

## Research Article

# Stereocontrol of Methyl Methacrylate during Photoinduced Nitroxide-Mediated Polymerization in the Presence of Photosensitive Alkoxyamine

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Photosensitive alkoxyamine 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidin-4-yl quinoline-2-carboxylate (PE-TEMPO-Q) was synthesized. Photochemical properties of PE-TEMPO-Q were studied to develop photoinduced nitroxide-mediated polymerization of methyl methacrylate (MMA). Rapid and facile polymerization at ambient temperature with PE-TEMPO-Q as an initiator was confirmed to proceed in a controlled mechanism based on the linear growth in molecular weight combined with relative narrow polydispersity index (1.4–1.8) of the resulting polymers. The stereochemistry of obtained polymers was also investigated, and the syndiotacticity slightly increased compared with the typical photopolymerization. Dual-controlled photopolymerization of MMA was achieved in the presence of synthesized alkoxyamine.

## 1. Introduction

The design and preparation of well-defined polymers at the molecular level has been one of the major concerns in synthetic polymer chemistry over the past several decades. Controlled/living radical polymerization (CRP) methods, which mainly include nitroxide-mediated polymerization (NMP) [1], atom transfer radical polymerization (ATRP) [2], and reversible addition-fragmentation chain transfer (RAFT) [3], have been developed primarily to prepare polymers with predetermined molecular weights, low polydispersities, and specific topologies. The stereochemical control is also an important issue in developing excellent novel polymer materials because physical and mechanical properties are highly dependent on tacticity. Anionic and coordination polymerizations have been applied to achieve various stereochemical control polymers [4, 5]. However, radical polymerization is much less successful in controlling tacticity because of the radical nature of the propagation step such that the planarity of the generated radicals ( $sp^2$  hybridization) offers similar probabilities of meso and racemic addition, resulting in atactic polymers. Several approaches have been established

to control tacticity by polymerization under confined media such as the addition of solvents or additive-mediated system, even by polymerizing monomer with inherent stereospecificity [6–8].

A further target in radical polymerization is the attempt to synthesize polymers by controlling the molecular weight and tacticity [9, 10]. Since the way has been paved by the developments in each control, an increased number of studies in this topic have been reported. Lutz et al. [11] and Jiang et al. [12] combined ATRP polymerization with Lewis acid-mediated system to obtain stereospecific polymers with controlled molecular weights and narrow polydispersities. Miura et al. [13] and Wang et al. [14] studied ATRP polymerization in the presence of fluoroalcohol and successfully obtained dual-controlled polymerization. Great progress in controlling microstructures and macromolecular architectures has been achieved in recent year by combining either Lewis acid with RAFT polymerization [15]. However, most of these studies are performed in a thermoinitiated polymerization system with long polymerization period or extremely low temperature conditions (approximately  $-70^\circ\text{C}$ ), resulting in time- and energy-consuming strategies.

UV irradiation, as an easy and effective activation method, offers a mild technique for dual control. Contrary to thermally based applications, typical photochemistry can be performed in mild temperatures, indicating its suitability for thermally sensitive monomers and substrates [16]. Fang et al. [17] applied UV irradiation to initiate controlled/living radical polymerization of acrylamide under the stereocontrol of a Lewis acid by the decomposition of dibenzyl trithiocarbonate into free radicals under UV irradiation. The polymerization took place at ambient temperature in a relatively rapid manner. Shim et al. [18] studied the photoinitiated polymerization of vinyl acetate with a photochemically inert RAFT agent under low reaction temperature in fluoroalcohols to obtain polymers with enhanced stereocontrol and molecular weight control. Shanmugam and Boyer [19] reported a simple method for the tacticity and temporal control of RAFT polymerization of poly(*N,N*-dimethylacrylamide) by combining Lewis acids in the presence of photoredox catalysts. However, such techniques only allow the simultaneous control of the molecular weight and stereoregularity with limited types of monomers, such as (meth) acrylamides. Therefore, expanding the applicable monomers, such as methyl methacrylate (MMA), is vital.

The combination of stereocontrol and molecular weight control of MMA, which is one of the most applied monomers, has been achieved by ATRP and RAFT polymerizations using various Lewis acids or polar solvents [15, 20]. Nevertheless, rigorous reaction conditions are usually required. The in-depth investigation of photoinduced control/living polymerization provides an efficient, mild, and robust method strategy to prepare well-defined PMMA. We have successfully carried out the photopolymerization of MMA using photoinitiator/photosensitive nitroxide as a bimolecule-mediated system [21]. In this study, a photosensitive alkoxyamine was synthesized, and its photochemical behavior was investigated. Moreover, the photoinduced NMP polymerization of MMA with simultaneous control of molecular weight and stereoregularity was examined.

## 2. Experimental

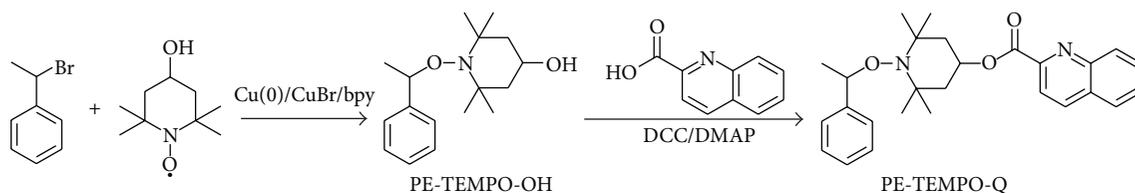
**2.1. General.** MMA (Tianjin Damao Chemical Reagent Factory, China) was distilled under vacuum before use. 4-Hydroxy-2,2,6,6-tetramethyl-piperidinyl-1-oxy [TEMPO-OH, 98%, Aladdin Industrial Corporation (AIC), USA] was purified by recrystallization from cyclohexane. Quinaldic acid (98%, AIC), 1-bromoethyl benzene (97%, AIC), 2,2'-bipyridyl (bpy, 99%, AIC), CuBr (99%, AIC), Cu(0) powder (99.9%, AIC), *N,N'*-dicyclohexylcarbodiimide (DCC, 99%, AIC), 4-dimethylaminopyridine (DMAP, 99%, AIC), and 2,2-dimethoxy-2-phenyl acetophenone (DMPA, BASF) were used as received. All solvents were commercially available and used without further purification.

FT-IR spectra were measured between 4000  $\text{cm}^{-1}$  and 500  $\text{cm}^{-1}$  for 32 scans at 4  $\text{cm}^{-1}$  resolution in KBr pellets using a Nicolet Magna 360 spectrophotometer.  $^1\text{H}$  NMR spectra were recorded on a Bruker spectrometer (400 MHz) with DMSO- $d_6$  as solvent at 25°C and tetramethylsilane (TMS) as the internal reference. Elemental analyses were performed

under a  $\text{N}_2$  atmosphere using Elementar Vario EL CHNS equipment, and the C, H, and N contents in the product were determined. Electron spin resonance (ESR) was measured using Bruker BioSpin A300-10-12 to test for unpaired electrons in the product. The sample was dissolved in a quartz cylindrical tube with  $\text{CH}_2\text{Cl}_2$  as the inert solvent. UV-vis spectra of the samples were obtained using a Shimadzu UV-450 spectrophotometer. Fluorescence spectra were measured using a Shimadzu RF-5301PC spectrophotometer. Gel permeation chromatography (GPC) measurements were obtained from a Viscotek VE112 instrument equipped with a VF7510 pump, a VF1122 variable wavelength detector, and a M302 refractive index detector with THF as the eluent at a rate of 1.0 mL/min at 40°C. The injection volume was 20  $\mu\text{L}$ , and the concentration was 5–10 mg/mL. Calibration was performed using narrow molecular weight polystyrene standards (polymer index < 1.1), ranging from  $2 \times 10^3$  g/mol to  $6 \times 10^4$  g/mol.

**2.2. Synthesis of Photosensitive Alkoxyamine 2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidin-4-yl Quinoline-2-carboxylate (PE-TEMPO-Q).** The photosensitive alkoxyamine PE-TEMPO-Q was prepared by a two-step reaction sequence. First, a mixture of TEMPO-OH (1.293 g, 7.50 mmol), Cu(0) powder (0.480 g, 7.50 mmol), CuBr (1.080 g, 7.50 mmol), 1-bromoethyl benzene (0.925 g, 5.00 mmol), and bpy (1.170 g, 7.50 mmol) in benzene (50 mL) was mixed in a flask and stirred at 70°C for 8 h under an inert atmosphere. The reaction mixture was then filtered and successively washed thrice with 1 mol/L  $\text{CuSO}_4$  solution and distilled water. After drying with magnesium sulfate and evaporating benzene, the crude product was purified by silica gel column chromatography (ethyl acetate/ether = 1/20) to obtain a white solid. Analytical data are as follows: Yield: 70.26%. Melting point: 98.9–99.6°C. Found: C, 73.61; H, 9.81; N, 5.05%. Calc. for  $\text{C}_{17}\text{H}_{27}\text{NO}_2$ : C, 74.01; H, 9.79; N, 5.04%.  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm, TMS): 7.29–7.22 (m, 5H, Ar-H), 4.74 (q, 1H, CH), 4.43 (d, 1H, -OH), 3.74 (m, 1H, CH), 1.74–1.60 (d, 2H, - $\text{CH}_2$ -), 1.42 (d, 3H, - $\text{CH}_3$ ), 1.38–1.22 (q, 2H, - $\text{CH}_2$ -), 1.28 (s, 3H, - $\text{CH}_3$ ), 1.17 (s, 3H, - $\text{CH}_3$ ), 1.02 (s, 3H, - $\text{CH}_3$ ), 0.60 (s, 3H, - $\text{CH}_3$ ).

Then, the obtained PE-TEMPO-OH (2.770 g, 10.0 mmol), quinaldic acid (1.903 g, 11.0 mmol), and DMAP (0.122 g, 1.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 mL) were charged to a flask and stirred under an inert atmosphere. The DCC (2.060 g, 10.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was slowly dropped to the mixture for 1 h at -10°C and allowed to react for 24 h after returning to room temperature. The reaction mixture was then filtered and washed thrice with 1 mol/L HCl and distilled water. After drying with magnesium sulfate and evaporating  $\text{CH}_2\text{Cl}_2$ , the crude product was purified by silica gel column chromatography (ethyl acetate/ether = 1/50) to obtain a transparent sticky liquid. Analytical data are as follows. Yield: 62.87%. Found: C, 74.97; H, 7.46; N, 6.48%. Calc. for  $\text{C}_{17}\text{H}_{27}\text{NO}_2$ : C, 75.05; H, 7.62; N, 6.13%.  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm, TMS): 8.58–7.76 (m, 9H, Quinoline-H), 7.38–7.25 (m, 5H, Ar-H), 5.28 (t, 1H, CH), 4.80 (q, 1H, - $\text{CH}_3$ ), 2.10–1.96 (d, 2H, - $\text{CH}_2$ -), 1.74–1.62 (t, 2H, - $\text{CH}_2$ -), 1.46 (d, 3H, - $\text{CH}_3$ ), 1.37 (s, 3H, - $\text{CH}_3$ ), 1.31 (s, 3H, - $\text{CH}_3$ ), 1.16 (s, 3H, - $\text{CH}_3$ ), 0.75 (s, 3H, - $\text{CH}_3$ ).



SCHEME 1: Synthesis of photosensitive alkoxyamine PE-TEMPO-Q.

**2.3. Typical Procedure for Photoinduced NMP of MMA.** The quantitated PE-TEMPO-Q was generally dissolved in MMA (1 mL) and placed in a quartz tube. The reaction mixture was deoxygenated by nitrogen bubbling and stirred for 30 min. Afterward, the tube was sealed and irradiated by a photoreactor (Mejiro Genossen CHG-200) equipped with a Hg lamp. Light intensity was  $20 \text{ mW/cm}^2$  measured by a UV radiometer (Photoelectric Instrument Factory of Beijing Normal University, China). The resulting polymers were precipitated in methanol and then dried at  $40^\circ\text{C}$  for 12 h under reduced pressure. Conversion of the monomer was directly monitored by weighing method. The number-average molecular weights and polydispersity index (PDI) were determined by GPC.

### 3. Results and Discussion

**3.1. Photosensitive Alkoxyamine.** It has been proved that photosensitive alkoxyamine with a chromophore could be applied to the control/living free radical polymerization according to similar observations from the unimolecular thermal alkoxyamines [22, 23]. The chromophore attached to the alkylated TEMPO can act as a light absorber and then transfer the energy to the photolysis of NO–C bond via intramolecular quenching of the excited state of the chromophore [24]. We first synthesized a traditional alkoxyamine with hydroxyl group originally developed by Matyjaszewski et al. [25], in which the reaction of the alkyl halide in the presence of Cu(0)/CuBr/bpy complex was used as a convenient source of alkyl radicals. Then, the photosensitive alkoxyamine PE-TEMPO-Q was obtained by a simple esterification reaction with quinaldic acid (Scheme 1).

The results of the structural characterization of obtained products are shown in the supporting information (Figures 1 and 2). The  $^1\text{H}$  NMR spectra (Figure 1) revealed that signals observed in the range of 0.65–1.43 ppm and 1.55–2.60 ppm are assigned to the methyl and methylene groups of the TEMPO moiety, respectively. The methyl protons resonate as two singlets and the methylene protons resonate as two doublets of doublets because the nonplanar TEMPO ring leads to different chemical shifts of two methyl groups on the same side. The two methylene protons on the same carbon are also not equivalent. These two types of methylene protons in TEMPO are coupled to each other and the methine proton. Compared with the  $^1\text{H}$  NMR result of PE-TEMPO-OH, the signal at 4.43 ppm assigned to the hydroxyl protons disappears completely, and the  $>\text{CH}-$  proton signal of TEMPO moiety is shifted from 3.74 to 5.28 for the change of

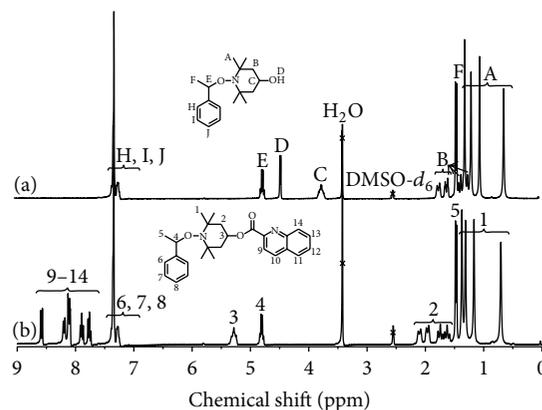
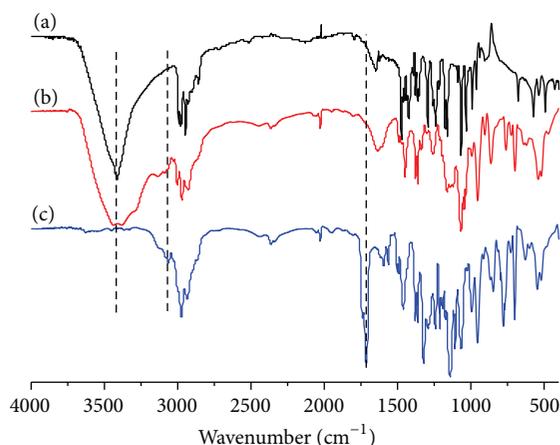
FIGURE 1:  $^1\text{H}$  NMR spectra of (a) PS-TEMPO-OH and (b) PS-TEMPO-Q.

FIGURE 2: FT-IR spectra of (a) TEMPO-OH, (b) PS-TEMPO-OH, and (c) PS-TEMPO-Q.

the chemical environment after esterification. The new signals at 7.71–8.64 ppm are attributed to the protons of quinoline ring. The FT-IR spectra of PE-TEMPO-Q (Figure 2) show an apparent disappearance of the characteristic hydroxyl group after esterification and a strong absorption at  $1713 \text{ cm}^{-1}$  assigned to infrared absorption peak of the ester carbonyl. Absorption bands are also observed at approximately  $3002\text{--}3125 \text{ cm}^{-1}$  for the typical unsaturated C–H stretching vibration and at  $1634 \text{ cm}^{-1}$  for benzene skeleton vibration. The spectral characterization supports the successful covalent attachment of quinoline chromophore to PE-TEMPO-OH.

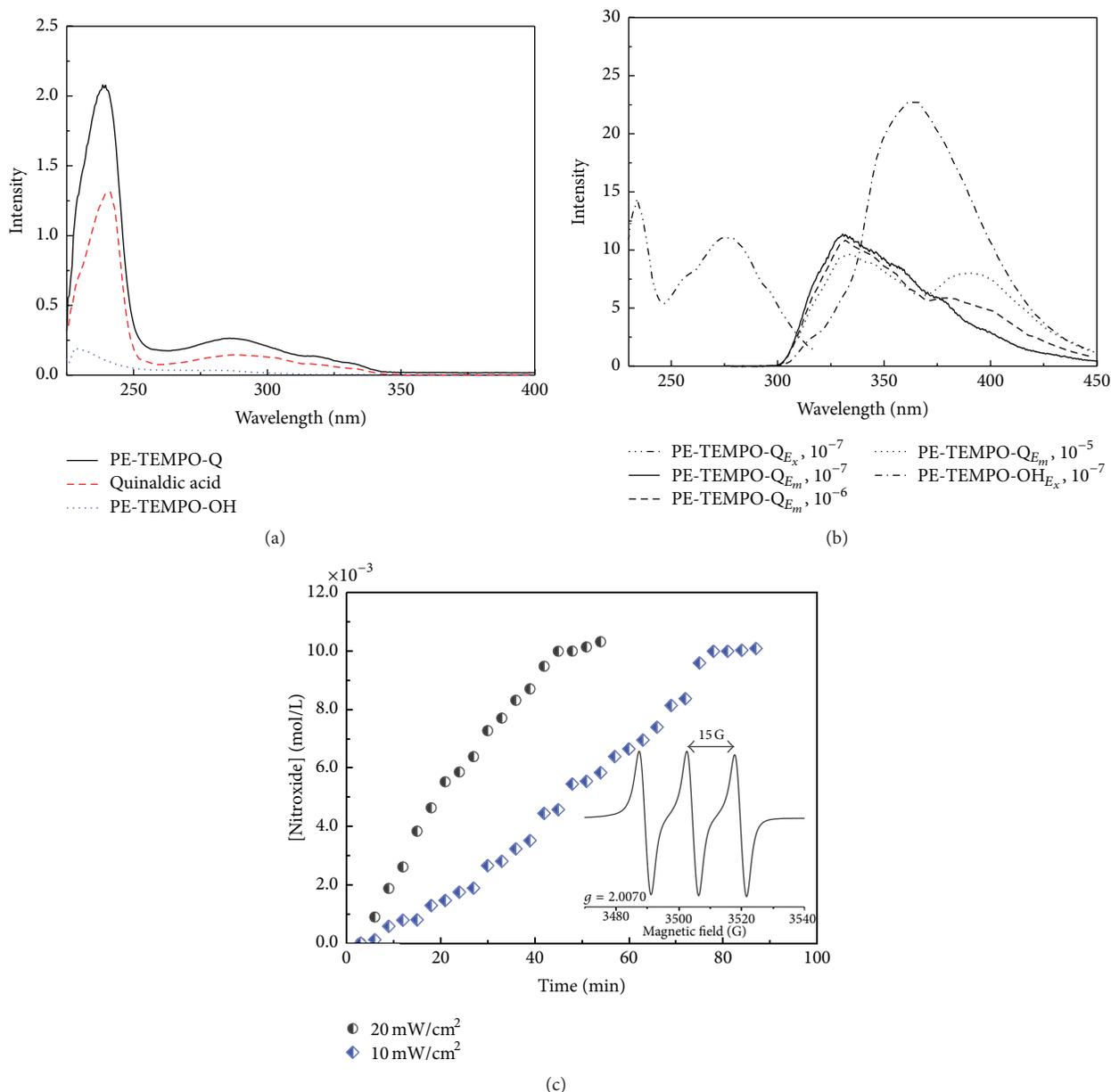


FIGURE 3: (a) UV absorption spectra. (b) Fluorescence spectra,  $E_x$  = excitation spectrum, and  $E_m$  = emission spectrum. (c) Plot of nitroxide concentration versus irradiation time under inert atmosphere, initial concentration of PE-TEMPO-Q is  $10^{-2}$  mol/L; the inset shows the EPR spectrum of obtained nitroxide after photolysis at 60 min at 20 mW/cm<sup>2</sup>.

The UV-visible absorption spectra of the investigated nitroxides in  $\text{CH}_2\text{Cl}_2$  ( $10^{-6}$  mol/L) are depicted in Figure 3(a). Compared with PE-TEMPO-OH, substitution by the quinoline moiety in PE-TEMPO-Q induces a change in the absorption at 270–350 nm, which is associated with the  $n-\pi^*$  transition of the corresponding chromophores. These results indicate that the synthesized alkoxyamine is absorbed in a more convenient spectral range for photopolymerization irradiated by Hg lamp. In addition, the fluorescence spectra of PE-TEMPO-Q in  $\text{CH}_2\text{Cl}_2$  using 276 nm as excitation wavelength are shown in Figure 3(b). A slight blue shift is shown, but the intensity decreases drastically compared

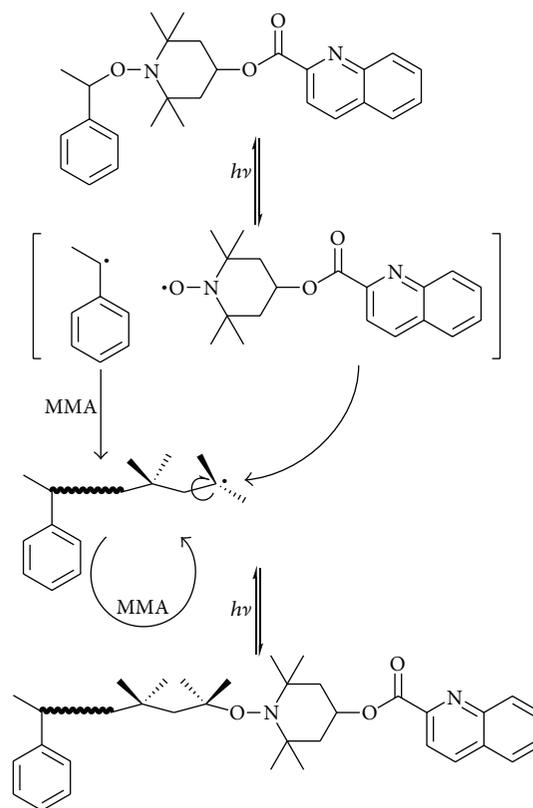
with the quinaldic acid for the intramolecular quenching of the excited chromophore by electron exchange interactions [26]. This phenomenon suggests that an efficient energy transfer from the chromophore moiety to the nitroxide radical moiety of TEMPO can occur across the molecular distances. Meanwhile, the fluorescence intensity slightly decreases with increase in concentration because of the minor intermolecular sensitization. However, a new shoulder peak appears at  $10^{-6}$  mol/L and increases with concentration. This phenomenon is probably due to the fact that the structure of PE-TEMPO-Q with two adjacent aromatic rings improves the molecular planarity, facilitating the formation of excimers at

certain level of concentration. Such bulky substituent group also have some effects on polymer stereoregularity and will be discussed in the next section. The photolysis of PE-TEMPO-Q in  $\text{CH}_2\text{Cl}_2$  ( $10^{-2}$  mol/L) was performed at room temperature at different light intensities and recorded *in situ* by TR-ESR [Figure 3(c)]. With PBN as an active radical trapping agent, the ESR signals after photolysis corresponded to the TEMPO-based nitroxide because the spectra presented the typical  $g$  value and characteristic hyperfine coupling constant. The concentration of nitroxide linearly increases over time, and the growth rate becomes higher with increasing light intensity. The final concentration reached a stable level at  $10^{-2}$  mol/L, which indicates that the alkoxyamine almost entirely decomposes. Thus, PE-TEMPO-Q is a potential candidate for subsequent controlled photopolymerization because of its photochemical properties.

**3.2. Photoinduced NMP by PE-TEMPO-Q.** The photoinduced NMP of MMA was investigated in the presence of PE-TEMPO-Q at ambient temperature. The control of the molecular weight of MAA was first investigated with photosensitive alkoxyamine as a unimolecular initiator. The mechanism is proposed to occur as shown in Scheme 2. PE-TEMPO-Q is activated by UV irradiation, and the weak C–ON bond in PE-TEMPO-Q splits into a benzyl radical and a TEMPO-based nitroxide radical with a quinolone group. The former initiates the polymerization and forms a chain radical, whereas the latter scavenges the chain radical to form a dormant macro-alkoxyamine. The intramolecular sensitization in the formed macro-alkoxyamine reversibly furnishes a TEMPO radical and a chain radical again. Termination of polymerization by combining polymer radicals is minimized by the rapid reaction of nitroxide radicals combined with carbon-centered radicals. The linker between the sensitizer and the NO–C moiety does not change with the course of the polymerization. Thus, the efficiency of the photoinduced cleavage is maintained, and photo-controlled polymerization should proceed during the entire polymerization process, similar to the typical thermal-initiation polymerization.

Figure 4(a) shows the plot of time versus the photoinduced NMP of MMA with different PE-TEMPO-Q concentrations. In the early stage of polymerization at low [PE-TEMPO-Q] ( $2.19 \times 10^{-2}$  mmol, conversion < 30%), the plot provides an almost straight line, which indicates that the ambient temperature polymerization of MMA under UV irradiation is first-order kinetics. However, the slope of the plot increases at higher temperatures, suggesting an increase in the stationary concentration of the growing radicals and in the polymerization rate. When [PE-TEMPO-Q] is improved, a linear increase is obtained during the whole polymerization process. The polymerization rate dramatically decreases at high conversion. This phenomenon may have been caused by the typical decay in the concentration of TEMPO-based nitroxide in the polymerization process, which will be investigated in further studies.

The evolution of molecular weight and distribution versus conversion is shown in Figure 4(b). A regular increase in number-average molecular weight ( $M_n$ ) of the controlled



SCHEME 2: Polymerization mechanism of MMA in the presence of PE-TEMPO-Q.

polymerization is observed. This behavior suggests a partial controlled photopolymerization. Nevertheless, the experimental  $M_n$  values are much higher than the theoretical ones. Such high  $M_n$  values could be explained by the low efficient photolysis of PE-TEMPO-Q, leading to very small amounts of alkyl and nitroxide radicals. The alkyl radicals initiate the polymerization of methacrylate with a relatively high propagation rate constant. Meanwhile, the amount of nitroxide is not sufficient to trap the alkyl macroradicals and stop or moderate the propagation. The combination of these phenomena leads to polymers with high  $M_n$ , as already observed in NMP [27]. The PDI is found to be quite large (>1.8) at low conversion (<10%), demonstrating that the control process is not perfect in the early stage of polymerization for the low photocleavage efficiency of PE-TEMPO-Q. The excess of initiating radical created at the beginning of polymerization leads to the self-termination reaction for the alkyl radical competing with the (macro-)alkoxyamine reformation. In addition, the competitive dissociation between C–O bond and N–O bond in (macro-)alkoxyamine induces a lack of persistent radicals [28]. The disproportionation side reaction induced by intramolecular hydrogen transfer of PMMA polymer chain could lead to a distinct increase in the PDI [29, 30]. However, once the equilibrium has been established, controlled polymerization can be obtained such that the molecular weight distribution becomes narrow as the conversion increases and becomes close to 1.37 at nearly 75%. The GPC analysis of the resulting polymers also

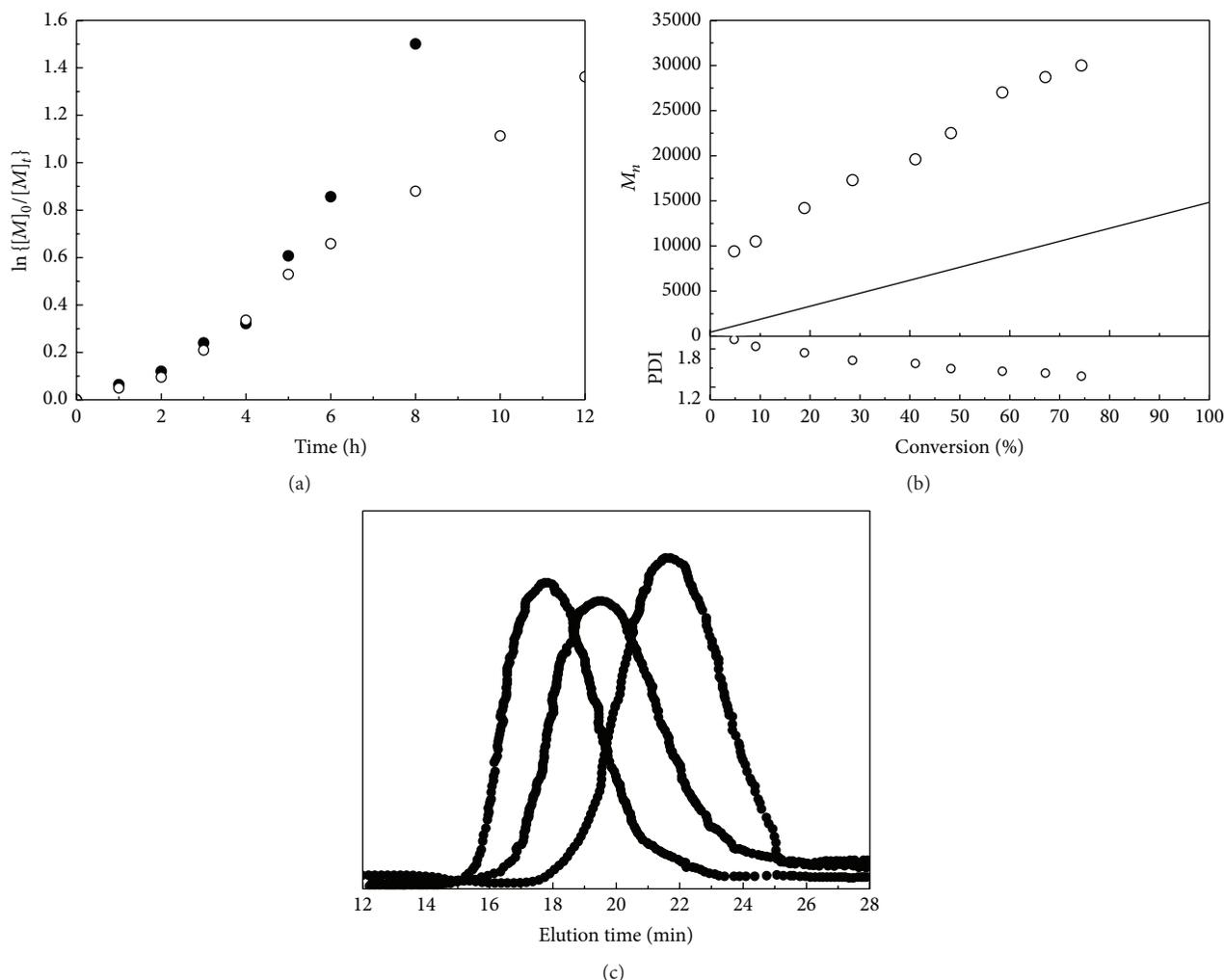


FIGURE 4: Photopolymerization of MMA in the presence of photosensitive alkoxyamine, light intensity = 20 mW/cm<sup>2</sup>, [MMA] = 9.42 mmol, [PE-TEMPO-Q] = (●)  $2.19 \times 10^{-2}$  mmol or (○)  $6.56 \times 10^{-2}$  mmol. (a) Kinetics plot; (b) plots of molecular weights and distributions versus conversion, the solid line corresponds to theoretical  $M_n$ ; (c) GPC traces of the MMA homopolymers at different conversion: Table 1, runs 9, 12, and 15 ([PE-TEMPO-Q] =  $6.56 \times 10^{-2}$  mmol).

supported the controlled radical polymerization mechanism. Figure 4(c) shows the GPC profiles of the polymers produced for different conversion. The curves are shifted to the higher molecular weight with an increase in the conversion.

**3.3. Polymer Stereochemistry.** Previous study has shown a significant penultimate group effect on the homopolymerization of PMMA, resulting in the change of tacticity [31]. The photosensitive alkoxyamine with bulky chromophore is presumed to display a certain effect on the conformation change during the reversible equilibrium process, thus affecting the stereoregularity of polymer. Meanwhile, the syndiotactic triad content of PMMA increases with decreasing temperature of polymerization, and the segment motion is restrained for the relative low reactive temperature of photopolymerization in favor of high stereotacticity [32].

The tacticity of PMMA was determined by analyzing  $\alpha$ -methyl signals attributed to the syndiotactic (*rr*), isotactic

(*mm*), and heterotactic (*mr*) triads in the <sup>1</sup>H NMR spectrum. The results are summarized in Table 1. Contrasting experiments are initially tested directly using DMPA (2.0 wt.%) as an initiator in bulk condition (runs 1–3). Figure 5 shows the examples of comparative results of the <sup>1</sup>H NMR spectra of PMMA synthesized with or without PE-TEMPO-Q. In general, the polymer formed is predominantly syndiotactic but with relative low fraction (*rr* < 50%). This phenomenon is due to the fact that when PMAA radical is added to MMA, a marked preference is observed for the new chiral center to adopt a configuration opposite to that of the preceding (penultimate) unit in the chain. Thus, a racemic dyad for the steric hindrance and electrostatic repulsion is formed. In the presence of PE-TEMPO-Q, PMMA with a slightly high degree of syndiotacticity is obtained as syndiotactic triads *rr* = 62%–65%. The isotacticity fraction decreases compared with the results obtained from typical photopolymerization and decreases gradually with increasing conversion. This

TABLE 1: Experiment data of PMMA by photopolymerization.

Initiator	Run <sup>(a)</sup>	Time (h)	Conv. (%)	$M_{n,theo}$ (g/mol) <sup>(e)</sup>	$M_n$ (g/mol) <sup>(f)</sup>	PDI	Tacticity ( <i>mm:mr:rr</i> ) <sup>(g)</sup>	$m/r$ <sup>(h)</sup>
DMPA	1 <sup>(b)</sup>	—	17.07	—	18900	2.20	27.0/27.9/45.1	40.95/59.05
	2	—	53.17	—	28300	2.74	27.4/26.1/46.5	40.45/59.55
	3	—	77.52	—	43500	2.63	24.4/27.8/47.8	35.80/60.20
PE-TEMPO-Q	4 <sup>(c)</sup>	2	11.31	5317	17700	2.09	8.7/31.2/60.1	24.30/75.70
	5	3	21.34	9650	28500	1.86	6.8/32.1/61.1	22.85/77.15
	6	4	27.49	12307	35300	1.74	4.9/34.7/60.4	22.25/77.75
	7	5	45.51	20092	43000	1.69	4.8/34.5/60.7	22.05/77.95
PE-TEMPO-Q	8	6	57.52	25280	49800	1.59	4.5/34.1/61.4	21.55/78.45
	9 <sup>(d)</sup>	2	9.11	1743	10500	1.84	9.9/32.6/57.5	26.20/73.80
	10	3	18.87	3149	14200	1.74	7.1/34.3/58.6	24.25/75.75
	11	4	28.52	4539	17300	1.62	5.9/35.9/58.2	23.85/76.15
	12	5	41.10	6351	19600	1.57	4.9/34.9/60.2	22.35/77.65
	13	6	48.23	7377	22500	1.49	4.4/35.4/60.2	22.10/77.90
	14	8	58.52	8859	27000	1.45	4.4/34.7/60.9	21.76/78.25
	15	10	67.13	10098	28700	1.42	4.5/34.5/61.0	21.75/78.25
	16	12	74.38	11142	30000	1.38	4.5/34.6/61.1	21.80/78.40

(a) Light intensity was 20 mW/cm<sup>2</sup>,  $v_{MMA} = 1$  mL; (b) DMPA = 2 wt.%; (c) [PE-TEMPO-Q] =  $2.19 \times 10^{-2}$  mmol; (d)  $6.56 \times 10^{-2}$  mmol; (e)  $M_{n,theo.} = ([MMA]_0/[Alkoxyamine]_0 \times M_{monomer} \times Conv.%) + M_{Alkoxyamine}$ ; (f) measured by GPC in THF; (g) *mm* = isotactic triads; *mr* = atactic triads; *rr* = syndiotactic triads; (h) calculated based on triad tacticity ( $m = rr + mr/2$ ,  $r = rr + mr/2$ ).

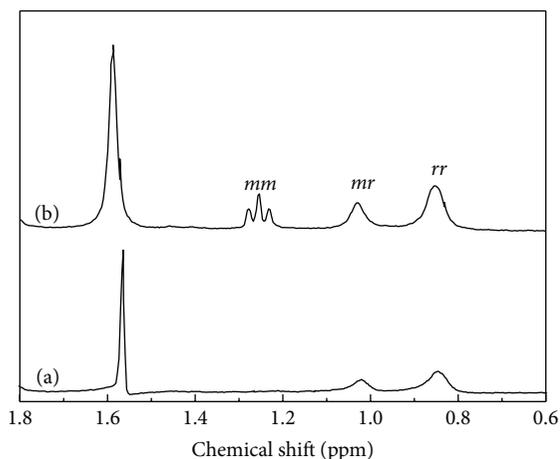


FIGURE 5: <sup>1</sup>H NMR spectra of *a*-CH<sub>3</sub> of PMMA in CDCl<sub>3</sub> for PMMA synthesized with PE-TEMPO-Q, (a) Table 1, run 10; (b) Table 1, run 1.

phenomenon is probably due to the fact that when the PE-TEMPO-Q is combined with the propagating chain radical, the sp<sup>2</sup> carbon-centered radical prefers to form lower syndiotactic propagation because of the enormous steric effect produced by rigidity and bulkiness of the cyclic structure. However, these results further confirm that the amount of PE-TEMPO-Q has little or no influence on polymer stereotacticity for MMA, thus providing more information to the understanding of stereocontrol mechanism.

#### 4. Conclusion

In this study, the photoproperties of alkoxyamine PE-TEMPO-Q bearing a quinolone group are investigated. The

dual-controlled polymerization of MMA is determined in the presence of PE-TEMPO-Q under mild UV irradiation. A linear growth in the polymer chain combined with a comparatively narrow molecular weight distribution in the range of 1.4–1.8 is observed. The syndiotactic content of PMMA derived from the photoinduced NMP is approximately 59%–61% and higher than the ones obtained by typical photopolymerization. These results indicate that PE-TEMPO-Q affected stereocontrol in the polymerization of MAA to produce syndiotactic-rich polymers. To the best of the authors' knowledge, this study is the first to report the use of an efficient photosensitive alkoxyamine to achieve dual-controlled polymerization under UV irradiation.

#### Competing Interests

The authors declare that they have no competing interests.

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