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Controlled/living radical polymerization of styrene catalyzed by cobaltocene

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ABSTRACT

Controlled/living radical polymerization of styrene has been achieved by atom transfer radical polymerization (ATRP) catalyzed by cobaltocene (PDI = 1.27–1.41). The effects of the initiators, temperatures and solvents were studied. The end group of PS–Br was characterized by ^{1}H NMR. Block copolymerization proved that the polymer end is still living and the PMMA-*b*-PSt block copolymer was synthesized.

1. Introduction

Transition-metal-mediated living radical polymerization, especially atom transfer radical polymerization, has developed into a versatile tool to precisely synthesize well-defined (co)polymer with well controlled compositions, functionalities, topologies, even hybrids, new nanostructured materials and bioconjugates [1–18]. Since Matyjaszewski and Sawamoto first reported two different catalyst systems independently in 1995 [19,20], a number of different transition metal complexes have been successfully applied to living radical polymerization, including systems based on Cu [21], Ru [22], Fe [23], Ni [24], Pd [25], Rh [26], Re [22i,27], Mo [28], Co [29,30]. 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 dynamics equilibrium to keep low radical concentration and restrict irreversible termination [31,32]. Metallocene complexes have been extensively studied as olefin polymerization catalysts over the past 20 years. It has been found that their catalytic behavior can be significantly affected by slight structural variations of the bridging group and ring substituents in metallocene catalysts [33]. The sandwich metallocene complexes are the most studied organometallic complexes [34]. With a view to develop a new ATRP catalyst system with two cyclopentadienyl ligands, we decided to study the sandwich metallocene complexes. They show good reversibility between the reduced and oxidized forms; especially, ferrocene has been used as the standard sample for the cyclic voltammetry experiment. Besides, metallocene complexes can be readily modified by introduction of a bridging group or ring substituents in the cyclopentadienyl rings. This will make us further understand the steric and electronic factors influencing the behavior of the metallocene ATRP catalysts.

Some time ago, we successfully employed cobaltocene/ethyl 2-bromoisobutyrate (EBiB) for MMA living radical polymerization [29]. The polydispersities of PMMA obtained were very narrow (<1.15). In this paper, we examined the polymerization of styrene catalyzed by cobaltocene. The results showed that the polymerization can be controlled though the polydispersities of polystyrenes were a little broad. To support the mechanism, the end group of PS–Br was characterized by ^{1}H NMR. Block copolymerization experiment also proved the living end group.

2. Experimental

2.1. General considerations

Styrene was dried over calcium hydride, distilled twice under reduced pressure, degassed and stored under argon at −15 °C. Cobaltocene, ethyl 2-bromoisobutyrate (EBiB), and 1-phenyl ethylbromide (PEBr) were prepared according to the literatures [35–37]. All solvents were distilled from appropriate drying agents and deoxygenated before use.

2.2. Polymerization of styrene

All manipulations were conducted under argon with standard Schlenk techniques. Polymerizations were carried out in 100-mL Schlenk flasks fitted with a Teflon stopcock. A typical polymerization

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procedure of styrene 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). Cobaltocene (58 mg, 3×10^{-4} mol) was added, oxygen was removed again. Styrene (6.249 g, 6.0×10^{-2} mol), toluene (5 mL) and EBiB (58 mg, 3×10^{-4} mol) were added via gastight degassed syringes under the protection of argon at room temperature. 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 (0.8 mL) were withdrawn via a degassed syringe, diluted with THF (8 mL), added to methanol (100 mL), and white polymers were obtained, dried under vacuum. The conversions were determined by gravity.

2.3. *Block copolymerization*

The general procedure was conducted as described above, only the initiator EBiB was added later, when the solution was preheated in oil bath for 20 min. The reaction was carried out at 70 °C with MMA, after 24 h, MMA was almost consumed. A second and equal St was added under argon. The same procedure was used to get polymers as described above. The copolymer was obtained without further purification.

2.4. *Characterizations*

The number- and weight-average molecular weights and polydispersities of polystyrene 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 of 1 mL min^{-1}, and the column temperature was 25 °C). Calibration was made with standard samples of polystyrene. ^{1}H NMR spectra were recorded on a VARIAN AS-400 spectrometer at room temperature in $CDCl_3$, using tetramethylsilane as internal standard.

3. Results and discussion

3.1. *Temperature effect on controlled radical polymerization of styrene with Cp_2Co*

The results of the polymerization of styrene initiated with EBiB/Cp_2Co in toluene at 60–90 °C are shown in Figs. 1 and 2. When the molar ratio is $[St]_0$:$[Cp_2Co]_0$:$[Initiator]_0 \approx 200{:}1{:}1$, at higher reaction temperature, the higher rate of polymerization (0.005 h^{-1}, 0.014 h^{-1}, 0.031 h^{-1}, and 0.040 h^{-1} for 60, 70, 80, and 90 °C, respectively) was observed. From 60 °C to 90 °C, the polymerizations were all pseudo-first order reactions (Fig. 1), and the number-average molecular weight (M_n) of the obtained polystyrene increased in direct proportion to monomer conversion (Fig. 2). The efficiency (*f*) of initiator increased slowly with increasing temperature (0.38, 0.46, 0.42, and 0.50). The polydispersities (M_w/M_n) (1.27–1.41) at 80 °C were narrower than those at other temperatures. This is possibly due to that cobaltocene is just a precatalyst, which should be converted to the active catalyst first (see Section 3.5). At low temperatures (60 °C, 70 °C) the conversion may be slow and incomplete, but high temperature (90 °C) may cause some side reactions. So 80 °C is the most appropriate temperature for styrene polymerization catalyzed by Cp_2Co. The end group of PS–Br was also characterized by ^{1}H NMR (Fig. 3).

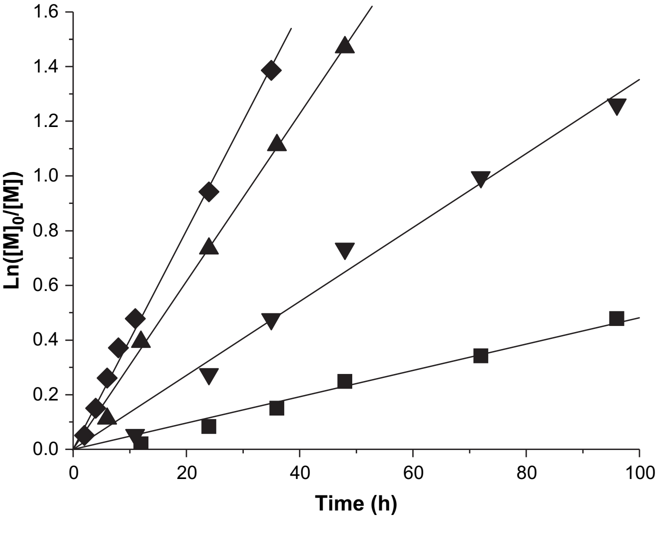


Fig. 1. Time dependence of ln$[M]_0/[M]$ in toluene. $[St]_0 \approx 12.0$ M; $[Cp_2Co]_0 = 60$ mM; $[initiator]_0 = 60$ mM.; 60 °C (■), 70 °C (▼), 80 °C(▲), 90 °C(◆).

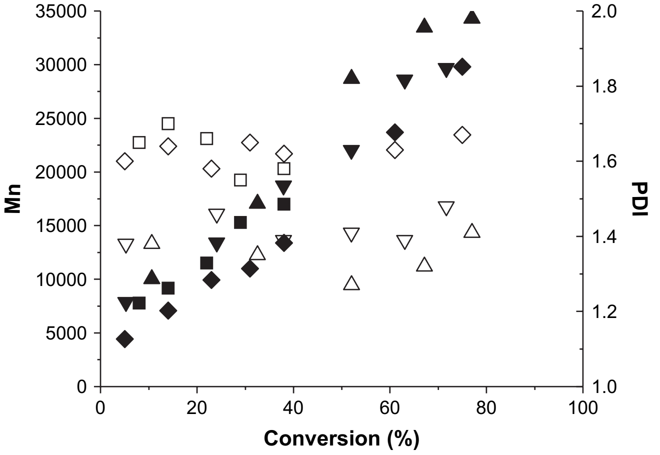


Fig. 2. Dependence of the molecular weights and polydispersities of PSt on monomer conversion in toluene (conditions as Fig. 1); 60 °C (■□), 70 °C (▼▽), 80 °C(▲△), 90 °C(◆◇).

3.2. *Initiator effect on controlled radical polymerization of styrene with Cp_2Co*

The polymerization of styrene was initiated with EBiB and PEBr catalyzed by cobaltocene in toluene at 80 °C under same conditions. When it was initiated by EBiB, the plot of ln($[M]_0/[M]_t$) *vs.*

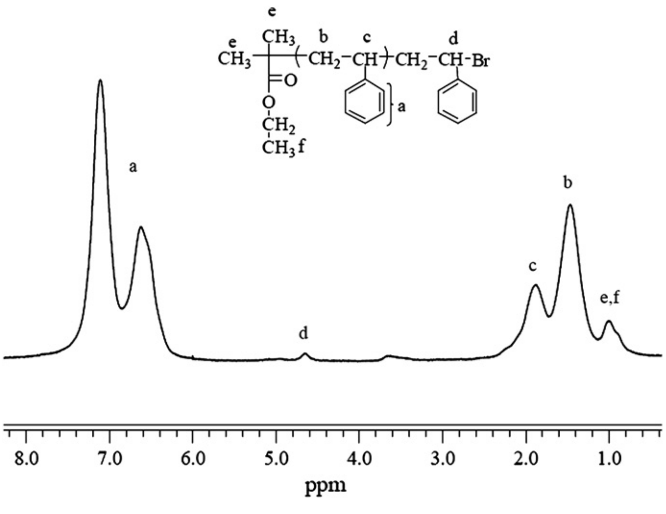


Fig. 3. ^{1}H NMR (400 MHz) of PS-Br in $CDCl_3$.

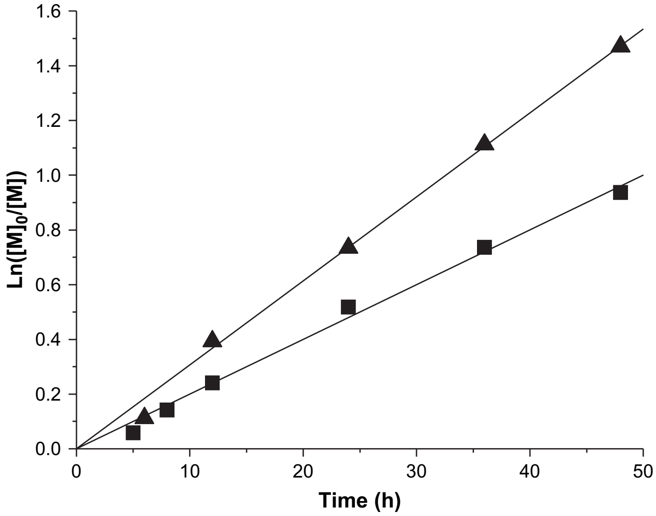


Fig. 4. Time dependence of ln[M]$_0$/[M] at 80 °C in toluene. [St]$_0$ ≈ 12.0 M; [Cp$_2$Co]$_0$ = 60 mM; [initiator]$_0$ = 60 mM, EBiB as initiator (▲); PEBr as initiator (■).

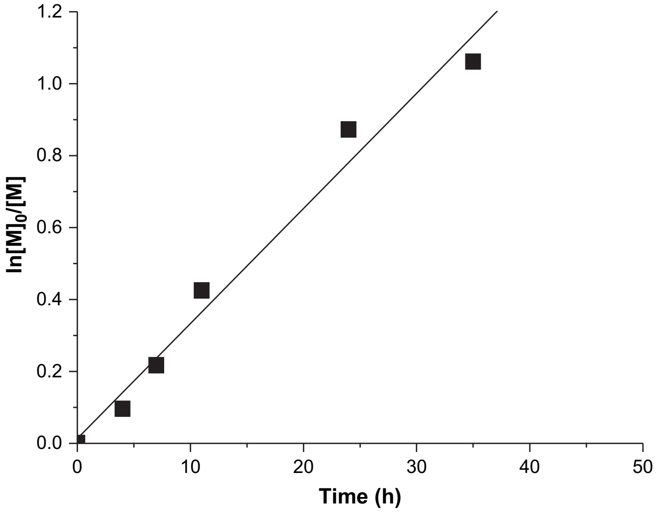


Fig. 6. Time dependence of ln[M]$_0$/[M] at 80 °C in dioxane. [St]$_0$ = 12.0 M; [Cp$_2$Co]$_0$ = 60 mM; [EBiB]$_0$ = 60 mM.

time (Fig. 4) was linear with a pseudo-first order rate constant (k_{obs}) of 0.031 h^{-1}, indicating that the radical concentration is constant throughout the polymerization. The molecular weight (M_n) increased linearly with conversion (Fig. 5). The polydispersities (M_w/M_n) are low (1.27–1.41), and the efficiency (*f*) of initiator as computed from $f = M_{n(th)}/M_{n(GPC)}$ was 0.42. When it was initiated by PEBr, the plots of ln([M]$_0$/[M]$_t$) *vs.* time (Fig. 4) and the molecular weight (M_n) *vs.* conversion (Fig. 5) were also linear. The polymerization rate was reduced evidently ($k_{obs} = 0.020$ h^{-1}), the polydispersities increased (1.43–1.71), and the efficiency (*f*) of initiator was a little higher to 0.46. The results showed that EBiB is much better than PEBr as initiator for styrene living polymerization catalyzed by Cp$_2$Co. The different performance between the two initiators is mainly due to the different C–Br bond strengths of EBiB and PEBr. Matyjaszewski has determined the activation rate constant and found that EBiB was 16 times faster than PEBr [38].

3.3. *Solvent effects on controlled radical polymerization of styrene with Cp$_2$Co*

In order to examine the solvent effect, dioxane was employed as a solvent for the polymerization of styrene with EBiB/Cp$_2$Co at 80 °C. The polymerization was also pseudo-first order reaction (Fig. 6), and the M_n increased linearly with conversion (Fig. 7). In comparison to the non-polar solvent (toluene), the pseudo-first order rate constant (k_{obs}) was almost unchanged and the efficiency (*f*) was improved to 0.52, but the polydispersities (M_w/M_n) were broader than that in toluene. The results indicated that toluene is better than dioxane as solvent for this polymerization.

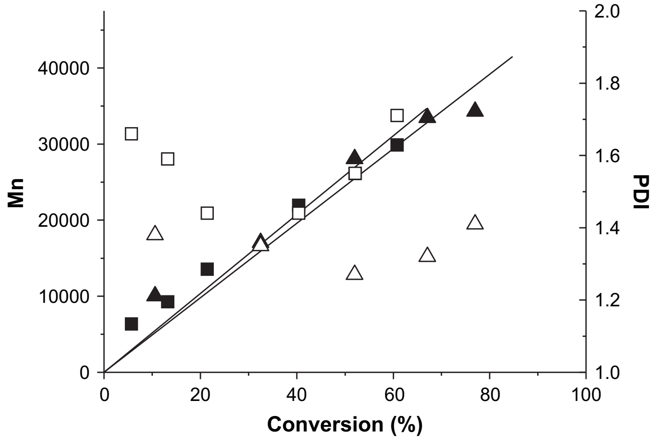


Fig. 5. Dependence of the molecular weights and polydispersities of PSt on monomer conversion at 80 °C in toluene (condition as Fig. 1), EBiB as initiator (▲ △); PEBr as initiator (■ □).

3.4. *Block copolymerization*

To examine the living nature of the polymerization catalyzed by cobaltocene/EBiB system, an equal amount of fresh styrene was added to the reaction system, when the initial MMA had almost been consumed (86.4%) (Fig. 8). The second step polymerization went on successfully. The conversion of St reached 61.8% after 72 h, and the M_n increased from 24,500 to 35,200, while the polydispersities increased from 1.11 to 1.40 (Fig. 9). ^{1}H NMR spectrum proved that the block copolymer was synthesized and the end was living (Fig. 10).

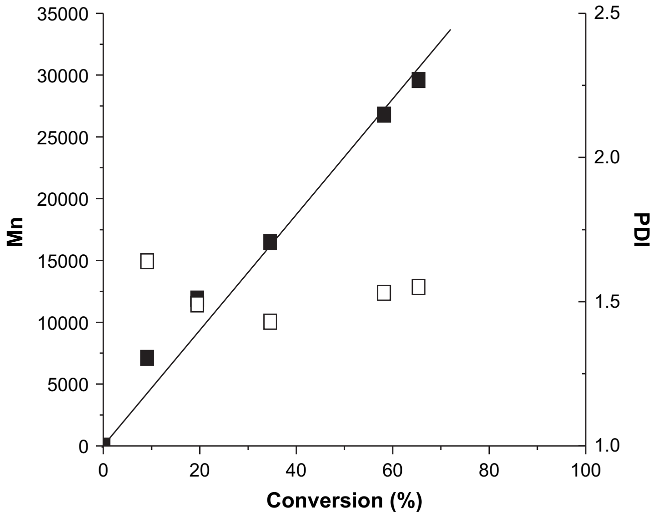


Fig. 7. Dependence of the molecular weights and polydispersities of PSt on monomer conversion at 80 °C in dioxane (conditions as Fig. 6).

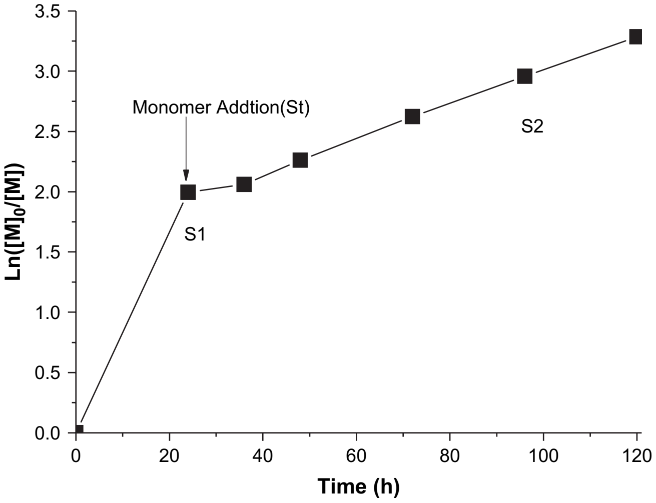


Fig. 8. Block copolymerization results. Time dependence of $\ln[M]_0/[M]$ at 70 °C in toluene. $[MMA]_0 = [St]_0 = 60$ M; $[Cp_2Co]_0 = 60$ mM; $[EBiB]_0 = 60$ mM.

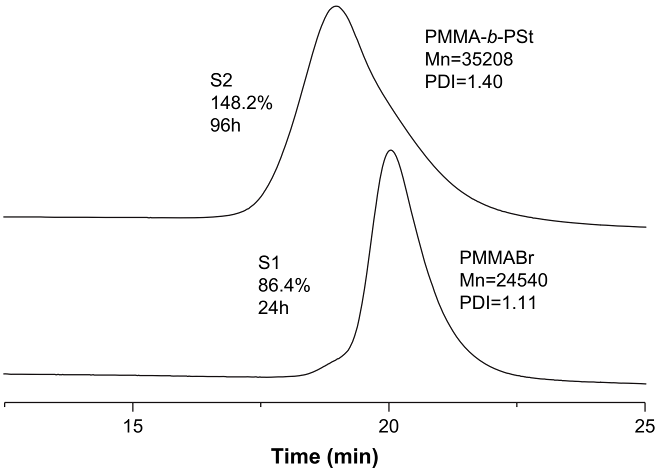


Fig. 9. GPC curves of S1 and S2.

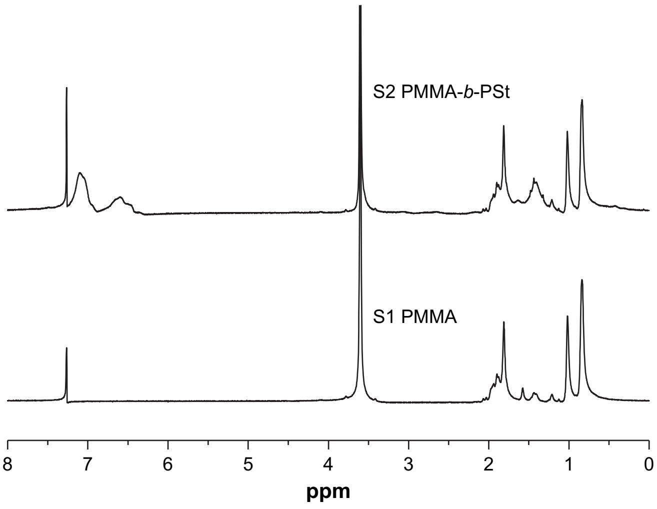
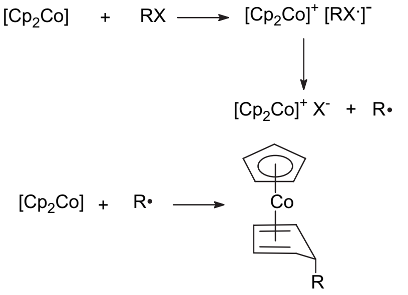


Fig. 10. ^{1}H NMR (400 MHz) of S1 and S2.

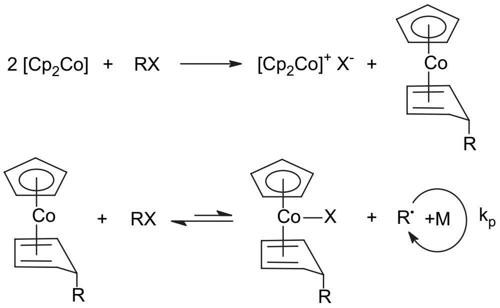
3.5. Mechanism

Cobaltocene is a 19-electron compound; it is easily oxidized. Sheats [34,36] has exactly investigated the reaction between cobaltocene with organic halides and got equal molar amount of the cobalticinium halide and the *exo*-substituted η^4-cyclopentadiene complex. He found a number of evidences to support this reaction by a charge-transfer radical course and proposed a possible mechanism for the reaction. The first step is generally thought that an electron is transferred from cobaltocene to the organic halide to form the 18-electron cobalticinium and a radical anion $RX^{\bullet-}$, which then releases a radical $R^{\bullet}$ and X^-. In the second step, the $R^{\bullet}$ radical further reacts with cobaltocene to give the *exo*-substituted η^4-cyclopentadiene complex (Scheme 1).

To confirm this mechanism, reaction of cobaltocene with EBiB under the polymerization condition was done and a yellow solid and a red oil were obtained. They were characterized by MS and ^{1}H NMR spectra to be Cp_2CoBr [MS (ESI): *m*/*z* 189.32 (Cp_2Co^+), 79.01 (Br^-); ^{1}H NMR ($CDCl_3$) δ: 5.95 (s, 10H, C_5H_5)] and the *exo*-substituted η^4-cyclopentadiene Co(I) complex [MS (ESI): *m*/*z* 304.28 (M^+); ^{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)]. So in our previous report [29] we suggested that the mechanism of the controlled radical polymerization catalyzed by cobaltocene is similar. We considered that the polymerization is controlled through the reversible activation of halide initiator by cobaltocene, and the second step is a side reaction, which will irreversibly terminate the polymerization. However, recently Poli [39] in his review article pointed out that the active catalyst may be the *exo*-substituted η^4-cyclopentadiene Co(I) complex, due to the low initiation efficiency. We retested the polymerization with a Cp_2Co/EBiB ratio of 2:1, and no polymerization was found. The polymerization started again by further addition of 1 equiv of initiator. This indicated that the *exo*-substituted η^4-cyclopentadiene Co(I) complex was indeed the active catalyst and the reaction of cobaltocene



Scheme 1. The reaction mechanism of cobaltocene with RX.



Scheme 2. The possible mechanism of controlled/living radical polymerization catalyzed by cobaltocene.

with RX was irreversible. So the mechanism of the controlled radical polymerization catalyzed by cobaltocene may follow as described in Scheme 2. The polymerization was controlled through the reversible activation of halide initiator by the *exo*-substituted η^4-cyclopentadiene Co(I) complex. Cobaltocene is just a precatalyst, which can be converted to the active catalyst by reaction with halide initiator. The detailed mechanism study is still under progress.

4. Conclusions

In conclusion, we have demonstrated that Cp_2Co/EBiB system can catalyze the controlled living radical polymerization of styrene. The molecular weight increased linearly with conversion and narrow polydispersities (1.27–1.41) were achieved at 80 °C. Block copolymerization proved that the polymer end is still living and the PMMA-*b*-PSt block copolymer was synthesized.

Acknowledgments

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