Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 1581−1585

polymer

www.elsevier.com/locate/polymer

$AlCl_3$ promoting living-radical polymerization of MMA based on *sec*-butyl chlorine in *n*-butanol

Ying Feng*, Jinhua Feng, Jiruo Zhao, Yuling Wang

Key Laboratory of Rubber-Plastics, Ministry of Education, School of Polymer Science and Engineering, Qingdao University of Science and Technology, 53 Zhengzhou Road, Qingdao, Shandong 266042, China

Received 25 August 2006; received in revised form 21 November 2006; accepted 13 December 2006
Available online 20 December 2006

Abstract

The effect of metal halide $AlCl_3$ as additive on the living-radical polymerization of methyl methacrylate (MMA) in *n*-butanol at 80 °C was investigated. The initiator was *sec*-butyl chlorine (SBC), which was used as a model initiator containing secondary R−Cl bond and the catalyst was $FeCl_2/(PPh_3)_4$. The polymerization reaction of MMA, using SBC/$FeCl_2$ $(PPh_3)_4$ as initiating system, was very slow or even did not take place without $AlCl_3$. The addition of $AlCl_3$ accelerated the polymerization to some great extent and the polymers obtained have almost controlled molecular weights and narrow molecular weight distribution. These experimental results were different from those of the literatures, in which metal chlorides would slow down the polymerization rate of MMA for ATRP reactions.

Keywords: Living polymerization; MMA; ATRP

1. Introduction

A significant attention has been attracted since 1994 that living-radical polymerizations were reported. Atom transfer radical polymerization (ATRP) is one of the most significant living-radical polymerization systems, in which alkyl halides were used as initiators and transition metal complexes as catalysts [1−3]. Large amount of well-defined linear polymers has been synthesized by ATRP techniques. If the initiator is a polymeric macromolecule, novel and well-defined polymer materials will be possibly synthesized by ATRP procession.

However, a number of halogen-containing polymers, such as chlorinated polyolefins and chlorinated poly(vinyl chloride), which might be utilized as ATRP macromolecule initiators for the preparation of functionalized derivatives, cannot initiate ATRP reactions effectively [4] because those polymers contain just secondary R−Cl bond and it has been reported that secondary chlorine atoms containing alkyl halide, such as $-CH_2-ClCH_2-CH_2-$, can only achieve 26.5% conversion of monomer in MMA polymerization, when catalyzing with CuBr in 120 °C for 115 h [4].

Some interesting experiments [5−12] have demonstrated that the metal alkoxide additives such as Al(O-*i*Pr)$_3$ and MeAl(ODBP)$_2$ could accelerate atom transfer radical polymerizations, however, the metal chlorides such as $SnCl_4$ and $TiCl_4$ would slow down the polymerizations catalyzed by transition metals such as Ni, Fe, Re and Cu. How these additives functioned is still unknown so far.

Here we design a route in which the initiator is inactive *sec*-butyl chlorine (SBC), which worked as a model initiator containing secondary R−Cl bond, the catalyst is $FeCl_2/(PPh_3)_4$, and $AlCl_3$, a typical cationic polymerization cocatalyst, is used as additive agent.

It has been found that when the molar ratio of [MMA] and [SBC] was as high as 4:1, there was only 17% conversion of the monomer obtained, using SBC/$FeCl_2/(PPh_3)_4$ initiating system in *n*-butanol solution at 80 °C for 120 h. The conversion was increased to 62% in the same conditions when adding a little

---

* Corresponding author.
E-mail address: yingfeng@qust.edu.cn (Y. Feng).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.12.027

amount of $AlCl_3$, where the molar ratio of [SBC]:[$AlCl_3$] was 1:3.04×10^{-2} and the $[MMA]_0$:$[AlCl_3]_0$ was 1:7.56×10^{-3}.

2. Experimental section

2.1. Materials

MMA (purity > 99%) was distilled under reduced pressure before use. $Fe_2Cl_2 \cdot 4H_2O$, PPh_3 (purity > 98%), and $AlCl_3$ (purity > 99%) were used as received. *sec*-Butyl chlorine (purity > 99%) and *n*-butanol (purity > 99%) were also used as received.

2.2. Polymerization procedures

Polymerization was carried out in sealed glass tubes. A typical example is as follow. Firstly, the *n*-butanol solution of $FeCl_2$ and PPh_3 was mixed with the *n*-butanol solution of SBC and $AlCl_3$ in a glass tube. Secondly, the tube was closed with a septum. After three freeze–pump–thaw cycles, the mixing solution with SBC, $AlCl_3$, $FeCl_2$ and PPh_3 was aged for 1 h at designed temperatures. Lastly, MMA was added (the total volume of the reaction mixture was about 20–30 ml) using syringe and then the sealed glass tube with the resulting solution was immediately placed in an oil bath, keeping at 80 °C for designed time.

White precipitation was observed as the polymerization proceeds. In designed time, the reaction mixture was cooled to ambient atmosphere temperature and subsequently methanol was added to precipitate the product. The product was filtrated, washed with ethanol and dried under vacuum at 50 °C until constant weight. Monomer conversion was determined from the amount of PMMA obtained precipitately.

2.3. Measurements

The MWD, M_n, and M_w/M_n ratios of the polymers were measured by gel-permeation chromatography (GPC) in tetrahydrofuran (THF) on a Waters 515-410 instrument and SHIMADZU system composed of a set of KF-1, KF-2, KF-3, KF-4, KF-6. Tetrahydrofuran was used as the eluent and the flow rate was 1.00 ml/min. Before the manipulations, two steps were taken: (1) about 0.2 g of the light red products was dissolved in cyclohexanone (10 ml) and precipitated in 25 ml of ethanol. (2) The resulting samples were re-dissolved in THF and eluted on a column of Al_2O_3 with THF, and then precipitated in ethanol again. This procedure gave white polymers for NMR and GPC experiments. ^1H NMR spectra were recorded using a Varian Unity-500 spectrometer in $CDCl_3$, operating at 400 MHz.

3. Results and discussion

3.1. Polymerization of MMA

MMA was polymerized in *n*-butanol at 80 °C using SBC/$AlCl_3$/$FeCl_2$/$(PPh_3)_4$ initiating system. No PMMA was obtained when polymerizing for 24 h at 80 °C, if SBC did not exist, only with $AlCl_3$/$FeCl_2$/$(PPh_3)_4$. PMMA was observed when polymerizing for 24 h at room temperature in the presence of SBC/$AlCl_3$/$FeCl_2$/$(PPh_3)_4$. Fig. 1 shows the effects of $AlCl_3$ and polymerization time on polymerizations of MMA based on SBC/$AlCl_3$/$FeCl_2$/$(PPh_3)_4$ initiating system in *n*-butanol at 80 °C. The rate of polymerization was comparable to that of MMA–CCl_4/$NiCl_2(PPh_3)_2$/$Al(Oi\text{-}Pr)_3$ system polymerized in benzene at 80 °C [5] and lower than that of MMA–CCl_4/$RuCl_2(PPh_3)_3$/MeAl $(ODBP)_2$\{methylaluminum bis-(2,6-di-*tert*-butylphenoxide)\} system polymerized in benzene at 60 °C [6].

It has been found that the polymerization rate was highly dependent on the molar ratio of $AlCl_3$ and $FeCl_2/(PPh_3)_4$ in these experiments. An obvious acceleration was observed when changing the Al and Fe ratio from 1.5:1 to 1:1 (Fig. 1) and only little amount of PMMA was achieved when the ratio of Al and Fe was 2:1 or 1:1.5.

Polymerization rate was also dependent on the molar ratio of SBC/$AlCl_3$ (Table 1).

It can be seen from Table 1 that conversions of MMA, initiated by inactive secondary alkyl halides (SBC), increased in the presence of $AlCl_3$. It can also be found that although conversions of monomer were increased, the number-average molecular weight (M_n) of PMMA was decreased in the same time, as increasing $AlCl_3$ molar mass, contrasting Run 2 to Run 3 and Run 6 to Run 7. These could belong to forming more number of active species.

Contrasting Run 8 to Run 9 and Run 10 to Run 11, not only molecular weight of PMMA raised, but also MMA conversions increased for increasing $AlCl_3$ molar mass. Since the increasing extents of MMA conversions were only about 5–6%, the decreasing of M_n cannot show out in these cases.

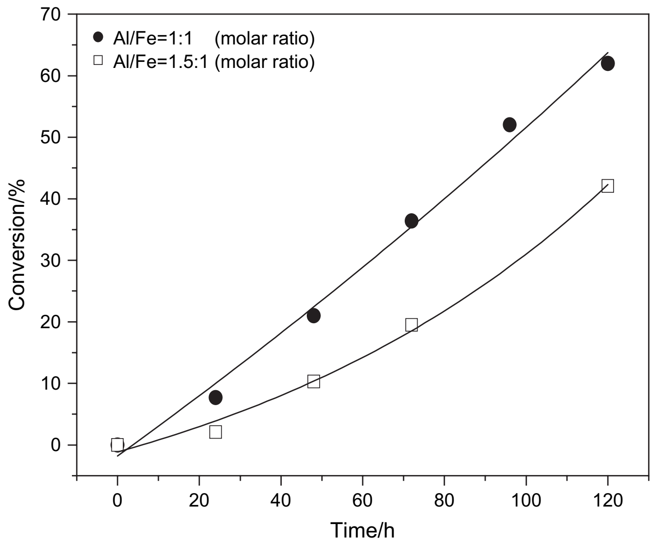

Fig. 1. Polymerization of MMA with SBC/$AlCl_3$/$FeCl_2$/$(PPh_3)_4$ initiation system in *n*-butanol at 80 °C. $[MMA]_0 = 18.84$ mM; $[SBC]_0 = 4.705$ mM; $[FeCl_2/(PPh_3)_4]_0 = 1.42 \times 10^{-1}$ mM; ● – $[AlCl_3]_0 = 1.42 \times 10^{-1}$ mM, □ – $[AlCl_3]_0 = 2.13 \times 10^{-1}$ mM aging for 1 h at designed temperature.

Table 1
Polymerization of MMA initiated from *sec*-butyl chlorine (SBC) in butanol at 80 °C

Run	Temperature (°C)	Time (h)	[M]/[SBC]/[$AlCl_3$]/[$FeCl_2$]/[$(PPh_3)_4$] (molar ratio)	Conversion (%)	$M_{n,GPC}$	M_w/M_n
1	25	48	100/24.90/0.000/0.756/3.03	0	–	–
2	80	120	100/24.90/0.000/0.756/3.03	17	*44,000*	1.17
3	80	120	100/24.90/0.756/0.756/3.03	62	*34,000*	1.19
4	80	24	100/24.90/0.756/0.756/3.03	7	18,000	1.41
5	80	24	100/24.9/1.134/1.134/4.545	7.7	–	–
6	80	48	100/24.90/0.756/0.756/3.03	13	*19,000*	1.47
7	80	48	100/24.9/1.134/1.134/4.545	21	*13,000*	1.48
8	80	72	100/24.90/0.756/0.756/3.03	30	26,000	1.12
9	80	72	100/24.9/1.134/1.134/4.545	36	31,000	2.35
10	80	96	100/24.90/0.756/0.756/3.03	47	29,000	1.63
11	80	96	100/24.9/1.134/1.134/4.545	52	55,000	1.62

Aging for 1 h at designed temperature for each experiment except for Run 1.

Fig. 2 shows the logarithmic conversion data of MMA, i.e., $\ln([M]_0[M])$ vs t, where $[M]_0$ and [M] denote the monomer concentrations at time 0 and t, respectively. It can be seen from Fig. 2 that the rate of polymerization was also related with SBC and $AlCl_3$ molar ratios. Higher molar ratio of $AlCl_3$/SBC leads to higher conversion of monomer of MMA. Almost first-order rate plots were observed after 50 h, indicating that the polymerization could be internally of first order with respect to monomer and that the concentration of the growing species remains constant after a long polymerization period, for example 50 h in above two particular cases. These results showed that the formation of active species and getting to constant numbers were related with polymerization time. Prior to 24 h, there were only a few amounts of active species, in the period of 24–50 h, the number of active species was growing up. After 50 h, the number of active species remained constant.

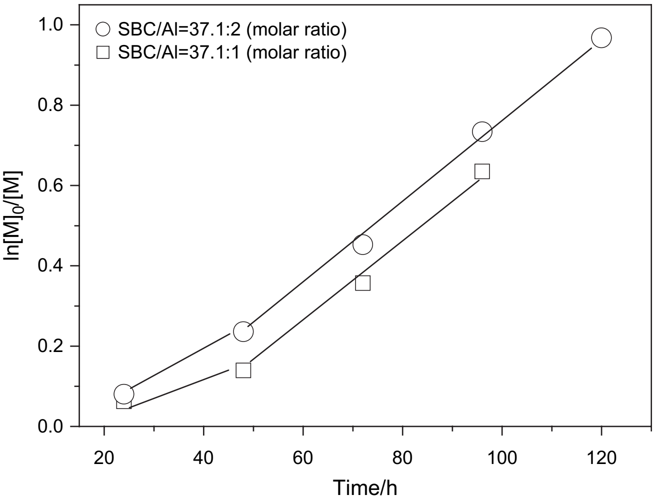

Fig. 2. The logarithmic conversion data of MMA as a function of time, where $[M]_0$ and [M] denote the monomer concentrations at time 0 and t, respectively. The butanol solution of SBC + $AlCl_3$ + $FeCl_2/(PPh_3)_4$ was aged for 1 h at designed temperature before polymerization at 80 °C. $[MMA]_0 = 18.84$ mM; $[SBC]_0 = 4.75$ mM; Al:Fe = 1:1; ○ – $[AlCl_3]_0 = 2.84 \times 10^{-1}$ mM, □ – $[AlCl_3]_0 = 1.42 \times 10^{-1}$ mM.

Fig. 3 shows the relative number-average molecular weights (M_n), the polydispersities (M_w/M_n), and the molecular weight distributions (MWDs) of the polymers obtained with the SBC/$AlCl_3$/$FeCl_2$/$(PPh_3)_4$ initiating system. The M_n increased almost linearly with polymerization time or monomer conversion (C, %). A long inducing period was present according to Figs. 2 and 3. Because butanol is a non-solvent for the polymer of PMMA, the polymer chain would precipitate from butanol and the collapsed coil structure of the polymer chain would lead the reaction frequency of chain-end with catalyst reduced greatly, although $FeCl_2$, $FeCl_3$, PPh_3 and $AlCl_3$ were soluble in butanol. In the experiments, a very few amounts of precipitates can be found when polymerization conducted for 5 h. A few amounts of precipitates were obtained when polymerization was conducted for 24 h, the conversion of PMMA was 7% and the molecular weight was 18,000 g/mol at the moment. Such high molecular weight in the conversion of only 7% could belong to not establishing out rapid reverse balance of active species and dormant species, and the lifetime of chain-end active species was long and the number of active species was small at the beginning of polymerization. The number-average molecular weight of polymers increased with the conversion growth indicating that the chain end was active. The MWDs were between 1.17 and 2.35 showing that the controllability of reactions was not so good in terms of no chain transferring and no chain ending in the condition of polymerization.

For detailed research on the early period of polymerization, PMMA precipitate in *n*-butanol can be observed at about 1% conversion, and M_n is 12,000–18,000 from the result of GPC. There is nearly no oligomer in the methanol solution, which was used as precipitating agent. Since there was only solid phase and solution phase, the issues of catalysts partition did not discussed.

Assuming that one polymer chain was formed by one molecule of SBC activated from each molecule of $AlCl_3$, the calculated relative number-average molecular weights ($M_{n,cal}$) may be obtained using the formula $M_{n,cal} = (([M]_0 \times C)/(\alpha[AlCl_3]_0)) \times M_{MMA}$. The data of Fig. 3 were the results of designing $\alpha = 100\%$. It can be seen that the

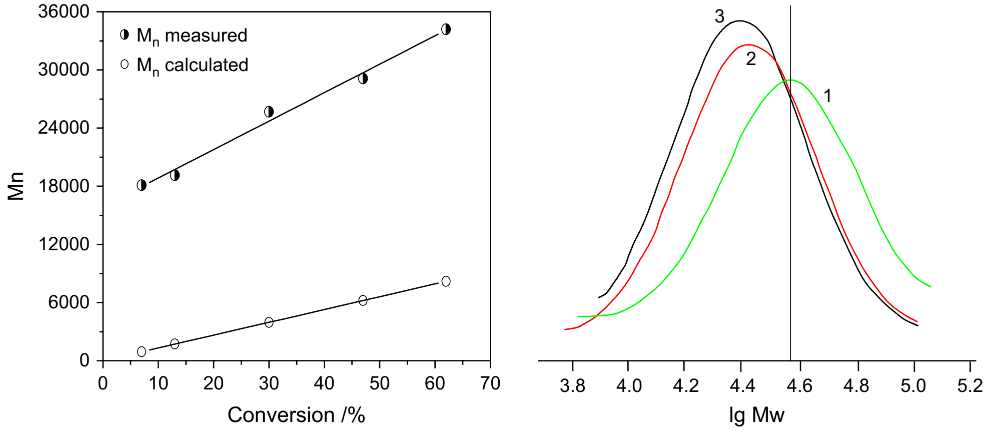

Fig. 3. M_n and MWD curves of PMMA versus conversion obtained with SBC/$AlCl_3$/$FeCl_2$/$(PPh_3)_4$ initiating system in butanol at 80 °C. $[MMA]_0 = 18.84$ mM; $[SBC]_0 = 4.75$ mM; $[AlCl_3]_0 = 1.42 \times 10^{-1}$ mM; $[FeCl_2/(PPh_3)_4]_0 = 1.42 \times 10^{-1}$ mM. (Peak 1: $M_n = 34200$, $M_w/M_n = 1.19$, conversion = 60%; peak 2: $M_n = 27677$, $M_w/M_n = 1.12$, conversion = 30%; peak 3: $M_n = 19138$, $M_w/M_n = 1.47$, conversion = 13%.)

relative number-average molecular weights measured are larger than those of calculated. α is about 20%, which implied that 20% of $AlCl_3$ added would be used to activate SBC if ignoring SBC initiation alone.

3.2. Polymerization mechanism of MMA initiated via SBC/$AlCl_3$/$FeCl_2$/$(PPh_3)_4$ system

The MMA polymerization with such initiating system apparently conducted by a radical mechanism because it has been known that ionic polymerization cannot take place in protonic solution. The polymerizations of MMA using SBC/$AlCl_3$/$FeCl_2$/$(PPh_3)_4$ initiating system in this paper were carried out in *n*-butanol solution, and additionally, MMA cannot perform cationic polymerization. The other evidence was that the polymerization was perfectly inhibited by the addition of radical inhibitors. Along with the relationship of molecular weights and polymerization time (Fig. 3) and other experiments described above, it can be said that a living-radical polymerization of MMA occurred. Fig. 4(a,b) showed the IR and ^{1}H NMR spectra of PMMA obtained by SBC/$AlCl_3$/$FeCl_2$/$(PPh_3)_4$ initiation system.

3.3. The effects of aging

Sawamoto et al. [12] investigated the polymerizations of MMA with CCl_4/$RuCl_2$/PPh_3 in the presence of weak Lewis acid such as MeAl(ODBP)$_2$, Al(O*i*-Pr)$_3$, and strong Lewis acid such as $SnCl_4$ in toluene at 80 °C. They found that Al(O*i*-Pr)$_3$ and MeAl(ODBP)$_2$ can accelerated the polymerization successfully to produce polymers with controlled molecular weights and narrow MWDs, and metal chlorides such as $SnCl_4$ and $TiCl_4$ were not effective additives, they slowed down the polymerizations.

Contrasting to Sawamoto's experiments in this paper, polar solvent and stronger Lewis acid $AlCl_3$ were used and an aging procedure was employed before polymerization. It has been found that methods of aging affected polymerization rate greatly. For example (Table 2) of the SBC/$AlCl_3$ aging system, the conversion of MMA was 21% when the butanol solution of SBC and $AlCl_3$ was aged for 1 h, following adding $FeCl_2$/$(PPh_3)_4$ and MMA, and then polymerizing for 48 h at 80 °C. In the same condition, except for aging 1.5 h, the conversion was 50%.

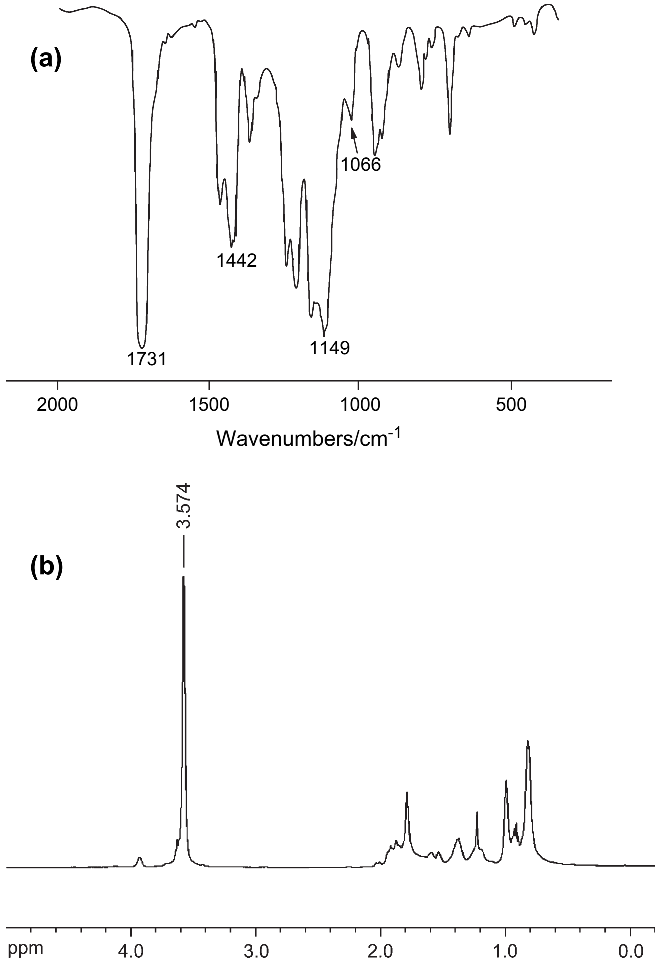

Fig. 4. IR (a) and ^{1}H NMR (b) spectra of PMMA obtained by SBC/$AlCl_3$/$FeCl_2$/$(PPh_3)_4$ initiation system.

Table 2
The effects of aging on MMA conversion of polymerization

Aging method	Aging time (h)	Polymerizing time (h)	Conversion (%)
SBC/$AlCl_3$	1	48	21
	1.5	48	50
SBC/$AlCl_3$/$FeCl_2$/$(PPh_3)_4$	1	72	30
	2	72	14

Polymerizing temperature: 80 °C; $[MMA]_0 = 18.84$ mM; $[SBC]_0 = 4.75$ mM; $[AlCl_3]_0 = 1.42 \times 10^{-1}$ mM; $[FeCl_2/(PPh_3)_4]_0 = 1.42 \times 10^{-1}$ mM.

However, for the SBC/$AlCl_3$/$FeCl_2$/$(PPh_3)_4$ aging system, the conversion was only 14% when the butanol solution of SBC, $AlCl_3$ and $FeCl_2$/$(PPh_3)_4$ together was aged for 2 h, following adding MMA, and then polymerizing for 72 h at 80 °C. Since polymerizing and aging would take place in the same time and different aging times gave different conversions for the same aging systems, these results indicated that the formation of active centers would be greatly related to polymerization times.

4. Conclusion

A controlled or living-radical polymerization of MMA has been achieved with secondary alkyl chloride initiating system, consisting of *sec*-butyl chlorine, $FeCl_2(PPh_3)_4$, and Lewis acid $AlCl_3$. The polymerization most likely proceeds via the radical mechanism. Aging reaction of initiator and Lewis acid played an important role.

References

[1] Mardare D, Matyjaszewski K. Macromol Rapid Commun 1994;15: 37–44.

[2] Greszta D, Mardare D, Matyjaszewski K. Macromolecules 1994;27: 638–44.

[3] Mardare D, Matyjaszewski K. Macromolecules 1994;27:645–9.

[4] Percec V, Asgarzadeh F. J Polym Sci Part A Polym Chem 2001;39: 1120–35.

[5] Uegaki H, Kotani Y, Kamigaito M, Sawamoto M. Macromolecules 1997;30:2249–53.

[6] Kato M, Kamigaito M, Sawamoto M, Higashimura T. Macromolecules 1995;28:1721–3.

[7] Granel C, Dubois Ph, Jérôme R, Teyssié Ph. Macromolecules 1996;29: 8576–82.

[8] Uegaki H, Kotani Y, Kamigaito M, Sawamoto M. Macromolecules 1998;31:6756–61.

[9] Ando T, Kamigaito M, Sawamoto M. Macromolecules 1997;30:4507–10.

[10] Matyjaszewski K, Wei M, Xia J, McDermott NE. Macromolecules 1997;30:8161–4.

[11] Kotani Y, Kamigaito M, Sawamoto M. Macromolecules 1999;32: 2420–4.

[12] Ando T, Kamigaito M, Sawamoto M. Macromolecules 2000;33: 6732–7.