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The exo-substituted η^4-cyclopentadiene CpCo(I) complexes: A new kind of ATRP catalysts and the actual catalyst for the cobaltocene-catalyzed ATRP

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ABSTRACT

The exo-substituted η^4-cyclopentadiene CpCo(I) complexes were found to be the actual catalyst for the cobaltocene-catalyzed ATRP. Cobaltocene is just a precatalyst, which can be converted to the catalyst by the reaction with halide initiator. As a new kind of ATRP catalyst, the exo-substituted η^4-cyclopentadiene CpCo(I) complexes can catalyze the living radical polymerization of MMA, styrene, and the block copolymerization of MMA with styrene.

1. Introduction

Transition-metal-mediated living radical polymerization is one of the most important advances in polymer science in the 1990s. It is now a versatile tool to precisely synthesize well-defined (co)polymer with well controlled compositions, functionalities, topologies, even hybrids, new nanostructured materials, bioconjugates [1–9]. Among these approaches, ATRP is the most attractive one. Since Matyjaszewski and Sawamoto firstly reported two different catalyst systems independently in 1995 [10,11], a number of different transition metal complexes have been successfully applied to living radical polymerization, including systems based on Cu [12], Ru [13], Fe [14], Ni [15], Pd [16], Rh [17], Re [18], Mo [19], Co [20,21]. The transition metal complexes have critical effects in ATRP. It can induce reversible activation of a dormant carbon–halogen bond at a terminal *via* a single-electron transfer redox reaction to establish rapid dynamic equilibrium to keep low radical concentration and restrict irreversible termination (Scheme 1) [2,3].

A few years ago, our group reported the cobaltocene-catalyzed ATRP of MMA [20a]. Cobaltocene is a 19-electron complex, which can be easily oxidized. Sheats et al. [22,23] have exactly investigated the reactions between cobaltocene and organic halides in the ratio of 2:1 and obtained equal molar amounts of cobaltocenium halide and exo-substituted η^4-cyclopentadiene CpCo(I) complex. He has found a number of evidences to support that the reaction proceeded through a single-electron transfer process and proposed a possible mechanism for the reaction. The first step is generally thought to be that an electron transfers from cobaltocene to organic halide to form the 18-electron cobaltocenium and the radical anion $RX^{-}\bullet$, which then releases the radical $R\bullet$ and X^-. In the second step, the radical $R\bullet$ reacts with another equivalent of cobaltocene to give the exo-substituted η^4-cyclopentadiene CpCo(I) complex. In our previous report [20a], we suggested a possible mechanism for the ATRP catalyzed by cobaltocene as described in Scheme 2. According to this mechanism, the polymerization is controlled by the reversible activation of halide initiator by cobaltocene, and the second reaction is a side reaction, which will irreversibly terminate the polymerization. However, Poli pointed out in his recent review article that the actual catalyst may be the CpCo(I) or CpCo(II) complex, owing to the low efficiency factor ($f = 0.25$) [24]. To further explore the mechanism of cobaltocene-catalyzed ATRP, a systematic study was done in this paper, and the exo-substituted η^4-cyclopentadiene CpCo(I) complex was found to be the actual catalyst for the cobaltocene-catalyzed ATRP. The exo-substituted η^4-cyclopentadiene CpCo(I) complexes were also developed as a new kind of ATRP catalysts.

2. Experimental

2.1. General considerations

Methyl methacrylate (MMA) and styrene were dried over calcium hydride, distilled twice under reduced pressure, degassed

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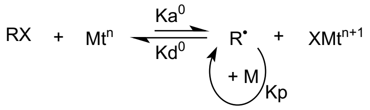
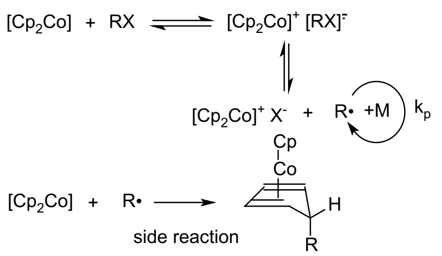


Scheme 1. ATRP of MMA with transition metal complexes.



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

and stored under argon at −15 °C. Cobaltocene and ethyl 2-bromoisobutyrate (EBiB) were prepared according to the literature [25,26]. Toluene was distilled from appropriate drying agents and deoxygenated before use.

2.2. Preparation of the CpCo(I)[η^4-$C_5H_5(Me_2CCO_2Et)$] (**1**)

Cobaltocene (1.021 g, 5.4 mmol) and ethyl 2-bromoisobutyrate (EBiB) (0.505 g, 2.6 mmol) were dissolved in 25 mL of toluene and stirred at 40 °C for 20 h. Then the mixture was filtered through a 3 cm plug of CuCl. After removal of solvent under reduced pressure, 0.752 g (94%) of complex **1** was obtained as a red oil. ^{1}H NMR ($CDCl_3$): δ 5.14 (br s, 2H diene-H), 4.71 (br s, 5H, C_5H_5), 4.02 (br s, 2H, CH_2CH_3), 2.97 (br s, 1H, Allyl-H), 2.69 (br s, 2H diene-H), 1.22 (br s, 3H, CH_2CH_3), 0.68 (s, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ 176.3, 78.9, 75.3, 59.7, 59.1,47.5, 41.0, 21.2, 14.2 ppm. MS (ESI): *m*/*z* 304.2 (M^+), 303.3 ($M^+ - 1$). IR (KBr): ν_{co} 1721(s) cm^{-1}. Anal. Calcd for $C_{16}H_{21}CoO_2$: C, 63.16; H, 6.96. Found: C, 62.86; H, 6.90.

2.3. Preparation of the CpCo(I)[η^4-$C_5H_5(Me_2CCN)$] (**2**)

Complex **2** was prepared according to the literature [27]. ^{1}H NMR ($CDCl_3$): δ 5.27 (br s, 2H diene-H), 4.75 (br s, 5H, C_5H_5), 2.82 (br s, 1H, Allyl-H), 2.79 (br s, 2H diene-H), 0.87 (s, 6H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ 123.9, 78.2, 74.7, 57.5, 38.2, 36.8, 21.8 ppm. MS (ESI): *m*/*z* 257.06 (M^+), 256.4 ($M^+ - 1$). IR (KBr): $\nu_{C\equiv N}$ 2227(s) cm^{-1}. Anal. Calcd for $C_{14}H_{16}CoN$: C, 65.37; H, 6.27; N, 5.45. Found: C, 65.08; H, 6.53; N, 5.35.

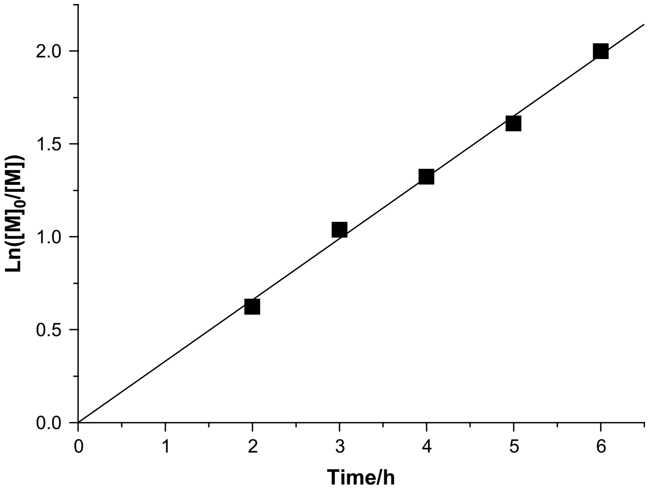


Fig. 1. Time dependence of ln($[M]_0/[M]$) at 80 °C with $[MMA]_0$:$[Cp_2Co]_0$:$[EBiB]_0$:$[EBiB]_0$ (initiator) = 200:2:1:1.

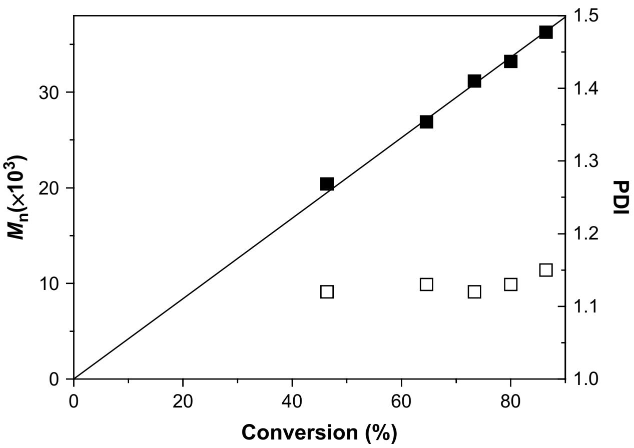


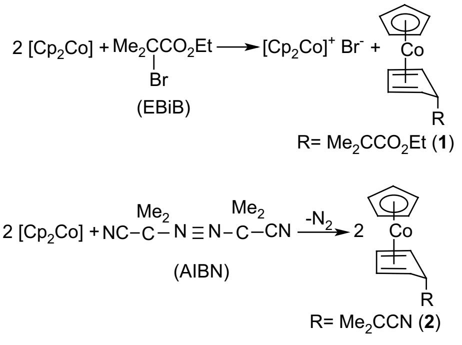
Fig. 2. Dependence of M_n and PDI on conversion at 80 °C with $[MMA]_0$:$[Cp_2Co]_0$:$[EBiB]_0$:$[EBiB]_0$ (initiator) = 200:2:1:1.

2.4. Polymerization

All manipulations were conducted under argon with standard Schlenk techniques. Polymerizations were carried out in 50 mL Schlenk flasks fitted with a Teflon stopcock. A typical polymerization procedure of MMA was as follows. 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). The catalyst (3×10^{-4} mol) was added, and oxygen was removed again. MMA (6.007 g, 6.0×10^{-2} mol), toluene (5 mL), and EBiB (58 mg, 3×10^{-4} mol) were added via gastight degassed syringe under the protection of argon. The flask was sealed with Teflon stopcock by three freeze–pump–thaw cycles to remove oxygen, and then immersed in an oil bath at 80 °C. At timed intervals, samples were withdrawn via a degassed syringe, diluted with THF, added to mass methanol, and the white polymers were obtained, dried under vacuum. The conversions were determined by gravity.

2.5. Characterizations

The number- and weight-average molecular weight and polydispersities of polystyrene were measured by GPC (Waters 510



Scheme 3. Preparation of complexes **1** and **2**.

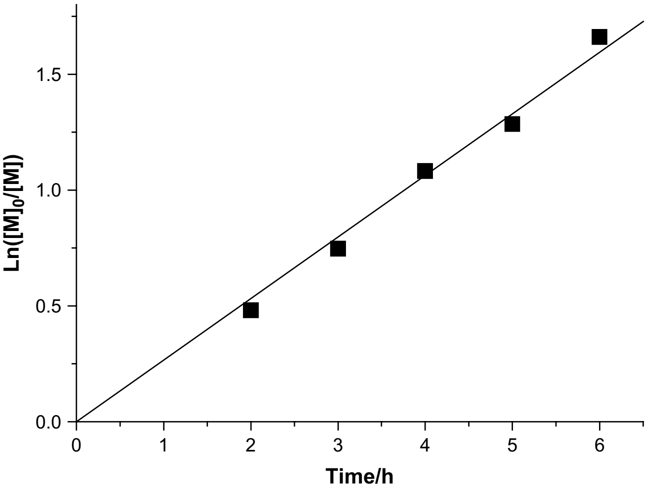


Fig. 3. Time dependence of ln([M]$_0$/[M]) at 80 °C with [MMA]$_0$:[**1**]$_0$:[EBiB]$_0$ = 200:1:1.

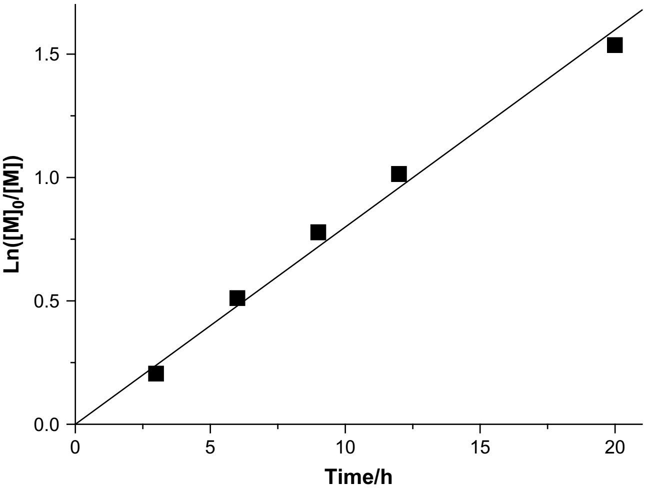


Fig. 5. Time dependence of ln([M]$_0$/[M]) at 80 °C with [St]$_0$:[**1**]$_0$:[EBiB]$_0$ = 200:1:1.

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 35 °C). Calibration was made with standard samples of polystyrene. ^{1}H and ^{13}C NMR spectra were recorded on a VARIAN AS-400 spectrometer in $CDCl_3$, using tetramethylsilane as the internal standard. IR spectra were recorded as KBr disks on a Nicolet 380 FT-IR spectrometer. Mass spectra were recorded on a TRACE DSQ instrument. Elemental analyses were performed on a Perkin–Elmer 240C analyzer.

2.6. Block copolymerization

The general procedure was conducted as described above. The reaction was carried out at 80 °C with MMA. After 7 h the MMA was almost consumed and an equal St was added under argon. After 24 h, the copolymer was obtained without further purification.

3. Results and discussion

To further explore the mechanism of cobaltocene-catalyzed ATRP, the reaction of MMA in the presence of cobaltocene and EBiB was carried out in toluene at 80 °C under argon atmosphere with [MMA]$_0$:[Cp_2Co]$_0$:[EBiB]$_0$ = 200:2:1. After 16 h, no polymer was obtained, indicating that the initiator EBiB was fully consumed by cobaltocene. But when another 1 equiv of EBiB was added, the polymerization was initiated. The plot of ln([M]$_0$/[M]) *vs.* time (Fig. 1) was linear with a pseudo-first order rate constant (k_{obs}) of 0.33 h^{-1}, indicating that the radical concentration was constant. The molecular weight (M_n) increased linearly with conversion and the polydispersities were very low (~1.1) (Fig. 2). The efficiency factor (f) of total EBiB was 0.24. In fact, half of EBiB was consumed by cobaltocene, the effective f should be 0.48. These results indicated that the exo-substituted η^4-cyclopentadiene CpCo(I) complex should be the actual catalyst for the cobaltocene-catalyzed ATRP and the reaction of cobaltocene with RX was irreversible. However, there is another possibility, as Poli pointed [24], the CpCo(II) complex, formed by reaction of the exo-substituted η^4-cyclopentadiene CpCo(I) complex with halide initiator, may also be the actual catalyst. Then, the polymerization of MMA under the same condition with [MMA]$_0$:[CpCo(I)]$_0$:[EBiB]$_0$ = 200:2:1 was carried out and polymer was formed (40% conversion was achieved in 4 h). This result excluded the possibility of the CpCo(II) complex as the actual catalyst. Besides, the dimer $(Cp^*CoBr)_2$ was also synthesized [28] and it could not catalyze the polymerization of MMA under the above condition.

To further support this mechanism, two exo-substituted η^4-cyclopentadiene CpCo(I) complexes CpCo(I)[η^4-$C_5H_5(Me_2CCO_2Et)$]

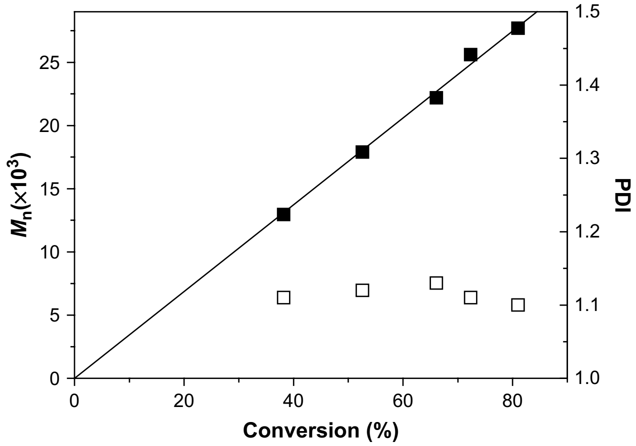


Fig. 4. Dependence of M_n and PDI on conversion at 80 °C with [MMA]$_0$:[**1**]$_0$:[EBiB]$_0$ = 200:1:1.

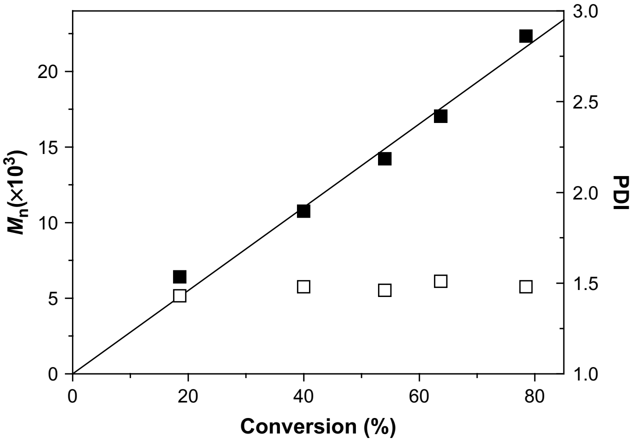


Fig. 6. Dependence of M_n and PDI on conversion at 80 °C with [St]$_0$:[**1**]$_0$:[EBiB]$_0$ = 200:1:1.

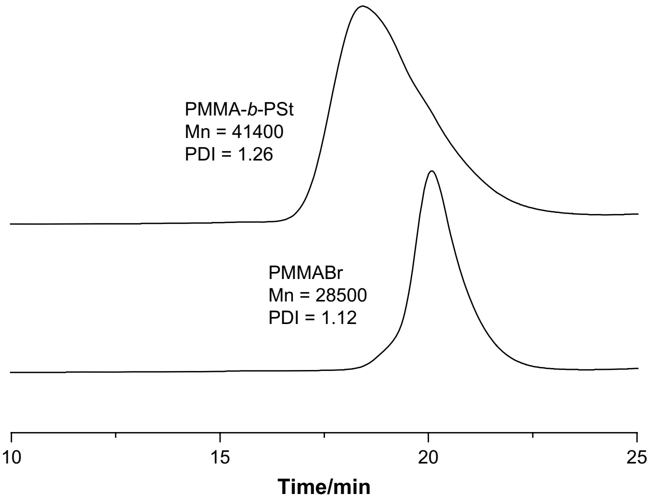


Fig. 7. GPC curves of PMMABr and PMMA-*b*-PSt.

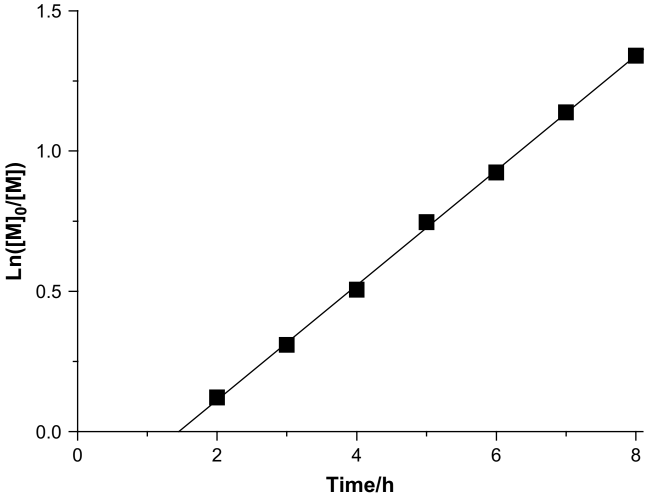


Fig. 9. Time dependence of $\ln([M]_0/[M])$ at 80 °C with $[MMA]_0$:$[\mathbf{2}]_0$:$[EBiB]_0 = 200:1:1$.

(**1**) and CpCo(I)[η^4-$C_5H_5(Me_2CCN)$] (**2**) were synthesized by the reactions of cobaltocene with EBiB and AIBN [27], respectively (Scheme 3), fully characterized by ^{1}H NMR, ^{13}C NMR, ESI-MS, elemental analysis, and applied successfully to the ATPP.

The polymerization of MMA catalyzed by complex **1** with 1 equiv of EBiB as initiator was carried out in toluene at 80 °C ($[MMA]_0$:$[\mathbf{1}]_0$:$[EBiB]_0 = 200:1:1$). The plot of $\ln([M]_0/[M])$ *vs.* time (Fig. 3) was linear with a pseudo-first order rate constant (k_{obs}) of 0.27 h^{-1}, which is slightly smaller than that for the *in situ* polymerization from cobaltocene (0.33 h^{-1}). The molecular weight (M_n) increased linearly with conversion and the polydispersities were quite low (~ 1.1) (Fig. 4). The efficiency factor was 0.59, a little higher than that for the Cp_2Co/EBiB system.

Complex **1** was also applied to the ATRP of styrene with $[St]_0$:$[\mathbf{1}]_0$:$[EBiB]_0 = 200:1:1$. The plot of $\ln([M]_0/[M])$ *vs.* time (Fig. 5) was linear with a pseudo-first order rate constant (k_{obs}) of 0.08 h^{-1}, which is much smaller than that for MMA polymerization. The molecular weight (M_n) also increased linearly with conversion, but the polydispersities were slightly broader (~ 1.5) (Fig. 6). The efficiency factor was 0.73.

To examine the living nature of the polymerization catalyzed by the η^4-cyclopentadiene CpCo(I) complex, the block copolymer PMMA-*b*-PSt was synthesized successfully through the ATRP catalyzed by complex **1**. Fig. 7 shows that the M_n increased from 28,500 to 41,400, while the polydispersities increased from 1.12 to 1.26. The ^{1}H NMR spectrum of the copolymer proved that the block copolymer was synthesized and the polymer end was living (Fig. 8).

Complex **2** was also applied successfully for the ATRP of MMA and styrene with 1 equiv of EBiB as initiator ($[Monomer]_0$:$[\mathbf{2}]_0$:$[EBiB]_0 = 200:1:1$). The plots of $\ln([M]_0/[M])$ *vs.* time (Figs. 9 and 10) were linear with a pseudo-first order rate constant (k_{obs}) of 0.21 and 0.068 h^{-1}, respectively, but both with a retardation for about 1.5 h. The molecular weight (M_n) increased linearly with conversion (Figs. 11 and 12). The polydispersities were quite low (~ 1.1) for PMMA but slightly broader (~ 1.5) for polystyrene. The efficiency factors were 0.68 and 0.78, respectively. The *y*-intercepts were *ca.* 20,000 and 3000, respectively, which may be attributed to the different property of the cyano group from the ester group.

All these results have proved that the exo-substituted η^4-cyclopentadiene CpCo(I) complex must be the actual catalyst for the cobaltocene-catalyzed ATRP, and the reaction of cobaltocene with organic halide is irreversible. So the mechanism of cobaltocene-catalyzed ATRP may follow as described in Scheme 4. The polymerization was controlled by the reversible activation of halide initiator by the exo-substituted η^4-cyclopentadiene CpCo(I)

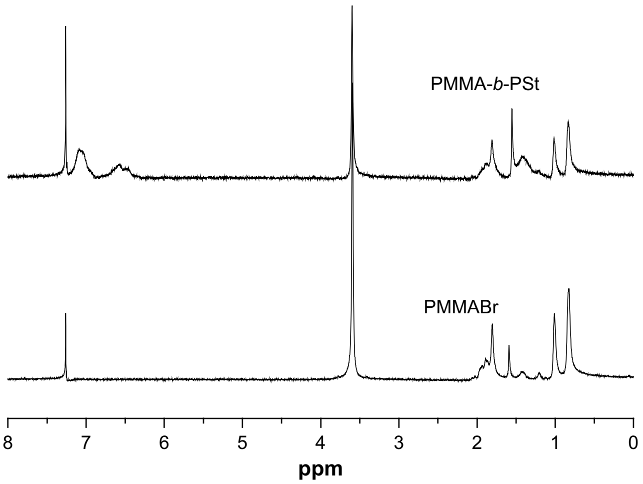


Fig. 8. The ^{1}H NMR spectra of PMMABr and PMMA-*b*-PSt.

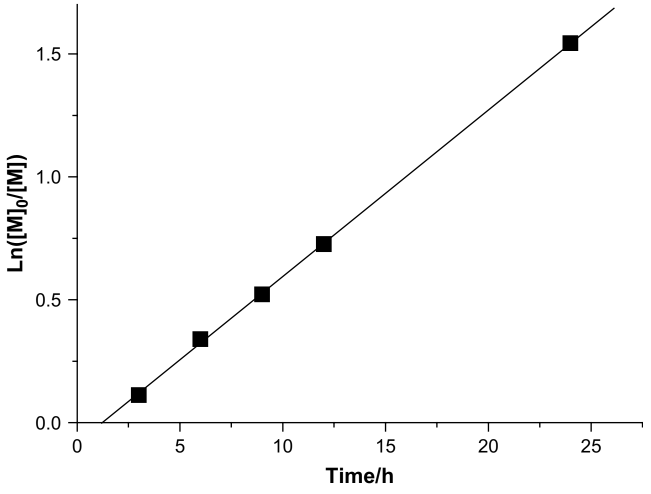


Fig. 10. Time dependence of $\ln([M]_0/[M])$ at 80 °C with $[St]_0$:$[\mathbf{2}]_0$:$[EBiB]_0 = 200:1:1$.

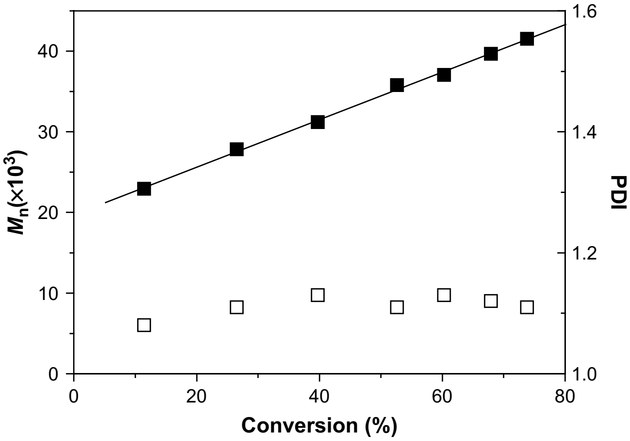


Fig. 11. Dependence of M_n and PDI on conversion at 80 °C with $[MMA]_0$:$[\mathbf{2}]_0$:$[EBiB]_0 = 200:1:1$.

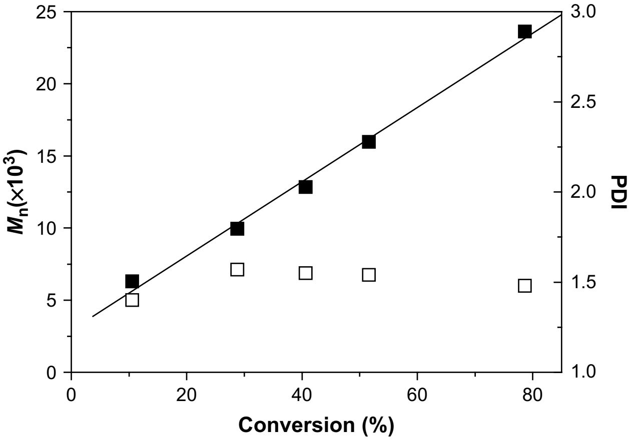
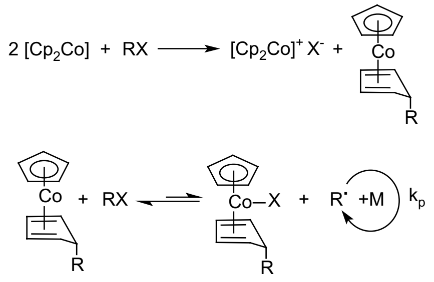


Fig. 12. Dependence of M_n and PDI on conversion at 80 °C with $[St]_0$:$[\mathbf{2}]_0$:$[EBiB]_0 = 200:1:1$.

complex. Cobaltocene is just a precatalyst, which can be converted to the actual catalyst by reaction with halide initiator. However, there are still some problems. Although the efficiency factors of the initiator were much improved by using the exo-substituted η^4-cyclopentadiene CpCo(I) complexes instead of cobaltocene, the efficiency factors are still not very high. The system may be more complicated than those as suggested. Some side reactions [such as the oxidation addition of CpCo(I) with alkyl halide initiator] may exist and reduce the initiator efficiency. The more clear and detailed mechanism needs further investigation.



Scheme 4. The mechanism of cobaltocene-catalyzed ATRP.

4. Conclusions

In conclusion, we have demonstrated that the exo-substituted η^4-cyclopentadiene CpCo(I) complex is the actual catalyst for the cobaltocene-catalyzed ATRP. Cobaltocene is just a precatalyst, which can be converted to the actual catalyst by reaction with halide initiator. As a new kind of ATRP catalysts, the exo-substituted η^4-cyclopentadiene CpCo(I) complexes can catalyze the living radical polymerization of MMA, styrene, and the block copolymerization of MMA with styrene. Cobaltocene is a good precatalyst due to the high performance and easy availability.

Acknowledgments

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