Atom Transfer Radical Polymerization of Styrene and Methyl Methacrylate Catalyzed by FeCl₂/Iminodiacetic Acid

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ABSTRACT: The atom transfer radical polymerization of styrene and methyl methacrylate with FeCl₂/iminodiacetic acid as the catalyst system in bulk was successfully implemented at 70 and 110 °C, respectively. The polymerization was controlled: the molecular weight of the resultant polymer was close to the calculated value, and the molecular weight distribution was relatively narrow (weight-average molecular weight/number-average molecular weight ~ 1.5). Block copolymers of polystyrene-b-poly[(methyl methacrylate) and poly(methyl methacrylate)-b-poly(methyl acrylate) were successfully synthesized, confirming the living nature of the polymerization. A small amount of water added to the reaction system increased the reaction rate and did not affect the living nature of the polymerization system. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 4308–4314, 2000

Keywords: atom transfer radical polymerization; styrene; methyl methacrylate; iron chloride; iminodiacetic acid

INTRODUCTION

Transition-metal-catalyzed atom transfer radical addition gives a unique and efficient procedure for carbon—carbon bond formation in organic syntheses.1 Research groups, including those of Matyjaszewski,2,3 Sawamoto,4 Percec,5 and Teyssie,6 have successfully introduced this approach into polymerization chemistry as a novel living/controlled radical polymerization process, that is, atom transfer radical polymerization (ATRP), which has stimulated many polymer chemists to study this sort of polymerization. The key mechanism of ATRP is the reversible formation of radicals from alkyl halides accompanied by reduction/oxidation of the copper halide/ligand complex. The choice of ligand and transition metal becomes one of the key points for tailoring the reactivity of the catalyst. Until now, multidentate nitrogen ligands work very well for copper-mediated ATRP by providing the desired reactivity.7–9 Multidentate nitrogen ligands consist of three types of nitrogen donors: aromatic nitrogens,2,7 imine-type nitrogens,8 and aliphatic nitrogens.9 However, ligands used in an ATRP catalyst system, such as 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen),10 may be carcinogens to human beings because of their conjugated aromatic ring structure. It seems necessary to explore commercialized ligands with low toxicity and low cost. Iminodiacetic acid (IDA), which is nontoxic and commercially available, complexes with both FeII and FeIII more easily than copper.11–13 In this work, we developed a new catalytic system based on the complex of iron with IDA for the controlled/living radical polymerization of styrene (St) or methyl methacrylate (MMA).
EXPERIMENTAL

Materials
St was vacuum-distilled over CaH₂ just before polymerization. Fe²⁺Cl₂ was washed with acetone and dried under vacuum before use. IDA was used as received, without purification. α-Bromoethyl benzene and ethyl 2-bromopropionate were used as received from Aldrich. N,N-Dimethylformamide (DMF) was distilled at reduced pressure and stored over 4-Å molecular sieves until use.

Polymerization
The general procedure for the polymerization was as follows: The catalyst, ligand, and monomer were added to a flask with stirring; three cycles of vacuum nitrogen were applied to remove oxygen; and after the mixture was stirred at 25 °C for 1 h, the initiator was added. Then, the flask was immersed in an oil bath at the required temperature. After a given time, the flask was opened, and a certain amount of tetrahydrofuran (THF) was added to the reaction system to dissolve the resulting polymer. The polymer was obtained by being precipitated in methanol and dried in vacuo at 60 °C for 24 h.

Characterization
The monomer conversion was determined gravimetrically. Molecular weights and molecular weight distributions were obtained by gel permeation chromatography (GPC) carried out with a PE series 200 instrument equipped with mixed 5-μm polystyrene (PS) columns (refractive index detector). All samples were run in THF at 25 °C with a flow rate of 1.0 mL/min, and calibration was done with PS standards. 1H NMR spectra were recorded on a Bruker Avance 500 500-MHz NMR spectrometer at room temperature in CDCl₃. Differential scanning calorimetry (DSC) was carried out with a PE Pyris-1 thermal analyzer. Infrared spectra were performed on KBr pellets with a PE Paragon 1000 spectrophotometer.

RESULTS AND DISCUSSION

Polymerization of St in Bulk
The polymerization of St was well controlled with RX/Fe²⁺Cl₂/HN(CH₂COOH)₂ as the catalyst under heterogeneous conditions. St was polymerized in bulk at 70 °C with [St]₀/[RBr]₀/[FeCl₂]₀/[NH(CH₂COOH)₂]₀ = 130/1/1/2, [St]₀ = 8.7 mol L⁻¹, and [I]₀ = 0.067 mol L⁻¹, where the initiator is α-bromoethyl benzene (■) at 70 °C or CCl₄ (▲, △) at 110 °C.

Figure 1. $M_n$ (open symbols) and $M_w/M_n$ (filled symbols) dependence on the monomer conversion for the heterogeneous ATRP of St in bulk. [FeCl₂]/[NH(CH₂COOH)₂]₀/2 = 0.067 mol L⁻¹, [St]₀ = 8.7 mol L⁻¹, and [I]₀ = 0.067 mol L⁻¹, where the initiator is α-bromoethyl benzene (■, □) at 70 °C or CCl₄ (▲, △) at 110 °C.
It was reported by Matyjaszewski et al. that most of the chain ends of the polymer obtained are chlorinated (i.e., 80–90% RCl). Decomposition may occur more easily in an RCl system than in an RBr system because of the weaker CCl bond in the former at a long reaction time. The dehalogen of the minority bromide on the active chain ends may result in increased Mw/Mn with conversion.

A first-order kinetic plot of the polymerization is shown in Figure 2. The plot is almost linear, although slow initiation is initially observed. After a small induction period created by the limited solubility of the catalyst in the reaction medium, a living polymerization occurs. The linear plot of ln([M]0/[M]) versus time indicates that the polymerization of St in bulk was first-order with respect to the monomer, and the concentration of active centers was constant throughout the polymerization. This implies that no obvious termination reactions occurred during the polymerization process. The end group of the resulting PS with an Mw of 4100 (as measured by GPC) was investigated with 1H NMR. The 1H NMR spectrum of PS is shown in Figure 3. The signals of the multiplets at 4.4 ppm were attributed to the methine proton geminal to the halide end group. From the ratio of the peak intensity of the 4.4 group to that of the phenyl group at 6.4–7.2 ppm, the Mw(H NMR) was calculated to be 4500.

Block Copolymerization of St-b-MMA

The resultant PS with an ω-halogen in the chain end was used as a macroinitiator for block copolymerization. From the halogen-terminated PS macroinitiator (Mn(GPC) = 3320, Mw/Mn = 1.26), polystyrene-b-polymethyl methacrylate (PS-b-PMMA) copolymer (Mn = 32,510, Mw/Mn = 1.51) was prepared in DMF catalyzed by FeCl2/IDA. In the Fourier transform infrared spectrum of the

Figure 2. Semilogarithmic kinetic plot for the bulk ATRP of St at 70 °C. [FeCl2]/[NH(CH2COOH)2]/2 = 0.067 mol L⁻¹; [St]0 = 8.7 mol L⁻¹; [RBr]0 = 0.067 mol L⁻¹.

Figure 3. 1H NMR spectrum of PS prepared with FeCl2 coordinated by IDA as the catalyst (Mn(GPC) = 4100).
PS-b-PMMA block copolymer, the characteristic peaks at 1731 and 1193 cm\(^{-1}\) corresponded to the ester carbonyl of PMMA, and 3060, 3026, 756, and 700 cm\(^{-1}\) represented the existence of the benzene ring in the block copolymer. GPC curves of the polymers in Figure 4 show that molecular weight shifted from a lower weight (3320) to a higher weight (32,510), indicating that the PS-b-PMMA block copolymer was successfully synthesized. These results demonstrate the living nature of the reaction system.

**Polymerization of MMA in Bulk**

The polymerization of MMA was carried out with FeCl\(_2\)/HN(CH\(_2\)COOH)\(_2\) as the catalyst under heterogeneous conditions with [MMA]\(_0\)/[RBr]\(_0\)/[FeCl\(_2\)]\(_0\)/[NH(CH\(_2\)COOH)]\(_2\)_0 = 130/1/1/2, [MMA]\(_0\) = 9.4 mol L\(^{-1}\); [RBr]\(_0\) = 0.072 mol L\(^{-1}\). The reaction color changed from light yellow to orange during the reaction. The molecular weight distribution of the resulting polymer was narrow (M\(_n\)/M\(_w\) = 1.21) before the monomer conversion reached about 50%. However, the molecular weight distribution became wider (M\(_w\)/M\(_n\) ~ 1.5) when the monomer conversion exceeded 50%. A linear increase of M\(_n\) versus the monomer conversion was found (Fig. 5). The M\(_n\)(GPC) was close to the predetermined values [calculated for the bulk polymerization of MMA in the presence of 1 molar equiv of Fe\(^{1+}\)Cl\(_2\) and 2 molar equiv of NH(CH\(_2\)COOH)\(_2\)] at 90 °C.

**Block Copolymerization of PMMA-b-PMA**

The block copolymer was synthesized to confirm the living nature of the reaction system. The mac-
roinitiator \( (M_n = 5560, M_w/M_n = 1.56) \) was prepared at 90 °C with \([\text{MMA}]_0 = 4.7 \text{ mol L}^{-1}\), \([\text{ethyl 2-bromopropionate}]_0 = 0.075 \text{ mol L}^{-1}\), and \([\text{MMA}]_0/[\text{RBr}]_0/[\text{FeCl}_2]_0/[\text{NH(CH}_2\text{COOH)}_2]_0 = 62.7/1/1/2 \) in DMF. The block copolymer of PMMA-\(b\)-PMA was obtained with \([\text{PMMA–X}]_0 = 0.0001 \text{ mol L}^{-1}(\text{MA}]_0 = 2 \text{ mol L}^{-1}\), and \([\text{PMMA–X}]_0/[\text{FeCl}_2]_0/[\text{NH(CH}_2\text{COOH)}_2]_0 = 1/1/2 \) in DMF. GPC curves of the resulting polymers are shown in Figure 8. The molecular weight increased to 12,030 from 5560, and the PDI was reduced to 1.30 from 1.56. The block copolymer was characterized by DSC. DSC curves in Figure 9 shows that there were two glass-transition temperatures at 20 and 92 °C (the glass-transition temperatures of PMMA and PMA are 100 and 10 °C, respectively.). This indicates the formation of the block copolymer of PMMA-\(b\)-PMA.

Effect of H\(_2\)O

A small amount of water was introduced into the reactor to modify the solubility of the catalyst. The addition of 1 mL of H\(_2\)O resulted in a faster polymerization, and the monomer conversion reached 82.4% within 1.5 h because of the improvement of the solubility of the catalyst. After heating, a heterogeneous red-yellow solution was obtained. As demonstrated in Figure 10, a linear increase in the measured molecular weight with conversion was displayed. The plot of \(\ln([M_0]/[M])\) versus time in Figure 11 indicates that the polymerization of St in the presence of water was essentially first-order with respect to the monomer. However, the molecular weight distribution...
became broader than that of the polymerization system without water. This presumably happened because the halogen transfer equilibrium shifted more or less to active species from dormant ones in the presence of water.

Effect of the Different Transition-Metal Ions

The effect of the different transition metals on ATRP was investigated in the polymerization of St with $[\alpha$-bromoethyl benzene]/[CuBr]/[NH(CH$_2$COOH)$_2$]$_0$/[St]$_0$ = 1/2/4 and [St]$_0$ = 8.7 M in bulk at 70 °C ($M_n$(th) = 10,000). Table I shows the outcomes for the polymerization of St with CuBr/ NH(CH$_2$COOH)$_2$ as the catalyst system. From Table I, we can see that the molecular weight increased with monomer conversion, which showed somewhat living characteristics. However, the measured molecular weight was much higher than the calculated values, and the molecular weight distribution was rather wide. The living species seemed rather active, which led to radical–radical termination as reported by Xia and Matyjaszewski.$^{17}$

CONCLUSIONS

The ATRP of St and MMA catalyzed by an RX/FeCl$_2$/IDA/ST system proceeded via a living/controlled mechanism. The molecular weights were essentially proportional to the reciprocal of the concentration of the initiator. Furthermore, the experimental molecular weights were close to the calculated ones, and the PDIs of the resulting PS and PMMA were as low as 1.3 and 1.5, respectively. Although a small amount of water added to the reaction system resulted in a relatively wider molecular weight distribution, it did not affect the living nature of the polymerization system.

Table I. Polymerization of St in Bulk

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>$M_n$(th)</th>
<th>$M_n$(exp)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10</td>
<td>1000</td>
<td>41,000</td>
<td>2.30</td>
</tr>
<tr>
<td>17</td>
<td>20</td>
<td>2000</td>
<td>55,076</td>
<td>2.18</td>
</tr>
<tr>
<td>40</td>
<td>50</td>
<td>5000</td>
<td>69,796</td>
<td>1.27</td>
</tr>
</tbody>
</table>

$[\text{St}]_0 = 8.7 \text{ mol L}^{-1}$; [α-bromoethyl benzene]$_0 = [\text{CuBr}]_0/2 = [\text{NH(CH}_2\text{COOH)}_2]_0/4 = 0.09048 \text{ mol L}^{-1}$ at 70 °C.
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REFERENCES AND NOTES

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