Controlled Grafting of a Well-Defined Glycopolymer on a Solid Surface by Surface-Initiated Atom Transfer Radical Polymerization

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ABSTRACT: The atom transfer radical polymerization (ATRP) technique using the copper (Cu)/4,4′-di-*n*-heptyl-2,2′-bipyridine (dHbipy) complexes was applied to the graft polymerization of a sugar-carrying methacrylate, 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (MAIpGlc), on the substrate on which the monolayer of the initiator, 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane, was immobilized by the Langmuir−Blodgett technique. Ellipsometric and atomic force microscopic analyses confirmed that the polymerization carried out in the presence of the (sacrificing) free initiator, *p*-toluenesulfonyl chloride, afforded a homogeneous graft layer on the substrate. The thickness *d* of the graft layer in a dry state increased with reaction time and in proportion to the number-average molecular weight M_n of the (low-polydispersity) free polymers produced in the solution. This proportional relationship between *d* and M_n strongly suggests a controlled growth of the graft chains, as well as of the free chains, with the graft density kept constant. Grazing-angle reflection−absorption FTIR studies revealed that the isopropylidenyl groups of the poly(MAIpGlc) grafts were quantitatively converted to the hydroxyl groups by treatment with formic acid, thus producing the first solid surface densely grafted with a well-defined glucose-carrying polymer.

Introduction

Recently much interest has been directed toward the modification of solid surfaces for their potential applicabilities in various fields of materials science. Surface-graft polymerization is one of the most effective and versatile methods widely used for this purpose. While the graft polymerization starting with initiating sites fixed on a surface is effective to yield a high graft density, it usually results in a poor control of molecular weight and molecular weight distribution.[1−3] Recently, living polymerization techniques were successfully applied to the surface-initiated graft polymerization to control these molecular parameters.[4−9] We were the first to succeed in grafting a low-polydispersity poly(methyl methacrylate) with an exceptionally high graft density on a silicon substrate.[4] In that work, we made a combined use of the Langmuir−Blodgett (LB) technique[10,11] and the atom transfer radical polymerization (ATRP) technique,[12] a variant of living radical polymerization.[13] The former technique provided a well-organized set of initiating sites on the substrate, and the latter achieved a controlled graft polymerization.

This success encouraged us to attempt to prepare a solid surface grafted with a low-polydispersity glycopolymer, a polymer with pendant saccharide residues. Glycopolymers have attracted much attention as a model system to study the specific molecular recognition functions of saccharide.[14−20] Such a recognition process is considered to be cooperative and hence strongly dependent on the spatial distribution of saccharide residues.[21−24] To elucidate the multivalent interactions in the recognition process, it is required to control the structural parameters of glycopolymers. Thus, the controlled synthesis of structurally well-defined glycopolymers have been attempted by cationic polymerization,[25] ring-opening methathesis polymerization,[26,27] and ring-opening polymerization.[28] We also succeeded in synthesizing a glycopolymer and a glycopolymer-carrying amphiphile with a low polydispersity by living radical polymerization.[29] The glycopolymers grafted on a surface should present a particularly interesting model system to the molecular recognition process. This paper is the first report on the grafting of a well-defined glycopolymer on a solid substrate.

Synthetic chemical interest in this work concerns the graft polymerizability of a monomer with a bulky side group. A sugar-carrying monomer such as 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (MAIpGlc) with protected hydroxyl groups is very bulky in size compared with methyl methacrylate. Will this difference in monomer size bring about any significant difference in the graft polymerization behavior? This is a question to be answered below.

Experimental Section

Materials. 3-*O*-Methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (MAIpGlc) was synthesized by the reaction of 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose and methacrylic anhydride in pyridine and purified by flash silica gel column chromatography.[29c] Chloroform (Spectrograde, Dojindo Laboratories, Kumamoto, Japan), 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CTS, Gelest Inc., Tullytown, PA), and CuBr (99.999%, Aldrich Chemical Co., Inc., Milwaukee, WI,) were used as received. 4,4′-Di-*n*-heptyl-2,2′-bipyridine (dHbipy) was prepared by the method of Matyjaszewski et al.[30] Veratrole (1,2-dimethoxybenzene, Nacalai Tesque, Kyoto, Japan) was dried over molecular sieves (4 Å) for several days before use. All other reagents were commercially obtained and used without further purification.

Preparation of Monolayer. CTS was spread from a chloroform solution (ca. 0.01 wt %) on the clean water surface in a Langmuir trough (200 × 500 × 3 mm^3), the temperature of which was kept at 25 °C by circulating thermostated water. The subphase water was purified by means of a reverse-osmosis module, an ion-exchange column, and a double distiller, and its acidity was adjusted to pH = 4.5. The surface pressure was measured by a Whilhelmy-type film balance. After spreading the solution, 30 min was allowed for the

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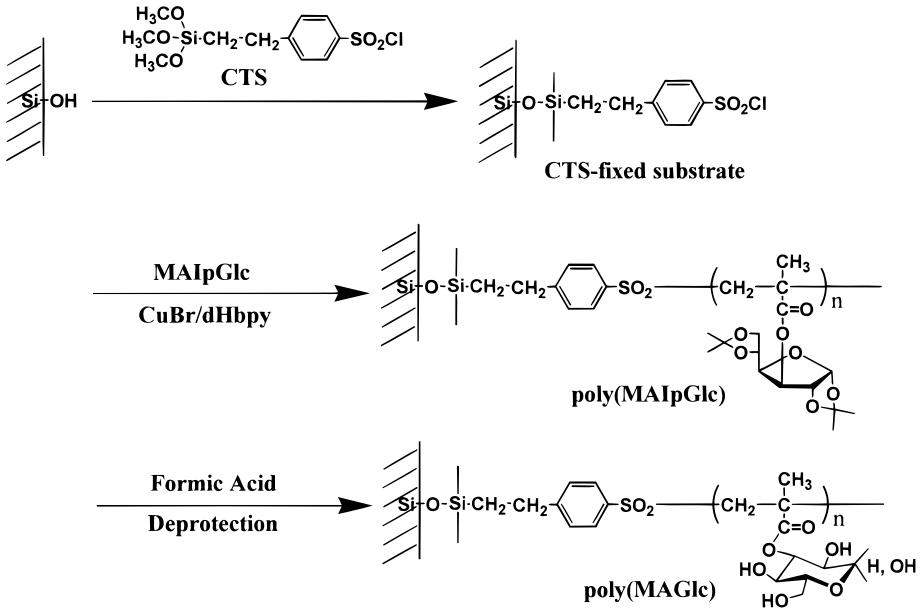

Figure 1. Schematic illustration of controlled grafting of a well-defined glycopolymer.

evaporation of the solvent and the hydrolysis of the methoxysilyl groups of CTS.[31] After the surface monolayer was compressed at a constant speed of 15 cm^2/min and annealed for 30 min at a surface pressure of 10 mN/m, it was transferred by the lifting-up method onto the oxidized silicon substrate that had been cleaned by ultrasonication in chloroform and sputtered with air under a reduced pressure to make the surface hydrophilic. For the measurements of grazing-angle reflection−absorption infrared (GIR) spectra, the CTS monolayer was fixed on a SiO_2/Au/Cr-coated glass plate. This plate was prepared by the following procedure: a 5 nm thick Cr layer and then a 100 nm thick Au layer were vacuum-evaporated on a cleaned glass plate, on which a 5−10 nm thick SiO_2 layer was deposited by a reactive evaporation of silicon monooxide in the presence of a 10^{-4} Torr of oxygen. The Cr layer was used for the improvement of adhesion between the glass surface and the gold layer. The transfer ratio, defined as the difference between the water surface areas before and after the deposition divided by the substrate surface area, was approximately unity in all cases, indicating successful deposition and the formation of a monolayer film with hydrophilic groups adherent to the substrate surface. Thermal treatment of this substrate at 110 °C for 20 min promoted the reaction of the unreacted silanol groups of CTS with those on the substrate, forming covalent bonds between the CTS film and the substrate. The successful immobilization of CTS was confirmed by the GIR measurement on the SiO_2/Au/Cr/glass substrate: the GIR bands due to the chlorosulfonyl group of CTS little decreased by washing with solvent.

Graft Polymerization and Deprotection. The graft polymerization was carried out as follows: a degassed veratrole solution of CuBr (15 mM), dHbipy (30 mM), MAIpGlc (1.5 M), and *p*-toluenesulfonyl chloride (TsCl, 7.6 mM), in which the CTS-fixed substrate (fixed CTS:TsCl ≈ 1:5000 by mole) was dipped, was sealed in a glass tube under vacuum and heated for a prescribed period of time at 80 °C. TsCl was added as a free initiator for the two purposes described later. To remove ungrafted but physically adsorbed (free) polymers, the substrate was immersed in chloroform for at least 24 h or extracted with toluene by a Soxhlet apparatus for 12 h.

The deprotection of the isopropylidenyl group on the poly(MAIpGlc) grafts was conducted by dipping the substrate in 80% formic acid for 48 h at room temperature.

Measurements. Monomer conversion and number- and weight-average molecular weights (M_n and M_w) of the free polymers produced in the solution were determined by polystyrene-calibrated GPC (by an 8010 high-speed liquid chromatograph, Tosoh Corp., Tokyo, Japan). Topographic images of the grafted substrate were observed by an atomic force microscope (AFM: SPI3600+SPA300, Seiko Instruments Inc., Chiba, Japan) with a V-shaped cantilever (Park Scientific Instruments, Sunnyvale, CA, spring constant 0.064 N/m). To determine the thickness of the graft layer, the graft layer was scratched and the height difference between the scratched and unscratched regions was measured by AFM. (It was confirmed that the silicon substrate had no damage by the scratching procedure.) The thickness of the graft layer was also estimated by an analyzer−rotating ellipsometer (DVA ellipsometer, Mizojiri Optical Co., Ltd., Tokyo, Japan) equipped with a He−Ne laser (632.8 nm). The polarizer angle and the incident angle were fixed at 30° and 70°, respectively. The thickness was calculated from the ellipsometric angle, Δ and Ψ, by assuming that the refractive index of the graft layer is 1.49, which is the value for a poly(methyl methacrylate) film. Grazing-angle reflection−absorption infrared (GIR) spectra were recorded with a BioRad FTS-6000 Fourier transform spectrometer (Bio-Rad Laboratories Inc., Hercules, CA) equipped with a reflection accessory and a liquid nitrogen-cooled MCT detector, in which p-polarized light was directed onto the substrate at an incident angle of 80°. The contact-angle measurements were carried out in the air by a sessile droplet technique just after each sample was cleaned by ultrasonication in water for 5 min.

Results and Discussion

As schematically illustrated in Figure 1, the glucose-carrying glycopolymer was grafted by the surface-initiated ATRP of MAIpGlc on the CTS-fixed substrate, followed by deprotection. First, CTS was homogeneously immobilized by the Langmuir−Blodgett technique. The details of the immobilization process were previously reported.[4] A chlorosulfonylphenyl group (−Ph−SO_2Cl) of CTS is one of the best initiating groups for ATRP.[32] The graft polymerization was carried out in the presence of the free initiator, TsCl, the role of which was previously discussed in relation to the key reaction of ATRP:[4]

$$P{-}X + Cu^{I}X/2L \rightleftarrows P^{\bullet} + Cu^{II}X_2/2L \qquad (1)$$

where X = Cl or Br and L = dHbipy in this study. In brief, the propagating radical $P^{\bullet}$ produced by the halogen-atom transfer from P−X to the Cu^{I} complex will undergo polymerization until it is deactivated by the Cu^{II} complex, and a number of such activation−deactivation

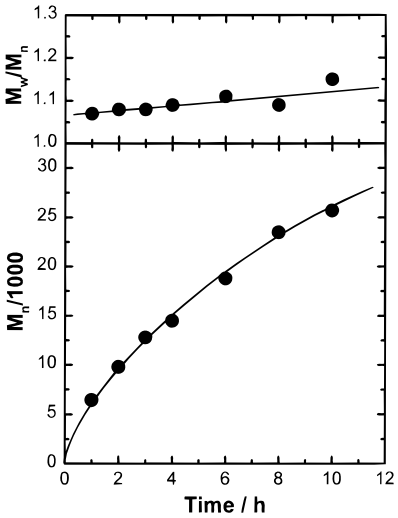

Figure 2. Plots of M_n and M_w/M_n of free polymers vs polymerization time.

cycles and a low concentration of the active species (relative to that of the dormant species P−X) are essential to yield polymers with low polydispersities.[33−35] In the polymerization without an additional initiator, the concentration of the Cu^{II} complex produced from the reaction at the substrate surface is too low to reversibly deactivate P• with a sufficiently high rate. The additional initiator would increase and adjust the concentration of the Cu^{II} complex as in a free ATRP system. Alternatively, the adjustment of the Cu^{II} concentration could be made by directly adding an appropriate amount of the Cu^{II} complex.[9] Another advantage of the additional initiator is that it produces free polymers, which can be used as a measure of the molecular weight and molecular weight distribution of the graft chains. In fact, in the graft polymerization of methyl methacrylate, the thickness of the graft layer increased in proportion to the M_n value of the free polymer.[4] In more recent work,[36] methyl methacrylate was graft polymerized on initiator-fixed silica particles with a large surface area, and the direct GPC analysis of the graft chains cleaved off the silica particles by treatment with a HF solution confirmed that the graft chains have nearly the same molecular weight and molecular weight distribution as the free polymers.

Controlled Graft Polymerization of MAIpGlc. Figure 2 shows the plot of the M_n value and polydispersity index (M_w/M_n) of the free polymer produced in the solution as a function of polymerization time, where the M_n and M_w/M_n values were estimated by a polystyrene-calibrated GPC. The M_n value increased with polymerization time and reached ca. 25 000 in 10 h. The absolute M_n value determined by the light scattering method is ca. 2.4 times larger than the M_n value estimated by a polystyrene-calibrated GPC.[29c] GPC value of 25 000, therefore, corresponds to the absolute value of about 60 000. The polydispersity of the free polymer reached less than 1.1 in 1 h, slightly increasing with polymerization time (still less than 1.2 even at 12 h). This suggests that the activation rate of P−X to P• should be sufficiently high and that the side reactions, which resulted in the observed increase of polydispersity, have only a minor effect under the studied conditions. The obtained polydispersity values of about 1.1 in all cases are lower than those (M_w/M_n = 1.2−1.3 for polymers in the same molecular weight range) previously obtained by the solution polymerization with ethyl 2-bromoisobutylate as an initiator.[29c] This indicates that chlorosulfonylphenyl group is a better initiator for the ATRP of MAIpGlc.

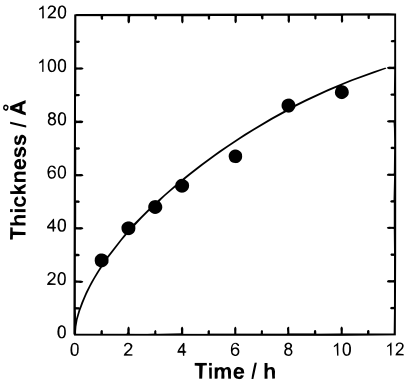

Figure 3. Plots of graft layer thickness vs polymerization time.

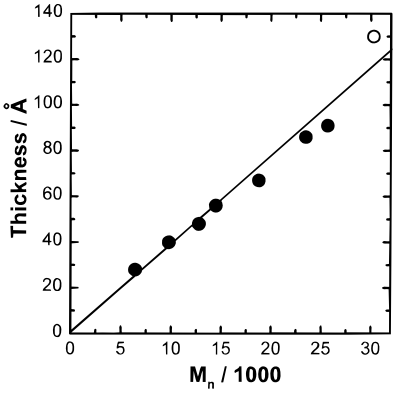

Figure 4. Relationship between graft layer thickness d and M_n of free polymer: (●) on the silicon substrate; (○) on the SiO_2/Au/Cr/glass substrate.

We observed the thickest sample grafted on the oxidized silicon substrate at different locations by AFM: the surface roughness was about 1 nm in a 10 × 10 μm^2 scanning area at any location, and the thickness determined by AFM imaging across the scratch boundary was nearly constant. These suggest that a homogeneous polymer layer was formed on the substrate. By repeatedly washing the substrate with chloroform and measuring the thickness of the polymer layer, we confirmed that the polymer chains were not physically adsorbed but chemically anchored onto the substrate. The dry thickness of the grafted polymer layer was also determined by ellipsometry, where the refractive index n of the graft layer was assumed to be equal to that of PMMA (n = 1.49). For the thickest sample, the AFM and ellipsometry values were very close to each other. This justifies the assumed value of the refractive index of the graft layer.

Figure 3 shows the layer thickness d estimated by ellispometry: d increased with the polymerization time. Since the molecular weight of the polymer grafted on the substrate should be somehow correlated to that of the free polymer produced in the solution as mentioned above, the graft layer thickness d was plotted against M_n of the free polymer in Figure 4. Like in the graft polymerization of MMA, a proportional relationship was obtained between them from low through high conversions, suggesting a controlled growth of the graft chains, as well as of the free chains, with the number of graft

chains kept constant. This strongly suggests that the M_n of the graft polymer is almost equal or at least proportional to that of the free polymer, and the graft density, i.e., the number of graft sites per unit area, is essentially constant throughout the course of polymerization.

Now, we discuss the graft density, assuming that the M_n of the graft chain be the same as that of the free chain. From the slope of the line in Figure 4, the graft density σ was estimated to be ca. 0.1 chain/nm^2. (The apparent M_n value (by GPC) was multiplied by the factor of 2.4 to convert it to the absolute value.) This graft density is to be compared to the σ value of 0.4 chain/nm^2 similarly estimated for the PMMA grafts.[4] To take the size difference of the two monomers into account, we consider the dimensionless surface density σ^* defined as the number of graft chains per monomer cross-sectional area, a ($\sigma^* = \sigma a$). Here, we consider a polymer chain as a cylinder with a cross-sectional area equal to a. When the contour length per monomer unit is set equal to the length of the C−C−C bond (0.25 nm) with the bulk density assumed to be unity, we obtain $a = 0.66$ and 2.2 nm^2, and hence $\sigma^* = 0.26$ and 0.22 for the PMMA and poly(MAIpGlc) grafts, respectively. The reasonable agreement of the σ^* values means that the observed difference in the graft density σ can primarily be ascribed to the difference in size of the two monomer units and hence that the bulkiness of the monomer unit has a steric, but little chemical, effect on the graft polymerization behavior. Perhaps, any monomer with a bulky functional group could be grafted on a substrate in a controlled fashion if its solution polymerization proceeds in a living radical process.

Deprotection of MAIpGlc to MAGlc Units. The surface of poly(MAIpGlc)-grafted substrate showed contact angles around 80°. After the treatment with formic acid, the contact angle was found to become too low to be measured by the present simple method (less than 20°).[37] This confirmed that this treatment made the surface hydrophilic, indicating that the MAIpGlc unit was converted to the MAGlc unit. To obtain the infrared spectrum of the graft layer before and after deprotection, poly(MAIpGlc) was grafted on the SiO_2/Au/Cr/glass substrate. The thickness of the graft layer was measured to be 13.0 nm by ellipsometry, and the M_n and M_w/M_n values of the free polymer produced in the solution were estimated to be 3.1×10^4 and 1.17, respectively, by GPC. These data, shown by the open circle in Figure 4, fall closely on the line obtained for the graft polymerization on the silicon substrate. This suggests that the SiO_2 was homogeneously evaporated on the gold layer, and thus CTS was successfully immobilized with the same density as on the oxidized silicon substrate. Parts a and b of Figure 5 show the GIR spectra of the graft layer before and after deprotection, respectively. Before deprotection, absorption bands due to the isopropylidenyl group were observed. The absorption bands at 3000, 1450, and 1380 cm^{-1} are assignable to the C−H stretching and the C−H asymmetric and symmetric deformation modes, respectively. The C−O stretching band of the isopropylidenyl group, which was overlapped with the absorption band due to the SiO_2 layer (Si−O−Si stretching), was also detected in the region between 1200 and 1000 cm^{-1}. After deprotection, these bands were missing, and a broad absorption band appeared at around 3500 cm^{-1}, which is assignable to the hydroxyl group formed by the deprotection of the isopropylidenyl group. These spectra were found to be comparable to those recorded for the spin-coated films of the free polymers, poly(MAIpGlc) and poly(MAGlc), shown in Figure 6. Here, the free polymer poly(MAGlc) used as a reference was confirmed by ^{1}H NMR to be completely deprotected. Hence, we conclude that, like the free polymer, the poly(MAIpGlc) grafted on the substrate was completely deprotected by the treatment with formic acid and converted to poly(MAGlc). The possibility of the degrafting or chain breaking of the graft polymers during this treatment was ruled out by comparing the intensity and peak position of the absorption band at 1730 cm^{-1} due to the C═O stretching of the ester group before and after deprotection; the small increase (about 10%) in intensity may be ascribed to the decrease in thickness, since the sensitivity of the GIR measurement has a maximum at

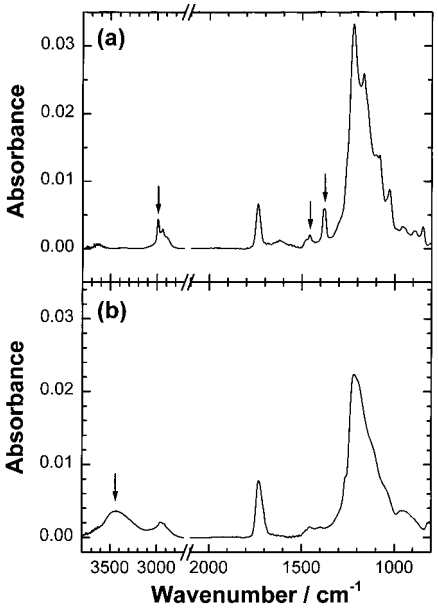

Figure 5. Grazing-angle reflection−absorption FTIR spectra of poly(MAIpGlc) grafted on a SiO_2/Au/Cr/glass substrate (a) before and (b) after deprotection.

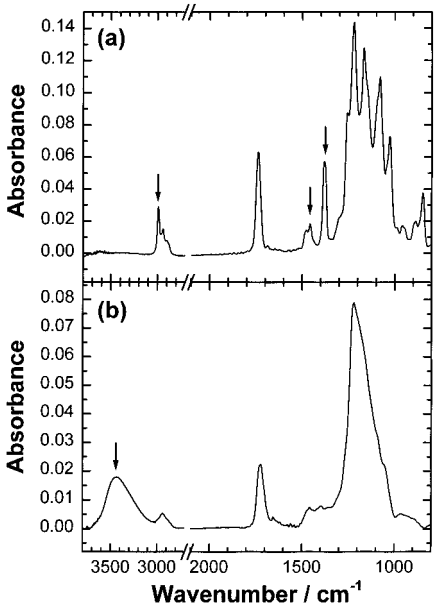

Figure 6. Grazing-angle reflection−absorption FTIR spectra of free polymers, (a) poly(MAIpGlc) and (b) poly(MAGlc), spin-coated on a SiO_2/Au/Cr/glass substrate.

the substrate surface and decays exponentially with increasing distance from the surface.

Conclusions

We have succeeded in the controlled graft polymerization of MAIpGlc by the surface-initiated ATRP, yielding a homogeneous graft polymer layer with a high graft density. The grazing-angle reflection−absorption FTIR measurement revealed that, by treatment with formic acid, the poly(MAIpGlc) graft on the substrate was quantitatively deprotected and converted to the glucose-carrying polymer, poly(MAGlc), without degrafting or chain breaking.

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