Atom Transfer Radical Polymerizations of Methyl Methacrylate and Styrene with an Iniferter Reagent as the Initiator

Wei Zhang, Xiulin Zhu, Zhenping Cheng, Jian Zhu

Key Laboratory of Organic Synthesis of Jiangsu Province, School of Chemistry and Chemical Engineering of Suzhou University, Suzhou 215123, China

ABSTRACT: Three novel iniferter reagents were synthesized and used as initiators for the polymerizations of methyl methacrylate (MMA) and styrene (St) in the presence of copper(I) bromide and N,N,N',N'',N''-pentamethyl-diethylenetriamine at 90 and 115°C, respectively. All the polymerizations were well controlled, with a linear increase in the number-average molecular weights during increased monomer conversions and relatively narrow molecular weight distributions (weight-average molecular weight/number-average molecular weight $\leq$ 1.36) throughout the polymerization processes. The polymerization rate of MMA was faster in bulk than that in solution and was influenced by the different polarities of the solvents. A slight change in the chemical structures of the initiators had no obvious effect on the polymerization rates of MMA and St. The initiator efficiency toward MMA was lower than that toward St. The results of ^{1}H-NMR, matrix-assisted laser desorption/ionization time-of-flight mass spectrum analysis, and chain-extension experiments demonstrated that well-defined poly(methyl methacrylate) and polystyrene bearing photolabile groups could be obtained via atom transfer radical polymerization (ATRP) with three iniferter reagents as initiators. The polymerization mechanism for this novel initiation system was a common ATRP process. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 230–237, 2007

Key words: atom transfer radical polymerization (ATRP); living polymerization

INTRODUCTION

Controlled/living free-radical polymerization (LFRP) has become the focus of extensive research in the past few years.[1–5] Through LFRP, the molecular weights and molecular weight distributions of the resulting polymers can be well controlled. The iniferter technique was first developed by Otsu and coworkers[1,2,6] as a powerful method for synthesizing well-designed functional polymers. Vinyl polymers containing the N,N-diethyldithiocarbamate (DC) derivative groups were synthesized by the radical polymerization of the corresponding monomers with an iniferter reagent. However, the structures and compositions of the obtained polymers were poorly controlled with relatively high molecular weight distributions [weight-average molecular weight/number-average molecular weight (M_w/M_n) > 1.50].[2] Fortunately, much significant progress has been made in the development of controlled/living radical polymerizations, such as stable free-radical polymerization,[7,8] reversible addition–fragmentation chain transfer polymerization,[9–11] and atom transfer radical polymerization (ATRP).[12–15] Among them, ATRP may be one of the most versatile living free-radical polymerization techniques because of its high degree of compatibility with a wide range of functional monomers, controllable macromolecular architectures with low molecular weight distributions, functional end groups, and mild reaction conditions.[4,5]

As one component of an ATRP system, the initiator plays an important role because it will give rise to an initiating radical species via homolytic cleavage of its labile bond, such as a carbon–halogen bond, by the catalysts.[4,5] The initiating radical species resulting from the initiator can initiate the polymerization of the monomer. The fast initiation is vital to obtaining well-defined polymers with narrow molecular weight

distributions. Up to now, most of the initiators for successful ATRP have been organic halides with a potentially active carbon–halogen bond, and the obtained polymers usually have halogen atoms in the chain ends. Moreover, the dehalogenation of the terminated polymers needs radical or ionic reactions, and the reaction is incomplete.[16,17]

Qiu and coworkers[18,19] focused on extending the scope of ATRP initiators. In their studies, they first successfully introduced C—C-type thermal iniferter regents, such as 1,1,2,2-tetraphenyl-1,2-ethanediol,[18] 2,3-dicyano-2,3-diphenylsuccinate,[20] and 2,3-dicyano-2,3-di(p-tolyl) succinate,[21] and a photoiniferter reagent (tetraethylthiuram disulfide[19]) to ATRP system as initiators. Therefore, it became possible to synthesize well-defined polymers with a DC group as the end group, which can be used as a macroiniferter to synthesize block copolymers via an iniferter technique. Qiu et al.[16] also reported that the DC group could be transferred by the mediation of the dormant–active species equilibrium in the process of ATRP. Recently, well-defined polymers bearing photolabile groups [N,N-(diethylamino)dithiocarbamoyl (DC)] were prepared via an ATRP technique using cuprous N,N-diethyldithiocarbamate [Cu(S$_2$CNEt)][22] and a mixed-ligand copper(II) [Cu(S$_2$CNEt)Cl].[23] However, exchange reactions between the DC group and the halogen atoms in the catalyst were found because of the different bond lengths of Cu—S and Cu—X (X = Br or Cl).[16,22,23] Ishizu and Kakinuma[24] also synthesized nanocylinders consisting of graft block copolymers by the photoinduced ATRP technique. We synthesized well-defined DC-ended poly (methyl methacrylate) (PMMA), using copper(II) N,N'-n-butyldithiocarbamate {Cu[SC(S)N(C$_4$H$_9$)$_2$]$_2$}[25] as a catalyst, and well-defined DC-ended polystyrene (PS), using ethyl 2-N,N-(diethylamino)dithiocarbamoyl butyrate (EDDCB)[26] and (1-naphthyl)methyl N,N-diethyldithiocarbamate (NMDC)[27] as initiators via ATRP. Moreover, in the styrene (St)/EDDCB/copper(I) bromide (CuBr)/N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA)[26] and St/NMDC/CuBr/PMDETA[27] systems, we found that almost no exchange reactions occurred between the DC group and the halogen atoms (Br or Cl) in the catalyst, although the results were different from those reported by Qiu and coworkers.[16,22,23]

In this work, we synthesized three novel iniferter reagents with different structures and studied their properties as initiators in ATRPs of methyl methacrylate (MMA) and St.

EXPERIMENTAL

Materials

St and MMA (chemically pure; Shanghai Chemical Reagent Co., Shanghai, China) were washed with a 5% sodium hydroxide aqueous solution and then with deionized water until neutralization. After being dried with anhydrous sodium sulfate overnight, the monomers were distilled under a vacuum and stored at −18°C. PMDETA (98%; Jiangsu Liyang Jiangdian Chemical Factory, Jiangsu, China) was dried with a 4-Å molecular sieve and distilled under a vacuum. Copper(I) chloride (CuCl; analytical reagent; Shanghai Zhenxin Chemical Reagent Factory, Shanghai, China) was dissolved in hydrochloric acid, precipitated into a large amount of deionized water, filtered, washed with absolute ethanol, and dried under a vacuum. CuBr (chemically pure; Shanghai Chemical Reagent) was purified through washing with acetic acid and acetone and then dried under a vacuum. Toluene and anisole were distilled before use. Tetrahydrofuran (THF; analytical reagent; Shanghai Chemical Reagent) and methanol (commercially available) were used as received. Carbon disulfide, dibenzyl amine, diethylamine, 2,2′-azobisisobutyronitrile, tetraethylthiuram disulfide, sodium hydroxide, and other reagents (analytical reagent; Shanghai Chemical Reagent) were used as received. 2-(N,N-Diethyldithiocarbamyl) isobutyric acid ester (DCIA),[28] ethyl 2-N,N-(diethylamino)dithiocarbamoyl isobutyrate (EDCIB), and ethyl 2-N,N-(dibenzylamino)dithiocarbamoyl isobutyrate (EBDCIB)[29] were synthesized according to the references, respectively.

DCIA (C$_9$H$_{16}$N$_2$S$_2$). ^{1}H-NMR (CDCl$_3$, δ, ppm): 3.66–3.98 (m, 4H), 1.89–1.92 (s, 6H), 1.26–1.30 (s, 6H). ANAL. Calcd: C, 49.96%; H, 7.54%; N, 12.95%. Found: C, 50.13%; H, 7.57%; N, 12.80%.

EDCIB (C$_{11}$H$_{21}$NO$_2$S$_2$). ^{1}H-NMR (CDCl$_3$, δ, ppm): 4.17–4.22 (m, 2H), 3.69–3.95 (m, 4H), 1.73–1.89 (s, 6H), 1.23–1.30 (s, 9H). ANAL. Calcd: C, 50.15%; H, 8.04%; N, 5.32%. Found: C, 50.23%; H, 8.37%; N, 5.10%.

EBDCIB (C$_{21}$H$_{25}$NO$_2$S$_2$). ^{1}H-NMR (CDCl$_3$, δ, ppm): 7.19–7.52 (s, 10H), 4.64–5.02 (m, 4H), 4.18–4.23 (m, 2H), 1.21–1.31 (s, 9H). ANAL. Calcd: C, 65.08%; H, 6.50%; N, 3.61%. Found: C, 65.11%; H, 6.47%; N, 3.53%.

The purities of the aforementioned compounds were characterized with a Waters 515 high-performance liquid chromatograph and were all above 99%.

Characterization

The molecular weights and molecular weight distributions of the polymers were determined with a Waters 1515 gel permeation chromatography (GPC) instrument equipped with a refractive-index detector and using HR1, HR3, and HR4 columns with a molecular weight range of 100–500,000 g/mol calibrated with PMMA or PS standard samples. THF was used as the eluent solvent at a flow rate of 1.0 mL/min and at 30°C. ^{1}H-NMR spectra of the polymers were recorded on an Inova 400-MHz NMR instrument with CDCl$_3$ as the solvent and tetramethylsilane as

the internal standard. The elemental analyses for C, H, and N were performed on a Leco CHNS microanalyzer. The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained with a Biflex II (Bruker, Germany) equipped with a nitrogen laser (λ = 337 nm). The accelerating voltage was 19 kV. A stainless steel target was used as the MALDI substrate, and Ag^+ was used as the cationizing agent. The purity of the products was determined on a Waters 515 high-performance liquid chromatograph with a mixed solvent of methanol and water as the eluent solvent at a ratio of 80 : 20 (v/v), and the column temperature was 30°C.

General procedures of the polymerization

A typical ATRP procedure can be described as follows: A solution of MMA (2 mL, 18.9 mmol) and DCIA (0.0205 g, 0.0945 mmol) was added to a dry glass tube filled with CuBr (0.0272 g, 0.0189 mmol) and PMDETA (0.12 mL, 0.0567 mmol) with a predetermined molar ratio ([MMA]$_0$/[DCIA]$_0$/[CuBr]$_0$/[PMDETA]$_0$ = 200 : 1 : 2 : 6) under an argon atmosphere. Then, the mixture was degassed under a vacuum and charged with argon (five times). The glass tube was sealed under argon and was placed in an oil bath held by a thermostat at 90°C. At timed intervals, the tube was cooled in ice water to stop the polymerization. Afterwards, the tube was opened, and the contents were dissolved in THF; the solution was passed through a neutral Al_2O_3 column with THF as the eluent solvent to remove the catalyst and precipitated into a large amount of methanol. The samples were dried to a constant weight at 50°C. The conversion of the monomer was determined by gravimetry. A similar procedure was conducted for all the polymerizations.
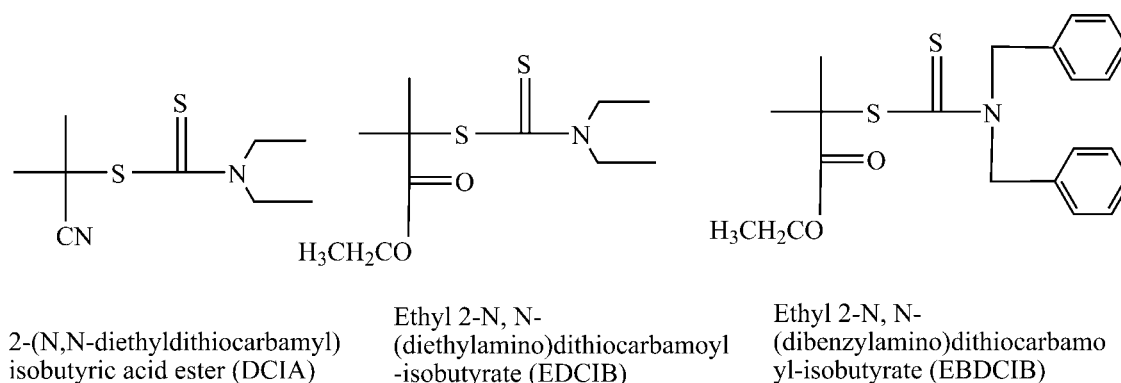
Photopolymerization

The PMMA obtained as described previously was dissolved in fresh MMA with a predetermined molar ratio ([MMA]$_0$/[Macroinitiator]$_0$ = 200 : 1). After the degassing process was performed five times, the tube was sealed under argon and was left to stand under a 250-W high-pressure mercury lamp from a distance of 15 cm at room temperature. At the determined time, the tube was removed. The reaction mixture was treated according to the previously described procedures.

RESULTS AND DISCUSSION

ATRPs of MMA

In recent years, some iniferter reagents have been expanded to be used as initiators in ATRP to synthesize well-defined polymers bearing DC groups.[24,26,27] In this work, three novel iniferter reagents, DCIA, EDCIB, and EBDCIB (Scheme 1), were used as initiators to initiate the polymerization of MMA at 90°C, and the results are presented in Table I and Figures 1 and 2. The results of comparison experiments in Table I show that the monomer conversion was only 3.89% in 120 min in the MMA/EDCIB system, and this indicated that EDCIB could not initiate the polymerization of MMA alone at 90°C; the thermal-initiation polymerization of MMA was also negligible. The cause is the fact that EDCIB is a photoiniferter, not a thermal iniferter. The polymerization of MMA was successfully carried out in bulk or in solution when EDCIB/CuBr/PMDETA was used as an initiation system, and the molecular weight distributions of the obtained polymers were also relatively narrow (M_w/M_n = 1.19–1.24). The existence of a catalyst (CuBr/PMDETA) improved the C—S bond dissociation by the coordination of copper with the initiator through a Cu—S bond.[30,31] The polymerization rate in solution was slower than that in bulk because of the lower concentration of the initiator in solution. The faster polymerization rate in anisole versus that in toluene was attributed to the different homogeneities of the reaction system in different solvents, and this was consistent with the results reported.[26,32] As

Scheme 1 Chemical structures of DCIA, EDCIB, and EBDCIB.

2-(N,N-diethyldithiocarbamyl) isobutyric acid ester (DCIA)

Ethyl 2-N, N-(diethylamino)dithiocarbamoyl -isobutyrate (EDCIB)

Ethyl 2-N, N-(dibenzylamino)dithiocarbamo yl-isobutyrate (EBDCIB)

TABLE I
Results of Comparison Experiments for the Polymerization of MMA Initiated by EDCIB

$[MMA]_0/[EDClB]_0/$ $[CuBr]_0/[PMDETA]_0$	Time (min)	Conversion (%)	$M_{n(GPC)}$	$M_{n(th)}$	M_w/M_n
$200 : 1 : 0 : 0^a$	40	Trace	—	—	—
	120	3.89	$<10^5$	—	—
$200 : 1 : 2 : 6^a$	20	46.25	27,600	9,500	1.21
	40	68.72	32,800	13,900	1.22
$200 : 1 : 2 : 6^b$	20	14.31	20,300	3,100	1.19
	40	29.14	23,500	6,000	1.20
$200 : 1 : 2 : 6^c$	20	24.27	20,500	5,100	1.20
	40	43.02	22,500	8,800	1.24

The polymerization temperature was 90°C.
[a] $[MMA]_0 = 9.46$ mol/L.
[b] $[MMA]_0 = 4.73$ mol/L; MMA/toluene = 1/1 (v/v).
[c] $[MMA]_0 = 4.73$ mol/L; MMA/anisole = 1/1 (v/v).

shown in Table I and Figure 2, the M_ns were higher than the theoretical number-average molecular weights ($M_{n(th)}$s) determined with the following equation: $M_{n(th)} = ([M]_0/[I]_0) \times M_M \times$ Conversion $+ M_I$, where $[M]_0$ and $[I]_0$ are the initial concentrations of the monomer and initiator, respectively, and M_M and M_I are the molecular weights of the monomer and initiator, respectively. This indicated that the initiator efficiencies ($M_{n(th)}/M_n$) were relatively low. We also changed the molar ratios between the monomer and other components and carried out similar experiments at other temperatures (80 and 100°C); however, the initiator efficiency was not obviously elevated. That M_n was higher than $M_{n(th)}$ predicted by $[M]_0/[I]_0$ indicated either inefficient initiation or chain coupling (at most, one twice higher than the predicted $M_{n(th)}$ can be formed by bimolecular radical coupling).[33] Okamoto et al.[34] reported similar results. As shown Figure 1, the linearity of

the semilogarithmic plots of ln $[M]_0/[M]$ versus the polymerization time indicated that the polymerizations were pseudo-first-order with respect to the monomer in all cases. Figure 1 shows that the slight change in the chemical structures of the initiators had no obvious effect on the polymerization rates of MMA. As shown in Figure 2, the $M_{n(GPC)}$s of PMMA increased linearly with the monomer conversions. This evidence together with the narrow molecular weight distributions of the polymers ($M_w/M_n \leq 1.36$ in all cases) indicated that well-defined PMMA could be obtained via ATRP initiated by these systems.

ATRPs of St

In our previous studies, we found that initiators bearing DC groups or DC derivative groups, such as EDDCB,[26] NMDC,[27] and BDC,[35] were highly efficient initiators for ATRP of St. To further investigate the
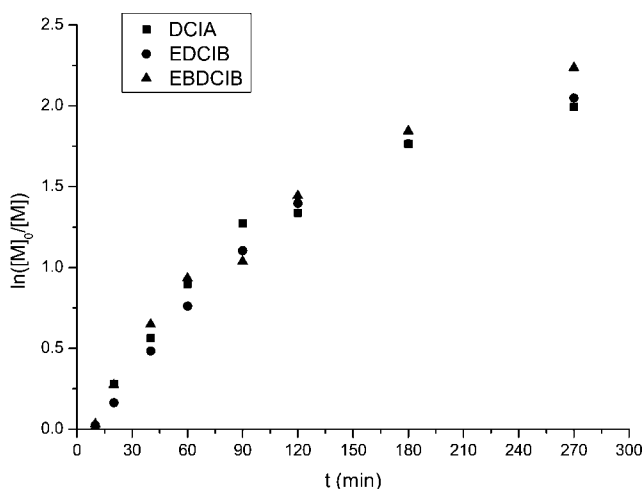

Figure 1 Kinetics of the solution ATRPs of MMA at 90°C with anisole as a solvent initiated by three different initiators (polymerization conditions: $[MMA]_0/[I]_0/[CuBr]_0/[PMDETA]_0 = 200 : 1 : 2 : 6$; MMA/anisole = 1/1 (v/v).
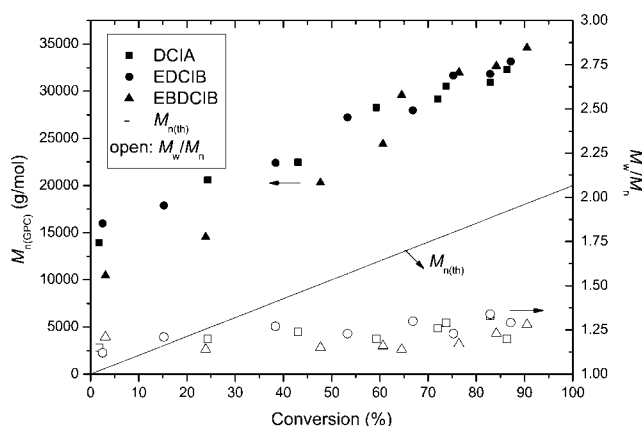

Figure 2 Dependence of the molecular weight and the molecular weight distribution (M_w/M_n) on the monomer conversion for the solution ATRPs of MMA in anisole. For the polymerization conditions, see Figure 1.

TABLE II
Results for the Bulk Polymerization of St Initiated by Different Systems

$[St]_0/[I]_0/[CuBr]_0/$ $[PMDETA]_0$	Temperature (°C)	Time (h)	Conversion (%)	$M_{n(GPC)}$	$M_{n(th)}$	M_w/M_n
$100:1:0:0^a$	115	6	40.93	32,000	4,200	1.84
		16	69.26	33,500	7,500	1.78
$100:1:2:6^a$	115	6	69.17	8,100	7,400	1.06
		16	99.76	11,400	10,600	1.11
$100:1:2:6^b$	115	6	69.54	8,000	7,500	1.06
		16	99.87	11,500	10,700	1.07
$100:1:2:6^c$	115	6	68.79	7,900	7,300	1.05
		16	99.39	12,700	10,600	1.07
$100:1:2:6^c$	100	16	31.37	3,600	3,300	1.08
$100:1:2:6^c$	90	16	Trace	—	—	—

The initial St concentration was 8.68 mol/L.
[a] EDCIB.
[b] EBDCIB.
[c] DCIA.

properties of this kind of initiator, the polymerizations of St initiated by different systems were carried out, and the results are presented in Table II. From Table II, we can see that the polymerizations could occur only in the presence of EDCIB without the CuBr/PMDETA system; however, almost no PMMA was obtained in a similar system presented previously (Table I). This observation could be ascribed to the fact that the thermal-initiation polymerization of St was easier than that of MMA because the monomer radicals from St are more easily produced than those from MMA;[36–39] moreover, the three iniferter reagents in this article are photoiniferters, not thermal iniferters, so they mainly produce radicals under ultraviolet (UV)-irradiation conditions without other catalysts.[2] The molecular weights were much higher than the theoretical ones, and the value of the molecular weight distribution was high ($M_w/M_n \geq 1.78$) in the St/EDCIB system; this indicated that the polymerization was uncontrolled. When the catalyst (CuBr/PMDETA) was added to the system, the polymerization of St was carried out via an ATRP mechanism. The polymerization rate of St in the EDCIB/CuBr/PMDETA system was faster than that in the St/EDCIB system. The effect of the chemical structures of the initiators on the polymerization of St was also negligible. Moreover, the molecular weights of the obtained polymers were close to the theoretical values, and this indicated a high initiator efficiency. The molecular weight distributions of the synthesized polymers in the presence of the catalyst were very narrow in all cases ($M_w/M_n = 1.05$–1.11). From Table II, we also can see that the polymerization rate decreased with the polymerization temperature, and almost no polymer was obtained in 16 h when the reaction temperature decreased to 90°C ($[St]_0/[DCIA]_0/[CuBr]_0/[PMDETA]_0 = 100:1:2:6$). Therefore, for this polymerization system, the

reaction temperature should not be below 90°C. These results indicated that the polymerizations of St initiated by EDCIB (EBDCIB or DCIA)/CuBr/PMDETA systems were well controlled.

End-group analysis of the polymer and chain extension

According to our reported results,[26,27,35] there were almost no exchange reactions between the DC group and the halogen atoms in the catalyst system. To further confirm this conclusion, we also prepared well-defined PMMA samples, using EBDCIB/CuBr (CuCl)/PMDETA systems, and PS samples, using DCIA/CuBr (CuCl)/PMDETA systems. The samples were both characterized by ^{1}H-NMR spectroscopy, as shown in Figures 3 and 4. We chose EBDCIB as the initiator to synthesize PMMA because the chemical shifts of phenyl could be seen clearly in the ^{1}H-NMR spectroscopy of PMMA and were not affected by other signals. As shown in Figure 3, the signals at $\delta = 7.01$–7.52 ppm correspond to the phenyl of the initiator, and the chemical shifts at $\delta = 4.75$–5.40 ppm due to the methylene protons of N,N-(dibenzylamino)dithiocarbamoyl [$—S_2CN(CH_2Ph)_2$] were all seen clearly. In Figure 4, we also can see the corresponding signals at 3.40–4.20 ppm (b), which are assigned to the methylene protons of the diethylthiocarbamoylthiyl group [$—S_2CN(CH_2CH_3)$]. The chemical shifts at $\delta = 4.60$–5.21 ppm (a) are ascribed to the St unit adjacent to the terminal DC group, which departed from the repeated units in the main chain because of the effect of an ω-DC end group. In these two systems, the same results were obtained when the catalyst was the CuCl/PMDETA complex. These data demonstrate the existence of the DC groups at the end of the polymer chains under different experimental conditions. About the question of halogen-
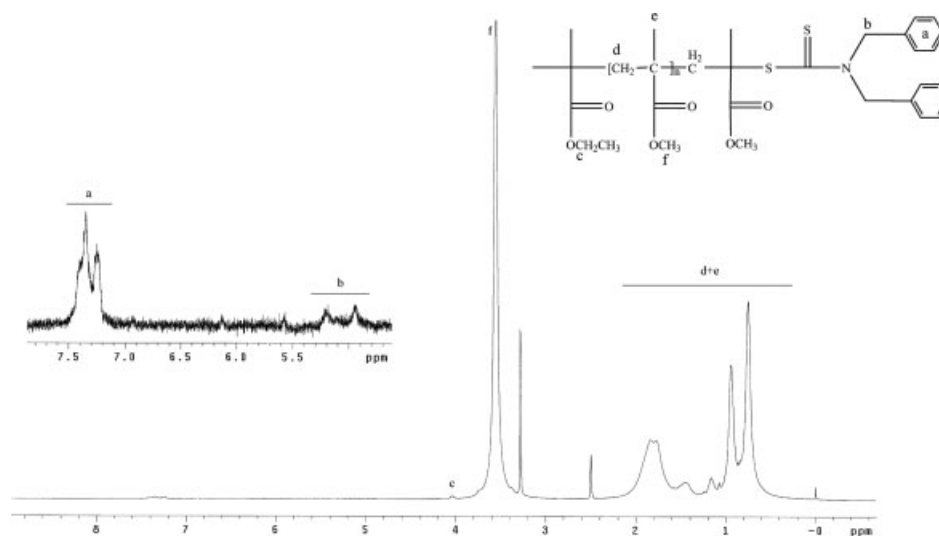
Figure 3 ^{1}H-NMR spectroscopy (400 MHz) of PMMA initiated with the EBDCIB/CuBr/PMDETA system in anisole at 90°C (in CDCl$_3$; [MMA]$_0$/[EBDCIB]$_0$/[CuBr]$_0$/[PMDETA]$_0$ = 200 : 1 : 2 : 6; MMA/anisole = 1 : 1 (v/v); sample $M_{n(GPC)}$ = 26,900; sample M_w/M_n = 1.25).

exchange reactions, different research groups have presented different results. Sawamoto et al.[40] and Matyjaszewski et al.[41] both reported a mixture of Cl and Br in the ω-end groups; however, Haddleton et al.[42] found results differing from our results. In our research system, no similar exchange reactions were found, and this may have been influenced by the different reaction conditions.

As we know, MALDI-TOF mass spectrometry has been recently employed for the analysis of polymers obtained by LFRP techniques to provide structural and molecular mass information that is not obtainable by other analytical methods.[43–46] The molecular weight of the polymer sample used in MALDI-TOF analysis is usually relatively low to enhance its accuracy.[43] Therefore, we selected PS sample prepared with the DCIA/CuBr(CuCl)/PMDETA system to conduct MALDI-TOF experiments because a PS sample with a low molecular weight was easier to synthesize than PMMA in this case. In Figure 5, the MALDI-TOF mass spectrum of PS is presented and shows only one distribution consisting of a number of peaks with a peak-to-peak mass increase of about 104 g/mol, corresponding to the molar mass of the monomer unit, in the range of experimental error ($\pm$4 amu in a linear mode).[45] However, the mass val-
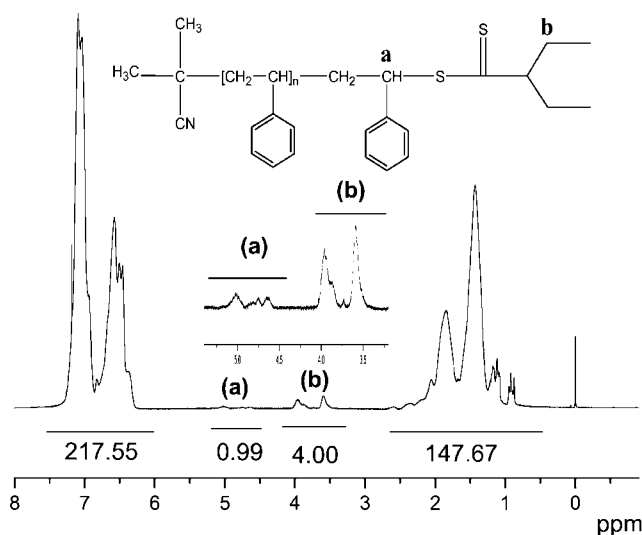

Figure 4 ^{1}H-NMR spectroscopy (400 MHz) of PS prepared with the DCIA/CuBr/PMDETA system in bulk ([St]$_0$/[DCIA]$_0$/[CuBr]$_0$/[PMDETA]$_0$ = 50 : 1 : 2 : 6) at 115°C (CDCl$_3$; sample $M_{n(GPC)}$ = 4400; sample M_w/M_n = 1.12).
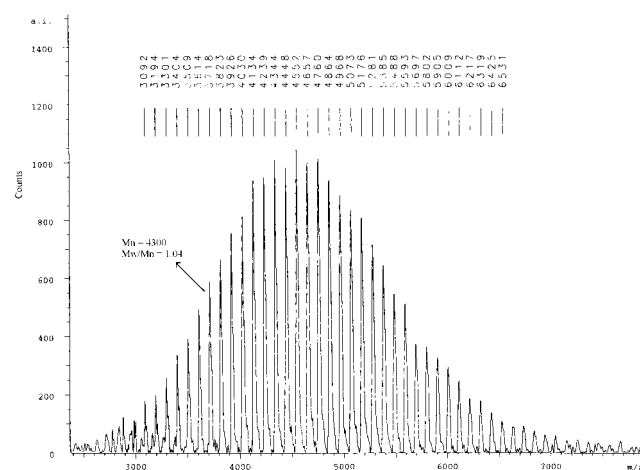

Figure 5 MALDI-TOF mass spectrum of PS. PS was synthesized with the DCIA/CuBr/PMDETA system as the initiating system ([St]$_0$/[DCIA]$_0$/[CuBr]$_0$/[PMDETA]$_0$ = 50 : 1 : 2 : 6) in bulk at 115°C (time = 5 h; conversion = 80.20%; $M_{n(th)}$ = 4400).

ues indicated that the PS samples carried not DC groups but an olefin, and this agreed with the values for $\{[(CH_3)_2(CN)—(St)_{n-1}CH=CHPh]/Ag\}^+$. As already shown by ^{1}H-NMR spectra (Fig. 4), the unsaturated ω-end does not result from side reactions during the process of polymerization but is due to the decomposition of the DC terminus of PS samples under laser ionization, as reported.[43] Furthermore, the molecular weight values obtained by NMR ($M_{n(NMR)}$ = 4500 g/mol, calculated from Fig. 4), MALDI-TOF (M_n = 4300 g/mol), and GPC ($M_{n(GPC)}$ = 4400 g/mol) were consistent with the theoretical value ($M_{n(th)}$ = 4400 g/mol). The other PS sample obtained with the DCIA/CuCl/PMDETA system also was investigated with MALDI-TOF analysis, and the results were similar to those already mentioned. These observations led us to conclude that the polymerization of St was well controlled.

Another method for proving the existence of DC and DC derivatives was the chain-extension experiment under UV-light-irradiation conditions. The obtained PMMA samples were used as macroinifers to carry out the chain-extension experiments under UV irradiation, and the results are exhibited in Figure 6. M_n of the synthesized polymers increased from 26,900 to 86,900 g/mol, and this confirmed the presence of DC groups. The increases in the molecular weight distribution values from 1.25 to 1.78 could be attributed to the side reactions under UV-irradiation conditions and some terminated chains in macroiniferters.[26,27,35]

Mechanism of polymerization

On the basis of the data above, a possible polymerization mechanism is depicted in Scheme 2. As presented in Scheme 2(I), the redox reaction of the initiator and Cu(I) species results in a free radical, which initiates the monomer and produces a mono-
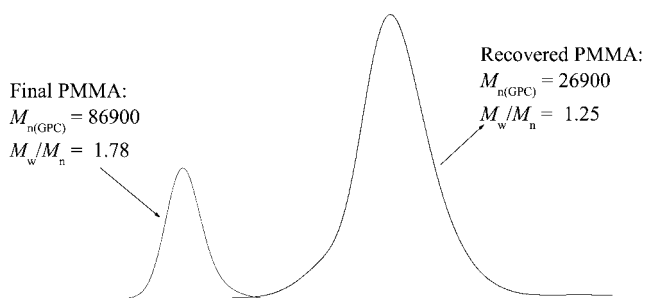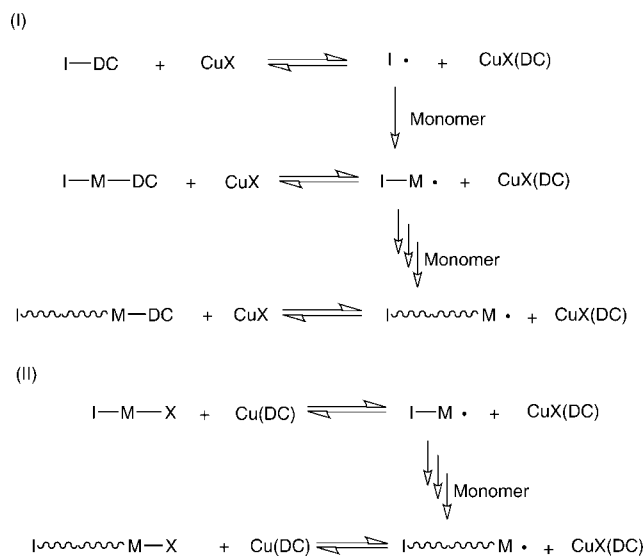

Scheme 2 Supposed mechanism of polymerization with the DCIA (or EDCIB or EBDCIB)/CuBr/PMDETA system.

mer radical in the initiating step. The following propagation is well controlled because of a low and stationary concentration of actives species resulting from the fast dynamic equilibrium between the active and dormant species. In this equilibrium, DC or a DC derivative group acts as a transfer atom instead of a halogen atom (X = Br or Cl). As shown in Scheme 2(II), side reactions are avoided, as proven by the reported results. Therefore, the mechanism of polymerization is a common ATRP process, as reported by Sawamoto et al.[4] and Matyjaszewski and Xia.[5]

CONCLUSIONS

Well-defined PMMA and PS bearing photolabile groups were successfully synthesized via ATRPs of MMA and St initiated by three novel initiators. The effects of different chemical structures of the initiators on the polymerization of MMA and St were negligible. The polymerization rate of MMA in toluene was slower than that in anisole. The initiator efficiency of this kind of initiator to MMA was lower than that to St. Exchange reactions between the DC group and the halogen atoms (Br or Cl) in the catalyst were not found.

Figure 6 GPC curves of the recovered PMMA and final PMMA. The PMMA used in the chain-extension experiment was synthesized with the EBDCIB/CuBr/PMDETA system ([MMA]$_0$/[EBDCIB]$_0$/[CuBr]$_0$/[PMDETA]$_0$ = 200 : 1 : 2 : 6) in anisole at 90°C (chain-extension experimental conditions: [MMA]$_0$/[Macroinitiator]$_0$ = 200 : 1; 20 h under UV-light irradiation at room temperature; conversion = 34.8%).

References

1. Ostu, T.; Yoshida, M. Makromol Chem Rapid Commun 1982, 3, 127.
2. Ostu, T. J Polym Sci Part A: Polym Chem 2000, 38, 2121.
3. Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. PCT Int. Pat. Appl. WO 9801478 Al (1998).
4. Kamigaito, M.; Ando, T.; Sawamoto, M. Chem Rev 2001, 101, 3689.

5. Matyjaszewski, K.; Xia, J. H. Chem Rev 2001, 101, 2921.

6. Ostu, T.; Yoshida, M.; Tazaki, T. Makromol Chem Rapid Commun 1982, 3, 133.

7. Georges, M. K.; Veregin, P. R. N.; Kazmaier, P. M.; Hamer, G. K. Macromolecules 1993, 26, 2987.

8. Hawker, C. J.; Bosman, A. W.; Harth, E. Chem Rev 2001, 101, 3661.

9. Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Macromolecules 1998, 31, 5559.

10. Moad, G.; Rizzardo, E.; Tang, S. H. Aust J Chem 2005, 8, 379.

11. Barner-Kowollik, C.; Davis, T. P.; Heuts, J. P. A.; Stenzel, M. H.; Vana, P.; Whittaker, M. J Polym Sci Part A: Polym Chem 2003, 41, 365.

12. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. Macromolecules 1995, 28, 1721.

13. Wang, J. S.; Matyjaszewski, K. Macromolecules 1995, 28, 7901.

14. Wang, J. S.; Matyjaszewski, K. J Am Chem Soc 1995, 117, 5614.

15. Percec, V.; Narboiu, B. Macromolecules 1995, 28, 7970.

16. Li, P.; Qin, S. H.; Qin, D. Q.; Qiu, K. Y. Polym Int 2004, 53, 756.

17. Kroeze, E.; ten Brinke, G.; Hadziioannou, G. Macromolecules 1995, 28, 6650.

18. Chen, X. P.; Qiu, K. Y. Macromolecules 1999, 32, 8711.

19. Li, P.; Qiu, K. Y. Polymer 2002, 43, 3019.

20. Qin, D. Q.; Qin, S. H.; Qiu, K. Y. J Polym Sci Part A: Polym Chem 2000, 38, 101.

21. Qin, D. Q.; Qin, S. H.; Qiu, K. Y. Macromolecules 2000, 33, 6987.

22. Li, P.; Qiu, K. Y. J Polym Sci Part A: Polym Chem 2002, 40, 2093.

23. Li, P.; Qiu, K. Y. Macromol Rapid Commun 2002, 23, 1124.

24. Ishizu, K.; Kakinuma, H. J Polym Sci Part A: Polym Chem 2005, 43, 63.

25. Zhang, W.; Zhu, X. L.; Zhu, J.; Cheng, Z. P. Macromol Chem Phys 2004, 205, 806.

26. Zhang, W.; Zhu, X. L.; Zhu, J.; Chen, J. Y. J Polym Sci Part A: Polym Chem 2006, 44, 32.

27. Zhang, W.; Zhou, N. C.; Zhu, J.; Sun, B.; Zhu, X. L. J Polym Sci Part A: Polym Chem 2006, 44, 510.

28. Ishizu, K.; Katsuhara, H.; Kawauchi, S.; Furo, M. J Appl Polym Sci 2005, 95, 413.

29. Ishizu, K.; Khan, R. A.; Ohta, Y.; Furo, M. J Polym Sci Part A: Polym Chem 2004, 42, 76.

30. Li, P.; Qiu, K. Y. J Polym Sci Part A: Polym Chem 2001, 39, 4001.

31. Zhang, W.; Zhu, X. L.; Cheng, Z. P.; Zhu, J.; Xu, W. J. J Macromol Sci Pure Appl Chem 2004, 41, 49.

32. Zhang, H. Q.; Schubert, U. S. J Polym Sci Part A: Polym Chem 2004, 42, 4882.

33. Matyjaszewski, K.; Davis, T. P. In Handbook of Radical Polymerization; Matyjaszewski, K.; Davis, T. P., Eds.; Wiley: New York, 2002; Chapter 8, p 361.

34. Miura, Y.; Satoh, T.; Narumi, A.; Nishizawa, O.; Okamoto, Y.; Kakuchi, T. J Polym Sci Part A: Polym Chem 2006, 44, 1436.

35. Zhang, W.; Zhu, X. L.; Zhu, J.; Cheng, Z. P. Presented at the 8th Society of Polymer Science Japan International Polymer Conference, Fukuoka, Japan, 2005.

36. Devonport, W.; Michalak, L.; Malmstron, E.; Mate, M.; Kurdi, B.; Hawker, C. J. Macromolecules 1997, 30, 1929.

37. Matyjaszewski, K.; Shigemoto, T.; Frechet, J. M. J.; Leduc, M. Macromolecules 1996, 29, 4167.

38. Acar, A. E.; Yagci, M. B.; Mathias, L. J. Macromolecules 2000, 33, 7700.

39. Nanda, A. K.; Hong, S. C.; Matyjaszewski, K. Macromol Chem Phys 2003, 204, 1151.

40. Ando, T.; Kamigaito, M.; Sawamoto, M. Tetrahedron 1997, 53, 1545.

41. Matyjaszewski, K.; Wang, J. L.; Grimaud, T.; Shipp, D. A. Macromolecules 1998, 31, 1527.

42. Haddleton, D. M.; Heming, A. M.; Kukulj, D.; Jackson, S. G. Chem Commun 1998, 1719.

43. Nonaka, H.; Ouchi, M.; Kamigaito, M.; Sawamoto, M. Macromolecules 2001, 34, 2083.

44. Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. Macromolecules 1997, 30, 2190.

45. Matyjaszewski, K.; Jo, S. M.; Paik, H. J.; Gaynor, S. G. Macromolecules 1997, 30, 6398.

46. He, T.; Zheng, G. H.; Pan, C. Y. Macromolecules 2003, 36, 5960.