

Elucidation of Acceleration Mechanisms by a Photosensitive Onium Salt for Nitroxide-Mediated Photocontrolled/Living Radical Polymerization

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Abstract

The acceleration mechanisms by a photosensitive onium salt for the nitroxide-mediated photocontrolled/living radical polymerization (photo-NMP) were determined. The photo-NMP of methyl methacrylate was performed by irradiation at room temperature using 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) as the mediator and (2RS, 2'RS)-azobis(4-methoxy-2,4-dimethylvaleronitrile) as the initiator. The polymerization was accelerated in the presence of (4-*tert*-butylphenyl)diphenylsulfonium triflate (^tBuS) to produce a polymer with a molecular weight distribution as narrow as the polymerization in its absence. (±)-Camphor-10-sulfonic acid or 2-fluoro-1-methylpyridinium *p*-toluenesulfonate had no effect on the polymerization speed, suggesting that ^tBuS did not serve as the photo-acid generator for the photo-NMP. It was found that the acceleration of the polymerization was based on the electron transfer from MTEMPO into ^tBuS in the excited state to temporarily generate a free radical propagating chain end and an oxoaminium salt (OAS), the one-electron oxidant of MTEMPO. This electron transfer mechanism was verified on the basis of the fact that the photo-NMP in the presence of ^tBuS was still accelerated by triphenylamine, the electron transfer inhibitor, to partly produce a polymer with an uncontrolled molecular weight. The formation of an uncontrolled molecular weight polymer indicated the generation of a free radical propagating chain end due to the deactivation of the OAS by the triphenylamine. It was deduced that ^tBuS served as the electron acceptor from MTEMPO in the excited state to temporarily produce a free radical propagating chain end along with OAS, resulting in the acceleration of the polymerization.

Keywords

Photocontrolled/Living Radical Polymerization, Acceleration Mechanisms, Electron Transfer,

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(4-*tert*-Butylphenyl)Diphenylsulfonium Triflate, 4-Methoxy-2,2,6,6-Tetramethylpiperidine-1-Oxyl, Oxoaminiun Salt

1. Introduction

The controlled/living radical polymerization (CLRP) has been an indispensable technique to design and create highly functional and efficient materials supporting today's cutting-edge technologies in many fields, such as drug and gene deliveries [1]-[4] and anti-bacterial treatment [5] in medical care, photolithography in electronics [6]-[8], water purification in environmental engineering [9], and surface modifications of wettability in the textile and vehicle industries [10]-[12]. The significance of the CLRP is the improvement of the functions by unifying the physical properties based on strict control of the molecular weight related to the structure of the polymers. Many CLRP systems have been established using various catalysts to provide well-controlled molecular weight polymers; e.g., the atom transfer radical polymerization (ATRP) [13] [14], reversible addition-fragmentation chain transfer (RAFT) [15], organoheteroatom-mediated polymerization [16], nitroxide-mediated polymerization (NMP) [17], iniferter polymerization [18], and iodide transfer polymerization [19] [20]. These thermal CLRPs produced a number of architectures with precisely controlled structures including supra molecules with high dimensional structures.

The photo-induced CLRP provides an environmental benefit, local application, and processing without thermal damage. The photo-CLRP to strictly control the molecular weights for various monomers was achieved by Yamago and coworkers using the organotellurium complex [21]. The photo-induced systems were also developed for the ATRP [22]-[24], RAFT [25], and iniferter polymerization [26] [27], although some of them still required heating to proceed [23] [24]. On the other hand, the photo-induced NMP to highly control a molecular weight have not been attained in spite of the fact that many efforts have been made using the mediators supported on the photosensitive groups [28]-[33]. In recent years, the photo-NMP using 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) has been reported to proceed at room temperature to produce polymers with a comparatively narrow molecular weight distribution ($M_w/M_n \approx 1.4$) [34]-[47]. This photo-NMP was accelerated in the presence of an iron-arene complex [48] and photosensitive onium salts, such as the diaryliodonium salts [34] [35] and triarylsulfonate salts [49] [50]. These onium salts served only as the accelerator for the polymerization and had no influence on the molecular weight control. However, the mechanisms of the acceleration by the onium salts were unclear, although possible mechanisms were proposed [51]-[53]. The present study determined that the acceleration by the onium salts for the photo-NMP was based on the electron transfer mechanism from MTEMPO to the onium salt in the excited state. This paper describes the acceleration mechanisms of the photo-NMP using a photosensitive triarylsulfonium salt.

2. Experimental

2.1. Instrumentation

The photopolymerization was carried out using an Ushio optical modulex BA-H502, an illuminator OPM2-502H with a high-illumination lens UI-OP2SL, and a 500 W super high-pressure UV lamp (USH-500SC2, Ushio 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 *N,N*-dimethylformamide as the eluent at 40°C.

2.2. Materials

MTEMPO [54] and oxoaminiun hexafluoroantimonate (OASbF₆) [55] were prepared as reported previously. (2RS, 2'RS)-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (*r*-AMDV) was obtained by separation from a mixture of the racemic and meso forms of 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) [56]. Methyl methacrylate (MMA) was washed with 5 wt.% sodium hydroxide solution and water, then distilled over calcium hydride. (4-*tert*-Butylphenyl)diphenylsulfonium triflate ('BuS) was purchased from Sigma-Aldrich. (±)-Camphor-10-

sulfonic acid (CSA) was obtained from Wako Pure Chemical Industries. 2-Fluoro-1-methylpyridinium *p*-toluenesulfonate (FPT) and triphenylamine were purchased from Tokyo Chemical Industry. These chemicals were used as received. Exrapure N₂ gas with over 99.9995 vol% was purchased from Taiyo Nippon Sanso Corporation.

2.3. The Photo-NMP Using MTEMPO: General Procedure

MMA (936.0 mg, 9.35 mmol), *r*-AMDV (14.0 mg, 0.0454 mmol), MTEMPO (9.0 mg, 0.0483 mmol), and ^tBuS (12.0 mg, 0.0256 mmol) were placed in an ampoule. The contents in the ampoule were degassed several times using a freeze-pump-thaw cycle and were charged with N₂. The photopolymerization was carried out in the nitrogen atmosphere at room temperature for 5.5 h using a reflective light from a mirror in order to avoid any thermal polymerization caused by the direct irradiation. The product was dissolved in dichloromethane (10 mL). The solution was concentrated by an evaporator to remove the dichloromethane and unreacted monomer and was freeze-dried with benzene (15 mL) at 40°C to obtain the product as white powder (657.1 mg). The monomer conversion was estimated gravimetrically. The product was dissolved in dichloromethane (5 mL) and poured into hexane (500 mL). The precipitate collected by filtration and dried in vacuo for several hours was subjected to GPC analysis.

2.4. The Photo-NMP Using OAS: General Procedure

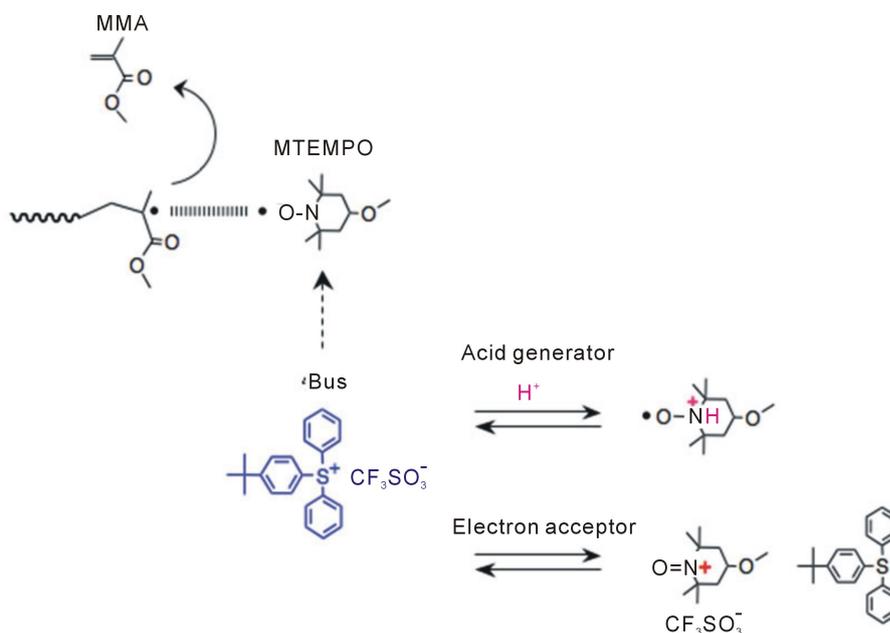
MMA (936.0 mg, 9.35 mmol), *r*-AMDV (14.0 mg, 0.0454 mmol), and OASbF₆ (20.4 mg, 0.0483 mmol) were placed in an ampoule. The contents in the ampoule were degassed several times using a freeze-pump-thaw cycle and were charged with N₂. The photopolymerization was carried out in the nitrogen atmosphere at room temperature for 5.5 h using a reflective light from a mirror. The product was dissolved in dichloromethane (10 mL). The solution was concentrated by an evaporator to remove the dichloromethane and unreacted monomer and was freeze-dried with benzene (10 mL) at 40°C to obtain the product as white powder (299.0 mg). The monomer conversion was estimated gravimetrically. The product was dissolved in dichloromethane (1.5 mL) and poured into hexane (200 mL). The precipitate collected by filtration and dried in vacuo for several hours was subjected to GPC analysis.

3. Results and Discussion

The photo-NMP of MMA was performed at room temperature for 5.5 h using MTEMPO as the mediator and *r*-AMDV as the initiator in the presence of ^tBuS. The polymerization was accelerated by ^tBuS at a 0.53 molar ratio to MTEMPO to produce poly(MMA) at a 68% MMA conversion (M_n = 13,600, M_w/M_n = 1.43), whereas the polymerization in the absence of ^tBuS yielded a polymer at a 35% conversion (M_n = 8490, M_w/M_n = 1.40). It was confirmed that ^tBuS played a role only as the accelerator because the polymerization provided a molecular weight distribution as narrow as that by the polymerization in its absence. The photosensitive onium salts are often used as a proton source in many photoreactions by eliminating a proton from the solvent or monomer in the excited state [57]. While the photosensitive onium salts serve as a photo-acid generator, the salts also act as an electron acceptor in the presence of an electron donor in the excited state [58] [59]. Hence, two mechanisms are considered for the cause of the acceleration by ^tBuS for the MTEMPO-mediated photopolymerization as shown in **Scheme 1**. The polymerization should be accelerated by the protonation to MTEMPO when ^tBuS serves as the photo-acid generator, whereas the acceleration is caused by the temporary generation of a free radical propagating chain end along with the formation of an oxoaminium salt (OAS), the one-electron oxidant of MTEMPO, when ^tBuS acts as the electron acceptor.

In order to clarify the mechanisms of the acceleration by ^tBuS, the possible mechanism of ^tBuS as the photo-acid generator was first explored. For the thermal nitroxide-mediated controlled/living radical polymerization, CSA and FPT accelerated the polymerization by serving as a proton donor or a Lewis acid [60]. These acids were adopted as the accelerator instead of ^tBuS for the MTEMPO-mediated photopolymerization (**Table 1**). Neither CSA nor FPT produced a significant difference in the MMA conversion and molecular weight distribution of the resulting polymers, indicating that the polymerization was not accelerated in the presence of the acid. Consequently, the role of ^tBuS as the photo-acid generator is negated for the acceleration of the polymerization.

When ^tBuS acts as the electron acceptor from MTEMPO, the OAS is temporarily generated in the excited state. In order to verify this electron transfer mechanism for the acceleration, the polymerization using OASbF₆



Scheme 1. The acceleration mechanisms of the photo-NMP by $t\text{BuS}$.

Table 1. The photo-NMP using MTEMPO in the presence of acid^a.

Acid	Conversion (%)	Mn ^b	Mw/Mn ^b
CSA	30	7990	1.36
FPT	42	9250	1.40
—	35	8490	1.40

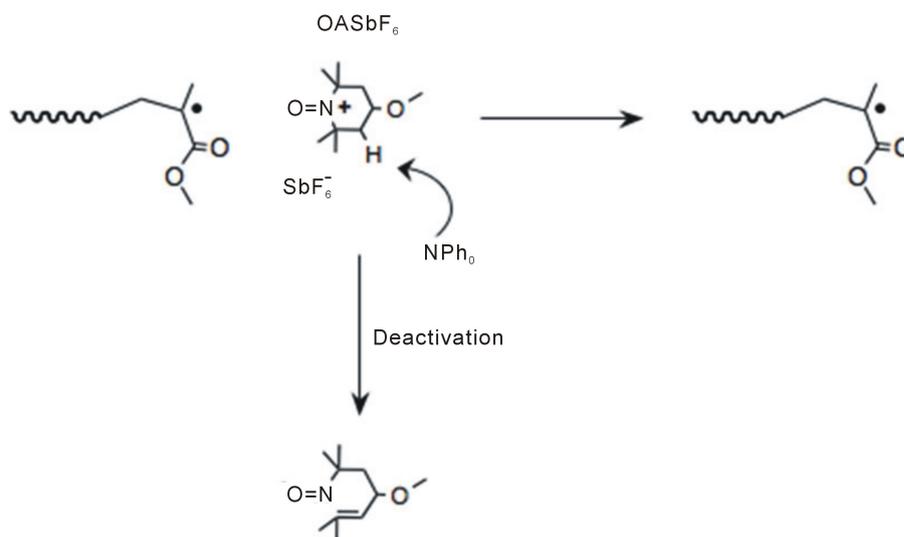
a. Acid/MTEMPO = 0.53, MTEMPO/ r -AMVD = 1.06. Polymerization time = 5.5 h. b. Estimated by GPC based on PMMA standards.

instead of MTEMPO was investigated. The polymerization using OASbF_6 in the absence of $t\text{BuS}$ produced a polymer at a 31% conversion ($M_n = 9670$, $M_w/M_n = 1.35$) at a 1.06 molar ratio of OASbF_6/r -AMVD, while the MTEMPO-mediated polymerization yielded a polymer at a 35% conversion ($M_n = 8490$, $M_w/M_n = 1.40$) at the identical molar ratio of MTEMPO/ r -AMVD. The polymerization by OASbF_6 produced a polymer with a comparatively narrow molecular weight distribution at a conversion similar to that for the polymerization by MTEMPO, implying that OASbF_6 served as the mediator to control the molecular weight as did MTEMPO. It is expected that the oxoammonium cation eliminated an electron from the counter anion to convert into MTEMPO in the excited state because it is difficult to eliminate an electron from the propagating radical chain end attached to the electron-withdrawing group. The conversion of the oxoammonium cation to MTEMPO by the electron elimination from the counter anion is supported by previous reports that the OAS eliminated an electron from electron donors to provide their radical cations, and converting into MTEMPO [61]–[65]. Accordingly, the polymerization was examined in the presence of the electron transfer inhibitor, triphenylamine. These results are summarized in **Table 2**. The MTEMPO-mediated polymerization was retarded by triphenylamine. This retardation was caused by preventing the bond cleavage between the propagating radical and MTEMPO due to more electron-donating triphenylamine, resulting in no influence on the molecular weight distribution. On the other hand, the OASbF_6 -mediated polymerization was accelerated by the triphenylamine, accompanied by the formation of a polymer with an uncontrolled molecular weight over 1,000,000. The ratio of the polymer with the uncontrolled molecular weight to that with the controlled molecular weight was estimated to be 0.454/0.546 for $M_n = 1,630,000/10,300$ based on the area percent by the GPC analysis. The formation of the polymer with the uncontrolled molecular weight implies the generation of a free radical propagating chain end without the counter radical of the mediator, indicating the deactivation of OASbF_6 . This deactivation is considered to occur by the β -elimination of OASbF_6 by the triphenylamine (**Scheme 2**). The triphenylamine has the potential to act as the

Table 2. The photo-NMP in the presence of triphenylamine ^a.

Mediator	Ph ₃ N/Mediator	Time (h)	Conversion (%)	Mn ^b	Mw/Mn ^b
MTEMPO	1.0	7.0	22	5200	1.35
MTEMPO	0	5.5	35	8490	1.40
OASbF ₆	1.0	5.5	49	1,630,000 ^c	2.88
OASbF ₆	0	5.5	31	10,300	1.47
OASbF ₆	0	5.5	31	9670	1.35

a. Mediator/*r*-AMVD = 1.06. b. Estimated by GPC based on PMMA standards. c. The ratio of the area % for Mn = 1,630,000/10,300 was 0.454/0.546.

**Scheme 2.** The generation of a free radical propagating chain end based on the deactivation of OASbF₆ by the triphenylamine.

electron donor to OASbF₆, however this possibility is negated because OASbF₆ should be converted into MTEMPO to control the molecular weight if the electron transfer occurs from the triphenylamine to OASbF₆.

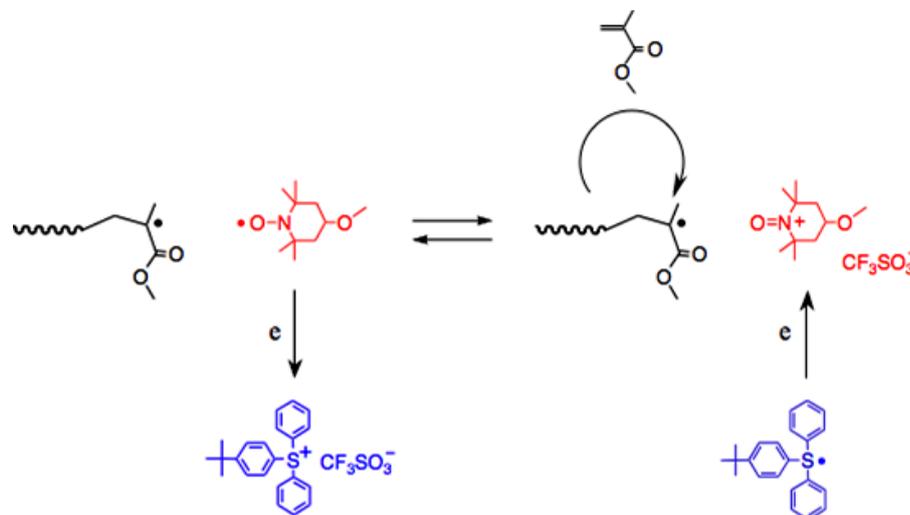
In order to verify the formation of the OAS in the excited state by the electron transfer from MTEMPO to ^tBuS, the acceleration by ^tBuS for the MTEMPO-mediated photopolymerization was explored in the presence of the triphenylamine. The results are shown in **Table 3**. The triphenylamine significantly increased the polymerization rate, accompanied by broadening of the molecular weight distribution, indicating the formation of a polymer with an uncontrolled molecular weight. This uncontrolled molecular weight along with the rapid polymerization is caused by the generation of a free radical propagating chain end losing the mediator radical based on the deactivation of the OAS by the triphenylamine. It was confirmed that the OAS was formed in the excited state by the electron transfer from MTEMPO to ^tBuS (**Scheme 3**). ^tBuS served as the electron acceptor to temporarily produce the OAS along with a free radical propagating end. The electron transfer from MTEMPO in the excited state lengthens the time for which the propagating radical is in the free state, causing an increase in the number of monomers inserted between the propagating radical and MTEMPO. Hence, this longer free state time of the propagating radical resulted in the acceleration of the polymerization. The propagating radical is coupled again with MTEMPO formed by the reverse electron transfer from the ^tBuS radical to the OAS. This reverse electron transfer maintains the molecular weight control of the polymerization against the acceleration by ^tBuS.

The electron transfer mechanism for the acceleration by ^tBuS is supported by the photo-NMP of glycidyl methacrylate (GMA) [66]. The uncontrolled photopolymerization initiated by *r*-AMDV in the presence of ^tBuS provided a gel product due to the simultaneous progress of the free radical polymerization of the vinyl groups by *r*-AMDV and the cationic ring-opening polymerization of the epoxy group by ^tBuS serving as the photo-acid generator [60]. On the other hand, the photo-NMP using MTEMPO in the presence of ^tBuS produced a poly(GMA) obtained only by the vinyl group polymerizing and retained the epoxy groups in the structure, supporting the fact

Table 3. The acceleration by triphenylamine for the photo-NMP in the presence of ^tBuS^a.

Ph ₃ N/ ^t BuS	Time (h)	Conversion (%)	Mn ^b	Mw/Mn ^b
1.0	2.5	88	18,600	2.32
0	5.5	68	13,600	1.43

a. MTEMPO/*r*-AMVD = 1.06, ^tBuS/MTEMPO = 0.53. b. Estimated by GPC based on PMMA standards.

**Scheme 3.** The electron transfer mechanism for the acceleration of the photo-NMP by ^tBuS.

that ^tBuS served as the electron acceptor from MTEMPO during the photo-NMP.

4. Conclusion

The acceleration mechanisms by the photosensitive onium salts for the photo-NMP were determined. The onium salts did not serve as the photo-acid generator, but as the electron acceptor from MTEMPO to temporarily produce the OAS along with a free radical propagating end in the excited state. The formation of the OAS by the electron transfer was confirmed by obtaining a polymer with an uncontrolled molecular weight by the polymerization in the presence of the electron transfer inhibitor. The conversion from MTEMPO into the OAS in the excited state lengthened the time for which the propagating radical was in the free state, resulting in the acceleration of the polymerization. MTEMPO that was reproduced by the reverse electron transfer from the onium radical to the OAS controlled the molecular weight.

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