Controlled/"Living" Radical Polymerization. Homogeneous Reverse Atom Transfer Radical Polymerization Using AIBN as the Initiator

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ABSTRACT: Atom transfer radical polymerization using AIBN/CuBr₂/2dNbipy as the initiating system has been successfully carried out for styrene, methyl acrylate, and methyl methacrylate. Well-defined polymers with low polydispersities have been obtained. High apparent initiation efficiencies were observed for both styrene and methyl acrylate polymerizations at 110 °C. With an increase of the [AIBN]_o/[CuBr₂/2dNbipy]_o ratio, apparent initiation efficiency decreased and polydispersity increased. Low initiation efficiencies were observed for the polymerizations of methyl methacrylate at both 110 and 90 °C, with higher polydispersities at higher temperature. The changes in polydispersity with respect to the changes in [AIBN]_o/[CuBr₂/2dNbipy]_o ratio and the temperature can be explained by the differences in the rate of deactivation by the copper(II) halide species.

Introduction

Well-defined polymers with low polydispersities and complex architectures can be achieved by living polymerization processes in which there is neither chain transfer nor termination. Until recently, most of the living polymerization systems were reported for an-ionic,^{1,2} cationic³ or group transfer polymerizations.⁴ However, the industrial applications of these techniques have been limited by the need for high-purity monomers and solvents, reactive initiators, and anhydrous conditions. In contrast, free radical polymerization is probably the most important commercial process leading to high molecular weight polymers. A large variety of monomers can be polymerized and copolymerized radically under relatively simple experimental conditions which require the absence of oxygen but can be carried out in the presence of water. However, free radical polymerization processes often yield polymers with illcontrolled molecular weights and high polydispersities. The idea of combining the advantages of both living polymerization and radical polymerization has attracted much attention. Indeed, recent years have witnessed a rapid progress in the development of controlled/ "living" radical polymerization. $^{5-16}\,$

Recently, we reported the transition metal catalyzed atom transfer radical polymerization (ATRP), a novel controlled/"living" radical process using alkyl halides as initiators, CuX ($X = Cl^-$ and Br^-) as a catalyst and 2,2′-bipyridine, bipy, as a complexing ligand.^{9,10} In this process, a dynamic equilibrium is established where the dormant polymer chains are reversibly activated via a halogen atom transfer reaction (eq 1).

$$P_{n} \cdot X \xrightarrow{k_{act}} P_{n} \cdot + X \cdot$$
(1)
$$(k_{p})_{Monomer}$$

A variety of monomers such as styrene,¹³ methyl acrylate,¹⁷ methyl methacrylate,¹⁸ and acrylonitrile¹⁹ were polymerized in a well-controlled manner.

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Scheme 1. Mechanism of Reverse ATRP Initiation:

 $I - I \xrightarrow{\Delta} 2 I^{*}$ $I^{*} + X M_{t}^{n+1} \xrightarrow{} I - X + M_{t}^{n}$ $k_{i} \downarrow + M$ $I - P_{1}^{*} + X M_{t}^{n+1} \xrightarrow{} I - P_{1} - X + M_{t}^{n}$

Propagation:

$$I - P_n - X + M_t^n$$
 \longrightarrow $I - P_n^* + X M_t^{n+1}$
 $(+M)_{k_p}$

Reverse ATRP differs from normal ATRP in its initiation process, where a conventional radical initiator, such as AIBN, is used.²⁰ As shown in Scheme 1, in the initiation step, once generated, the initiating radicals or the propagating radicals, I• or $I-P_1$ •, can abstract the halogen atom X from the oxidized transition-metal species, XM_t^{n+1} , to form the reduced transition-metal species, M_t^n , and the dormant species, I-X or $I-P_1-X$. In the subsequent steps, the transition-metal species, M_t^n , promotes exactly the same ATRP process as normal ATRP where $R-X/M_t^n/L_x$ are used as the initiation system. Instead of first activation of a dormant species, R-X, with M_t^n , as in the case of normal ATRP, reverse ATRP originates from the deactivation reaction between radicals, I• or $I-P_1$ •, and XM_t^{n+1} .

Previously, we reported the reverse ATRP of styrene under heterogeneous conditions employing unsubstituted bipyridine as the ligand. However, up to 10 equiv of copper(II) halide was needed to gain good control of the polymerization.²⁰ As a result of the excess copper-(II) halide, the polymerizations proceeded very slowly. In addition, uncontrolled heterogeneous reverse ATRP were observed for both methyl acrylate and methyl methacrylate.

By using alkyl substituted bipyridine ligands, such as 4,4'-di-5-nonyl-2,2'-bipyridine (dNbipy), reverse ATRP can be carried out under homogeneous conditions. In this paper, we report the kinetic investigation of the homogeneous reverse ATRP of styrene, methyl acrylate, and methyl methacrylate.



Figure 1. Effect of $[AIBN]_o/[CuBr_2/2dNbipy]_o$ ratio on the homogeneous reverse ATRP of styrene at 110 °C in bulk, varying $[CuBr_2/2dNbipy]_o$. [styrene]_o = 8.7 M; $[AIBN]_o = 0.045$ M; $[CuBr_2]_o = [dNbipy]_o/2 = 0.090$ M (1:2.0), 0.073 M (1:1.6), and 0.054 M (1:1.2).

Experimental Section

Materials. Styrene, methyl acrylate (MA), and methyl methacrylate (MMA) from Aldrich were vacuum distilled over CaH₂ and stored under an argon atmosphere at -15 °C. The ligand, 4,4'-di-5-nonyl-2,2'-dipyridyl (dNbipy) was prepared according to the reported procedure.¹³ The initiator, AIBN, was recrystallized from ether and stored at -15 °C. Anisole (solvent, 99.7%) and CuBr₂ were obtained from Aldrich and used without any further purification. MA, MMA and anisole were bubbled with dry argon for at least 15 min immediately before polymerization.

Polymerization. Bulk. To dry glass tubes with $CuBr_2$ and dNbipy under argon was added a solution of AIBN dissolved in the monomer. Three freeze-pump-thaw cycles were performed, and the tubes were sealed under vacuum and placed in an oil bath at 50 °C for 30 min until the mixture became a homogeneous solution. Then, the tubes were put in an oil bath held by a thermostat at the desired temperature. At timed intervals, the polymerizations were stopped by cooling the tubes into ice-water. Afterwards, the tubes were opened and the contents dissolved in THF.

Solution. A dry round-bottomed flask was charged with $CuBr_2$ and dNbipy. The flask was sealed with a rubber septum and was cycled between vacuum and argon three times to remove the oxygen. Degassed monomer and solvent were added using degassed syringes. The flask was immersed in an oil bath held by a thermostat at the desired temperature and allowed to stir until the mixture became homogeneous. Then, AIBN, dissolved in a small amount of monomer, was added. At timed intervals, samples were withdrawn from the flask using a degassed syringe and added to THF.

Characterization. Monomer conversion was determined from the concentration of residual monomer, with THF (for styrene) and anisole (for MA and MMA) as internal standards, using a Shimadzu GC-14 gas chromatograph equipped with a J&W Scientific 30 m DB-WAX column with a Shimadzu CR501 Chromatapac. Molecular weights and molecular weight distributions were measured using a Waters 712 WISP autosampler and the following Phenogel GPC columns: guard, linear, 1000 Å, and 100 Å. Polystyrene and poly(MMA) standards were used to calibrate the columns.

Results and Discussion

Homogeneous Reverse ATRP of Styrene. First, a series of reactions were carried out using copper(II) halide at different concentrations. As can be seen from Figure 1, when 2 equiv of copper(II) halide with regard to AIBN was employed, the first-order kinetic plots were rather linear, indicating that the concentration of the growing species remained constant.

The rate of polymerization increased when less than 2 equiv of copper(II) halide with regard to AIBN was used, since the copper(II) was the deactivating reagent. The previously reported kinetic investigations showed



Figure 2. Dependence of molecular weight, M_{n} , on monomer conversion for the homogeneous reverse ATRP of styrene at 110 °C in bulk, varying [CuBr₂/2dNbipy]_o. See Figure 1 for conditions.



Figure 3. Dependence of molecular weight distribution, M_w , M_n , on monomer conversion for the homogeneous reverse ATRP of styrene at 110 °C in bulk, varying [CuBr₂/2dNbipy]_o. See Figure 1 for conditions.

ATRP generally has a negative order with respect to copper(II) halide concentration.^{13,17} A decrease of the polymerization rate after an initial rapid polymerization was observed when the AIBN to copper(II) halide ratio of 1:1.2 was used. This was due to the fact that the amount of copper(II) halide at the beginning of the reaction was not sufficient to deactivate all of the radicals generated by AIBN. Thus, some of the polymer chains terminated by coupling, resulting in a decrease in the radical concentration.

Figure 2 is a plot of the number-average molecular weight (M_n) vs conversion for these polymerizations. The plots of polydispersities (M_w/M_n) vs conversion are shown in Figure 3. The M_n values increased linearly with conversion and polydispersities remained relatively low, indicating a well-controlled polymerization process. Based on the assumption that one molecule of AIBN initiator generated two polymer chains, the theoretical molecular weight $(M_{n,Cal})$ for reverse ATRP was calculated according to eq 2, where $[M]_0$ and $[AIBN]_0$ represent the initial concentrations of monomer and AIBN initiator, and $(MW)_0$ is the molecular weight of the monomer.

$$M_{n, Cal} = \{ [M]_o / (2[AIBN]_o) \} x (MW)_o x \text{ conversion}$$
(2)

As shown in Figure 2, a very good correlation of the calculated molecular weight with the experimental one was found for different [AIBN]₀/[CuBr₂/2dNbipy]₀ ratios, indicating a high apparent initiator efficiency (>95%).²¹ This was not surprising as the initiator efficiency of AIBN increases with increasing temperature.²² Also, in reverse ATRP, once generated, the initiating radicals or the propagating radicals, I[•] or I-P₁[•], can be rapidly



Figure 4. Effect of $[AIBN]_0/[CuBr_2/2dNbipy]_0$ ratio on the homogeneous reverse ATRP of styrene at 110 °C in bulk, varying $[AIBN]_0$. [styrene]_0 = 8.7 M; $[CuBr_2]_0 = [dNbipy]_0/2 = 0.090$ M; $[AIBN]_0 = 0.045$ M (0.50:1), 0.056 M (0.62:1), and 0.075 M (0.83:1).

deactivated by copper(II) halide to form the organic halide dormant species, I-X or $I-P_1-X$ (Scheme 1). Figure 2 also shows molecular weights were dependent on AIBN and not on CuBr₂ when the CuBr₂ concentration was varied. The experimental molecular weights were slightly lower than the calculated ones when the [AIBN]₀/[CuBr₂/2dNbipy]₀ ratio of 1:2.0 was used, presumably due to some new chains generated by styrene thermal self-initiation because of the overall slow polymerization (Figure 1).

From Figure 3, the lowest polydispersities were obtained when the $[AIBN]_0/[CuBr_2/2dNbipy]_0$ ratio of 1:1.6 was used. At a $[AIBN]_0/[CuBr_2/2dNbipy]_0$ ratio of 1:2.0, after an initial drop, an increase of polydispersities with conversion was observed, presumably due to side reactions, such as the elimination of HBr from the dormant polystyryl bromide chains, when more CuBr_2 was present in the ATRP system.²³ The higher polydispersities for the $[AIBN]_0/[CuBr_2/2dNbipy]_0$ ratio of 1:1.2 were attributed to the presence of less CuBr_2/dNbipy, resulting in insufficient deactivation, especially at the initial stage.

Another series of homogeneous reverse ATRP were performed at $[CuBr_2/2dNbipy]_0 = 0.1$ M with varying concentrations of AIBN. The rate of polymerization increased with an increase of AIBN concentration as shown in Figure 4. This was a result of more radicals being generated by the decomposition of AIBN.

At [AIBN]₀/[CuBr₂/2dNbipy]₀ ratios greater than 0.5, especially in the case of the [AIBN]₀/[CuBr₂/2dNbipy]₀ ratio of 0.83:1, nonlinear kinetics at the beginning of the reaction was observed as a result of termination reactions due to insufficient deactivation by copper(II) halide. The $M_{\rm n}$ values increased linearly with conversion as depicted in Figure 5 and polydispersities remained relatively low throughout the reaction as shown in Figure 6. At $[AIBN]_0/[CuBr_2/2dNbipy]_0 = 0.83:1$, the apparent initiator efficiency was about 85% possibly due to termination reactions caused by the insufficient deactivation by CuBr₂ at the beginning of the polymerization which resulted in the decrease of the number of propagating chains. Similar to the previous set of experiments, the lowest polydispersities were obtained with $[AIBN]_0/CuBr_2/2dNbipy]_0 = 0.62:1$. Higher or lower CuBr₂ concentrations led to increased polydispersities due to either side reactions of CuBr₂ at higher concentrations or insufficient deactivation by CuBr₂ at lower concentrations.

Homogeneous Reverse ATRP of Methyl Acrylate. The kinetic plots of homogeneous reverse ATRP



Figure 5. Dependence of molecular weight, M_n , on monomer conversion for the homogeneous reverse ATRP of styrene at 110 °C in bulk, varying [AIBN]₀. See Figure 4 for conditions.



Figure 6. Dependence of molecular weight distribution, M_w , M_n , on monomer conversion for the homogeneous reverse ATRP of styrene at 110 °C in bulk, varying [AIBN]_o. See Figure 4 for conditions.



Figure 7. Effect of $[AIBN]_0/[CuBr_2/2dNbipy]_0$ ratio on the homogeneous reverse ATRP of MA at 110 °C in anisole, varying $[AIBN]_0$. $[MA]_0 = 5.27$ M; $[CuBr_2]_0 = [dNbipy]_0/2 = 0.045$ M; $[AIBN]_0 = 0.022$ M (0.50:1) and 0.028 M (0.62:1).

of methyl acrylate in anisole solution at different AIBN concentrations are displayed in Figure 7, and the plots of number-average molecular weights and polydispersities vs conversion are shown in Figure 8. As shown in Figure 7, the kinetics was first-order in monomer, indicating a constant concentration of growing radicals. The rate of polymerization increased significantly with an increase of AIBN concentration. Both reverse ATRP reactions were well controlled with $M_{\rm n}$ values increasing linearly with conversion and polydispersities remaining very low. Although the apparent initiator efficiency appeared to be unity, because the experimental molecular weights were based on polystyrene standards, the actual molecular weights of the produced poly(methyl acrylate) could be higher. Nevertheless, it can be concluded that very high initiator efficiencies have been observed for both polymerizations.



Figure 8. Molecular weight, M_n , and molecular weight distribution, M_w/M_n , dependence on monomer conversion for the homogeneous reverse ATRP of MA at 110 °C in anisole, varying [AIBN]_o. See Figure 7 for conditions.



Figure 9. Effect of temperature on the homogeneous reverse ATRP of MMA in anisole at 110 and 90 °C: $[MMA]_0 = 4.67$ M; $[AIBN]_0 = [CuBr_2]_0/2 = [dNbipy]_0/4 = 0.011$ M.

Compared to styrene, a more pronounced increase of the polymerization rate was observed for methyl acrylate with an increase of the $[AIBN]_0/[CuBr_2/2dNbipy]_0$ ratio, as shown in Figures 4 and 7. This was ascribed to the fact that there was more excess copper(II) halide when a lower $[AIBN]_0/[CuBr_2/2dNbipy]_0$ ratio was used, and the rate of ATRP of methyl acrylate decreases stronger than that of styrene with increasing CuBr₂ concentration.^{13,17}

Homogeneous Reverse ATRP of Methyl Methacrylate. The kinetic plots of the homogeneous reverse ATRP of methyl methacrylate in anisole solution at different temperatures are displayed in Figure 9. At 110 °C, the temperature at which successful homogeneous reverse ATRP were carried out for both styrene and methyl acrylate, the kinetic plot of homogeneous reverse ATRP of methyl methacrylate showed significant curvature, indicating a possible termination reaction. At this temperature, the deactivation of the growing PMMA chains was not fast enough compared to the PMMA propagation under such ATRP conditions. When the homogeneous reverse ATRP of MMA was carried out at 90 °C, the linear semilogarithmic plot of ln([M]_o/[M]) vs time indicates constant concentration of growing species; however, an approximately 30 min induction period was observed. This can be attributed to the fact that AIBN decomposed slower at a lower temperature. Thus, in the first 30 min of the polymerization, copper(II) halide was in great excess compared to the radicals generated. As a result, the polymerization was retarded/inhibited during this induction period.

Figure 10 shows the number-average molecular weights and polydispersities vs conversion. In both cases, molecular weights increased with conversion; however, these were higher than the calculated values,



Figure 10. Molecular weight, $M_{\rm n}$, and molecular weight distribution, $M_{\rm w}/M_{\rm n}$, dependence on monomer conversion for the homogeneous reverse ATRP of MMA in anisole at 110 and 90 °C. See Figure 9 for conditions.

indicating low apparent initiator efficiency. The low apparent initiator efficiencies could be caused by the possible termination reactions due to the insufficient deactivation of the propagating PMMA radicals. In general, AIBN initiator efficiency decreases with the decrease of temperature.²² Polydispersities remained relatively low, with those at 90 °C lower than at 110 °C due to better control of polymerization and fewer termination reactions.

Conclusions

In conclusion, homogeneous reverse ATRP using AIBN/CuBr₂/2dNbipy as the initiating system has been successfully carried out for styrene, methyl acrylate and methyl methacrylate. Well-controlled polymerizations with low polydispersities have been achieved. For both styrene and methyl acrylate, high apparent initiator efficiencies were observed. The apparent initiator efficiency decreased with an increase of the [AIBN]₀/ [CuBr₂/2dNbipy]₀ ratio. The apparent initiator efficiency is affected by the termination reactions of the growing radicals by coupling which become more important at a higher [AIBN]₀/[CuBr₂/2dNbipy]₀ ratio. For styrene, the lowest polydispersity was obtained with a [AIBN]₀/[CuBr₂/2dNbipy]₀ ratio of 1:1.6. Increased polydispersities were obtained at higher CuBr₂ concentration due to side reactions by CuBr₂ or lower CuBr₂ concentration as a result of insufficient deactivation. In agreement with previous results, the rate of ATRP of methyl acrylate showed a stronger dependence on excess copper(II) halide.^{13,17} For methyl methacrylate, low apparent initiator efficiencies were observed for both polymerizations at 110 and 90 °C, with higher polydispersities at higher temperature due to relatively slower deactivation compared to PMMA propagation. It was also observed that styrene could undergo thermal selfinitiation which was more evident with an overall slow polymerization when a [AIBN]₀/[CuBr₂/2dNbipy]₀ ratio of 1:2.0 was employed.

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