Chemistry Letters Vol.34, No.10 (2005)

Fabrication and Electrochemical Properties of High-density Graft Films with Ferrocene Moieties on ITO Substrates

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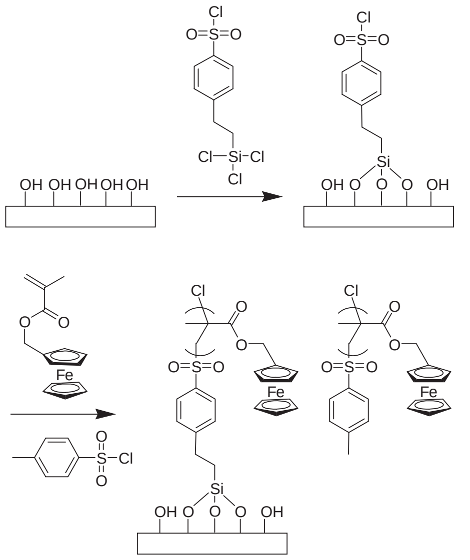
(Received July 5, 2005; CL-050867)

High-density graft films bearing ferrocene (Fc) moieties were fabricated on quartz and indium tin oxide (ITO) substrates by surface-initiated atom transfer radical polymerization (ATRP). The thickness of the film increased with the increase in the molecular weight of the polymer. We successfully observed quantitative electrochemical redox signals on the ITO substrates coated with a graft polymer. The cyclic voltammograms showed that all ferrocene moieties were electrochemically active.

Recently, high-density graft films have been developed using the living radical polymerization technique.[1–4] The surface density of the polymer chains is so high that the polymer chains are forced to stretch along the direction normal to the grafting surface.[5] This configuration is quite different from that of graft films obtained by the conventional polymerization technique. Focusing attention on the availability of various monomers for the living radical polymerization technique, we previously reported a precise method of synthesizing photofunctional polymers,[6] and also demonstrated preparation of photofunctional graft films.[7] Here, we demonstrate the surface-initiated ATRP, that is a kind of living radical polymerization, for the monomer bearing an electrochemically active ferrocene moiety, ferrocenylmethyl methacrylate (FMMA), and its electrochemical property was investigated by cyclic voltammetry.

PFMMA graft films were prepared as shown in Scheme 1. Quartz substrates and ITO-coated substrates (10 Ω per square) were ultrasonicated in acetone, ethanol, deionized water (Quartz), and in toluene, acetone, ethanol (ITO) for 10 min, respectively, and then dried with N_2. The substrates were subsequently cleaned with a UV–O_3 cleaner for 1 h to make the surface hydrophilic. The cleaned substrates were immersed in a dry toluene solution with 2-wt % 2-(4-chlorosulfonylphenyl)-ethyltrichlorosilane (CTCS) for 2 h at room temperature to immobilize CTCS from which polymerization proceeds. These substrates were washed with THF and dried under vacuum.



Scheme 1. Procedure of PFMMA graft films on quartz and ITO substrates.

A dry anisole solution with FMMA, TsCl, CuBr, and sparteine was degassed by four freeze–pump–thaw cycles. Free initiator TsCl was added not only to control the catalytic balance in the ATRP system but also to estimate the molecular weight of the grafted polymer, which has a molecular weight and molecular weight distribution similar to those of the free polymer. The substrates chemically modified with CTCS were immersed in this solution and sealed under vacuum. After polymerization at 90 °C, a part of the solution was diluted with THF and passed through alumina column to remove CuBr, and then analyzed by gel permeation chromatography (GPC). The substrates were ultrasonicated in THF for 10 min and rinsed in THF with a Soxhlet extractor for 12 h to remove physisorbed free polymers.

Figure 1 shows the plots of M_n and M_w/M_n against the monomer conversion. The value of M_n increased with monomer conversion and agreed with the theoretical value calculated from the initial monomer concentration $[M]_0$ and initiator concentration [I]. This indicates that the initiation efficiency is close to unity and the polymerization proceeds in well-controlled fashion. Furthermore, M_w/M_n value was retained at around 1.2.

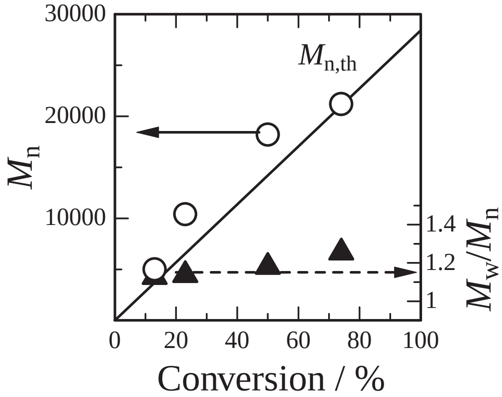


Figure 1. Plots of M_n and M_w/M_n vs monomer conversion for polymerization of FMMA. The solid line was obtained by theoretical calculation from $[M]_0/[I] = 100$ and monomer conversion.

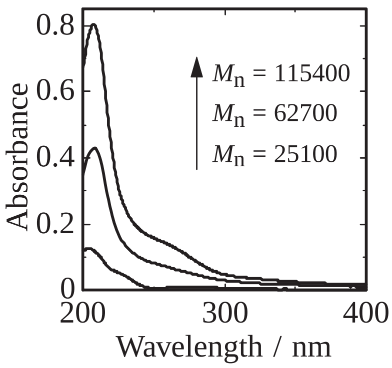


Figure 2. Absorption spectra of PFMMA graft films on quartz substrates.

These facts show that the ATRP catalysis system operates well in the case that FMMA is used as a monomer, and that FMMA is applicable to the surface-initiated ATRP.

Figure 2 shows the absorption spectra of the PFMMA graft films on quartz substrates with various molecular weight polymers. The peak around 206 nm was assigned to the absorption of Fc moiety, and the absorbance increased with the molecular weight of the polymer. The thickness of the film for $M_n = 115,400$ was evaluated to 23 nm from AFM measurement. This suggests that we can fabricate the PFMMA graft films on solid substrate, and the thickness of a graft film can be controlled precisely according to the degree of polymerization. The graft density was estimated to 0.12 chains nm^{-2} from the peak absorbance. When methyl methacrylate (MMA) is used as a monomer, the graft density of 0.70 chains nm^{-2} is achieved.[8] The graft density of this PFMMA graft film was lower than that of PMMA films, but this is because FMMA chains have a higher steric hindrance due to a bulky Fc group; the monomer unit volume is 0.34 and 0.14 nm^{-3} for FMMA and MMA, respectively. Considering this difference, the graft density of the PFMMA film is as high as that of the PMMA graft film.

Figure 3 shows cyclic voltammograms of PFMMA graft films on the ITO substrate measured with a conventional three-electrode cell where reference electrode and counter electrode were Ag/0.1 M Ag^+ in acetonitrile and Pt, respectively. The electrolyte solution was 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) acetonitrile. The current signals around 0.17 V were ascribed to redox reaction of Fc^+/Fc. The cyclic voltammograms showed characteristics of surface waves: symmetrical current about potential axis. The potential difference between cathodic and anodic peaks was negligible, and the peak current was proportional to the scan rate ranging from 10 to 50 $mV\,s^{-1}$. These findings suggest that the electrode reaction rate is substantially fast compared with these scan rates, and all the redox active Fc moieties in the film contribute to redox current, that is, this PFMMA graft film has a hole transport property. Then graft density was evaluated from quantity of charge, which is the integral of current density. This film had a graft density estimated at 0.10 chains nm^{-2}. This is in good agreement with the graft density on quartz substrate estimated from the absorption spectra, indicating that all the Fc moieties in the graft film are electrochemically active.

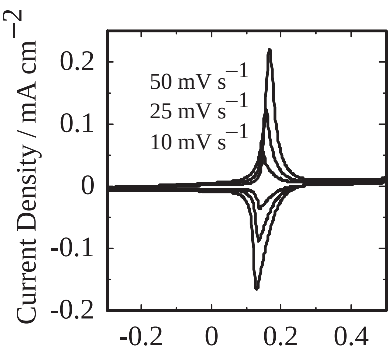


Figure 3. Cyclic voltammograms of PFMMA graft film on ITO in acetonitrile with 0.1 M Bu_4NBF_4.

In this study, we fabricated an ultrathin graft film on quartz and ITO substrates by the surface-initiated ATRP technique for a redox monomer. The redox polymer synthesized by ATRP had a narrow molecular weight distribution. The redox films had a higher graft density than those fabricated by the conventional technique and were electrochemically active. Generally, it is difficult to measure cyclic voltammetric signals with polymer-coated electrodes because of the poor permeability of electrolyte solution into the polymer film. Furthermore, it is impossible to use good solvents because of dissolution of polymers. In the current study, however, we detected quantitative oxidation and reduction current through the graft-polymers, showing highly efficient hole transport among the ferrocene moieties. These results indicate that the electrochemical reactions could be controlled by the well-defined nano-structure of high-density graft polymers fabricated in a living fashion of ATRP.

This work was partly supported by a Grant-in-Aid for Young Scientists (B) (No. 16750187) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, the 21st Century COE program, COE for a United Approach to New Materials Science, and the Integrative Industry–Academia Partnership (IIAP) including Kyoto University, Nippon Telegraph and Telephone Corporation, Pioneer Corporation, Hitachi, Ltd., Mitsubishi Chemical Corporation, and Rohm Co., Ltd.

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Published on the web (Advance View) September 10, 2005; DOI 10.1246/cl.2005.1366