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

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The atom transfer radical polymerization technique using the copper/ligand complexes was applied to the graft polymerization of methyl methacrylate on the Si wafer on which the monolayer of the initiator, 2-(4-chlorosulfonylphenyl) ethyl trimethoxysilane, was immobilized by the Langmuir-Blodgett technique. Atomic force microscopic and ellipsometric studies revealed that the polymerization with an additional initiator afforded a homogeneous graft layer, the thickness of which increased proportionally to the number-average molecular weight of the narrow-polydispersity homopolymers produced in the solution. This suggests that the graft polymerization is successfully controlled by the Cu/ligand complexes in the same way as the solution polymerization.

Keywords: Surface modification / Monolayer / Immobilization / Controlled radical polymerization / Graft layer / Ellipsometry

Recently much interest has been directed towards new ways to modify surfaces of solid substrates for potential applicability. Graft polymerization starting with the initiating sites fixed on the surface is one of the most effective and versatile methods for such surface modification. However, it is usually very difficult to control molecular weight, molecular weight distribution, and surface density of graft chains. We attempted to precisely control all these three parameters by the combined use of two independent techniques: one is the Langmuir-Blodgett (LB) technique 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 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.

In this work, we have examined the graft polymerization of methyl methacrylate (MMA) by ATRP on an initiator-fixed substrate. 2-(4-Chlorosulfonylphenyl) ethyl trimethoxysilane (CTS) was used as an initiator which can be immobilized on an oxidized silicon substrate; the Cl atom of a chlorosulfonyl group (-SO₂Cl) is easily abstracted by the Cu/L complex, and the produced -SO₂* radical initiates the radical polymerization.

Immobilization of Initiator

Figure 1 schematically illustrates the immobilization...
process of the initiating groups. CTS was spread from a chloroform solution on the clean water surface in a Langmuir trough, where methoxysilyl groups (≡Si-OCH₃) of CTS were presumably hydrolyzed to silanol groups (≡Si-OH). The surface pressure (π) – occupied area (A) isotherm of CTS suggests the formation of a monolayer on the water surface. 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 value. This initial decrease in A might be due to the polycondensation between silanol groups formed by the hydrolysis of CTS on the water surface.

After the surface monolayer was annealed for 30 min at π = 10 mN/m, it was transferred by the lifting-up method onto the oxidized silicon substrate. The transfer ratio, defined as the difference in the water surface area before and after the deposition divided by the substrate surface area, was approximately unity, indicating successful deposition and the formation of a Z-type monolayer film. 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 silicon substrate, forming covalent bonds between the CTS film and the substrate. The atomic force microscopic (AFM) observation suggests that homogeneous immobilization of CTS has been achieved.

Controlled Graft Polymerization

The graft polymerization on the initiator-fixed substrate was carried out for various periods at 90 °C in a degassed diphenyl ether solution of CuBr, 4,4’-di-n-heptyl-2,2’-bipyridine (ligand), MMA, and an additional initiator, p-toluenesulfonyl chloride (TsCl). The polymerization without TsCl gave free homopolymers with high polydispersities (Mₘ/Mₙ > 3) like the conventional radical polymerization. This is presumably because the concentration of graft-layer thickness and Mₙ of free homopolymers produced in solution.

REFERENCES