Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Zhang, Weidong , Zhang, Wei , Cheng, Zhenping , Zhou, Nianchen and Zhu, Xiulin(2008) 'Atom Transfer Radical Polymerization of Methyl Methacrylate High Efficiently Initiated by Azo-containing Iniferter', Journal of Macromolecular Science, Part A, 45: 10, 850 — 856

To link to this Article: DOI: 10.1080/10601320802300776

URL: http://dx.doi.org/10.1080/10601320802300776

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2008) **45**, 850–856
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ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320802300776

Atom Transfer Radical Polymerization of Methyl Methacrylate High Efficiently Initiated by Azo-containing Iniferter

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Received February 2008 and accepted April 2008

Two novel azo-containing iniferters, (4,4′-(diazene-1,2-diyl) bis(4,1-phenylene) bis(2-(diethylca-rbamothioylthio)-2-methylpropanoate (BDCMP) and 4-((4-bromophenyl)diazenyl)phenyl-2-(diethylcarbamothioylthio)-2-methylpropanoate (PDCMP) were synthesized and used successfully as the initiators for atom transfer radical polymerization of methyl methacrylate (MMA). The kinetic plots were first order and the molecular weights of the polymers with narrow molecular weight distributions increased with the monomer conversions. Furthermore, the results showed that the apparent initiation efficiencies (f was close to 0.90 defined as $M_{n(\mathrm{th})}/M_{n(\mathrm{GPC})}$) of BDCMP and PDCMP were both higher than that (f was lower than 0.5) of 2-N,N-(diethylamino)dithiocarboyl-isobutyrate (EDCIB), which was reported previously by us (14). The obtained mono- and bi-functional PMMAs containing azo and N,N-diethyldithiocarbamate (DC) groups were confirmed by ^{1}H-NMR and ultraviolet absorption spectra, respectively. The block copolymer, poly (methyl methacrylate)-*b*-polystyrene (PMMA-*b*-PS), was also successfully prepared via the ATRP chain-extension experiment using the obtained PMMA as a macroinitiator.

Keywords: Atom transfer radical polymerization (ATRP), azobenzene, methyl methacrylate, *N*, *N*-diethyldithiocarbamate

1. Introduction

In recent years, atom transfer radical polymerization (ATRP) has been paid considerable attention due to its great versatility with a wide range of monomers (1–5), and good controllability of macromolecular architectures, with both low molecular weight distributions and various functional end groups. As a multi-component system, the reactive system is mainly composed of the monomer, an initiator, the catalyst (composed of a transition metal species with any suitable ligand) and some additives. Among these components, the initiators is considered very important components since it determines the number of growing chains and the final molecular weight of the polymer. As a good initiator of the ATRP system, the initiation should be fast and quantitative, based on which the well-defined polymers can be obtained with narrow molecular weight distributions.

Until now, most of the initiators for the successful ATRP systems are common organic halides with a potentially active carbon-halogen or carbon-sulfur bond, such as α-haloester, benzylic halide and sulfonyl halides. However, the obtained polymers are usually captured with halogen atom in the ω-ends of the polymers, which prepared using the initiators above. In order to expand the scope of ATRP initiators, Qiu et al. first successfully introduced the iniferter reagents as the initiators into ATRP systems (6, 7). In particular, a well-defined polymer bearing photo-labile, i.e., N,N-(diethylamino)dithiocarbamoyl (DC) group can be prepared via ATRP technique using some iniferter reagents as the initiators or using some special catalysts, such as cuprous N,N-diethyldithiocarbamate $\mathrm{Cu(S_2CNEt)}$ (8–11) and a mixed-ligand copper (II), $\mathrm{Cu(S_2CNEt)Cl}$ (8, 9). Our group reported the ATRP of vinyl monomers initiated by some functional photoiniferter reagents, such as ethyl 2-N,N-(diethylamino)dithiocarbamoyl-butyrate (EDDCB)(12), (1-naphthyl)methyl N,N-diethyldithiocarbamate (NMDC)(13), 2-(N,N-diethyldithiocarbamyl) isobutyric acid ester (DCIA) (14), ethyl 2-N,N-(diethylamino)dithiocarbamoyl-isobutyrate (EDCIB) (14) and ethyl 2-N,N-(dibenzylamino)dithiocarbamoyl-isobutyrate (EBDCIB) (14). In the above systems, we found this kind of initiators mentioned above were very low apparent initiation efficiency to polymerization of methyl methacrylate (MMA). As is well known, increasing electron-withdrawing of the initiator can

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enhance the initiation efficiency in conventional ATRP systems. In this work, our interest is to heighten the initiation efficiency of this kind of initiators above by increasing electron-withdrawing effect of the iniferter agents.

Polymers containing a azobenzene unit, which undergo conversion from trans-to cis-forms on irradiation with UV light, have gained great attention due to their many possible optical applications (15), for example, a new optical switch (16–18), optical polyelectrolyte (19), and nonlinear optical materials (20–22). In addition, azobenzene-terminated polymers have been used as photochromic probes (23, 24). Recently, several initiators containing azobenzene were synthesized and used successfully as the initiators in ATRP system (25–27). Percec et al. reported an azobenzene-functional sulfonyl chloride initiator for ATRP of MMA to prepare azobenzene-terminated polymers (28). Hizal et al. synthesized a novel multi-arm star A_2B_2 copolymer with an azobenzene unit as a core via combination of ATRP and nitroxide-mediated free radical polymerization (NMP) methods. The photoresponsive properties of the polymers were investigated (29). Our group also reported monofunctional and difunctional azobenzene-based initiators to prepare azobenzene-terminated PMMA via ATRP method (25). We found that all those initiators substituted by azobenzene moiety had relatively high initiation efficiency.

In order to improve the initiator efficiency and functionalize the polymer, in this work, we synthesized two novel initiators containing azo and DC units, (4,4′-(diazene-1, 2-diyl) bis (4,1-phenylene) bis (2-(diethylcarbamothioylthio)-2-methylpropanoate (BDCMP) and 4-((4-bromophenyl)diazenyl)phenyl-2-(diethylcarbamothioylthio)-2-methylpropanoate (PDCMP), and successfully used them in ATRP of MMA. Most significantly, the experimental results showed that initiators with azo and DC units had higher initiation efficiency and better controllability than that of ethyl 2-*N*,*N*-(diethylamino)dithiocarbamoyl-isobutyrate (EDCIB) (14) under similar experiment conditions.

2. Experimental

2.1. *Materials*

Methyl methacrylate (MMA) (99%; chemically pure, from Shanghai Chemical Reagent Co., China) was washed with a 5% sodium hydroxide aqueous solution and then with deionized water until neutralization. After being dried with anhydrous sodium sulfate overnight, it was finally distilled under reduced pressure and kept in a refrigerator under 0°C before use. 2-Bromo-2-methylpropionyl bromide was purchased from Aldrich Chemical Co. PMDETA (98%; Jiangsu Liyang Jiangdian Chemical Factory, Liyang, China) was dried with 4-Åmolecular sieve and distilled in vacuum. Copper bromide (98%; Aldrich) was stirred with acetic acid for 12 h, washed with ethanol and diethyl ether, and then dried in vacuum. Ethyl-2-*N*, *N*-(diethylamino) dithiocarbamoyl-isobutyrate (EDCIB) was synthesized according to the reference (14). Tetrahydrofuran (THF) (Analytical reagent, from Shanghai Chemical Reagent Co. Ltd.) and dimethyl formamide (DMF) (analytical reagent, Shanghai Chemical Reagent Co.), and methanol (commercially available) were used as received.

2.2. *Synthesis of 4-(4-bromo-phenylazo phenol (BPP)*

4-(4-Bromo-phenylazo)-phenol was synthesized according to the literature (30) and purified by means of column chromatography on silica oxide, with mixed petroleum ether and ethyl acetate (3:1, v/v) as the eluent. The BPP was obtained as a golden yellow crystal (Yield: 82%), HPLC (Waters 515) indicated that the purity was above 98%. ^{1}H-NMR ($CDCl_3$, δ): 7.92 (d, 2H), 7.82 (d, 2H), 7.63 (d, 2H), 6.95 (d, 2H) Elemental Analysis Calculated: (%) C, 52.01, H 3.27, N, 10.11; Found: (%) C, 51.53, H, 3.24; N, 9.82.

2.3. *Synthesis of 4,4′-(diazene-1, 2-diyl)diphenol (DDP)*

4, 4′-(Diazene-1, 2-diyl) diphenol was synthesized as the literature (31). The crude product was obtained by recrystallizing three times from mixed ethanol and water (3:1, v/v). The DPP was obtained as a violet red crystal (Yield: 18%). ^{1}H-NMR (DMSO-d_6): 10.09 (s, 2H), 7.72 (d, 2H), 7.70 (d, 2H), 6.92 (d, 2H), 6.89 (d, 2H). Elemental Analysis Calculated: (%) C, 67.28; H, 4.71, N, 13.08; Found: (%) C, 67.63; H, 4.23, N, 13.46.

2.4. *Synthesis of 4-((4-bromophenyl) diazenyl) phenyl 2-bromo-2-methylpropanoate (PBMP) and 4,4′-(diazene-1,2-diyl) bis (4,1-phenylene) bis(2-bromo-2-methylpropanoate) (BPMP)*

PBMP and BPMP were synthesized with a procedure similar to that reported in the literature (25) The crude product was recrystallized three times from ethanol, and the pale yellow powder was obtained (yield: 72%).

PBMP: Elemental Analysis Calculated: (%) C, 45.1, H, 3.31, N, 6.57; Found: (%) C, 44.75, H, 3.46, N, 6.55. ^{1}H-NMR ($CDCl_3$, δ): 7.9 (d, 2H), 7.8 (d, 2H), 7.6 (d, 2H), 6.95 (d, 2H), 1.91 (m, 6H). The purity was above 98%. BPMP (62% yield): Elemental Analysis Calculated: (%) C, 46.9; H, 3.94; N, 5.47; Found: (%) C, 46.55; H, 3.65; N, 5.23. ^{1}H-NMR ($CDCl_3$, δ): 6.93–7.89 (m, 8H), 1.92 (m, 12H).

2.5. *Synthesis of 4-((4-bromophenyl) diazenyl) phenyl-2-(diethylcarbamothioylthio)-2-methylpropano-ate (PDCMP)*

PDCMP was prepared as the following procedure: PBMP 4.26 g (10 mmol) was added dropwise to the suspension of sodium diethyl-dithiocarbamate trihydrate 2.25 g (10 mmol) in acetone (100 mL). The solution was stirred for 6 h at room temperature. The mixture was filtered and the solvent was removed *in vacuo*. The obtained crude product was purified by recrystallization three times from ethyl acetate and a pale yellow solid was obtained (78% yield).

PDCMP: Elemental Analysis Calculated: (%) C, 51.01; H, 4.89; N, 8.50; Found (%): C, 51.09; H, 4.94; N, 8.45. ^{1}H NMR ($CDCl_3$, δ): 6.93–7.89 (m, 8H), 3.65-3.90 (m, 2H), 1.90-1.94 (s, 6H), 1.20–1.54 (s, 6H).

2.6. *Synthesis of (4,4′-(diazene-1,2-diyl)-bis(4,1-phenylene)bis(2-(diethyl-carbamothioylthio)-2-methylpropanoate (BDCMP)*

The method of synthesis of BDCMP is similar to that described for the synthesis of PDCMP. The crude product was recrystallized three times from ethyl acetate and a pale yellow solid was obtained (67%, yield).

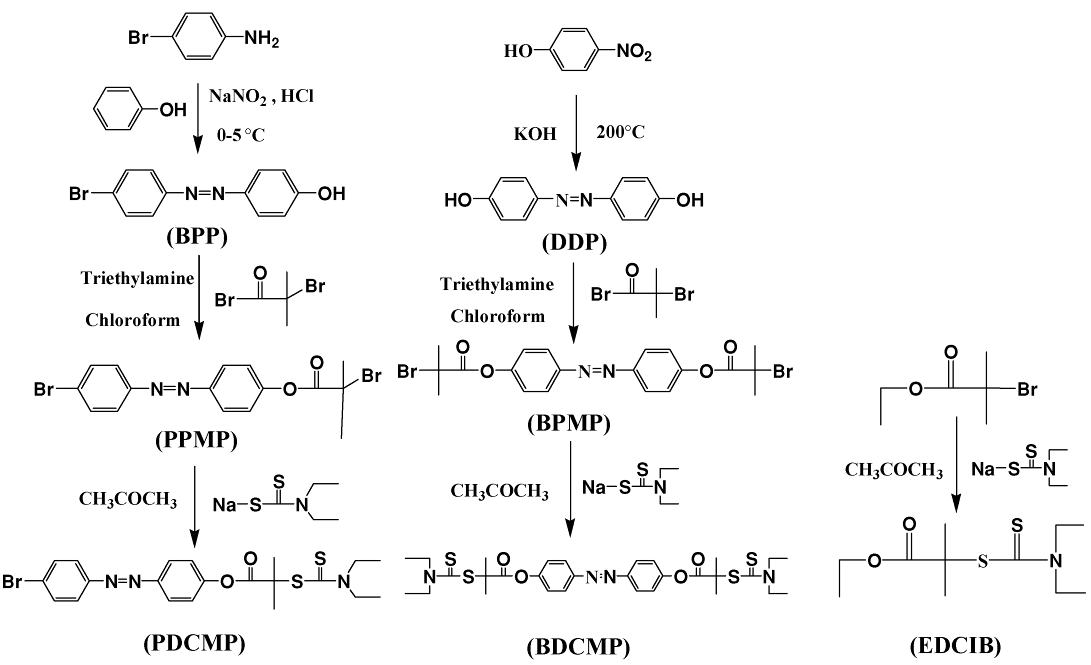
BDCMP: Elemental Analysis Calculated: (%) C, 51.01; H, 4.89; N, 8.50. Found: (%) C, 51.09; H, 4.94; N, 8.45. ^{1}H-NMR ($CDCl_3$, δ): 6.93–7.89 (m, 8H), 3.65–3.95 (m, 8H), 1.83–1.94 (s, 12H), 1.20–1.34 (s, 12H).

2.7. *Characterization*

^{1}H-NMR spectra were recorded on an INOVA 400MHz nuclear magnetic resonance (NMR) instrument, using tetramethylsilane (TMS) as the internal standard. Ultraviolet visible (UV-vis) absorption spectra of the polymers and initiator in THF solutions were performed on a Shimadzu (Kyoto, Japan) UV-240 recording spectrophotometer at ambient temperature. The elemental analyses for C, H, and N were tested by a LECO-CHNS microanalyzer. The purity of products was determined on HPLC (mode 515 high-performance liquid chromatograph, Waters) with a mixed solvent of methanol and water as the eluent at the ratio of 80 : 20 (v/v) at 30°C. The molecular weights and molecular weight distributions of the polymers were determined with a Waters 1515 gel permeation chromatography (GPC) equipped with a refractive index detector, using a HR1, HR3, and HR4 column with molecular weight range 100-500,000 calibrated with PMMA standard samples. THF was used as the eluent at a flow rate of 1.0 mL min^{-1} operated at 30°C.

2.8. *General polymerization procedures*

A typical ATRP procedure was carried out as follows: a solution of MMA (1 mL, 9.46 mmol) and PDCMP (11.65 mg, 0.0236 mmol) was added to a dry glass tube filled with copper bromide (6.76 mg, 0.0473 mmol), PMDETA (24.49 mg, 0.141 mmol) in sequence. After the reaction mixture was bubbled with argon for approximately 10 min to eliminate the oxygen, the tube was sealed under an argon atmosphere and then immersed in an oil bath at a desired temperature. At timed intervals, the tube was cooled in ice water to stop the polymerization. Afterwards, the tube was opened, and the contents were diluted with THF, then it was precipitated into a large amount of methanol. The samples were dried to constant weight at 50°C. The



Sch. 1. The synthetic routes of initiators.

conversion of the monomer was determined by gravimetry. The similar procedures were conducted for the other polymerizations.

3. Results and discussion

3.1. *ATRP of MMA*

Recently, some iniferter reagents were expanded to be used as the initiators in ATRP to synthesize well-defined polymers bearing DC groups (7–8, 32–34). In our previous study, we found that the initiation efficiency of this type of initiators were high for ATRP of styrene, but relatively low for ATRP of MMA. In order to improve the initiation efficiency of this kind of initiator and expand more functional initiators of ATRP, we introduced the azobenzene unit to the structures of the initiators as shown in Scheme 1. The homopolymerizations of MMA were carried out with PDCMP, BDCMP and EDCIB as the initiators, respectively, CuBr/PMDETA complex as the catalyst in DMF solution ($[\mathrm{MMA}]_0/[\mathrm{Initiator}]_0/[\mathrm{CuBr}]_0/[\mathrm{PMDETA}]_0 =$ 400:1:2:6; MMA/DMF = 1/1 (v/v)) at 80^{circ}C. The results were presented in Figures 1 and 2. As shown in Figure 1, the kinetic plots were all approximately first-order with respect to the monomer in all cases, indicating that the radical concentration of each system was constant during the reaction. Furthermore, the polymerization rates were apparently effected by the initiator structures and decreased in the order of BDCMP > EDCIB > PDCMP. The polymerization rate in the case of BDCMP was faster than that in the case of PDCMP since the radical concentration in the case of BDCMP was higher than that in the case of PDCMP using the same concentration of initiator. The different polymerization rate between EDCIB and PDCMP may be attributed to the different initiator structures (35, 36). Figure 2 showed the dependence of the molecular weights and molecular weight distributions ($M_{\mathrm{w}}/M_{\mathrm{n}}$) on the monomer conversions for the ATRP of MMA. The molecular weights ($M_{\mathrm{n(GPC)}}$) of PMMAs increased linearly with the monomer conversions. Moreover, the $M_{\mathrm{n(GPC)}}$s using BDCMP and PDCMP as initiators were very close to the theoretical ones ($M_{\mathrm{n(th)}}$s), which indicated that the initiation efficiencies of BDCMP and PDCMP were relatively high ($f$was close to 0.90 defined as $M_{\mathrm{n(th)}}/M_{\mathrm{n(GPC)}}$). $M_{\mathrm{n(th)}}$was determined by$M_{\mathrm{n(th)}} = ([\mathrm{M}]_0/[\mathrm{I}]_0) \times M_{\mathrm{M}} \times$ Conversion $+M_{\mathrm{I}}$, where $[\mathrm{M}]_0$ and $[\mathrm{I}]_0$ are initial concentrations of monomer and initiator, respectively, M_{M} and M_{I} are the molecular weight of MMA and the initiator, respectively. However, the initiation efficiency of EDCIB was relatively low which was similar to the results reported by our group (14). This result is in good agreement with our intention to improve the initiation efficiency of this kind of initiator. The high initiation efficiencies of BDCMP and PDCMP should be ascribed to electron-withdrawing group of azo moiety in BDCMP and PDCMP, which increased the electrophilicity effect of the initiating radical (37). As shown in Figure 2, the molecular weight distributions ($M_{\mathrm{w}}/M_{\mathrm{n}}$) of the polymers in the cases of PDCMP and BDCMP were relatively lower ($M_{\mathrm{w}}/M_{\mathrm{n}} < 1.45$) than those in the case of EDCIB ($M_{\mathrm{w}}/M_{\mathrm{n}} = 1.5$–$2.0$).

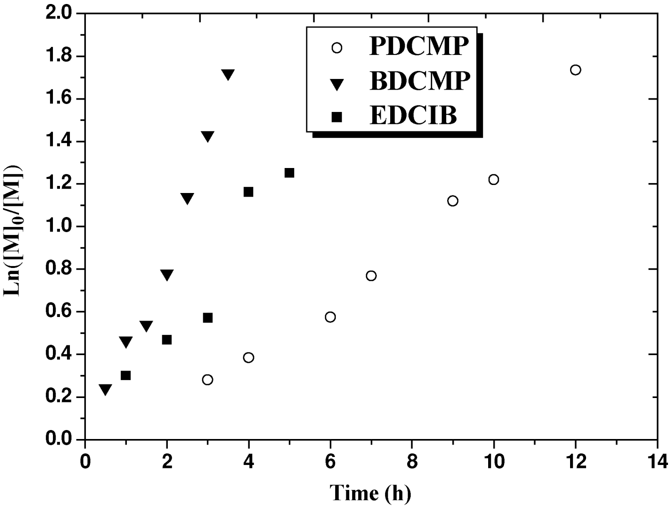


Fig. 1. Kinetic plots of the solution ATRPs of MMA. Conditions: $[\mathrm{MMA}]_0/[\mathrm{Initiator}]_0/[\mathrm{CuBr}]_0/[\mathrm{PMDETA}]_0 = 400:1:2:6$, 80^{o}C. MMA/DMF = 1/1 (v/v). Initiators are PDCMP, BDCMP and EDCIB, respectively.

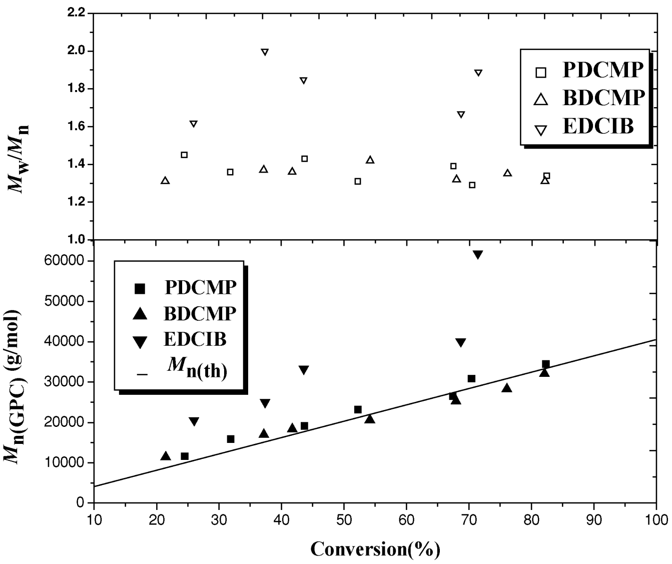


Fig. 2. The dependence of the molecular weights and molecular weight distributions on the monomer conversion for the ATRPs of MMA. Conditions are the same as in Figure 1.

According to the literature (38), the concentrations of different components and reaction temperature obviously influence the polymerization behaviors. In this section, we also investigated the effect of them on the polymerization and the results are given in Table 1.

Table 1. The solution ATRPs of MMA with different ratios of $[MMA]_0/[Initiator]_0/[CuBr]_0/[PMDETA]_0$ and temperatures in the presence of BDCMP

Entry	$[MMA]_0/[Initiator]_0/[CuBr]_0/[PMDETA]_0$	*T (°C)*	*Time (h)*	*Conversion (%)*	$M_{n(GPC)}$	$M_{n(th)}$	M_w/M_n
1	200 : 1 : 2 : 6	80	2.5	83.1	21000	17100	1.31
2	400 : 1 : 2 : 6	80	2.5	67.9	25300	27100	1.32
3	800 : 1 : 2 : 6	80	2.5	56.8	35800	45800	1.32
4	400 : 1 : 2 : 6	70	2.5	63.1	26900	25600	1.40
5	400 : 1 : 2 : 6	90	2.5	86.6	31400	35200	1.38
6	400 : 1 : 1 : 3	80	2.5	61.1	34200	24800	1.37
7	400 : 1 : 0.5 : 3	80	2.5	39.6	23000	16000	1.34

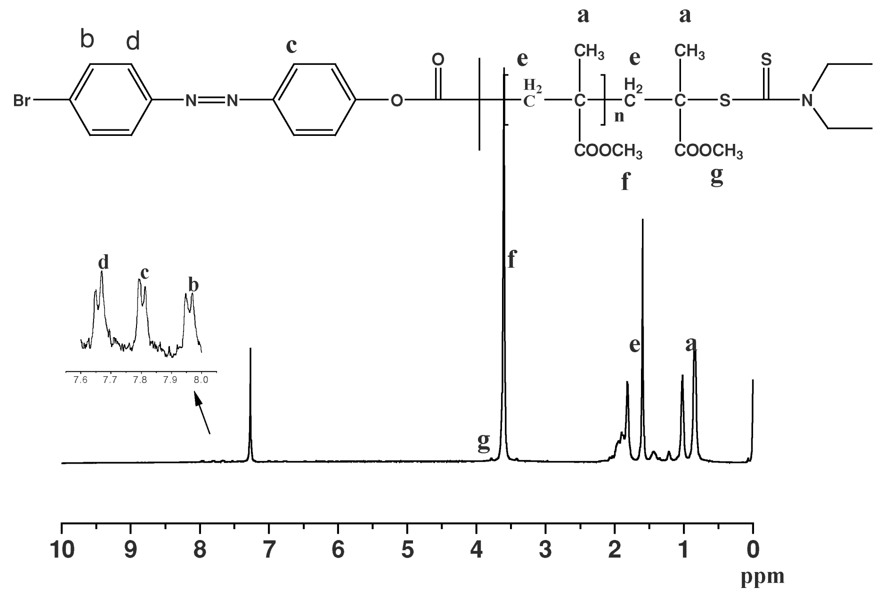


Fig. 3. ^{1}H-NMR spectrum of the PMMA initiated PDCMP/CuBr/PMDETA in solution ($[MMA]_0/[PDCMP]_0/[CuBr]_0/[PMDETA]_0 = 400{:}1{:}2{:}6$, MMA/DMF = 1:1 (v/v)) at 80°C (in $CDCl_3$). Sample: $M_{n(GPC)} = 19100$ g/mol, $M_w/M_n = 1.43$.

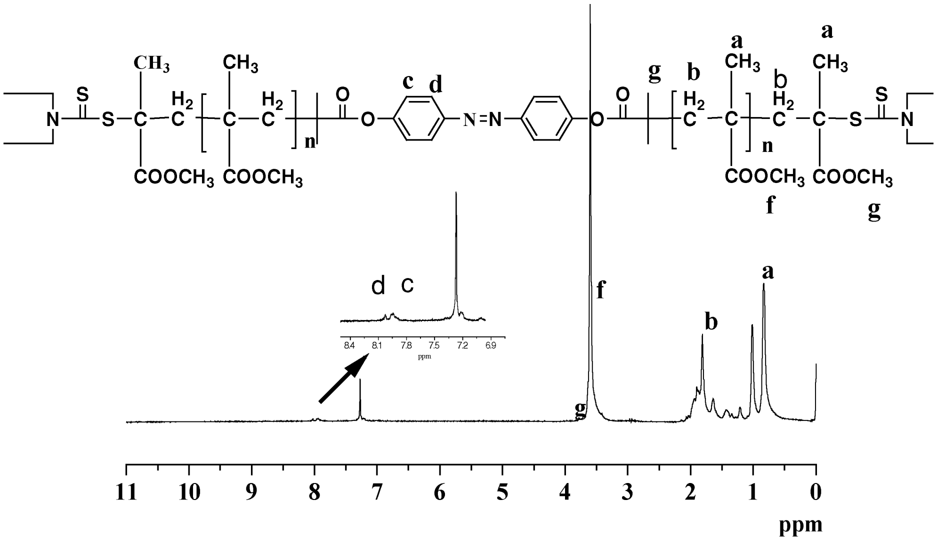


Fig. 4. ^{1}H-NMR spectrum of the PMMA initiated BDCMP/CuBr/PMDETA in solution ($[MMA]_0/[BDCMP]_0/[CuBr]_0/[PMDETA]_0 = 400{:}1{:}2{:}6$, MMA/DMF = 1:1 (v/v)) at 80°C (in $CDCl_3$). Sample: $M_{n(GPC)} = 11400$ g/mol, $M_w/M_n = 1.31$.

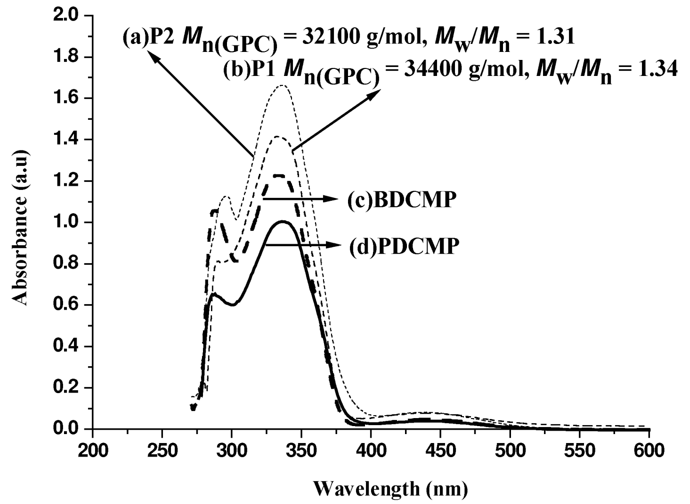


Fig. 5. Ultraviolet absorption spectra of initiators and polymers: (a) P2 initiated by BDCMP; (b)P1 initiated by PDCMP; (c) BDCMP; (d) PDCMP; concentration of initiators and polymers are 5.0×10^{-5}M with THF as a solvent.

From Table 1, it can be seen that the polymerizations were all well-controlled in all cases of different ratios of $[MMA]_0/[initiator]_0/CuBr]_0/[PMDETA]_0$ and temperatures. When the ratios of $[MMA]_0/[initiator]_0/CuBr]_0/[PMDETA]_0$ was changed from 200:1:2:6 to 800:1:2:6, the monomer conversion decreased from 83.1% to 56.8% (entries 1–3) at the same temperature, which was due to the different concentration of initiator and catalyst. Table 1 also showed that the polymerization rate increased with the reaction temperature (entries 1, 4 and 5). When the initial concentration of ratio of MMA to BDCMP was constant (400:1), the polymerization rate decreased with the concentration of catalyst complex (CuBr/PMDETA) and the polymerization was still well controlled at a relatively low concentration of catalyst complex. The molecular weights were close to the theoretical ones ($M_{n(th)}$s) while keeping the relatively narrow molecular weight distributions, which indicated the 'living' nature of the polymerization.

3.2. *End group analysis and the chain extension*

To certificate the polymer enveloped by azo and DC group, the polymer was characterized by^{1}H-NMR and ultraviolet absorption spectra. Figures 3 and 4 showed the ^{1}H-NMR spectra of PMMA obtained using PDCMP and BDCMP as initiators, respectively. The characteristic signals corresponding to the phenyl protons of the azo group were observed at around 7.15–7.95 ppm and the signal attributed to the methyl protons of $COOCH_3$ in the MMA unit connected to DC group was observed at approximately 3.78 (39). The similar results also can be obtained as to the polymer prepared with BDCMP as the initiator. Owing to the high sensitivity of the DC group to the ultraviolet light, we also do the ultraviolet absorption of the polymer and initiator in THF to confirm the polymer ended with DC group. As shown in Figure 5, both the initiator and the polymer had a strong absorption at about 282 nm. The results were in agreement with the previous results reported by Qiu et al. (11), that is, the characteristic absorption peak of DC group. In addition, the peak around at 320-350 nm is the characteristic intense $\prod$–$\prod^*$ transition of azobenzene (25). The data above demonstrated the existence of the azo and DC group.

A chain-extension reaction was also used to verify the functionality and 'living" nature of the polymer. We used

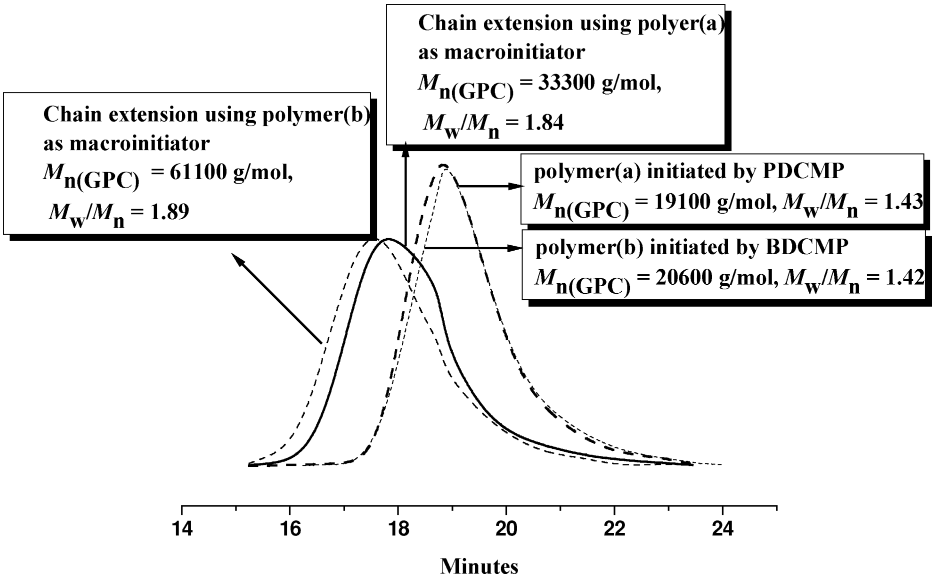


Fig. 6. GPC curves of polymer of macroinitiators and final polymers by chain-extension. Conditions: $[St]_0/[Macroinitiator]_0/[CuBr]_0/[PMDETA]_0 = 400:1:2:6$; 115°C. St/DMF = 1/1 (v/v).

the obtained polymer as a macroinitiator and styrene as the second monomer to carry out chain extension reaction. A typical chain extension experiment was carried out at 115°C with $[St]_0/[Macroinitiator]_0/[CuBr]_0/[PMDETA]_0 = 400/1/2/6$ in DMF solution and St/DMF = 1:1 (v/v) as shown in Figure 6. The molecular weights and molecular weight distributions of the polymers had an obvious change, such as the molecular weight increased from 19100 to 33300 g/mol and molecular weight distribution increased from 1.43 to 1.84 for PDCMP, the molecular weight increased from 20600 to 61100 g/mol and molecular weight distribution increased from 1.42 to 1.89 for BDCMP.

4. Conclusions

Two novel iniferter reagents containing DC and azo groups, PDCMP and BDCMP were synthesized and used as the initiators for ATRP of MMA. The well-defined functional PMMA containing azo and *N*, *N*-diethyldithiocarbamate (DC) group was successfully obtained. Both PDCMP and BDCMP were highly efficient initiators for ATRP of MMA, other than EDCIB, due to the introduction of azo groups in the iniferter reagents.

Acknowledgments

The financial support of this work by the National Nature Science Foundation of China (No.20574050), the Science and Technology Development Planning of Jiangsu Province (No. BK2007702 and BK2007048), and the Nature Science Key Basic Research of Jiangsu Province for Higher Education (No. 05KJA15008) are gratefully acknowledged.

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