Halide Anions as Ligands in Iron-Mediated Atom Transfer Radical Polymerization

Mircea Teodorescu,† Scott G. Gaynor, and Krzysztof Matyjaszewski*

Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received September 28, 1999; Revised Manuscript Received December 14, 1999

ABSTRACT: Halide anions have been used as complexing ligands in iron-mediated ATRP, in both direct and reverse ATRP. In direct ATRP, iron(II) bromide complexed with ammonium and phosphonium chloride, bromide, or iodide salts has been shown to catalyze the polymerization of both styrene and (meth)acrylates in a controlled manner under appropriate conditions. The experimental molecular weights increased linearly with monomer conversion and were close to the calculated values. The polymerization rates and polydispersities ($M_w/M_n = 1.1-1.4$) were dependent on the monomer employed. Reverse ATRP, initiated by AIBN/$FeBr_3$/onium salts, led to a controlled polymerization of both methyl methacrylate and methyl acrylate, while for styrene uncontrolled molecular weights and high polydispersities were obtained, presumably due to the involvement of the cationic polymerization. It is suggested that different iron complexes may be involved in ATRP, depending on the onium salt/$FeBr_3$ ratio. Because of their ionic nature, the iron complexes could be removed easily from the reaction mixture by washing the polymerization mixture with water.

Introduction

Since 1995, when it was discovered,[1,2] atom transfer radical polymerization (ATRP) has been expanding continuously, with a large effort being directed toward both better understanding of the reaction mechanism and enlargement of the fields of application. The role of, and the selection criteria for, each component of the polymerization mixture—monomer, initiator, transition metal, ligand, solvent—have been investigated in detail. Presently, most vinyl monomers can be polymerized in a controlled/"living" manner by using this technique, the main exceptions being vinyl acetate and vinyl chloride.[3−5] Also, an increasing number of transition metals, like copper,[1,6] ruthenium,[2] iron,[7,8] nickel,[9,10] rhodium,[11,12] and rhenium,[13] in conjunction with different ligands can be used to catalyze the polymerization reaction. Many ligands are available for each transition metal used in ATRP, but despite this, a steady effort is directed toward designing new ligands, those that are cheaper and able to form catalytic complexes with improved reactivities.

This paper reports on a new class of ligands able to complex iron, leading to active catalysts for ATRP. Up to now, the ligands used in iron-based ATRP have been selected from the classes of phosphines (tributylphosphine,[8,14] triphenylphosphine[7,15]), aliphatic amines (tributylamine,[8,14] trioctylamine[14]), substituted bipyridines (4,4′-di(5-nonyl)-2,2′-bipyridine, dNbpy[8]), tetradentate Schiff bases,[16] or carbon monoxide and cyclopentadienyl.[17,18] The iron complexes with these ligands display either tetrahedral (triphenylphosphine, tributylamine, carbon monoxide, and cyclopentadienyl) or square-planar (tetradentate Schiff base) configuration. The only complex that may possess a different structure, $FeBr_2$:dNbpy = 1:2, was employed for styrene and MMA polymerization.[8]

Following this route, we decided to investigate the activity of some of the tetrahedral complexes of iron as catalysts for ATRP. Among them, those with halide anions as ligands and bulky organic counterions (tetrabutylammonium, tetrabutylphosphonium, etc., Figure 1) proved to be the best ATRP catalysts. The paper presents the results obtained by employing halide anions as ligands in iron-based ATRP. Two approaches were used: direct ATRP, as well as the reverse approach, in which the ATRP initiating system is formed in situ by the reaction of a conventional radical initiator with the complex of the transition metal in its upper oxidation state. Previously, Asscher and Vofsi used diethylammonium chloride and triethylammonium chloride to solubilize copper and iron chlorides, employed as catalysts in ATRA of chloroform and carbon tetrachloride to different olefins.[19−21] However, these complexes have not been used in ATRP. Moreover, the reported here halide-based iron complexes can polymerize acrylates in a controlled way, in contrast to earlier reports focused on nitrogen- and phosphorus-based ligands.

Experimental Section

Materials. Styrene, methyl methacrylate (MMA), and methyl acrylate (MA) were vacuum distilled from CaH_2 and stored at −15 °C. The onium salts, all from Aldrich, were dried under vacuum at 90 °C for at least 8 h and kept in a desiccator over anhydrous $CaCl_2$. Iron(II) bromide and iron(III) bromide, from Aldrich, were used as received. 1-Phenylethyl bromide (PEBr), methyl 2-bromopropionate (MBP), and ethyl 2-bromoisobutyrate (EBIB), from Aldrich, were used as received. AIBN was recrystallized from methanol at 50 °C and stored in the freezer. All the solvents were used without further purification. In many cases, monomers and solvents were bubbled with argon for at least 15 min immediately before polymerization.

Polymerizations. The experimental conditions (temperature, concentrations, etc.) were chosen so as to ensure a proper polymerization rate, while keeping termination reactions at a low level. Therefore, MMA polymerizations were more diluted than those of styrene and MA, whereas styrene polymerizations were carried out at higher temperature, under the conditions described before.[3]

Single-Point Experiments. A glass tube was loaded with the solid compounds ($FeBr_2$/onium salt or $FeBr_3$/onium salt/AIBN),

† Current address: Polytechnic University, Faculty of Industrial Chemistry, 1 Gh. Polizu Street, 78126, Bucharest, Romania.

10.1021/ma991652e CCC: $19.00
Published on Web 03/09/2000

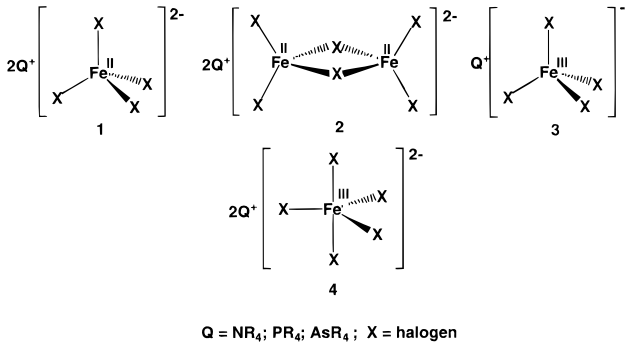


Figure 1. Structures of the complexes of iron with halide anions described in the literature that may be involved in the polymerization processes presented in this paper.

capped with a rubber septum, and cycled three times between vacuum and argon in order to remove oxygen. Then, all liquid components (monomer, solvent, GC standard, initiator), previously degassed, were added via a syringe. The tube was sealed under argon and placed in an oil bath thermostated at the desired temperature. After a certain time interval, the tube was cooled and opened, and the contents were dissolved in THF or toluene.

Kinetic Experiments. A Schlenk flask was charged with $FeBr_2$ and the onium salts. The flask was sealed with a rubber septum and was cycled three times between vacuum and argon. The degassed liquid components, except for the initiator, were added through degassed syringes, and the mixture was stirred at room temperature until the catalytic complex formed. In the case of MA, the initiator was added and the reaction mixture was quickly transferred into tubes, which were immediately sealed and placed in the oil bath. In the case of styrene and MMA, the flask was placed in the oil bath and the initiator added. After certain time intervals, tubes were removed from the oil bath and processed as described above, or samples were withdrawn from the reaction mixture using degassed syringes and dissolved in THF or toluene. A few drops of a 10% solution of hydroquinone in THF were added to polyMA GPC samples in order to prevent further polymerization of the monomer. In the case of reverse ATRP, AIBN was loaded into the Schlenk flask together with $FeBr_3$ and the onium salt.

Measurements. Monomer conversion was determined by GC in THF (styrene, MMA) or toluene (MA) solution using chlorobenzene or *o*-xylene as internal standards. A Shimadzu GC-14 gas chromatograph equipped with a J&W Scientific DB-WAX column with a Shimadzu CR501 Chromatapac was used. Molecular weights and polydispersities (M_w/M_n) were measured by GPC in THF using a Waters 717 Plus autosampler, PSS guard, 10^5, 1000, and 100 Å columns, and a Waters 410 differential refractometer.

Results

A. Direct ATRP. 1. Polymerization of Styrene. Polymerization experiments using different molar ratios of onium salt/$FeBr_2$ (Table 1) showed that the reaction was slow, the rate decreasing with increasing amounts of salt. The molecular weights agreed well with the theoretical values, and the polydispersities were low, $M_w/M_n < 1.2$, except for where the salt/$FeBr_2$ molar ratio was 0.5. Here, a cationic polymerization appeared to occur, leading to much lower molecular weights and a bimodal molecular weight distribution. Tetrabutylammonium bromide (TBABr) and tetrabutylphosphonium bromide (TBPBr) were employed as salts. In both cases, the optimum molar ratio salt/$FeBr_2$ was in the range 1−1.5. The reaction mixture was heterogeneous at both room temperature and 110 °C.

A kinetic experiment carried out using a ratio TBABr/$FeBr_2$ = 1.5 showed a nonlinear first-order kinetic plot,

Table 1. Styrene Polymerization Catalyzed by $FeBr_2$/Onium Salts[a]

salt	salt/$FeBr_2$ (mol/mol)	conv (%)	$M_{n,th}$	$M_{n,SEC}$	M_w/M_n
TBABr	0.5	28	5600	2570	1.53
TBABr	1	23	4600	4670	1.18
TBABr	1.5	19	3800	4000	1.11
TBABr	2	12	2400	2460	1.18
TBPBr	0.5	70	14000	3030	2.18
TBPBr	1	29	5800	5450	1.18
TBPBr	1.5	16	3200	3240	1.10
TBPBr	2	6	1200	1050	1.15

[a] Experimental conditions: $[St]_0 = 8.7$ M; $[PEBr]_0 = [FeBr_2]_0 = 45.3$ mM; 110 °C; time = 7 h.

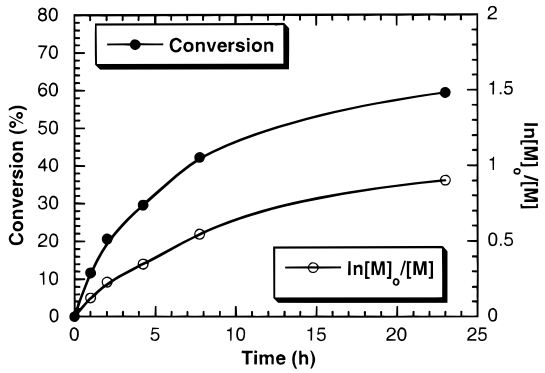


Figure 2. Kinetic plot for the bulk polymerization of styrene. $[St]_0 = 8.7$ M; $[PEBr]_0 = [FeBr_2]_0 = 45.3$ mM; $[TBABr]_0 = 67.9$ mM; 110 °C.

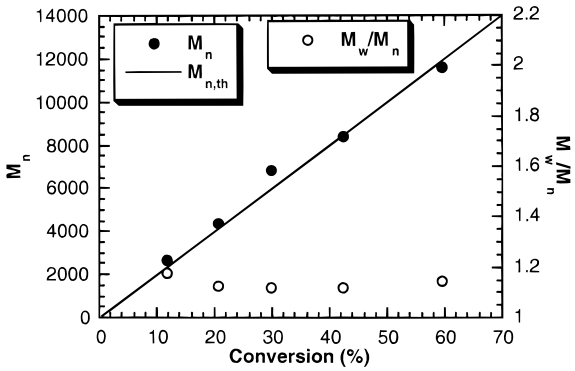


Figure 3. Dependence of molecular weights and polydispersities on monomer conversion for the bulk polymerization of styrene. Experimental conditions as in Figure 2.

but good agreement between the theoretical and experimental M_n's was observed with polydispersities in the range $M_w/M_n = 1.1-1.2$ (Figures 2 and 3).

2. Polymerization of MMA. Test experiments carried out at different TBPBr/$FeBr_2$ molar ratios in xylene at 80 °C showed an optimum value around 0.5−1. The results of the kinetic experiment performed under these conditions are shown in Figures 4 and 5. The reaction was fast (80% conversion after 5 h), but the first-order kinetic plot was not linear, indicating the presence of termination reactions. The reaction mixture was slightly heterogeneous. The molecular weights increased linearly with conversion, but they were higher than the theoretical values. Polydispersity decreased at the beginning of the reaction until a minimum value of 1.34 was reached and increased again after 60% conversion.

3. Polymerization of Methyl Acrylate. Single-point polymerization experiments showed that $FeBr_2$ complexes with either chloride, bromide, or iodide anion

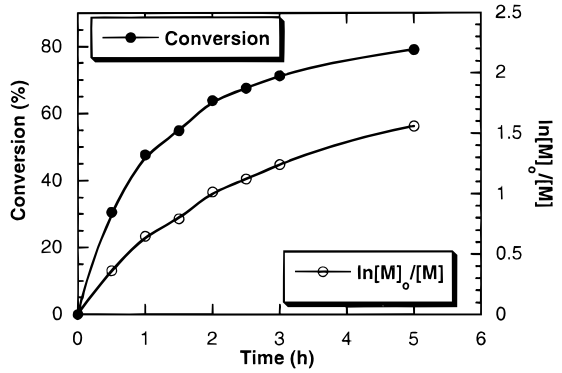


Figure 4. Kinetic plot for the solution polymerization of MMA. $[MMA]_0 = 4.68$ M; $[EBIB]_0 = [FeBr_2]_0 = [TBPBr]_0 = 15.6$ mM; solvent = *o*-xylene; 80 °C.

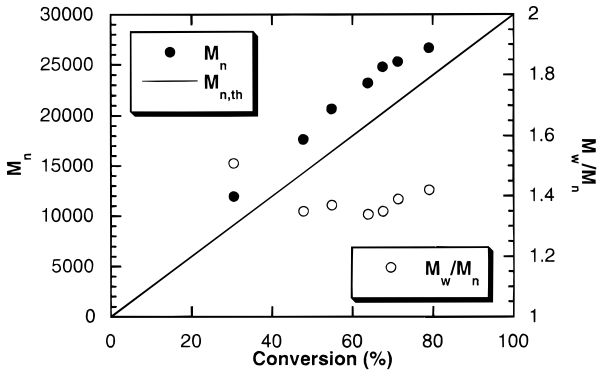


Figure 5. Dependence of molecular weights and polydispersities on monomer conversion for the solution polymerization of MMA. Experimental conditions as in Figure 4.

Table 2. Methyl Acrylate Polymerization Catalyzed by $FeBr_2$/Onium Salts[a]

salt	salt/$FeBr_2$ (mol/mol)	time (h)	conv (%)	$M_{n,th}$	$M_{n,SEC}$	M_w/M_n
TBACl	0.5	8.5	5	1000	1150	1.53
TBACl	1	8.5	16	3200	3960	1.39
TBACl	1.5	8.5	34	6800	8060	1.90
TBACl	2	8.5	29	5800	12400	1.92
TBABr	0.5	22.17	5	1000	1230	1.35
TBABr	1	22.17	22	4400	4620	1.34
TBABr	1.5	22.17	32	6400	6830	1.22
TBABr	2	22.17	34	6800	6800	1.69
TBAI	0.5	22	4	800	750	1.17
TBAI	1	22	13	2600	2700	1.17
TBAI	1.5	22	25	5000	5120	1.15
TBAI	2	22	16	3200	3510	1.12
TBAI	2.5	22	19	3800	3720	1.13
TBPBr	0.5	23.17	4	800	1200	1.30
TBPBr	1	23.17	24	4800	4820	1.21
TBPBr	1.5	23.17	27	5400	5980	1.20
TBPBr	2	23.17	32	6400	6680	1.23
TBPBr	2.5	23.17	14	2800	2590	1.52

[a] Experimental conditions: $[MA]_0 = 11.1$ M; $[MBP]_0 = [FeBr_2]_0 = 47.7$ mM; 90 °C.

were active for methyl acrylate ATRP (Table 2). The experimental molecular weights agreed very well with the theoretical values, and the polydispersities were low, indicating a controlled process. The polydispersity indices depended on the nature of the complexing halide anion and decreased in the order $Cl^- > Br^- > I^-$. Also, the polydispersity was lower in the case of tetrabutylphosphonium salt than for its tetrabutylammonium counterpart, very likely due to a better solubility of the first one. The reaction mixtures were slightly heterogeneous in all cases. Similar results were obtained in the case of butyl acrylate.

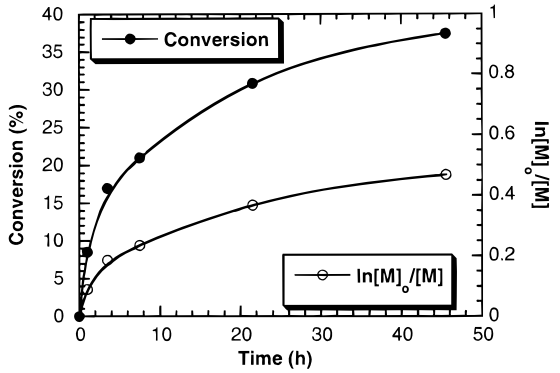


Figure 6. Kinetic plot for the bulk polymerization of methyl acrylate. $[MA]_0 = 11.1$ M; $[MBP]_0 = [FeBr_2]_0 = 47.7$ mM; $[TBPBr]_0 = 71.5$ mM; 90 °C.

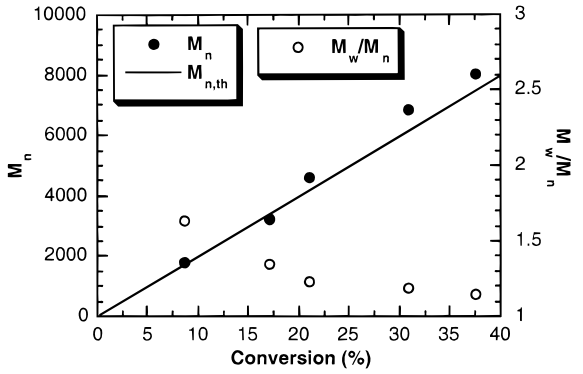


Figure 7. Dependence of molecular weights and polydispersities on monomer conversion for the bulk polymerization of methyl acrylate. Experimental conditions as in Figure 6.

A kinetic experiment carried out at a ratio TBPBr/$FeBr_2 = 1.5$ showed that the polymerization was very slow, with only 38% conversion being reached after 46 h. The first-order kinetic plot was nonlinear, indicating the presence of termination reactions (Figure 6). The molecular weights agreed well with the theoretical values, and the polydispersities decreased with conversion to values as low as 1.15 (Figure 7).

B. Reverse ATRP. Reverse ATRP has been previously demonstrated for both copper[22−25] and iron[15] complexes. The procedure uses as an initiating system a conventional radical initiator, such as AIBN, together with a complex of a transition metal in its upper oxidation state, which at higher temperature and in the presence of the monomer is converted to a classical ATRP initiating system, by decomposition of the radical initiator to form radicals which then react with the higher oxidation state transition metal to form the organic halide and the complex of the transition metal in its lower oxidation state. The previously described iron-mediated reverse ATRP employed the system AIBN/$FeCl_3$/triphenylphosphine to polymerize MMA in a well-controlled manner.[15] This section shows our results on reverse ATRP promoted by iron(III) bromide complexed with halide anions.

1. Polymerization of MMA. Polymerization experiments at different onium salt/$FeBr_3$ ratios were carried out (Table 3). The experimental conditions were chosen to ensure a fast decomposition of AIBN (approximately 10 min lifetime at 100 °C), and a rapid trapping of the radicals resulted from the decomposition of the initiator ($FeBr_3$/AIBN = 4). In all cases, a bottom red layer

Table 3. Reverse ATRP of MMA Catalyzed by $FeBr_3$/TBPBr[a]

entry	TBPBr/$FeBr_3$ (mol/mol)	conv (%)	$M_{n,th}$	$M_{n,SEC}$	M_w/M_n
1	0.5	41	12 300	13 330	1.43
2	1	63	18 900	20 110	1.65
3	1.5	63	18 900	21 210	1.62
4	2	38	11 400	13 650	1.30
5	2.5	26	7 800	9 510	1.30

[a] Experimental conditions: $[MMA]_0 = 3.12$ M; $[AIBN]_0 = 5.2$ mM; $[FeBr_3]_0 = 20.8$ mM; solvent *o*-xylene; 100 °C; time = 2.17 h.

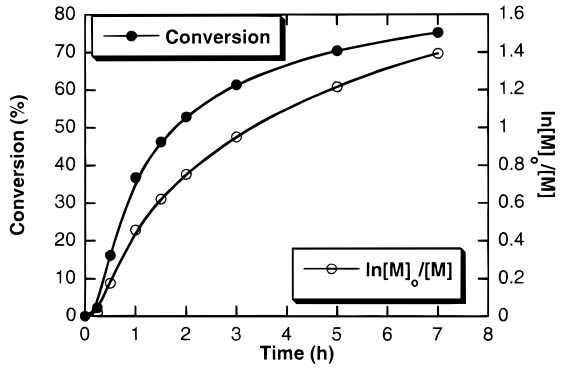


Figure 8. Kinetic plot for the solution polymerization of MMA by reverse ATRP. $[MMA]_0 = 3.12$ M; $[AIBN]_0 = 5.2$ mM; $[FeBr_3]_0 = 20.8$ mM; $[TBPBr]_0 = 41.6$ mM; solvent *o*-xylene; 100 °C.

formed in the reaction mixture shortly after heating at 100 °C. The theoretical molecular weights were calculated assuming 100% initiation efficiency for the primary radicals generated from AIBN (eq 1).

$$M_{n,th} \approx [MMA]_0/2[AIBN]_0 \times MW_{MMA} \times \text{conversion} \quad (1)$$

The experimental molecular weights were higher by 10−20% than the theoretical values, indicating a 80−90% initiation efficiency of AIBN, similar to previously reported reverse ATRP with Cu complexes.[23] Higher salt/iron ratios afforded lower polydispersities (Table 3).

A kinetic experiment, carried out under the experimental conditions corresponding to the best results in terms of both control of the polymerization and reaction rate (Table 3, entry 4), showed a short induction period at the beginning of the reaction and a nonlinear first-order kinetic plot, indicating the presence of termination reactions (Figure 8). The molecular weights increased linearly with conversion, but they were higher than the predicted values. Polydispersity indices increased during the polymerization from below 1.3 to about 1.45 (Figure 9).

2. Polymerization of Styrene and Methyl Acrylate. Attempts to polymerize styrene in a controlled manner by reverse ATRP failed, presumably due to the occurrence of the cationic process induced by the $FeBr_3$ present in a large amount in the reaction mixture. Experiments performed in bulk, at 110 °C, for TBABr/$FeBr_3$ ratios varying from 0.5 to 2.5 afforded much lower molecular weights than the values calculated based on conversion (eq 1) and polydispersities ranging from 3.7 to 6.7.

Reverse ATRP of methyl acrylate displayed a slow polymerization rate as in the case of the direct approach (Table 4). The experimental molecular weights were

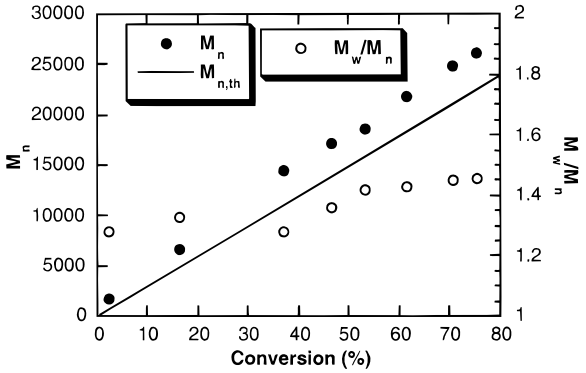


Figure 9. Dependence of molecular weights and polydispersities on monomer conversion for the solution polymerization of MMA by reverse ATRP. Experimental conditions as in Figure 8.

Table 4. Reverse ATRP of Methyl Acrylate Catalyzed by $FeBr_3$/TBPBr[a]

entry	TBPBr/$FeBr_3$ (mol/mol)	conv (%)	$M_{n,th}$	$M_{n,SEC}$	M_w/M_n
1	0.5	3	600	480	1.11
2	1	10	2000	3400	1.84
3	1.5	23	4600	5980	1.67
4	2	26	5200	7500	1.31
5	2.5	30	6000	7350	1.30

[a] Experimental conditions: $[MA]_0 = 11.1$ M; $[AIBN]_0 = 23.9$ mM; $[FeBr_3]_0 = 95.6$ mM; 100 °C; time = 22 h.

higher by 20−50% than the theoretical values. As in the case of MMA, the lowest polydispersities were obtained for salt/$FeBr_3$ ratios higher than 2. The reaction mixture was heterogeneous in all cases due to the formation of a red phase, shortly after heating at 100 °C.

Discussions

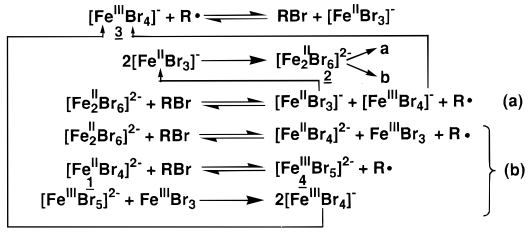
Iron complexes with halide anions as ligands have been known for many years.[26−29] They are negatively charged and are usually accompanied by bulky organic onium counterions. Figure 1 shows the structures of the complexes described in the literature that may be involved in the polymerization processes presented in this paper. In most cases, they are formed by the direct reaction of onium halides with iron halides in solution.[26]

Complexes **1** and **3** have been isolated for both chlorine and bromine, while **2** and **4** are known only for X = Cl.[29,30] It is also worth mentioning that, unlike chlorine-based complexes, mononuclear iron(III) complexes with more than four bromine atoms have not been isolated, presumably due to their lower stability.[28,31]

Complex **1** is very likely the active species involved in the direct ATRP process. However, the assistance of complex **2** cannot be excluded at onium salt/$FeBr_2$ ratios lower than 2. By abstracting the halogen atom from the initiator or the polymeric "dormant" species, the $[Fe^{II}Br_4]^{2-}$ complex is converted to a $[Fe^{III}Br_5]^{2-}$ species, **4**, which has not yet been isolated but could be present in solution. The formation of the $[Fe^{III}Br_5]^{2-}$ complex anion is supported by the reverse ATRP experiments, which will be discussed later. The redox potential of the $[Fe^{II}Br_4]^{2-}$ complex seems to be relatively high, as indicated by the low polymerization rates displayed by styrene and methyl acrylate.

In the reverse ATRP process, different complexes may be involved, depending on the onium salt/$FeBr_3$ ratio,

Scheme 1



as suggested by the variable polydispersities obtained for different salt/$FeBr_3$ ratios (Tables 3 and 4, entries 2, 3 vs 4, 5). As the $[Fe^{III}Br_4]^-$ complex anion, **3**, is formed at the equimolar amounts of onium bromide and $FeBr_3$ in solution at room temperature,[26,27] we can assume that it is also present when a onium salt/$FeBr_3$ ratio equal to 1 is employed in the reverse ATRP experiments (Tables 3 and 4, entry 2). Because of its higher stability, the deactivation step is slow, leading to a higher polydispersity, even though iron(III) is in relatively high concentration.

A mixture of complexes of type **1** and **2** is very likely to be responsible for the activation step. Their plausible formation is shown in Scheme 1. The abstraction of a bromine atom from $[Fe^{III}Br_4]^-$ may lead to a $[Fe^{II}Br_3]^-$ species which is unstable and dimerizes quickly to a complex of type **2**. Through reaction with the alkyl bromide, complex **2** may form an unstable $Fe^{II}-Fe^{III}$ mixed complex, which decomposes very fast according to either route a or route b (Scheme 1). Following route b, $FeBr_3$ forms along with the complex **1**, which reacts with RBr in the activation step leading to $[Fe^{III}Br_5]^{2-}$. $[Fe^{III}Br_5]^{2-}$ can participate in the deactivation process, and also, it may react fast with $FeBr_3$ forming the more stable $[Fe^{III}Br_4]^-$ complex. The contribution of each of these species to the reaction should depend also on their solubilities in the organic medium, which may be very different as ionic species carrying a variety of electric charges are involved.

The lower polydispersities obtained for salt/iron ratios higher than 2 (Tables 3 and 4, entries 4 and 5) suggest the involvement of the $[Fe^{III}Br_5]^{2-}$ complex, which may allow for easier abstraction of a bromine atom due to its lower stability and therefore faster deactivation. In this case, the resulting $[Fe^{II}Br_4]^{2-}$ complex could be responsible for the activation step.

The ionic nature of the iron complexes involved in the polymerization allowed for easy removal of the catalyst by simply washing the final reaction mixture with water. This procedure was tested in the case of styrene polymerization through direct ATRP and MMA polymerization by the reverse approach. Both final polymerization mixtures were diluted with benzene and washed with water (2−3 times) until the red organic layer became colorless. After drying and removing the organic solvent under vacuum, white solid polymers were obtained.

Conclusions

Ionic iron complexes with halide anions as ligands and bulky onium cations can be used to control the polymerization of styrene and (meth)acrylates by both direct and reverse ATRP. In the direct approach, iron(II) bromide complexed with either chloride, bromide, or iodide onium salts allowed for the preparation of polymers with predetermined molecular weights and low polydispersities. However, styrene and acrylate polymerizations were slow, while that of MMA was quite fast. The first-order kinetic plot was nonlinear in all cases, indicating the presence of termination reactions.

Reverse ATRP was successfully applied to MMA. The molecular weights increased with conversion, and they were close to the values calculated based on the initial monomer/AIBN ratio. Methyl acrylate displayed the same slow polymerization rate as in the case of the direct approach, while for styrene the occurrence of the cationic process led to uncontrolled molecular weights and high polydispersities. Depending on the onium salt/$FeBr_3$ ratio, different iron complexes may be involved in the polymerization.

Acknowledgment. Support from the Industrial Members of the ATRP Consortium at Carnegie Mellon University is gratefully appreciated.

References and Notes

(1) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(2) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
(3) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901.
(4) Matyjaszewski, K. *Chem. Eur. J.* **1999**, *5*, 3095.
(5) Patten, T. E.; Matyjaszewski, K. *Acc. Chem. Res.* **1999**, *32*, 895.
(6) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.
(7) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 4507.
(8) Matyjaszewski, K.; Wei, M.; Xia, J.; McDermott, N. E. *Macromolecules* **1997**, *30*, 8161.
(9) Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1996**, *29*, 8576.
(10) Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamotao, M. *Macromolecules* **1997**, *30*, 2249.
(11) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, *29*, 3665.
(12) Moineau, G.; Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1998**, *31*, 542.
(13) Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromlecules* **1999**, *32*, 2420.
(14) Wei, M.; Xia, J.; McDermott, N. E.; Matyjaszewski, K. *Am. Chem. Soc. Polym. Prepr.* **1997**, *38* (2), 231.
(15) Moineau, G.; Dubois, P.; Jerome, R.; Senninger, T.; Teyssie, P. *Macromolecules* **1998**, *31*, 545.
(16) Wolfe, P. S.; Nguyen, S. T. *Am. Chem. Soc. Polym. Prepr.* **1998**, *39* (2), 552.
(17) Kamigaito, M.; Sawamoto, M. *Am. Chem. Soc. Polym. Prepr.* **1999**, *40* (2), 325.
(18) Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 6877.
(19) Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1962**, 1887.
(20) Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1963**, 3921.
(21) Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1964**, 4962.
(22) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7572.
(23) Xia, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7692.
(24) Xia, J.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 5199.
(25) Zhu, S.; Wang, W.; Tu, W.; Yan, D. *Acta Polym.* **1999**, *50*, 267.
(26) Gill, N. S. *J. Chem. Soc.* **1961**, 3512.
(27) Clausen, C. A.; Good, M. L. *Inorg. Chem.* **1970**, *9*, 220.
(28) Sproul, G. D.; Stucky, G. D. *Inorg. Chem.* **1972**, *11*, 1647.
(29) Dunbar, K. R.; Quillevere, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 293.
(30) James, B. D.; Liesegang, J.; Bakalova, M.; Reiff, W. M.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1995**, *34*, 2054.
(31) Nelson, S. M. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1987; Vol. 4, p 217.

MA991652E