina. 2-(2-Bromoisobutyryloxy)ethyl methacrylate (BIEM) was synthesized by the reaction of 2-hydroxylethyl methacrylate (HEMA, Wako Pure Chemicals, 99%) and 2-bromoisobutyryl bromide in the presence of triethylamine, following a procedure described elsewhere.[39] 2-((4-Azidobenzoyl)oxy)ethyl methacrylate (ABEM) was synthesized by the reaction of HEMA and 4-azidobenzoyl chloride, obtained from 4-azidobenzoic acid (TCI, 98%) and thionyl chloride (TCI, 98%), in the presence of triethylamine.[40] 2,2′-Azobis(isobutyronitrile) (AIBN, 98%) was purchased from Wako Pure Chemicals. Poly(ethylene glycol) methyl ether methacrylate (PEGMA; molecular weight = 475) was purchased from Aldrich and purified by passing through an activated alumina column. PET pellets (intrinsic viscosity = 0.58) were purchased from Aldrich. Water was purified by a Milli-Q system (Milli-Q Advantage, Nippon Millipore Ltd., Tokyo, Japan) to a specific resistivity about 18 MΩ·cm.

Synthesis of a Random Copolymer with Azido Groups and ATRP-Initiating Sites. A Pyrex glass tube was charged with MMA (1.90 g, 20.0 mmol), BIEM (6.65 g, 23.8 mmol), ABEM (1.30 g, 4.72 mmol), AIBN (79 mg, 0.48 mmol), and DMF (70 g) under ambient atmosphere. The system was degassed by three freeze−pump−thaw cycles and sealed off under vacuum. The polymerization was carried out in a shaking oil bath thermostated at 75 °C for 7 h. The polymerization mixture was poured into a mixed solvent of hexane/diethyl ether = 2/8 to obtain crude polymer, which was redissolved in dichloromethane and reprecipitated in a mixture of *n*-hexane/diethyl ether = 8/2 and further purified by reprecipitation with a system of dichloromethane (solvent) and *n*-hexane (nonsolvent). The final product was dried *in vacuo* at room temperature overnight to obtain a slightly yellow powder (yield = 70%). Gel permeation chromatography (GPC) (PMMA calibrated): number-average molecular weight M_n = 20 000 and polydispersity index $M_w/M_n = 1.84$.

Preparation of AIP-Immobilized Polymeric Substrates. A thin film of PET was prepared by spin-coating a 4 wt % PET solution in *o*-chlorophenol, which had been passed through a Teflon filter (Cosmonice Filter S, pore size = 0.45 μm, Nihon Millipore Ltd., Tokyo, Japan) beforehand, onto a silicon wafer, which had been surface-treated with *p*-aminophenyltrimethoxysilane beforehand, at 600 rpm for 10 s and then 3000 rpm for 60 s. The spin-coated PET film was annealed under vacuum at 80 °C for 15 min and then cooled immediately to room temperature. A 0.5 wt % solution of AIP polymer in toluene was spin-coated onto the PET film at 600 rpm for 10 s and then 3000 rpm for 60 s. The coated film was irradiated by a UV lamp (H-400P, Toshiba, Japan, 400 W) for 5 min and finally washed with toluene to remove unreacted AIP. Commercially available PET, PE, PP, and polylactide (PLA) films were similarly spin-coated with an AIP solution in toluene and UV-irradiated. For polystyrene (PS) substrate, acetic acid was used as a solvent for spin-coating AIP.

Surface-Initiated Polymerization of PEGMA with AIP-Immobilized Polymeric Substrates. In a typical run, bipy (13.0 mg, 83.2 μmol) was dissolved in water (6 g) and deoxygenized by bubbling with dry argon. The deoxygenated mixture was transferred into an argon-purged Schlenk tube with CuCl (0.40 mg, 4.04 μmol) and $CuCl_2$ (5 mg, 37.2 μmol) and stirred with a magnetic stir bar at room temperature until no trace of copper powder was observed in the system. After this solution was added to a deoxygenated mixture of PEGMA (2 g, 4.21 mmol) and PEGBr (15.0 mg, 21.0 μmol), the reaction solution was immediately transferred into an argon-purged Schlenk tube containing the AIP-immobilized polymeric substrate. All the procedures were carried out in Schlenk tubes with rubber septum through cannulas under dry argon atmosphere. The polymerization was carried out in an oil bath thermostated at 30 °C and, after a prescribed time *t*, quenched to 0 °C. An aliquot of the solution was taken out for NMR measurement to estimate monomer conversion and for GPC measurement to determine molecular weight and its distribution. The polymeric substrate was thoroughly washed with water to remove physisorbed free polymer.

Measurements. GPC analysis was carried out at 40 °C on a Shodex GPC-101 high-speed liquid chromatography system equipped with a guard column (Shodex GPC KF-G), two 30 cm mixed columns (Shodex GPC KF-804 L, exclusion limit = 400 000), and a differential refractometer (Shodex RI-101). *N*,*N*-Dimethylformamide (DMF) containing 10 mM LiBr was used as an eluent at a flow rate of 0.8 mL/min. Poly(methyl methacrylate) (PMMA) standards were used to calibrate the GPC system. Sample

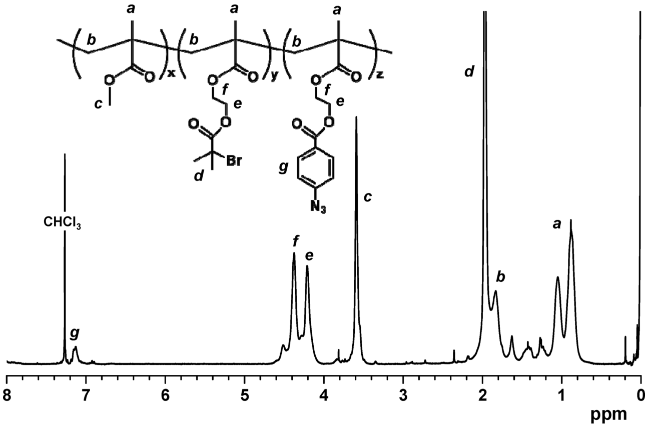

Figure 2. ^{1}H NMR spectrum of initiator-carrying random copolymer (AIP). The solvent was $CDCl_3$.

detection was also made with a multiangle laser light scattering (MALLS) detector (DAWN EOS, Wyatt Technology, Santa Barbara, CA) equipped with a Ga−As laser (λ = 690 nm). The refractive index increment, dn/dc, in DMF solution of poly(PEGMA) (PPEGMA) was determined to be 0.047 mL/g by a Wyatt Technology OPTILAB DSP differential refractometer (λ = 690 nm).

Ellipsometric analysis was performed on a variable angle-of-incidence spectroscopic ellipsometer (M-2000U, J.A. Woollam Co., Inc.). Measurements were taken at three incidence angles of 65°, 70°, and 75°. The ellipsometric angles were recorded in a wavelength range from 242 to 999 nm. The data were processed and fitted by the software WVASE32 (J.A. Woollam Co., Inc.). The thickness of the PPEGMA graft was converted to its weight assuming a bulk density of PPEGMA to be 1.0 g/cm^3.

Static contact angle measurements were performed at 20 °C and ambient humidity on a CA-X contact angle meter (Kyowa Interface Science Co., Ltd.) equipped with a video capture apparatus. A drop of water as a probe liquid (1 μL) was deposited on a sample surface with a microsyringe. Contact angles were measured at three different positions for each sample and averaged.

Results and Discussion

Synthesis of Random Copolymer Having Phenylazido and ATRP Initiator Groups (AIP). We have carried out the random (statistical) copolymerization of MMA (monomer to control the number of functional groups), BIEM (ATRP initiator-carrying monomer), and ABEM (pheny azide-carrying monomer) with AIBN in DMF at 75 °C. PMMA-calibrated GPC measurement of the purified polymer (AIP) revealed that the M_n and M_w/M_n values of the copolymer were 20 000 and 1.84, respectively. Figure 2 shows the ^{1}H NMR spectrum of AIP, from which the molar composition of the copolymer MMA:BIEM:ABEM was calculated to be 0.4/0.5/0.1, which is almost equal to the feed ratio. The molar composition is an important factor for the subsequent grafting. (For instance, the number of BIEM units affects polymer-grafting density. Note that 50% molar fraction of BIEM units provides sufficient number of initiating sites to achieve high grafting density of polymer, as will be described below.) The AIP copolymer was soluble in good solvents for PMMA.

Immobilization of AIP on Polymeric Substrates. To demonstrate the versatility of our strategy for the introduction of ATRP-initiating sites on the surface of polymeric substrates, we have used several types of polymeric substratesz spin-coated with AIP. To quantitatively characterize a series of processes from the initiator immobilization to the subsequent surface-initiated polymerization, we, at first, used a PET thin film coated onto a silicon wafer as a polymeric substrate because this system can easily be analyzed in terms of thickness by ellipsometry thanks to the high reflectivity of silicon. For this purpose, a PET thin film was prepared by spin-casting a 4 wt % PET solution in *o*-chlorophenol on a silicon wafer. Atomic force microscopic (AFM) measurement revealed the formation of the homogeneous PET film with a relatively smooth surface (mean square surface smoothness, rms = 1.3 nm) and the ellipsometric measurement determined its film thickness to be 110 nm on average. The PET film was subsequently coated with AIP by spin-coating a 0.5 wt % AIP solution in toluene. Ellipsometric measurement of the multilayer revealed a thickness of AIP layer of about 20 nm. The surface roughness of the AIP layer was confirmed by AFM to be similar to that of the PET first layer. The multilayer film was subjected to UV irradiation, washed with toluene, and analyzed by ellipsometry. Almost no change in the film thickness was detected before and after the processes of UV irradiation and washing. When a photomask was used during UV irradiation, the unexposed region of AIP layer almost completely disappeared after washing with toluene (*vide infra*). In addition, in a reference experiment we used poly(MMA-*r*-BIEM), a copolymer without ABEM units, instead of AIP. A thin film of this copolymer-coated PET surface was almost completely removed by toluene washing. These results indicate that AIP was immobilized through the photoreactivity of the phenylazido group of the ABEM units which can generate highly reactive nitrene to spontaneously form covalent bonds with neighboring hydrocarbons.[27] This immobilization method could be applied to various polymeric substrates including PE, PP, PS, PLA, PC, and so on. However, a choice of appropriate solvent for spin-coating of AIP solution should be required; otherwise, a polymeric substrate of interest would be damaged. For instance, we chose acetic acid as a cast solvent for the immobilization of AIP on a PS surface.

Surface-Initiated ATRP of PEGMA on AIP-Immobilized Polymeric Substrates. One of the most important requirements for the fabrication of a well-defined, concentrated polymer brush on a polymeric substrate is the proper choice of the polymerization media to prevent the polymeric substrate from swelling.[26] In a swollen substrate, chain can grow from its inside, forming some boundary layer of graft and substrate polymers, leading to a poorly defined graft system in both structure and properties, even if the graft amount may be large. Therefore, we decided to use water as a polymerization solvent, which is nonsolvent for all the polymeric substrates used here as well as the AIP layer.

We carried out the solution polymerization of PEGMA in water in the presence of the free ATRP initiator (PEGBr) and the AIP-immobilized PET film on a silicon wafer. The polymerization was carried out at 30 °C and catalyzed by mixed copper/ligand complexes (containing CuCl and $CuCl_2$) which had been well used in aqueous ATRP systems.[41,42] Figure 3 shows the first-order kinetic plot of monomer concentration for the polymerization. The plot is almost linear, indicating that the radical concentration stays constant during the polymerization. Figure 4 shows the evolution of M_n and M_w/M_n of the free polymer produced from the free initiator PEGBr as a function of monomer conversion. It can be seen that the M_n values increase in proportion to monomer conversion. However, the values of M_n estimated by PMMA-calibrated GPC ($M_{n,GPC}$) slightly deviated from the theoretical values $M_{n,theo}$ calculated from the initial molar ratio of monomer to the free initiator. This may be due to the difference in the hydrodynamic volume of the PMMA and the PPEGMA. To confirm this, GPC-MALLS

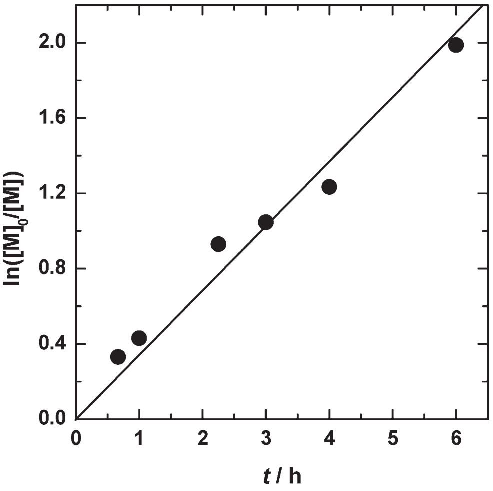

Figure 3. Plot of ln([M]$_0$/[M]) vs time for the solution polymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA) (25 wt %) in water at 30 °C in the presence of initiator-carrying random copolymer (AIP)-coated substrate (ca. 1 × 1 cm): [PEGMA]$_0$/[water-soluble atom transfer radical polymerization initiator (PEGBr)]$_0$/[copper(I) chloride (CuCl)]$_0$/[copper(II) dichloride (CuCl$_2$)]$_0$/[2,2′-biyridine (bipy)]$_0$ = 200/1/0.2/1.8/4.

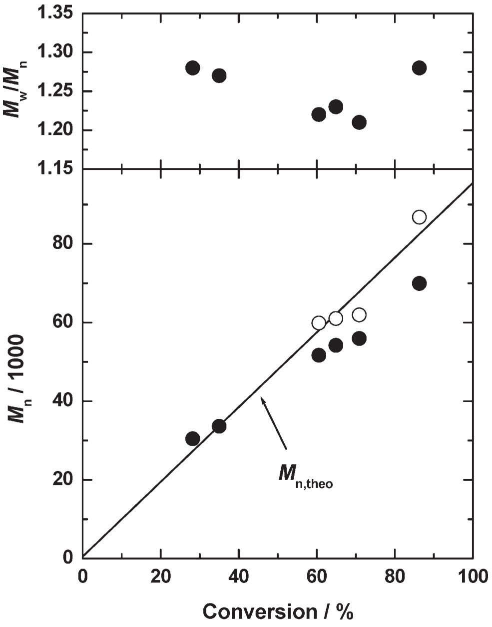

Figure 4. Evolution of number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the free polymer as a function of monomer conversion for the solution polymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA) (25 wt %) in water at 30 °C in the presence of initiator-carrying random copolymer (AIP)-coated substrate (ca. 1 × 1 cm): [PEGMA]$_0$/[water-soluble atom transfer radical polymerization initiator (PEGBr)]$_0$/[copper(I) chloride (CuCl)]$_0$/[copper(II) dichloride (CuCl$_2$)]$_0$/[2,2′-biyridine (bipy)]$_0$ = 200/1/0.2/1.8/4. The filled and open circles represent the data obtained by poly(methyl methacrylate)-calibrated gel permeation chromatography (GPC) and GPC-MALLS (multiangle laser light scattering), respectively. The full line represents the theoretical prediction.

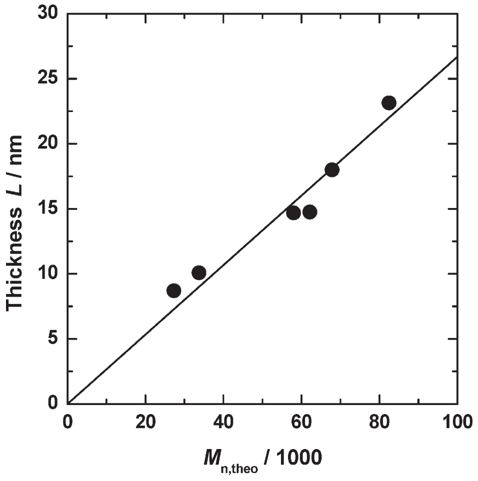

Figure 5. Plot of dry thickness *L* of poly(poly(ethylene glycol) methyl ether methacrylate) (PPEGMA) layer vs $M_{n,theo}$ of PPEGMA free chain. The theoretical number-average molecular weight $M_{n,theo}$ was calculated from the initial molar ratio of monomer to the free initiator. The slope of the straight line gives the graft density to be 0.18 chains/nm^2, which corresponds to a surface occupancy σ of 0.53 by taking the monomer volume into account (see text).

measurement was made for some PPEGMA samples prepared by the same method. The GPC-MALLS-determined M_n value ($M_{n,MALLS}$, open circles in Figure 4) was larger than the $M_{n,GPC}$ value (filled circles in Figure 4) and close to the $M_{n,theo}$ value (full line in Figure 4). This may allow us to adopt the theoretical M_n value as an absolute value in the following discussion. As shown in Figure 4, the M_w/M_n ratio remains low around 1.2 for most samples. All these results confirm that the aqueous ATRP of PEGMA proceeded in a controlled fashion, giving a low-polydispersity PPEGMA with a predictable molecular weight.

We measured the dry thickness *L* of the PPEGMA graft layer on the AIP-immobilized substrate by ellipsometry. It has been well recognized that in surface-initiated LRPs the molecular characteristics of free polymers generated from free initiators are essentially the same as those of graft polymers. Therefore, we plotted the thickness *L* as a function of the $M_{n,theo}$ value of the free polymers simultaneously produced in the solution, as shown in Figure 5. The proportional relationship was obtained, meaning that the surface grafting was controlled as well as the polymerization in the solution phase. From the slope of the line in Figure 5, we calculated the graft density to be 0.18 chains/nm^2, which was converted to the surface occupancy σ of 0.53 by taking the monomer volume into account. The σ value is comparable with that (0.4) for concentrated PMMA brushes previously attained on silicon wafer, indicating that the resultant PPEGMA brush is undoubtedly in the concentrated brush regime. Incidentally, when a similar surface-initiated polymerization was carried out in methanol or a mixture of methanol/water = 1/1 in volume, the σ values were more than 4, which obviously indicates the presence of a boundary layer coexisting graft and AIP polymers, as mentioned above, ascribed from the swelling of the AIP layer in the solvent systems.

The PPEGMA brush (L = 20 nm) on the polymeric substrate was subjected to contact angle measurement with water as a probe liquid. The contact angle of water was determined to be about 40° on average. This value is much lower than the water contact angles of 78° and 65° of PET and the AIP-immobilized substrate before the polymerization, respectively. This result suggests that the outermost layer of the substrate is almost completely covered by the PPEGMA brush.

Photopatterning and Protein Repellency of Polymer Brush. Since the AIP immobilization takes place only on a UV-irradiated portion, UV irradiation thorough a photomask would produce a pattern composed of AIP-immobilized and unimmobilized regions on polymeric substrates. To demonstrate this, we here used a copper microgrid as a photomask

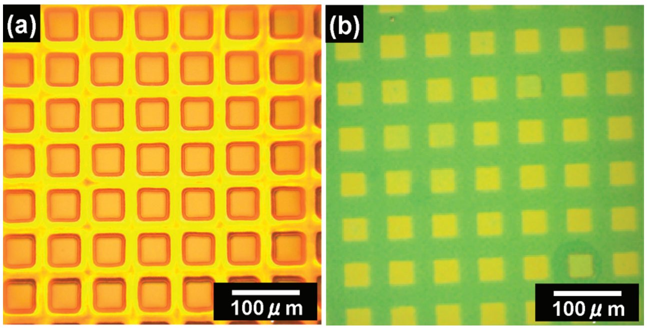

Figure 6. Optical micrographs of (a) a copper microgrid used as a photomask and (b) an initiator-carrying random copolymer (AIP)/poly(ethylene terephthalate) (PET)/silicon substrate after UV-irradiation through the photomask and subsequent washing with toluene.

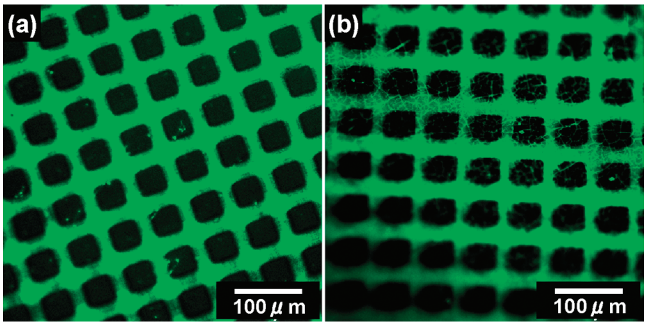

Figure 7. Confocal laser scanning microscopy images of patterned poly(poly(ethylene glycol) methyl ether methacrylate) (PPEGMA) brushes on (a) poly(ethylene terephthalate) (PET) and (b) polylactide (PLA) substrates after the treatment with fluorescein isothiocyanate (FITC)-labeled bovine serum albumin (BSA).

and irradiated the AIP/PET/silicon substrate with UV light through the mask. Figure 6 show the optical micrographs of the photomask used here as well as the substrate after UV-irradiation and subsequent washing with toluene. It can be clearly seen that the micropattern of the AIP layer, with size and shape corresponding to those of the photomask, was generated. The micropatterned substrate was then subjected to the surface-initiated ATRP of PEGMA in a similar way as described above.

It was previously reported that the concentrated brushes of hydrophilic polymers, e.g., PPEGMA, poly(2-hydroxyethyl methacrylate), and poly(2-methacrycryloyloxyethylphosphorylcholine), synthesized by surface-initiated LRP could effectively suppress the nonspecific adsorption of proteins mainly due to the unique size-exclusion property of concentrated polymer brushes.[43−47] In order to visually verify the formation of PPEGMA brushes in a given pattern, the substrate after the polymerization was immersed in a 1 wt % fluorescein isothiocyanate (FITC)-labeled bovine serum albumin (BSA) aqueous solution for 12 h, thoroughly rinsed with a buffer solution, and observed by confocal laser scanning microscopy (CLSM) in fluorescence mode. Figure 7a shows the CLSM image of the BSA-treated substrate. The fluorescence-emitting region, where FITC-labeled BSA molecules adsorb, was selectively observed in the region that was not irradiated with UV light during the AIP-immobilization process. On the contrary, the fluorescence emission was hardly detected on the AIP-immobilized regions from which PPEGMA brushes should have been generated. This suggests the successful achievement of the patterning of the AIP layer which leads to the formation of the patterned polymer-brush surface.

Similarly, we modified the surfaces of some polymeric substrates (film, sheet, and plate) made of different materials including PET, PLA, PP, PE, and PS. As an example, Figure 7b shows the CLSM image of a PLA film after patterning AIP layer, conducting ATRP, and treating with FITC-labeled BSA. The selective adsorption of BSA on the non-UV-irradiated region was observed, which suggests again the successful generation of the concentrated PPEGMA brush on the photopatterned initiator layer. As might be expected, similar results were obtained with other substrates such as PP, PE, and PS, thanks to the high reactivity of azide moiety. This demonstrates the versatility of the system developed here for the introduction of ATRP initiator moieties on polymeric substrates.

Conclusions

In order to graft a polymer brush on the surface of polymeric materials, a novel approach was demonstrated for the immobilization of ATRP initiating sites on the surface of organic polymeric substrates. The surface of polymeric substrate was coated with a thin layer of random copolymer (AIP) synthesized by radical copolymerization of MMA, an ATRP initiator-carrying monomer, and a photoreactive phenylazide-carrying monomer. The AIP-coated substrate was UV-irradiated to immobilize the copolymer by utilizing the photoreactivity of the phenylazido groups of the copolymer. Surface-initiated ATRP of PEGMA in water with thus-functionalized polymeric substrate proceeded in a living fashion, yielding polymeric substrates grafted with well-defined, concentrated PPEGMA brush. The aid of a photomask during the UV-irradiation process enabled the patterning of both the AIP and the brush layers. More importantly, it was demonstrated that these techniques were applicable to a variety of polymeric substrates. There should be no limitation in the range of organic materials that can be used with this technique, as the reactivity of nitrene produced by phototransformation of azide has significantly high reactivity for hydrocarbons. In addition, the method is simple and can be performed in mild reaction conditions without any costly equipment. These advantages should broaden the range of potential applications of polymer brushes.

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