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ORIGINAL PAPER

SET LRP of MMA mediated by Fe(0)/EDTA in the presence of air

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Abstract In this work, single electron transfer-living radical polymerization (SET LRP) of methyl methacrylate was successfully carried out using CCl_4 as initiator and Fe(0)/ethylenediaminetetraacetic acid (EDTA) as catalyst at 25 °C in dimethyl sulfoxide in the presence of air. In addition, ascorbic acid (VC) was used as reducing agent in the polymerization. Kinetics experiments demonstrated that the SET LRP is a 'living' polymerization, for example, the $\ln([M]_0/[M])$ versus time is linear and the number-average molecular weight values increases with respect to monomer conversion with narrow polydispersities. The amount of EDTA and VC had a profound effect on the polymerization. The 'living' characteristics were further verified by chain extension.

Keywords SET LRP · Living polymerization · Fe(0)-mediated/EDTA

Introduction

It is one of major research directions to synthesize the explicit composition and structural polymer compounds in polymer field. The free-radical polymerization (FRP) is one of the effective methods. Conventional FRP provides a spectrum of nearly 50 % of all commercial synthetic polymers for various markets. However, the major drawback of traditional radical polymerization lies in the degree of control over molecular weight distribution, end-functionality, and macromolecular

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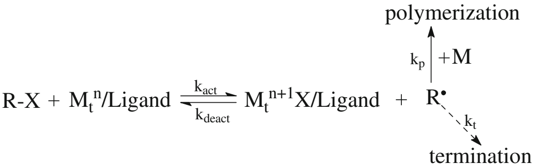
Scheme 1 Proposed mechanism for ATRP



architecture. These drawbacks have been overcome by the development of process so-called controlled/living radical polymerization (CLRP). During the past decade, CLRP processes have been extensively studied such as stable free-radical polymerization (SFRP) [1], best exemplified by nitroxide-mediated radical polymerization (NMRP) [2, 3], atom transfer radical polymerization (ATRP) [4–7], and reversible addition-fragmentation chain transfer [8–10]. Among them, ATRP is one of the most powerful, versatile, simple, and inexpensive living polymerization techniques to synthesize the well-defined polymers with narrow dispersities. ATRP is mediated by a transition-metal complex that establishes a dynamic equilibrium between the dormant polymer and active polymeric radical. The mechanism of ATRP is shown in Scheme 1.

A variety of transition metal complexes with various ligands have been used as catalysts for ATRP including ruthenium [6], iron [11, 12], rhodium [13], palladium [14], and copper [15, 16]. The most commonly used for ATRP is copper complexes. In comparison to copper complexes, iron-based ATRP is a very attractive catalyst system due to the low toxicity and low price. Most of iron catalysts have been recently used for CLRP of styrene and methyl methacrylate (MMA). For instance, Matyjaszewski and coworkers [17, 18] reported ATRP of MMA with ppm amount of Fe(III)Br_3 or Fe(II)Br_2 catalyst and ATRP of MMA catalyzed in the presence of triflate anions. Kamigaito and coworkers [19] reported the first example of controlled radical polymerization of styrene and MMA with FeO-based heterogeneous system. Zhu and coworkers [20, 21] reported an iron-mediated ICAR ATRP of MMA, iron-mediated AGET ATRP of styrene, and MMA under various conditions. In addition, iron-mediated ARGET ATRP of acrylonitrile was reported by Chen et al. [22]. Many ligands in combination with iron-mediated ATRP have been reported, including phosphines [12, 23], nitrogen-based ligands [24–26], and more environmentally friendly carboxylic acids [27–29]. However, many of the transition metals as well as ligands are expensive and harmful to the environment and human beings.

Single electron transfer-living radical polymerization (SET LRP) is an improved ATRP, which was firstly proposed by Percec et al. [30]. ATRP is mediated by transition metals through inner sphere electron transfer process [31]. However, SET LRP is mediated by transition metals through outer sphere electron transfer process [32, 33]. SET LRP has been demonstrated to be a reliable, robust, and straightforward tool to synthesize well-defined polymers. SET LRP technique has many advantages over other living radical polymerization, such as low temperature, fast polymerization, small amount of catalyst, and higher molecular weight polymers with narrow polydispersities.

In typical SET LRP, the concentrations of Cu(0) activating species and Cu(II) deactivating species are self-regulated by the disproportionation of Cu(I) generated in situ in the presence of appropriate ligands and solvents. Therefore, ligands are an important component of catalyst system used in SET LRP. It helps to solubilize the transition metal salts in organic media and alter the redox potential of the metal center for the appropriate dynamics of exchange between the dormant and active species. A variety of ligands have been successfully used in SET LRP, such as bipyridine, tris(2-aminoethyl)amine, tris(2-(dimethylamino)ethyl)amine, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, and poly(ethylene imine). Comparing with ligands mentioned above, ethylenediaminetetraacetic acid (EDTA) is less harmful to environment and human beings. EDTA forms especially strong complexes with Fe(II) and Fe(III). $FeCl_2$/EDTA as a novel mediator used for the controlled polymerization of styrene has been reported in homogeneous [34] and heterogeneous systems [35], the presence of EDTA had no effect on the living polymerization with narrow dispersities. The polymerization was performed under argon and at higher temperature. However, the polymerization of MMA was not unsuccessful with $FeCl_2$/EDTA in this system.

The SET LRPs of MMA, in *N*,*N*-dimethylformide (DMF) [36], acetic acid [37], and dimethyl sulfoxide (DMSO) [38], were done at ambient temperature using Cu(0)-based complexes. The polymerization has high rate, and the obtained polymer has higher molecular weights with narrow dispersities.

Iron powder can be directly used as catalyst for SET LRP, which is cheap and easy to handle. Liu et al. [39] firstly discussed SET LRP of acrylonitrile at 65 °C by using Fe(0) as catalyst in the presence of hexamethylenetetramine as ligands and *N*,*N*-dimethylformamide as the solvents. The polymerization proceeded in a ‘living’ manner with CCl_4 as initiator.

Ascorbic acid (VC) is a reducing agent used in ARGET ATRP and AGET ATRP. In this work, Fe powder was used in combination with EDTA/VC as complex catalyst system for the SET LRP of MMA at 25 °C with CCl_4 as initiator and DMSO as solvent in the presence of air.

Experimental

Materials

MMA, purchased from Tianjin Fuchen Chemical Reagents Factory, China, was distilled under reduced pressure prior to use. Carbon tetrachloride (CCl_4, 99 %), obtained from Hunan HuiHong Reagent Co., Ltd., was used without further purification. Fe powder (75 um, 99 %) was obtained from ShangHai ShenLe Iron wire Co., Ltd., China. DMSO, purchased from Tianjin Tianda Chemical Reagents Factory, China, was distilled under reduced pressure prior to use. VC (AR), obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. EDTA, purchased from JinJinLe Industry Co., Ltd., Shanghai, China, dried at 60 °C for a day before use. Other reagents were used without further purification.

Polymerization

The single electron transfer living radical polymerizations of MMA were carried out in the presence of air. A typical solution polymerization procedure for the ratio of $[MMA]_0/[CCl_4]_0/[Fe]_0/[EDTA]_0/[VC]_0 = 500{:}1{:}0.1{:}0.2{:}0.1$ is as follows: 5 g MMA (50 mmol), 0.0006 g Fe powder (0.01 mmol), 0.0058 g EDTA (0.02 mmol), 0.0018 g VC (0.01 mmol), 10 mL DMSO, and 0.0154 g CCl_4 (0.1 mmol) were in turn placed into a 100-mL three-neck round-bottom flask equipped with a magnetic stirring bar. The flask with the reaction mixture was placed in oil bath at 25 °C. After a desired time, the polymer was precipitated in a large excess of methanol. The resultant polymer was filtered and dried at 60 °C in vacuo. The monomer conversions were determined gravimetrically.

Characterization

^{1}H NMR spectra of the copolymer samples were recorded with Bruker 400 MHz Spectrometer in deuterated chloroform solvent and tetramethyl silane as standard. The molecular weight and polydispersity were obtained with gel permeation chromatography (GPC), carried out at 30 °C using Waters 1515 system. The system was equipped with refractive index detector, using HR1, HR3, and HR4 column. Polystyrene (PSt) narrow standards were used for calibration, the range of the molecular weight is 100–500,000. The universal calibration can be used to correct the molecular weights obtained for polystyrene to poly(methyl methacrylate) (PMMA). Flow rate of mobile phase THF was set at 1.0 mL/min and with column temperature of 30 °C.

Results and discussion

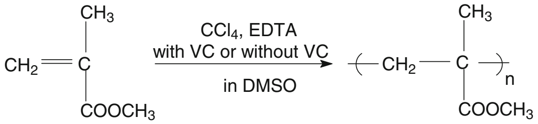
Fe powder-mediated single electron transfer-living radical polymerization of MMA at ambient temperature in the presence of air.

PMMA was prepared by SET LRP process using Fe powder/EDTA/CCl_4 as catalyst system in the presence of air as described in Scheme 2.

The feasibility of Fe powder-mediated single electron transfer living radical polymerizations of MMA were investigated at 25 °C in the presence of air in DMSO using EDTA as ligand and CCl_4 as initiator with VC or without VC, and the molar ratio of $[MMA]_0/[CCl_4]_0/[Fe]_0/[EDTA]_0/[VC]_0$ was fixed at 500:1:0.1:0.2:0.1. The results are depicted in Fig. 1.

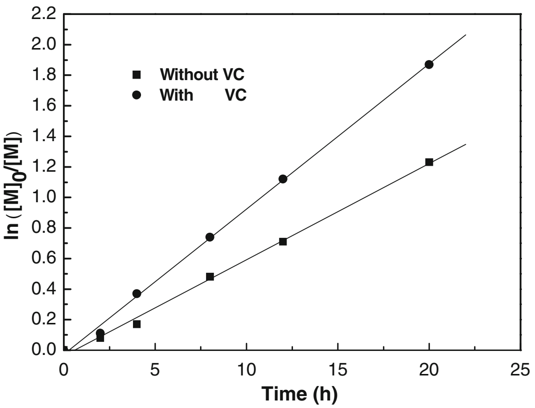
As can be seen from Fig. 1, first order is observed with respect to MMA concentration with VC and without VC, indicating the concentration of living

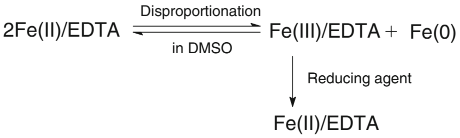
Scheme 2 SET LRP of MMA with Fe powder/EDTA heterogeneous system



$$CH_2{=}C(CH_3)(COOCH_3) \xrightarrow[\text{in DMSO}]{CCl_4,\ EDTA \text{ with VC or without VC}} \left(CH_2 - C(CH_3)(COOCH_3) \right)_n$$

Fig. 1 Kinetic plot of $\ln([M]_0/[M])$ versus time for SET LRP of MMA in DMSO in the presence of Fe powder with VC and without VC





Scheme 3 Proposed mechanism of disproportionation of Fe(II) complex in situ to generate Fe(0) and Fe(III) in DMSO in the presence of VC

species remained constant during the polymerization process. The induction periods were estimated to be 40 min and 18 min, respectively, and became shorter in the presence of VC. The corresponding values of the apparent rate constant (k_p^{app}), which derived from $\ln([M]_0/[M]) = k_p^{\text{app}}t$, are 2.65×10^{-5} and $1.74 \times 10^{-5}\ \text{s}^{-1}$ according to the slopes of Fig. 1. This indicated that the polymerization became faster in the presence of VC. This was probably because VC reduced the Fe(III)/EDTA to the active Fe(II)/EDTA, and thus, the concentration of Fe(II)/EDTA increased and the polymerization rate correspondingly increased. The proposed mechanism is illustrated in Scheme 3. In this mechanism, activation of dormant chains occurred through the heterolytic bond cleavage of the carbon halide bond activated by Fe(0) to generate Fe(II) and primary radicals, Fe(II)complex was disproportioned in the presence of DMSO to produce Fe(III) complex and Fe(0), and then Fe(III) complex was reduced by reducing agent (VC) to generate Fe(II) complex.

Figure 2 shows that the molecular weight of obtained PMMA increases with increasing MMA conversion and agrees well with the theory values when the conversion is beyond about 20 % with VC and without VC. However, the polydispersities index (PDI) values of obtained PMMA were 1.35 in the absence of VC and 1.28 in the presence of VC, but leveled off around conversion about 20 %. It indicates that the polymerization is a controlled polymerization. At the very early stages of polymerization, probably, high concentration of the growing radicals resulted in excessive termination. On the basis of results above, it can be concluded that Fe(0)/EDTA is an effective catalyst for SET LRP of MMA in DMSO.

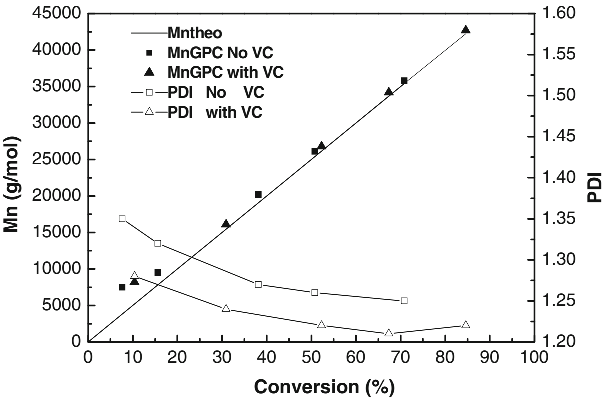


Fig. 2 Dependence of the molecular weight on the monomer conversion for SET LRP of MMA in DMSO in the presence of Fe powder with VC and without VC

Effect of amount of EDTA on the polymerization

Ligand plays a vital role in SET LRP, especially, the ratio of [ligand]/[catalyst] is an important parameter when preparing a catalyst complex for SET LRP because it has a strong effect on the polymerization rate and the level of control attained in the polymerization. In order to further investigate the effect of amount of EDTA on the polymerization, a series of experiments were carried out and the results are complied in Table 1.

As shown in Table 1, the conversion increased from 0 to 68.8 % with the ratio of [Fe]/[EDTA] varying from 1:0 to 1:5. When no EDTA was added, no polymerization occurred. The $M_{n,GPC}$ values increased with increasing amount of EDTA and were in good with the $M_{n,theo}$ values. In addition, the PDI values were low, indicating that the Fe(0)/EDTA-mediated SET LRP of MMA had characteristics of living polymerization.

Table 1 Experimental data of EDTA on the polymerization for SET LRP of MMA in DMSO at 25 °C in the presence of air

Entry	[Fe]/[EDTA]	Time (h)	Conversion (%)	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PDI
1	No EDTA	24	0	0	0	0
2	1:0.5	18	41.3	20,650	21,800	1.19
3	1:1	12	67.4	33,700	34,200	1.21
4	1:2	12	68.8	34,400	35,600	1.23
5	1:5	10	72.4	36,200	37,100	1.25

[MMA] = 5 M. $[MMA]_0/[CCl_4]_0/[Fe]_0/[VC]_0 = 500:1:0.1:0.1$

$M_{n,theo} = ([M]_0/[CCl_4]_0) \times M_{w,MMA} \times \text{conversion}\%$

Table 2 Different solvents on the SET LRP of MMA at 25 °C in the presence of air

Entry	Solvent	Time (h)	Conversion (%)	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PDI
1	DMSO	12	67.4	33,700	34,200	1.21
2	DMSO/H_2O (V/V = 90:10)	12	70.3	35,200	36,300	1.22
3	DMSO/H_2O (V/V = 50:50)	12	77.4	38,700	40,500	1.21
4	Benzene	18	22.8	11,400	16,400	1.24
5	Toluene	24	23.5	11,800	15,200	1.26

[MMA] = 5 M

Effect of different solvents on the polymerization

In SET LRP, the disproportionation of in situ active species was facilitated by solvent. Consequently, the solvents have a strong effect on the polymerization. A series of experiments were conducted in different solvents in the ratio of $[MMA]_0/[CCl_4]_0/[Fe]_0/[EDTA]_0/[VC]_0 = 500:1:0.1:0.2:0.1$. The results are shown in Table 2.

From Table 2, it can be seen that the highest conversion (77.4 %) occurred in DMSO/H_2O (V/V = 50:50) after 12 h. It indicated that H_2O added facilitated the disproportionation of Fe(II). The conversions were higher in polar solvent than those in apolar solvent. The $M_{n,GPC}$ values were consistent with the corresponding $M_{n,theo}$ values with narrow PDI values.

Effect of amount of VC on the polymerization

In Fe-mediated SET LRP, Fe(III) and Fe(0) was prepared from the disproportionation of Fe(II). Fe(III) was reduced to Fe(II) by VC, thus, the amount of VC affected the polymerization. To study the effect of amount of VC on the polymerization, a series of experiments were performed under different concentration of VC. The results were shown in Table 3.

It can be seen from Table 3 that, the conversion increased with increasing amount of VC. The experimental $M_{n,GPC}$ values were in good agreement with the corresponding theoretical $M_{n,theo}$ values. Increasing amount of VC, the concentration of Fe(II) increased by the reduction of Fe(III) and leaded in the increase of polymerization rate. Thus, excessive VC resulted in the broader PDI values.

Analysis of chain end and chain extension of PMMA

The resulting PMMA-Cl was characterized by ^1H NMR spectroscopy (Fig. 3). The signal at 3.79 ppm (Fig. 3b) was correlated with the methyl ester group at the chain end which deviated from the signal at 3.61 ppm (Fig. 3a) of other methyl ester groups because of the chain end of Cl atom. This result was consistent with what Sawamoto reported [12].

Table 3 Different concentrations of VC on the SET LRP of MMA at 25 °C in the presence of air

Entry	$[Fe]_0/[VC]_0$	Time (h)	Conversion (%)	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PDI
1	1:1	12	32.6	16,300	18,400	1.20
2	1:5	12	51.7	25,850	26,500	1.21
3	1:10	12	67.4	33,00	34,200	1.21
4	1:20	12	71.2	35,600	37,100	1.23
5	1:50	12	75.7	37,850	39,500	1.26
6	1:100	12	77.8	38,600	40,300	1.29

$[MMA] = 5$ M. $[MMA]_0/[CCl_4]_0/[Fe]_0/[EDTA]_0 = 500{:}1{:}0.1{:}0.2$

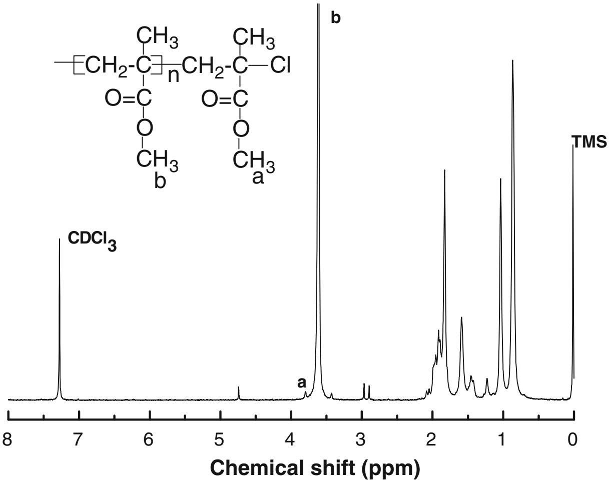


Fig. 3 ^{1}H NMR spectrum of PMMA-Cl obtained via ($M_{n,GPC}$ = 9,400 g/mol, PDI = 1.21) with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard

In next study, CCl_4 was replaced by the synthesized PMMA as macroinitiator, and the experiment of chain extension was conducted in the same way mentioned above. The results are shown in Fig. 4. The GPC trace of the obtained PMMA was narrow and symmetric, and shifted towards higher molar masses. The successful chain extension experiment further verified the living feature of SET LRP of MMA.

Conclusion

A new ligand, EDTA, was firstly used for SET LRP of MMA in combination with Fe(0), using ascorbic acid as reducing agent. The use of Fe(0)/EDTA as catalyst enables the production of well-controlled polymers. The conversion increased with the amount of EDTA and VC, solvent had profound effect on the polymerization. Kinetics results showed that the polymerization has ‘living’ characteristics. The

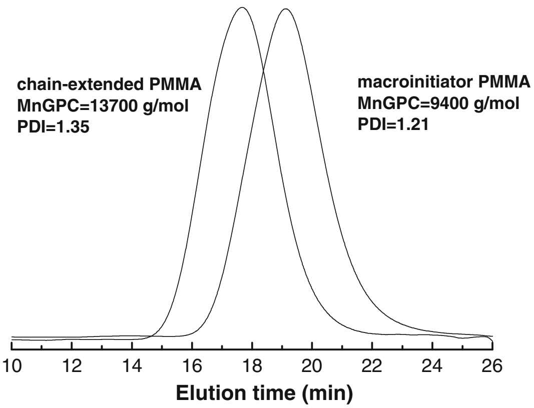


Fig. 4 GPC traces of macroinitiator and chain-extended PMMA

polymerization followed first order kinetics and the molecular weights increased linearly with conversion and were in consistent with theoretical values. The living feature was further verified by chain extension of PMMA.

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