Controlled/“Living” Radical Polymerization of Styrene and Methyl Methacrylate Catalyzed by Iron Complexes[1]

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ABSTRACT: Controlled/“living” radical polymerization of styrene and methyl methacrylate has been achieved by atom transfer radical polymerization (ATRP) catalyzed by iron halide complexes under both homogeneous and heterogeneous conditions. A variety of coordinating ligands have been used including 4,4′-bis(5-nonyl)-2,2′-bipyridine, trialkylamines, triphenylphosphine, trialkylphosphines, and trialkylphosphites. The polymer number-average molecular weight (M_n) increases linearly with monomer conversion and matches the predicted molecular weight. The polymerization rate and molecular weight distribution ($M_w/M_n = 1.1-1.5$) are affected by the structure of the coordinating ligands and the monomers employed.

Introduction

Radical polymerization processes play a dominant role in the industrial preparation of a wide variety of polymeric materials because of their mild reaction conditions, compatibility with a wide range of monomers, and high tolerance to impurities, water, functional groups, and additives. However, radical reactions are difficult to control because of irreversible biradical termination processes. Only in recent years has controlled/“living” radical polymerization become a reality because of the discovery of several polymerization systems that are based on rapid and reversible exchange between a low concentration of growing radicals and various types of dormant species.[2−16] One of the approaches to controlled/living radical polymerization is based on the transition metal-catalyzed atom transfer radical polymerization (ATRP). Several transition metal systems have been reported to control the radical polymerization of various monomers using alkyl halides (RX) as initiators (X = Cl, Br); for examples, CuX/2,2′-bipyridines,[7−10,13,14] $RuX_2/PPh_3/Al(OR)_3$,[11,12] NiX/*o,o*′-$(CH_2NMe_2)_2C_6H_3$,[15] and NiX_2/PPh_3.[16]

Iron complexes have been used widely in organic chemistry for carbon-carbon bond formation by atom transfer radical addition;[17−19] however, controlled radical polymerization by iron complexes has not been extensively studied.[20] This paper reports a new class of catalytic systems based on iron complexes containing various coordinating ligands for controlled/living radical polymerization of styrene and methyl methacrylate.

Experimental Section

Materials. Styrene and methyl methacrylate (MMA) were passed through a column of alumina to remove the inhibitor and were then stored under argon. 4,4′-Bis(5-nonyl)-2,2′-bipyridine (dNbipy) was synthesized via a coupling reaction of 4-(5-nonyl)pyridine using Pd−C as the catalyst. Other reagents, such as $FeBr_2$, organic ligands (trialkylamines, trialkylphosphines, etc.), and initiators (1-phenylethyl bromide, benzyl bromide, ethyl 2-bromoisobutyrate, *p*-toluenesulfonyl chloride, 2-bromopropionitrile, etc.), were purchased from commercial sources and used as received.

Polymerization of Styrene. The polymerization of styrene was carried out by the following general procedure: $FeBr_2$, coordinating ligands, initiator, 1-phenylethyl bromide (1-PEBr), and monomer (styrene, 1.0 mL) in appropriate ratios were added to a glass tube that was purged with argon. The solution was deaerated by three “freeze−pump−thaw” cycles and sealed under vacuum. The tubes were placed in an oil bath thermostatted at 110 °C, and were removed from the oil bath at timed intervals. The polymerization of styrene with $FeBr_2/N(nBu)_3$ as catalyst was carried out in a Schlenk flask with a magnetic stir bar and 10.0 mL of styrene and 0.5 mL of chlorobenzene as an internal standard for gas chromatography (GC) measurement.

Polymerization of MMA. The polymerization of MMA with various catalysts was carried out by a procedure similar to that described here for the polymerization catalyzed by $FeBr_2/N(nBu)_3$. First, $FeBr_2$ (34.0 mg, 0.16 mmol), deaerated MMA (5.0 mL, 46.7 mmol), *o*-xylene (4.0 mL), and $N(nBu)_3$ (0.11 mL, 0.47 mmol) were added to a dry round-bottomed Schlenk flask that was purged with argon. The solution was stirred for 10 min at room temperature, and then *p*-toluenesulfonyl chloride (30.0 mg, 0.16 mmol) was added as a solution in *o*-xylene (1.0 mL). The flask was sealed with a rubber septum and deaerated by three freeze−pump−thaw cycles to remove oxygen. The flask was immersed in an oil bath thermostatted at 80 °C. At timed intervals, samples were withdrawn from the flask with a deaerated syringe and diluted with tetrahydrofuran (THF).

Characterization. Monomer conversions were determined in THF solvent with *o*-xylene or *p*-dimethoxybenzene as an internal standard with a Shimadzu (GC-14A) gas chromatography. The number- and weight-average molecular weights (M_n and M_w, respectively) and polydispersities (M_w/M_n) of polystyrene and poly MMA (PMMA) were measured with a Waters 712 WISP autosampler and the following Phenogel gel permeation chromatography (GPC) columns: guard, linear, 1000 Å, and 100 Å. Molecular weights of polystyrene and PMMA were calibrated with polystyrene and PMMA standards, respectively.

Results

Polymerization of Styrene. The bulk polymerization of styrene was relatively well controlled by several RX/FeX_2/ligand (X = Cl, Br) initiating systems under both homogeneous and heterogeneous conditions. In all of the polymerizations, the molecular weight increased with monomer conversion, and the molecular weights measured by GPC matched the theoretical values calculated from eq 1 where $\Delta[M]$, $[R - X]_o$, and $(MW)_o$

$$M_n = (\Delta[M]/[R - X]_o)(MW)_o \qquad (1)$$

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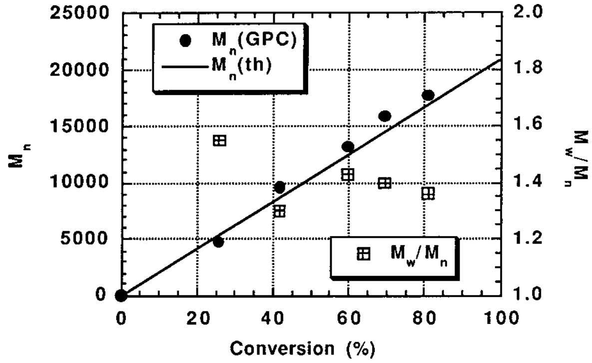


Figure 1. Dependence of molecular weights and polydispersities on monomer conversion in the bulk polymerization of styrene at 110 °C (1-PEBr:FeBr$_2$:P(nBu)$_3$:styrene = 1:1:3:200).

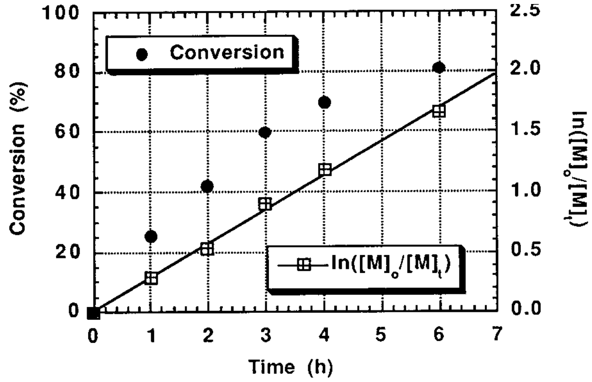


Figure 2. First-order kinetic plot of ln($[M]_0/[M]_t$) versus time in the bulk polymerization of styrene at 110 °C (1-PEBr:FeBr$_2$:P(nBu)$_3$:styrene = 1:1:3:200).

represent the concentration of consumed monomer, the initial concentration of initiator, and the molecular weight of monomer, respectively. Both the polymerization rate and polydispersity, however, varied depending on the coordinating ligands employed.

When tri-*n*-butylphosphine, P(nBu)$_3$, was used as a coordinating ligand (FeBr$_2$:P(nBu)$_3$ = 1:3) and 1-PEBr as an initiator, the reaction mixture was homogeneous and nearly colorless. The M_n increased linearly with monomer conversion, however, the polydispersities were relatively high (1.3−1.4, Figure 1). The polymerization was fast, and the straight semilogarithmic kinetic plot of ln($[M]_0/[M]_t$) vs time (Figure 2) indicated that the concentration of growing radicals was constant.

When tri-*n*-butyl-amine, N(nBu)$_3$, was used as a coordinating ligand (FeBr$_2$:N(nBu)$_3$ = 1:3), although the reaction mixture was heterogeneous, polymers with controlled molecular weights and even lower polydispersities were obtained (Figure 3). The polymerization was relatively fast, again with a linear semilogarithmic kinetic plot (Figure 4).

dNbipy has been widely used in the copper-based ATRP system, with excellent control of styrene polymerization.[10] When dNbipy was used as the coordinating ligand in the iron-based ATRP system (FeBr$_2$:dNbipy = 1:2), the molecular weights measured by GPC were close to the predicted molecular weights, but the polymerization rate was very slow, requiring 21 h to reach 64% conversion (Table 1). The polymerization rate was dramatically increased when dNbipy was mixed with P(nBu)$_3$ or N(nBu)$_3$, and polymers with better molecular weight control and lower polydispersities (< 1.2) were produced. For example, the polymerization reached 82% conversion in 5 h with 1:1 of dNbipy:P(nBu)$_3$ and 87% conversion in 8 h with 1:1 of dNbipy:N(nBu)$_3$ as the coordinating ligands, (Table 1). It is interesting to note that triethylphosphite, which has been used as the coordinating ligand in atom transfer radical addition (ATRA), gave an uncontrolled polymerization of styrene (Table 1). Another commonly used ligand, triphenylphosphine, also yielded a poorly controlled polymerization of styrene, with a slow polymerization rate and high polydispersity (Table 1).

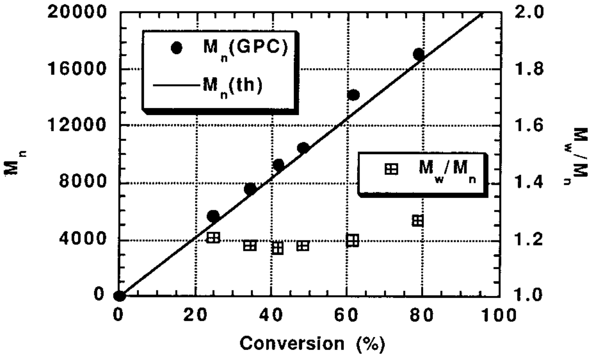


Figure 3. Dependence of molecular weights and polydispersities on monomer conversion in the bulk polymerization of styrene at 110 °C (1-PEBr:FeBr$_2$:N(nBu)$_3$:styrene = 1:1:3:200).

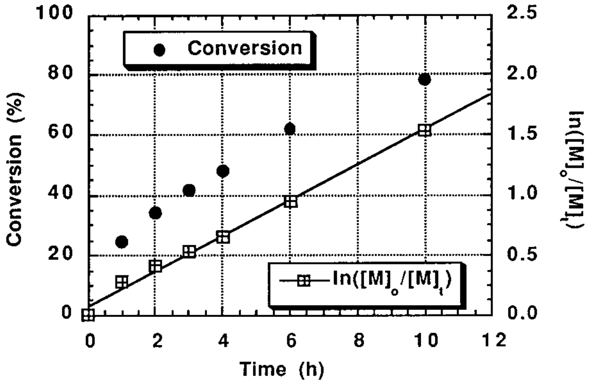


Figure 4. First-order kinetic plot of ln($[M]_0/[M]_t$) versus time in the bulk polymerization of styrene at 110 °C (1-PEBr:FeBr$_2$:N(nBu)$_3$:styrene = 1:1:3:200).

Table 1. Results of Bulk Polymerization of Styrene with Different Initiating Systems at 110 °C

system[a]	time (h)	conv (%)	$M_{n(th)}$	$M_{n(GPC)}$	M_w/M_n
A	21.0	64	6840	6470	1.27
B	5.0	82	8720	9600	1.13
C	8.0	87	9240	9800	1.20
D	15.0	87	9240	30500	6.14
E	15.0	47	5100	4200	1.76

[a] A, 1-PEBr:FeBr$_2$:dNbipy:styrene = 1:1:2:100; B, 1-PEBr:FeBr$_2$:dNbipy:P(nBu)$_3$:styrene = 1:1:1:1:100; C, 1-PEBr:FeBr$_2$:dNbipy:N(nBu)$_3$:styrene = 1:1:1:1:100; D, 1-PEBr:FeBr$_2$:P(OEt)$_3$:styrene = 1:1:3:100; E, 1-PEBr:FeBr$_2$:PPh$_3$:styrene = 1:1:3:100.

Polymerization of MMA. When the polymerization of MMA was carried out at 80 °C with FeBr$_2$/dNbipy as the catalyst and 2-bromopropionitrile (BPN) as the initiator, the reaction mixture was homogeneous. The M_n(GPC) increased linearly with monomer conversion (Figure 5) and the polydispersity remained relatively low (< 1.3). The nearly straight semilogarithmic kinetic plot of ln($[M]_0/[M]_t$) vs time (Figure 6) indicated that the concentration of growing radicals was constant during the polymerization. Additional studies showed that polymerizations with both 1 and 2 equivalents of dNbipy to FeBr$_2$ yielded similar molecular weight control and polymerization kinetics.

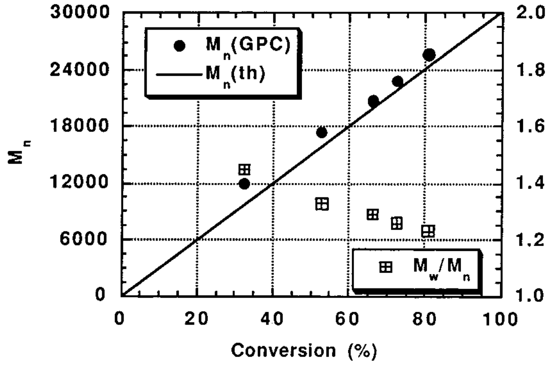


Figure 5. Dependence of molecular weights and polydispersities on monomer conversion in the solution polymerization of MMA (50% *o*-xylene, v/v) at 80 °C (BPN:$FeBr_2$:dNbipy:MMA = 1:1:1:300).

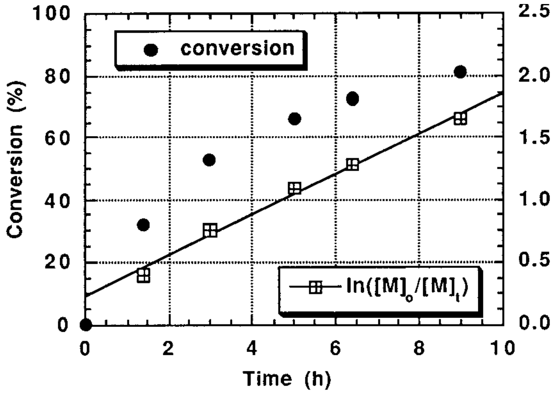


Figure 6. First-order kinetic plot of $\ln([M]_0/[M]_t)$ versus time in the solution polymerization of MMA (50% *o*-xylene, v/v) at 80 °C (BPN:$FeBr_2$:dNbipy:MMA = 1:1:1:300).

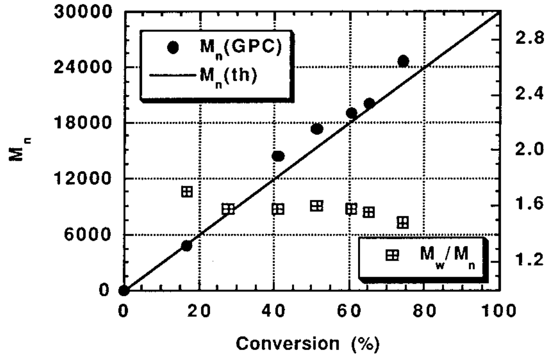


Figure 7. Dependence of molecular weights and polydispersities on monomer conversion in the solution polymerization of MMA (50% *o*-xylene, v/v) at 80 °C (TSCl:$FeBr_2$:$N(nBu)_3$:MMA = 1:1:3:300).

When $N(nBu)_3$ was employed as the coordinating ligand and *p*-toluenesulfonyl chloride (TSCl) as the initiator,[13] the reaction mixture was heterogeneous. The molecular weight increased linearly with monomer conversion, however, the polydispersities were relatively high (≈1.5, Figures 7 and 8), presumably in part because of the heterogeneous nature of the catalyst. When a more soluble ligand such as tri-*n*-octylamine was used, the polydispersities dropped to <1.4.

PMMA of higher molecular weight up to 80 000 was also prepared with both $FeBr_2$/dNbipy and $FeBr_2$/$N(nBu)_3$ as catalysts when a monomer-to-initiator ratio of 1000:1 was used. The molecular weights matched the theoretical values and the polydispersities were relatively low, but higher than that for Cu-based ATRP (Table 2).[21]

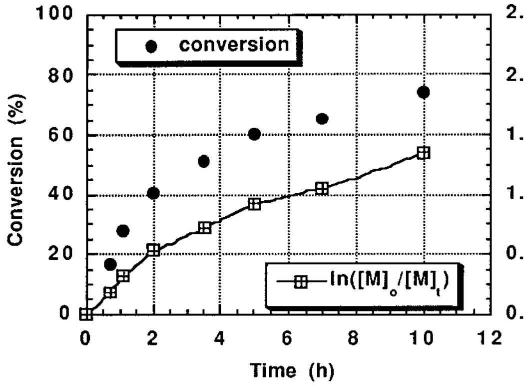


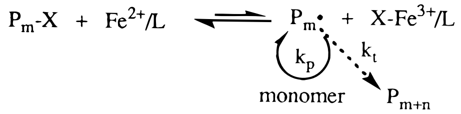
Figure 8. First-order kinetic plot of $\ln([M]_0/[M]_t)$ versus time in the solution polymerization of MMA (50% *o*-xylene, v/v) at 80 °C (TSCl:$FeBr_2$:$N(nBu)_3$:MMA = 1:1:3:300).

Table 2. Polymerization of Methyl Methacrylate in 50% *o*-Xylene (v/v) at 80 °C

ligand	time (h)	conv (%)	$M_{n(th)}$	$M_{n\,(GPC)}$	M_w/M_n
dNbipy[a]	19.0	75	75 100	75 100	1.24
$N(nBu)_3$[b]	24.0	86	86 400	85 800	1.35

[a] TSCl:$FeBr_2$:dNbipy:MMA = 1:4:4:1000. [b] TSCl:$FeBr_2$:$N(nBu)_3$:MMA = 1:2:6:1000.

Scheme 1



Discussion

The polymerization of styrene and MMA in the presence of iron halide complexes plausibly proceeds by the same atom transfer mechanism as proposed for the other ATRP systems. The polymeric halide (P_m-X) may be repeatedly activated by an Fe^{2+} species to form the growing radical $P_m^{\bullet}$, and X-Fe^{3+}. The X-Fe^{3+} species may rapidly react with a propagating polymeric radical, which has incorporated several monomer molecules, to regenerate P_m-X and the Fe^{2+} species. Repetition of these reactions results in the formation of well-defined polymers. Contribution of biradical termination reactions is small in the presence of a low stationary concentration of growing radicals (Scheme 1).

The radical mechanism is supported by the fact that addition of a molar equivalent of galvinoxyl (relative to initiator) effectively inhibits the polymerization and that the stereochemistry of the resulting PMMA by $FeBr_2$/dNbipy at 80 °C (rr:rm:mm = 59:37:4) is very similar to that of PMMA radically prepared by AIBN in toluene at 80 °C (rr:rm:mm = 58:38:4).[16,20]

Some Fe(III) complexes with amines or phosphines as the ligands were reported to be unstable[22]; however, others have been isolated.[23,24] The stability of Fe(III) complexes may depend on the reaction conditions. In the studied ATRP systems there seems to be a sufficient concentration of Fe(III) species in solution to control the polymerization. The details of the mechanism are still under investigation.

Apparently, the nature of the ligands strongly affects the kinetics of the polymerization and the polydispersity by influencing the thermodynamics and kinetics of the exchange process. It seems that more nucleophilic ligands better stabilize the Fe^{+3} species and accelerate the polymerization rate. At the same time, the exchange process is sufficiently fast to maintain a low

Table 3. Polymerization of Methyl Methacrylate by $FeBr_2$/dNbipy with Different Initiators[a]

initiator[b]	conv (%)	$M_{n(th)}$	$M_{n(GPC)}$	M_w/M_n
BzBr	59.5	11 900	21 430	1.60
EBiB	72.3	14 460	15 210	1.38
BPN	60.6	12 120	12 830	1.25
TSCl	53.0	10 600	10 710	1.24

[a] Reaction conditions: 3 h at 90 °C in 50% toluene solution (v/v); [MMA]:[initiator]:[$FeBr_2$]:[dNbipy] = 200:1:1:1. [b] BzBr, benzyl bromide; EBiB, 2-ethyl bromoisobutyrate; BPN, 2-bromopropionitrile; TSCl, *p*-toluenesulfonyl chloride.

polydispersity. In the polymerization of styrene, the overall polymerization rates with various catalysts proceed in the following order: $FeBr_2/P(nBu)_3 > FeBr_2/N(nBu)_3 > FeBr_2/dNbipy/P(nBu)_3 > FeBr_2/dNbipy/N(nBu)_3 > FeBr_2/PPh_3 > FeBr_2/P(OEt)_3 > FeBr_2/dNbipy$.

In the mixed-ligand systems, it is not clear whether only one iron complex [such as $FeBr_2/dNbipy/P(nBu)_3$ or $FeBr_2/dNbipy/N(nBu)_3$] is formed or rather two different iron complexes [such as $FeBr_2$/dNbipy and $FeBr_2/P(nBu)_3$ or $FeBr_2/N(nBu)_3$] are present. It is possible that several catalytic species exist in an equilibrium in solution. Because ATRP is proposed to proceed by a free radical polymerization mechanism, the halogen-terminated polymer chains and propagating radicals can freely react with iron(II) halides and iron(III) halides, respectively. Because of a fast dynamic exchange between halogen-terminated polymer chains and propagating radicals, polymers with unimodal molecular weight distribution are produced regardless of the number of catalytic species in solution.

The molecular weight is controlled by the initial monomer-to-initiator ratio and monomer conversion. The amount of catalyst does not affect the molecular weight control but does affect the polymerization rate. Reducing the amount of catalyst leads to slower polymerization when all other conditions are kept the same. The choice of initiator is important especially in the polymerization of MMA, fast initiation is required to obtain good molecular weight control. For example, when an initiator that yields slow initiation [such as benzyl bromide (BzBr)] is used, the molecular weight is higher than the predicted value and the polydispersity is high (Table 3). When initiators giving faster initiation [such as 2-ethyl bromoisobutyrate (EBiB), 2-bromopropionitrile (BPN), and *p*-toluenesulfonyl chloride (TSCl)] are used, the molecular weights are close to the predicted values and polydispersities are relatvely low (Table 3).

In summary, we have demonstrated that the radical polymerization of styrene and MMA can be controlled by iron complexes using a variety of coordinating ligands. The polymerization rate and molecular weight distribution vary depending on the coordinating ligands. The polymerization presumably proceeds by the same atom transfer mechanism proposed for other transition metal-catalyzed polymerizations, such as the Cu-based ATRP system. The easy access and versatility of coordinating ligands suggest that many organic ligands could be used for various transition metal catalysts to control the radical polymerization of vinyl monomers.

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