Reverse atom transfer radical polymerization of styrene using BPO as the initiator under heterogeneous conditions

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Reverse atom transfer radical polymerization of styrene in the presence of a conventional radical initiator (benzoylperoxide, BPO) in bulk was successfully implemented via a new polymerization procedure. The system first reacts at 70 °C for ten hours, then polymerizes at 110 °C, which results in a well-controlled radical polymerization with high initiation efficiency and narrow molecular weight distribution of the resulting polymer, i. e., the polydispersity is as low as $M_w/M_n = 1.32$. The initiation mechanism of BPO is different from that of AIBN because there is redox reaction between BPO and Cu^I generated from the reaction of radicals with Cu^{II}. The initiation mechanism of BPO/$Cu^{II}Cl_2$/bpy is deduced through the experimental data. The molecular weight of the resultant polymer is in agreement with the theoretical value calculated in accordance with the aforementioned mechanism.

1. Introduction

The transition-metal-catalyzed atom transfer radical addition, ATRA, gives a unique and efficient way for carbon-carbon bond formation in organic synthesis [1]. Research groups such as 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, i. e., atom transfer radical polymerization, ATRP, which stimulated many polymer chemists to study this sort of polymerization. It is important in this research area to find a new initiator system. Wang and Matyjaszewski [7] reported that in addition to a typical ATRP initiating system (using a alkyl halide, R—X, as an initiator and a transition-metal species complexed with suitable ligand(s), Mtn/Lx, as a catalyst, R—X/Mtn/Lx), a 'living'/controlled polymerization was observed using a conventional radical initiator (azodiisobutyronitrile, AIBN) and a transition-metal compound at higher oxidation state (e. g., $Cu^{II}Cl_2$) complexed with suitable ligands (e. g., 2,2′-bipyridine, bpy) as a catalyst. Afterward, Xia and Matyjaszewski [8] reported that by using alkyl substituted bipyridine ligands, such as 4,4′-nonyl-2,2′-bipyridine (dNbipy), reverse ATRP of methyl acrylate can be carried out under homogeneous conditions. Most recently, Wang and Yan [9] developed a new procedure for reverse ATRP of MA under heterogeneous conditions. Authors usually use AIBN as an initiator hitherto. What will happens if BPO is used in reverse ATRP. This article is devoted to the topic as mentioned. When BPO is used in the living/controlled radical polymerization of styrene, the initiation mechanism is different from that of AIBN because there is redox reaction between BPO and Cu^I generated from the reaction of radicals with Cu^{II}. Consequently, A new mechanism is suggested which conforms mental results.

2. Experimental

2.1. Materials

Styrene was vacuum distilled over CaH_2 just before polymerization. BPO was used after ordinary purification. $CuCl_2$ and 2,2′-bipyridine was used as received without purification.

2.2. Polymerization

Catalyst, ligand, initiator, monomer were added to a flask with stirrer. The heterogeneous mixture was first degassed (three times), secondly immersed in an oil bath, heated at 70 °C for 10 h, then reacted at 110 °C. After a given time, the flask was opened and THF was added to the sample to dissolve the polymer.

2.3. Polymer characterization

The monomer conversion was determined by gravimetry. Molecular weight and molecular weight distribution were obtained by gel permeation chromatography (GPC) that was carried out with a Waters 208 instrument, using tetrahydrofuran as eluent, and calibration with polystyrene standards.

^{1}H NMR spectrum was taken on 300 MHz spectrometers at room temperature in $CDCl_3$.

3. Result and discussion

In the reaction system of this work, BPO can result in a well-controlled radical polymerization with high initiation efficiency 90% and rather low polydispersity $M_w/M_n = 1.32$. Figures 1 and 2 show that the measured molecular weight linearly increases with increasing monomer conversion, and it matches the theoretical value calculated from Eq. (1) for bulk polymerization of styrene initiated with BPO in the presence of 2 molar equiv. of $Cu^{II}Cl_2$ and 4 molar equiv. of bpy at 110 °C.

$$M_{n,th} = 104 \times \{\Delta[M]/([BPO])\} \times \text{conv.} \qquad (1)$$

Figures 3 and 4 show the first-order kinetic plot, indicating that the concentration of the growing species remained constant. The first point is beyond the experimental error from the linear plot, and the monomer conversion at this moment is apparently higher than that in a living polymer-

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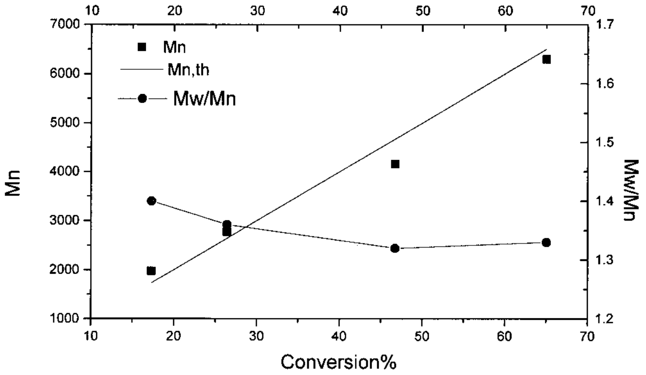


Fig. 1. Molecular weight, M_n, and molecular weight distribution, M_w/M_n, dependence on monomer conversion for the heterogeneous reverse ATRP of styrene at 110 °C in bulk, [styrene]:[BPO]:[$CuCl_2$]:[bpy] = 100:1:2:4.

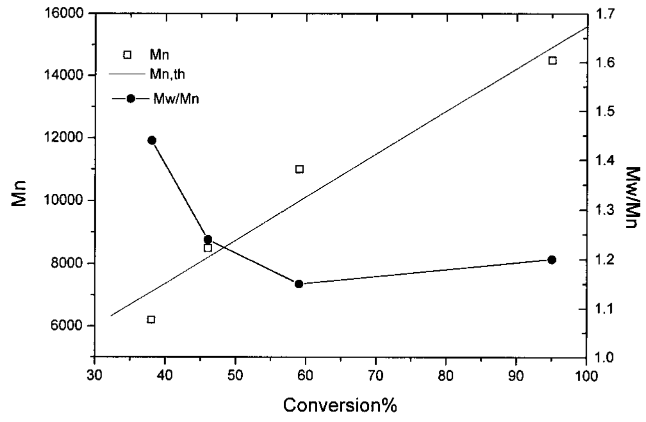


Fig. 2. Molecular weight, M_n, and molecular weight distribution, M_w/M_n, dependence on monomer conversion for the heterogeneous reverse ATRP of styrene at 110 °C in bulk, [styrene]: [BPO]: [CuCl2]:[bpy] = 150:1:2:4.

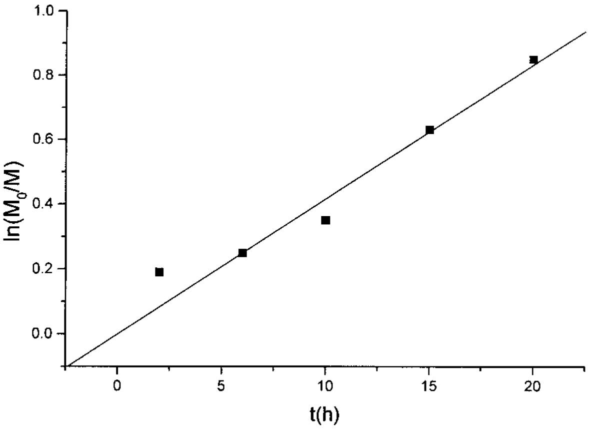


Fig. 3. Semilogarithmic kinetic plot for the bulk reverse ATRP of styrene at 110 °C [styrene]:[BPO]:[$CuCl_2$]:[bpy] = 100:1:2:4.

ization. It seems that the polymerization occurred partially at low temperature.

These experiments data indicated that the polymerization of styrene initiated by the BPO/$Cu^{II}Cl_2$/bpy system proceeded via a living/controlled polymerization mechanism. The molecular weight was essentially proportional to the reciprocal of the concentration of BPO. Furthermore, a good correlation between the calculated molecular weight and the experimental one was found, and the polydispersity is lower than 1.39, indicating a high initiation efficiency of BPO. The structure of resulting polystyrene was studied by ^{1}H-NMR. The ^{1}H-NMR spectrum of PS is illustrated in Fig. 5. Signals were observed at 1.2~2.1 ppm, originating from the methene and methine protons of the main chain. A signal was discerned at 7.9 ppm, assigned to the aromatic protons at ortho position of the benzoyl moiety attached to the polymer head group, The broad triplets at 4.4 ppm are attributed to the end group chlorine. Moreover, comparison of the integration of the signals of end

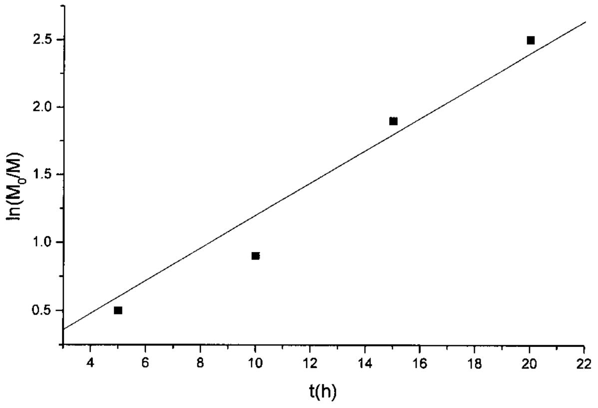
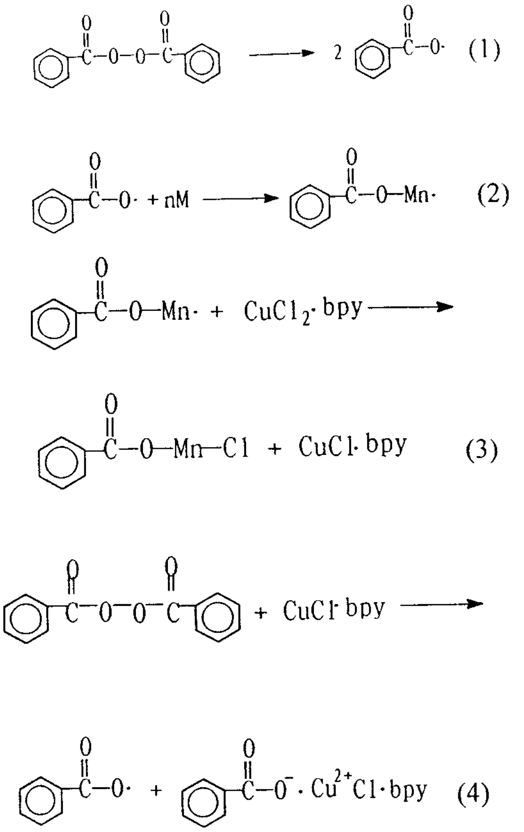


Fig. 4. Semilogarithmic kinetic plot for the bulk reverse ATRP of styrene at 110 °C [styrene]:[BPO]:[$CuCl_2$]:[bpy] = 150:1:2:4.



Scheme 1.

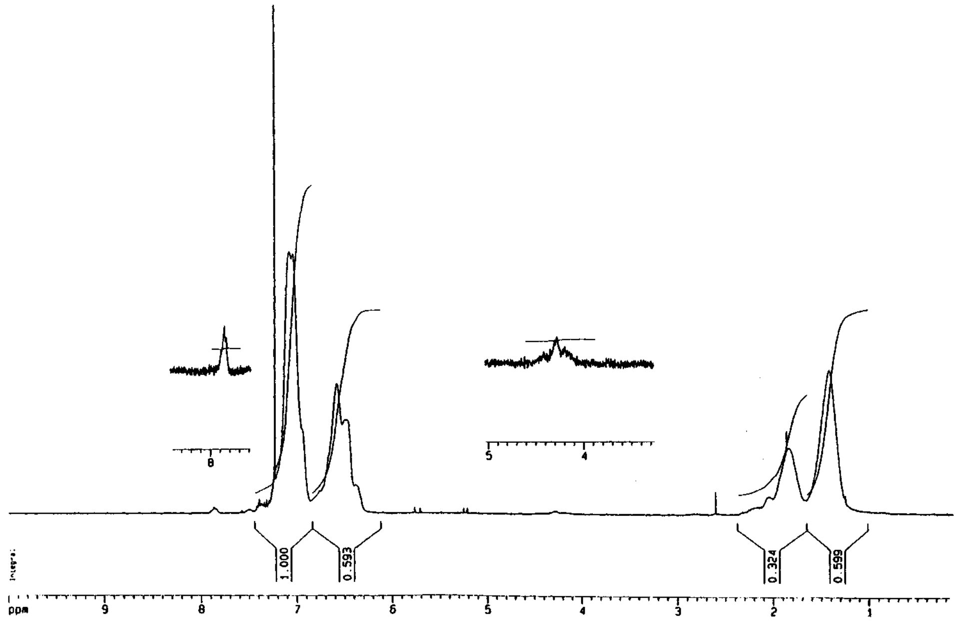


Fig. 5. ^{1}H-NMR of the polystyrene with BPO/$Cu^{II}Cl_2$/bipy.

group with those of methene and methine in the main chain of PS gives a molecular weight, $M_{n,NMR} = 12\,000$, close to the one from GPC based on PS standards, $M_{n,GPC} = 11\,000$. The reaction scheme is suggested as below:

The present outcomes can be explained in terms of Scheme 1. First, one molecule of BPO decompose into two primary radicals, Cu^{II} can not take electron from primary radicals due to the strong oxidation of primary radicals from BPO; second, after a monomer adds to a primary radical, the oxidation of the radical decreases greatly; third, now $Cu^{II}Cl_2$ can get rid of electron from this radical, forming dormant species and Cu^I; finally, redox reaction between BPO and Cu^I takes place and produces one primary radical. This process continually repeats at lower temperature. From the analysis we can see that one mole of BPO will result in one mole of radicals. During this period the inhibited reaction is predominant, little polymer was generated. So the initiation mechanism of BPO/$Cu^{II}Cl_2$/bpy is somewhat different from that of AIBN/$Cu^{II}Cl_2$/bpy. After ten hours at 70 °C, most of BPO was exhausted while the reduced transition-metal species, Cu^I, and the dormant species were accumulated. When the system is heated to 110 °C, however, in the presence of a coordinative ligand a reversible activation of the resulting alkyl chlorides was observed, and the polymerization under consideration proceeded via the ATRP mechanism.

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