Azobenzene-Based Initiator for Atom Transfer Radical Polymerization of Methyl Methacrylate

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> ABSTRACT: 2-Bromopropionic acid 2-(4-phenylazophenyl)ethyl ester, 2-bromopropionic acid 6-(4-phenylazophenoxy)hexyl ester (BPA₆), 2-bromopropionic acid-(4-phenylazoanilide), and 2-bromopropionic acid 4-[4-(2-bromopropionyloxy)phenylazo]phenyl ester (BPPE) were used as initiators with monofunctional or difunctional azobenzene for the heterogeneous atom transfer radical polymerization of methyl methacrylate with a copper(I) chloride/N,N,N',N",N"-pentamethyldiethylenetriamine catalytic system. The rates of polymerizations exhibited first-order kinetics with respect to the monomer, and a linear increase in the number-average molecular weight with increasing monomer conversion was observed for these initiation systems. The polydispersity indices of the polymer were relatively low (1.15-1.44) up to high conversions in all cases. The fastest rate of polymerization and the highest initiation efficiency were achieved with BPA₆, and this could be explained by the longer distance between the halogen and azobenzene groups and the better solubility of the BPA_6 initiator. The redshifting of the UV absorptions of the polymers only occurred for the BPPEinitiated system. The intensity of the UV absorptions of the polymers were weaker than those of the corresponding initiators in chloroform and decreased with the increasing molecular weights of the polymers in all cases. © 2005 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 43: 2358-2367, 2005

> **Keywords:** atom transfer radical polymerization (ATRP); azobenzene-based initiators; gel permeation chromatography; methyl methacrylate; UV–vis spectroscopy

INTRODUCTION

Azobenzene-containing polymers have attracted significant interest because of their specific properties,¹ and they can be used to prepare new optical switchs,^{2,3} novel azo-containing pH-sensitive hydrogels,^{4,5} optical polyelectrolyte,⁶ and nonlinear optical materials and photore-cording materials.^{7–9} Recently, liquid-crystalline properties have been observed for some derivatives with an azobenzene moiety in the side

chain.^{10–12} Furthermore, azobenzene-terminated polymers have been used as photochromic probes.^{1,13,14} Various methods have been developed to attach azobenzene moieties selectively to the side chains, main chain, crosslinks, or chain ends of polymers.^{15–25}

Atom transfer radical polymerization (ATRP) is a method for controlled radical polymerization, $^{26-28}$ and it has great tolerance for functional groups on the monomers and initiators. $^{26-30}$ Polymers with various α functionalities have been prepared with initiators containing hydroxyl, amino, allyl, vinyl, and epoxyl groups. ³¹ ATRP or a combination of ATRP and other methods has been used to synthesize azobenzene-containing polymers. ^{7,32–36} Zhao et al. ³² reported

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Scheme 1. Structure of the azo-based initiators.

the preparation of a series of liquid-crystalline diblock copolymers composed of polystyrene and polymethacrylate with an azobenzene moiety in the side chain, but the initiation efficiency of the polymerization was rather low (<40%); this was probably due to incomplete initiation during the early stage of polymerization. Iyoda et al.33 synthesized well-defined poly{11-[4-(4-butylphenylazo)phenoxy]-undecyl methacrylate} containing an azobenzene mesogen via ATRP with 2-bromoisobutyrate as an initiator and copper(I) chloride (CuCl)/1,1,4,7,10,10-hexamethyldiethylenetriamine as the catalyst with a high initiation efficiency (>80%). Recently, Xi et al.⁷ reported the copolymerization of 4-[N-ethyl-(2-methacryloyloxyethylamino]-4'-nitroazobenzene and methyl methacrylate (MMA) with poly(p-chloromethyl styrene) as a multicenter initiator by ATRP. Lu et al.³⁴ reported the synthesis of a series of hyperbranched homopolymers and copolymers with functional azobenzene units in the side chain with the newly developed self-condensing vinyl polymerization and self-condensing vinyl copolymerization methods. Photoresponsive polymethacrylates containing different bisazo chromophores were also prepared with ATRP by Lu et al.³⁶ The irradiation of these polymer films with a linearly polarized laser induced birefringence because of the reorientation of the bisazo chromophores through transcis-trans isomerization cycles of double azo bonds. Percec et al.³⁵ reported a sulfonyl chloride based initiator with an azobenzene moiety for ATRP of MMA, but no detailed information about the relationship between the initiation efficiency and the structure of the initiator was provided.

This work reports ATRP of MMA with various initiators with monofunctional or difunctional azobenzene (Scheme 1). The aim of this research was to study the structural effect of different ester-type initiators with monofunctional or difunctional azobenzene on the controllability of polymerization and the ultraviolet–visible (UV–vis) spectra of obtained polymers. The initiator, 2-bromopropionic acid 6-(4-phenylazophenoxy)-hexyl ester (BPA₆), with the longer distance between the halogen and azobenzene groups and

better solubility afforded well-controlled polymerizations with an initiator efficiency of 0.9– 1.0. The difference in the initiator efficiency was attributed to the distance between the halogen and azobenzene groups and the solubility of the initiator in the reaction solution. The UV absorption of the azobenzene-based initiators and corresponding polymers were measured, and the redshift of the maximum wavelength (λ_{max}) only occurred for the 2-bromopropionic acid 4-[4-(2bromopropionyloxy)phenylazo]phenyl ester (BPPE) initiated system.

EXPERIMENTAL

Materials

MMA (chemically pure; Shanghai Chemical Reagent Co., Ltd., China) was washed with a 5% sodium hydroxide aqueous solution and then with deionized water until neutralization. After being dried with anhydrous sodium sulfate MMA was distilled in overnight, vacuo. N, N, N', N'', N''-Pentamethyldiethylenetriamine (PMDETA; 98%; Jiangsu Liyang Jiangdian Chemical Factory, China) was dried with 4-A molecular sieves and distilled in vacuo. CuCl (analytical reagent; Shanghai Zhenxin Chemical Reagent Factory, China) was dissolved in hydrochloric acid and precipitated into a large amount of deionized water; it was then filtered, washed with absolute ethanol, and dried in vacuo. Copper(I) bromide (CuBr; chemically pure; Shanghai Chemical Reagent Co., Ltd., China) was purified via washing with acetic acid and acetone and then dried in vacuo. 4-Phenylazophenylamine (chemically pure; Shanghai Chemical Reagent) and 1-chloro-6-hydroxyhexane (Acros; 95%) were used as received. 4-Hydroxyazobenzene (HZO) and 4,4'-dihydroxyzaobenzene (HZO_2) were synthesized according to the literature.^{37,38} The analytical results are given next.

HZO. Yield: 80%. ELEM. ANAL.: C, 72.39% (calcd. 72.71%); H, 5.18% (calcd. 5.08%); N, 14.00% (calcd. 14.14%). ¹H NMR (CDCl₃, δ): 7.88 (d, 4H), 7.48 (m, 3H), 6.95 (d, 2H).

HZO₂. Yield: 20%. ¹H NMR [dimethyl sulfoxide- d_6 (DMSO- d_6), δ]: 10.09 (br, 2H), 7.72 (d, 2H), 7.70 (d, 2H), 6.92 (d, 2H), 6.89 (d, 2H). ¹³C NMR (δ): 159.93 (2s), 145.25 (2s), 115.73 (4d).

All other reagents and solvents were used as received without further purification.

Synthesis of 2-Bromopropionic Acid 2-(4-Phenylazophenyl)ethyl Ester (BPA)

Triethylamine (1.53 g, 15.2 mmol) was added to a solution of HZO (1.5 g, 7.6 mmol) in dry chloroform (130 mL). The solution was stirred in an ice bath, and 2-bromopropionyl bromide (3.29 g, 15.2 mmol) in dry chloroform (20 mL) was added dropwise over a period of 1 h under an argon atmosphere; the mixture was then stirred at room temperature overnight. The solution was filtered, washed with deionized water three times, and dried with anhydrous magnesium sulfate overnight, and the solvent was removed *in vacuo*. The obtained crude product was purified by recrystallization three times from ethanol, and a pale yellow solid was obtained (1.6 g, 63% yield).

ELEM. ANAL.: C, 53.84% (calcd. 54.05%); H, 4.0% (calcd. 3.9%); N, 8.26% (calcd. 8.40%). UV–vis (chloroform): λ_{max} [nm; ε , molar absorption coefficient (L mol⁻¹ cm⁻¹)] = 320 nm. ¹H NMR (CDCl₃, δ): 8.01–7.92 (m, 4H), 7.56–7.27 (m, 5H), 4.66–4.54 (m, 1H), 1.99–1.91 (m, 3H). ¹³C NMR (δ): 168.95 (s, -C=O), 155.2 (s), 152.89 (s), 150.92 (s), 131.68 (s), 129.50 (d), 122.23 (d), 124.62 (d), 123.36 (d), 21.887 (s), 40.00 (s).

Synthesis of BPA₆

5-(4-Phenylazophenoxy)-pentan-1-ol was synthesized with a procedure similar to that reported in the literature.³⁹ The yield was 85%. The crude products were used for further reaction without any purification. The ester was prepared via a procedure similar to that described previously for the synthesis of BPA. The crude product was recrystallized three times from *n*-hexane, and a pale yellow powder was obtained.

Yield: 34%. ELEM. ANAL.: C, 58.86% (calcd. 58.20%); H, 5.81% (calcd. 5.71%); N, 6.31% (calcd. 6.47%). UV–vis (chloroform): λ_{max} [nm; ε (L mol⁻¹ cm⁻¹)] = 340 nm. ¹H NMR (CDCl₃, δ): 7.94–7.92 (d, 2H), 7.89–7.7.87 (d, 2H), 7.52–7.49 (m, 3H), 7.26–6.99 (m, 2H), 4.40–4.35 (m, 1H), 4.25–4.14 (m, 2H), 4.07–4.04 (m, 2H), 1.86–1.82 (m, 3H), 1.77–1.72 (m, 2H), 1.62–1.55 (d, 2H), 1.53–1.48 (m, 4H). ¹³C NMR (δ): 170.82 (s, –C=O), 162.10 (s), 153.15 (s), 147.29 (s), 130.84 (s), 129.52 (d), 125.30 (s), 123.01 (s), 115.15 (d), 68.54 (s), 66.36 (s), 40.69 (s), 29.52 (s), 28.80 (s), 26.15 (s), 26.04 (s), 22.13 (s).

Synthesis of 2-Bromopropionic Acid-(4-phenylazoanilide) (BPN)

This was produced via a procedure similar to that described for the synthesis of BPA. The crude product was recrystallized three times from ethanol, and a yellow powder was obtained.

Yield: 36%. ELEM. ANAL.: C, 54.27% (calcd. 54.22%); H, 4.30% (calcd. 4.22%); N, 12.66% (calcd. 12.65%). UV–vis (chloroform): λ_{max} [nm; ε (L mol⁻¹ cm⁻¹)] = 350 nm. ¹H NMR (CDCl₃, δ): 8.22 (s, NH), 7.98–7.91 (m, 4H), 7.74–7.72 (d, 2H), 7.53–7.46 (m, 3H), 4.62–4.57 (m, 1H), 2.01–1.99 (m, 3H). ¹³C NMR (δ): 167.77 (s, -C=O), 153.01 (s), 149.84 (s), 140.00 (s), 131.42 (s), 129.57 (d), 124.48 (d), 123.26 (d), 120.4 (d), 45.73 (s), 23.43 (s).

Synthesis of BPPE

This was produced via a procedure similar to that described for the synthesis of BPA. The crude product was recrystallized three times from ethyl acetate, and an orange, needlelike crystal was obtained.

Yield: 38%. ELEM. ANAL.: C, 44.61% (calcd. 44.63%); H, 3.41% (calcd. 3.31%); N, 5.37% (calcd. 5.79%). UV–vis (chloroform): λ_{max} [nm; ε (L mol⁻¹ cm⁻¹)] = 330 nm. ¹H NMR (CDCl₃, δ): 7.99–7.98 (m, 4H), 7.32–7.27 (m, 4H), 4.64–4.62 (m, 2H), 1.98–1.92 (m, 6H). ¹³C NMR (δ): 168.97 (s, –C=O), 152.86 (2s), 150.78 (2s), 124.69 (4d), 122.81 (4d), 39.93 (2s), 21.88 (2q).

Polymerizations

A typical polymerization procedure was as follows. A dry glass tube was filled with CuCl (Br; 0.0094 g), PMDETA (20 μ L), an initiator (4.73 \times 10^{-5} mol), anisole (1 mL), and MMA (1 mL). Then, it was degassed in vacuo, charged with argon (five times), sealed under N2, and placed in an oil bath held by a thermostat at the desired temperature for polymerization. At timed intervals, the tube was immersed into cold water to stop the polymerization. Afterwards, the tube was opened, and the contents were dissolved in tetrahydrofuran (THF); the solution was passed through a neutral Al_2O_3 column with THF as an eluent for the removal of the catalyst. Then, the solution was precipitated into a large amount of *n*-hexane. The conversion of the monomer was determined by gravimetry.

Characterization

Elemental analyses of C, H, and N were measured with an EA1110 CHNO-S instrument. The molecular weights and molecular weight distributions of the polymers were determined with a Waters 1515 gel permeation chromatograph equipped with a refractive-index detector, with HR 1, HR 3, and HR 4 columns (molecular weight = 100-500,000) calibrated with poly(methyl methacrylate) (PMMA) standard samples. THF was used as the eluent at a flow rate of 1.0 mL min⁻¹ at 30 °C. ¹H NMR and ¹³C NMR spectra of the polymers were recorded on an Inova 400-MHz NMR instrument with $CDCl_3$ or $DMSO-d_6$ as the solvent and tetramethylsilane (TMS) as the internal standard. The UV-vis absorption spectra of the polymers and initiator in chloroform solutions were determined on a Shimadzu RF540 spectrophotometer.

RESULTS AND DISCUSSION

Four azobenzene-based initiators were synthesized through the condensation of phenols, alcohol, or aniline with 2-bromopropionyl bromide. The structures of the initiators and the synthetic procedures used in the preparation of the initiators are described in Schemes 1 and 2, respectively.

Initially, the polymerization of MMA was carried out with BPA as a monofunctional initiator along with CuBr/PMDETA/50% (v/v) anisole at 60 °C, and a polymer with a broad molecular weight distribution [polydispersity index (PDI) = 1.48] was obtained; it also required longer polymerization times (46 h for 86% monomer conversion). Therefore, a mixed halogen (R-Br/ CuCl)⁴⁰ catalytic system was used to improve the control level of the polymerization. Figure 1 shows the UV-vis spectra of the azobenzenebased initiators and the corresponding polymers. These four azobenzene-based initiators showed $\lambda_{\rm max}$ at 320–350 nm. The difference λ_{\max} values of these initiators could be ascribed to the different substituent groups on the azobenzene. As shown in Figure 1, for all the initiators, both the initiator and corresponding polymer exhibited two strong absorption peaks; the first peak appeared in the shorter wavelength region (ca. 240-250 nm) and corresponded to the absorption by the biphenyl



Scheme 2. Synthetic routes of the initiators.

moiety,⁴¹ and the second peak appeared at the characteristic intense π - π * transition of azobenzene at 320-350 nm. In addition, a much weaker $n-\pi^*$ transition was observed at 440 nm. λ_{\max} of the azo chromophores attached to polymeric chains was almost the same as that of the corresponding azo-based initiators, except for the BPPE-initiated system. λ_{max} of corresponding PMMA initiated by BPPE was redshifted by about 10 nm (340 nm) in comparison with that for BPPE (330 nm). It is well known that azobenzene and its derivatives undergo trans-cis isomerization when subjected to UV or visible light. For example, for trans-azobenzene, λ_{max} should be 444 nm, whereas for *cis*azobenzene, λ_{max} decreases to 439 nm.^{42,43} Generally, the trans form is more stable than the cis form upon irradiation with UV or visible light. The stereochemistry factor has influence on the trans-cis isomerization of azobenzene to some extent. In the case of a monoinitiator, the obtained polymers attach to one side of

azobenzene, and the effect of the stereochemistry factor on trans-cis isomerization can be negligible. For a difunctional azobenzene initiator, the azobenzene group is located in the middle of the polymer chain, each side of azobenzene is capped with a polymer chain, and so the trans-cis isomerization of azobenzene is hindered by the larger molecular motion resistance raised by the long polymer chain attached at each side of the azobenzene group. This may be unfavorable for the formation of cis-azobenzene. Therefore, the redshift of λ_{\max} of corresponding PMMA was only observed when it was initiated by BPPE. In addition, the intensities of the UV absorptions of the polymers were weaker than those of the corresponding initiators in chloroform and decreased with increasing molecular weights of the polymers in all cases; this was due to the decreasing concentration of the azo chromophores attached to polymeric chains with the increasing molecular weights of the polymers.



Figure 1. UV–vis spectra of azo polymethacrylates and corresponding azo initiators in chloroform solutions. The solution concentration was 8×10^{-5} mol/L.

Polymerization of MMA with Monofunctional Azobenzene Initiators

The polymerizations of MMA were carried out with a monomer/initiator molar ratio of 200, and a final number-average degree of polymerization of 200 was targeted; this produced a theoretical number-average molecular weight $(M_{\rm n,th})$ of approximately 20,000 g mol⁻¹ at 100% conversion.

Figure 2 shows first-order plots for the polymerizations of MMA with initiators BPA, BPN, and BPA_6 in all cases; the propagating radical concentration was constant, and there were no significant termination reactions during the polymerizations. For the BPA/CuCl initiation system, the polymerization rate was slowest. An induction period was observed for the BPA and BPN initiation system, and it was due to the poor solubility of BPA and BPN in the reaction medium. For BPA₆, the induction period was eliminated, and the rate of polymerization was increased; this could be explained by the longer distance between the halogen and azobenzene groups and the better solubility with the increasing length of the alkyl chain in BPA_6 . Figure 3 shows the dependence of the numberaverage molecular weight determined by gel permeation chromatography $(M_{n,GPC})$ on the monomer conversion. $M_{n,GPC}$ increased linearly with the monomer conversion in all cases, and a relatively high initiation efficiency was observed with the BPA₆ initiator. However, $M_{n,GPC}$ was higher than $M_{
m n,th}$ ($M_{
m n,th}$ = conversion imes $M_{
m MMA}$ imes $[MMA]_0/[initiator]_0 + MW_{initiator}$, where M_{MMA} is the molecular weight of MMA and M_{initiator} is the molecular weight of the initiator) with initiators BPA and BPN, and this indicated low initiation efficiency. The low initiation efficiency $(M_{n,th}/M_{n,GPC})$ of BPA and BPN was attributed to the poor solubility of the initiators in the reaction medium, which resulted in insufficient initiation during the early stage of the polymerization.

Figure 3 also shows that PDI of the polymer decreased with increasing conversion, and most PDIs were lower than 1.44. The PDIs of the polymers were relatively low up to high conversions in all cases. The PDIs ranged from 1.44 (10.0% conversion) to 1.18 (98.8% conversion) for the BPA initiator, from 1.44 (53.6% conver-



Figure 2. Kinetic plots for the polymerizations of MMA with monofunctional azobenzene-based initiators BPA, BPN, and BPA₆ in anisole solutions (50% v/v) at 60 °C ([MMA]₀/[initiator]₀/[CuCl]₀/[PMDETA]₀ = 200/1/2/2).



Figure 3. Evolution of $M_{n,GPC}$ and PDI with the conversion for the polymerizations of MMA with monofunctional azobenzene-based initiators BPA, BPN, and BPA₆ in anisole solutions (50% v/v) at 60 °C ([MMA]₀/[initiator]₀/[CuCl]₀/[PMDETA]₀ = 200/1/2/2).

sion) to 1.36 (98.6% conversion) for the BPN initiator, and from 1.39 (44.0% conversion) to 1.23 (96.1% conversion) for the BPA₆ initiator. Relatively narrow molecular weight distributions were observed for the BPA initiator (PDI = 1.18-1.44).

Polymerization of MMA with a Difunctional Azobenzene Ester Initiator

Figure 4 shows a first-order plot for the polymerization of MMA with BPPE as a difunctional initiator up to a high conversion. The apparent rate constant of the polymerization with BPPE as a difunctional initiator, calculated from the slope, was 3.86×10^{-5} s⁻¹, which was almost identical to that of monofunctional initiator BPA. A similar phenomenon was observed by Haddleton and Waterson.⁴⁴ However, the induction period (ca. 2 h) in the BPPE/CuCl system was shorter than that (ca. 6 h) in the BPA/CuCl system. This may be ascribed to the increased solubility of the difunctional initiator with one more ester group. Figure 5 shows the dependence of $M_{n,GPC}$ on the monomer conversion. $M_{\rm n \ GPC}$ increased linearly with the monomer conversion up to high conversions and was close to $M_{n,th}$; this indicated a relatively high initiation efficiency. The PDIs of the polymers were relatively low up to 98% conversions. The PDIs



Figure 4. Kinetic plots for the polymerizations of MMA with difunctional azobenzene-based initiator BPPE in anisole solutions (50% v/v) at 60 °C ([MMA]₀/ [initiator]₀/[CuCl]₀/[PMDETA]₀ = 200/1/2/2).

ranged from 1.31 (16.2% conversion) to 1.24 (98.0% conversion).

¹H NMR Analysis of the Polymer Structure

Figure 6(a–d) shows the ¹H NMR spectrum of PMMA obtained by initiation with BPA, BPN, BPA_6 , and BPPE, respectively. The characteristic signals corresponding to the phenyl protons of the azo group were observed at 7.95 and 7.65 ppm, respectively. The signal corresponding to the methyl protons of $COOCH_3$ in the MMA unit connected to the halide end group was observed at approximately 3.78.45 The signals at 0.83–1.21 ppm (a) were assigned to the protons of methyl groups of $-C(CH_3)$ $(COOCH_3)$, the signals from 1.44 to 2.07 ppm (e) were attributed to the methylene group of $-CH_2-$, and the peaks at 3.60 ppm (f) were assigned to methoxy groups in the main chain. These verified the presence of a halide end group in the polymer and the occurrence of polymerization according to the described ATRP mechanism. Furthermore, the numberaverage molecular weights calculated by a comparison of the integration values of the phenyl protons in azobenzene and the protons in $-COOCH_3$ of the MMA units ($M_{n,NMR}$) were determined to be 9900, 15,000, 20,100, and 15,800 for the polymers initiated by BPA (PMMA1), BPN (PMMA2), BPA₆ (PMMA3), and BPPE (PMMA4), respectively (Table 1).

The degree of functionalization (DF) of the azobenzene moiety for polymers initiated by different initiators was evaluated from the ratio of $M_{\rm n,GPC}$ to $M_{\rm n,NMR}$. The results showed that approximately 90% of the polymer chains were functionalized by the azobenzene moiety in all cases.

CONCLUSIONS

Well-defined PMMA containing azobenzene groups was prepared via ATRP with monofunctional and difunctional azobenzene-based initiators. The rates of polymerizations exhibited first-order kinetics with respect to the monomer, and a linear increase in the number-average molecular weight with increasing monomer conversion was observed for these initiation systems. The PDIs of the polymer were relatively low up to high conversions in all cases. The PDIs ranged from 1.44 (10.0% conversion) to 1.18 (98.8% conversion) for the BPA initiator, from 1.44 (53.6% conversion) to 1.36 (98.6% conversion) for the BPN initiator, from 1.39 (44.0% conversion) to 1.23 (96.1% conversion) for the BPA_6 initiator, and from 1.31 (16.2% conversion) to 1.24 (98.0% conversion)for the BPPE initiator. The fastest rate of polymerization and the highest initiation efficiency were achieved with the BPA₆ initiator. The redshift of the UV absorptions of the polymers only occurred with the BPPE-initiated



Figure 5. Evolution of $M_{n,GPC}$ and PDI with the conversion for the polymerizations of MMA with difunctional azobenzene-based initiator BPPE in anisole solutions (50% v/v) at 60 °C ([MMA]₀/[initiator]₀/[CuCl]₀/[PMDETA]₀ = 200/1/2/2).



Figure 6. ¹H NMR spectra (CDCl₃, TMS, 20 °C, 400 MHz) of PMMA obtained with (a) BPA/CuCl/PMDETA, (b) BPN/CuCl/PMDETA, (c) BPA₆/CuCl/PMDETA, and (d) BPPE/CuCl/PMDETA in anisole.

Table 1. $M_{n,GPC}$, $M_{n,NMR}$, PDI, and DF Values of Azobezene-Containing PMMAs

Polymer	$M_{ m n,NMR}$	$M_{ m n,GPC}$	PDI	DF^{a}
PMMA1	9,900	11,100	1.36	0.90
PMMA2	15,000	13,500	1.40	0.90
PMMA3	20,100	18,600	1.35	0.92
PMMA4	15,800	13,450	1.36	0.86

^a DF = $M_{n,GPC}/M_{n,NMR}$.

system. The intensities of the UV absorptions of the polymers were weaker than those of the corresponding initiators in chloroform and decreased with the increasing molecular weights of the polymers in all cases. This research was supported by Science and Technology Development Planning of Jiangsu Province (BG2004018) and Suzhou City (SG0413).

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