

Triphenylphosphine as Reducing Agent for Copper(II)-catalyzed AGET ATRP*

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Abstract Triphenylphosphine (TPP) was used as reducing agent to continuously generate the Cu(I) activator in copper(II)-catalyzed activators generated by electron transfer atom transfer radical polymerization (AGET ATRP). For example, the polymers prepared with a molar ratio of $[MMA]_0/[EBiB]_0/[CuCl_2]_0/[PMDETA]_0/[TPP]_0 = 500/1/0.1/0.5/0.5$ had controlled molecular weights and low molecular weight distribution (M_w/M_n) values (~ 1.2). TPP as a commercial reducing agent provides a convenient copper-catalyzed AGET ATRP procedure for the preparation of well-defined polymers.

Keywords: ATRP; AGET ATRP; Reducing agent; Triphenylphosphine (TPP).

INTRODUCTION

Reversible-deactivation radical polymerizations (RDRPs) are the robust methods to prepare well-defined polymers^[1]. Among them, atom transfer radical polymerization (ATRP) is one of the powerful techniques to synthesize well-defined polymers with complex architecture, such as block, stars and graft copolymers^[2–7]. Some methods of ATRP including reverse ATRP^[8,9], simultaneous reverse and normal initiation (SR&NI) ATRP^[10–12], initiators for continuous activator regeneration (ICAR) ATRP^[13,14] and activators (re)generated by electron transfer (A(R)GET) ATRP^[15–23] were developed to reduce the amount of catalyst.

In these systems, oxidatively stable Cu(II) complexes were reduced to the Cu(I) complexes at the beginning of the reaction with radicals formed by decomposition of radical initiators or various reducing agents. These initiating systems laid foundation for the development of the next generation of ATRP systems, carried out in the presence of small amounts (ppm) of the Cu-complex in which the activator catalyst complexes, the Cu(I) species, are continuously regenerated during the polymerization. In A(R)GET ATRP, the presence of a large excess of the reducing agent enables the polymerization to be conducted with very small amounts of catalysts. Therefore, the absolute amount of copper catalyst in A(R)GET ATRP can be decreased under that in normal ATRP conditions without affecting the rate of polymerization. Development of A(R)GET ATRP has profound biological implications because it lowers the amount of necessary catalyst, while still allowing excellent control over molecular weight and molecular weight distribution.

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Reducing agents, which are unable to initiate new polymer chains were regularly used in A(R)GET ATRP. Following early reports that zero-valent Cu could be used as a reducing agent to react with Cu(II) and enhance the rate of polymerization in ATRP^[24], the A(R)GET principle was demonstrated using tin(II) 2-ethylhexanoate ($\text{Sn}(\text{EH})_2$)^[25], ascorbic acid (AsAc)^[26] or triethylamine^[27] as the reducing agents, which reacted with the Cu(II) complexes to generate the Cu(I) ATRP activators. Apart from these, zero-valent metals^[28], glucose^[29], phenol^[30], methylaluminoxane^[31] and N_2H_4 ^[32] were also successfully used as an efficient reducing agent in A(R)GET ATRP.

Phosphorus-containing compounds are rarely used in copper-catalyzed ATRP. They were commonly used in most transition metals-catalyzed ATRP^[33], including rhenium, ruthenium, iron, rhodium, nickel and palladium. However, phosphorous ligands are less effective due to the inappropriate electronic effects or unfavorable binding constants for copper-catalyzed ATRP. Using oxidatively stable FeCl_3 /phosphorus ligands^[34] as a catalyst complex, the iron-mediated AGET ATRP of MMA and St can be conducted successfully in the presence of a limited amount of air. Recently, Noh and coworkers developed the iron(III)-catalyzed ATRP with phosphorus ligands in the absence of any conventional radical initiator or reducing agent but with the normal ATRP initiators^[35–40]. The components often include vinyl monomer, ATRP initiator, higher oxidation state iron(III)-catalyst and phosphorus-containing ligand. Various types of phosphorus-containing ligands can be used as ligand and reducing agent, simultaneously. As one of the frequently used ligands, triphenylphosphine (TPP) has been successfully applied to coordinate all the aforementioned transition metals. The reducing of CuCl_2 and CuBr_2 with TPP was also reported for a long time^[41]. Therefore, TPP has a possibility to be used as a reducing agent for AGET ATRP. Herein, TPP was successfully applied as a reducing agent for copper-catalyzed AGET ATRP. Polymerization of MMA was well-controlled to prepare polymers with predetermined molecular weights and with low M_w/M_n values. The use of TPP provides a commercial and controlled ATRP procedure, and reduced the costs of removing catalyst from polymers.

EXPERIMENTAL

Materials

Monomers methyl methacrylate (MMA) (> 99%), styrene (St) (> 99%) and glycidyl methacrylate (GMA) (> 99%) were purchased from Shanghai Chemical Reagents Co. Ltd (Shanghai, China). The monomers were washed three times with an aqueous solution of sodium hydroxide (NaOH) (5 wt%), followed by washing with deionized water until the solution was neutralized. The resulting solution was then dried over anhydrous magnesium sulfate, distilled twice at reduced pressure, and stored at $-18\text{ }^\circ\text{C}$. Ethyl 2-bromoisobutyrate (EBiB) (98%) and (1-bromoethyl) benzene (PEBr) (97%) were purchased from Acros and used as received. Copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (> 99%), Copper(II) bromide (CuBr_2) (> 99%), N,N,N',N'',N'' -pentamethyldiethylenetriamine (PMDETA) (98%) and ascorbic acid (AsAc) (> 99.7%) were purchased from Shanghai Chemical Reagents Co. Ltd (Shanghai, China) and used as received. Triphenylphosphine (TPP, 99%, Sigma-Aldrich Co. Ltd) was recrystallized to constant melting point (m.p. $79.5\text{--}80\text{ }^\circ\text{C}$.) from absolute alcohol. Tetrahydrofuran (THF) (99.9%, Shanghai Chemical Reagents Co. Ltd.) and methanol (99.9%, Shanghai Chemical Reagents Co. Ltd.) were used as received. All other chemicals were obtained from Shanghai Chemical Reagents Co. Ltd and used as received unless mentioned.

Typical Procedure for AGET ATRP of MMA

A typical bulk polymerization procedure with the molar ratio of $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{CuCl}_2]_0/[\text{PMDETA}]_0/[\text{TPP}]_0 = 500/1/0.1/0.5/0.5$ is as follows. A mixture was obtained by adding $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.64 mg, 0.00376 mmol), TPP (4.9 mg, 0.0188 mmol), MMA (2.0 mL, 18.8 mmol), EBiB (5.7 μL , 0.0376 mmol), PMDETA (3.9 μL , 0.0188 mmol) to a dried ampoule with a stir bar. The ampoule was flame-sealed and then transferred into an oil bath held by a thermostat at the desired temperature ($90\text{ }^\circ\text{C}$) to polymerize under stirring. After the desired polymerization time, the ampoule was cooled by immersing into iced water. Afterward, the ampule was opened, and the contents were dissolved in THF ($\sim 2\text{ mL}$) and passed through a small basic Al_2O_3 chromatographic

column to remove copper salts. The resulting solution was precipitated into a large amount of methanol (~200 mL) with stirring. The polymer obtained by filtration was dried under vacuum until constant weight at 50 °C. The monomer conversion was determined gravimetrically.

Typical Procedures for Chain Extension Using PMMA as Macroinitiator

The PMMA sample ($M_{n,SEC} = 17600$ g/mol, $M_w/M_n = 1.07$) obtained with the molar ratio of $[MMA]_0/[EBiB]_0/[CuCl_2]_0/[PMDTA]_0/[TPP]_0 = 500/1/0.1/0.5/0.5$ in the presence of air was used as the macroinitiator for the chain extension reaction at the molar ratio of $[MMA]_0/[PMMA]_0/[CuCl_2]_0/[PMDTA]_0/[TPP]_0 = 500/1/0.1/0.5/0.5$. The polymerization procedure is as follows: PMMA (330.9 mg, 0.0188 mmol) was dissolved in $CuCl_2 \cdot 2H_2O$ (0.32 mg, 0.00188 mmol), TPP (2.5 mg, 0.0094 mmol), MMA (1.0 mL, 9.4 mmol) and PMDTA (2 μ L, 0.0094 mmol) were added. The rest of the procedure was the same as that described above. The chain-extension reaction was carried out in bulk under stirring at 90 °C. The monomer conversion was 22.9% in 6 h. The M_n and M_w/M_n values were determined by SEC ($M_{n,SEC} = 31800$ g/mol, $M_w/M_n = 1.25$).

Characterization

The number-average molecular weight ($M_{n,SEC}$) and molecular weight distribution (M_w/M_n) values of the resulting polymers were determined using a Waters 1515 size exclusion chromatography (SEC) equipped with a refractive-index detector (Waters 2414), using HR 1 (pore size: 10 nm, 100–5000 Da), HR 2 (pore size: 50 nm, 500–20000 Da) and HR 4 (pore size 1000 nm, 50–100000 Da) columns (7.8×300 mm, 5 μ m beads size) with measurable molecular weights ranging from 10^2 – 5×10^5 g/mol. THF was used as the eluent at a flow rate of 1.0 mL/min and 30 °C. SEC samples were injected using a Waters 717 plus autosampler and calibrated with poly(methyl methacrylate) standards purchased from Waters. ^1H -NMR spectrum of the obtained polymer was recorded on an INOVA 400 MHz nuclear magnetic resonance instrument using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard. The UV-Vis spectra were recorded on a Shimadzu UV3150 spectrophotometer with a quartz UV-Vis cell (1 mm path length) and acetonitrile (CH_3CN) was using as solvent. Matrix assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF) measurement was performed using a Bruker Autoflex III (MALDI-TOF) mass spectrometer equipped with a 337 nm nitrogen laser.

RESULTS AND DISCUSSION

In order to analyze the reduction, the experiments were carried out at a molar ratio of $CuCl_2/PMDTA = 1:1$ in the presence or absence of TPP for comparison (Table 1, entry 1, 3). The controllability of the polymerization was obviously improved by adding TPP. When PMDTA in entry 1 was replaced by TPP (entry 2), the polymerization had bad controllability. The polymerizations using bpy as ligand were also carried out in presence or absence of TPP (Table 1, entries 4, 5). However, there was no polymer produced without TPP even after 4 days. The controlled polymer ($M_{n,SEC} = 27900$ g/mol, $M_w/M_n = 1.21$) was obtained in the presence of TPP after 2 days. Then, UV-Visible spectroscopy was used to confirm the reduction of Cu(II) to Cu(I) by TPP as shown in Fig. 1. Acetonitrile was chosen as a solvent because the Cu(II) complex has high solubility in it. The UV-Visible spectrum of $CuCl_2/PMDTA/TPP$ complexes indicated a remarkably decrease of absorption compare with that of $CuCl_2/PMDTA$, confirming the effect of TPP on reduction of Cu(II) to Cu(I).

Table 1. AGET ATRP of MMA under different experimental conditions

Entry	Time (h)	Polymerization conditions	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,SEC}$ (g/mol)	M_w/M_n
1 ^a	8.0	500:1:1:1:0	54.9	27400	30200	1.33
2 ^a	24.0	500:1:1:0:1	2.7	1300	high	high
3 ^a	4.0	500:1:1:1:1	60.3	30100	31900	1.15
4 ^b	96.0	500:1:1:2:0	0	–	–	–
5 ^b	48.0	500:1:1:2:2	52.6	26300	27900	1.21

Polymerization conditions: ^a $[MMA]_0/[EBiB]_0/[CuCl_2]_0/[PMDTA]_0/[TPP]_0$;

^b $[MMA]_0/[EBiB]_0/[CuCl_2]_0/[bpy]_0/[TPP]_0$, MMA = 2.0 mL, temperature = 90 °C.

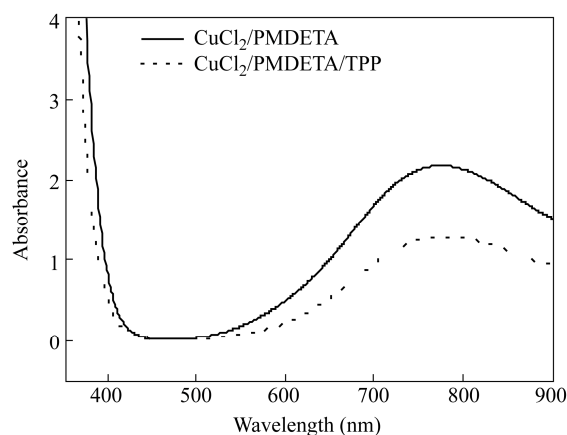


Fig. 1 UV-Visible spectra of $\text{CuCl}_2/\text{PMDETA}$ in the absence (solid) or presence (dot) of TPP in acetonitrile at 25 °C ($[\text{CuCl}_2]_0 = 10^{-2}$ mol/L, $[\text{PMDETA}]_0 = 10^{-2}$ mol/L and TPP = 10^{-2} mol/L if added)

As an efficient catalyst system, it is necessary to reduce the amount of catalyst. In AGET ATRP, a sufficiently large excess of PMDETA or TPP were usually used to reduce the Cu catalyst. The additional reducing agent can improve the controllability, and excess aliphatic nitrogen-based ligands^[42, 43] can serve not only as ligands but also as reducing agents in copper-mediated AGET ATRP. Table 2 illustrates the results of AGET ATRP of MMA, GMA and St in the presence of various amounts of $\text{CuCl}_2/\text{PMDETA}$ complexes and TPP, respectively. Firstly, the result of the polymerization in the presence of TPP (entry 2 in Table 2) with the similar conversion of entry 1, showed the significantly lower M_w/M_n (~1.14). The amount of copper was varied from 340 down to $\delta = 34$ versus MMA. The controllability of $M_{n,\text{SEC}}$ and M_w/M_n was good by reducing the amount of Cu catalyst (from $\delta = 340$ to $\delta = 68$, Table 2, entries 3–5). However, with $\delta = 34$ Cu catalyst (Table 2, entry 6), the molecular weight was higher than the theoretical one with broad M_w/M_n (1.45), which indicates that there was not enough Cu to assure a fast exchange between active and dormant species. In order to further investigate the systems for other monomers, TPP as reducing agent for copper-mediated AGET ATRP of GMA and St was studied, and the results are listed in entries 7–8. The $M_{n,\text{SEC}}$ values were close to their corresponding theoretical ones and M_w/M_n values of the obtained polymers were low, indicating a well-controlled polymerization process. Therefore, we demonstrated that TPP can be used as efficient reducing agents for copper(II)-catalyzed AGET ATRP for the first time.

Table 2. Synthesis of PMMA, PGMA and PST by A(R)GET ATRP using TPP as reducing agent

Entry	Time (h)	Polymerization conditions	Cu	Conv. (%)	$M_{n,\text{th}}$ (g/mol)	$M_{n,\text{SEC}}$ (g/mol)	M_w/M_n
1 ^a	5.5	500:1:0.1:0.5:0	340	60.4	37000	30100	1.53
2 ^a	6.5	500:1:0.1:0.5:0.5	340	62.5	36200	31900	1.14
3 ^a	6.0	500:1:0.1:0.5:0.5	340	57.9	25200	26200	1.14
4 ^a	6.0	500:1:0.05:0.5:0.5	170	60.4	30200	31100	1.19
5 ^a	6.0	500:1:0.02:0.5:0.5	68	62.7	31300	33800	1.24
6 ^a	6.0	500:1:0.01:0.5:0.5	34	68.1	34000	39600	1.45
7 ^b	6.0	500:1:0.1:0.5:0.1	355	57.7	28800	25700	1.13
8 ^c	12.0	500:1:0.1:0.5:0.5	300	42.1	21900	20900	1.21

Polymerization conditions: $[\text{M}]_0:[\text{EBiB}]_0:[\text{CuCl}_2]_0:[\text{PMDETA}]_0:[\text{TPP}]_0$, ^a MMA = 2.0 mL, temperature = 90 °C;

^b St = 2.0 mL, anisole = 1.0 mL, temperature = 110 °C; ^c GMA = 2.0 mL, anisole = 1.0 mL, temperature = 60 °C.

To reduce the interference of PMDETA, a molar ratio of $\text{CuCl}_2/\text{PMDETA} = 1:1$ was investigated in Table 3, it can be seen that no polymer was obtained when $[\text{CuCl}_2]_0/[\text{TPP}]_0 = 0.1:0.1$ (Table 3, entry 1). The polymerization rate increased with the increasing TPP amount and M_w/M_n kept low (< 1.15). The results proved further that TPP can act as reducing agent for Cu(II)-catalyst AGET ATRP.

Table 3. Effect of TPP amount on copper-mediated AGET ATRP

Entry	Time (h)	Polymerization conditions	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,SEC}$ (g/mol)	M_w/M_n
1	10.0	500:1:0.1:0.1:0.1	0	—	—	—
2	10.0	500:1:0.1:0.1:0.2	26.0	13000	15200	1.14
3	10.0	500:1:0.1:0.1:0.5	35.4	17700	18400	1.12

Polymerization conditions: $[MMA]_0/[EBiB]_0/[CuCl_2]_0/[PMDETA]_0/[TPP]_0$; MMA = 2.0 mL, temperature = 90 °C.

In order to further investigate the polymerization with adding TPP as reducing agent in detail, the kinetics were studied in the absence and presence of TPP in bulk. Figure 2(a) shows the kinetics of AGET ATRP of MMA using the molar ratio of $[MMA]_0/[EBiB]_0/[CuCl_2]_0/[PMDETA]_0/[TPP]_0 = 500/1/0.1/0.5/(0.5)$ at 90 °C, respectively. From Fig. 2(a), it can be seen that the kinetics in the absence and presence of TPP showed linear plots, indicating that the polymerizations were approximately first-order with respect to the monomer concentration, and that the number of active species remained constant throughout the polymerization. However, the polymerization rate for the AGET ATRP in the absence of TPP was much faster than that in the presence of TPP. By calculating the apparent rate constant of the polymerization, k_p^{app} ($R_p = -d[M]/dt = k_p[P_n \cdot][M] = k_p^{app}[M]$), as determined from the kinetic slopes, a k_p^{app} of $8.84 \times 10^{-5} s^{-1}$ for the bulk polymerization in the presence of TPP and k_p^{app} of $1.26 \times 10^{-4} s^{-1}$ without TPP were obtained, respectively. Meanwhile, an induction period (~ 3.4 h) was observed under both polymerization conditions. This is due to that there needs some time to establish a dynamic equilibrium between the concentration of Cu(II) and Cu(I) species as the reaction proceeded^[44–47]. Figure 2(b) shows the evolution of $M_{n,SEC}$ and M_w/M_n values of PMMA on the conversion for the bulk AGET ATRP of MMA at 90 °C. As shown in Fig. 2(b), it can be seen that the controllability over molecular weight distribution was poor (~ 1.4) without additional reducing agent, which indicated that a suitable reducing agent should be needed for a well-controlled polymerization process. In the presence of TPP, the $M_{n,SEC}$ values of the polymers, being close to the corresponding theoretical ones, increased linearly with monomer conversion while keeping low M_w/M_n values (≤ 1.2). The SEC traces of PMMA showed monomodal profiles in Fig 3. From above discussion, TPP as the reducing agent played an important role in the control of the copper-mediated AGET ATRP of MMA.

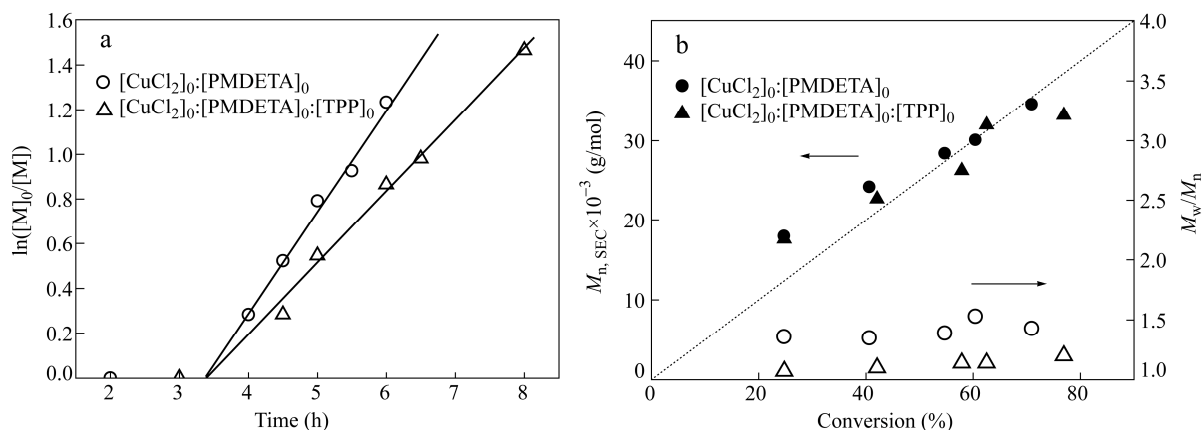


Fig. 2 $\ln([M]_0/[M])$ as a function of time (a) and number-average molecular weight ($M_{n,SEC}$) and molecular weight distribution (M_w/M_n) versus conversion (b) for bulk copper-mediated ATRP of MMA using TPP as the additive. Polymerization conditions: $[MMA]_0/[EBiB]_0/[CuCl_2]_0/[PMDETA]_0/[TPP]_0 = 500/1/0.1/0.5/(0.5)$, MMA = 2.0 mL, temperature = 90 °C.

One of the advantages of the AGET ATRP is to allow the polymerization to be carried out in the presence of limited amounts of air due to the excess use of the reducing agent. Therefore, the bulk AGET ATRP of MMA was investigated without special deoxygenation procedures. Figure 4(a) shows the corresponding kinetics in both cases (with and without TPP, respectively). The first-order kinetics was observed in each case. The

polymerization rate for the AGET ATRP using TPP as the additives was slower than that without TPP. A k_p^{app} of $9.09 \times 10^{-5} \text{ s}^{-1}$ in the case of TPP and k_p^{app} of $1.21 \times 10^{-4} \text{ s}^{-1}$ in the absence of TPP were obtained, respectively. Meanwhile, it can be seen that an induction period in the presence of air ($\sim 5.5 \text{ h}$) was longer than that without air. This is due to that oxygen from air in the reaction system should consume some reducing agent as reported in our previous works^[16]. From Fig. 4(b), it can also be seen that the $M_{n,\text{SEC}}$ values of the polymers, being close to the corresponding theoretical ones, increased linearly with monomer conversion in the presence of TPP. At the same time, the M_w/M_n values in the presence of TPP (< 1.21) were relatively narrower than that without TPP. The SEC traces of PMMA showed monomodal profiles in Fig 5. These results further demonstrated that both the polymerization rate and controllability over molecular weight of the polymers could be enhanced with TPP as reducing agent in the presence of limited amounts of air.

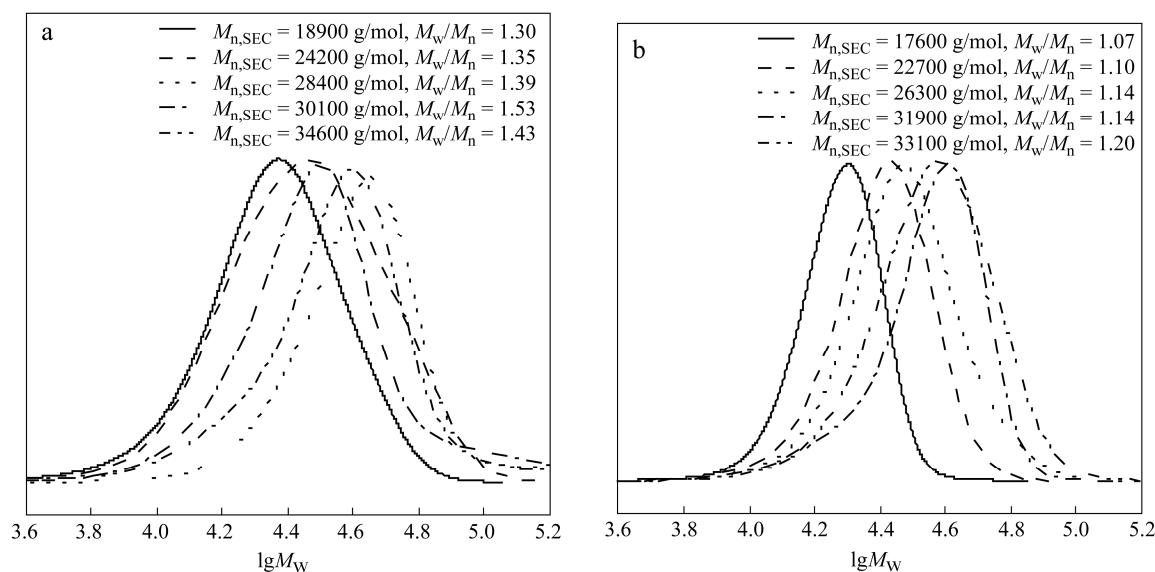


Fig. 3 Evolution of SEC traces: (a) $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{CuCl}_2]_0/[\text{PMDETA}]_0 = 500/1/0.1/0.5$; (b) $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{CuCl}_2]_0/[\text{PMDETA}]_0/[\text{TPP}]_0 = 500/1/0.1/0.5/0.5$ (Reaction conditions are the same as in Fig. 2.)

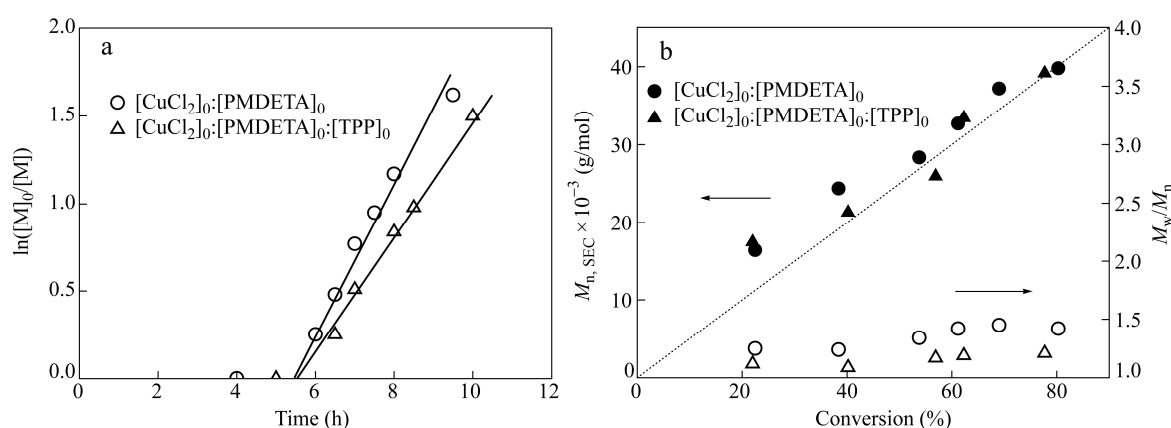


Fig. 4 $\ln([M]_0/[M])$ as a function of time (a) and number-average molecular weight ($M_{n,\text{SEC}}$) and molecular weight distribution (M_w/M_n) versus conversion (b) for bulk copper-mediated ATRP of MMA using TPP as the additive. Polymerization conditions: $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{CuCl}_2]_0/[\text{PMDETA}]_0/[\text{TPP}]_0 = 500/1/0.1/0.5/(0.5)$, $\text{MMA} = 2.0 \text{ mL}$, temperature = 90°C , $[\text{O}_2] = 3.0 \times 10^{-2} \text{ mol/L}$.

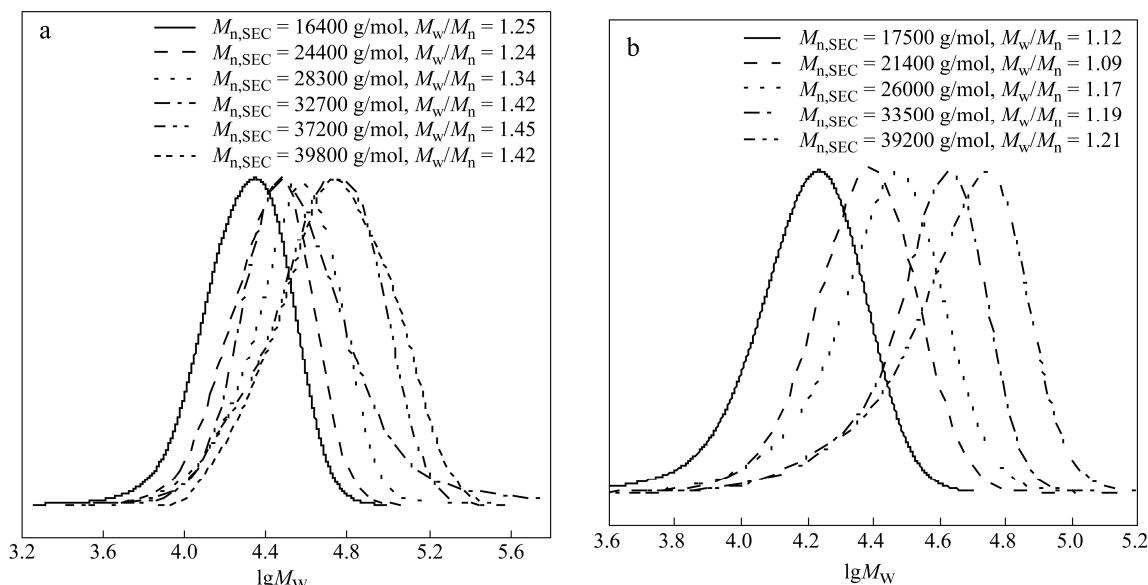


Fig. 5 Evolution of SEC traces: (a) $[MMA]_0/[EBiB]_0/[CuCl_2]_0/[PMDETA]_0 = 500/1/0.1/0.5$; (b) $[MMA]_0/[EBiB]_0/[CuCl_2]_0/[PMDETA]_0/[TPP]_0 = 500/1/0.1/0.5/0.5$ (Reaction conditions are the same as in Fig. 4.)

In Fig. 6, another copper salt ($CuBr_2$) was also used to evaluate the copper-mediated AGET ATRP of MMA in the presence of TPP as reducing agent. The corresponding k_p^{app} was $1.53 \times 10^{-4} s^{-1}$ in the presence of TPP, and an induction period (~ 2.0 h) was observed. As similar as that using $CuCl_2$ as the catalyst, the $M_{n,SEC}$ values of the obtained PMMA using $CuBr_2$ with TPP increased linearly with monomer conversion while keeping low M_w/M_n values ($M_w/M_n = 1.06$ – 1.24). The SEC traces of PMMA showed monomodal profiles in Fig 7. All these results indicated that the AGET ATRP of MMA using $CuBr_2$ or $CuCl_2$ as the catalyst in the presence of TPP showed the well-controllability over the molecular weights and molecular weight distributions.

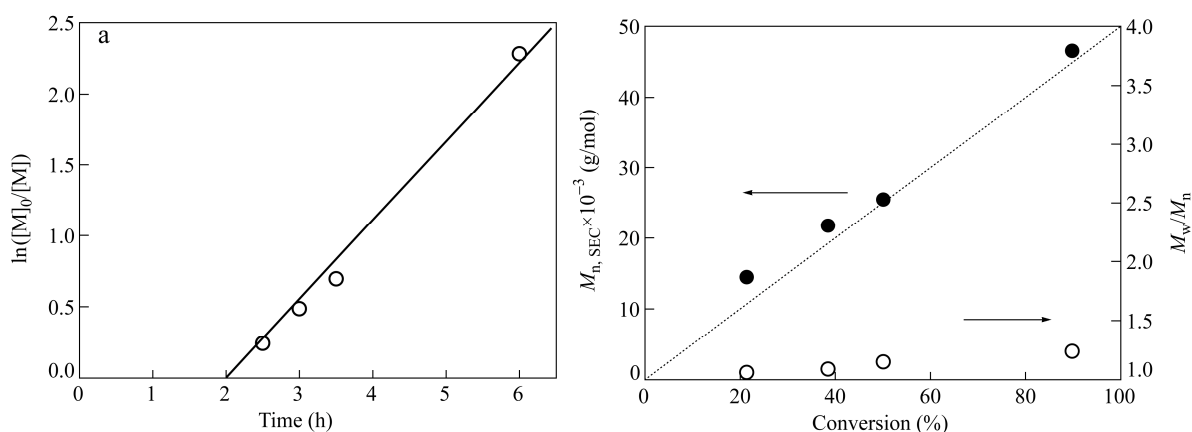


Fig. 6 $\ln([M]_0/[M])$ as a function of time (a) and number-average molecular weight ($M_{n,SEC}$) and molecular weight distribution (M_w/M_n) versus conversion (b) for bulk copper-mediated ATRP of MMA using TPP as the additive. Polymerization conditions: $[MMA]_0/[EBiB]_0/[CuBr_2]_0/[PMDETA]_0/[TPP]_0 = 500/1/0.1/0.5/0.5$, MMA = 2.0 mL, temperature = 90 °C.

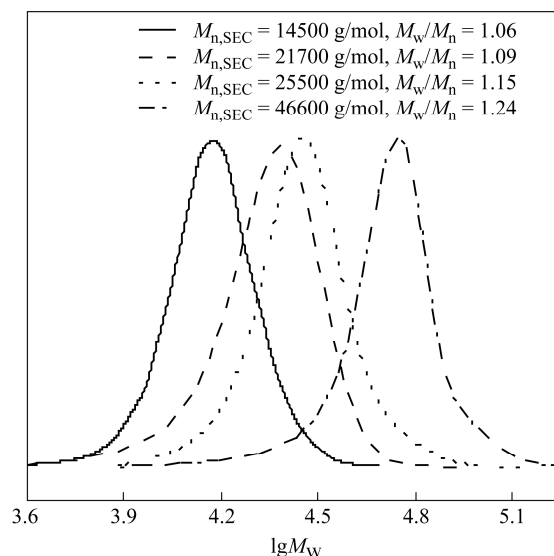


Fig. 7 Evolution of SEC traces: $[MMA]_0/[EBiB]_0/[CuBr_2]_0/[PMDTA]_0/[TPP]_0 = 500/1/0.1/0.5/0.5$ (Reaction conditions are the same as in Fig. 6.)

The chain ends of the obtained PMMA ($M_{n,SEC} = 17600$ g/mol, $M_w/M_n = 1.07$) were analyzed by ^1H -NMR spectroscopy, as shown in Fig. 8. The chemical shift at 4.09 could be assigned to the protons of the methylene (CH_3-CH_2-O , a in Fig. 8) from the initiator moieties of EBiB. The chemical shift at 3.75 (c in Fig. 8) was attributed to the methyl ester group at the chain end, as mentioned by Sawamoto *et al.*, which deviated from the chemical shift 3.60 (b in Figure 8) of other methyl ester group in PMMA because of the electron-attracting function of ω -X atom^[48]. Meanwhile, the percentage of chain-end functionality can be estimated by a comparison of the integrals of the peaks H_c/H_a (~ 1.5). The molecular weights of PMMA sample calculated from the ^1H -NMR spectrum ($M_{n,NMR}$) was 1.55×10^4 g/mol [$M_{n,NMR}$ (g/mol) = $115.2 + 100.1 \times (227.8/1.5 + 1) + 35.5$], which was close to the SEC value (1.76×10^4 g/mol), according to Eq. (1) where 115.2, 100.1 and 35.5 are the molecular weights of EBiB moieties, MMA and Cl, respectively.

$$M_{n,NMR} \text{ (g/mol)} = 115.2 + 100.1 \times (2I_b/3I_a + 1) + 35.5 \quad (1)$$

To obtain the more accurate molecular weight of PMMA, the polymers were characterized by MALDI-TOF mass spectrometry. To avoid halogen exchange^[49] between EBiB and $CuCl_2$, The PMMA sample ($M_{n,SEC} = 1.45 \times 10^4$ g/mol, $M_w/M_n = 1.06$) obtained with $[MMA]_0/[EBiB]_0/[CuBr_2]_0/[PMDTA]_0/[TPP]_0 = 500/1/0.1/0.5/0.5$ was used. It can be found from Fig. 9 that there was one main series of peaks whose interval was regular, about 100.1, the molar mass of MMA, and the experimental isotopic mass distribution values in main peak series of MALDI-TOF spectrum (with the subtraction of m/z value of potassium cation (Ag^+ , 107.8 g/mol)) are in good agreement with the theoretical values.

$$M_{theo} = 115.2 + n \times 100.1 + 79.9 \quad (2)$$

M_{theo} refers to the theoretical mass value given by Eq. (2). 115.2 and 79.9 refer to the molecular weights of ethyl moisobutyrate and bromine species of EBiB, respectively. Here, 100.1 and n are the average mass of MMA repeat unit and number of the MMA unit in the polymer chains. The molecular weight of the PMMA sample calculated from the MALDI-TOF ($M_{n,MALDI-TOF}$) was about 1.42×10^4 g/mol, which was close to the SEC value (1.45×10^4 g/mol), indicating that the PMMA was end-capped by EBiB species with high fidelity.

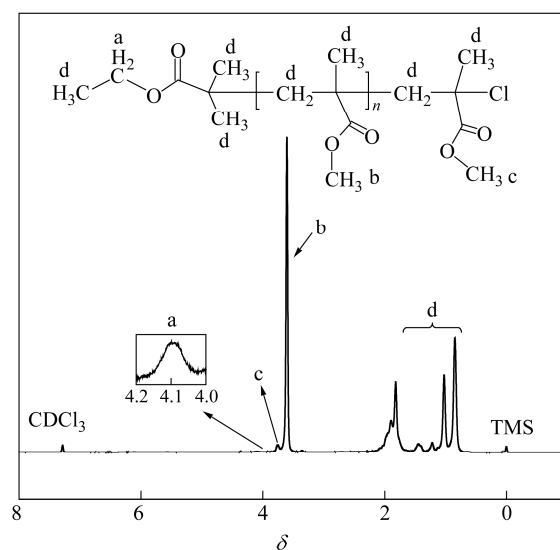


Fig. 8 ^1H -NMR spectrum of PMMA ($M_{n,\text{SEC}} = 17600$ g/mol, $M_w/M_n = 1.07$) obtained using CDCl_3 as solvent and tetramethylsilane (TMS) as internal standard
Polymerization conditions: $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{CuCl}_2]_0/[\text{PMDETA}]_0/[\text{TPP}]_0 = 500/1/0.1/0.5/0.5$, $\text{MMA} = 2.0$ mL, temperature = 90°C , time = 4.0 h, conversion = 24.8%.

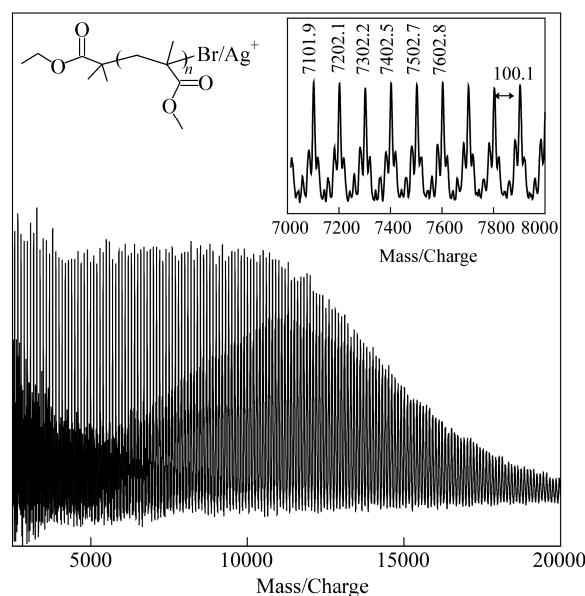


Fig. 9 Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry of poly(methyl methacrylate) (PMMA, $M_{n,\text{SEC}} = 1.45 \times 10^4$ g/mol, $M_w/M_n = 1.06$)
polymerization conditions: $[\text{MMA}]_0/[\text{EBiB}]_0/[\text{CuBr}_2]_0/[\text{PMDETA}]_0/[\text{TPP}]_0 = 500/1/0.1/0.5/0.5$, $\text{MMA} = 2.0$ mL, temperature = 90°C .

These results showed that the EBiB moieties were successfully attached onto the chain ends of the obtained PMMA. According to the mechanism of RDRPs, the resultant polymer can be used as macro-initiators to conduct chain-extension reaction. Therefore, the obtained PMMA sample ($M_{n,\text{SEC}} = 17600$ g/mol, $M_w/M_n = 1.07$) was used as the macroinitiator in chain-extension experiment. From Fig. 10, there was a peak shift from the macroinitiator to the chain-extended PMMA with $M_{n,\text{SEC}} = 31800$ g/mol and $M_w/M_n = 1.25$. The successful chain-extension reaction further confirmed the features of ATRP.

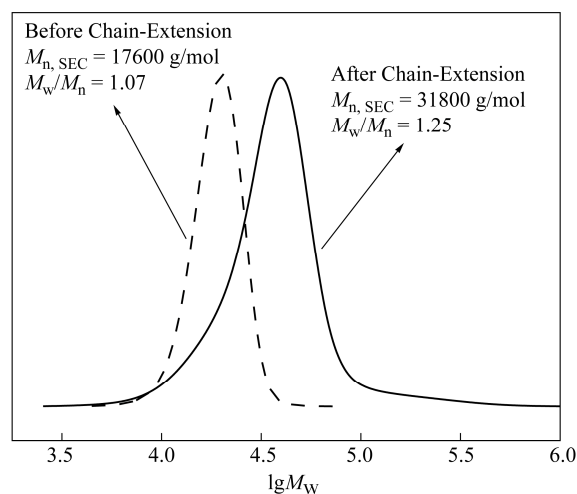


Fig. 10 SEC traces of before and after chain extension using PMMA prepared by ATRP of MMA as the macroinitiator

Original PMMA: $[MMA]_0/[EBiB]_0/[CuCl_2]_0/[PMDETA]_0/[TPP]_0 = 500/1/0.1/0.5/0.5$, MMA = 2.0 mL, temperature = 90 °C, time = 4.0 h, conversion = 24.8%; Chain extended PMMA: $[MMA]_0/[PMMA]_0/[CuCl_2]_0/[PMDETA]_0/[TPP]_0 = 500/1/0.1/0.5/0.5$, MMA = 1.0 mL, temperature = 90 °C, time = 6.0 h, conversion = 22.9%, $M_{n,th} = 29050$ g/mol ($M_{n,th}$ (g/mol) = $500 \times 100 \times 20.9\% + 17600$).

CONCLUSIONS

In conclusion, we have demonstrated that triphenylphosphine (TPP) can be used as efficient reducing agents for copper-catalyzed AGET ATRP for the first time. Well-controlled AGET ATRP has been successfully achieved in the presence or absence of air and demonstrated features of RDRPs. We believe that this work is a more promising step toward the development of practical AGET ATRPs because TPP are stable, commercial, and cost-effective.

REFERENCES

- 1 Jenkins, A.D., Jones, R.G. and Moad, G., *Pure Appl. Chem.*, 2010, 82: 483
- 2 Pintauer, T. and Matyjaszewski, K., *Chem. Soc. Rev.*, 2008, 37: 1087
- 3 Matyjaszewski, K. and Tsarevsky, N.V., *Nature Chem.*, 2009, 1: 276
- 4 Tsarevsky, N.V. and Matyjaszewski, K., *Chem. Rev.*, 2007, 107: 2270
- 5 Zhang, F.J. and Liu, X.H., *Chinese J. Polym. Sci.*, 2013, 31(12): 1613
- 6 Xin, Y., Wang, H., Liu, B.W. and Yuan, J.Y., *Chinese J. Polym. Sci.*, 2015, 33(1): 36
- 7 Sun, T., Zhang, Y.F., Chen, C.L., Gong, X.Z. and Meng, J.Q., *Chinese J. Polym. Sci.*, 2014, 32(7): 880
- 8 Kubisa, P., *Prog. Polym. Sci.* 2004, 29: 3
- 9 Xia, J. and Matyjaszewski, K., *Macromolecules*, 1997, 30: 7697
- 10 Gromada, J. and Matyjaszewski, K., *Macromolecules*, 2001, 34: 7664
- 11 Li, M., Min, K. and Matyjaszewski, K., *Macromolecules*, 2004, 37: 2106
- 12 Li, M., Jahed, N.M., Min, K. and Matyjaszewski, K., *Macromolecules*, 2004, 37: 2434
- 13 Mueller, L., Jakubowski, W., Tang, W. and Matyjaszewski, K., *Macromolecules*, 2007, 40: 6464
- 14 Plichta, A., Li, W.W. and Matyjaszewski, K., *Macromolecules*, 2009, 42: 2330
- 15 Jakubowski, W. and Matyjaszewski, K., *Macromolecules*, 2005, 38: 4139
- 16 Bai, L.J., Zhang, L.F., Pan, J.L., Cheng, Z.P. and Zhu, X.L., *Polym. Chem.*, 2012, 3: 2685

- 17 Kwiatkowski, P., Jurczak, J., Pietrasik, J., Jakubowski, W., Mueller, L. and Matyjaszewski, K., *Macromolecules*, 2008, 41: 1067
- 18 Dong, H.C. and Matyjaszewski, K., *Macromolecules*, 2010, 43: 4623
- 19 Luo, R. and Sen, A., *Macromolecules*, 2008, 41: 4514
- 20 Bai, L.J., Zhang, L.F., Pan, J.L., Cheng, Z.P. and Zhu, X.L., *Macromolecules*, 2013: 46, 2060
- 21 Pan, J.L., Li, Z., Zhang, L.F., Cheng, Z.P. and Zhu, X.L., *Chinese J. Polym. Sci.*, 2014, 32(8): 1010
- 22 Davis, K.A. and Matyjaszewski, K., *Chinese J. Polym. Sci.*, 2014, 32(1): 195
- 23 Jakubowski, W., Min, K. and Matyjaszewski, K., *Macromolecules*, 2006, 39: 39
- 24 Matyjaszewski, K., Coca, S.N., Gaynor, S.G., Wei, M.L. and Woodward, B.E., *Macromolecules*, 1997, 30: 7348
- 25 Jakubowski, W. and Matyjaszewski, K., *Angew. Chem., Int. Ed.*, 2006, 45: 4482
- 26 Min, K., Gao, H. and Matyjaszewski, K., *J. Am. Chem. Soc.*, 2005, 127: 3825
- 27 Tang, H., Radosz, M. and Shen, Y., *Macromol. Rapid Commun.*, 2006, 27: 1127
- 28 Zhang, Y.Z., Wang, Y. and Matyjaszewski, K., *Macromolecules*, 2011, 44: 683
- 29 Dong, H.C., Tang, W. and Matyjaszewski, K., *Macromolecules*, 2007, 40: 2974
- 30 Hizal, G., Tunca, U., Aras, S. and Mert, H., *J. Polym. Sci., Part A: Polym. Chem.*, 2006, 44: 77
- 31 Yamamura, Y. and Matyjaszewski, K., *J. Macro. Sci., Part A: Pure and Appl. Chem.*, 2007, 44: 1035
- 32 Matyjaszewski, K., Jakubowski, W., Min, K., Tang, W., Huang, J., Braunecker, W.A. and Tsarevsky, N.V., *Proc. Natl. Acad. Sci. U.S.A.*, 2006, 103: 15309
- 33 Matyjaszewski, K. and Xia, J., *Chem. Rev.*, 2001, 101: 2921
- 34 Zhang, L.F., Cheng, Z.P., Tang, F., Li, Q. and Zhu, X.L., *Macromol. Chem. Phys.*, 2008, 209: 1705
- 35 Xue, Z.G., He, D., Noh, S.K. and Lyoo, W.S., *Macromolecules*, 2009, 42: 2949
- 36 Xue, Z.G., Oh, H.S., Noh, S.K. and Lyoo, W.S., *Macromol. Rapid Commun.*, 2008, 29: 1887
- 37 Xue, Z.G., Linh, N.T.B., Noh, S.K. and Lyoo, W.S., *Angew. Chem. Int. Ed.*, 2008, 47: 6426
- 38 Xue, Z.G., Lee, B.W., Noh, S.K. and Lyoo, W.S., *Macromol. Rapid Commun.*, 2008, 29: 1887
- 39 He, D., Xue, Z.G., Khan, M.Y., Noh, S.K. and Lyoo, W.S., *Polymer*, 2007, 48: 4704
- 40 Chen, X.X., Khan, M.Y. and Noh, S.K., *Polym. Chem.*, 2012, 3: 1971
- 41 Jardine, F.H., Rule, L. and Vohra, A.G., *J. Chem. Soc. (A)*, 1970, 238
- 42 Kwak, Y.W. and Matyjaszewski, K., *Polym. Int.*, 2009, 58: 242
- 43 Hu, Z.Q., Shen, X.R., Qiu, H.Y., Lai, G.Q., Wu, J.R. and Li, W.Q., *Eur. Polym. J.*, 2009, 45: 2313
- 44 Bai, L.J., Zhang, L.F., Zhang, Z.B., Zhu, J., Zhou, N.C. and Cheng, Z.P., *J. Polym. Sci., Part A: Polym. Chem.*, 2011, 49: 3980
- 45 Bai, L.J., Zhang, L.F., Zhang, Z.B., Zhu, J., Zhou, N.C., Cheng, Z.P., and Zhu, X.L., *J. Polym. Sci., Part A: Polym. Chem.*, 2011, 49: 3970
- 46 Bai, L.J., Zhang, L.F., Zhu, J., Cheng, Z.P. and Zhu, X.L., *J. Polym. Sci., Part A: Polym. Chem.*, 2009, 47: 2002
- 47 Zhang, L.F., Cheng, Z.P., Lü, Y.T. and Zhu, X.L., *Macromol. Rapid Commun.*, 2009, 30: 543
- 48 Ouchi, M., Terashima, T. and Sawamoto, M., *Chem. Rev.*, 2009, 109: 4963
- 49 Matyjaszewski, K., Paik, H.J., Shipp, D.A., Isobe, Y. and Okamoto, Y., *Macromolecules*, 2001, 34: 3127