

Photofunctional Ultrathin Films Prepared by High-Density Graft Polymerization

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High-density graft polymers having photo-functional units at the side chains were prepared on solid substrates by surface-initiated atom transfer radical polymerization (ATRP). In this study, methacrylate esters with carbazolyl and terephthaloyl moieties were employed as electron-donating and accepting monomers, respectively. The average molecular weight M_n obtained had a narrow distribution and was proportional to the monomer conversion, showing that the polymerization proceeded in a "living" fashion. The thickness of the graft polymer film on the surface was proportional to the molecular weight and it was controlled to a few nanometers by adjusting the reaction time. Fluorescence spectroscopy was applied to the diblock and triblock copolymers prepared on a quartz substrate in order to investigate electron transfer and exciplex formation between the block-layers with emphasis on the structural control of photophysical processes. These results indicate the feasibility of the high-density graft films as a novel nano-material based on the "tailored polymerization".

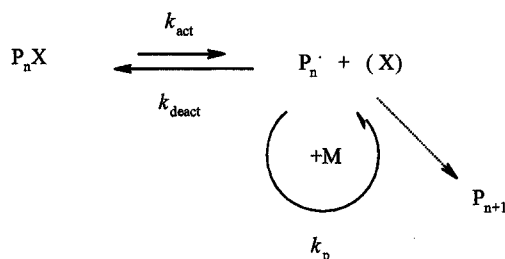
Key words: High density graft polymer, Ultrathin film, Layered structure, Photofunctional surface, Atom transfer radical polymerization

1. INTRODUCTION

Photo- and electronic functions of polymeric materials have attracted much attention because of the wide range of fascinating applications such as displays, sensors, and solar cells. The functions depend strongly on the nano-structures of polymer assemblies, which are also determined by the chemical structures of individual polymer chains, including the molecular weight and the molecular weight distribution.

Living radical polymerization was developed as a novel polymer synthesis method to control precisely the molecular weight and the molecular weight distribution.¹ Among the various living radical polymerization methods (nitroxide-mediated controlled radical polymerization,² atom transfer radical polymerization (ATRP),³ reversible addition-fragmentation chain transfer (RAFT)⁴), ATRP proceeds under the equilibrium of the activated state and the dormant state through all the processes as shown in Scheme 1.^{5,6} Here, k_{act} , k_{deact} and k_p are the rate constants of the activation, deactivation and the propagation reactions, respectively.

ATRP is applicable to graft polymerization initiated



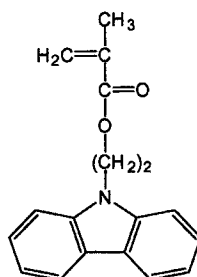
Scheme 1

with 2-(4-chlorosulfonyl-phenyl)ethyl-trichlorosilane (CTCS) fixed on a solid surface. The high-density graft polymers thus obtained possesses particular characteristics different from those prepared by conventional polymerization methods.

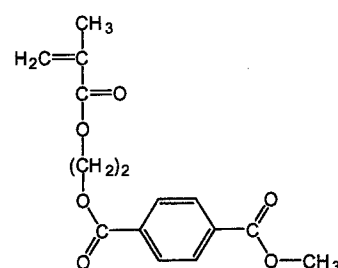
In this study, we investigated the surface initiated ATRP for two kinds of methacrylate monomers (Scheme 2): 1) 2-(9-carbazolyl)ethyl methacrylate (CzEMA), which has an electron donating carbazole chromophore, and 2) 2-(methyl terephthaloyloxy)ethyl methacrylate (TPEMA), which has an electron-accepting unit. Block copolymers of these special monomers were synthesized using the ATRP method in living mode. We investigated the photophysical interaction between the block polymers by fluorescence spectroscopy.

2. EXPERIMENTAL

A glass tube was charged with predetermined amounts of Cu(I)Br and sparteine, to which a monomer solution containing *p*-toluenesulfonyl chloride (TsCl) was quickly added.⁷ The mixture was immediately degassed



CzEMA



TPEMA

Scheme 2

by three freeze-thaw cycles, sealed under vacuum and finally placed in an oil bath thermostatted at 90°C. After a prescribed period, the tube was quenched to room temperature, and a part of the sample solution was studied by size exclusion chromatography (SEC) after appropriate dilution with tetrahydrofuran (THF). The monomer conversion was estimated by comparing the SEC peaks of the polymer and the monomer. The surface graft polymerization was carried out by the ATRP method. The fixed CTCS initiator on the quartz substrate was used and TsCl was also added as a free initiator not only to control the polymerization but also to provide free polymers, which are produced in solution and useful as a measure of the molecular weight and molecular weight distribution of the graft chain. After polymerization, the substrate was rinsed in a Soxhlet extractor with dichloromethane for 12 h to remove physisorbed polymers and impurities. The molecular weight of this polymer was determined from the area ratio for the methyl proton of the side chain and the methylene proton of the initiator on the ^1H NMR spectrum. The evaluation of the layer thickness was done by UV absorption spectroscopy and atomic force microscopy (AFM) (Shimadzu SPM-9500J).

3. RESULTS AND DISCUSSION

Figure 1 shows SEC curves for PCzEMA obtained by the ATRP method. The molecular weight increases with increasing monomer conversion, keeping the polydispersity index M_w/M_n remarkably small.

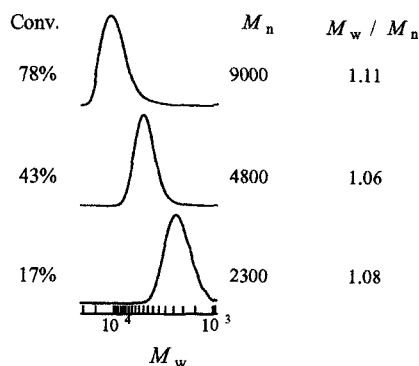


Figure 1 SEC curves of PCzEMA obtained by ATRP with TsCl/CuBr/Sp in anisole at 90°C. THF was used as eluent (40°C).

Figure 2 shows the plot of the number-average molecular weight M_n and M_w/M_n to the monomer conversion. The M_n linearly increased with the monomer conversion. The solid line in the figure is the theoretical molecular weight which was calculated from the following eq. 1 where $[M]_0$ is the concentration of the monomer preparation, $[I]_0$ is the concentration of the initiator, MW_0 is the molecular weight of the monomer, p is the amount of monomer converted, and IW is the molecular weight of the initiator. The experimental values of M_n agreed well with the calculated values, and this fact shows that one initiator molecule generates one propagation chain. Also, the M_w/M_n ratio stayed around 1.2 at all conversions. These results show that M_w/M_n is

very low and the reaction proceeds with quick exchanges between the activated species and

$$M_{n,th} = \frac{[M]_0}{[I]_0} \times MW_0 \times p + IW \quad (1)$$

the dormant species.

The absorption spectra of PCzEMA grafted on the quartz substrate were measured as shown in Fig. 3. All samples exhibited similar absorption spectra consisting of the carbazole (Cz) chromophore (295, 330, 345 nm), and the absorbance was gradually increased with the progress of polymerization. This result suggests that the film thickness is adjustable by choosing the reaction time of polymerization.

Figure 4 shows an AFM image for a PCzEMA sample grafted on a quartz substrate. The left side of this picture was scratched, hence, showing the bare surface of the

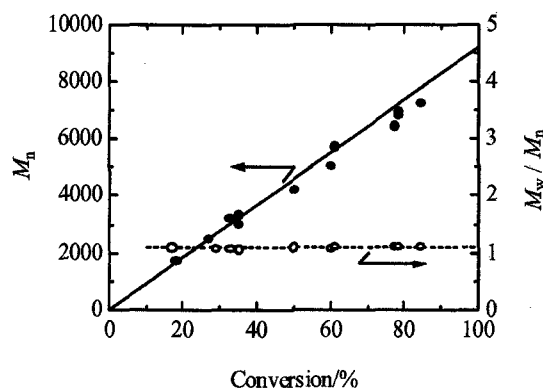


Figure 2 Dependence of molecular weight and polydispersity on monomer conversion for polymerization at 90°C with $[\text{CzEMA}]_0 = 1.72 \times 10^{-3} \text{ mol L}^{-1}$, $[\text{TsCl}]_0 = 5.2 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{CuBr}]_0 = 5.2 \times 10^{-5} \text{ mol L}^{-1}$, $[\text{Sp}] = 1.04 \times 10^{-4} \text{ mol L}^{-1}$. The solid line was calculated from the eq. 1.

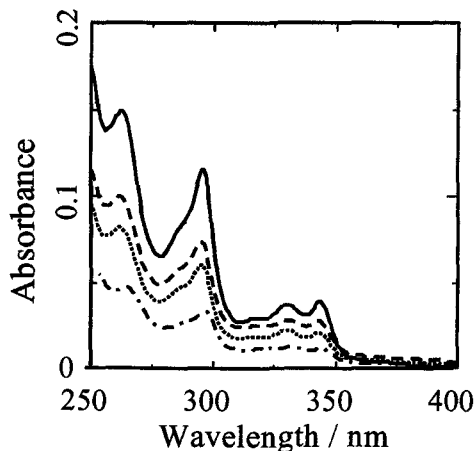


Figure 3 UV absorption spectra of PCzEMA grafted on substrates. The molecular weights of polymers are 6,600, 12,100, 14,600, and 21,300 from the bottom.

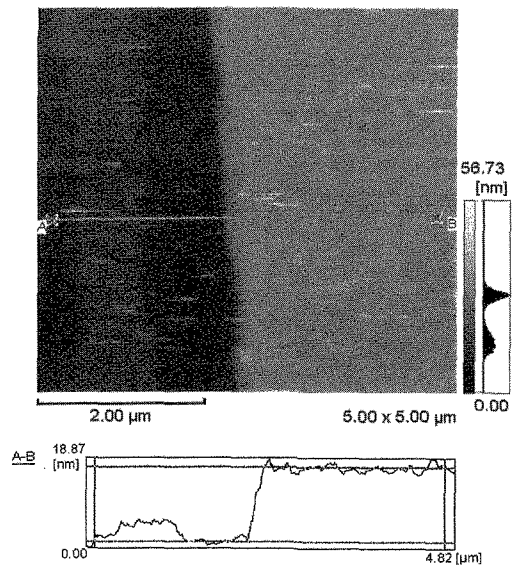


Figure 4 Topographic AFM image of the grafted polymer surface (right) and the bare surface of quartz plate.

quartz plate. The image on the right side clearly shows that a polymer film was formed within a flatness of 1 nm in altitude difference. The film thickness L was evaluated from the height difference between the film surface and the bare surface of the quartz substrate as indicated by the line profile at the lower part of Fig. 4. In this example, the thickness was evaluated to be 16 nm.

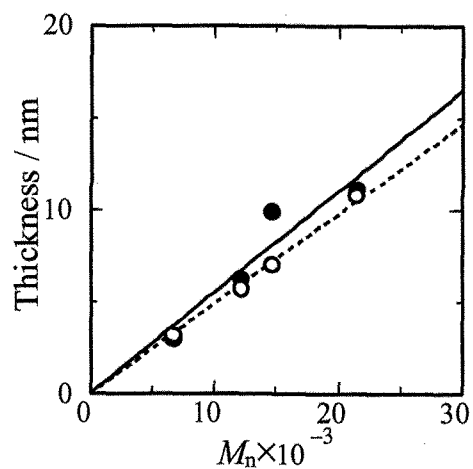


Figure 5 Relationship between M_n of the free polymer and the film thickness measured by AFM(●) and the thickness calculated from UV absorbance(○), assuming the bulk density as 1.23 g cm^{-3} .

Figure 5 depicts the plot of film thickness and M_n of the free polymer in solution. The measured thickness showed a proportional relationship with M_n , again showing that the thickness L is simply given by the polymer chain length, i.e., the degree of polymerization (DP). More important is the value of thickness. For example, the sample of $M_n = 10,000$, corresponding to

DP=30, has a thickness of ca. 5 nm. It is easy to control the DP in the order of a few tens. Therefore it is safely said that this ATRP method can be used to fabricate well-defined layers with a precision of a few nanometers.

From the relationship shown in Fig. 5, the graft plane density ρ on the surface was calculated to be $0.35 \text{ chains nm}^{-2}$, from the following eq. 2, assuming that the film density d is the same as the density of bulk.

$$\rho = N_A L d / M_n \quad (2)$$

where N_A is the Avogadro number. Table 1 lists the plane densities of the polymers examined in this study.

Table 1		
polymer	plane density /chains nm^{-2}	monomer unit volume / nm^3
PCzEMA	0.35	0.19
PTPEMA	0.29	0.19
PMMA	0.70	0.07

Poly(methyl methacrylate) (PMMA) gives the highest plane density among the samples, and the value $\rho = 0.7 \text{ chains nm}^{-2}$ is at least 10 times larger than the density of conventional graft polymers.⁸ The plane densities of PCzEMA and PTPEMA show also high values around $0.3 \text{ chains nm}^{-2}$, which are half of that for PMMA, probably due to the large volume of chromophores at the side chain. These results indicate that the high-density graft polymer bearing photo-functional chromophores can be synthesized on the surface in a living fashion.

To fabricate "layered structures" with high-density graft polymers, we tried to prepare diblock and triblock copolymers on solid surfaces. First, diblock graft copolymers were synthesized in the sequence of Quartz-PMMA-PCzEMA. In these samples, the sulfonyl- phenyl moiety of the initiator CTCS, which was fixed at a quartz plate, has the ability of an electron acceptor and quenches fluorescence from photo-excited carbazole unit. Therefore, the PMMA part in the block copolymer acts as a spacer segment between the CTCS and PCzEMA part. The fluorescence spectra of Quartz-PMMA-PCzEMA are shown in Fig. 6. All the samples exhibit similar emission spectra assigned to the monomer fluorescence bands of the carbazole chromophore at 350 and 365 nm. However, with the decrease of M_n of the PMMA segment, the intensity decreased rapidly, and finally very weak fluorescence was observed associated with a small amount of broad emission at long wavelengths around 450 nm ~ 600 nm. This additional emission was assigned to exciplex of the carbazole unit probably formed with the sulfonyl-phenyl moiety of the initiator. For the Quartz-PCzEMA sample, most of the excitation energy was quenched at the surface as a result of efficient energy migration among the carbazole chromophores. The introduction of PMMA segments effectively prevents the interaction between the carbazole chromophores and the surface, yielding the strong monomer fluorescence.

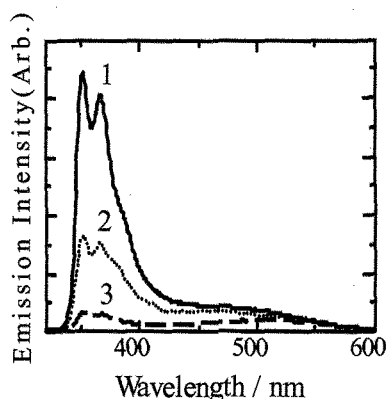


Figure 6. Fluorescence spectra of PCzEMA segments in diblock copolymers grafted on the quartz substrate. The spectra were measured in the air. 1 : Quartz - PMMA (121) - PCzEMA (41), 2 : Quartz - PMMA (14) - PCzEMA (35). 3 : Quartz - PCzEMA(39) without PMMA segments. The excitation wavelength was 295 nm. The numbers in parenthesis present the degree of polymerization DP.

Figure 7 shows the fluorescence spectra of triblock copolymers, Quartz-PTPEMA-PMMA-PCzEMA, in which the PTPEMA segment contains terephthaloyl (TP) units as electron acceptor moieties, and the interaction with the carbazole units was controlled by the spacer block of PMMA segments. The schematic illustration inserted in Fig. 7 indicates the chemical structure of triblocks. The upper figure shows spectra monitored in THF which is a good solvent for methacrylate polymers. The polymer chains take expanded and stretched conformations in the solvent, consequently, the spectra consist of mainly the carbazole monomer emission, indicating little interaction with the TP units. On the other hand, the lower spectra were measured in the air, the copolymers being in the solid state. Compared with the spectra in Fig. 6, the triblock copolymers show much strong interaction between donors and acceptors, irrespective of the M_n of the PMMA segments. This result suggests that the triblock chains were folded in the middle PMMA segments due to their small unit volume as listed in Table 1. The plane density is restricted by the first step polymerization of TPEMA, therefore, the plane density becomes rare for the PMMA chains in the middle part. The excess free volume in the middle part gives rise to the flexibility of triblock polymers, resulting in conformational changes depending on the surrounding medium.

4. CONCLUSION

This study exemplified a novel nano-structures composed of high-density graft copolymers, which were fabricated by surface-initiated ATRP for the photo- and electro-functional methacrylate esters. The living radical polymerization successfully proceeded, yielding graft polymers with a narrow molecular weight distribution. The obtained polymers gave a flat and thin film on the substrate with a thickness of a few nanometers. Fluorescence spectroscopy for the diblock and triblock

copolymers showed that the photophysical interaction between the electron donor and acceptor blocks could be controlled by the layered nano-structures.

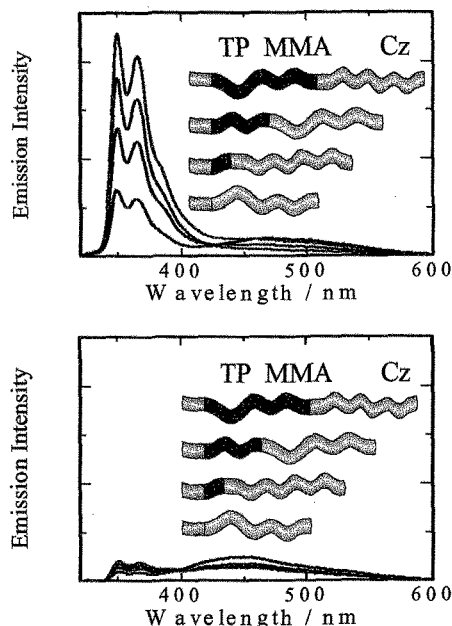


Figure 7 Fluorescence spectra of triblock copolymers grafted on a quartz substrate in the sequence of Quartz-PTPEMA-PMMA-PCzEMA. Inserted are schematic illustrations of triblockes, where the DPs are 6 for TP units, ca.160 for Cz units, and 0, 23, 68, 135 from the bottom to the top for MMA units at the middle part. The upper spectra were measured in THF solvent, and the lower spectra were in the air. The excitation wavelength was 295 nm.

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