

## Research Article

# Aqueous Photo-Living Radical Polymerization of Sodium Methacrylate Using a Water-Soluble Nitroxide Mediator

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The aqueous photo-living radical polymerization of sodium methacrylate (NaMA) was attained using 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]-propionamide} (V-80) as the initiator and 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (HTEMPO) as the mediator in the presence of (4-fluorophenyl)diphenylsulfonium triflate (FS). The polymerization was carried out in water at room temperature by irradiation using a high-pressure mercury lamp. Whereas the polymerization by V-80 and/or FS in the absence of HTEMPO produced polymers with very high molecular weights and broad molecular weight distributions, the HTEMPO-mediated polymerization provided still lower-molecular-weight distributions using both V-80 and FS. The first-order time-conversion plots had an induction period up to 2.5 h; however, they thereafter showed a linear increase. The conversion-molecular weight plots also exhibited a linear correlation. A linear correlation was also obtained for the plots of the molecular weights versus the reciprocal of the initiator concentration. Based on these three correlations, it was found that the HTEMPO-mediated photopolymerization proceeded by a living mechanism.

## 1. Introduction

Poly(sodium methacrylate) (PNaMA), a water-soluble polyelectrolyte, has been used for many objectives, such as surface modification of the wettability and friction [1], suppression of cell adhesion and protein adsorption [1, 2], and self-assembly studies on amphiphilic block copolymers in aqueous media [3–7]. While PNaMA and its copolymers were prepared through the living anionic or living radical polymerizations of methacrylates with protecting groups of *tert*-butyl and benzyl, followed by deprotection [3–7], those were also directly obtained by the controlled/living radical polymerization of sodium methacrylate (NaMA) in water. For instance, the atom transfer radical polymerization (ATRP) of NaMA produced PNaMA with a well-controlled molecular weight [8]. This aqueous ATRP was used for the preparation of polymer brushes including PNaMA segments on gold [9, 10] and glass [11] surfaces. The photo-iniferter polymerization using a dithiocarbamate catalyst also succeeded in fabricating a PNaMA-branched graft copolymer on glass [12] and a poly(ethylene terephthalate) film [1].

In recent years, the nitroxide-mediated photo-controlled/living radical polymerization has been established for methyl methacrylate (MMA) using the derivatives of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) in the presence of the photo-acid generator (PAG) of diaryliodonium hexafluorophosphate [13–17], triarylsulfonium triflate [18–22], and an iron-arene complex [23]. This polymerization was used for the photodispersion polymerization of MMA in an alcoholic medium that produced monodispersed microspheres [24].

It was found that the nitroxide-mediated photo-controlled radical polymerization could be used for the NaMA polymerization in water using the water-soluble mediator and PAG. This paper describes the photo-living radical polymerization of NaMA in an aqueous medium using 4-hydroxy-TEMPO (HTEMPO) as the mediator, (4-fluorophenyl)diphenylsulfonium triflate (FS) as the water-soluble PAG, and 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide} (V-80) as the initiator.



TABLE 1: The photopolymerization of NaMA in water.

Run no.	V-80 (mM)	HTEMPO (mM)	FS (mM)	Time (h)	Conversion (%)	$M_n^a$	$M_w/M_n^a$
1	—	—	—	1	98	208,000	29.36
2	44.8	—	—	1	100	86,800	10.66
3	—	—	25.3	1	95	202,000	46.27
4	44.8	—	25.3	1	98	93,800	15.04
5	44.8	47.6	—	6	61	101,000	3.19
6	—	47.6	25.3	5	53	52,500	2.36
7	44.8	47.6	25.3	9	78	60,400	2.05
8	44.8	95.2	25.3	5	0	—	—
9	44.8	47.6	50.6	5	55	65,700	2.58
10	8.96	9.52	5.06	20	92 <sup>b</sup>	20,300	3.71

[NaMA]<sub>0</sub> = 9.25 mM.

<sup>a</sup>Estimated by GPC based on PNaMA standards.

<sup>b</sup>[NaMA]<sub>0</sub> = 1.85 mM.

TABLE 2: The HTEMPO-mediated polymerization of NaMA by V-80.

V-80 (mM)	Time (h)	Conversion (%)	$M_n^a$	$M_w/M_n^a$
14.9	3.5	71	86,700	2.22
22.5	5	76	75,800	2.16
44.8	9	78	60,400	2.05

[NaMA]<sub>0</sub> = 9.25 mM, HTEMPO/V-80 = 1.06, FS/HTEMPO = 0.53.

<sup>a</sup>Estimated by GPC based on PNaMA standards.

**2.2. Materials.** V-80 was purchased from Wako Chemicals and used as received. HTEMPO was prepared as reported previously [25]. FS and NaMA were purchased from Sigma-Aldrich and used as received. Distilled water was purchased from Wako Chemicals and used without further purification.

**2.3. Photopolymerization. General procedure** NaMA (1 g, 9.25 mmol), V-80 (18.3 mg, 0.0448 mmol), HTEMPO (8.2 mg, 0.0440 mmol), FS (10.9 mg, 0.0253 mmol), and distilled water (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 9 h by irradiation with a 500 W high-pressure mercury lamp. Distilled water (10 mL) was added to the product to dissolve it completely. A small amount of the resulting solution (0.1 mL) was withdrawn to determine the monomer conversion by <sup>1</sup>H NMR. The residual solution was dried in vacuo for several hours to obtain a polymer (1.2441 g).

### 3. Results and Discussion

The photoradical polymerization of NaMA was performed in water using HTEMPO as the mediator, V-80 as the initiator, and a water-soluble photo-acid generator, FS, as the accelerator at room temperature by irradiation (Scheme 1). The results of the polymerization are listed in Table 1. The monomer conversion was estimated by <sup>1</sup>H NMR using the signal intensity of the methyl protons at 1.85 ppm for unreacted NaMA and the methyl and methylene protons

at 0.6–2.2 ppm for the polymer main chain (Figure 1). The NaMA had a high reactivity for radical polymerizations and caused autopolymerization that produced a very high-molecular-weight polymer with a broad MWD. The polymerization was also initiated by V-80 and yielded a polymer with a lower molecular weight and MWD. Furthermore, the polymerization by FS caused an increase in the MWD. On the other hand, the polymerization using HTEMPO as the mediator significantly decreased the MWD. This HTEMPO-mediated polymerization produced a still lower MWD using both V-80 and FS than the polymerization in the presence of either V-80 or FS. The HTEMPO-mediated polymerization is decelerated due to the control of the propagating radicals by HTEMPO. Hence, the autopolymerization competitively occurs during the slow polymerization initiated only by V-80, resulting in the higher MWD. Figure 2 shows GPC profiles of the PNaMA obtained by the polymerization in the absence and presence of HTEMPO. The doubling amount of HTEMPO obstructed the polymerization process. An excess of HTEMPO hinders the cleavage of the C-ON bond at the propagating polymer chain end. It has been reported that the PAG accelerated the polymerization of MMA without an increase in the MWD [14, 18, 21]. However, the doubling amount of FS rather caused broadening of the MWD. It is considered that the propagating radicals are much freer in the aqueous medium by the interaction of the water-soluble HTEMPO and FS in the excited state. The proposal mechanism of the HTEMPO-mediated polymerization is shown in Scheme 2. In addition, the dilution of the polymerization system caused a further increase in the MWD.

In order to confirm the living nature of the polymerization, the first-order time-conversion plots were evaluated under the conditions at the HTEMPO/V-80 molar ratio of 1.06 and FS/HTEMPO of 0.53. The yellow solution gave rise to polymer precipitates after 2.5 h of the polymerization. Figure 3 shows the time-conversion and its first-order plots for the polymerization.  $[M]$  denotes the monomer concentration. The induction period was observed up to 2.5 h. This induction period can be accounted for by the capture of the initiator radicals generated from V-80 by HTEMPO during the initial stage of the polymerization. The  $\ln([M]_0/[M]_t)$

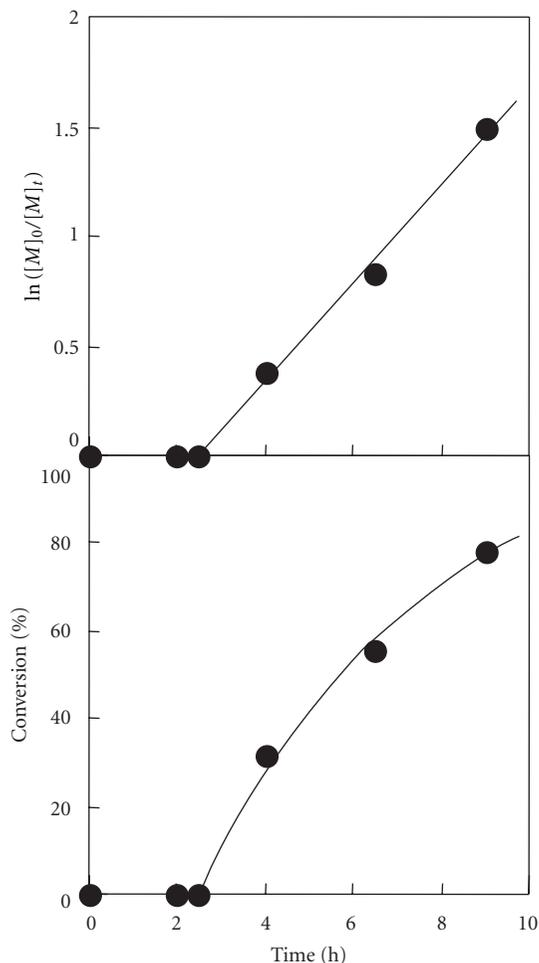


FIGURE 1: The  $^1\text{H}$  NMR spectrum of the resulting mixture obtained by the HTEMPO-mediated photopolymerization of NaMA in water at HTEMPO/V-80 of 1.06 and HTEMPO/FS of 0.53. Solvent:  $\text{D}_2\text{O}$ . Conversion = 78%.

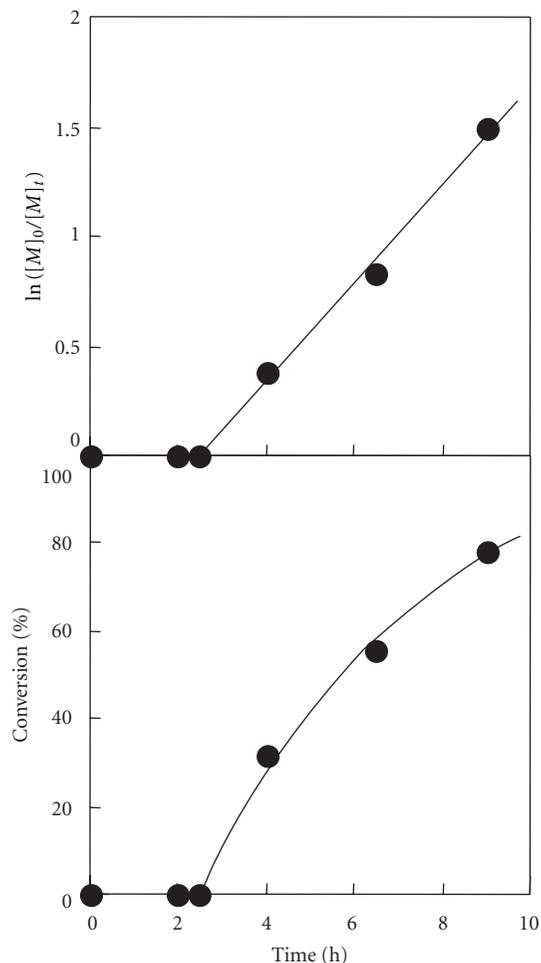


FIGURE 3: The time conversion and its first-order plots for the NaMA polymerization. HTEMPO/V-80 = 1.06, HTEMPO/FS = 0.53.

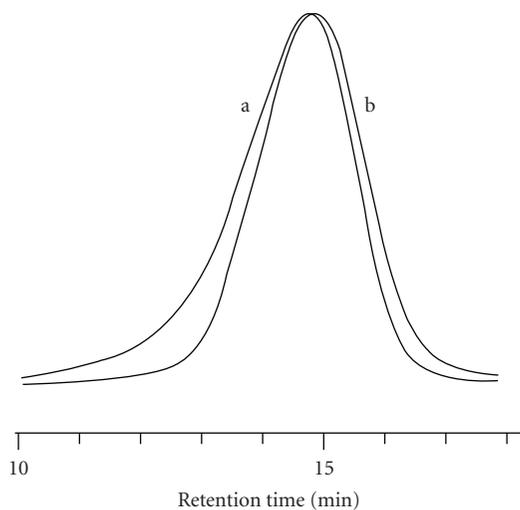


FIGURE 2: GPC profiles of the PNaMA obtained by the photopolymerization in the absence (a, Table 1, Run 4) and presence (b, Table 1, run 7) of HTEMPO.

linearly increased over 2.5 h, indicating that the number of polymer chains was constant throughout the course of the polymerization. The relationship between the conversion and the molecular weight of the polymer revealed the living polymerization. The conversion-molecular weight plots are shown in Figure 4. The observed molecular weight exhibited a linear increase with the increasing conversion. However, the observed molecular weights were in poor agreement with the theoretical values. This poor agreement suggested the low initiator efficiency and the existence of the nonsteady state during the very early stage of the polymerization. The MWD was constant around  $M_w/M_n = 2.0$ . The MWD is broad when the controlled polymerization is taken into consideration. This broad MWD is due to the fact that the polymers precipitated during the polymerization even at the 32% conversion. The GPC analysis endorsed the living nature of the polymerization. Figure 5 shows the GPC profiles of the polymers produced for each conversion. The curves were shifted to the higher molecular weight side with an increase in the conversion.

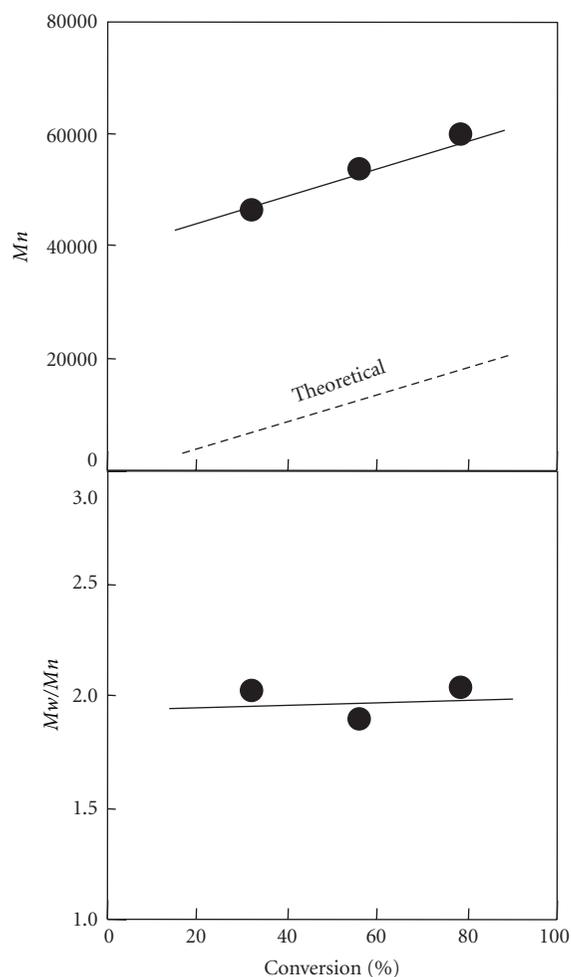


FIGURE 4: The plots of the molecular weight and its distribution versus the conversion for the polymerization. HTEMPO/V-80 = 1.06, HTEMPO/FS = 0.53.

The livingness of the polymerization was also confirmed on the basis of the correlation between the initial concentration of the initiator and the molecular weight of the polymer. Table 2 shows the results on the HTEMPO-mediated polymerization at three different concentrations of V-80. The molecular weight decreased with an increase in the initiator concentration, while the MWD was constant at ca. 2. The plotted molecular weight versus the reciprocal of the initial concentration of V-80 showed a linear increase in the molecular weight (Figure 6). Therefore, it can be deduced that the HTEMPO-mediated photoradical polymerization of NaMA in water proceeded by a living mechanism using V-80 and FS.

#### 4. Conclusion

The photo-living radical polymerization of NaMA was attained in an aqueous solution using the HTEMPO mediator in the presence of V-80 and FS. The polymerization produced polymers with an MWD around  $Mw/Mn = 2$ . This somewhat broad MWD was attributed to the precipitation

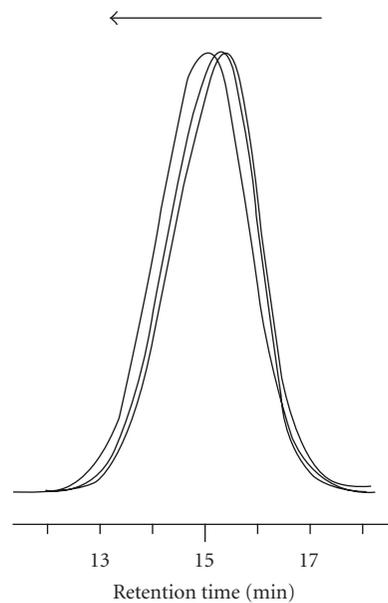


FIGURE 5: The variation in the GPC curves versus the conversion: 32% (4 h), 56% (6.5 h), and 78% (9 h) from the right.

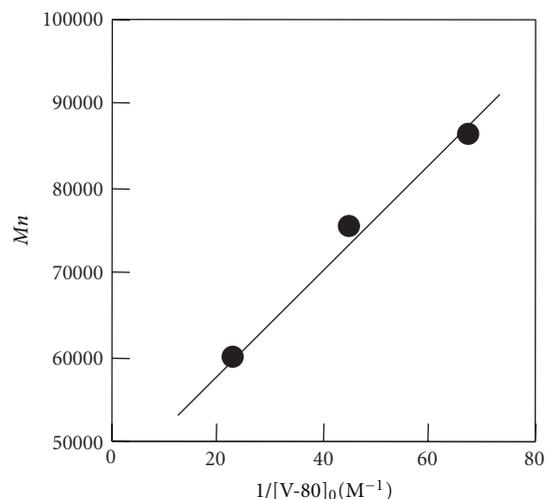


FIGURE 6: The plots of the molecular weight and its distribution versus the reciprocal of the initiator concentration for the polymerization. HTEMPO/V-80 = 1.06, HTEMPO/FS = 0.53.

of the polymers during the polymerization. The first-order time-conversion plots included an induction period up to 2.5 h; however, they thereafter showed a linear increase. The conversion-molecular weight plots also exhibited a linear increase, although the observed molecular weights were in poor agreement with the theoretical values due to the low initiator efficiency and the nonsteady state during the very early stage of the polymerization. Furthermore, a linear increase was obtained for the plots of the molecular weight versus the reciprocal of the initiator concentration. Based on these three linear correlations, it can be deduced that the HTEMPO-mediated photoradical polymerization of NaMA proceeded in accordance with a living mechanism.

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