

## Organic-inorganic composite materials as photoinitiator for controlling/living polymerization

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**ABSTRACT:** Titanium dioxide (TiO<sub>2</sub>)/graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) composites were first used as photoinitiator for photochemically mediated controlled/living polymerization of methyl methacrylate. The polymerization was successfully carried out in polyethylene glycol at room temperature with FeCl<sub>3</sub>·6H<sub>2</sub>O/*N,N,N',N',N''*-pentamethyldiethylenetriamine as complex catalyst and ethyl 2-bromoisobutyrate as initiator in this case. A pseudo-first-order dependence of the monomer concentration on the polymerization time was observed. TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> was verified to be an efficient photoinitiator. The polymerization was controlled to produce poly(methyl methacrylate) with narrow molecular weight distribution and controlled number average molecular weight (*M<sub>n,GPC</sub>*). The *M<sub>n,GPC</sub>* matched well with the theoretical values when using both UV and sunlight irradiation as light source. The effects of reaction conditions on the polymerization were investigated. The polymerization could be started and stopped through periodically switching on/off the light. The living nature was further supported by the chain extension experiments. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42891.

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### INTRODUCTION

Living free radical polymerization provides an efficient method for preparation of polymers with well defined structures, compositions, and architectures.<sup>1–3</sup> Controlled radical polymerizations, like atom transfer radical polymerizations (ATRP),<sup>4,5</sup> reversible addition-fragmentation chain transfer polymerization (RAFT),<sup>6</sup> and nitroxide-mediated polymerizations (NMP)<sup>7</sup> were the most extensively studied techniques. ATRP is mediated by transition metal/ligand complexes with an alkyl halide as initiator. A dynamic equilibrium between the activator and deactivator is established. ATRP does not require strict purification of monomer and solvent and is suitable for a number of monomers. Furthermore, some improved ATRP techniques are tolerant to a small amount of air during polymerization.<sup>8</sup>

TiO<sub>2</sub> has been used as photocatalyst in many fields and it is very suitable for industrial use due to its good photoactivity, high stability, low cost and adequate energy band gaps. In recent years, TiO<sub>2</sub> has received much attention especially as photocatalytic material in polymer preparation. More recently, TiO<sub>2</sub> was used as photoinitiator to synthesize well-defined

poly(methyl methacrylate) (PMMA).<sup>9</sup> However, a major disadvantage is that TiO<sub>2</sub> is active only under the ultraviolet region due to its wide band gap, which restricts the use of TiO<sub>2</sub> under sunlight.

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is a robust and stable visible-light-driven polymeric semiconductor photocatalyst. g-C<sub>3</sub>N<sub>4</sub> has been reported to initiate Cu-mediated ATRP of methyl methacrylate (MMA) in the presence of light.<sup>10</sup> Nevertheless, g-C<sub>3</sub>N<sub>4</sub> has some shortcomings, for example, a small specific surface area, a low visible light utilization efficiency, and rapid recombination of photo-generated electron-hole pairs. There are some reports on overcoming these limitations of C<sub>3</sub>N<sub>4</sub> by modification with TiO<sub>2</sub>.

Solvents play a key role in ATRP process. In ATRP, the most used solvents were organic solvents. These organic solvents are toxic, hazardous, and are harmful to the environment and human body. Researchers are trying to find green solvents for ATRP. PEG-400 has been proved to be a kind of green solvents and is inexpensive and of course recyclable. Our group have successfully carried out ATRP in PEG-400.<sup>11,12</sup> More recently,

photo-induced ATRP of MMA was successfully performed in poly(ethylene glycol)-400 with nanosized  $\alpha\text{-Fe}_2\text{O}_3$  as photoinitiator by our group.<sup>13</sup>

To our knowledge, the organic-inorganic composite material  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  is still not reported and not used in living polymerization. In the present work, we prepared  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  composite material and used it as photoinitiator in ATRP of MMA with  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}/\text{PMDETA}$  as complexes catalyst. Furthermore, the photocatalytic performance of  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  was investigated.

## EXPERIMENTAL

### Materials

$\text{TiO}_2/\text{g-C}_3\text{N}_4$  was synthesized according to the literature.<sup>14</sup> MMA was purchased from Tianjin Fuchen Chemical Reagent Factory (Tianjin, China) and distilled by reduced pressure prior to the experiments. Ethyl 2-bromoisobutyrate (EBiB) (98%) and  $N,N,N',N',N''$ -pentamethyldiethylenetriamine (PMEDTA) were obtained from Aladdin (China) and were used without further purification. Polyethylene glycol (PEG-400) was obtained from Sinopharm Chemical Reagent (Shanghai, China) and was used as received. Ferric chloride hexahydrate was obtained from Shanghai Qingfeng Chemical Factory (Shanghai, China). Other chemicals were commercially available and used as received.

### Polymerization Procedure

A three-neck flask was used as the polymerization reactor, which was equipped with a magnetic stirrer. A typical experiment procedure was performed as follows: MMA (2 g, 0.02 mol), EBiB (0.0195 g, 0.0001 mol),  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  (0.0027 g, 0.00001 mol), PMEDTA (0.0052 g, 0.00003 mol),  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  (0.03 g), and PEG-400 (10 mL) were added to the flask. The flask was gassed three times with  $\text{N}_2$  and was placed in a thermostat water bath. Then a 500-W high pressure mercury lamp and sunlight were used separately to initiate polymerization at 25°C in dry nitrogen atmosphere. The light intensity was 100  $\text{W}/\text{cm}^2$ . After a desired time, an excess of methanol was added to precipitate PMMA. The obtained polymers were dried under vacuum. Monomer conversions were determined gravimetrically.

### Characterizations

A gel permeation chromatography (GPC) (Waters 1515) was used to evaluate molecular weight ( $M_{n,\text{GPC}}$ ) and molecular weight distribution (MWD) of the resulting PMMA at 35°C. Tetrahydrofuran was employed an eluent and set to 1.0 mL/min. Standard PMMA was chosen to calibrate the curves.  $^1\text{H-NMR}$  spectrum was collected in  $\text{CDCl}_3$  on a Bruker ARX 400 NMR spectrometer at room temperature. Tetramethylsilane was used as internal standard.

## RESULTS AND DISCUSSION

### Photo-Induced ATRP of MMA

To check the optical properties of  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  and the mixture of  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  and  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  in PEG-400 during the polymerization, we performed the comparison of the corresponding UV-vis spectra of  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  and the mixture of  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$

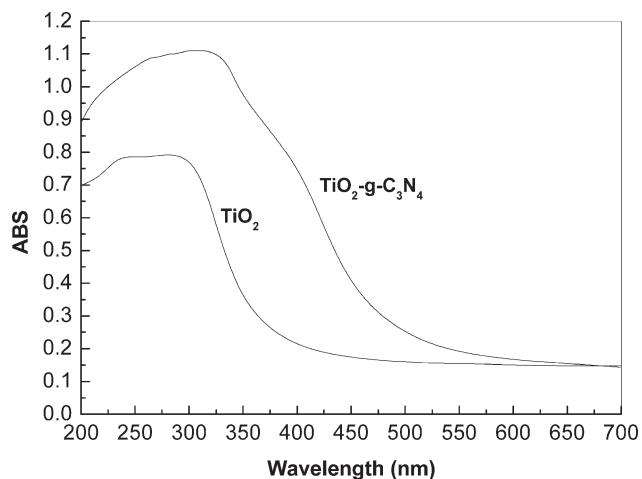


Figure 1. UV-Vis spectra of  $\text{TiO}_2$  and  $\text{TiO}_2\text{-g-C}_3\text{N}_4$ .

and  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  in PEG-400. Representative results of UV-vis experiments are shown in Figure 1. As can be seen from Figure 1, the absorption peaks of  $\text{TiO}_2$  exhibited less than 350 nm and the absorption peaks of  $\text{TiO}_2\text{-g-C}_3\text{N}_4$  exhibited less than 450 nm, respectively.

The living behaviors were examined by the investigation of  $M_{n,\text{GPC}}$  evolution and MWD. The experiments of photo-induced ATRP of MMA by  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}/\text{PMEDTA}$ -mediated living radical polymerization technique was performed at 25°C with PEG-400 as solvent and  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  as photoinitiator. The volume ratio of MMA to PEG-400 was fixed at 1 : 4. The light intensity was 100  $\text{W}/\text{cm}^2$ . The molar ratio of  $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{FeCl}_3\cdot 6\text{H}_2\text{O}]_0/[\text{PMEDTA}]_0$  was kept at 200/1/0.1/0.3. 0.03 g of  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  was introduced to this system. The results are shown in Figure 2.

Figure 2 indicated the dependence of the measured  $M_{n,\text{GPC}}$  and the MWD on the monomer conversion. The  $M_{n,\text{GPC}}$  values of the obtained PMMAs increased in direct proportion to monomer conversions. Furthermore, the measured  $M_{n,\text{GPC}}$  values of the obtained PMMAs were in good agreement with the theoretical values ( $M_{n,\text{th}}$ ). It indicated that the biradical terminations

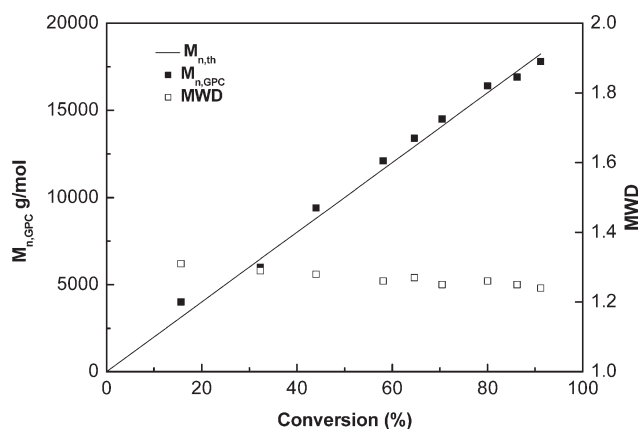


Figure 2.  $M_{n,\text{GPC}}$  and MWD versus the conversion for the photoinduced ATRP of MMA in PEG-400 with  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  as photoinitiator. The experimental conditions were the same as Figure 2.

**Table I.** The Results of Photoinduced ATRP of MMA Using  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  as Photocatalyst under UV Irradiation<sup>a</sup>

Entry	$R^b$	$\text{TiO}_2/\text{g-C}_3\text{N}_4$ (g)	Conversion (%)	$M_{n,\text{th}}$ (g/mol)	$M_{n,\text{GPC}}$ (g/mol)	MWD
1	200 : 1 : 0.1 : 0.3	0	0	0	0	0
2	200 : 1 : 0.1 : 0.3	0.01	14.25	2850	3900	1.31
3	200 : 1 : 0.1 : 0.3	0.02	30.34	6068	6500	1.29
4	200 : 1 : 0.1 : 0.3	0.03	44.01	8802	9400	1.28
5	200 : 1 : 0.1 : 0.3	0.04	52.13	10426	11100	1.26
6	200 : 1 : 0.1 : 0.3	0.05	64.73	12946	13700	1.27

<sup>a</sup>  $[\text{MMA}]_0 = 2$  g, time = 1.5 h. MMA/PEG-400 = 1/4 (v/v), temperature = 25°C. The light intensity was 100  $\text{W}/\text{cm}^2$ .

<sup>b</sup>  $R = [\text{M}]_0/[\text{RX}]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{L}]_0$ .

**Table II.** The Results of Photoinduced ATRP of MMA Using  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  as Photocatalyst under UV or Sunlight Irradiation<sup>a</sup>

Entry	$R^b$	Conversion (%)	$M_{n,\text{th}}$ (g/mol)	$M_{n,\text{GPC}}$ (g/mol)	MWD
1	200 : 1 : 0.1 : 0.1	9.83	1966	3200	1.33
2	200 : 1 : 0.1 : 0.2	21.57	4314	4500	1.31
3	200 : 1 : 0.1 : 0.3	32.29	6458	6000	1.29
4	200 : 1 : 0.05 : 0.3	12.45	2490	11100	1.32
5	200 : 1 : 0.15 : 0.3	40.63	8126	13700	1.27
6	200 : 1 : 0.3 : 0.3	28.78	7156	13700	1.34
7 <sup>c</sup>	200 : 1 : 0.1 : 0.3	45.55	9110	9800	1.29

<sup>a</sup>  $[\text{MMA}]_0 = 2$  g, time = 1 h. MMA/PEG-400 = 1/4 (v/v),  $\text{TiO}_2/\text{g-C}_3\text{N}_4 = 0.03$  g, temperature = 25°C. The light intensity was 100  $\text{W}/\text{cm}^2$ .

<sup>b</sup>  $R = [\text{M}]_0/[\text{RX}]_0/[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]_0/[\text{L}]_0$ .

<sup>c</sup> Sunlight irradiation. The experiment was carried out at noon (2015.4.13) in Yueyang, Hunan Province, China. Temperature = 25°C. The weather is sunny (2015.4.13). The light intensity was kept 100  $\text{W}/\text{cm}^2$ .

were negligible and the initiating efficiency was high. Lower MWD values (below 1.35) were found during the polymerization process.

On the basis of discussion above, it indicated that the photoinduced ATRP of MMA possessed the characteristics of living radical polymerization.

#### Effect of $\text{TiO}_2/\text{g-C}_3\text{N}_4$ On the Photoinduced ATRP of MMA

To investigate the effects of  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  on the photoinduced ATRP of MMA, a series of experiments were performed, and the results are listed in Table I. No conversion was achieved without  $\text{TiO}_2/\text{g-C}_3\text{N}_4$ . When increasing the amount of  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  (Entry 2–6), faster polymerization rate were observed after the same reaction time, implying that the amount of  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  played an important role on the polymerization reaction rate.

#### Effect of the Ligand

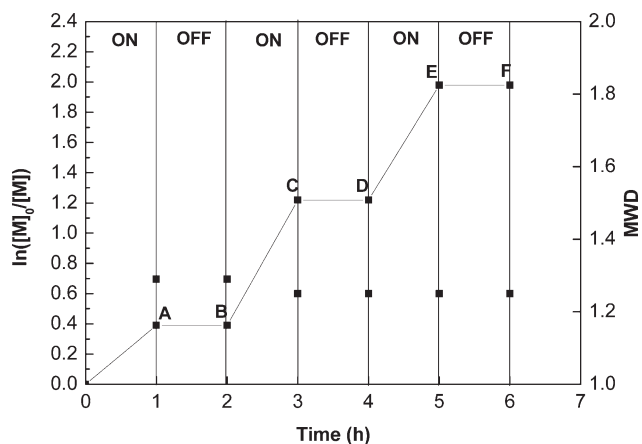
To demonstrate the utility of ligand on the photoinduced ATRP of MMA, the effect of amounts of ligand on the photoinduced ATRP of MMA was examined. The results are compiled in Table II (Entry 1–3).

As can be seen from Table II, increasing the concentration of ligand resulted in a faster polymerization rate, implying a higher ratio of activation/deactivation rate. These results demonstrated that the concentration of PMEDTA had a favorable influence

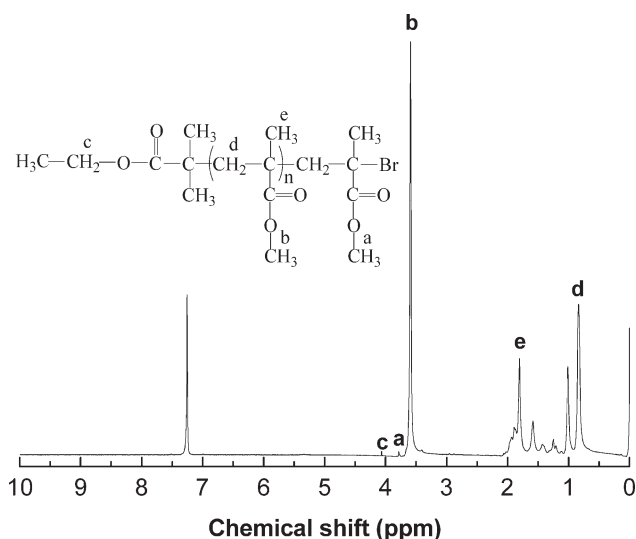
on the polymerization rate. Moreover, all the obtained MWD values were lower than 1.35 within the same reaction time. When sunlight was used as light source, a significant increase of polymerization rate occurred. A similar phenomenon has been reported by Yagci.<sup>10</sup>

#### Effect of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{PMEDTA}$

The effect of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{PMEDTA}$  on the photoinduced ATRP of MMA was investigated (Entry 3–6 in Table II). An increased



**Figure 3.** Effect of turning on/off light for the photoinduced ATRP of MMA at room temperature with  $\text{TiO}_2/\text{g-C}_3\text{N}_4$  as photoinitiator.



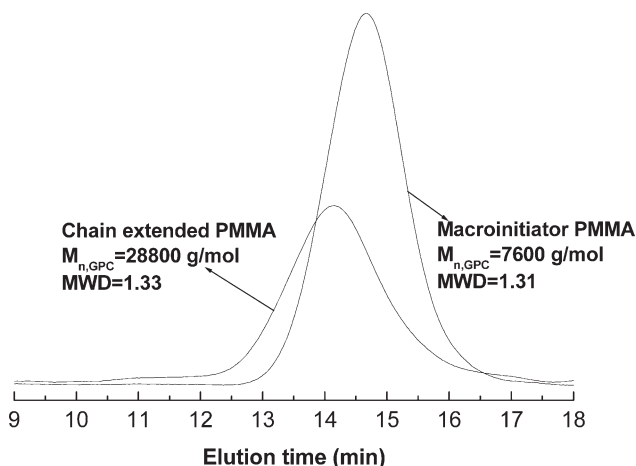
**Figure 4.**  $^1\text{H-NMR}$  spectrum of PMMA ( $M_{n,\text{GPC}} = 7600$  g/mol,  $\text{MWD} = 1.31$ ).

molar ratio of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{PMEDTA}$  was introduced from 0.05 : 0.3 to 0.3 : 0.3 to obtain higher polymerization rate.  $\text{MWD}$  values remained low throughout the polymerization and were all less than 1.35. It indicated that the concentration of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  played an important role on the controllability over the polymerization.

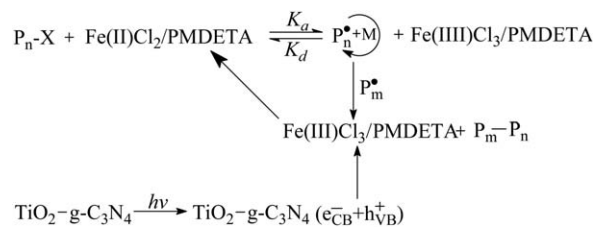
#### Effect of Turning Periodically on/off Light

One of the advantages of photochemically mediated polymerization is that the polymerization can be controlled by turning periodically on/off the light.<sup>10</sup> The effect of turning periodically on/off light on the photoinduced ATRP of MMA was investigated. The light intensity was kept  $100 \text{ W/cm}^2$ . The results are shown in Figure 3.

The predetermined mixture of MMA, EBiB,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , PMEDTA,  $\text{TiO}_2/g\text{-C}_3\text{N}_4$ , and PEG-400 was irradiated under light for 1 h. Enough amounts of initial radicals were achieved. As can be seen from Figure 3, the polymerization ceased when the lamp was turned off, indicating a very slow polymerization



**Figure 5.** GPC traces of (a) the macroinitiator PMMA-Cl and (b) the chain extended PMMA.



**Scheme 1.** Mechanism of photoinduced ATRP of MMA in PEG-400 using  $\text{TiO}_2\text{-g-C}_3\text{N}_4$  as photoinitiator.

rate. The polymerization proceeded fast when the lamp was turned on.

#### Analysis of Chain End of PMMA and Chain Extension of PMMA-Br

The  $^1\text{H-NMR}$  NMR spectrum of the resulting PMMA-Br synthesized by photoinduced ATRP with  $\text{TiO}_2/g\text{-C}_3\text{N}_4$  as photoinitiator is displayed in Figure 4. As shown in Figure 4, the peaks corresponded to  $-\text{OCH}_3-$  protons of PMMA-Br resonating at 3.58 and 3.78 ppm, respectively (a and b in Figure 4). It is probably the electron attracting function of  $\omega$ -Br atom, which was reported by Sawamoto.<sup>15</sup> The  $-\text{CH}_3$  and  $-\text{CH}_2-$  protons of PMMA appeared at 0.63–1.13 ppm (d in Figure 4) and 1.30–2.12 ppm (e in Figure 4), respectively. The  $-\text{CH}_2-$  protons of EBiB appeared at 4.06 ppm (c in Figure 4). The chain extension experiments were performed using the obtained PMMA-Br ( $M_{n,\text{GPC}} = 7600$  g/mol,  $\text{MWD} = 1.31$ ) as macroinitiator. Figure 5 shows the GPC curves of the macroinitiator PMMA-Br and chain extended PMMA. It was found that the molecular weight of the chain extended PMMA increased and the GPC curve of the chain extended PMMA was monomodal and symmetrical, indicating the “living” features of the chain end.

#### Mechanism Analysis

The mechanism is shown in Scheme 1. An electron and a positive hole were produced when the  $\text{TiO}_2\text{-g-C}_3\text{N}_4$  was irradiated under the UV and sunlight. According to the reported literature,<sup>16</sup>  $g\text{-C}_3\text{N}_4$  generated firstly an electron due to higher conduction band than that of  $\text{TiO}_2$ . Then, the photo-generated electrons can be transferred to the conduction band of  $\text{TiO}_2$ . In the meantime,  $\text{TiO}_2$  generated a positive hole to transfer  $g\text{-C}_3\text{N}_4$ . The electron reacted with  $\text{Fe(III)Cl}_3/\text{PMDETA}$  to generate  $\text{Fe(II)Cl}_2/\text{PMDETA}$ . Then  $\text{Fe(II)Cl}_2/\text{PMDETA}$  reacted with  $\text{P}_n\text{-X}$  to generate radical  $\text{P}_n^{\bullet}$  and  $\text{Fe(III)Cl}_3/\text{PMDETA}$ . Finally,  $\text{P}_n^{\bullet}$ -initiated the living polymerization.

#### CONCLUSIONS

Using  $\text{TiO}_2/g\text{-C}_3\text{N}_4$  as photoinitiator, photoinduced ATRP of MMA was successfully carried out in PEG-400 at ambient temperature with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{PMEDTA}$  as complexes catalyst. Kinetic study of photoinduced ATRP showed that the polymerization proceeded in a controlled way. All obtained PMMAs have relatively narrow molecular weight distributions ( $\text{MWD} < 1.35$ ). The experimental results of periodically turning on/off light indicated that the polymerization ATRP of MMA

can be manipulated by light. Furthermore, the polymerization rate increased under sunlight irradiation

#### ACKNOWLEDGMENTS

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