ABSTRACT

A well-defined poly(n-butyl acrylate) (PBA) homopolymer was prepared by activators generated by electron transfer (AGET) ATRP at 90°C in N,N-dimethylformamide using ferric chloride hexahydrate (FeCl₃·6H₂O)/succinic acid (SA) as a catalyst and ethyl 2-bromoisobutyrate as an initiator. Ascorbic acid was selected as a reducing agent. The kinetic results showed that a linear increase of molecular weights of polymers with monomer conversion and a relatively narrow polydispersity (<1.25), when the conversion is beyond 40%, is an indication of a polymerization controlled by AGET ATRP of n-butyl acrylate (nBA). That is to say, (FeCl₃·6H₂O)/SA catalyst complex is demonstrated to be highly efficient for the AGET ATRP of nBA. The effects of different molar ratios of [FeCl₃·6H₂O]/[SA] and the concentration of ascorbic acid on polymerization rate were investigated. The maximum polymerization rate was obtained at molar ratio of [FeCl₃·6H₂O]/[SA] = 1:2 and gave the best control of molecular weight and the distribution of polymer molecular weight. The polymerization reaction rate decreased when the higher or lower molar ratio of [FeCl₃·6H₂O]/[SA] was employed. The polymerization rate increased with higher content of ascorbic acid. The effects of different solvents on the polymerization were investigated. The experimental results showed that the polymerization rate was faster in polar solvent (such as DMF) than that in non-polar solvent (such as benzene). The obtained polymers had higher molecular weights with narrow distribution of molecular weight in DMF than that in benzene. Moreover, the obtained PBA was used as a macroinitiator in the chain extension experiment via AGET ATRP. The molecular weight of polymer increased after chain extension experiment. The chain extension experiment confirmed the living character of the polymerization system. The resultant PBA was characterized by ¹H NMR, FTIR and gel permeation chromatography.

INTRODUCTION

Traditional free radical polymerization is favoured in industry for the preparation of an extensive spectrum of materials due to a broadly available polymerizable monomers, mild reaction conditions and its tolerance to impurities such as moisture [1]. However, the traditional radical polymerization is incapable of controlling the molecular weight (MW) and the distribution of molecular weight of polymer. At present, this problem is addressed by controlled radical polymerizations (CRP) [2]. CRP produces polymers with varied well-defined architectures, such as block, graft, or star shaped copoly-
mers under a relatively mild condition.

Atom transfer radical polymerization (ATRP) [3] has developed into one of the most robust synthetic tools within the spectrum of CRP processes [4-9]. However, some drawbacks also should be considered. For example, the low oxidation state metals used in CRP processes are sensitive to air and moisture, and some special handling procedures and storage are usually required. This brings forth some inconvenience for the experiment operations. In addition, some traces of transition metal catalyst employed in such polymerization system would remain in the industrial productions, which may cause environmental problems.

In order to improve ATRP technique a new method of an activator, generated by electron transfer for atom transfer radical polymerization (AGET ATRP), has been proposed by Matyjaszewski’s group [10-12]. In an AGET ATRP, the activators are generated by electron transfer. The reducing agent reacts with the higher oxidation metal complex but it is unable to initiate new chains. Scheme I summarizes the general mechanism of AGET ATRP. For a successful AGET ATRP process, the reducing agents should be selected so that the reduction occurs without formation of intermediates or products that could form new initiators for an ATRP.

Compared with the traditional ATRP, the AGET ATRP has the advantages of facile preparation, storage and handling of ATRP catalysts, better control over the polymerization [13]. The transition metal copper [14-16] and iron [17-20] are usually used for the catalyst in ATRP techniques. In comparison to Cu catalysts, Fe catalysts are less toxic and have better biocompatibility. It has been reported that the poly(methyl methacrylate) was prepared via AGET ATRP process catalyzed by iminodiacetic acid and FeCl₃ complex [21].

Poly(n-butyl acrylate) can be used as a soft segment in thermoplastic elastomers due to its low glass transition temperature and durability [22]. There were some reports on the ATRP homopolymerization of n-butyl acrylate [23-25]. To the best of our knowledge, there have been no reports on AGET ATRP of n-butyl acrylate mediated by FeCl₃.6H₂O/succinic acid catalyst system. This system is more challenging, since the more polar acrylate could potentially affect the catalyst performance. In our research, all reaction materials are perfectly dissolved in N,N-dimethylformamide (DMF).

In this study, AGET ATRP of n-butyl acrylate (BA) was carried out in DMF at 90°C in the presence of a catalyst system of FeCl₃.6H₂O/succinic acid (SA) and an ATRP initiator of ethyl 2-bromoisobutyrate (EBiB). The kinetics and the effects of the ratio of [FeCl₃.6H₂O]/[SA], and the amount of ascorbic acid on the polymerization rate were investigated. The aim of the present work is to study the control of AGET ATRP mediated by the catalyst system.

**EXPERIMENTAL**

**Materials**

n-Butyl acrylate (nBA, Shanghai Chemical Reagents Co., AR grade) was distilled under reduced pressure after removal of inhibitor and stored at low temperature. Ethyl 2-bromoisobutyrate (EBiB, AlfaAesar Chemical Co., China, 99%) was used without further purification. N,N-Dimethylformamide (DMF, AR
grade) was distilled at reduced pressure before use. Ferric chloride hexahydrate (FeCl₃·6H₂O) (AR grade), succinic acid (SA, AR grade), ascorbic acid, and other reagents were used as received (China).

Polymerization of n-Butyl Acrylate
In a typical experiment, 12.82 g of n-butyl acrylate (0.10 mol), 97.50 mg of EBiB (0.50 mmol) and 20 mL of DMF were first placed in a three-necked bottle. The flask was then degassed with nitrogen for 30 min, and then 135.15 mg of FeCl₃·6H₂O (0.50 mol) and 118.09 mg of succinic acid (1.00 mmol) were added. Finally, 88.10 mg of ascorbic acid was added. The ratio of [nBA]₀/[EBiB]₀/[FeCl₃·6H₂O]₀/[SA]₀/[ascorbic acid]₀ was fixed to be 200/1/1/2/1. After degassing with nitrogen three times to remove air and moisture, the round flask was sealed and then placed in an oil bath at 90°C under stirring. After the desired polymerization time, the polymerization was terminated by pouring the product into a large amount of methanol. After filtration, the obtained poly(n-butyl acrylate) (PBA) was dried at 60°C in vacuo for overnight.

Polymer Characterization
Monomer conversion was determined by gravimetry. The molecular weight and molecular weight distribution of the polymer were determined with a Waters 1515 gel permeation chromatography (GPC) (Wyatt Technology Corporation, USA) equipped with refractive index detector, using HR1, HR3 and HR4 column with molecular weight ranging from 100 to 500,000 calibrated with polystyrene standard sample. Polystyrene standards were used to calibrate the columns. Tetrahydrofuran was used as a mobile phase at a flow rate of 1.0 mL/min and with column temperature of 30°C. The Mₙ(th) of nBA was calculated by the following equation:

$$M_{n(th)} = ([nBA]₀/[I]₀) \times W_{nBA} \times x$$

where, [nBA]₀ as the initial concentration of nBA; [I]₀ the initial concentration of EBiB; W_{nBA} the molecular weight of nBA and x the monomer conversion.

FTIR Spectrum was recorded on a Nicolet 370 FTIR spectrometer (USA) from powder-pressed KBr pellets in the wavelength range of 4000-400 cm⁻¹. The nominal resolution for all spectra was 4 cm⁻¹ and there were 32 scans for each spectrum. Proper corrections for atmospheric water vapour and carbon dioxide in air were made and the spectrum contained information that was characteristics only of the sample.

¹H NMR Spectrum was recorded on a Bruker nuclear magnetic resonance (¹H NMR) instrument (400 MHz Spectrometer, Germany) using CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard.

RESULTS AND DISCUSSION

Characterization of n-Butyl Acrylate
Figure 1 shows the ¹H NMR spectrum of the synthesized PBA. The chemical shift, δ = 0.9 ppm (c in Figure 1) was attributed to the protons of CH₃. The chemical shift, δ = 1.6 ppm (g in Figure 1) was assigned to the protons of -CH₂-. The chemical shift, δ = 1.8 ppm (f in Figure 1) corresponded to the backbone protons of -CH-. The chemical shift, δ = 1.9 ppm (b in Figure 1) was attributed to the backbone protons of -CH₂-. The chemical shift, δ = 3.6 ppm (a in Figure 1) corresponded to the protons of backbone -CH₂ in the chain ends of PBAs because of the electron-attracting function of ω-Cl atom. The chemical shift, δ = 3.9 ppm (e in Figure 1) was
Figure 2. FTIR Spectrum of poly(n-butyl acrylate) (PBA).

assigned to the protons of -OCH₂-. The characteristic absorption bands of the C=O group stretching vibration appeared at 1737 cm⁻¹, and the characteristic absorption bands of the C-H stretching vibration and the C-H in-plane bending vibration appeared at 2876, 2930 cm⁻¹ and 1380, 1470 cm⁻¹, respectively.

Polymerization Kinetics of AGET ATRP of n-Butyl Acrylate

The AGET ATRPs of n-butyl acrylate were performed using succinic acid (SA) and FeCl₃.₆H₂O as the catalyst, and EBiB was used as the initiator. Figure 3 shows the kinetic plot of ln([M]₀/[M]) versus time for the solution AGET ATRP of nBA. The plot of ln([M]₀/[M]) versus time (where M₀, the initial concentration of the monomer, and M, the monomer concentration at any time) is linear, demonstrating that the number of the active species remains constant during the polymerization process. The apparent rate k_app (k_app = dln([M]₀/[M])), that the slope of ln([M]₀/[M]) versus reaction time is obtained to be 4.51×10⁻⁶ s⁻¹.

The dependence of the number average molecular weight, Mₙ, on the monomer conversion is demonstrated in Figure 4. As indicated in Figure 4, a linear increase of Mₙ versus conversion can be observed. In additional, M_n(exp) values are higher than the theoretical M_n(thero) at high monomer conversion. A possible reason for this observation might be due to the deactivation of chain ends and termination reactions, which are more pronounced at higher monomer conversion. In the meanwhile, the values of PDI are broad at the beginning of polymerization when the conversion is less than 30% (PDI > 1.33). When the conversion is beyond 40%, the values of PDI are narrow (PDI < 1.25). This suggests that the convernsional radical polymerization takes place in the early stage.
Effect of \([\text{FeCl}_3\cdot6\text{H}_2\text{O}]/[\text{SA}]\) Ratio

As a very important parameter for AGET ATRP, the ratio of \([\text{FeCl}_3\cdot6\text{H}_2\text{O}]/[\text{SA}]\) has a strong effect on the polymerization rate and the level of control attained in polymerization process. A series of experiments with various ratios of \([\text{FeCl}_3\cdot6\text{H}_2\text{O}]/[\text{SA}]\) were performed at 90°C. The experimental results are shown in Figure 5. A linearly first-order plot with respect to monomer was observed in AGET ATRP of nBA solution. A rate dependency on the ratio of \([\text{FeCl}_3\cdot6\text{H}_2\text{O}]/[\text{SA}]\) was observed. The polymerization rate reached its maximum when the molar ratio was 1:2. In contrast, slow polymerization rate occurred when the molar ratios were 1:1 and 1:3. This might be ascribed to the degradative chain transfer to the ligand which would decrease the rate of polymerization due to the loss of active chains from the reaction process.

Figure 6 shows that the molecular weights increase with monomer conversion. It is clear that the molecular weights of the prepared polymers are actually higher than the theoretical values indicating low initiation efficiency. As shown in Figure 7, the PDI is narrow when the conversion is beyond 40% and the value of PDI reaches 1.19. A broader PDI is obtained when the conversion is less than 40%. This could be ascribed to the lower amount of Fe species and relatively a slow deactivation rate.

Effect of Ascorbic Acid

In AGET ATRP process, the active Fe(II) complexes were produced by an in situ reduction mechanism between the reducing agent ascorbic acid and the Fe(III) complexes. Therefore, this reducing agent plays an important role in the AGET ATRP process [10]. The effect of ascorbic acid on the solution polymerization of BA was investigated in this work. The results are listed in Table 1.

From Table 1, it can be seen that the poly-
merization conversion increases from 31.22% to 62.15% with ascorbic acid increases, whereas the PDI is almost kept constant. The increase in polymerization rate has originated from the increased concentrations of the propagating radicals in the polymerization system. The corresponding GPC traces and PDI values are shown in Figure 8. The traces shift cleanly and completely, confirming the increase of the molecular weights of polymers with increases in ascorbic acid concentration.

**Effect of Solvent**

The solvent plays an important role in ATRP process. To know the effect of solvent on polymerization, the AGET ATRPs of n-butyl acrylate in various solvents were investigated with the ratio of \([nBA]_0/[EBiB]_0/\left[FeCl_3\cdot6H_2O\right]/[SA]_0/[\text{ascorbic acid}]_0\) fixed to be 200/1/1/2/1. Solvents employed were benzene and DMF. The results have been compiled in Table 2.

As shown in Table 2, the polymerization rate is faster in DMF than in benzene under the same conditions. The polydispersities of the obtained PBA remain lower with higher molecular weight in DMF than in benzene, which is an indication of the polarity of solvent having a vital effect on the AGET ATRP of n-butyl acrylate. This probably is because during polymerization the system remains homogeneous in DMF and heterogeneous in benzene.

**Chain Extension of PBA**

In order to verify the active nature of the chain end of the obtained poly(nBA), chain extensions of the obtained chlorine-terminated poly(nBA) (M_n: 8396 g/mol, PDI: 1.33) were performed in DMF in the presence of FeCl_3\cdot6H_2O/SA. The solution mixture of the obtained chlorine-terminated poly(nBA), FeCl_3\cdot6H_2O/SA and ascorbic acid in DMF in a round-bottom flask was thermostated at 90°C under nitrogen atmosphere. The chain extensions were successful.

### Table 1. Effect of reducing agent content on AGET ATRP of BA at 90°C in DMF.

<table>
<thead>
<tr>
<th>Entry</th>
<th>FeCl_3\cdot6H_2O/ ascorbic acid</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>(\bar{M}_{n(\text{theo})}) (g/mol)</th>
<th>(\bar{M}_n) (g/mol)</th>
<th>PDI</th>
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<td>1</td>
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<td></td>
<td>62.15</td>
<td>15932</td>
<td>21031</td>
<td>1.35</td>
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<tr>
<td>2</td>
<td>1:3</td>
<td></td>
<td>57.71</td>
<td>14793</td>
<td>18672</td>
<td>1.25</td>
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<td>13645</td>
<td>17524</td>
<td>1.22</td>
</tr>
<tr>
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<td>48</td>
<td>41.56</td>
<td>10653</td>
<td>14725</td>
<td>1.21</td>
</tr>
<tr>
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<td></td>
<td>31.22</td>
<td>8003</td>
<td>10384</td>
<td>1.19</td>
</tr>
</tbody>
</table>

### Table 2. Effect of solvent on AGET ATRP of BA at 90°C in DMF and benzene.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>(\bar{M}_{n(\text{theo})}) (g/mol)</th>
<th>(\bar{M}_n) (g/mol)</th>
<th>PDI</th>
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</tbody>
</table>
Figure 9. GPC Curves before and after chain extension with PBA as a macroinitiator.

The chain-extended PBA number average molecular weight, $\bar{M}_n$, was 14206 g/mol and the PDI value was 1.41. The reason was that the nBA was initiated by chlorine-terminated poly(nBA), thus the chain-extended PBA number average molecular weight, $\bar{M}_n$, increased. The results are evident in Figure 9. It is clear from this result that the end groups of the polymers are active in the chain extension reaction.

CONCLUSION

The AGET ATRP of nBA was successfully performed in DMF at 90°C using EBiB and FeCl$_3$.6H$_2$O/SA as initiator and catalyst, respectively. The kinetics experiment indicated that the polymerization of BA is a living/controlled polymerization. The obtained poly(nBA) possessed a chlorine-terminated atom, as was proved by chain extension reaction. The polymerization rate reached the maximum when the ratio of [FeCl$_3$.H$_2$O]/[SA] was 1:2. The polarity of solvent had a profound effect on the AGET ATRP of nBA. The polymerization rate is faster in DMF than that in benzene. The reducing agent ascorbic acid plays an important role in the AGET ATRP process, and the polymerization rate is increased with its higher content.

REFERENCES


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