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SHORT COMMUNICATION

Nitroxide-mediated photo-living radical polymerization of methyl methacrylate in solution

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Abstract The photoradical polymerization of methyl methacrylate (MMA) was performed in an acetonitrile solution at room temperature using (2RS,2′RS)-azobis(4-methoxy-2,4-dimethylvaleronitrile) as the initiator, 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl as the mediator, and (4-*tert*-butylphenyl)diphenylsulfonium triflate as the photoacid generator. This solution polymerization showed a non-steady-state during the very early stage followed by a steady-state. The polymerization produced oligomers with several thousand molecular weights at a very low conversion under the non-steady-state. It was confirmed that the polymerization proceeded in accordance with a living mechanism under the steady-state based on the linear correlations for both the first-order time-conversion plots and the conversion–molecular weight plots. The molecular weight distributions of the polymers obtained in the steady-state were approximately 1.8. The block copolymerization with isopropyl methacrylate (^{i}PMA) demonstrated that the growing polymer chain ends of the MMA prepolymer were stabilized even at a high conversion and efficiently initiated the ^{i}PMA polymerization.

Keywords Photo-living radical polymerization · Solution polymerization · 4-Methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) · Methyl methacrylate · Non-steady-state · Steady-state · Block copolymerization · Isopropyl methacrylate

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Introduction

A significant number of investigations have been conducted on the nitroxide-mediated living radical polymerization based on its advantages over other living polymerizations in controlling the molecular weight by its simple procedure, using easily available and nonmetallic catalysts and widely creating macromolecules with a variety of nitroxide derivatives. The investigations concerned the kinetics and mechanisms of the polymerization [1–6], rate enhancement [7–10], stability of the propagating radicals [11–13], deactivation mechanism of the growing chain end [14, 15], influence of a substituent position for styrene derivatives on the polymerization rate [13], relationship between the structure of the nitroxides and the bond dissociation energy of NO-C [16], and effect of the nitroxide structure on the molecular weight distribution [17, 18]. Based on these findings, various architectures were created using the nitroxide-mediated living radical polymerization, the end-functional polymers [15], random copolymers [19–21], block copolymers including the random block [22–34], graft copolymers [35], star polymers including the hetero-arms [36–38], comb polymers [39, 40], etc. All these studies were made using the thermal nitroxide-mediated polymerization. The thermal polymerization ordinarily requires a high temperature over 120°C and takes some dozens of hours to obtain a high conversion. Therefore, the bulk polymerization is typically adopted over the solution polymerization, since the solution polymerization retards the propagation rate. However, the growing polymer chain ends are more stabilized in a solution than in the bulk [26] because their deactivation occurs at the end stage of the polymerization where most monomers are consumed. The stability of the growing polymer chain ends is significant in the molecular design using the living polymerization.

It has recently been reported that the nitroxide-mediated polymerization could be applied to photopolymerization [41–48]. The photopolymerization mediated by 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) had a living nature and controlled the homopolymerization of methyl methacrylate (MMA) that was unsuccessful by the thermal polymerization. The photopolymerization needed less time due to the rate enhancement by the photo-acid generators when compared to the thermal polymerization. On the other hand, the deactivation of the growing polymer chain ends occurred during the end stage of the bulk polymerization, as well as the thermal polymerization [49]. In order to obtain more stable growing polymer chain ends, the solution polymerization was explored, resulting in that the growing chain ends was more stabilized in a solution even at a high conversion. Furthermore, it was found that the solution polymerization produced a significant difference from the bulk polymerization in involving the non-steady-state that was not observed in the bulk polymerization. This short communication describes the MTEMPO-mediated photopolymerization of MMA in the acetonitrile solution using (2RS,2′RS)-azobis(4-methoxy-2,4-dimethylvaleronitrile) (*r*-AMDV) as the initiator and (4-*tert*-butylphenyl)diphenylsulfonium triflate (^{t}BuS) 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 (BMO-500D1, Wacom Co. Ltd.). 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. ^{1}H NMR measurements were conducted using a Varian 300 FT NMR spectrometer.

Materials *r*-AMDV was obtained by separation from a mixture of the racemic and meso forms of 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) [50]. MTEMPO was prepared as reported previously [51]. ^{t}BuS was purchased from Sigma-Aldrich and was used without further purification. MMA and ^{i}PMA were washed with 5 wt.% sodium hydroxide solution and water and then distilled over calcium hydride. Acetonitrile was purified by distillation over calcium hydride.

Photopolymerization of MMA: general procedure MMA (936 mg, 9.35 mmol), *r*-AMDV (7 mg, 0.0227 mmol), MTEMPO (9 mg, 0.0483 mmol), ^{t}BuS (23 mg, 0.0491 mmol), and acetonitrile (1 mL) were placed in an ampoule. After degassing the contents, the ampoule was sealed under vacuum. The polymerization was carried out at room temperature for 24 h with irradiation by reflective light using a mirror with a 500 W high-pressure mercury lamp at 7.0 A (30.1 W/cm^2). Dichloromethane (10 mL) was added to the resulting viscous solution. The solution was concentrated by an evaporator to remove the monomer unreacted, acetonitrile, and dichloromethane. The residue was freeze-dried with benzene (30 mL) at 40°C to obtain the product as white powder (946 mg). The conversion was estimated with the weight. The product was dissolved in dichloromethane (10 mL) and poured into hexane (500 mL). The precipitate was collected by filtration and dried in vacuo for several hours to be subjected to GPC analysis.

Block copolymerization of MMA with ^{i}PMA MMA (936 mg, 9.35 mmol), *r*-AMDV (7 mg, 0.0227 mmol), MTEMPO (9 mg, 0.0483 mmol), ^{t}BuS (23 mg, 0.0491 mmol), and acetonitrile (1 mL) were placed in an ampoule. After degassing the contents, the ampoule was sealed under vacuum. The polymerization was carried out at room temperature for 14 h with irradiation using a 500 W high-pressure mercury lamp. ^{i}PMA (3.539 g, 27.6 mmol) degassed by bubbling nitrogen for 15 min was added to the resulting solution. Part of the mixture (1 mL) was withdrawn to determine the molecular weight of the PMMA prepolymer and was freeze-dried with benzene (20 mL) at 40°C to obtain the prepolymer as white powder (126 mg). The residual mixture in the ampoule was degassed and the ampoule was sealed under vacuum. The block copolymerization was carried out at room temperature for 19 h with the irradiation. The resulting white suspension was dissolved in dichloromethane (15 mL) and poured into hexane (500 mL) to precipitate a polymer. The precipitate was collected by filtration and freeze-dried with benzene (30 mL) at 40°C to obtain the block copolymer as white powder (2.598 g).

Results and discussion

The photoradical polymerization of MMA was performed in acetonitrile at room temperature using the *r*-AMDV initiator and the MTEMPO mediator in the presence of the

Table 1 The photopolymerization of MMA in acetonitrile

MTEMPO/ *r*-AMDV	^{t}BuS/ MTEMPO	Conversion (%)	Mn[a]	Mw/Mn[a]
1.06	0.53	80	7,930	1.72
2.13	0.53	67	10,100	1.67
2.13	1.02	97	11,700	1.78

Irradiation time: 24 h. $[MMA]_0$=9.35 M, $[MTEMPO]_0$=0.0483 M

[a] Estimated by GPC based on PMMA standards

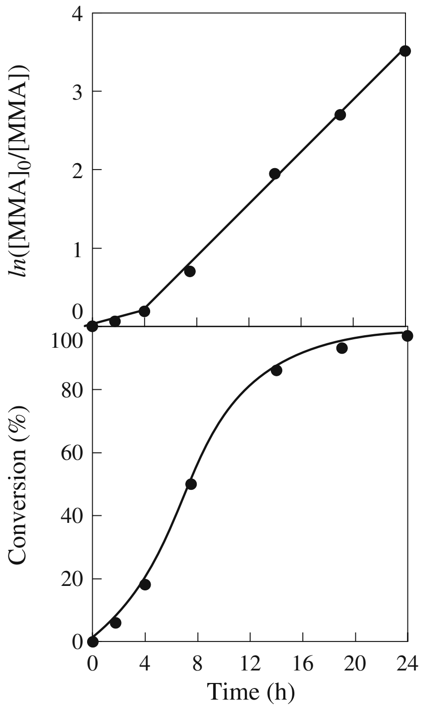


Fig. 1 The time-conversion and its first-order plots for the polymerization of MMA in acetonitrile. [MMA]$_0$=9.35 M, MTEMPO/*r*-AMDV=2.13, ^{t}BuS/MTEMPO=1.02

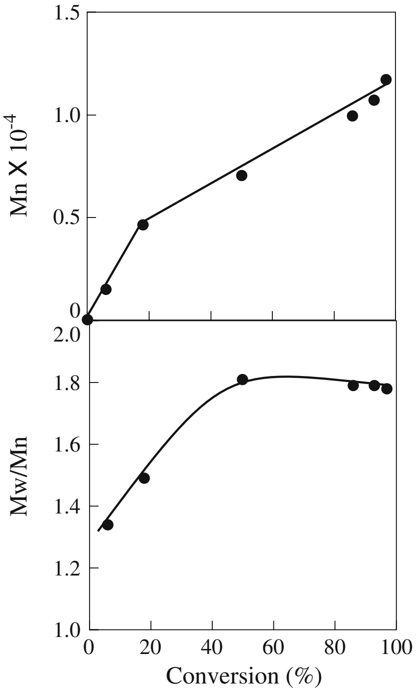


Fig. 2 The plots of the molecular weight and molecular weight distribution vs. the conversion for the polymerization of MMA in acetonitrile. [MMA]$_0$=9.35 M, MTEMPO/*r*-AMDV=2.13, ^{t}BuS/MTEMPO=1.02

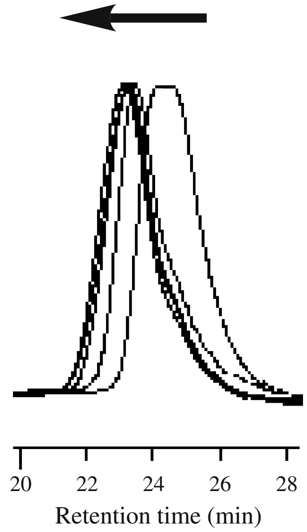
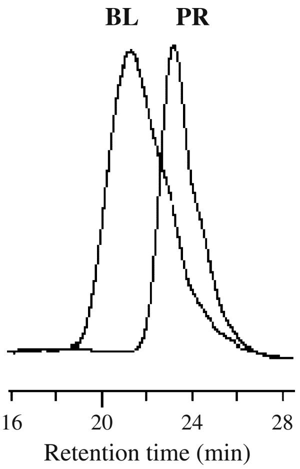


Fig. 3 The GPC profiles of the PMMA obtained at each conversion: 18% (4 h), 50% (7.5 h), 86% (14 h), 93% (19 h), and 97% (24 h) from the *right*

^{t}BuS photo-acid generator. The results are shown in Table 1. As a result of increasing the amount of MTEMPO, the rate of the polymerization decreased. However, the polymerization rate was enhanced by increasing the amount of ^{t}BuS. The solution polymerization allowed the conversion to reach 97%, whereas it was difficult for the bulk polymerization to increase the conversion over 85% [46].

The livingness of the solution polymerization was explored at the MTEMPO/*r*-AMDV of 2.13 and ^{t}BuS/MTEMPO of 1.02. The time-conversion and its first-order plots for the polymerization are shown in Fig. 1. The *ln*([MMA]$_0$/[MMA]) plots showed different lines before and after 4 h, indicating that the radical concentrations were different for these two lines. The polymerization should be under the non-steady-state below 4 h and reached the steady-state over this time. The non-steady-state was not observed in the bulk polymerization [46]. It is suggested that MTEMPO could not effectively trap the propagating

Fig. 4 The GPC profiles of the resulting block copolymer (*BL*) and prepolymer (*PR*)



radical due to its low concentration in the solution polymerization, causing occurrence of a normal termination between the propagating radicals under the non-steady-state. However, the proportion of the polymers produced by the normal termination is low based on its conversion (<18%). Figure 2 shows the plots of the molecular weight vs. the conversion for the solution polymerization. It was observed that oligomers with several thousand molecular weights were formed under the non-steady-state below the 18% conversion. The molecular weight linearly increased with the conversion under the steady-state, indicating that the polymerization proceeded by the living mechanism. The molecular weight distribution was around 1.8, somewhat higher than that for the bulk polymerization. This broader molecular weight distribution should be due to the presence of the oligomers produced under the non-steady-state.

The GPC profiles for the polymers obtained under the steady-state are shown in Fig. 3. The GPC curves were shifted to the higher molecular weight side as the conversion increased, thus supporting the living mechanism of the polymerization.

The stability of the growing polymer chain ends for the solution polymerization was also investigated through the block copolymerization. The PMMA prepolymer was prepared by a 14-h polymerization. The block copolymerization was performed for 19 h using ^{i}PMA as the second monomer. The solution containing the PMMA prepolymer and ^{i}PMA in acetonitrile was converted into a white suspension after 19 h. Figure 4 shows the GPC profiles of the prepolymer and the block copolymer. The GPC curve of the block copolymer was shifted to the higher molecular weight side, indicating that the prepolymer efficiently initiated the polymerization of ^{i}PMA. The growing polymer chain ends were stabilized even at a high conversion over 85% for the solution polymerization, whereas their stability was retained only for a conversion below 60% for the bulk polymerization. The molecular weights and molecular weight distributions were estimated to be Mn=8,650 and Mw/Mn=1.75 for the prepolymer and Mn=30,400 and Mw/Mn=2.61 for the block copolymer by the GPC based on the PMMA standards. The molecular weight of the P^{i}PMA blocks was determined to be Mn=30,300 by ^{1}H NMR based on the signal intensity of the methyl at 3.63 ppm for the PMMA blocks and the methine at 4.87 ppm for the P^{i}PMA blocks [49] and on the molecular weight by GPC for the prepolymer. The total molecular weight of the block copolymer was Mn=39,000 by ^{1}H NMR.

Conclusion

The photoradical polymerization of MMA in solution consisted of the non-steady-state and steady-state. Under the non-steady-state, the oligomers with several thousand molecular weights were formed, however, their conversion was low. The polymerization was confirmed to proceed in accordance with a living mechanism under the steady-state based on the linear correlations of the first-order time-conversion plots and the conversion–molecular weight plots. The molecular weight distributions of the polymers were somewhat broadened as compared to those for the bulk polymerization. The block copolymerization demonstrated that the growing polymer chain ends were stabilized in the solution even at a high conversion and efficiently initiated the polymerization of ^{i}PMA.

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