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Controlled/“Living” Radical Polymerization of MMA Catalyzed by Cobaltocene

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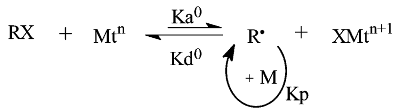
Transition-metal-mediated living radical polymerization, sometimes known as atom transfer radical polymerization (ATRP), is now one of the most rapidly developing areas in the past several years.[1,2] Since Matyjaszewski[3] and Sawamoto[4] first reported two different catalyst systems independently in 1995, a number of different transition-metal complexes have been successfully used in living radical polymerization, including systems based on Cu,[5] Ru,[6] Fe,[7] Ni,[8] Pd,[9] Rh,[10] Re,[11] and Mo.[12] The transition-metal complex in ATRP plays a key role in controlling the chain growth, polymerization rate, and polydispersities. As a catalyst, the complex induces reversible activation of a dormant carbon−halogen bond at a terminal via a one-electron redox reaction of the metal center (Scheme 1). Thus, the metal center must possess at least two readily accessible oxidation states separated by one electron, and there should be good reversibility between the reduced and oxidized forms of the catalyst.

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.[13] With a view to develop a new ATRP catalyst system with two cyclopentadienyl ligands, we decided to study the sandwich metallocene complexes. The sandwich metallocene complexes are the most studied organometallic complexes.[14] They have good reversibility between the reduced and oxidized forms; especially, ferrocene has been used as the standard sample for the cyclic voltammetry experiment. Another advantage of the metallocene complexes is that they 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 metallocenes have been used as the catalysts for polymerization of acrylic acids.[15] In this case, the metallocenes are presumably oxidized by accepting a halogen radical in the polymerization. In this paper, we report the controlled/“living” radical polymerization of MMA based on cobaltocene and ethyl 2-bromoisobutyrate (EBiB), which produces polyMMA with very narrow polydispersities (PDI < 1.15).

Scheme 1



Cobaltocene was easily prepared by a literature procedure[16] or purchased from Aldrich. The homogeneous polymerization of MMA initiated with EBiB and cobaltocene was carried out in toluene at 70 °C under an argon atmosphere with $[\mathrm{MMA}]_0$:$[\mathrm{EBiB}]_0$:$[\mathrm{Cp_2Co}]_0$ = 235:1:1. The semilograithmic plot of $\ln([\mathrm{M}]_0/[\mathrm{M}]_t)$ vs time (Figure 1) is linear with a pseudo-first-order rate constant (k_{obs}) of 0.083 h^{-1}, indicating that the radical concentration is constant throughout the polymerization. There an obvious retardation was observed. The molecular weight (M_n) increases linearly with time. The polydispersities (PDI) are quite low (∼1.1) (Figure 2), but the $M_{\mathrm{n(calc)}}$ is larger than $M_{\mathrm{n(GPC)}}$, and the efficiency (f) of the initiator as computed from $f = M_{\mathrm{n(th)}}/M_{\mathrm{n(GPC)}}$ is low (0.25). When the reaction temperature was increased to 80 °C, the polymerization is also controllable (see Supporting Information). The initiation efficiency was nearly no change ($f = 0.24$), but the polydispersities was increased slightly (<1.2), and the pseudo-first-order rate constant (k_{obs}) was increased to 0.15 h^{-1}. The retardation time was much decreased than that at 70 °C. When the reaction temperature was decreased to 60 °C, the polymerization was much slower.

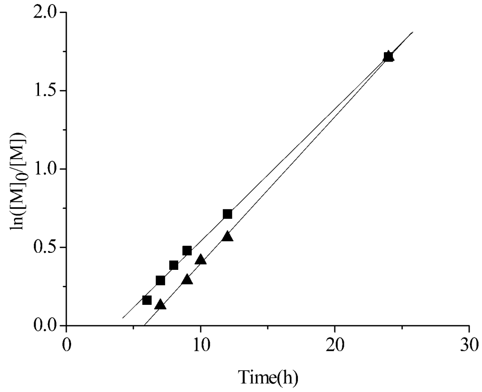


Figure 1. Time dependence of $\ln[\mathrm{M}]_0/[\mathrm{M}]$ at 70 °C in toluene. $[\mathrm{MMA}]_0$ = 14.1 M; $[\mathrm{Cp_2Co}]_0$ = $[\mathrm{EBiB}]_0$ = 60 mM (■) and $[\mathrm{MMA}]_0$ = 13.0 M; $[\mathrm{Cp_2Co}]_0$ = 100 mM; $[\mathrm{EBiB}]_0$ = 60 mM (▲).

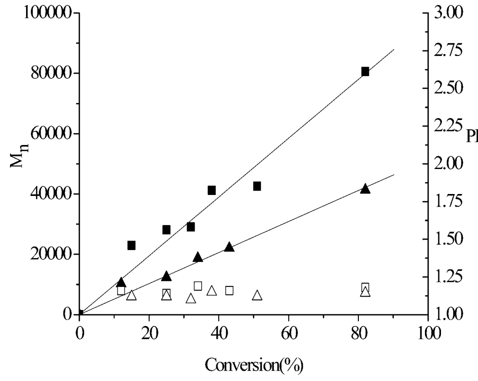


Figure 2. Dependence of the molecular weights and polydispersities of PMMA on conversion at 70 °C. $[\mathrm{MMA}]_0$ = 14.1 M; $[\mathrm{Cp_2Co}]_0$ = $[\mathrm{EBiB}]_0$ = 60 mM (■, □) and $[\mathrm{MMA}]_0$ = 13.0 M; $[\mathrm{Cp_2Co}]_0$ = 100 mM; $[\mathrm{EBiB}]_0$ = 60 mM (▲, △).

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Table 1. Results of MMA Polymerization Catalyzed by Cobaltocene/EBiB[a]

temp (°C)	catalyst	solvent	reaction time (h)	conv (%)	M_n(calc)	M_n(GPC)	f	PDI
60	cobaltocene	toluene	25	32				
60	cobaltocene	toluene	35	52				
60	cobaltocene	toluene	48	69				
70[b]	cobaltocene	toluene	6	15	3 320	22 300	0.25	1.12
70[b]	cobaltocene	toluene	12	51	11 700	42 600	0.25	1.12
70[b]	cobaltocene	toluene	24	82	18 700	80 600	0.25	1.14
70[c]	cobaltocene	toluene	7	12	2 620	10 000	0.41	1.16
70[c]	cobaltocene	toluene	12	43	9 130	22 000	0.41	1.16
70[c]	cobaltocene	toluene	24	82	17 300	41 300	0.41	1.18
70	cobaltocene	DMF	4	32	6 910	32 900	0.21	1.38
70	cobaltocene	DMF	6	50	10 900	46 400	0.21	1.29
70	cobaltocene	DMF	9	63	13 700	64 700	0.21	1.32
80	cobaltocene	toluene	3	19	4 240	14 100	0.24	1.12
80	cobaltocene	toluene	6	55	12 200	44 700	0.24	1.17
80	cobaltocene	toluene	12	80	17 700	75 400	0.24	1.18
80[d]	cobaltocene	toluene	3	26	5 270	6 930	0.63	1.16
80[d]	cobaltocene	toluene	5	51	10 100	13 900	0.63	1.21
80[d]	cobaltocene	toluene	10	78	15 600	26 600	0.63	1.23
80	ferrocene	toluene	72	24		154 000		2.95

[a] Experimental conditions: [MMA]:[catalyst]:[EBiB] ≈ 217:1:1. [b] [MMA]:[catalyst]:[EBiB] = 235:1:1. [c] [MMA]:[catalyst]:[EBiB] = 650:5:3. [d] The solvent, catalyst, and monomer were preheated to 80 °C for 20 min, and then the initiator was added.

If the polar solvent DMF was used, the polymerization was faster ($k_{obs} = 0.11$ h^{-1}), but the polydispersities were much higher (1.29−1.38) (Table 1).[17]

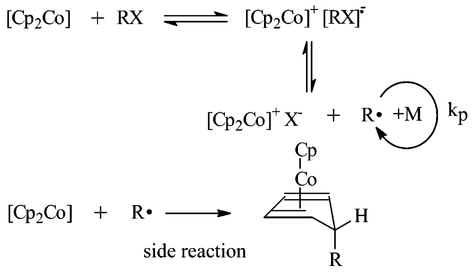
When the ratio of cobaltocene/initiator was slightly increased ($[EBiB]_0$:$[Cp_2Co]_0$ = 3:5, $[EBiB]_0$ = 60 mM, $[Cp_2Co]_0$ = 100 mM), the plots of $\ln([M]_0/[M]_t)$ vs time and M_n vs conversion show that the polymerization is still controllable (Figures 1 and 2). The initiation efficiency was increased to 0.41. When more catalyst was added to the reaction system, [EBiB]:[Cp_2Co] = 1:3 ($[EBiB]_0$ = 60 mM, $[Cp_2Co]_0$ = 180 mM), no polymer was produced in 24 h. These results indicate that the polymerization is influenced significantly by the amount of catalyst used.

To further increase the initiation efficiency, Cp_2Co, MMA, and toluene were mixed and preheated at 80 °C for 20 min, and then the EBiB was added. The plots of $\ln([M]_0/[M]_t)$ vs time and M_n vs conversion show that the polymerization is also controllable (see Supporting Information). The initiation efficiency was increased obviously ($f = 0.63$), although the polydispersities were increased slightly (1.16−1.23).

Polymerization of MMA using other metallocenes (ferrocene and nickelocene) was also examined under similar conditions. When nickelocene was employed, no polymerization was observed except the decomposition of the catalyst after 24 h. The polymerization of MMA with ferrocene is so slow that the conversion is only 24% after 72 h at 80 °C, and the polydispersities were much broader (Table 1).

Cobaltocene is a 19-electron complex. It is susceptible to radical addition to form the 18-electron η^4-cyclopentadiene complex. The reactions of organic halides with 2 equiv of cobaltocene afford equimolar amounts of cobalticinium halide and exo-substituted η^4-cyclopentadiene complexes (η^4-C_5H_5R)CpCo. A possible mechanism has been proposed to explain the reactions.[18] The initial step is generally thought to be an electron transfer, forming the 18-electron cobalticinium and the $RX^{\bullet-}$ radical anion, which then releases a $R^\bullet$ radical. In the second step, the $R^\bullet$ radical further reacts with cobaltocene to form the exo-substituted η^4-cyclopentadiene complexes. According to this mechanism, the possible polymerization mechanism may be suggested as described in Scheme 2. The polymerization was controlled through the reversible activation of halide initiator by cobaltocene. The second step is a side reaction for polymerization. Our experimental results gave some support for this mechanism. First, the polar solvent DMF can accelerate polymerization reaction, indicating the formation of a charged intermediate. Second, slightly increasing the ratio of cobaltocene/initiator to 5:3 increases the initiation efficiency because it can make the equilibrium in the first step shift to right. However, further increasing the ratio of cobaltocene/initiator (to 3:1) will promote the side reaction to form the exo-substituted η^4-cyclopentadiene cobalt complex irreversibly rather than polymerization. When the solvent, catalyst, and monomer were preheated, the side reaction, especially in the course of temperature increasing to the monomer polymerization temperature, was suppressed, and the initiation efficiency was increased evidently.

Scheme 2



In summary, we have demonstrated that controlled/"living" radical polymerization of MMA can be initiated by the cobaltocene/ EBiB catalyst system. Linear increase of molecular weights with conversion and low polydispersities (PDI < 1.15) were obtained. Fine-tuning of the complex sterics, electronics, and solubility characteristics as well as judicious choice of a compatible radical initiator would be expected to yield even more active and well-controlled polymerization systems. Further studies are examining these features and their effect on the polymerization of styrene and other monomers.

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Supporting Information Available: Plots of $\ln[M]_0/[M]$ vs time and M_n and PDI vs conversion at 80 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Polymerizations were performed under an inert atmosphere in a 100 cm^3 glass flask fitted with a Teflon stopcock. The flask was equipped with a magnetic stir bar. MMA was vacuum-distilled from CaH_2 twice and stored at −15 °C. All solvents were distilled from appropriate drying agents under argon prior to use. Cobaltocene was synthesized by a literature procedure.[16] In a typical solution polymerization, cobaltocene (57 mg, 60 mmol), MMA (6.825 g, 13.6 mol), toluene (5 mL), and ethyl 2-bromoisobutyrate (60 mg, 60 mmol) were added into the flask in this order at room temperature. After three freeze−pump−thaw cycles to remove oxygen, the flask was sealed and then immersed into a preheated oil bath at 80 °C. At timed intervals, an aliquot was removed (1.0 mL) with a degassed syringe and diluted with THF, then precipitated with methanol, and dried under vacuum. Conversion was measured by gravimetry and molecular weights determined by GPC [Waters 510 liquid chromatograph connected with four styragel GPC columns (guard, 10^3 Å, 10^4 Å, and 10^5 Å) and a Waters 410 differential refractometer; eluent, THF; flow rate, 1 mL/min; temperature, 25 °C]. Calibration was made with monodispersed polystyrenes as standards.

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