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ORIGINAL CONTRIBUTION

Photo-living radical polymerization of methyl methacrylate by 2,2,6,6-tetramethylpiperidine-1-oxyl in the presence of a photo-acid generator

Eri Yoshida

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Abstract The novel photo-living radical polymerization of methyl methacrylate (MMA) was determined using 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMDV) and 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) in the presence of bis(alkylphenyl)iodonium hexafluorophosphate (BAI). The polymerization provided a comparatively narrow molecular weight distribution in the range of 1.4–1.7. The resulting PMMA contained no BAI fragments in its structure and had the 1-cyano-1,3-dimethyl-3-methoxybutyl radical and MTEMPO at the 1:1 molar ratio. The experimental molecular weight was in close agreement with the theoretical one when the initiator efficiency was taken into consideration. The plots of $ln([MMA]_0/[MMA])$ vs. time and the molecular weight of PMMA vs. the conversion and vs. the reciprocal of the initial concentration of AMDV showed linear correlations, indicating that the polymerization proceeded in accordance with a living mechanism. It was found that the polymerization had a photo-switching ability, because the polymerization was interrupted by turning off the irradiation, and then restarted by the irradiation again.

Keywords Photo-living radical polymerization · 4-Methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl · 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) · Bis(alkylphenyl)iodonium hexafluorophosphate · Methyl methacrylate · Irradiation · Photo-switching ability

E. Yoshida (✉)
Department of Materials Science,
Toyohashi University of Technology,
1-1 Hibarigaoka, Tempaku-cho,
Toyohashi, Aichi 441-8580, Japan
e-mail: eyoshida@tutms.tut.ac.jp

Introduction

Photopolymerization has advantages over thermal polymerization, because it can be employed in local places and situations where heat cannot be applied such as vital tissues and electronic devices. Photopolymerization is composed of ionic polymerizations and radical polymerization. Whereas the photoionic polymerizations have the merits of the preparation of a variety of polymers with different backbone structures [1], a small volume contraction on cure based on ring opening [2–5], and no inhibition by oxygen, the polymerizations are inhibited by bases and water and have slow polymerization rates [6]. The photoradical polymerization provides a rapid polymerization rate and involves a wide range of applicable vinyl monomers. A great number of publications have been released on photoinitiators and photosensitizers for the radical polymerization [7]: peroxides [8], azo compounds [9, 10], organic carbonyls [11, 12], benzoxazines [13], organic polysulfides [14, 15], inorganic acids [16], and metal compounds such as $Mn_2(CO)_{10}$ [17], $Re_2(CO)_{10}$ [18], ZnO [19, 20], $PbEt_4$ [21], $Ce_2(SO_4)_3$ [22], and $UO_2(NO_3)_2$ [23]. Organic dyes of riboflavin, fluorescein, and acridine also served as photosensitizers for the polymerization [24, 25]. In spite of these many findings, there is no paper on the controlled photoradical polymerization with the exception of an iniferter polymerization discovered by Otsu using dithiocarbamate [26]. This dithiocarbamate system produced a variety of designed copolymers such as multi-block [27, 28], graft [29], and star copolymers [30] based on the living nature; however, it provided a normal molecular weight distribution (MWD) as well as the uncontrolled free radical polymerization (M_w/M_n=2.0–3.0) [31–33].

Recently, the novel photo-living radical polymerization of methyl methacrylate (MMA) has been determined by the

Table 1 Photoradical polymerization of MMA by AMDV and MTEMPO in the presence of BAI[a]

Run	MTEMPO/AMDV	BAI/MTEMPO	Time (h)	Conversion (%)	M_n^b	M_w/M_n^b
1	–	–	1	85	33,000	6.94
2	–	–[c]	1	87	32,300	5.86
3	1.1	–	31	40	11,600	1.47
4	1.1	0.5	3	68	16,200	1.66
5	1.1	0.75	2.5	88	19,800	2.88
6	1.1	1.5	2	95	20,600	3.16
7	1.4	0.5	9	68	13,600	1.41
8	2.0	0.5	12	68	10,600	1.55

[a] $[AMDV]_0=0.0454$ mol/L

[b] Estimated by GPC based on PMMA standards

[c] $[BAI]_0=0.0249$ mol/L

polymerization mediated by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) that provided a comparatively narrow MWD ($M_w/M_n=1.4$–1.8) [34]. The thermal TEMPO-mediated living radical polymerization also produces a comparatively narrow MWD ($M_w/M_n \fallingdotseq 1.3$) [35–37] and is important as a polymerization using a non-metallic catalyst converts into various derivatives [38–43]. The thermal TEMPO-mediated polymerization includes disadvantages such as no application to methacrylate monomers and limited performance at high temperature for a long period [35–37]. It was found that the TEMPO-mediated photo-living radical polymerization of MMA showed a significant polymerization rate at room temperature within several hours, and furthermore, it had a photo-switching ability. This paper describes the photo-living radical polymerization of MMA by 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (AMDV) as an initiator and 4-methoxy-TEMPO (MTEMPO) as a mediator in the presence of bis(alkylphenyl)iodonium hexafluorophosphate (BAI) as a photoacid generator.

Experimental

Instrumentation The photopolymerization was carried out using a Wacom HX-500 illuminator with a 500 W high-pressure mercury lamp. Gas chromatography (GC) 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 an 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. ^1H NMR measurements were conducted using a Varian 300 FT NMR spectrometer. UV analysis was performed with a Shimadzu UV-160A UV–Vis recording spectrophotometer.

Materials AMDV was recrystallized in methanol. MTEMPO was prepared as reported previously [44]. BAI in 50 wt.% propylene carbonate solution was supplied from Wako Pure Chemical Industries Ltd. and was used without further purification. MMA was washed with 5 wt.% sodium hydroxide solution and water and then distilled over calcium hydride. Methyl isobutylate was washed with saturated NaCl aqueous solution and was dried with sodium carbonate, then distilled over phosphorus oxide. Extrapure ethylbenzene was used as a standard for GC without further purification.

Photopolymerization of MMA by AMDV and MTEMPO in the presence of BAI: general procedure A mixture of MMA (1 mL, 936 mg, 9.35 mmol), AMDV (14 mg, 0.0454 mmol, 0.5 mol% to MMA), MTEMPO (9 mg, 0.0484 mmol, MTEMPO/AMDV=1.1), and BAI in 50 wt.% propylene carbonate solution (38 mg, 0.0249 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 3 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). Ethylbenzene was added as a standard to the dichloromethane solution; the solution was subjected to GC. The solution was concentrated to 5 mL with an evaporator and was poured into hexane (500 mL) to precipitate the polymer. The precipitate was collected by filtration and dried in vacuo for several hours to obtain the PMMA (623 mg, 67% in yield).

Initiator efficiency of AMDV A mixture of AMDV (14 mg, 0.0454 mmol), MTEMPO (34 mg, 0.183 mmol), and

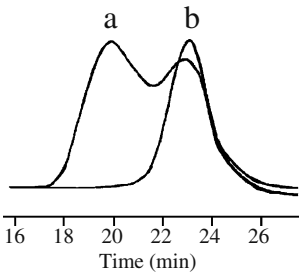


Fig. 1 GPC profiles of the PMMA obtained by the photoradical polymerization in the absence (**a**, Run 1 in Table 1) and presence (**b**, Run 4) of MTEMPO

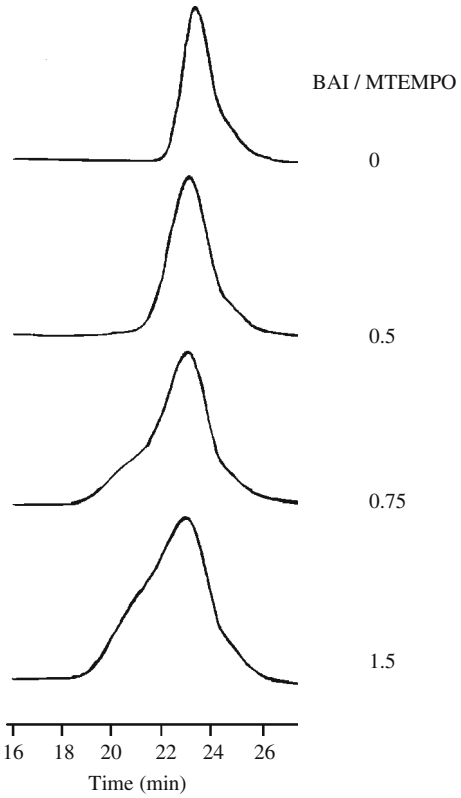


Fig. 2 GPC profiles of the PMMA obtained by the polymerization in the presence of BAI. MTEMPO/AMDV=1.1

methyl isobutylate (1 mL) was placed in an ampoule. After degassing the contents, the ampoule was sealed under vacuum. The reaction was carried out at room temperature for 1 h with irradiation in the same manner as the polymerization. The resulting solution was subjected to UV analysis.

Results and discussion

The photoradical polymerization of MMA was performed by AMDV as the initiator and MTEMPO as the mediator in the presence of BAI as the photo-acid generator. The polymerization was carried out in bulk at room temperature

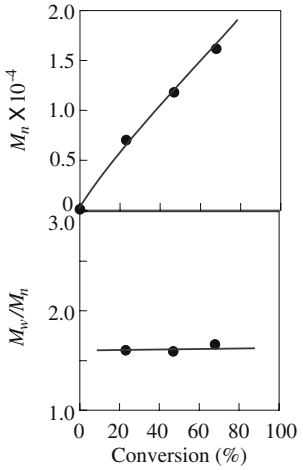


Fig. 4 The plots of the molecular weight of the PMMA vs. the conversion. MTEMPO/AMDV=1.1, BAI/MTEMPO=0.5

by irradiation with a high-pressure mercury lamp. The 10-h half-life temperature of AMDV is 30°C, while that of 2,2′-azobisisobutyronitrile (AIBN) is 65°C [45]. AMDV is expected to produce a polymer with a molecular weight distribution (MWD) narrower than AIBN by its rapid decomposition during the polymerization at room temperature. The orange-colored monomer solution turned colorless after the polymerization. These results are shown in Table 1. The polymerization in the absence of MTEMPO produced the PMMA with a broad MWD. BAI had a slight effect by decreasing the MWD, although the MWD was still broad. It was found that the MWD dramatically decreased in the presence of MTEMPO. Figure 1 shows the GPC profiles of the PMMA obtained in the presence and absence of MTEMPO. The PMMA in the presence of MTEMPO provided a unimodal GPC with a comparatively narrow MWD, whereas the PMMA prepared in its absence showed a bimodal GPC. BAI also affected the MWD in the presence of MTEMPO. As a result of increasing of the molar ratio of BAI to MTEMPO (BAI/MTEMPO), the MWD of the resulting polymer was broadened (Fig. 2). The increase in BAI also accelerated the polymerization. BAI should facilitate the scission between MTEMPO and the growing polymer radical. On the other hand, an increase in the molar ratio of MTEMPO to AMDV (MTEMPO/

Fig. 3 The first order time-conversion plots for the polymerization of MMA. MTEMPO/AMDV=1.1, BAI/MTEMPO=0.5

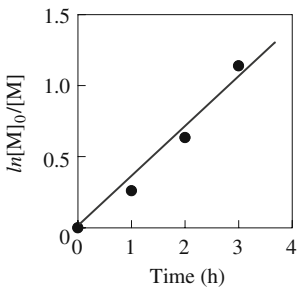


Fig. 5 The variation in the GPC curves vs. the conversion: 23% (1 h), 47% (2 h), and 68% (3 h) from the *right*

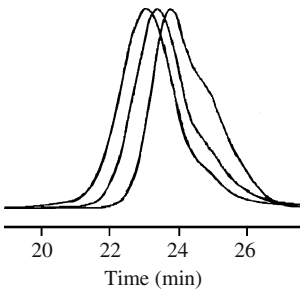


Table 2 Relationship between the initial concentration of AMDV and molecular weight of the resulting PMMA[a]

$[AMDV]_0$ ($\times 10^2$ mol/L)	Time (h)	Conversion (%)	M_n^b	M_w/M_n^b
2.59	19	76	23,800	1.62
4.54	3	68	16,200	1.66
6.48	5	72	10,600	1.72
12.3	3	79	7,900	1.53

[a] MTEMPO/AMDV=1.1, BAI/MTEMPO=0.5

[b] Estimated by GPC based on PMMA standards

AMDV) decreased the polymerization rate, indicating that an increase in MTEMPO shifted the equilibrium between MTEMPO and the growing polymer radical toward their recombination.

It was confirmed that the polymerization proceeded in accordance with a living mechanism based on the first order time-conversion plots and the plots of the PMMA molecular weight vs. the conversion. Figure 3 shows the first order time-conversion plots for the polymerization at MTEMPO/AMDV of 1.1 and BAI/MTEMPO of 0.5. The $ln([M]_0/[M])$ almost linearly increased over time. The number of polymer chains was constant throughout the course of the polymerization. The plots of the molecular weight of the resulting PMMA vs. the monomer conversion also linearly increased (Fig. 4). The MWD of the PMMA retained ca. 1.6 throughout the polymerization. As can be seen in Fig. 5, the GPC curve was shifted to the higher side of the molecular weight with an increase in the conversion, also supporting the living mechanism.

The relationship between the molecular weight of the resulting PMMA and the initial concentration of the initiator is summarized in Table 2. As a result of increasing the initial concentration of AMDV ($[AMDV]_0$), the molecular weight of the PMMA decreased. The MWDs were retained in the range of 1.5–1.7. Based on a plot of the molecular weight of the PMMA vs. the reciprocal of $[AMDV]_0$, a linear correlation was obtained (Fig. 6). It was deduced that the photoradical polymerization mediated by MTEMPO took place by a living mechanism.

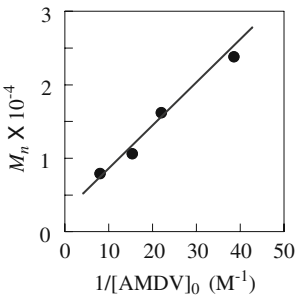


Fig. 6 The plots of the molecular weight of the PMMA vs. the reciprocal of $[AMDV]_0$. MTEMPO/AMDV=1.1, BAI/MTEMPO=0.5

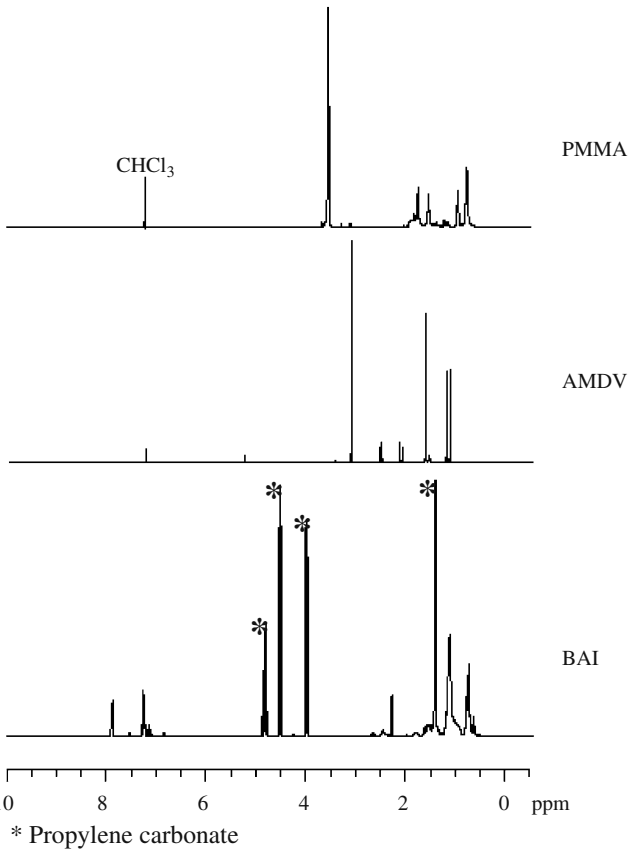


Fig. 7 ^{1}H NMR spectra of the PMMA, BAI, and AMDV. PMMA (M_n=7,030, M_w/M_n=1.60). Solvent: $CDCl_3$

The ^{1}H NMR analysis clarified the structure of the resulting PMMA. Figure 7 shows the ^{1}H NMR spectra of PMMA (M_n=7,030, M_w/M_n=1.60), BAI, and AMDV. No observed signals originating from BAI in the spectrum of the PMMA indicates that no fragments of BAI were contained in the polymer structure. It is suggested that the BAI fragments did not combine with the growing polymer chain end or MTEMPO, but just had the interaction with MTEMPO. The photo-living radical polymerization had no effect on the tacticity of PMMA based on the observation of the signals at 0.84 ppm (syndiotactic), 1.01 ppm (atactic), and 1.25 ppm (isotactic) [46]. It was found that

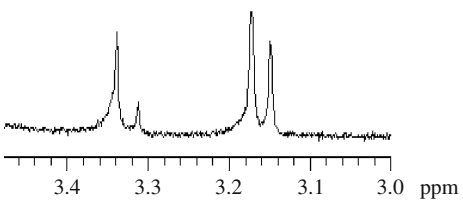
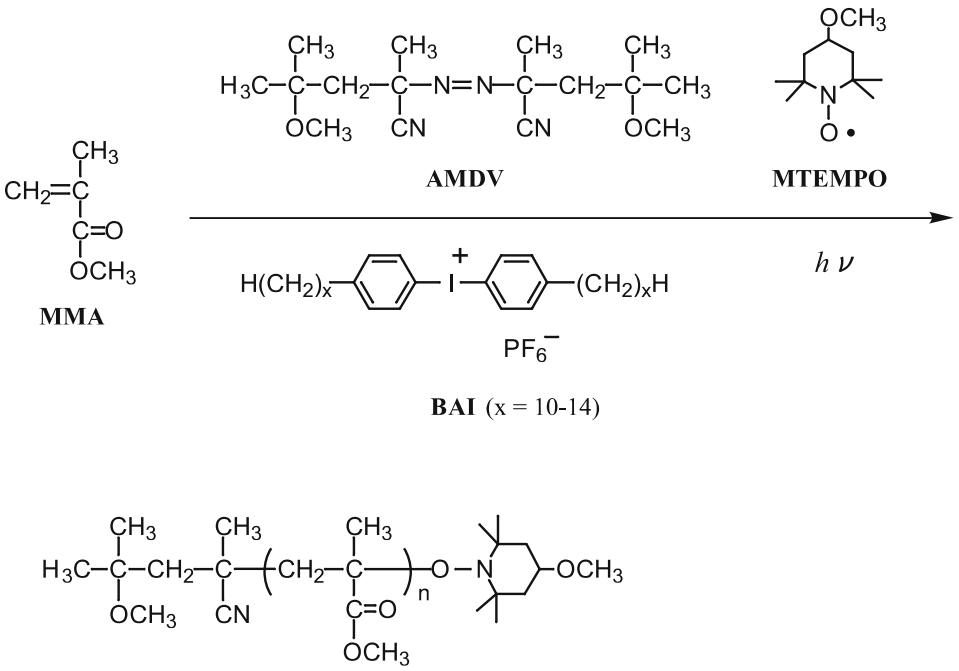


Fig. 8 ^{1}H NMR spectra of the methoxy protons originating from CDM and MTEMPO attached to the PMMA chain ends. Solvent: $CDCl_3$



Scheme 1 The photoradical polymerization of MMA by AMDV and MTEMPO in the presence of BAI

the PMMA involved the 1-cyano-1,3-dimethyl-3-methoxybutyl radical (CDM) and MTEMPO attached to the chain ends. Signals of the methoxy protons originating from CDM were discerned at 3.13–3.22 ppm, while those from MTEMPO were observed at 3.29–3.39 ppm (Fig. 8). The molar ratio of MTEMPO to CDM in the PMMA was estimated to be 0.952 based on their respective methoxy protons. This good agreement in the molar ratio of MTEMPO/CDM indicates that the growing radical generated by the CDM initiation was completely captured by MTEMPO (Scheme 1). The molecular weight of the PMMA was estimated to be M_n=6,500 based on the methoxy protons of CDM and the MMA units. The theoretical molecular weight based on the initial concentration of AMDV was M_n=2,370. This significant difference in the molecular weight between the theoretical and experimental values implies that the initiator efficiency was not unity.

The initiator efficiency (IE) was determined by a UV analysis. Figure 9 shows the UV spectra of MTEMPO before and after the reaction with AMDV in methyl isobutylate. The reaction was performed by irradiation at room temperature for 1 h. An excess of MTEMPO to AMDV was used for the reaction to effectively capture the CDM radicals. The reaction was carried out in the absence of BAI in order to prevent the CDM radicals captured by MTEMPO from regenerating by BAI. In addition, no change in the absorbance of MTEMPO by the irradiation

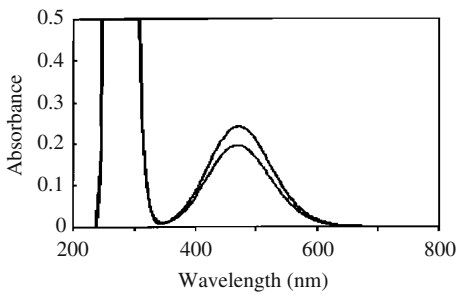
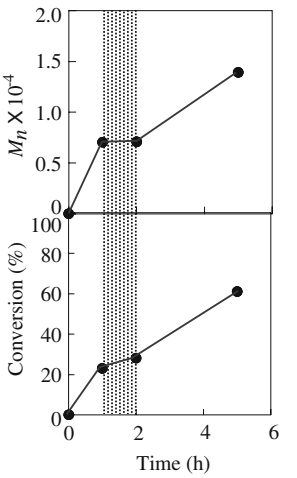


Fig. 9 UV spectra of MTEMPO before (*upper*) and after (*lower*) the reaction with AMDV. Solvent: methyl isobutylate

Fig. 10 The variation in the molecular weight of PMMA and conversion when the light was turned off in the middle of the polymerization. MTEMPO/AMDV=1.1, BAI/MTEMPO=0.5



in the absence of AMDV was confirmed. The IE was determined to be 0.378 based on the absorbance at 470 nm. The theoretical molecular weight when this IE was taken into account was calculated to be M_n=6,270, being in a close agreement with the molecular weight estimated by ^{1}H NMR (M_n=6,500).

The polymerization was revealed to have a photo-switching ability based on the investigation of the polymerization in the dark. Figure 10 shows the variation in the monomer conversion and molecular weight of PMMA when the light was stopped in the middle of the polymerization. The conversion and the molecular weight that increased by the irradiation stopped increasing when the light was cut off. However, they started increasing again when the system was exposed to the light. The progress of the polymerization can be controlled by on–off of light.

Conclusion

The photo-living radical polymerization of MMA was determined using AMDV and MTEMPO in the presence of BAI. The polymerization produced PMMA with a comparatively narrow MWD in the range of 1.4–1.7. The BAI fragments accelerated the polymerization by the interaction with MTEMPO attached to the polymer chain end; however, it was not inserted into the resulting polymer structure. The PMMA had the CDM and MTEMPO at the 1:1 molar ratio. The experimental molecular weight was in close agreement with the theoretical value when the initiator efficiency determined by UV was taken into account. The polymerization proceeded in accordance with a living mechanism, because the plots of $ln([M]_0/[M])$ vs. time and the molecular weight of PMMA vs. the conversion and vs. the reciprocal of the initial concentration of AMDV showed linear correlations. Furthermore, the polymerization had a photo-switching ability based on the fact that the polymerization was interrupted by turning off the irradiation, then restarted by further irradiation. This is the first study demonstrating that the TEMPO-mediated living radical polymerization had a photo-switching ability.

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