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Well-defined poly(methyl methacrylate) grafted to polyethylene with reverse atom transfer radical polymerization initiated by peroxides

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Abstract

A reverse atom transfer radical polymerization (ATRP) with $FeCl_3/PPh_3$/peroxides was applied to grafting of methyl methacrylate (MMA) to polyethylene (PE). Peroxides on PE were generated by γ-ray irradiation in air. A reverse ATRP of methyl methacrylate with benzoyl peroxide, cumene hydroperoxide, and di-*t*-butyl peroxide as models of the PE peroxides was confirmed to proceed successfully in living fashion. In an inhomogeneous (bulk) grafting system, the grafting ratio (GR) of PMMA to PE weights, molecular weight (M_n) and its distribution of grafted PMMA were not controlled with time, i.e. the grafting of MMA with a reverse ATRP to the oxidized PE failed in well-defined grafting. On the other hand, a homogeneous (in *o*-xylene solution) grafting system provided a well-controlled M_n, narrow polydispersity of grafted PMMA and a linear relation between M_n and GR, indicating a controlled grafting. The controlled grafting with a reverse ATRP combined to a radiation-induced grafting was achieved successfully. The grafting of MMA to polypropylene in this way also seemed to be controlled well.

Keywords: Reverse ATRP; Peroxide; Controlled grafting

1. Introduction

Polyethylene (PE) and polypropylene (PP) have been one of the most useful polymers among polyolefin's because of an impact resistance, a chemical stability, a thermal stability, etc. However, a low compatibility of such polymers with other polymers, dyes, fillers and so on has been the point at issue. The lack of reactive groups in the polyolefins has limited lots of there end uses. When the interaction with other materials is important, a modification of these polyolefins should be required. In order to improve these shortcomings, various techniques of chemical modifications of polyolefins have often been established. The grafting of other polymer to the polyolefins is one method of the modification.

The grafting method has been most frequently studied and applied to a wide range of the polymer materials in industry. Ionizing radiation (γ-ray, X-ray, and electron beam) in the presence of air, ozone treatment, UV radiation and free-radical initiators [1] have been used to oxidize polymeric materials and finally produce the polymeric peroxides on the chains. The oxidant is polar group that interact with other polar materials and the peroxides in the oxidant can act as initiators of radical polymerization. The heating the irradiated polymer in the monomer initiates the polymerization, which is in the category of 'graft-from'. However, it had been difficult to obtain the well-defined molecular weight of grafted polymer because the side reactions such as a recombination, a disproportionation, a cross-linking and a chain scission, resulting in loss of mechanical properties.

The 'living' polymerizations, including anionic [2] and cationic [3] polymerizations, have been used to obtain graft copolymers with well-defined structures [4–20]. Besides the stringent condition required for ionic polymerizations, they are limited by the scope of monomers used. In contrast, controlled free radical polymerization combine ease of polymerization. Some researchers have reported the controlled grafting techniques with living free radical

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polymerization in order to design a precise molecular weight of grafted polymer. Chung has developed an interesting approach to polyolefin/poly(methyl methacrylate) graft copolymers by careful introduction of oxygen to a borane-functionalized polyolefins [4–7]. Hawker reported a synthesis of PP-*graft*-polystyrene by a combination of metallocene and stable free radical polymerization (SFRP), in which the molecular weight and polydispersity were controlled [8]. Mülhaupt et al. synthesized highly branched polyethylene graft copolymers prepared by TEMPO-mediated graft polymerization [9]. Ying reported a synthesis of ethylene-propylene-diene terpolymer/poly(methyl methacrylate) graft copolymers with well-defined structure by atom transfer radical polymerization (ATRP) [10]. A synthesis of polyolefin grafted copolymers via living polymerization techniques in which a monomer of *n*-butyl acrylate having PE branch were polymerized by ATRP (‘graft-through’) method were reported [11]. We also recently developed control grafting of methyl methacrylate (MMA) to PE film with ATRP techniques [12]. These are excellent ways but it seems strenuous to synthesize initiators, reactive monomer, and modification of polymer before grafting. Recently, the facile approaches for controlled grafting were investigated. The controlled grafting without a specific modification was reported by Percec et al. who investigated that metal-catalyzed living radical graft copolymerization of olefins initiated from the structural defects of poly(vinyl chloride) [13,14]. Our previous works reported that controlled grafting of styrene (or styrene/*n*-BMA) to oxidized PE and PP by combination of SFRP and radiation-induced grafting that has been widely used for grafting [15–18].

In ATRP and SFRP, not to mention the controlled grafting with ATRP and SFRP, initiators, mediators, and ligands are rather costly. On the other hand, reverse ATRP are considerably cost-effective and useful for industry. Reverse ATRP differs from a typical ATRP in its initiation process, in which conventional radical initiators, including α,α'-azobisisobutylonitrile (AIBN) [21–26], BPO [27,28], 1,1,2,2-tetraphyenyl-1,2-ethandiol (TPED) [29,30], and others [31,32] are used with the transition-metal in its higher oxidation state. In this paper, we report a controlled grafting of methyl methacrylate (MMA) to oxidized PE and PP with a reverse ATPR that has not been known as far as we know. There are few studies for a controlled grafting with reverse ATRP. Using azo self-assembled membrane initiators, synthesis of polystyrene-*block*-PMMA brushes by reverse ATRP was only reported [33].

We first show that some peroxides play an effective role as initiators with $FeCl_3(PPh_3)_2$ catalyst for a reverse ATRP of MMA. The BPO, cumene hydroperoxide, and di-*tert*-butyl peroxides are proved to initiate successfully a reverse ATRP of MMA with the iron-catalyst. These peroxides can be models of polymeric peroxides. Thus, polymeric peroxides can be used as macroinitiators of controlled grafting with the iron catalyst. Presented grafting technique is easy and quite important for industry.

2. Experimental Section

2.1. Materials

High density PE (PE, H650W, $M_n = 1.3 \times 10^4$, $M_w = 8.0 \times 10^4$) and isotactic PP ($M_v = 4.0 \times 10^5$), which was supplied from Mitsubishi Chemical Co., Ltd., was dissolved in boiling toluene, cooled to room temperature, filtered, and dried in a vacuum oven. This procedure was repeated three times. MMA (reagent, Nacalai Tesque Co., Ltd.) was distilled under reduced pressure. Benzoyl peroxide (BPO) (reagent, Nacalai) was dissolved in chloroform, precipitated into methanol, and recrystallized. AIBN, $FeCl_3{\cdot}6H_20$, $FeCl_2{\cdot}4H_20$, di-*tert*-butyl peroxide (TBP), and cumene hydroperoxide (CHP) were purchased from Nacalai (Reagent) and used as received. Triphenylphosphine (PPh_3) (Reagent, Nacalai) recrystallized in a refrigerator from ethanol solution to remove oxidants. *o*-Xylene (Extra Pure, Nacalai), tetrahydrofuran (THF) (Extra Pure, Nacalai), and acetone (Extra Pure, Nacalai) were distilled before use. Hydriodic acid (reagent, 55%) was purchased from Aldrich Chemical Co., Ltd. and used as received.

2.2. Reverse ATRP of MMA with peroxides

Typical example is here. MMA (1.4×10^{-2} mol), peroxides (1.4×10^{-5} mol), and PPh_3 (1.68×10^{-4} mol) were put in a glass ampule and stirred to a complete homogeneous solution. After that, $FeCl_3$ (5.6×10^{-5} mol) was introduced in the glass ampule and stirred. This ampule was connected to a vacuum line, degassed from the solution by freeze-and-thaw method, and sealed under reduced pressure. The ampule was heated in an oil bath at polymerization temperature of 85 °C. After polymerization, the resultant was dissolved into acetone, precipitated into excess methanol, filtered, and dried under a vacuum oven. The dried polymer was weighed to obtain a monomer conversion. For solution polymerization, the same procedure was carried out except for an addition of *o*-xylene into a reaction ampule.

2.3. Controlled grafting of MMA to polyolefin

PE (or PP) was irradiated by γ-rays in air to generate peroxides on the polymer chains. Typical example is here. The oxidized PE (30 kGy, 0.5 g), MMA (2.9×10^{-2} mol), PPh_3 (1.39×10^{-4} mol), $FeCl_3$ (4.64×10^{-5} mol), and AIBN (1.16×10^{-5} mol) as a free initiator were put in a glass ampule. AIBN was used in the grafting to control a reaction system and a free polymer that was not grafted. The grafting in *o*-xylene was performed at 110 °C. After grafting, the resultant was completely dried and weighed

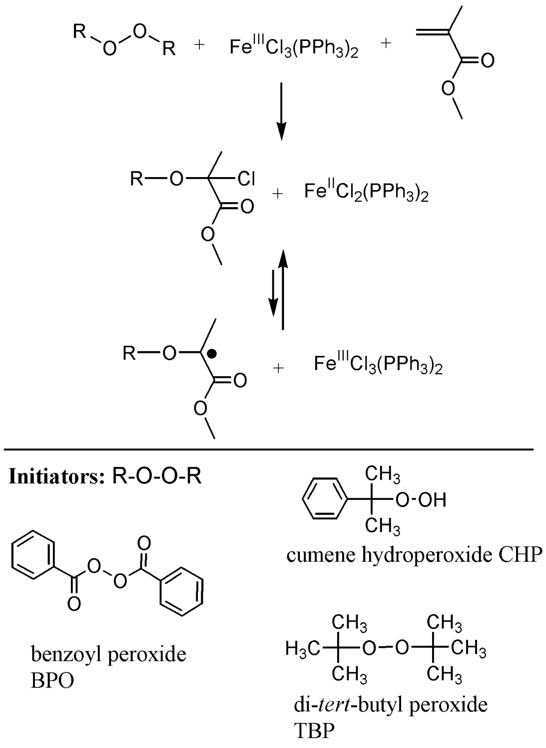

Fig. 1. Reverse ATRP of MMA with peroxides.

to determine a monomer conversion. The free PMMA was extracted with acetone and the grafted material was washed by Soxhlet extraction with THF. After completely drying the grafted material, the grafting ratio (GR) was estimated by FT-IR measurement.

2.4. Cleavage of the PMMA grafted to polyolefin

The grafted PMMA was cleaved from the PE and PP main chains by reaction with hydriodic acid. As a typical reaction, a sample of PMMA grafted to PE (ca. 0.2 g) in hydriodic acid (1.5 ml) and toluene (1.5 ml) mixture was allowed to stand at room temperature for three days and then was evaporated in vacuum. The dried sample was immersed into THF, and the grafted PMMA was extracted; thus, the grafted PMMA and the PE main chain were separated. The extracted grafted PMMA was precipitated in methanol, filtered, and dried in vacuum. The yield of PMMA was a few mg.

Table 1
Polymerization of MMA with BPO in the presence of Fe(II) catalysts at 85 °C

Run	$[MMA]_0/[BPO]_0$	Time (h)	Conversion (%)	M_n	M_w/M_n
11[a]	680	8.0	10.8	83,300	1.69
12[b]	1000	2.0	23.7	32,000	1.31
13[b]	1000	8.0	26.6	60,000	1.24
14[b]	1000	12.0	50.7	86,000	1.71
15[b]	1000	24.0	41.2	65,000	1.53

Conditions: MMA 1.1×10^{-2} mol (1.16 ml), $[BPO]_0/[FeCl_2]_0/[PPh_3]0 = 1/4/12$.

[a] In bulk.

[b] In acetone (1.0 ml).

2.5. Measurements

M_n and polydispersity of the grafted and free polymers were determined by gel permeation chromatography (GPC) in THF (1 ml/min) at 313 K on four polystyrene gel columns—Tosoh TSK gel GMH, G4000H, G2000H, and G1000H—that were connected to an online degasser (SD-8022 Tosoh), a Tosoh CCPE pump, and a ERC-7522 RI refractive index detector (ERMA Inc.). The columns were calibrated against standard PMMA (Polymer Laboratory, Inc.) samples. NMR was performed on a Bruker AVANCE 200 spectrometer using deuterated chloroform at 25 °C with tetramethylsilane as an internal reference. The grafting ratio (GR) was defined as follows:

$$GR(wt\%) = 100 \times (W_g - W_0)/W_0$$

Here W_g is the weight of the sample after grafting, and W_0 is the initial weight of the irradiated PE or PP. The GR was estimated by the FT-IR (IMPACT400D, Nicolet Instrument Co.; KBr) method because of a large experimental error involved in measuring the weight increase after grafting. Grafting ratios were calculated from the ratio of the IR absorbance of PMMA ($1730\ cm^{-1}$) to that of $1460\ cm^{-1}$, where the absorption at $1730\ cm^{-1}$ is assigned to the C=O stretching vibration of the carbonyl and that at $1460\ cm^{-1}$ to the CH_2 rocking vibration of the PE, PMMA, or PP main chains. In advance, some mixtures of PMMA and PE (or PP) were prepared to make a calibration curve of the grafting ratio (weight ratio of the mixture) against the absorbance ratio.

3. Result and discussion

3.1. Reverse ATRP of MMA with peroxides

Fig. 1 shows reaction scheme of reverse ATRP with peroxides. The peroxides decompose to generate free radicals. The free radicals react with MMA monomer, the MMA propagating radical abstracts chlorine from $FeCl_3$ into a dormant species (The $FeCl_3$ was reduced to $FeCl_2$). After that, the reaction proceeds in accordance to a typical ATRP process. Resulting polymer had protons (7.5–8.0 ppm) of benzene ring arising from a decomposed BPO at the PMMA α-end that were revealed from NMR measurement, indicating the initiation occurred from decomposed BPO radicals. At ω-end, a signal of methylene protons (2.5 ppm) with chlorine shifted toward lower magnetic field. As for the PMMA with M_n of 11700 estimated from GPC (run 7 in Table 1), the M_n's calculated from NMR were 13,500 and 12,800 using a signal intensity of protons on benzene ring at α- and methylene protons at

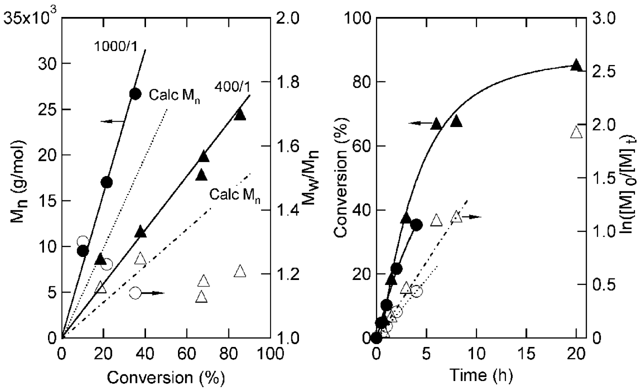

Fig. 2. Reverse ATPR of MMA with BPO in the presence of Fe catalysts at 85 °C in bulk. MMA 1.4×10^{-2} mol (1.48 ml), initial ratio of $[BPO]_0/[FeCl_3]_0/[PPh_3]_0 = 1/4/12$. Left: solid and open symbols indicate M_n and M_w/M_n, respectively. The dotted and dot-dashed lines indicate the calculated M_n for $[MMA]_0/[BPO]_0$ of 1000/1 (circles) and 400/1 (triangles). Right: conversion (solid) and $\ln([M]_0/[M]_t)$ vs. time.

ω-ends, respectively. Results of the polymerization are summarized in Fig. 2 and Table 1. The M_n of PMMA increased linearly with monomer conversion when the initial feed ratios of $[MMA]_0/[BPO]_0$ were 1000/1 (circles) and 400/1 (triangles) and the polydispersity's of PMMA were 1.14–1.30. Thus, the polymerization was controlled. The dotted and dot-dashed lines indicate the calculated M_n as follows

$$M_{n,calc} = ([MMA]_0/2[I]_0) \times M_{w,MMA} \times \text{conversion}$$

Here, $[I]_0$ is an initiator concentration and $M_{w,MMA}$ is a monomer molecular weight. The initiation efficiency $f(= M_{n,calc}/M_n)$ was obtained to be 0.67.

Table 2
Polymerization of MMA with peroxides in the presence of Fe catalysts

Run	Initiator	Time (h)	Conversion	M_n	M_w/M_n
1[a]	CHP	0.5	16.7	26,300	1.15
2[a]	CHP	1.0	35.8	38,800	1.20
3[a]	CHP	2.0	55.7	59,000	1.29
4[a]	CHP	4.0	59.7	64,500	1.35
5[a]	CHP	8.0	71.3	70,300	1.45
6[a]	CHP	12.0	72.5	75,300	1.42
7[a]	TBP	0.5	35.0	30,500	1.14
8[a]	TBP	1.0	56.9	46,500	1.15
9[a]	TBP	4.0	84.5	71,100	1.20
10[b]	CHP	3.0	7.3	37,500	1.23
11[b]	CHP	6.0	22.1	54,300	1.34
12[b]	CHP	12.0	31.2	78,000	1.30
13[b]	CHP	24.0	46.4	10,6000	1.39
14[b]	TBP	3.0	9.6	33,800	1.28
15[b]	TBP	6.0	24.5	49,900	1.33
16[b]	TBP	12.0	39.2	71,800	1.34
17[b]	TBP	24.0	55.2	97,200	1.42

[a] Conditions: at 110 °C in bulk, MMA 0.9×10^{-2} mol (0.953 ml), $[MMA]_0/[Peroxide]_0/[FeCl_3]_0/[PPh_3]_0 = 750/1/3/9$.

[b] Conditions: at 85 °C in acetone (1.0 ml), MMA 0.9×10^{-2} mol (0.953 ml), $[MMA]_0/[BPO]_0/[FeCl_2]_0/[PPh_3]_0 = 2000/1/3/9$. CHP: cumene hydroperoxide, TBP: di-*tert*-butyl peroxide.

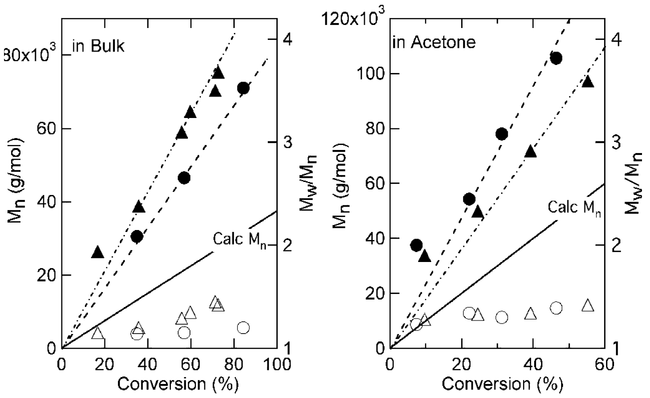

Fig. 3. Reverse ATRP of MMA with CHP (circles) and TBP (triangles) in bulk (left) and in acetone solution (right). Solid and open symbols indicate M_n and M_w/M_n, respectively. Solid lines are calculated M_n. In bulk: MMA 0.9×10^{-2} mol (0.953 ml), $[MMA]_0/[Peroxide]_0/[FeCl_3]_0/[PPh_3]_0 = 750/1/3/9$. Polymerization was carried out at 110 °C. In acetone (1.0 ml), MMA 0.9×10^{-2} mol (0.953 ml), $[MMA]_0/[BPO]_0/[FeCl_2]_0/[PPh_3]_0 = 2000/1/3/9$. Polymerization was carried out at 85 °C.

In a control experiment, we checked if $FeCl_2$ could be effective for a living radical polymerization of MMA. In the bulk polymerization, $FeCl_2$ was not dissolved well in MMA monomer. The result is listed in Table 1 run 1. The polymerization rate was relatively slow, the M_n was remarkably larger than $M_{n,calc}$, and the molecular weight distribution was broad, indicating an ill-controlled polymerization. In order to increase the solubility of $FeCl_2$ in a solution, acetone as a solvent was used and the results were in the Table 1 (run 2–5). Although the reaction rate increased and the polydispersity became a small value, the

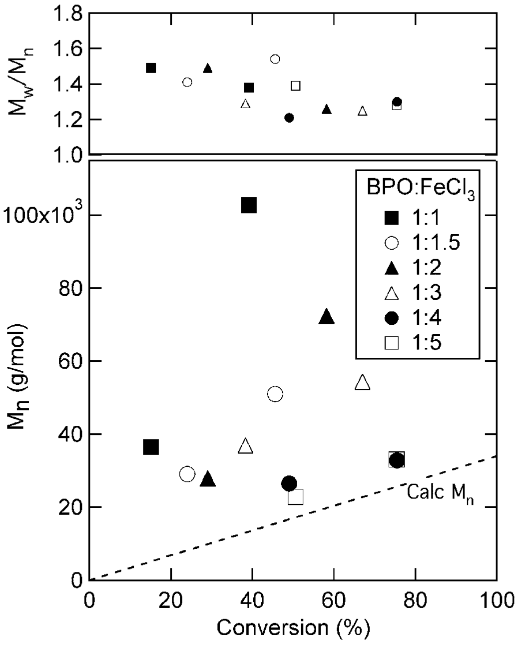

Fig. 4. Effect of initial concentration of $FeCl_3$ on the reverse ATRP. $[MMA]_0 = 1.4 \times 10^{-2}$ mol (1.48 ml), $[MMA]_0/[BPO]_0 = 680$. Polymerization was carried out at 85 °C. Polymerization times were 6 and 20 h for each condition (symbol) at lower and higher conversions, respectively.

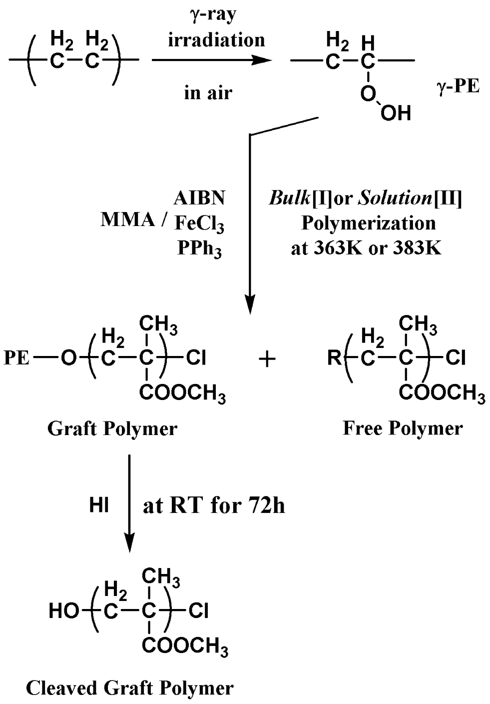

Fig. 5. Graft polymerization of MMA to irradiated PE with a reverse ATRP.

M_n was still quite high in comparison with the $M_{n,calc}$. The most likely reason of the slight improvement in solution polymerization was that $FeCl_2$ might act as effective catalyst by dissolving into acetone or some $FeCl_2$ might be oxidized before the polymerization and a small amount of $FeCl_3$ controlled the polymerization. However, we cannot explain the clear mechanism due to lack of data. Consequently, the large amount of $FeCl_2$ in the initiation system was not appropriate for a reverse ATRP in present case.

For other peroxides (CHP and TBP), bulk and solution polymerizations of MMA were carried out. The results of the polymerization are listed in Table 2. In both bulk and solution polymerization, the M_n of PMMA chains increased with monomer conversion and the range of polydispersity lied in between 1.14 and 1.45, indicating a living fashion as shown in Fig. 3. The initiation efficiency, however, was relatively low around 0.4. The iron catalyst concentration in the CHP or TBP initiation systems was smaller than the BPO system. The concentration effect of iron catalyst on the polymerization was checked. Fig. 4 shows the molecular weight of PMMA against monomer conversion with different initial concentration of Fe(III) ($[FeCl_3]_0$) in the BPO initiation system. The decrease in $[FeCl_3]_0$ depressed the polymerization rate (small value of the conversion at the same polymerization time) and the initiation efficiency of BPO ($M_{n,th} = 34,000$ at a conversion of 100%). When the ratio of $[BPO]_0/[FeCl_3]_0/[PPh_3]_0 = 1:3:9$, the efficiency was about 0.4 corresponding to the result in the CHP and TBP initiation systems. The low efficiency of CHP and TBP in the study was caused by a small concentration of iron catalyst relative to peroxides. When $[FeCl_3]_0$ increased more than four times as much as $[BPO]_0$, the effect of $[FeCl_3]_0$ concentration on the polymerization was not significant (just only the broader distribution of molecular weight). However, it is not clear that the small initial concentration of $FeCl_3$ made the initiation efficiency of peroxides low. In general, at the initiation, the peroxide decomposes to be radical and then it attacks MMA. The propagating radical abstracts chlorine atom from $FeCl_3$ and converts to dormant species. When $FeCl_3$ at the initiation is inadequate, effective atom transfer may not occur. Anyhow, these peroxides were confirmed to be effective for reverse ATRP of MMA. Since these peroxide including BPO are considered as models of peroxides generated on PE or PP by irradiation, a controlled grafting of MMA to PE or PP with a reverse ATRP initiated from polymer peroxides can be applied.

3.2. Controlled grafting of MMA to PE with reverse ATRP

The grafting scheme is shown in Fig. 5. The PE (PP) peroxides can initiate a graft polymerization of MMA with

Table 3
Bulk graft polymerization to PE film and powder in inhomogeneous at 90 °C

Run	Time (h)	Conversion (%)	GR (wt%)	$M_{n,free}$[a] (10^3)	$M_{w,free}/M_{n,free}$[a]	$M_{n,graft}$[b] (10^3)	$M_{w,graft}/M_{n,graft}$[b]	Ratio[c]
1[d]	1	26.5	45.0	14.2	1.13	1270	2.09	89.4
2[d]	2	56.9	56.2	19.9	1.19	1270	1.77	63.8
3[d]	24	88.8	53.9	27.8	1.07	1210	1.81	43.5
4[e]	4	58.2	34.0	55.5	1.35	119	1.84	2.14
5[e]	8	76.1	26.0	72.4	1.31	156	1.34	2.15
6[e]	24	92.5	44.6	90.7	1.33	180	1.34	1.98
7[f]	2	26.8	25.6	30.5	1.39	39.5	1.91	1.30
8[f]	6	53.7	39.4	57.2	1.27	58.6	2.00	1.02

[a] Free PMMA chains initiated from AIBN, which are not grafted.
[b] Grafted PMMA chains cleaved from PE bockbone.
[c] $M_{n,graft}/M_{n,free}$.
[d] Condition: PE (30 kGy, 500 μm) 0.1 g, $[MMA]_0/[AIBN]_0/[FeCl_3]_0/[PPh_3]_0 = 680/1/4/12$, MMA 2.3×10^{-2} mol (2.44 ml).
[e] Condition: PE (14.9 kGy, 50 μm) 0.06 g, $[MMA]_0/[AIBN]_0/[FeCl_3]_0/[PPh_3]_0 = 2500/1/4/12$, MMA 2.3×10^{-2} mol (2.44 ml).
[f] Condition: powder (30 kGy) 0.5 g, $[MMA]_0/[AIBN]_0/[FeCl_3]_0/[PPh_3]_0 = 2500/1/4/12$, MMA 3.7×10^{-2} mol (3.92 ml).

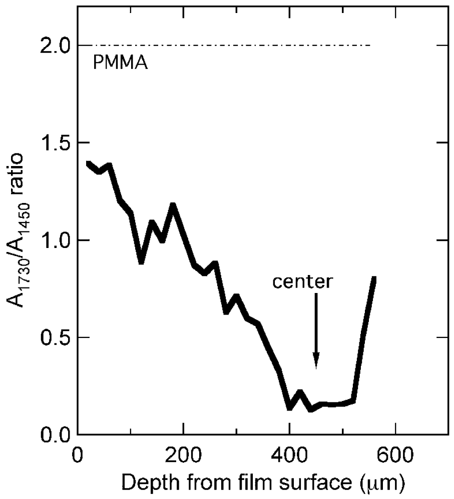

Fig. 6. Depth profile of PMMA chains in PE-*graft*-PMMA film with GR of 56.9 wt%. The absorbance ratios of 1730 cm^{-1}/1450 cm^{-1} were obtained from FT-IR measurement of sliced films at 20 μm each. The dot-dashed line indicates value of PMMA homopolymer.

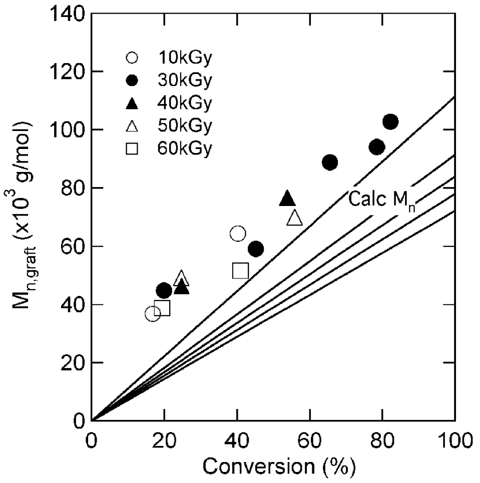

Fig. 7. Relation of conversion with M_n of the grafted PMMA prepared with irradiated PE with various doses (10–60 kGy, 0.5 g). MMA 0.029 mol (3.07 ml), $[MMA]_0/[AIBN]_0/[FeCl_3]_0/[PPh_3]_0 = 2500{:}1{:}4{:}12$, *o*-xylene = 0.4 ml, polymerization temperature was 110 °C. The dotted line indicates the calculated M_n. Each of the $M_{n,clac}$ was drawn with lines in the order of irradiation doses from upper (10 kGy) to bottom (60 kGy).

Fe-catalyst. The AIBN as a free initiator for a reverse ATRP is used in order to control the polymerization (including grafting) itself. AIBN is better initiator than BPO in this reverse ATRP and controls a polymerization of MMA in free chain (small M_w/M_n and a high initiation efficiency) [21–25]. Thus, AIBN was chosen as free initiators instead of BPO. Without free initiators, the grafting cannot be well controlled due to considerably low radical concentration.

In the case of bulk graft polymerization, the PE backbone polymer cannot be dissolved in MMA even at the polymerization temperature. The graft polymerization, thus, was carried out in inhomogeneous system. Bulk graft polymerizations of MMA to PE films (thickness 500 and 50 μm) and PE powder samples were conducted as shown in Table 3. Large difference of M_n of the grafted PMMA from the M_n of free PMMA, a broad molecular weight distribution, and scattered grafting ratios were obtained when the MMA was grafted to a thicker polyethylene film (thickness >50 μm). On the other hand, in the case of grafting to 'PE powder' samples, almost the identical M_n's were obtained for both grafted and free PMMA without improving its polydispersity. When the films was thick, it may safely be said that Fe-catalyst is inaccessible to inner region of the films but monomer can relatively easily diffuse into the inner sites. The diffused monomer in inner sites was grafted without mediation due to Fe-catalyst, resulting in much larger molecular weight of grafted PMMA. Fig. 6 show a depth profile of grafted PMMA from one side of the surface of the PE film (initial thickness was ca. 500 μm), which was estimated from the absorbance ratio (A_{1730}/A_{1450}) of IR spectrum of the sliced film at 20 μm each. After grafting, the PE film thickened to ca. 840 μm and the GR increased to 56.9 wt%. Although the amount of grafted PMMA gradually decreased toward film center, the grafted PMMA chains existed even at the film center. The diffusion of MMA was confirmed. This way was unable to determine the presence of Fe catalyst in the PE film because the measurement must be carried out after completely washing. Anyhow, the inhomogeneous system declared here cannot achieve well-controlled graft polymerization of MMA.

To cover the shortcoming, a graft polymerization of

Table 4
Solution graft polymerization to PE in homogeneous at 110 °C

Run	Time (h)	Conversion (%)	GR (wt%)	$M_{n,free}$[a] (10^3)	$M_{w,free}/M_{n,free}$[a]	$M_{n,graft}$[b] (10^3)	$M_{w,graft}/M_{n,graft}$[b]	Molar ratio[c]
1	5	19.9	14.0	34.4	1.19	44.8	1.15	0.106
2	9	45.2	27.6	47.1	1.27	59.1	1.28	0.093
3	20	65.6	39.9	59.2	1.38	88.8	1.32	0.078
4	30	78.5	46.8	74.7	1.36	94.1	1.30	0.097
5	40	82.2	49.7	76.0	1.43	102.8	1.49	0.080

[a] Free PMMA chains initiated from AIBN, which are not grafted.

[b] Grafted PMMA chains cleaved from PE bockbone.

[c] Molar ratio of graft to free PMMA, condition: PE (30 kGy, 500 μm) 0.5 g, $[MMA]_0/[AIBN]_0/[FeCl_3]_0/[PPh_3]_0 = 2500/1/4/12$, MMA 2.9×10^{-2} mol (3.07 ml), *o*-xylene 4.0 ml.

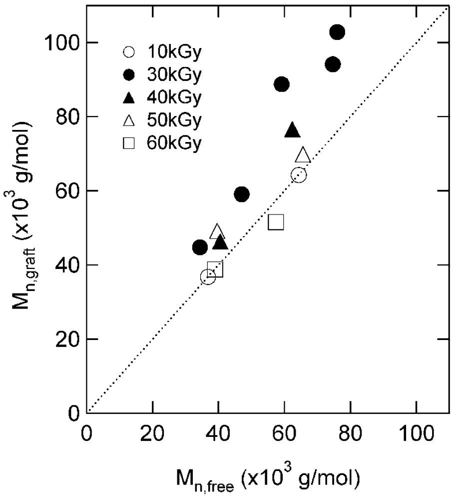

Fig. 8. The M_n relation of the grafted chains to free ones.

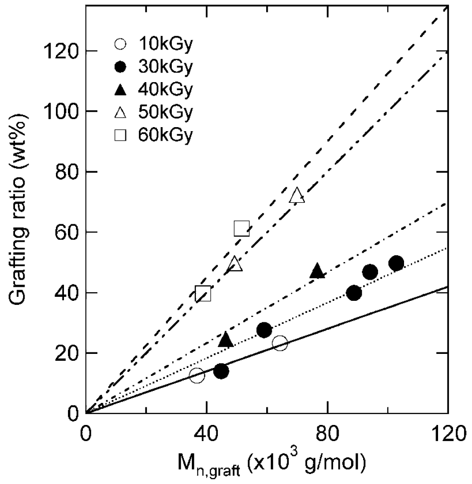

Fig. 9. The grafting ratio against $M_{n,graft}$. The slopes correspond to the average concentration of grafts along the PE main chain.

MMA to irradiated PE and PP was carried out in *o*-xylene (homogeneous system). The PE and PP are dissolved clearly at the grafting temperature of 110 °C. The free PMMA chains are generated simultaneously in solution during the grafting, which are initiated from AIBN. The M_n of grafted PMMA chains grew linearly with monomer conversion (Fig. 7) and their polydispersity's were small (< 1.4). The results (in the case using oxidized PE with a dose of 30 kGy) are summarized in Table 4. The molar ratios of grafted to free PMMA chains in all cases are nearly constant (ca. 0.09), indicating no change in the number of grafting sites even at a higher conversion. At the same dose, concentration of grafting site almost kept constant without generating new grafting sites. In addition, as expected, the molar ratio increased with irradiation dose. The concentration of the grafts relates to the PE peroxides concentration. In fact, the concentration of the PE peroxides formed by irradiation in air was quantified from FT-IR spectra of the nitrates generated quantitatively by a reaction of the peroxides with nitrogen monoxides [34] and the peroxide concentration per dose was estimated to be 1.7×10^{-7} mol/(g kGy). The $M_{n,clac}$ was calculated taking into account for the concentration of PE peroxides, that is, the initiator concentration $[I]_0$ was equal to $[AIBN]_0 + [Peroxide]_0$. Each of the $M_{n,clac}$ was drawn with lines in the order of irradiation doses from upper (10 kGy) to bottom (60 kGy). When the irradiation dose increased, the total initiation efficiency was found to decrease from Fig. 7. In other words, the increase in the initiator concentration made the efficiency to be decreased, which was consist with the result of the previous section except for a relatively smaller depression of the efficiency. This is because the initiation efficiency of AIBN was high in contrast to the BPO initiation system as previously reported [21–25].

As for the molecular weight, comparison of the M_n of the graft to that of free chains indicated almost the same values each other as shown in Fig. 8. This means that both graft and free PMMA chains were controlled and the characteristics of the free PMMA chains can be used as a measure of those of the graft PMMA chains. The GR was plotted against the $M_{n,graft}$ in Fig. 9. The GR increases linearly with conversion and the slope in the figure increases with irradiation dose. These facts indicate the controlled grafting was successful. The slopes correspond to the concentration of the grafts along the PE chain. The concentration of the grafts was plotted against the concentration of the peroxides generated in PE by the irradiation (Fig. 10). The solid line means the identical values of the concentration of the peroxides and the grafts along the PE chain. The dotted line shows that the average initiation efficiency of the peroxides on the PE was approximately 0.6, which coincides with the efficiency of the low molecular weight peroxides (previous section).

3.3. Controlled grafting of MMA to PP with reverse ATRP

The grafting of MMA to oxidized PP with reverse ATRP was applied. The grafting result is listed in Table 5. The molecular weight distributions were narrow and the M_n difference between graft and free PMMA chains are small,

Table 5
Graft polymerization of MMA to PP

Time (h)	Conversion (%)	GR (wt%)	$M_{n,graft}$	$M_{n,free}/M_{n,free}$	$M_{n,graft}$	$M_{n,graft}/M_{w,graft}$
2	20.5	47.2	35,600	1.21	33,200	1.26
24	43.1	58.8	55,900	1.39	45,400	1.49

Condition: irradiated PP (21 kGy) 0.4 mg, MMA 0.023 mol (2.44 ml), $[MMA]_0/[AIBN]_0/[FeCl_3]_0/[PPh_3]_0 = 2500/1/4/12$, at 110 °C in *o*-xylene.

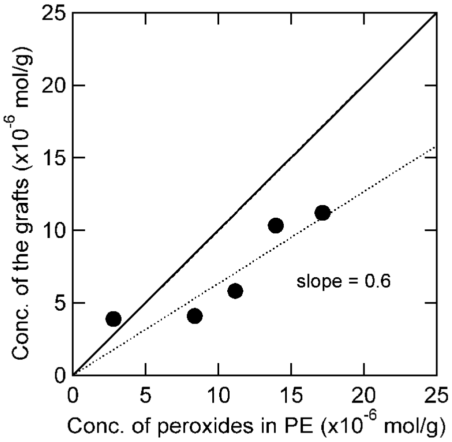

Fig. 10. Concentration of the grafts against that of peroxides in PE. The solid line means the identical value with each other. The dotted line corresponds to the initiation efficiency of the polymeric peroxides on irradiated PE.

indicating the grafting was also controlled. In addition, although the data point was only two, the linear relation of the GR to the $M_{n,graft}$ through the 'origin' can be drawn as shown in Fig. 11. The average concentration of the grafts on PP calculated from the slope of the line in the figure was ca. 1.3×10^{-5} mol/g (1.3×10^{-3} mol%/g). From our previous work [16], the concentration of the oxidized PP with irradiation dose of 21 kGy was analyzed to be about 1.7×10^{-7} mol/g according to the same method as the case of PE. The initiation efficiency of PP polymeric peroxides, therefore, can be calculated to be 0.76 that is close to that of peroxides of PE and low molecular weight compounds.

4. Conclusion

We verified the reverse ATRP of MMA proceeded successfully in the system of BPO (cumene hydroperoxide, di-*tert*-butyl peroxide)/$FeCl_3$/PPh_3. The initiation efficiency of these peroxides was estimated to be 60–70 % when the molar ratio of $FeCl_3$ to peroxides was four. Decrease in the ratio diminished the initiation efficiency and reduced the polymerization rate.

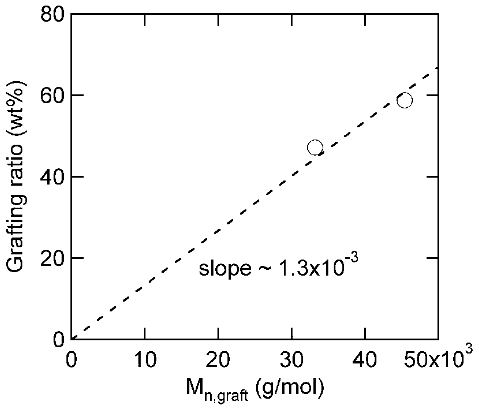

Fig. 11. Controlled grafting of MMA to irradiated PP (21 kGy, 0.4 mg) in *o*-xylene at 110 °C. MMA 0.029 mol (3.07 ml), $[MMA]_0/[AIBN]_0/[FeCl3]_0/[PPh3]_0 = 2500:1:4:12$, *o*-xylene = 0.4 ml. The grafting ratio against $M_{n,graft}$. The slopes corresponds to the average concentration of grafts along the PP main chain.

Well-controlled grafting of MMA to PE and PP was established by a combination of radiation-induced graft polymerization and reverse ATRP. The homogeneous grafting (solution) was well controlled, in contrast, the inhomogeneous grafting (bulk) showed no control. The initiation efficiency of polymeric peroxides was obtained to be around 60–76%, which were corresponding to the value in the reverse ATRP ($4[FeCl_3]_0 = [\text{peroxides}]_0$) of MMA initiated from low molecular weight peroxides.

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