

Photo-living radical polymerization of methyl methacrylate by a nitroxide mediator

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Abstract The novel photo-living radical polymerization was determined using 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) and bis(alkylphenyl)iodonium hexafluorophosphate (BAI) as the photo-acid generator. The polymerization of methyl methacrylate was performed using azobisisobutyronitrile as an initiator in the presence of MTEMPO and BAI at room temperature by irradiation with a high-pressure mercury lamp to produce poly(methyl methacrylate) with a comparatively narrow molecular weight distribution ($M_w/M_n=1.3-1.7$). The polymerization proceeded by a living mechanism based on the fact that the first-order time-conversion plots linearly increased. A linear increase in the plots of the molecular weight versus the conversion also supported the living nature of the polymerization. It was found that MTEMPO had an interaction with the propagation chain end to control the molecular weight, while BAI weakened the interaction of MTEMPO with the propagation chain end to reduce the molecular weight distribution and polymerization time.

Keywords Photo-living radical polymerization · 4-Methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl · Bis(alkylphenyl)iodonium hexafluorophosphate · A photo-acid generator · Methyl methacrylate · Poly(methyl methacrylate)

Introduction

The nitroxide-mediated living radical polymerization (NRP) is useful as a method using a nonmetallic catalyst to control of

molecular weight of polymers. The NRP has been utilized in creating resistant materials of semiconductors based on the fact that an infinitesimal amount of obstructive metals lowers efficiency of the semiconductors. The polymerization produces polymers with a narrow molecular weight distribution ($M_w/M_n=1.3$); however, it does not strictly control the molecular weights unlike the atom transfer radical polymerization (ATRP) [1] and reversible addition-fragmentation chain transfer (RAFT) polymerization ($M_w/M_n<1.1$) [2]. Another disadvantage is the fact that the NRP requires a high temperature over 120 °C and takes a few days to provide a high conversion of the monomers [3, 4]. In addition, it has been considered that the NRP cannot be applied to methacrylate monomers, although it inserts a small amount of the monomers into styrene and acrylate polymers through the copolymerization [5]. This is because the disproportionation termination predominates over the coupling termination during the methacrylate polymerization at high temperature [6].

The photoradical polymerization eliminates the side reactions caused by the high temperature during the polymerization. The most useful polymerization should be the photo-living radical polymerization with dithiocarbamate discovered by Otsu [7]. This polymerization has recently been often used in combination with the ATRP system [8]. While the polymerization by dithiocarbamate produced a number of designed copolymers, such as multi-block [9, 10], graft [11], and star copolymers [12] through its living nature, it has disadvantages in controlling the molecular weight. The polymerization with dithiocarbamate provided the normal molecular weight distribution as well as the uncontrolled free radical polymerization ($M_w/M_n=2.0-3.0$) [13–15].

A novel photo-living radical polymerization was determined using a nitroxide and a photo-acid generator. This polymerization of methyl methacrylate (MMA) produced poly(methyl methacrylate) (PMMA) with a comparatively

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Table 1 Photoradical polymerization of MMA by AIBN in the presence of MTEMPO and BAI

Run	AIBN (mol%)	MTEMPO/AIBN	BAI/MTEMPO	Time (h)	Conversion (%)	M_n	M_w/M_n
1	0.195	0	0	2	96	75,000	5.61
2	0.195	0	2.58 ^a	2	96	77,100	4.57
3	0.195	5.0	0.25	168	28	560	1.22
4	0.195	5.0	0.50	66	84	43,000	1.72
5	0.195	5.0	0.75	22	91	51,800	1.88
6	0.195	5.0	1.00	20	96	56,500	2.31
7	0.489	2.0	0.50	6	86	45,500	1.80
8	0.391	2.5	0.50	20	91	47,600	1.69
9	0.130	7.5	0.50	69	62	1,070,000 28,400 ^b	2.58 1.38
10 ^c	0.391	2.5	0.50	24	0	–	–
11 ^c	0.391	2.5	0.50	24+18 ^d	92	60,300	1.56

^a BAI/AIBN=2.58^b Bimodal GPC: M_n (area %)=1,070,000 (4%)+28,400 (96%)^c Polymerization in the dark^d Polymerization for 24 h in the dark and then for 18 h by irradiation

narrow molecular weight distribution. This short communication describes the photo-living radical polymerization of MMA by azobisisobutyronitrile (AIBN) as the initiator in the presence of 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) and bis(alkylphenyl)iodonium hexafluorophosphate (BAI) as the photo-acid generator.

Experimental

Instrumentation The photopolymerization was carried out using a Wacom HX-500 illuminator with a 500-W high-pressure mercury lamp. Gas chromatography was performed with Shimadzu GC 8A. Gel permeation chromatography (GPC) was performed using a Tosoh GPC-8020 instrument equipped with a DP-8020 dual pump, a CO-8020 column oven, and a RI-8020 refractometer. Three polystyrene gel columns, Tosoh TSKGEL G2000H_{XL}, G4000H_{XL}, and G6000H_{XL} were used with THF as the eluent at 40 °C.

Materials MTEMPO was prepared as reported previously [16]. MMA was washed with 5 wt.% sodium hydroxide solution and water and then distilled over calcium hydride. AIBN was recrystallized in methanol. BAI in 50 wt.% propylene carbonate solution was supplied from Wako Pure Chemical Industries and was used without further purification.

Photopolymerization of MMA by MTEMPO and BAI: general procedure A mixture of MMA (936 mg, 9.35 mmol), AIBN (6 mg, 0.0365 mmol, 0.4 mol% to MMA), MTEMPO (17 mg, 0.0914 mmol, MTEMPO/AIBN=2.5), and BAI in 50 wt.% propylene carbonate solution (72 mg, 0.0472 mmol, BAI/MTEMPO=0.5) was placed in an ampoule. After degassing the contents, the

ampoule was sealed under vacuum. The polymerization was carried out at room temperature for 20 h with irradiation by reflective light using a mirror with a 500-W high-pressure mercury lamp at 7.0 A. The resulting mixture was dissolved in dichloromethane (10 mL) and then poured into methanol (500 mL) to precipitate the polymer. The precipitate was collected by filtration and dried in vacuo for several hours to obtain the PMMA (604 mg, 65% in yield).

Results and discussion

The photoradical polymerization of MMA was performed using AIBN in the presence of MTEMPO and BAI at room temperature by irradiation with a high-pressure mercury lamp. The results are shown in Table 1. MTEMPO had an

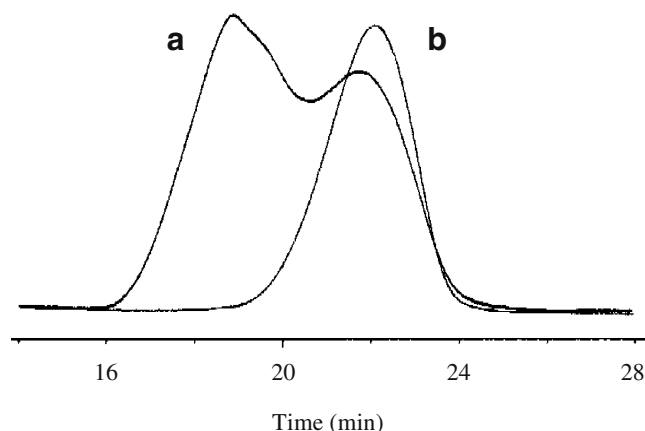


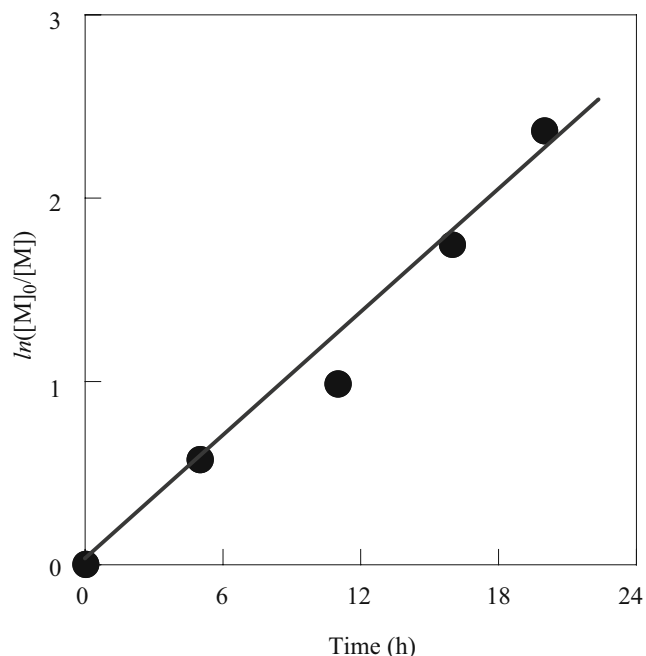
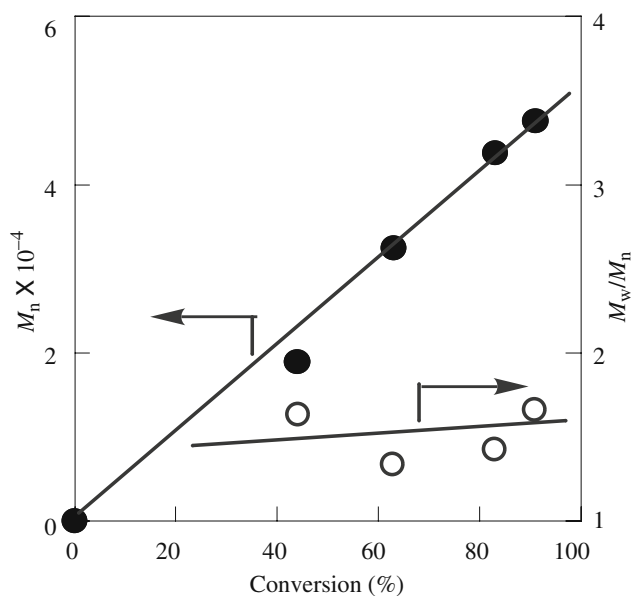
Fig. 1 GPC profiles of PMMA obtained by the photoradical polymerization in the absence (a run 1 in Table 1) and presence (b run 8) of MTEMPO

Table 2 Photo-living radical polymerization of MMA by MTEMPO

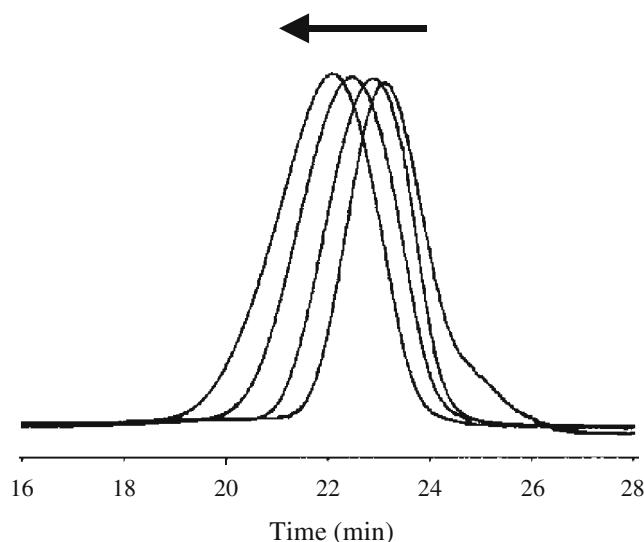
Time (h)	Conversion (%)	M_n	M_w/M_n
5	44	19,000	1.66
11	63	32,500	1.39
16	83	43,800	1.46
20	91	47,600	1.69

MTEMPO/AIBN=2.5, BAI/MTEMPO=0.5

effect on the molecular weight because the polymerization in the presence of MTEMPO produced PMMA with a narrower molecular weight distribution than the polymerization in the absence of MTEMPO. Figure 1 shows the GPC profiles of PMMA obtained by the polymerization in the presence and absence of MTEMPO. It was found that BAI itself did not have a direct effect on the molecular weight control based on the negligible difference between the polymerizations in the presence and absence of BAI without MTEMPO. As the molar ratio of BAI to MTEMPO increased, the molecular weight distribution (MWD) increased and the polymerization time was shortened, indicating that BAI played a role in weakening the interaction of MTEMPO with the propagation chain end. BAI showed such a function by the irradiation because the polymerization did not occur in the dark. However, the polymerization in the dark was initiated by exposure to light. The molar ratio of MTEMPO to AIBN also affected the MWD and polymerization time. As the MTEMPO/AIBN ratio increased, the MWD decreased, whereas the polymerization time was extended.

**Fig. 2** The first-order time-conversion plots for the polymerization of MMA. MTEMPO/AIBN=2.5, BAI/MTEMPO=0.5**Fig. 3** The plots of the molecular weight of the PMMA versus the conversion. MTEMPO/AIBN=2.5, BAI/MTEMPO=0.5

It was confirmed that the photoradical polymerization of MMA by AIBN in the presence of MTEMPO and BAI proceeded in accordance with a living mechanism. The variation in the monomer conversion, the molecular weight, and MWD of PMMA versus time is summarized in Table 2. As can be seen in Fig. 2, the first-order time-conversion plots $[\ln([M]_0/[M]) - t]$ linearly increased with the time. $[M]_0$ denotes the initial concentration of the monomer, and $[M]$ the concentration of the remaining monomer. This linear increase in the $\ln([M]_0/[M])$ vs. t indicates that the number of the polymer chains was constant throughout the course of the polymerization. The thermal polymerization

**Fig. 4** The variation in the GPC curves versus the conversion: 44% (5 h), 63% (11 h), 83% (16 h), and 91% (20 h) from the right

of styrene by MTEMPO took a few days to obtain a high conversion over 80% [3, 4], while the photopolymerization of MMA provided over a 90% conversion within 24 h. The plots of the molecular weight of PMMA versus the conversion also supported the living mechanism of the polymerization (Fig. 3). The MWD of PMMA was 1.3–1.7. Figure 4 shows the variation in the GPC curves versus the conversion. The curve was shifted to the higher molecular weight side with the increasing conversion. It is suggested that the photoradical polymerization mediated by MTEMPO and BAI well controlled the molecular weight of PMMA.

Conclusion

The photo-living radical polymerization of MMA was determined using the nitroxide radical and the photo-acid generator. The polymerization produced PMMA with a comparatively narrow MWD ($M_w/M_n=1.3-1.7$). The linear increases in the correlation of the first-order time-conversion and the molecular weight versus the conversion demonstrated that the polymerization proceeded by a living mechanism. MTEMPO interacted with the propagation chain end and controlled the molecular weight, while BAI weakened the interaction of MTEMPO with the propagation chain end to reduce the MWD and polymerization time. The system also had a photo-latent effect because the polymerization that did

not occur in the dark was initiated by the exposure to light. This is the first study demonstrating that the nitroxide-mediated living radical polymerization applied to the photopolymerization of MMA produced PMMA with a comparatively narrow molecular weight distribution.

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