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Controlled/“living” radical polymerization of methyl methacrylate catalyzed by CpCo(I) complexes conveniently generated from cobaltocene in situ

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ABSTRACT

Atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) catalyzed by a series of *exo*-substituted η^4-cyclopentadiene CpCo(I) complexes generated conveniently from cobaltocene in situ was studied. It is found that the steric and electronic effects of the *exo*-substituents at the η^4-cyclopentadiene ligand have significant effects on the polymerization. More bulky or weaker electron-withdrawing substituents lead to higher polymerization rate and better initiation efficiency. Polymerization of styrene, and the block copolymerization of MMA with styrene were also studied, using the selected catalyst system.

1. Introduction

Since Sawamoto [1] and Matyjaszewski [2] first reported two different catalyst systems in 1995, atom transfer radical polymerization (ATRP) of various monomers can be precisely controlled by using a number of different transition metal complexes [3–7]. Most of these systems involve a dynamic equilibrium between a minute amount of active propagating radicals and a large majority of dormant species. This equilibrium is established through the reversible activation of the dormant carbon–halogen bond at the terminal via a single-electron redox reaction of the transition metal center (Scheme 1) [8]. One of the potential advantages of the metal-mediated living radical polymerizations is the tunable activity of catalysts by changing the steric and electronic characters of their ligands.

A cobalt-mediated living radical polymerization, in which the radical generated from the homolysis of cobalt–carbon bond in the organometallic derivatives of cobalt(III), was first reported by Wayland et al. [9]. But living radical polymerizations through the reversible homolysis of carbon–halogen bond catalyzed by cobalt have not been reported adequately [10–19]. Recently, our group reported the ATRP of methyl methacrylate (MMA) and styrene catalyzed by cobaltocene to produce polymers with controlled molecular weights and narrow polydispersity index (PDI) values [10,18]. In this system, the actual catalyst turned out to be the *exo*-substituted η^4-cyclopentadiene CpCo(I) complex generated in situ from the reaction of cobaltocene with ethyl α-bromoisobutyrate (EBiB) [18,19]. In comparison with the well studied half-metallocene type ruthenium(II) catalyst system, in which the cocatalyst was a critical component for fast polymerization and good control [20–23], with the *exo*-substituted η^4-cyclopentadiene CpCo(I) complex, living radical polymerization of MMA can be well catalyzed ($PDI < 1.1$) without cocatalyst, and proceeded faster than that with half-metallocene type ruthenium(II) catalysts even in the presence of cocatalyst. So the CpCo(I) catalyst system is a very promising ATRP system. With the further study of the structure–property relationship, more efficient catalyst systems may be developed.

A number of *exo*-substituted η^4-cyclopentadiene CpCo(I) complexes have been prepared by the reaction of organic halides with cobaltocene [19,24–28]. In that type of reactions, an electron transferred firstly from cobaltocene to organic halide to form an 18-electron cobaltocenium and a radical anion $RX^{-\bullet}$, which rapidly transformed to $R^\bullet$ and X^-, followed by the reaction of $R^\bullet$ with another equivalent of cobaltocene to generate the *exo*-substituted η^4-cyclopentadiene CpCo(I) complex [29,30]. However, the influence of ligands has not been studied in Co(I) catalyzed ATRP, which prompts us to explore how the steric and electronic factors of the *exo*-substituents at the η^4-cyclopentadiene influence the activity of the *exo*-substituted η^4-cyclopentadiene CpCo(I) complex in ATRP. In this paper, we designed a model reaction (Scheme 2) to conveniently generate the CpCo(I) complexes from the reactions of cobaltocene with organic bromides in situ to catalyze the radical

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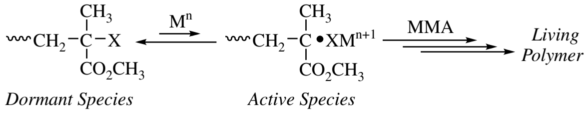


Scheme 1. ATRP of MMA with transition metal complexes.

polymerization of MMA. The results showed that the catalytic activity of the CpCo(I) complex was significantly dependent upon the *exo*-substituents at the η^4-cyclopentadiene ring. Thus, it is convenient to modulate the polymerization by adding different organic bromides.

2. Experimental

2.1. General considerations

MMA and styrene were dried over calcium hydride, distilled twice under reduced pressure, degassed and stored under argon at −15 °C. Ethyl α-bromoacetate was commercially available and was purified by distillation before use. Cobaltocene [31], EBiB [29], 1-phenyl ethylbromide [32], bromoacetone [33], α-bromoacetophenone [34], were prepared according to the literatures. All solvents were distilled from appropriate drying agents and deoxygenated before use.

2.2. Polymerization

All manipulations were conducted under argon with standard Schlenk techniques. Polymerizations were carried out in a 50-mL Schlenk flask fitted with a Teflon stopcock. A typical polymerization procedure of MMA was as following. Water and oxygen were removed from the flask with a magnetic bar by fire and applying high vacuum and back filling with argon (three times) before cobaltocene (113.5 mg, 6×10^{-4} mol), organic bromides (3×10^{-4} mol) and toluene (5 mL) were added under the protection of argon. All liquids were added via gastight dried degassed syringes under the protection of argon. The flask was then sealed with Teflon stopcock and stirred overnight at room temperature. Then MMA (6.067 g, 6.0×10^{-2} mol), and EBiB (58.5 mg, 3×10^{-4} mol) were added. The flask was sealed with Teflon stopcock by three freeze–pump–thaw cycles to remove oxygen, and immersed in an oil bath at 80 °C with stirring. Samples were taken out from the flask via a degassed syringe under the protection of argon at time intervals, diluted with THF (4 mL × 2), poured in methanol (100 mL) under vigorous stirring. The precipitated polymer was filtered with suction and dried overnight at 40 °C under vacuum. The conversions were determined by gravity.

2.3. Characterizations

The number- and weight-average molecular weight and polydispersities of PMMA were measured by GPC (Waters 510 liquid chromatograph connected with four styragel GPC columns (guard, 10^3 Å, 10^4 Å, 10^5 Å), and waters 410 differential refractometer). The eluent was THF at a flow rate of 1 mL min^{-1}, and the column temperature was 25 °C. Calibration was made with standard samples of polystyrene.

3. Results and discussion

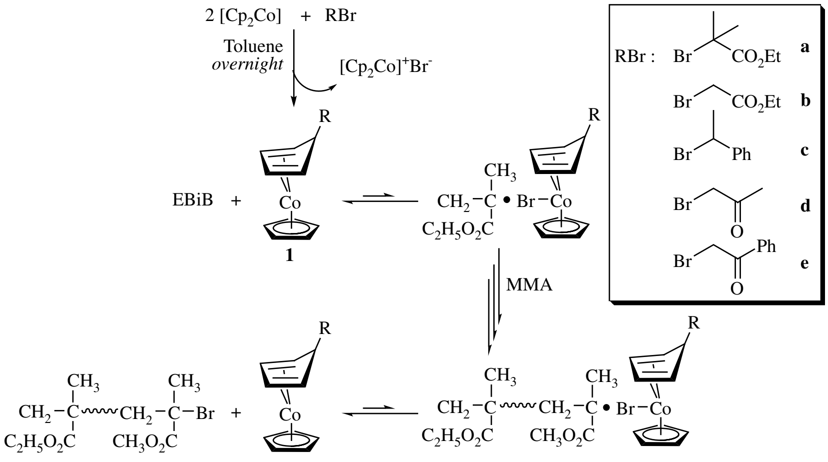
As we previously reported, the ATRP of MMA and styrene can be well controlled with the *exo*-substituted η^4-cyclopentadiene CpCo(I) [18,19]. Polymerization catalyzed by the separated *exo*-substituted η^4-cyclopentadiene CpCo(I) complex showed similar results to that generated in situ did. To avoid the complicated separation and purification, in this paper, MMA was polymerized with a series of *exo*-substituted η^4-cyclopentadiene CpCo(I) complexes generated in situ in conjunction with EBiB as an initiator in toluene at 80 °C under inert atmosphere.

Cobaltocene was reacted with organic bromides overnight in toluene at room temperature under argon to generate the corresponding *exo*-substituted η^4-cyclopentadiene CpCo(I) complexes. Then MMA and EBiB were added to start the polymerization.

3.1. Steric effect

The results of the polymerization catalyzed by **1a** and **1b** are shown in Figs. 1 and 2. The semilogarithmic plots of $\ln([M]_0/[M])$ vs. time were linear, with a pseudo-first order rate constant (k_{obs}) of $9.2 \times 10^{-5}\ s^{-1}$ (**1a**), $1.8 \times 10^{-5}\ s^{-1}$ (**1b**), indicating that the radical concentration was constant during the polymerization (Fig. 1). The polymerization proceeded quickly, while with some induction period for **1b**. The **1b** induced polymerization proceeded much slower than that with **1a**, informing that a less bulky substituent decreases the polymerization rate.

Fig. 2 shows the number-average molecular weights (M_ns) and polydispersity index (PDI) values of the polymers obtained with **1a**



Scheme 2. The model reaction to generate the Co(I) complex in situ to catalyze the ATRP of MMA.

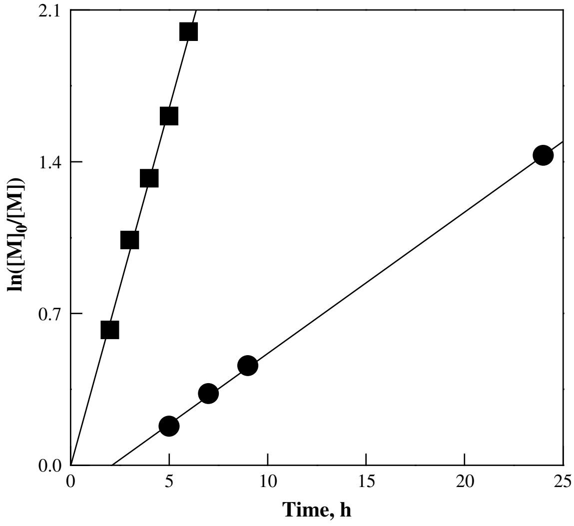


Fig. 1. Polymerization of MMA with CpCo(I)/EBiB in toluene at 80 °C; [MMA]$_0$:[EBiB]$_0$:[CpCo(I)]$_0$ = 200:1:1. CpCo(I): **1a** (■), **1b** (●).

and **1b**. The M_n values were directly proportional to monomer conversion. However, the M_n of the polymers obtained with **1b** was much higher than that with **1a**, noticing that the initiation efficiency was significantly decreased with a less bulky substituent. As shown in Table 1, the PDI values with **1b** were relatively narrow at low conversion (1.06) but became much broader (1.63) as the reaction proceeded, while the PDI values with **1a** were extremely narrow (below 1.2), as expected for a controlled polymerization. As a result of bulky substituent, the *exo*-substituted η^4-cyclopentadiene ligand may be more far away from the Co(I) centre in **1a** than that in **1b**. This would obtain a faster reaction rate and faster exchange between dormant and active species for **1a**, resulting faster polymerization and lower PDI values.

3.2. Electronic effect

The results of the polymerization catalyzed by **1b**, **1d**, and **1e** are shown in Figs. 3 and 4. The semilogarithmic plots of ln([M]$_0$/[M]) vs. time were linear for them, with a pseudo-first order rate constant (k_{obs}) of 5.5×10^{-5} s^{-1} (**1d**), 7.2×10^{-5} s^{-1} (**1e**), indicating a constant radical concentration during the polymerization (Fig. 3). The polymerization all proceeded quickly, while with some induction period. The reaction rate constant of **1b** was lower than that of **1d**, while the electron-withdrawing ability of the substituent in **1b** was stronger than that in **1d** according to their Taft σ^* constants (from Table 9.1 in Lange's Handbook of Organic Chemistry [35]), which are known for comparison of the electron-withdrawing ability, informing that weaker electron-withdrawing ability of the substituent results in high polymerization rate.

Table 1
Polymerizations of MMA with *exo*-substituted η^4-cyclopentadiene CpCo(I) complexes.

Catalyst	Time (h)	Conv, (%)	M_n	PDI
1a	2	46	20,400	1.12
	3	65	26,900	1.13
	4	73	31,200	1.12
	5	80	33,200	1.13
	6	86	36,300	1.15
1b	5	16	58,200	1.06
	6	28	67,500	1.08
	9	37	70,600	1.17
	24	76	97,400	1.63
1c	2	25	16,900	1.13
	3	46	21,800	1.14
	3.5	55	23,300	1.16
	4	62	25,300	1.15
	4.3	66	25,900	1.14
1d	5	37	37,000	1.09
	7	58	46,500	1.08
	8	65	51,400	1.05
	9	70	53,600	1.06
	9.5	75	55,600	1.05
1e	3	17	19,000	1.08
	4	36	29,800	1.07
	5	63	36,700	1.08
	6	71	43,000	1.06
	8	77	48,500	1.06

As shown in Fig. 4, the M_n values for **1b** and **1e** were directly proportional to monomer conversion. The molecular weights of the polymers obtained with **1d** were lower than that with **1b**,

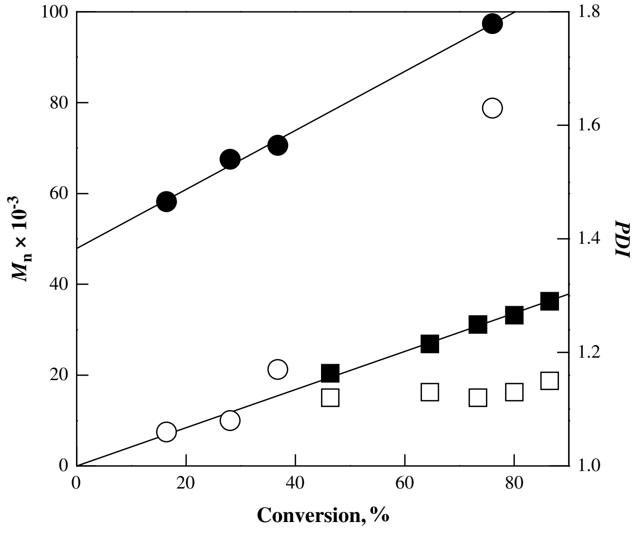


Fig. 2. M_n and PDI of poly(MMA) obtained with CpCo(I)/EBiB in toluene at 80 °C; [MMA]$_0$:[EBiB]$_0$:[CpCo(I)]$_0$ = 200:1:1. CpCo(I): **1a** (■), **1b** (●).

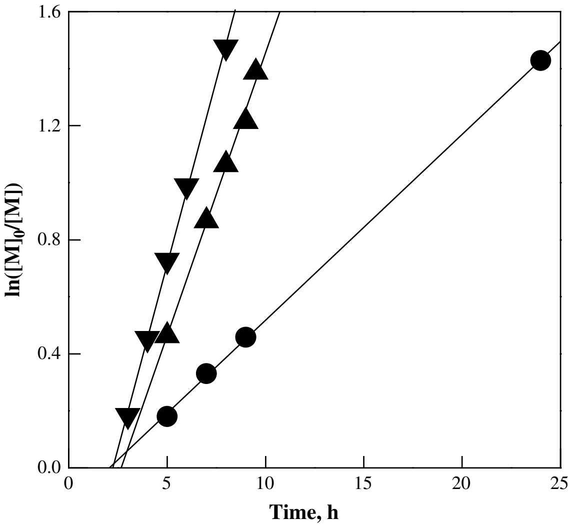


Fig. 3. Polymerization of MMA with CpCo(I)/EBiB in toluene at 80 °C; [MMA]$_0$:[EBiB]$_0$:[CpCo(I)]$_0$ = 200:1:1. CpCo(I): **1b** (●), **1d** (▲), **1e** (▼).

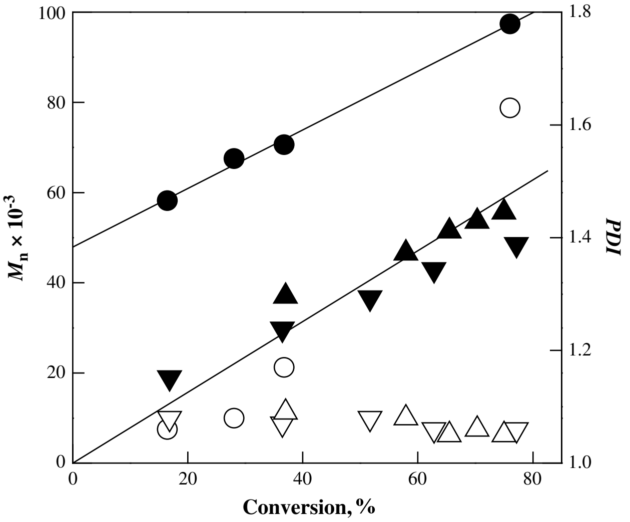


Fig. 4. M_n and PDI of poly(MMA) obtained with CpCo(I)/EBiB in toluene at 80 °C; $[MMA]_0$:$[EBiB]_0$:$[CpCo(I)]_0$ = 200:1:1. CpCo(I): **1b** (●), **1d** (▲), **1e** (▼).

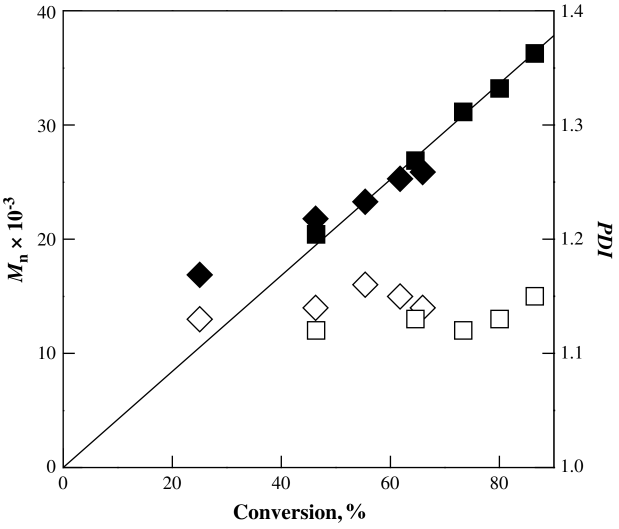


Fig. 6. M_n and PDI of poly(MMA) obtained with CpCo(I)/EBiB in toluene at 80 °C; $[MMA]_0$:$[EBiB]_0$:$[CpCo(I)]_0$ = 200:1:1. CpCo(I): **1a** (■), **1c** (□).

informing that weaker electron-withdrawing ability of the substituent results in higher initiation efficiency. While the substituents in **1d** and **1e** are very similar in steric and electronic effects, similar polymerization results were obtained. Both of the PDI values with **1d** and **1e** were extremely narrow (below 1.1, Table 1). The weaker electron-withdrawing abilities of the substituents in **1d** and **1e** could lower the redox potentials of these complexes and promote the redox reactions, causing a faster reaction rate and faster exchange between dormant and active species, and resulting faster polymerization, lower PDI values and improved conversion.

3.3. *Steric and electronic effects act together*

The results of the polymerization catalyzed by **1a** and **1c** are shown in Figs. 5 and 6. The semilogarithmic plot of $\ln([M]_0/[M])$ vs. time was linear for **1c**, with a pseudo-first order rate constant (k_{obs}) of 9.4×10^{-5} s^{-1}, indicating a constant radical concentration during the polymerization (Fig. 5). The polymerization with **1c** proceeded quickly, while with some induction period. The reaction rate constant of **1c** was almost the same as that of **1a**. As shown in Fig. 6, the M_n values for **1c** were also directly proportional to monomer conversion. The PDI values with **1c** were extremely narrow (below 1.2, Table 1), as expected for a controlled polymerization. The substituent in **1c** is less bulky than that in **1a**, but the electron-withdrawing ability of the substituent in **1c** was weaker than that in **1a**. These two factors acted together to make the polymerization catalyzed by **1c** as quickly as that by **1a**. The conversion with **1c** is evidently lower than those with others. This is probably due to the termination reaction, resulting from the decomposition of **1c**.

Our results confirm that the steric and electronic factors play an important role in the activity of ATRP catalysts. More bulky substituent makes the *exo*-substituted η^4-cyclopentadiene ligand more far away from the Co(I) centre, and weaker electron-withdrawing ability of substituent lower the redox potential of the Co(I) complexes facilitating halide abstraction from dormant species. This would shift the equilibrium toward active radical species and

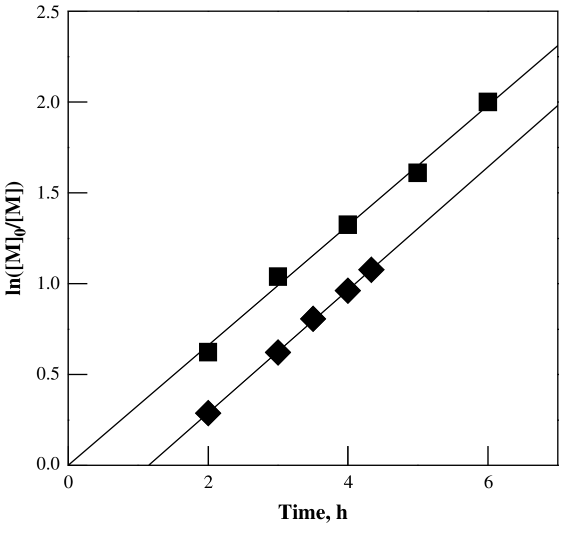


Fig. 5. Polymerization of MMA with CpCo(I)/EBiB in toluene at 80 °C; $[MMA]_0$:$[EBiB]_0$:$[CpCo(I)]_0$ = 200:1:1. CpCo(I): **1a** (■), **1c** (◆).

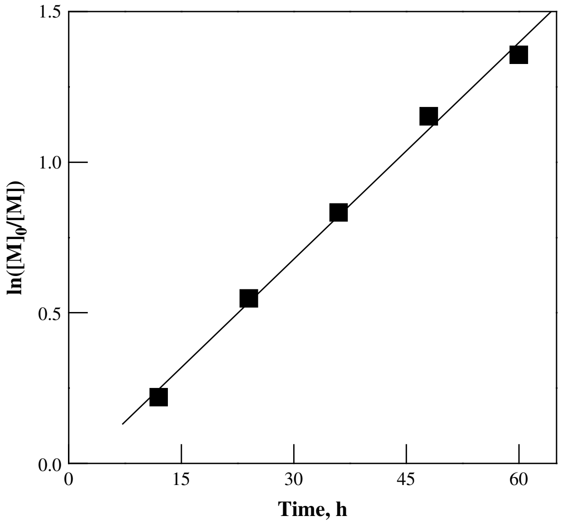


Fig. 7. Polymerization of styrene with **1e**/EBiB in toluene at 80 °C; $[styrene]_0$:$[EBiB]_0$:$[\mathbf{1e}]_0$ = 200:1:1.

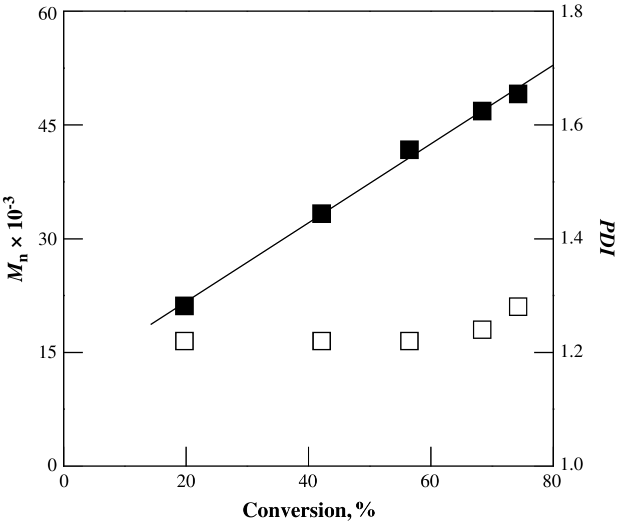


Fig. 8. M_n and PDI of polystyrene obtained with **1e**/EBiB in toluene at 80 °C; $[\text{styrene}]_0$:$[\text{EBiB}]_0$:$[\mathbf{1e}]_0 = 200:1:1$.

accelerate the exchange between dormant and active species, therefore increase the rate of polymerization without compromising the control.

3.4. Polymerization of styrene catalyzed by 1e

The PDI values of poly(MMA) catalyzed by **1d** and **1e** were extremely narrow (below 1.1, Table 1). That success in living radical polymerization of MMA prompted us to employ this catalyst to styrene. Thus, styrene was polymerized with **1e** coupled with EBiB as initiator.

A smooth polymerization occurred with an induction period, and the conversion reached 74% in 60 h (Fig. 7). As shown in Fig. 8, the M_n increased in direct proportion to monomer conversion. The PDI values of the obtained polystyrene were narrow throughout the reactions (below 1.3). The system with **1e** is superior to the reported **1a** system that gives broader PDI (1.3–1.4) in styrene polymerization under the similar condition [18].

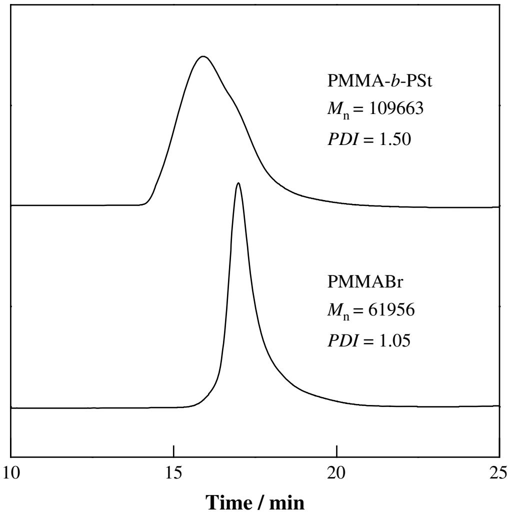


Fig. 9. GPC curves of PMMABr and PMMA-*b*-PSt.

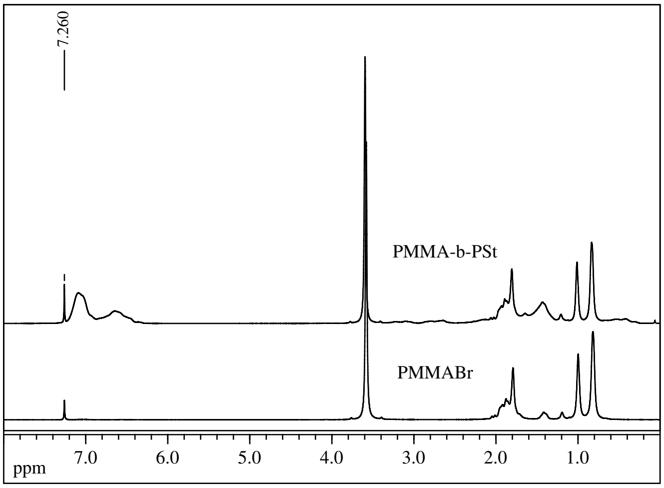


Fig. 10. ^{1}H NMR spectra of PMMABr and PMMA-*b*-PSt.

3.5. Block copolymerization with 1e

To examine the living nature of the polymerization catalyzed by **1e**/EBiB system, the block copolymer PMMA-*b*-PSt was synthesized successfully through the ATRP. Fig. 9 shows that the M_n increased from 62,000 to 109,700, while the polydispersities increased from 1.05 to 1.50. The ^{1}H NMR spectrum of the copolymer proved that the block copolymer was synthesized and the polymer end was living (Fig. 10).

4. Conclusions

In conclusion, a series of *exo*-substituted η^4-cyclopentadiene CpCo(I) complexes generated conveniently from cobaltocene in situ led to ATRP of MMA in conjunction with EBiB as initiator to give polymers with extremely narrow PDI (1.05–1.16) and controlled molecular weights. More bulky or weaker electron-withdrawing ability of *exo*-substituent at the η^4-cyclopentadiene ligand leads to higher rate and better initiation efficiency of polymerization catalyzed by the CpCo(I) complexes. Polymerization of styrene was catalyzed by **1e** with better control in comparison to **1a**. And the block copolymer PMMA-*b*-PSt was synthesized successfully by **1e**. Thus, it is convenient to modulate the polymerization with cobaltocene by adding different organic bromides, similar to modulating the polymerization catalyzed by Cu(I)X with different ligands. With the further study of the structure–property relationship, more efficient catalyst systems may be developed.

Acknowledgments

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