

“LIVING”/CONTROLLED RADICAL POLYMERIZATION OF ETHYL METHYLACRYLATE WITH 2,2'- AZOBISISOBUTYRONITRILE/FERRIC CHLORIDE/ TRIPHENYLPHOSPHINE INITIATION SYSTEM

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Abstract “Living”/controlled radical polymerization of ethyl methacrylate (EMA) was carried out with a 2,2'-azobisisobutyronitrile (AIBN)/ferric chloride (FeCl_3)/triphenylphosphine (PPh_3) initiation system at 85°C . The number average molecular weight (M_n) increases linearly with monomer conversion and the rate of polymerization is first order with respect to monomer concentration. The M_w of PEMA ranges from 3900 to 17600 and the polydispersity indices are quite narrow (1.09~1.22). The conversion can reach up to ~100% and M_w of the polymers obtained is close to that designed. The polymerization mechanism belongs to the reverse atom transfer radical polymerization (ATRP). The polymer was end-functionalized by chlorine atom, which acts as a macroinitiator to proceed extension polymerization in the presence of CuBr/bipy catalyst system via an ATRP process. The presence of ω -chlorine in the PEMA obtained was identified by ^1H -NMR spectrum.

Keywords “Living”/controlled radical polymerization, Reverse ATRP, Ethyl methacrylate, $\text{AIBN/FeCl}_3/\text{PPh}_3$, Bulk polymerization

INTRODUCTION

Free radical polymerization is the most important industrial process to prepare high molecular weight polymers. However, it often yields polymers with ill-controlled molecular weights and broad polydispersity indices due to the facile coupling and disproportion reactions between the propagating radicals during the polymerization. How to master the radical polymerization has been one of the most important topics in contemporary polymer chemistry. In recent years, a number of systems based on reversible termination of growing radicals have been reported in order to improve the chemoselectivity of radical polymerization, such as “living” radical polymerization with iniferters (initiator, transfer agent, and/or terminator)^[1], “living”/controlled radical polymerization with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) system^[2], “living”/controlled radical polymerization with $\text{RX/CuBr/2,2'-bipyridine}$ system via ATRP^[3-5], etc.

As reported in the literature, an initiation system of ATRP has two major demerits: the organic halide RX is usually toxic and the catalyst Mt^n/L_x is easily oxidized by the oxygen in air. A so-called reverse ATRP was recently explored^[6-8]. In reverse ATRP, a higher oxidation state transition-metal species $\text{Mt}^{n+1}\text{X}/\text{L}_x$ and a conventional radical initiator were used instead of lower oxidation state Mt^n/L_x and organic halide species, respectively. So far, two types of efficient reverse ATRP initiating systems, i.e., 2,2'-azobisisobutyronitrile ($\text{AIBN}/\text{CuCl}_2$ (or CuBr_2)/2,2'-bipyridine^[7-8] and $\text{AIBN/FeCl}_3/\text{PPh}_3$ ^[6] for “living”/controlled radical polymerization of MMA, MA, St have been reported.

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This article describes the main results of “living”/controlled polymerization of ethyl methacrylate (EMA) using an AIBN/FeCl₃/PPh₃ initiation system.

EXPERIMENTAL

Materials

FeCl₃ (anhydrous) was prepared from FeCl₃ · 6H₂O treated with thionyl chloride according to the reference procedure^[9]. AIBN was recrystallized from ethanol. EMA was dried over CaH₂ and distilled under vacuum. Triphenylphosphine (Aldrich) was recrystallized from ethanol to eliminate triphenylphosphine oxide.

Polymerization of EMA

The monomer was placed in a dry glass tube together with AIBN/FeCl₃/PPh₃. Three freeze-thaw cycles were performed. The tube was sealed under vacuum and placed in a constant temperature oil bath which was controlled by a thermostat. After the specified reaction time, the polymerization was stopped by chilling the tube in ice water. After the resultant polymer had been dissolved in THF, the PEMA was precipitated from heptane, and dried. The conversion of the polymerization was determined gravimetrically.

Characterizations

Molecular weights and molecular weight distributions of polymer samples were measured using a Waters 515 GPC with Styragel Columns (HT2 + HT3 + HT4) at 35 °C, THF as eluent (1.0 mL/min), polystyrene as calibration standards, and Waters Millennium 32 as data processing software. ¹H-NMR spectra were recorded with a Bruker ARX400 (400 MHz) spectrometer in CDCl₃ at 25 °C, using tetramethylsilane as the internal reference.

RESULTS AND DISCUSSION

Radical polymerization of EMA was carried out in bulk with the AIBN/FeCl₃/PPh₃ system ([EMA]₀: [AIBN]₀: [FeCl₃]₀: [PPh₃]₀ = 200:1:4:12) at 85 °C; the results are shown in Fig. 1. The plot of ln([M]₀/[M]) versus time appears as a straight line and indicates that the kinetics is first order in monomer concentration. This means that the concentration of propagating radicals is constant during the polymerization. The GPC curves of the PEMA obtained are shown in Fig. 2. The polydispersity indices are quite narrow ($M_w/M_n = 1.22 \sim 1.09$) when the conversion is from 29.0% to ~100%. Figure 3 shows that the $M_{n(GPC)}$ of PEMA increases linearly with increasing conversion. The initiation efficiency f ($f = M_{n(theory)}/M_{n(GPC)}$) is close to 1.0 (0.9~1.0). It suggests that the molecular weight of PEMA obtained is close to the expected one. These results convincingly reveal that a well-controlled radical polymerization of EMA could be carried out with the AIBN/FeCl₃/PPh₃ initiation system via a reverse ATRP.

Besides, we investigated the polymerization of EMA with the initiation system under different reaction conditions and the results are compiled in Table 1. At the same initial molar ratios of reaction agents as above, the polymerization carried out at 110 °C is also a well-controlled radical polymerization, with very narrow polydispersity indices, fast rate of polymerization and high conversion (see No. 1 in Table 1, the time = 1.5 h, the conversion = 99.6%, $M_{n(GPC)} = 12800$, $M_w/M_n = 1.09$, $f = 0.9$). When the ratio of initial concentration of EMA to AIBN is 400:1 and other conditions are fixed as mentioned above, the PEMA with $M_{n(GPC)} = 17600$, $M_w/M_n = 1.11$, and $f = \sim 1.0$ is obtained. Accordingly, it is a well-controlled polymerization. The above results show that EMA can be polymerized with the AIBN/FeCl₃/PPh₃ system in a well-controlled manner just as the monomer MMA reported by Moineau *et al.*^[6].

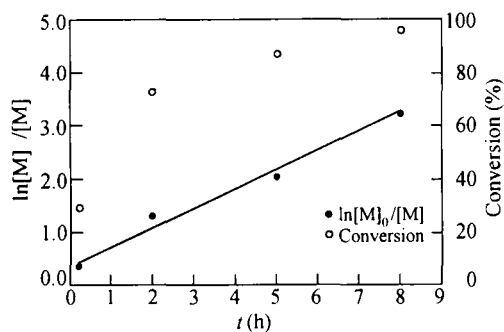


Fig. 1 Time dependence of $\ln[M]_0/[M]$ and conversion at 85°C where $[M]_0$ and $[M]$ are the EMA concentration at times 0 and t , respectively

Conditions: $[EMA]_0 = 8.0$ mol/L, $[AIBN]_0 = 4.0 \times 10^{-2}$ mol/L, $[FeCl_3]_0 = 1.6 \times 10^{-1}$ mol/L, $[PPh_3]_0 = 4.8 \times 10^{-1}$ mol/L, 85°C

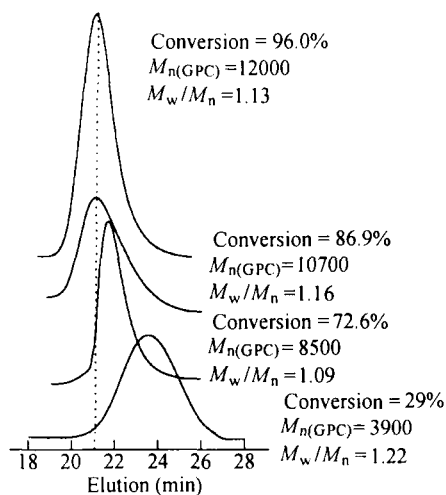


Fig. 2 GPC curves of PEMA obtained from bulk polymerization with AIBN/FeCl₃/PPh₃ at 85°C

Conditions: $[EMA]_0 = 8.0$ mol/L, $[AIBN]_0 = 4.0 \times 10^{-2}$ mol/L, $[FeCl_3]_0 = 1.6 \times 10^{-1}$ mol/L, $[PPh_3]_0 = 4.8 \times 10^{-1}$ mol/L

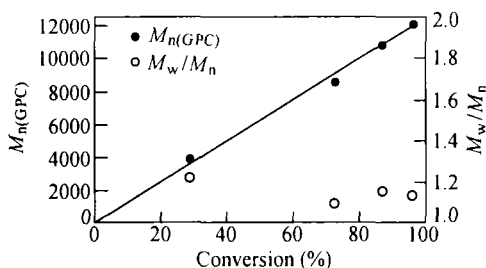


Fig. 3 Dependence of the number-average molecular weight and polydispersity of PEMA on the monomer conversion

Conditions: $[EMA]_0 = 8.0$ mol/L, $[AIBN]_0 = 4.0 \times 10^{-2}$ mol/L, $[FeCl_3]_0 = 1.6 \times 10^{-1}$ mol/L, $[PPh_3]_0 = 4.8 \times 10^{-1}$ mol/L, 85°C

Table 1. Bulk polymerization of EMA initiated with AIBN/FeCl₃/PPh₃^a

No	T^a (°C)	C^b	t^c (h)	Con. (%)	$M_{n(th)}^d$	$M_{n(GPC)}$	M_w/M_n	f^e
1	110	200:1	1.5	99.6	11400	12800	1.09	0.9
2	85	400:1	8.0	76.0	17300	17600	1.11	1.0

^a Conditions: $[EMA]_0 = 8.0$ mol/L, $[AIBN]_0$: $[FeCl_3]_0$: $[PPh_3]_0 = 1:4:12$

a) T = the reaction temperature; b) $C = [EMA]_0$: $[AIBN]_0$; c) t = the reaction time;

d) $M_{n(th)} = 114 \times ([M]_0/2[AIBN]_0) \times \text{conversion}$; e) $f = M_{n(th)}/M_{n(GPC)}$

End Group Analysis

A proposal concerning the reverse ATRP process of EMA with an AIBN/FeCl₃/PPh₃ initiating system is supported by the analysis of the end groups of the resultant polymer by ¹H-NMR spectroscopy. Figure 4 shows the ¹H-NMR spectrum of a sample of PEMA with $M_n = 3900$, $M_w/M_n = 1.22$.

The signal of *e* at 4.2 and *f* at 1.4 are assigned to the protons of the end groups, i.e., $-C(CH_3)(COOCH_2-CH_3)Cl$ and $-C(CH_3)(COOCH_2CH_3)Cl$, respectively. The result reveals that an ω -chlorine atom is an end group.

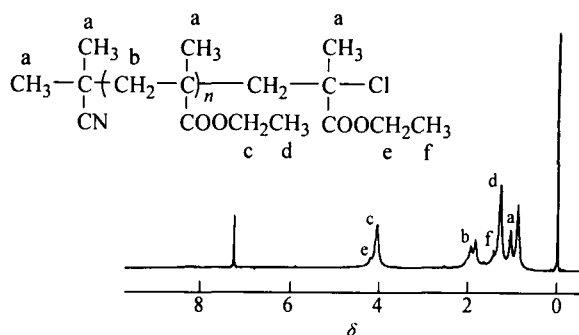
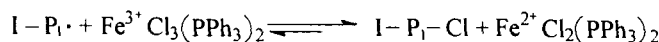
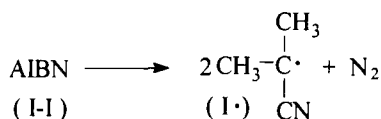


Fig. 4 ^1H -NMR spectrum of PEMA obtained from bulk polymerization with AIBN/ $\text{FeCl}_3/\text{PPh}_3$ at 85°C
 $M_n = 3900$, $M_w/M_n = 1.22$

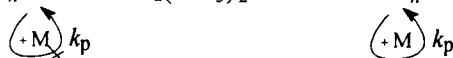
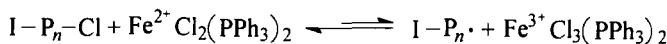
Mechanism of Polymerization

Based on the end group analysis, the mechanism of EMA polymerization with the AIBN/ $\text{FeCl}_3/\text{PPh}_3$ initiating system is proposed as shown in Scheme 1.

Initiation:



Propagation:



(where, M = monomer PPh_3 = the ligand)

Scheme 1

In the initiation reaction step, the initiator AIBN first cleaves to form primary radicals, which then react with monomers to form activated chain radicals ($\text{H}-\text{P}_1\cdot$). The monomer radical abstracts the chlorine atom from the highly oxidized transition-metal species, $\text{FeCl}_3(\text{PPh}_3)_2$, to form the reduced transition-metal species, $\text{FeCl}_2(\text{PPh}_3)_2$, and the dormant species, $\text{H}-\text{P}_1-\text{Cl}$. The chloride subsequently starts the propagation steps via an ATPR process.

Chain Extension of PEMA

The ^1H -NMR analysis of the PEMA obtained implies that an ω -chlorine atom exists as end group of the PEMA chain. Therefore, the PEMA can act as a macroinitiator for the extension polymerization of EMA. The extension polymerization of EMA was carried out in bulk at 85°C with PEMA ($M_n = 3900$, $M_w/M_n = 1.22$) in the presence of CuBr /bipyridine catalyst system. When $[\text{EMA}]_0 = 7.65 \text{ mol/L}$, $[\text{PEMA}]_0 = 5.42 \times 10^{-2} \text{ mol/L}$, $[\text{CuBr}]_0 = 5.42 \times 10^{-2} \text{ mol/L}$, $[\text{2,2'-bipyridine}]_0 = 5.42 \times 10^{-2} \text{ mol/L}$, $t = 10 \text{ h}$, the conversion was 95.8%. The M_n of chain-extended

PEMA increased to 16800, $M_w/M_n = 1.14$. The increase in the molecular weight is clearly demonstrated in the GPC curves as shown in Fig. 5.

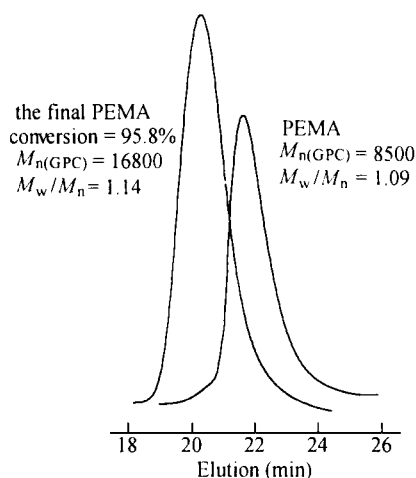


Fig. 5 The GPC curves of PEMA before and after extension polymerization with EMA in bulk at 85°C

The above results reveal that the “living”/controlled radical polymerization of EMA, with high conversion and very narrow polydispersity, can successfully be propagated using an AIBN/ FeCl_3 / PPh_3 initiating system. The mechanism of the polymerization belongs to a reverse ATRP.

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