

Reusable and environmentally friendly ionic trinuclear iron complex catalyst for atom transfer radical polymerization†

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Ionic iron complex $[(\text{Me}_3\text{tacn})_2\text{Fe}_2\text{Cl}_3]^+[(\text{Me}_3\text{tacn})\text{FeCl}_3]^-$ (**1**), which is readily soluble in methanol, acted as a powerful catalyst in controlled radical polymerization of styrene and MMA, and showed promising features of removal from the resulting polymers and was reusable after recovery from the crude products.

Controlled radical polymerization (CRP) is an important method for constructing polymers with fine structure. Metal-mediated atom transfer radical polymerization (ATRP) is a representative example of CRP, in which metal complexes composed of transition metals with various auxiliary ligands promote the polymerization of vinyl monomers with living nature, leading to polymers with precisely controlled molecular weight and molecular weight distribution and copolymers with block, graft, and star architectures.^{1,2} Nevertheless ATRP has an undesirable problem for its efficiency of the metal catalyst, for example, high quantity of metals are required to realize reasonable rates of the polymerization, which results in serious contamination such as toxic and deep-colored heavy metals in the resulting polymer. This problem has been noted early in the initial stage of the research of metal-catalyzed ATRP. Thus, several trials for efficient removal of the metal residues from the crude product, including in some cases recovery and reuse of the catalytically active metal species,³ were provided by immobilization^{4–12} of the catalyst and use of biphasic systems.^{13–16} The recent discovery of a highly active copper catalyst has provided another solution of this problem, which realizes well-controlled ATRP with low catalyst concentration.¹⁷ The simplest, but not fully investigated solution of this problem, is attended on solubility control of the catalyst species.^{18–26} Typically a catalyst with a good solubility in both polar and apolar solvents is useful not only for polymerization of apolar vinyl monomers, but also for separation of apolar polymer products by washing with polar solvents. Recently, Shen *et al.* have reported the ATRP of MMA with efficient removal of the copper residue from the resulting polyMMA and catalyst recycling (three times), in which the authors offered a solution of the solubility problem by ligand design.²⁷ While the challenge was successful; however, this system still has problems of low initiation efficiency and catalyst deactivation in the recycling experiments. Our method to overcome the solubility problem is based on employing cationic iron

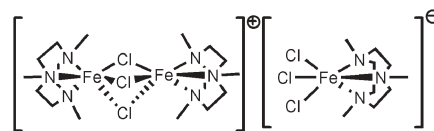
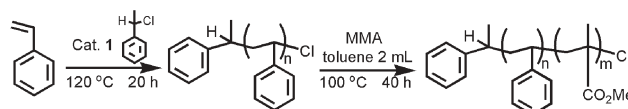


Fig. 1 Ionic iron complex **1**.

complexes with a tacn (1,4,7-trimethyltriazacyclononane) ligand (**1**) (Fig. 1); the cationic form is favorable to be dissolved in polar solvents, whereas the methyl groups on the tacn ligand induced soluble behavior of **1** in apolar solvents.²⁸ In this paper we report that **1** is a good catalyst for well-controlled polymerization and copolymerization of styrene, concomitant with facile separation of the catalyst from the polymer product *via* precipitation from methanol. The recovered catalyst species is reusable without loss of the catalytic activity.

The ionic complex **1** was synthesized according to a procedure described in the literature,²⁸ and was characterized by ¹H NMR and by ESI-MS.⁵ The complex **1** was used as catalyst in bulk polymerization of styrene initiated by halide compounds such as (1-chloroethyl)benzene and chlorodiphenylmethane (Scheme 1). For example, a polymerization of styrene by mixing catalyst **1**, the chloride, and styrene with a molar ratio of **1** : initiator : monomer = 1 : 2 : 1000 was performed at 100 °C under nitrogen atmosphere. The reaction mixture was heterogeneous (white suspension of the catalyst) at the initial stage, but gradually turned homogeneous with progress of the polymerization. This successfully produced the corresponding polymer. As shown in Fig. 2, plots of the molecular weight (M_n) vs. conversion (%) give a straight line. In addition, the molecular weight distribution (M_w/M_n) was broad (>1.5) at the initial stage of the reaction, but became narrow (around 1.2) with increase of the conversion. These two features are in accordance with so-called “controlled” atom transfer radical polymerizations. Table 1 shows the results of polymerization of styrene performed with alternating feeding ratios at 120 °C for 20 h. It can be seen that the molecular weight was decreased upon increasing the ratio of the initiator to the monomer. The polymerization proceeded slowly in toluene (volume of toluene : styrene = 1 : 1), though the conversion reached 100% with prolonged reaction time. In contrast, the M_w/M_n of the product obtained in toluene was



Scheme 1

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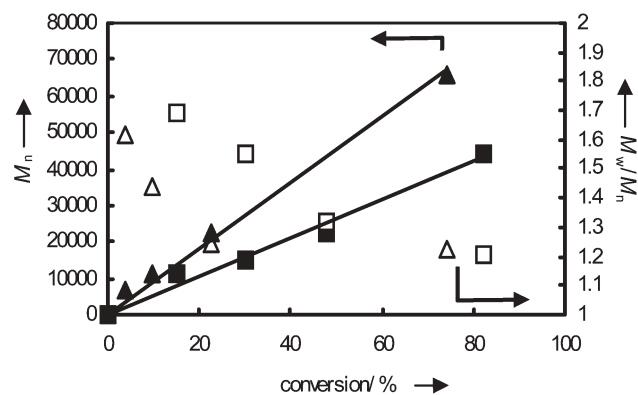


Fig. 2 Plots of M_n (■ and ▲) and M_w/M_n (□ and △) vs. conversion. Initiator: (1-chloroethyl)benzene (▲ and △) or chlorodiphenylmethane (■ and □). Temperature 100 °C. **1** : Initiator : St = 0.02 : 0.04 : 20 mmol.

somewhat narrower than that of the bulk polymerization with the same feeding ratio of catalyst/initiator/monomer. Initiation efficiency, which was dependent on the reaction conditions, was over 90% in only one case (ESI†).

The polymerization catalyzed by **1** gave polystyrene binding a chlorine atom at its chain end which is able to act as a macroinitiator. That is, the polystyrene is available in post polymerization by adding the second monomer to a reaction mixture. Therefore, we first polymerized styrene by the bulk polymerization (**1** : (1-chloroethyl)benzene : styrene = 1 : 2 : 500) at 120 °C for 20 h (conversion = >95%; M_n = 35 000, M_w/M_n = 1.3) and then added MMA (10 mmol) and toluene (2 mL) to the mixture which was stirred at 100 °C for further 40 h. This procedure resulted in PSt-b-PMMA with M_n = 75 000, M_w/M_n = 1.4 (conversion = >95%). The SEC charts are shown in the ESI.†

The good solubility of **1** in methanol is a crucial factor in separation of the catalyst from the polymer mixture by simple precipitation of the polymer from methanol. As an example, pouring a THF solution including the crude polystyrene produced (conditions: **1** : (1-chloroethyl)benzene : styrene = 1 : 2 : 1000; 100 °C, 70.5 h, conversion = 82%) into methanol (30 mL) afforded colorless polystyrene precipitates and a pale yellow supernatant containing the iron species. The polystyrene (M_n = 44 000, M_w/M_n = 1.2) purified *via* filtration and washing by methanol was subjected to ICP-mass analysis. It was found that only 14 ppm

Table 1 Polymerization of styrene^a

Entry	[Fe] : [I] : [St]	Conversion (%)	M_n (exptl.) ^b	M_n (calc.) ^c	M_w/M_n
1	1 : 1 : 1000	100	163 000	104 000	1.4
2	1 : 2 : 1000	95	54 000	49 000	1.3
3	1 : 6 : 1000	100	38 000	17 000	1.2
4	1 : 20 : 1000	100	16 000	5 000	1.3
5	1 : 1 : 1000	65	129 000	68 000	1.3
6	1 : 2 : 1000	68	52 000	35 000	1.2
7	1 : 6 : 1000	76	28 000	13 000	1.2
8	1 : 20 : 1000	93	13 000	4 800	1.2

^a Polymerization was carried out at 120 °C for 20 h in the presence of **1** as the catalyst and (1-chloroethyl)benzene as initiator. Concentration of **1** was 0.01 mol L⁻¹ (for entries 1–4, bulk) and 0.005 mol L⁻¹ (for entries 5–8, in toluene), respectively.

^b Determined by size exclusion chromatography (SEC) calibrated by PSt standards. ^c M_n (calc.) is calculated from the conversion of monomer.

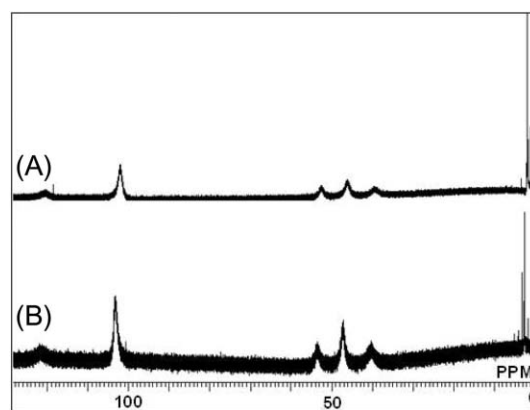


Fig. 3 ¹H NMR spectra measured in CD₃CN. (A) complex **1**, (B) recovered catalyst from the crude polystyrene formed by ATRP.

iron residue remained in the final product, indicating that the amount of charged iron (2300 ppm, calculated from 0.02 mmol of **1**) was almost completely removed.

Another unique property of **1** is its robustness due to the good coordination ability of triazacyclononane. This is evidenced by spectroscopy of the iron species recovered from the precipitation procedures described above. The colorless Fe(II) species **1** is sensitive to air, and easily oxidized to the brown Fe(III) species. Careful exclusion of air in the recovery process allowed the isolation of slightly yellow colored Fe species, of which ¹H NMR (Fig. 3) and ESI-mass spectra were identical to fresh **1**. In Table 2, results from reusing the catalyst recovered from the mixtures of polymerization of St are summarized. Very interestingly, from the first to the fourth run, the catalyst was not deactivated and thus repeatedly promoted the polymerization to give the corresponding PSt with nearly the same molecular weight and molecular weight distribution. Similar recycling of the catalyst was also achieved in the block copolymerization of styrene and MMA; the polymerization starting from styrene (conversion >95%, PSt-Cl M_n = 35 000, M_w/M_n = 1.2) followed by post-polymerization of MMA gave PSt-b-PMMA (M_n = 77 000, M_w/M_n = 1.4) with 95% conversion of MMA. The recovered catalyst *via* isolation treatment of the block copolymer was reused in the second block copolymerization of St and MMA. We found that the pre-polymerization of styrene gave PSt-Cl (conversion 90%, M_n = 43 000, M_w/M_n = 1.2), whereas the post-polymerization of MMA provided PSt-b-PMMA (M_n = 116 000, M_w/M_n = 1.7) with 95% conversion of

Table 2 Polymerization of styrene using reused catalyst^a

	Conversion (%)	M_n (exptl.) ^c	M_n (calc.) ^d	M_w/M_n
1st ^a	95	32 000	24 000	1.3
2nd ^b	93	29 000	23 000	1.3
3rd ^b	92	31 000	23 000	1.4
4th ^b	93	27 000	23 000	1.3

^a The first run of polymerization was carried out at 120 °C for 20 h in the presence of **1** (the catalyst) and (1-chloroethyl)benzene (the initiator) with the ratio of [I] : [I] : [St] = 0.02 : 0.04 : 10 mmol.

^b The 2nd, 3rd and 4th polymerizations were carried out with the recovered catalyst by the method described in the text. Other conditions were the same as those of footnote a. ^c Determined by size exclusion chromatography (SEC) with PSt calibration.

^d M_n (calc.) is calculated from the conversion of monomer.

MMA. It seems that in the case of the block-copolymerization, catalyst performance to provide a narrow molecular weight distribution in the pre-polymerization step was reduced somewhat at the post polymerization with MMA, although the catalyst recovery was successful.

In conclusion, the iron complex **1** proved to be an efficient catalyst for “living” ATRP, providing a clear solution of problematic isolation of the polymer from the catalyst residue by simple precipitation treatment. The robustness of **1** allows us to recover successfully it from the polymerization mixtures and to reuse it repeatedly without loss of the catalyst efficiency. Use of iron catalysts is one of the ultimate solutions for environmentally benign production of chemicals. Even in the chemical processes using iron reagents, which exhibit low biological toxicity, the catalyst recovery and reuse are key points which should be solved. The present work clearly demonstrates the importance of catalyst design for the recovery and reuse of the catalyst for ATRP.

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