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Controlled Graft Polymerization of Methyl Methacrylate on Silicon Substrate by the Combined Use of the Langmuir−Blodgett and Atom Transfer Radical Polymerization Techniques

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Recently much interest has been directed toward new ways to modify surfaces of solid substrates for their potential applicabilities.[1] Surface grafting of polymer chains is one of the most effective and versatile methods for this purpose, since surface properties can be widely changed by graft-polymerizing a variety of functional monomers. Graft polymerization starting with the initiating sites fixed on the surface is a promising method to yield a high graft density. However, it is usually very difficult in these experiments to control such parameters as molecular weight, molecular weight distribution, and surface density of graft chains.

This is the first report[2] of the precise control of all these three parameters. We will make combined use of two independent techniques: one is the Langmuir−Blodgett (LB) technique[3,4] to provide a well-organized set of initiating sites on the substrate, and the other is the atom transfer radical polymerization (ATRP) technique using copper (Cu)/ligand (L) complexes[5,6] to achieve a controlled graft polymerization. ATRP is one of the several techniques of controlled/“living” radical polymerization that has been attracting much attention as a new route to well-defined polymers with low polydispersities.[7] The key reaction of ATRP is the activation-deactivation reversible process

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

where X = Cl or Br, and L = 4,4′-di-*n*-heptyl-2,2′-bipyridine (dHbipy)[8] in this study. The propagating radical P* produced by the halogen-atom transfer from P−X to the $\mathrm{Cu^{I}X/2L}$ complex will undergo polymerization until it is deactivated by the $\mathrm{Cu^{II}X_2/2L}$ complex. A number of such activation−deactivation cycles and a low concentration of the active species (relative to that of the dormant species P−X) will give polymers with low polydispersities.[9−11]

In this work, we have examined the graft polymerization of methyl methacrylate (MMA) by ATRP on an initiator-immobilized substrate. 2-(4-Chlorosulfonylphenyl) ethyl trimethoxysilane (CTS, Chisso Co. Ltd., Tokyo, Japan) was used as an initiator which can be immobilized on an oxidized silicon substrate (normally, a silicon wafer is covered with a silicon oxide layer). A chlorosulfonylphenyl group ($\mathrm{-Ph-SO_2Cl}$) of CTS is one of the best initiating groups for ATRP;[5d,12] the Cl atom is easily abstracted by the $\mathrm{Cu^{I}X/2L}$ complex, and the produced $\mathrm{-Ph-SO_2^{*}}$ radical initiates the polymerization of MMA. In addition, CTS has methoxysilyl groups ($\mathrm{\equiv SiOCH_3}$), which can be hydrolyzed to silanol groups ($\mathrm{\equiv SiOH}$) and immobilized on an oxidized silicon substrate by forming the Si−O−Si covalent bond.[13,14] In recent years, some organosilane compounds with a long alkyl chain were reported to form a stable monolayer on the water surface, which could be transferred by the LB technique.[15] Here, we have applied this technique to the immobilization of CTS to control the graft−chain density.

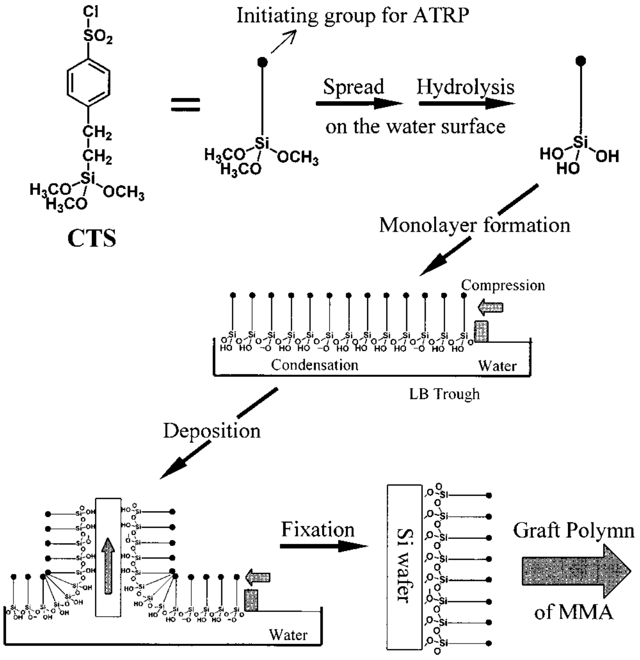

Figure 1. Schematic illustration of the immobilization process of the initiator by the LB technique.

Immobilization of Initiator. Figure 1 schematically illustrates the immobilization process of the initiator. CTS was spread from a chloroform solution on the clean water surface in a Langmuir trough (200 × 500 × 3 $\mathrm{mm^3}$), where methoxysilyl groups ($\mathrm{\equiv SiOCH_3}$) of CTS were presumably hydrolyzed to silanol groups (for effective hydrolysis, the acidity of the subphase water was adjusted to pH = 4−5). After the solution was spread, 30 min was allowed for the evaporation of the solvent and the hydrolysis of CTS to proceed completely. Figure 2 shows the surface pressure (π)−occupied area (A) isotherm of CTS recorded at a subphase temperature of 25 °C and a constant compression speed of 15 $\mathrm{cm^2/min}$. This figure indicates that π increases with decreasing A and the limiting area estimated by extrapolating the steepest tangent of the isotherm to zero surface pressure is approximately 0.35 $\mathrm{nm^2}$ per molecule, suggesting the formation of a monolayer on the water surface. The stability of the surface monolayer was checked by measuring the time dependence of A when π was kept 10 mN/m, at which the isotherm gave the steepest rise. The occupied area decreased by about 10%, approaching a constant. This initial decrease in A might be due to the polycondensation between silanol groups formed by the hydrolysis of CTS, and the constancy in A at the later stage suggests the formation of a stable monolayer.

After the surface monolayer was annealed for 30 min at π = 10 mN/m, it was transferred by the lifting-up method[16] onto the oxidized silicon substrate, which was

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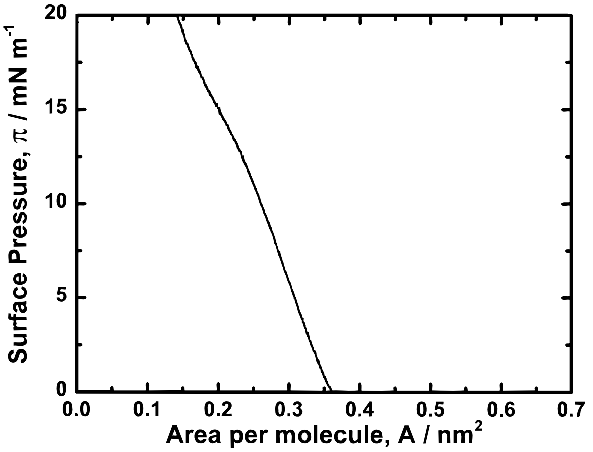

Figure 2. Surface pressure (π)−occupied area (A) isotherm of CTS spread from a chloroform solution at 25 °C

cleaned by ultrasonication in chloroform and sputtered with air under a reduced pressure to make the surface hydrophilic. 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, indicating successful deposition and the formation of a monolayer film with hydrophilic groups adherent to the substrate surface. Thermal treatment of thus obtained substrate at 110 °C for 20 min was carried out to promote the reaction of unreacted silanol groups of CTS with silanol groups on the substrate, forming covalent bonds between the CTS film and the silicon substrate. The atomic force microscopic (AFM) observation (by a SPI3600, Seiko Instruments Inc., Chiba, Japan) showed that the surface of the CTS-fixed substrate was similar to that of the original silicon substrate, exhibiting no characteristic structure. These results suggest that a homogeneous immobilization of CTS on the substrate has been achieved.

Graft Polymerization. The graft polymerization was carried out as follows; a degassed diphenyl ether solution of CuBr (10 mM), dHbipy (20 mM), MMA (4.7 M), and *p*-toluenesulfonyl chloride (TsCl, 2.4 mM or 4.8 mM), in which the initiator-fixed substrate was dipped, was sealed in a glass tube under vacuum and heated for various periods of time at 90 °C. TsCl was added as a free initiator to control the polymerization (see below). Like the conventional radical polymerization, the polymerization without TsCl gave free homopolymers with M_n values independent of monomer conversion and high polydispersities ($M_w/M_n > 3$). Hence, it might be termed “uncontrolled” polymerization, in which the concentration of initiator and hence the concentration of the Cu^{II} complex (see eq 1) in the solution was much too low to control the polymerization. On the other hand, addition of an appropriate amount of TsCl as a free initiator in solution brought about well-controlled polymerization. Figure 3 shows the plot of the number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the free polymer produced in the solution as a function of monomer conversion, where the M_n and M_w/M_n values were determined by polystyrene-calibrated GPC (by a 8010 high-speed liquid chromatograph, Tosoh Corp., Tokyo, Japan). The polydispersities of the free polymers were relatively low, and the M_n values were proportional to the monomer conversion with the slope very close to the theoretical value defined by the feed concentration of TsCl. This indicates that the number of polymer chains is kept constant during the polymerization and the polymerization process is controlled with a negligible contribution of transfer and termination reactions.

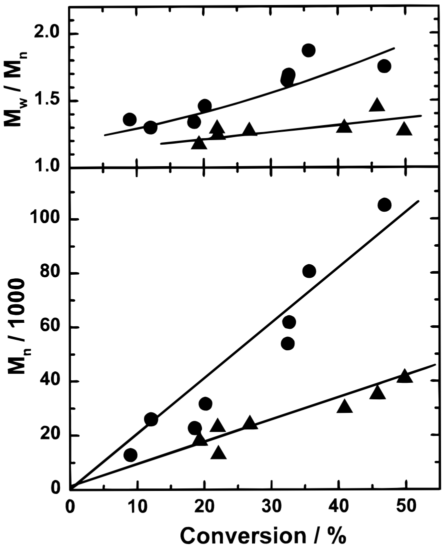

Figure 3. Plots of M_n and M_w/M_n of free polymers vs monomer conversion for the polymerization with TsCl. [TsCl] = 2.4 (●) and 4.8 mM (▲).

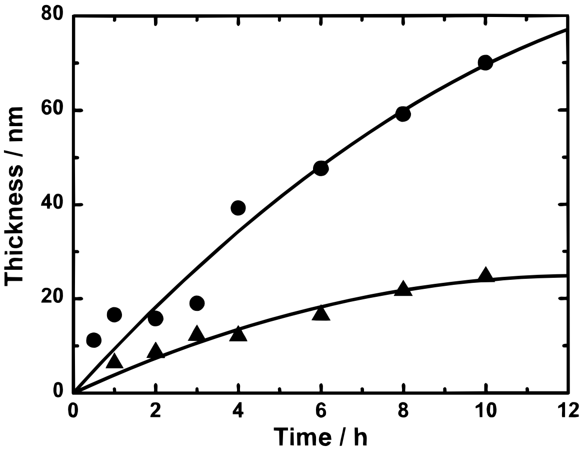

Figure 4. Plots of graft−layer thickness vs polymerization time. For symbols, see Figure 3.

The AFM observation revealed that a homogeneous polymer layer was formed on the substrate. By repeatedly rinsing the substrate with chloroform, we confirmed that the polymer chains were not physically adsorbed but chemically anchored onto the substrate. The thickness of the grafted polymer layer, determined by ellipsometry (by a DVA ellipsometer, Mizojiri Optical Co., Ltd., Tokyo, Japan), is plotted against the polymerization time in Figure 4. The layer thickness d increased with time, and polymerization with a lower concentration of TsCl gave a larger d after the same polymerization time.

The molecular weight of the polymer grafted on the substrate cannot be directly determined at present, but it should be somehow correlated to that of the free polymer produced in the solution. Figure 5 shows the plot of the graft layer thickness d vs M_n of the free polymer. A proportional relationship was obtained between them, and the slope of the line was independent of the concentration of TsCl. 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

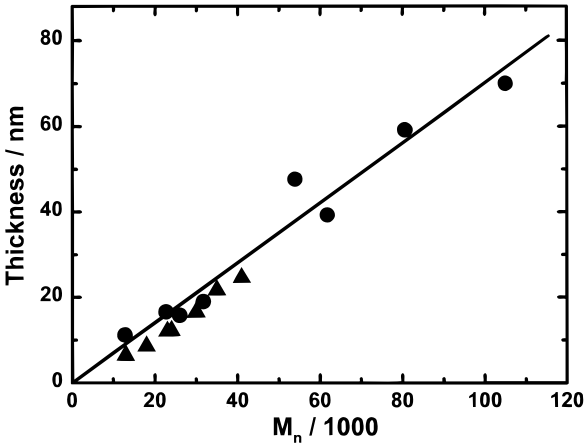

Figure 5. Relationship between graft−layer thickness and M_n of free polymers produced in solution. For symbols, see Figure 3.

constant during the course of polymerization. This can be interpreted as follows; in the presence of the additional initiator which would increases the concentration of the Cu^{II} complex (see eq 1), the activated radical P* is reversibly deactivated by the Cu^{II} complex so frequently that all the graft chains would grow slowly and more or less simultaneously with the number of chains constant.

In conclusion, we have succeeded in homogeneously immobilizing the initiator for the ATRP by the LB technique and controlling the graft polymerization of MMA on the initiator-immobilized substrate by the ATRP technique. The free initiator added in the solution plays the important role of increasing the Cu^{II} concentration, thus increasing the rate of deactivation process and thereby increasing the number of activation−deactivation cycles, an essential requirement of controlled radical polymerization. Since ATRP can be applied not only to the homopolymerizations but also to the block and/or random copolymerizations of a variety of monomers, this success will open up a new and wide route to "precision" surface modification.

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