

Atom Transfer Radical Polymerization of Graft Chains onto Polyethylene Film Initiated at Tribromomethyl Unit Introduced by Electron Beam Irradiation

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ABSTRACT: A novel process for graft polymerization onto a polyethylene (PE) film using atom transfer radical polymerization (ATRP) was examined. First, a PE film irradiated with an electron beam was treated with carbon tetrabromide, thereby introducing tribromomethyl groups. The number of tribromomethyl groups introduced onto the film could be controlled by adjusting the electron beam irradiation dose. Methyl methacrylate (MMA) was then graft-polymerized by ATRP in the initiator-intro-

duced PE film in the presence of a copper catalyst. Based on FTIR spectra from the PMMA grafted films, the behavior of graft polymerization reactions on the film surface and inside the film are discussed. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2533–2538, 2011

Key words: two-stage graft polymerization; radiation induced graft polymerization; atom transfer radical polymerization; functionalization of polymers

INTRODUCTION

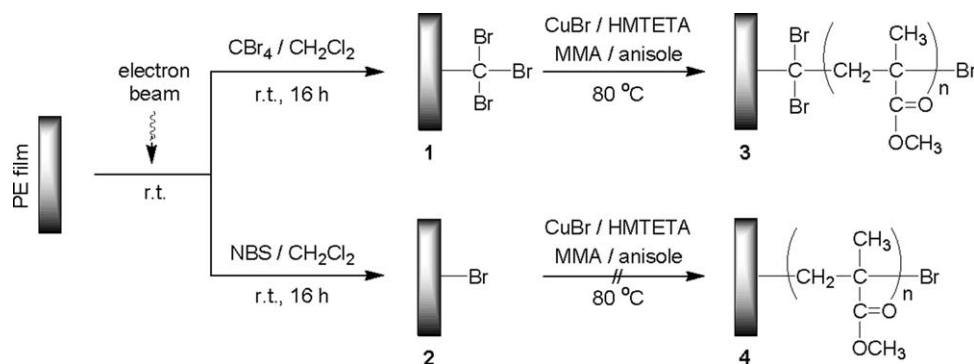
Radiation-induced graft polymerization (RIGP) is a highly versatile technique for introducing various functionalities onto diverse polyolefin substrates without changing the substrate shape.^{1–4} Covalent bonding of functional groups, which are responsible for functional expression, to a polyolefin substrate prevents them from easily volatilizing or eluting from the substrate. Materials produced by RIGP incorporating these features are applied to chemical filters for cleanroom use⁵ and filter materials for treating chemicals used in the semiconductor industry.⁶ Since free radicals in the irradiated substrate are extremely unstable, the RIGP process requires polymerization immediately following irradiation, otherwise cryogenically preserved with inert gas filling. Furthermore, RIGP is based on conventional radical polymerization and is accompanied by side reactions such as crosslinking reactions and terminations. Thus, RIGP cannot be used to precisely control the grafting ratio or the number and length of graft chains.

There have been many studies on atom transfer radical polymerization (ATRP), which can synthesize polymers with narrow molecular weight distribu-

tions by inhibiting side reactions.^{7–12} Some studies have demonstrated the use of ATRP for graft polymerization on the surface of inorganic materials, such as silicon wafers^{13–15} and silica gel particles.^{16–19} These studies reveal that the molecular weight distribution of graft chains is controllable. For these materials, ATRP is possible by the treatment of silanol groups in the substrate with 2-bromoisobutyryl bromide derivatives^{16–18} or thionyl chloride¹⁹ to introduce polymerization initiators. At the same time, ATRP-based graft polymerization in organic polymeric materials after molding presents several difficulties. First, polymerization without shape changes is difficult because the substrate has a lower melting point than that of inorganic materials.^{20,21} Second, a polyethylene (PE) or polypropylene (PP) substrate has no hydroxyl group and is chemically inert, making it difficult to introduce initiators. Some reports have shown that living radical polymerization allows graft polymerization onto shaped polyolefin substrates without shape changes.^{22–25} These reports show that a lengthy process is necessary before the introduction of initiators for ATRP graft polymerization.^{22–25} None of these reports have discussed the number of introduced initiators.

To address these issues, initiators available for ATRP on polyolefin substrates and a simple method for introducing initiators were examined. First, since the RIGP process generates free radicals in the polyolefin substrate through electron beam irradiation, the use of an electron beam for the introduction of

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Scheme 1 Introduction of initiator onto a PE film and ATRP of MMA onto the PE film.

initiators was considered. Next, in view of a recent study in which 2,2,2-tribromoethoxy groups were used as ATRP initiators,²² the direct introduction of tribromomethyl groups onto the substrate was considered. The present study has found a graft polymerization method based on ATRP that introduces tribromomethyl groups from carbon tetrabromide through electron beam irradiation of PE film and uses them as initiators (Scheme 1). By using this technique, grafting ratio and number or length of graft chain becomes controllable more accurately than RIGP. Consequently, it is expected that grafted polyolefin will be applied to high-performance separation such as a substrate for chromatography or biointerface.

EXPERIMENTAL

Materials

A commercially available linear low-density polyethylene (L-LDPE) film (T.U.X HZ#80, Tohcello) was used as the substrate. The thickness of the film was 80 μm and the density was 74 g m^{-2} . It was washed with acetone for 24 h, dried *in vacuo*, and stored under nitrogen before use.

Chemicals

N-bromosuccinimide (NBS, Wako Pure Chemical Industries) was recrystallized from water-methanol. Methyl methacrylate (MMA, Wako Pure Chemical Industries) was purified through a column containing alumina (Alumina B Super I, MP Biomedicals, LLC) before use. Carbon tetrabromide (Wako Pure Chemical Industries), anisole (Wako Pure Chemical Industries), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, Sigma-Aldrich Corporation), copper(I) bromide (Wako Pure Chemical Industries), copper(II) bromide (Wako Pure Chemical Industries), and dichloromethane (Wako Pure Chemical Industries) were used as received without any further purification.

Electron beam irradiation of PE film and treatment with carbon tetrabromide (general procedure for introduction of initiator)

A sheet of PE film (728.1 mg, 10.0 \times 10.0 cm^2) was placed in a zippered PE bag, which was sealed after nitrogen substitution, and irradiated with an electron beam by a curtain type accelerator (Model EC300/30/180L, Iwasaki Electric) at ambient temperature under a nitrogen atmosphere. The accelerator was operated at 0.3 mV for the acceleration voltage and 1.0 mA for beam current, respectively. The electron beam dose was set to 150 kGy. Immediately after irradiation, the bag containing the sample was placed in a glove box under a nitrogen atmosphere to prevent generated radicals from being lost. In the glove box, carbon tetrabromide (49.7 mg, 0.15 mmol) and dichloromethane (150 mL) were added to a glass tube, which was bubbled with nitrogen for 15 min. The irradiated PE film was placed and sealed in the glass tube. The glass tube was then removed from the glove box. Introduction of the tribromomethyl group was carried out by stirring at room temperature for 16 h. A functionalized PE film was obtained by washing the film removed from the glass tube with dichloromethane, further washing it with dichloromethane by a Soxhlet extractor for 16 h, and drying it *in vacuo* at 60°C for 3 h.

General procedure for ATRP of MMA onto CBr₄-treated PE film

Copper(I) bromide (21.5 mg, 0.15 mmol) and copper(II) bromide (11.2 mg, 0.05 mmol) were placed into a glass tube. This glass tube was placed in a glove box under a nitrogen atmosphere. A mixture of HMTETA (92.2 mg, 0.4 mmol), anisole (15 mL), and purified MMA (15 mL) was bubbled with nitrogen for 20 min and added to the glass tube. The solution was thoroughly stirred to dissolve the copper bromide. The CBr₄-treated PE film (147.1 mg, 2.0 \times 10.0 cm^2) was placed in the glass tube and sealed. The glass tube was removed from the glove box, and the graft polymerization reaction was carried out in a water bath at 80°C for 4 h. The film was

TABLE I
Irradiation Conditions Used for the Functionalization of PE Films and
Properties of the Functionalized PE Films

Entry	Treating agent (mmol)	Irradiation dose (kGy)	Elementary analysis (Br; ppm)	CBr ₃ group (μ mol/g)	Product
1	CBr ₄ (0.15)	0	0	0	–
2	CBr ₄ (0.15)	50	180	0.75	1a
3	CBr ₄ (0.15)	100	410	1.71	1b
4	CBr ₄ (0.15)	150	440	1.84	1c
5	CBr ₄ (1.5)	150	440	1.84	1c
6	CBr ₄ (0.15)	200	450	1.88	1d
7	CBr ₄ (0.15)	300	300	1.25	1e
8	NBS (0.15)	150	15	–	2

then removed from the glass tube, washed with acetone, then washed with THF in a Soxhlet extractor for 16 h and finally dried *in vacuo* at 60°C for 3 h. A MMA-grafted PE film (151.6 mg) with a grafting ratio of 3.1% was obtained.

Elemental analysis

Each film was collected on a platinum board and decomposed through combustion at 900°C in flowing Ar/O₂. The generated gas was absorbed by an absorbing solution and brought to a constant volume with pure water. Bromide ions in the test solution were quantified by ion chromatography using the ICS-3000 ion chromatography apparatus (Dionex Corp.) and the IonPac AS12A column (Dionex Corp.).

Measurement of grafting ratio

The grafting ratio (%) is expressed as:

$$R_g(\%) = 100 \times \frac{W_g - W_0}{W_0}, \quad (1)$$

where W_g is the weight of the sample after graft polymerization and W_0 is the weight of the PE film before graft polymerization.

Absorption infrared spectroscopy

Transmission FTIR spectra were recorded using a FT/IR-410 spectrometer (JASCO Corp.). Spectra were recorded at a 4-cm⁻¹ resolution and 48 scans were collected. The measurement was conducted at four different positions on the samples, and the mean of the data was determined. Attenuated total reflection (ATR) FTIR spectra were recorded using an FT/IR-410 spectrometer equipped with an ATR-300/H (JASCO Corp.) accessory and Zn-Se prism. Spectra were recorded at 4-cm⁻¹ resolution and 48 scans were collected. The measurement was conducted on both surfaces of the samples, and the mean of the data was determined.

RESULTS AND DISCUSSION

Treatment of electron beam irradiated polyethylene film with carbon tetrabromide

The results of elementary analysis of the PE film after carbon tetrabromide treatment are listed in Table I. The amount of bromine introduced to the PE film increased with the irradiation dose up to 200 kGy. However, the amount of bromine introduced increased only slightly in the irradiation dose range from 150 to 200 kGy and decreased at an irradiation dose of 300 kGy. This suggests that an excessively high irradiation dose induces crosslinking reactions between free radicals due to heat caused by irradiation, resulting in a decrease in the number of tribromomethyl groups. In fact, the PE film and PE bag containing the film were partially fused together after irradiation at 300 kGy.

Assuming that all the introduced functional groups are tribromomethyl groups as expected for the PE film treated with carbon tetrabromide, the amount of functional groups introduced, N_{CBr_3} (μmol g⁻¹), can be obtained from eq. (2), where X_{Br} is the value obtained from elementary analysis for bromine (μg g⁻¹), and M_{Br} is the atomic weight of bromine.

$$N_{\text{CBr}_3} = \frac{X_{\text{Br}}}{3M_{\text{Br}}} \quad (2)$$

For the irradiated PE film treated with NBS, instead of carbon tetrabromide, 15-ppm bromine was detected by elemental analysis (Table I, Entry 8). This suggests that bromine is bonded directly to all polyethylene chains.

Considering the PE film size used for this study (100 × 100 mm²), no variation in the introduced amount of functional groups was observed when the amount of carbon tetrabromide added was 0.15 mmol or more (Table I, Entries 4 and 5). The amount introduced depended only on the irradiation dose. This fact indicates that 0.15 mmol carbon tetrabromide was excessive in molar equivalent relative to the number of free radicals generated in the PE film through electron beam irradiation.

ATRP of MMA onto CBr_4 -treated PE film

Among the films treated with carbon tetrabromide, the ATRP of MMA onto **1a** and **1c** was carried out, in each case with different CuBr and CuBr_2 ratios for comparison. For both **1a** and **1c**, the graft polymerization of MMA progressed as expected, as shown in Figure 1, indicating that tribromomethyl groups introduced onto the PE film worked as ATRP initiators. It was considered that $\text{CuBr}/1,1,4,7,10,10$ -hexamethyl-triethylenetetramine (HMTETA) complexes cleaved the carbon-bromine bond in film **1a** and **1c**. The ATRP of MMA onto the NBS-treated PE film **2** was also carried out under the same conditions, but no polymerization occurred at least within the reaction time of 24 h. It was considered that the homolytic bond dissociation energy of the carbon-bromine bond in film **2** was excessively large, and bromine atoms were not withdrawn by $\text{CuBr}/\text{HMTETA}$ complexes.

The grafting of MMA into the PE film **1c** [Fig. 1(b)] yielded a higher grafting ratio than that for **1a** [Fig. 1(a)]. This is because of the larger number of tribromomethyl groups (initiators) introduced on the surface of the PE film **1c**. For both **1a** and **1c**, the grafting ratio decreased with increasing amount of CuBr_2 added to the solution. The use of $\text{CuBr}/\text{HMTETA}$ complexes alone provided the highest grafting ratio, but drastically lowered the polymerization rate, as is the case with conventional radical polymerization. This suggests that there was almost no regeneration of dormant species with $\text{CuBr}_2/\text{HMTETA}$ complexes, since the number of $\text{CuBr}/\text{HMTETA}$ complexes was more than five hundred times the number of initiators on each PE film, and the number of $\text{CuBr}/\text{HMTETA}$ complexes was also much larger than the number of $\text{CuBr}_2/\text{HMTETA}$ complexes after withdrawal of bromine atoms by the complexes. On the other hand, the addition of CuBr_2 allowed the regeneration of dormant species, with a relatively small drop in the polymerization rate over time. The low grafting ratio in a reaction time of 2 h may be attributable to the fact that it takes time for copper complexes to diffuse inside the films, delaying the start of the ATRP process within the films.

Transmission-FTIR measurements of the MMA-grafted PE film

The grafted films obtained in the present study are comprised of a PE trunk polymer and a PMMA graft polymer. The grafting ratio can be expressed by eq. (3):

$$R_g(\%) = 100 \times \frac{W_{\text{PMMA}}}{W_{\text{PE}}}, \quad (3)$$

where W_{PE} and W_{PMMA} are the weights of PE and PMMA in each film. Since the weights of PE (W_{PE}) and PMMA (W_{PMMA}) in each film are proportional to the mol concentrations of PE (c_1) and PMMA (c_2) in the

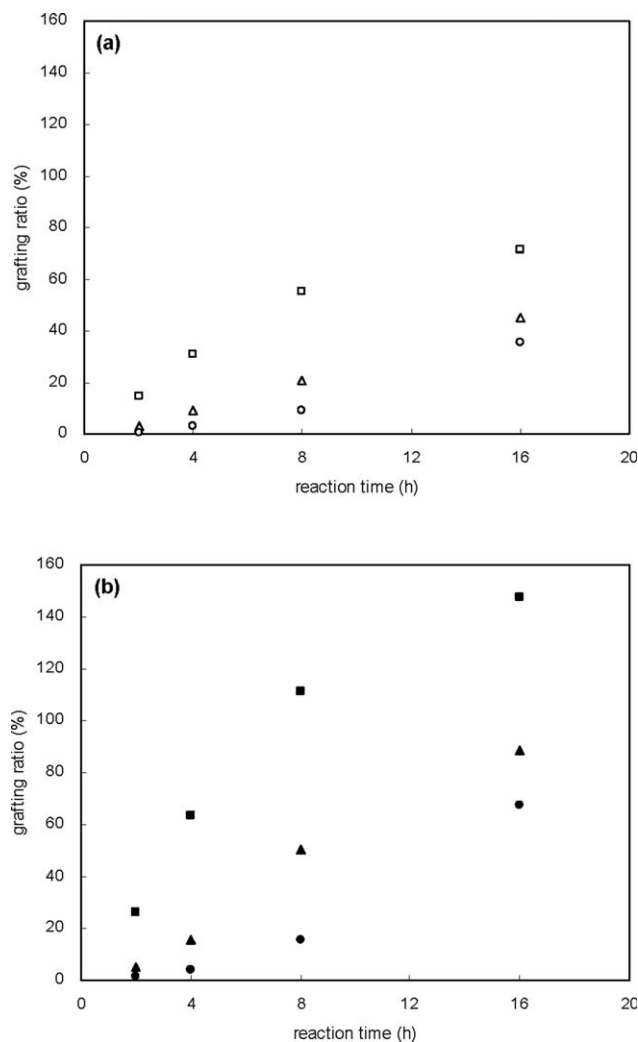


Figure 1 Grafting ratio of PMMA-grafted PE film as a function of the reaction time, (a) from the film **1a**, (b) from the film **1c**. $[\text{CuBr}] + [\text{CuBr}_2] = 2.0$ mmol. $[\text{HMTETA}] = 4.0$ mmol. $[\text{CuBr}_2]/([\text{CuBr}] + [\text{CuBr}_2])$: (□), (■) = 0; (△), (▲) = 0.1; (○), (●) = 0.25.

film, eq. (3) can be rewritten as eq. (4) with α as a proportional constant. Therefore, the grafting ratio is proportional to the ratio of the concentrations of PMMA and PE in each film.

$$R_g(\%) = \alpha \frac{c_2}{c_1} \quad (4)$$

The FTIR absorbance (A_1) of PE and that (A_2) of PMMA at the specific absorption wavelengths of the grafted films are proportional to c_1 and c_2 , respectively. Thus, eq. (5) can be derived from Beer's law as:

$$\frac{A_2}{A_1} = k \frac{c_2}{c_1}, \quad (5)$$

where k is a proportional constant taking into account the difference in molar absorbance coefficients between the two components. As given by eqs. (4) and (5), the grafting ratio is proportional to

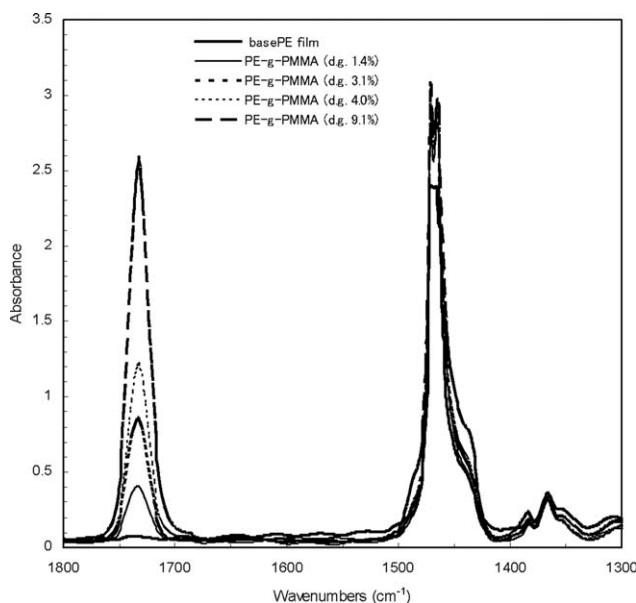


Figure 2 Transmission-FTIR spectra of PMMA-grafted PE film and base PE film.

A_2/A_1 . Consequently, it is expected that the grafting ratio of PMMA can be calculated by measuring the ratio of absorption band intensities of PE and PMMA (peak area ratio).²⁶

The transmission-FTIR spectra of various PMMA-grafted films for which the grafting ratio is already known were measured for comparison (Fig. 2). In the present study, PMMA has the stretching vibration of carbonyl groups (A_1) at 1732 cm^{-1} , while PE has the bending vibration of the C–H bond (A_2) at 1458 cm^{-1} . As shown in Figure 2, the absorption band (A_1) expanded as the grafting ratio of MMA increased. From the FTIR spectra, the peak areas P_1 and P_2 were determined based on the absorption bands (A_1 and A_2) to plot the grafting ratio and peak area ratio (P_2/P_1) of the films. The resultant calibration curve shows a comparatively high correlation between the grafting ratio and the peak area ratio (P_2/P_1) in the range of the grafting ratio of up to 5% or less (Fig. 3). When the grafting ratio was higher than 5%, the value of (P_2/P_1) became small. At a grafting ratio of more than 20%, the maximum value of the absorption band (A_1) exceeded an absorbance of 5, making it impossible to measure the value.

ATR-FTIR measurements of MMA-grafted PE film

The grafting ratio on the film surface was calculated using the calibration curve obtained and the ATR-FTIR spectra of the PMMA grafted films. The penetration depth d_p is expressed by eq. (6):

$$dp(\mu\text{m}) = \frac{\lambda}{2\pi\sqrt{\sin^2\theta - (n_s/n_c)^2}}, \quad (6)$$

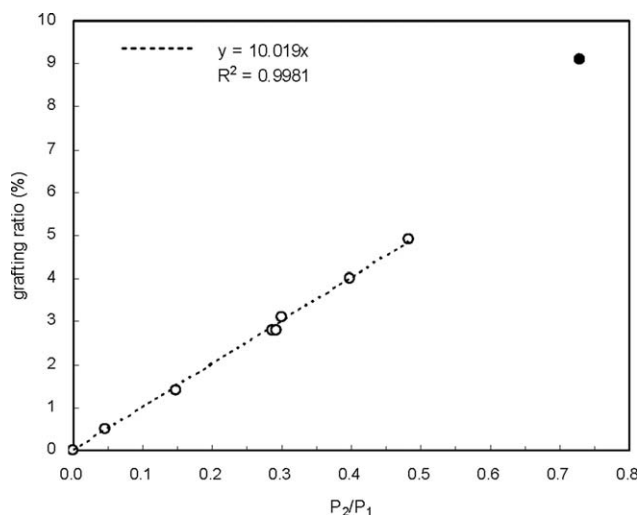


Figure 3 Degree of grafting of PMMA-grafted PE film as a function of the IR absorption peak ratio (P_2/P_1).

where λ is the wavelength of light in the prism, θ is the incidence angle of light, n_s is the refractive index of each sample, and n_c is the refractive index of the prism. In the present study, the incidence angle was 45° , and a Zn-Se prism (refractive index $n_c = 2.4$) was used. Assuming that the refractive index of the samples is 1.5, the penetration depth at 1458 and 1732 cm^{-1} is 1.38 and $1.16\text{ }\mu\text{m}$, respectively.

The ATR-FTIR spectra shown in Figure 4 indicate that the absorbance of PMMA increased over time. By obtaining the peak area ratio (P_2/P_1) from these spectra in the same manner as for the transmission-FTIR, the grafting ratio was calculated based on the calibration curve. The results obtained when the ratio ($[\text{CuBr}_2]/([\text{CuBr}] + [\text{CuBr}_2])$) was 0.25 are shown

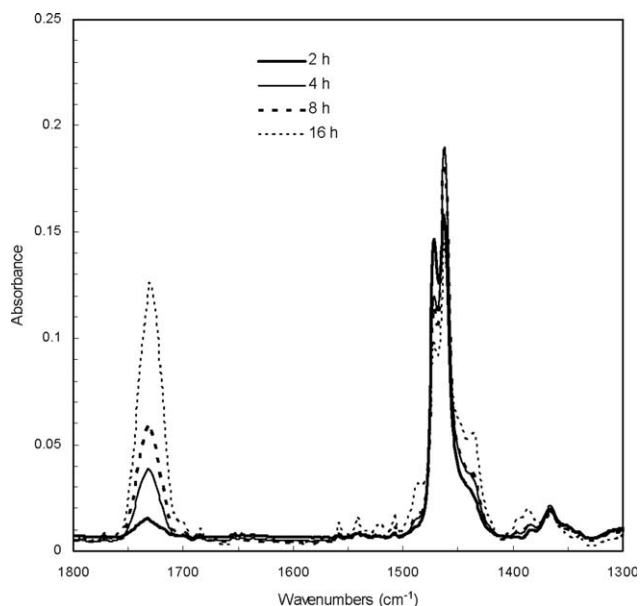


Figure 4 ATR-FTIR spectra of PMMA-grafted PE film from 1a.

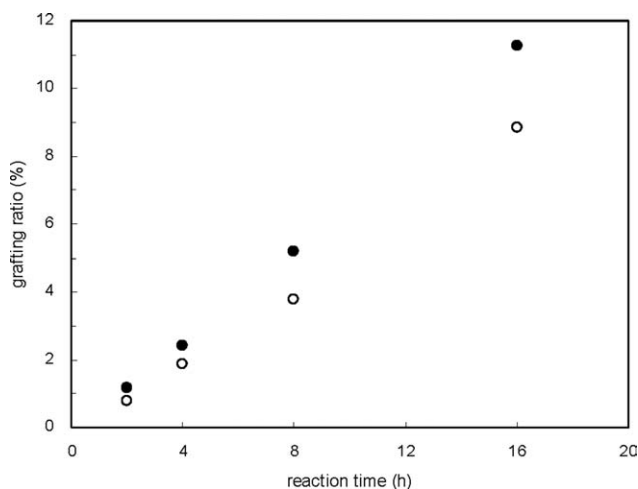


Figure 5 Surface grafting ratio of PMMA can be calculated from the IR absorption peak ratio (P_2/P_1) and the calibration curve. $[CuBr_2]/([CuBr] + [CuBr_2]) = 0.25$. Grafted from: (○), **1a**; (●), **1c**.

in Figure 5. For both **1a** and **1c**, this figure shows a relatively linear increase in the grafting ratio, indicating ideal ATRP behavior for polymerization with fewer side reactions. Under the same reaction conditions, the whole grafting ratio of the films (Fig. 1) increased drastically over time. This result may be attributable to the difference between the concentrations of copper catalyst near the film surface and inside the film. The copper catalyst can easily move toward initiators and terminals of graft chains in the vicinity of the film surface, facilitating the regeneration of dormant species with $CuBr_2/HMTETA$ complexes. On the contrary, the copper catalyst cannot easily diffuse from the surface into the inside of the film, resulting in a lower concentration of copper catalyst inside the film than on the surface. For graft chains in the process of polymerization, the regeneration of dormant species with $CuBr_2/HMTETA$ complexes is less likely to take place, and thus it may be the case that graft polymerization progresses at a reaction rate as high as conventional radical polymerization.

Consequently, this method can introduce graft chain onto molded PE substrate as well as RIGP. In addition, control and quantitative determination of initiator have been possible, which has been impossible in RIGP. Moreover, this method rarely causes the side reaction that has been observed in conventional radical polymerization, therefore, grafting ratio is accurately-controlled in this method rather than RIGP.

CONCLUSIONS

Tribromomethyl groups were introduced onto a PE film through electron beam irradiation and treat-

ment with carbon tetrabromide, and ATRP of MMA was carried out using tribromomethyl groups as initiators. The selection of a substrate with a comparatively large surface area is expected to facilitate ideal ATRP behavior for graft polymerization across the entire material. In addition, the finding of a reaction system that provides uniform graft polymerization across the entire material allows for the estimation of the number-average molecular weight of graft chains based on the introduced amount of initiators and the grafting ratio.

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References

- Saito, K.; Ito, K.; Yamagishi, M.; Furusaki, H.; Sugo, T.; Okamoto, T. *J Ind Eng Chem Res* 1989, 28, 1808.
- Saito, K.; Kaga, T.; Yamagishi, M.; Furusaki, S.; Sugo, T.; Okamoto, J. *J Membr Sci* 1989, 43, 131.
- Saito, K.; Tsuneda, S.; Kim, M.; Kubota, N.; Sugita, K.; Sugo, T. *Radiat Phys Chem* 1999, 54, 517.
- Komatsu, M.; Kaneko, M.; Fujiwara, K.; Takeda, K. *J. Ion Exchange* 2003, 14 (Suppl), 41.
- Okamoto, J.; Sugo, T.; Fujiwara, K.; Sekiguchi, H. *Radiat Phys Chem* 1990, 35, 113.
- Hashimoto, Y.; Amari, M.; Komatsu, M.; Fujiwara, K. *Solid State Phenomena* 2005, 103, 265.
- Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* 1995, 28, 1721.
- Sawamoto, M.; Kamigaito, M. *Trends Polym Sci* 1996, 4, 371.
- Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem Rev* 2001, 101, 3689.
- Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7901.
- Wang, J. S.; Matyjaszewski, K. *J Am Chem Soc* 1995, 117, 5614.
- Xia, J.; Matyjaszewski, K. *Macromolecules* 1997, 30, 7697.
- Ejaz, M.; Yamamoto, S.; Ohno, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* 1998, 31, 5934.
- Ejaz, M.; Ohno, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* 2000, 33, 2870.
- Ejaz, M.; Yamamoto, S.; Tsujii, Y.; Fukuda, T. *Macromolecules* 2002, 35, 1412.
- Chen, X.; Randall, D. P.; Perruchot, C.; Watts, J. F.; Patten, T. E.; Werne, T.; Armes, S. P. *J Colloid Interface Sci* 2003, 257, 56.
- Harrak, A. E.; Carrot, G.; Obserdisse, J.; Eychenne-Baron, C.; Boue, F. *Macromolecules* 2004, 37, 6376.
- Zhao, H.; Kang, X.; Liu, L. *Macromolecules* 2005, 38, 10619.
- Xu, F. J.; Cai, Q. J.; Kang, E. T.; Neoh, K. G. *Macromolecules* 2005, 38, 10541.
- Yamamoto, K.; Nakazono, M.; Miwa, Y.; Hara, S.; Sakaguchi, M.; Shimada, S. *Polym J* 2001, 33, 862.
- Yamamoto, K.; Tanaka, H.; Sakaguchi, M.; Shimada, S. *Polymer* 2003, 44, 7661.
- Yamamoto, K.; Miwa, Y.; Tanaka, H.; Sakaguchi, M.; Shimada, S. *J Polym Sci A* 2002, 40, 3350.
- Xing, C. M.; Deng, J. P.; Yang, W. T. *Polym J* 2002, 34, 801.
- Xing, C. M.; Deng, J. P.; Yang, W. T. *Polym J* 2002, 34, 809.
- Xing, C. M.; Deng, J. P.; Yang, W. T. *Polym J* 2003, 35, 613.
- Feng, J.; Haasch, R. T.; Dyer, D. J. *Macromolecules* 2004, 37, 9525.