Single Electron Transfer-Living Radical Polymerization of Methyl Methacrylate Catalyzed by Ytterbium Powder

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ABSTRACT: Zerovalent ytterbium (Yb) powder is firstly used as a catalyst in single electron transfer-living radical polymerization of methyl methacrylate initiated by carbon tetrachloride in N,N-dimethylformamide (DMF) and dimethyl sulfoxide, respectively. Polymerization proceeds in a “living”/controlled way as evidenced by kinetic studies and chain extension results, producing well-defined polymers with controlled degree of polymerization and narrow molecular weight distribution. The apparent activation energy of polymerization in DMF is accounted to be 36.2 kJ/mol, and the energy of equilibrium state is calculated to be 13.9 kJ/mol. An increase in the concentration of Yb(0) yields a higher monomer conversion. It is observed that polymerization rate experiments a rapid increase in the presence of more polar solvent water, and increasing in the content of H2O results in an increase in the apparent rate constant of polymerization, and a decrease in the molecular weight distribution. The reaction rate and molecular weight increase along with the decrease of DMF content. The effect of Yb(0) powder content, different ligands and concentration of initiator on the polymerization is also investigated.

INTRODUCTION

In recent years, living radical polymerization (LRP) is one of the most rapidly developing areas of polymer science, unlike conventional radical polymerizations, LRP allows syntheses of well-defined polymers with control over all aspects of molecular weights, narrow molecular weight distributions, terminal functionalities, topology, architectures, and compositions which have great impact on polymer’s mechanical and chemical properties. Some of the efficient LRP methods used nowadays are atom transfer radical polymerization, reversible addition fragmentation chain transfer, and nitroxide-mediated radical polymerization, which provide good versatility and functional group compatibility.

Recently, Percec’s group have developed an original LRP technique, named single electron transfer-living radical polymerization (SET-LRP). This technique provides extremely efficient and very mild conditions for the rapid syntheses of well defined polymers, such as functionalized acrylates, methacrylates, and vinyl chloride. SET-LRP relies on creation of a dynamic equilibrium between a large amount of a dormant species and a small amount of propagating radicals. It is proposed that the propagating species are generated through a reversible redox process catalyzed by a zerovalent copper complex Cu(0)/N-ligand that undergoes the outer-sphere one-electron oxidation with abstraction of a radically transferable atom or group, that the growing macroradicals react reversibly with the oxidized metal complex Cu(II)X2/N-ligand to reform the dormant species in a homogenous process, and that Cu(0) activating species and Cu(II)X2/N-ligand deactivating species are self-regulated by the disproportionation of Cu(I)X generated in situ in the presence of an appropriate combination of solvent and N-ligand, such as, Me6-TREN or TREN. This method provides a very simple way to incorporate desired functionality to either end groups or distributed along a polymer backbone. Indeed, the potential of SET-LRP has been fully attested by the synthesis of materials for unique applications such as dendritic macromolecules, mechanophore-linked polymers, graft copolymers, core-shell micelles, and vesicles formed from linear and four-arms star diblock polymers, AB2-type amphiphilic block copolymers, and has also been used in tandem with other radical reactions such as radical addition fragmentation chain-transfer polymerization and nitroxide-radical-coupling. Recent work suggests that the boundaries between heterogenous and homogenous systems catalysis and the presence of exothermic solution phase polymerization may have implications for the microscopic reversibility of the SET-LRP. However, SET-LRP process is almost activated by zero-valent copper or copper derivatives. The first examples of using...
transition metal Fe(0) and lanthanide metal Sm(0) catalyzed SET-LRP was provided recently by our group.\textsuperscript{57,58} Methacrylates in general exhibit an intrinsically lower rate constant of propagation in radical polymerization than acrylates. The unique reactivity of methyl methacrylate (MMA) toward radical addition makes the proper choice of the initiator crucial. Therefore, we chose carbon tetrachloride (CCl\textsubscript{4}) as initiator, as it is readily and commercially available that represents an efficient initiator for polymerization of methylmethacrylate.\textsuperscript{59}

In this work, we first report that SET-LRP catalyzed by Yb(0) powder could be utilized to synthesize poly(methyl methacrylate) (PMMA) with excellent control of molecular weight distribution. CCl\textsubscript{4} is selected to be initiator, \(N, N, N', N'\)-tetramethylethylenediamine (TEMED), \(N, N\)-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) are used as the solvent. The reactions are performed at various temperatures and thermodinamics of the polymerization is investigated. The effects of Yb(0) powder content, solvents, type of different ligands, and concentration of initiator are investigated.

**EXPERIMENTAL**

**Materials**

Analytical reagent grade MMA (98%, Tianjin FuChen Chemical Reagents, Tianjin, China) is distilled in vacuum and stored at 5 °C. CCl\textsubscript{4} (>99.5%), methanol (CH\textsubscript{3}OH) (>99.5%), and DMF (>99.5%) are purchased from Tianjin Chemical Reagents and used as received. Yb(0) powder, hexamethylethylenetramine, TEMED, and 1, 1, 4, 7, 10, 10-hexamethylenetetramine (HMTETA) are purchased from Aladdin Chemistry and used without further purification. All other chemical reagents are used as received.

**General Procedure for SET-LRP of AN**

A typical example of the general procedure is as follows. Yb(0) powder, N-ligand, solvent, MMA, and CCl\textsubscript{4} are added into a dry two-neck round-bottom flask which is immersed in ice water under stirring. Then, the mixture is degassed by 4 vacuum/N\textsubscript{2} cycles and sealed with N\textsubscript{2} finally. The flask is then immersed in an oil bath at the desired temperature maintained by a thermostat. After the desired polymerization time, the reaction is terminated by exposing the mixture to the air. The production is washed with a small amount of hydrochloric acid and precipitated by methanol-water (V:V, 1:1). The production is isolated by filtration and dried until a constant weight at 60 °C under vacuum.

**Chain Extension of Acrylonitrile with PMMA as Macroinitiator**

Chain extension of acrylonitrile (AN) with PMMA as macroinitiator is conducted using SET-LRP technology in DMF. PMMA macrorinitiator \(M_n = 14,570\), polydispersity index (PDI) = 1.25, Yb(0) powder, N-ligand, DMF, and AN are added into a dry two-neck round-bottom flask, which is bathed in ice water under stirring. The flask is then immersed in an oil bath at the desired temperature maintained by a thermostat. After a definite time, the polymerization is terminated by exposing the mixture to the air. The same aftertreatment procedure as in SET-LRP of MMA is applied for the polymerization product in chain extension of AN.

**Characterization**

The UV–vis spectra of SET-LRP of MMA catalyzed by Yb powder are determined on a Shimadzu UV 2550 spectrophotometer. The absorbance is recorded in the 200–800 nm range. Percentage conversion of MMA is measured by gravimetry. The number-average molecular weight \(M_n\) and the molecular weight distribution \(M_w/M_n\) are determined by gel permeation chromatography (GPC) which is performed with a Waters 1515 solvent delivery system (Milford, MA) at a flow rate of 1.0 mL/min through a combination of Waters HT3, HT4, and HT5 styragel columns. PMMA standards are used to calibrate the columns. A Waters 2414 differential refractometer is used as the detector. The analysis is undertaken at 35 °C with purified high-performance-liquid-chromatography-grade DMF as an eluent.

**RESULTS AND DISCUSSION**

A UV-vis spectroscopy study is performed to assess the stability of Yb(III)/TEMED and Yb(II)/TEMED in MMA/DMF and MMA/DMSO during the polymerization. Representative examples of UV-vis experiments are shown in Figure 1. UV–vis spectra were recorded after 4 h. As shown in Figure 1, with the presence of TEMED, the disappearance of the characteristic absorption peak of Yb(II) indicates that Yb(II) disproportionates into Yb(III) and Yb(0) completely and instantaneously in MMA/DMF and MMA/DMSO.

**SET-LRP of MMA Catalyzed with Yb(0) Powder**

To evaluate this process for the direct synthesis of well-defined PMMA, SET-LRP of MMA initiated with CCl\textsubscript{4} at 50 °C is conducted using Yb(0) powder as the catalyst at the radio of \([\text{MMA}]:[\text{CCl}_4]:[\text{Yb(0)}]:[\text{TEMED}] = 200:1:0.5:1\) (molar ratio). The volume ratio of MMA to solvent is fixed at 1:1. Two solvents are investigated using these conditions, DMF [Fig. 2(a,b)] and DMSO [Fig. 2(c,d)]. The kinetic plot concerning \(\ln([M]_0/\text{original concentration})/[M]/\text{current concentration})\) and conversion versus reaction time is shown as in
Figure 2(a). As expected, monomer conversion increases with reaction time. The linear kinetic plots of \(\ln([M]_0/\langle M \rangle)\) versus reaction time indicate that the polymerization is approximately first-order with respect to monomer concentration, the number of radical concentration is also constant, and the termination reactions can be neglected in the polymerization process, which is in tune with typical LRP. According to the slopes of the kinetic plot, the apparent rate constant of polymerization is calculated, 

\[
k_{\text{app}} = \frac{7.8 \times 10^{-6}}{C_2^{10}/C_0^{6}} \text{s}^{-1}
\]

The evolution of molecular weight and molecular weight distribution versus monomer conversion is depicted in Figure 2(b). From it, we can see that, the molecular weight increases almost in direct proportion to monomer conversion. The PDI decreases as the reaction progresses and the value of PDI is narrower with the range of 1.19–1.33, and it is observed that there is a decrease of PDI during the reaction until the formation of the solid phase. These results manifest the acceptable controllability of the polymerization. Figure 2(c,d) shows the kinetic experiments for SET-LRP of MMA in DMSO at 50 °C. A linear increase in the semilogarithmic kinetic plot is observed in Figure 2(c), and the polymerization proceeds faster in DMSO (apparent rate constant of propagation, \(k_{\text{app}}^{\text{prop}} = 10.6 \times 10^{-6} \text{s}^{-1}\)) than that in DMF (\(k_{\text{app}}^{\text{prop}} = 7.8 \times 10^{-6} \text{s}^{-1}\)). Despite the significant rate acceleration, SET-LRP of MMA catalyzed by Yb(0) powder also exhibits linearity between molecular weight measured by GPC and monomer conversion, and demonstrates excellent control of the molecular weight distribution as shown in Figure 2(d). These results indicate that this polymerization proceeded by SET-LRP showed the better control of polymerization is maintained. Moreover, the products are very pure without complicated aftertreatment. A polymerization mechanism is described in Scheme 1.
To derive activation energy parameters, the SET-LRP of MMA is also tested at 60, 70, and 80 °C with the ratio of [MMA]:[CCl₄]:[Yb(0)]:[TEMED] = 200:1:0.5:1, respectively. The results have been compiled in Table 1. With the rise of temperature from 50 to 80 °C, the conversion of MMA and the apparent rate constant of polymerization are increased from 27.6 to 61.7 and 5.6 × 10⁻⁶ s⁻¹ to 16.7 × 10⁻⁶ s⁻¹, respectively, while the values of PDI are widened from 1.25 to 1.33. The application of the SET-LRP methodology over a relatively broad temperature interval allows us to evaluate the Arrhenius plot of the polymerization process (Fig. 3).60 According to the slopes of the kinetic plot, the apparent activation energy of polymerization is deduced, ΔH_{app} = 36.2 kJ/mol. According to the formula ΔH_{eq} = ΔH_{app} - ΔH_{prop} the chain growth activation energy of polymerization (ΔH_{prop} = 22.3 kJ/mol), the energy of equilibrium state (ΔH_{eq}) is calculated to be 13.9 kJ/mol. These results indicate that SET-LRP of MMA can be conducted at mild conditions. The possibility to enhance the SET-LRP process with increasing temperature provides an excellent tool for the synthesis of functionalized PMMA in considerable time range.

Effect of Yb(0) Powder Content on SET-LRP of MMA

To further examine the effect of amount of Yb(0) powder content on the kinetics of SET-LRP of MMA, a series of experiments are conducted with different amounts of Yb(0) powder in DMF with V(MMA):V(DMF) = 1:1 and [MMA]:[CCl₄]:[Yb(0)]:[TEMED] = 200:1:0.5:1 at 50 °C, t = 16 h. The results have been summarized in Table 2. It is indicated that with an increase in the Yb(0) concentration, the conversion of MMA and the polymerization rate increase, however, the values of PDI decrease from 1.36 to 1.18. In addition, the molecular weights increase from 7460 to 17,260 with the increasing amount of Yb(0) powder.

Effect of Solvent on SET-LRP of MMA

As the control of polymerization relays on the disproportionation of in situ generated Cu(I), which is readily influenced by solvents. Therefore, a crucial role in SET-LRP processes is on the choice of a proper solvent. Cu(0)/Me₆-TREN catalyzed SET polymerization of methyl acrylate in solvents that do not mediate disproportionation such as MeCN and toluene results in nonfirst order kinetics and a nonliving polymerization, as reported by Nguyen et al.29 However, SET-LRP can be successfully conducted in toluene through the addition of 5–20% polar phenol additives.61 Nonpolar solvents such as toluene have been converted to an effective solvent via addition of polar phenol additives. H₂O is a kind of extremely polar solvents, to investigate effect of increasing H₂O on the set-LRP and PDI in the SET-LRP of MMA in DMF, a series of experiments are performed in mixtures of DMF and H₂O with V(MMA):V(solvent) = 1:1 and [MMA]:[CCl₄]:[Yb(0)]:[TEMED] = 200:1:0.5:1 at 50 °C. As shown in Figure 4, increasing the content of H₂O results in an increase in k_{app}^p.
and a decrease in PDI. At 0% H₂O, the $k^\text{app}_p$ is 5.6 × 10⁻⁶ s⁻¹ and PDI = 1.25 (27.6% conversion, $M_n = 14,570$). With 10% H₂O added to DMF, $k^\text{app}_p$ has increased to 8.1 × 10⁻⁶ s⁻¹ while the polydispersity has decreased to PDI = 1.18 (37.2% conversion, $M_n = 20,130$). The results have been listed in Table 3. The reason may be that as increasing the amount of H₂O in the reaction mixture increases the amount of disproportionation, thereby the increased control of molecular weight distribution can be attributed to more rapid production of sufficient levels of YbCl₂/TEMED. The effects of different electronic and stereo effects which affect disproportionation of Yb(II) diversely.

Effect of Initiator on SET-LRP of MMA

To investigate the role of CCl₄ in SET-LRP of MMA for further details, different concentrations of CCl₄ on the SET-LRP of MMA polymerizations are studied at 50 °C in DMF with [MMA]:[Yb(0)]:[TEMED] = 200:1:0.5:1 at 50 °C, $t = 16$ h. As shown in Table 5, in comparison with HMTETA, the conversion of MMA is much higher as well as molecular weight when TEMED and hexamethylenetetramine as the ligands. The phenomena might be contributed that N-ligands have different electronic and stereo effects which affect disproportionation of Yb(II) diversely.

Effect of Concentration of Initiator (CCl₄) on SET-LRP of MMA

The N-ligands play an important role in SET-LRP. The effect of different N-ligands on the kinetic of SET-LRP of MMA initiated with CCl₄ in DMF at 5 °C is examined with [MMA]:[CCl₄]:[Yb(0)]:[N-ligand] = 200:1:0.5:1. V(MMA):V(DMF) = 1:1. Table 4 summarizes a series of experiment results, in which conversion of MMA polymerizes is much with the volume ratio of AN:DMF at 1:1 and the molar ratio of [AN]:[CCl₄]:[Yb(0)]:[TEMED] at 4000:1:1.5:1, 1:1.5, and 1/2, respectively. It is also indicated that with an increase in the DMF volume, the conversion of MMA and molecular weights of PMMA measured by GPC decrease. Moreover, the PDI reduces from 1.30 to 1.20 as well. These results confirm further that the DMF can facilitate the SET-LRP of MMA with Yb(0) as catalyst, and the increase of DMF concentration can promote the polymerization.

Effect of N-Ligands on SET-LRP of MMA

Table 5 Effect of N-Ligands on SET-LRP of MMA

<table>
<thead>
<tr>
<th>Entry</th>
<th>N-Ligand</th>
<th>Conversion (%)</th>
<th>$M_n$ (kDa)</th>
<th>PDI</th>
<th>$k^\text{app}_p \times 10^{-6}$ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HTMA</td>
<td>36.9</td>
<td>17,860</td>
<td>1.27</td>
<td>8.0</td>
</tr>
<tr>
<td>2</td>
<td>TEMED</td>
<td>27.6</td>
<td>14,570</td>
<td>1.25</td>
<td>5.6</td>
</tr>
<tr>
<td>3</td>
<td>HMTETA</td>
<td>21.7</td>
<td>12,980</td>
<td>1.22</td>
<td>4.2</td>
</tr>
</tbody>
</table>

In DMF with V(MMA):V(DMF) = 1:1 and [MMA]:[CCl₄]:[Yb(0)]:[TEMED] = 200:1:0.5:1 at 50 °C, $t = 16$ h.

MMA is polymerized in the presence of different N-ligands. As shown in Table 5, in comparison with HMTETA, the conversion of MMA is much higher as well as molecular weight when TEMED and hexamethylenetetramine as the ligands. The phenomena might be contributed that N-ligands have different electronic and stereo effects which affect disproportionation of Yb(II) diversely.

Chain Extension of AN with PMMA as Macroinitiator

To verify the controlled/living natures of this polymerization system, block polymerization of AN using the above PMMA ([$M_n = 14,570$, PDI (GPC) = 1.25] as macroinitiator is carried out at 50 °C, with the volume ratio of AN:DMF at 1:1 and the molar ratio of [AN]:[CCl₄]:[Yb(0)]:[TEMED] at 4000:1:1.5:1. The block copolymer PMMA-b-PAN ($M_n$ (GPC) = 76,480; PDI (GPC) = 1.34) is obtained, which clearly reveals the living character of macroinitiator PMMA.

Table 6 Effect of Concentration of Initiator (CCl₄) on SET-LRP of MMA

<table>
<thead>
<tr>
<th>Entry</th>
<th>[CCl₄]:[Yb(0)]</th>
<th>Conversion (%)</th>
<th>$M_n$ (kDa)</th>
<th>PDI</th>
<th>$k^\text{app}_p \times 10^{-6}$ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5:0.5</td>
<td>20.3</td>
<td>13,660</td>
<td>1.21</td>
<td>3.9</td>
</tr>
<tr>
<td>2</td>
<td>0.75:0.5:2.5</td>
<td>24.1</td>
<td>13,980</td>
<td>1.24</td>
<td>4.8</td>
</tr>
<tr>
<td>3</td>
<td>1:0.5:2.5</td>
<td>27.6</td>
<td>14,570</td>
<td>1.25</td>
<td>5.6</td>
</tr>
<tr>
<td>4</td>
<td>1.25:0.5:2.5</td>
<td>31.6</td>
<td>15,390</td>
<td>1.28</td>
<td>6.6</td>
</tr>
<tr>
<td>5</td>
<td>1.5:0.5:2.5</td>
<td>36.3</td>
<td>16,230</td>
<td>1.32</td>
<td>7.8</td>
</tr>
</tbody>
</table>

In DMF with V(MMA):V(DMF) = 1:1 and [MMA]:[Yb(0)]:[TEMED] = 200:0.5:1 at 50 °C, $t = 16$ h.
CONCLUSIONS

Yb(0) is successfully used as catalyst for SET-LRP of well-defined PMMA in conjunction with CCl₄ as initiator and TEMED as N-ligand in DMF or DMSO. Both polymerizations proceed in the features of "living"/controlled free-radical polymerization, as evidenced by first-order kinetic plots of polymerization, the linear increase of molecular weight values with monomer conversions, and narrow PDI values of the polymers. According to the slopes of Arrhenius plot, the apparent activation energy of polymerization is accounted to be 36.2 kJ/mol, and the energy of equilibrium state is calculated to be 13.9 kJ/mol. It is observed that polymerization rate experiments a rapid increase in the presence of more polar solvent water, and increasing in the content of H₂O results in an increase in the apparent rate constant of polymerization (k_{app}), and decrease in PDI. With the decrease in the radio of V(DMF)/V(MMA), the reaction rate and molecular weights increase accordingly.

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REFERENCES AND NOTES