

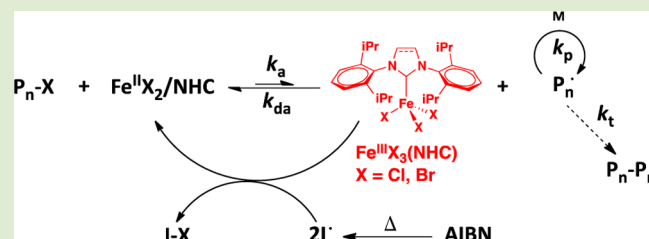
Initiators for Continuous Activator Regeneration Atom Transfer Radical Polymerization of Methyl Methacrylate and Styrene with *N*-Heterocyclic Carbene as Ligands for Fe-Based Catalysts

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Supporting Information

ABSTRACT: Iron-based *N*-heterocyclic carbene (FeX₃(NHC)) complexes were used in initiators for continuous activator regeneration atom transfer radical polymerization (ICAR ATRP). A series of ICAR ATRPs of methyl methacrylate (MMA) and styrene (St) were carried out using FeX₃(IDipp) where IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene with X = Cl (I–Cl) or Br (I–Br) and FeX₃(HIDipp) (HIDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene) with X = Cl (H–Cl) or Br (H–Br). The polymerizations showed good activity, resulting in polymers with controlled molecular weights and narrow molecular weight distribution (MWD) with low loading of catalysts (50 ppm). In particular, I–Br and H–Br generated polymers with narrower MWD. For example, ICAR ATRP of MMA with 50 ppm catalysts (H–Br) after 24 h at *T* = 60 °C in 50% v/v anisole resulted in PMMA with *M_w/M_n* = 1.20 at 65% monomer conversion. ICAR ATRP of St after 72 h resulted in PSt with *M_w/M_n* = 1.15 at 53% monomer conversion.



Iron (Fe)-based catalysts for atom transfer radical polymerization (ATRP) are attractive due to their low toxicity and biocompatibility and are less expensive than more common copper-based catalysts.¹ A variety of Fe-based catalysts have been prepared and studied for ATRP since the first reports in 1997.² Several ligands were used to enhance the catalytic activity of the Fe complexes, such as phosphines,³ multidentate amines,^{3c,4} imines,⁵ amine-bis(phenolate)s,⁶ hemins,⁷ thiocarbamates,⁸ organic acids,⁹ carbenes,¹⁰ metallocenes,¹¹ and triflates.¹² In addition, onium salts such as ammonium, phosphonium, imidazolium, and phosphazanium have been used to form complexes with Fe halides.¹³ *N*-Heterocyclic carbenes (NHCs) are among the strongest electron-donating ligands and form stable organometallic complexes. The electronic and steric properties of NHCs can be easily modified, and the ligands have lower toxicity than commercially available P- and N-based ligands. Therefore, NHCs are frequently used as ligands for organometallic complexes to improve the catalyst activity in various reactions.¹⁴ Indeed, Fe NHC complexes have been used for C–C bond formation, hydrosilylation, C–H activation, and borylation reactions.¹⁵

Iron trihalides (FeX₃) are stable in air and act as deactivators for Fe-catalyzed ATRP. Under activator (re)generation conditions, Fe^{III} can be reduced to Fe^{II} (activator) and can catalyze ATRP.^{3h,13f,g,16} For example, in *initiators for continuous activator regeneration* (ICAR) ATRP, thermally decomposable radical initiators, such as 2,2'-azobis(isobutyronitrile) (AIBN), are used to reduce Fe^{III} to Fe^{II}.^{3h,13f,g,17} ICAR ATRP with FeX₃ permits diminishing the catalyst loading condition (down to a parts per million level) while still resulting in well-defined

polymers. Chelating ligands with high electron-donating groups typically form more active catalysts, and they can be employed for ATRP with diminishing catalyst loading systems.^{3ij,5d} Fe–NHC, specifically FeX₃(NHC), complexes can generate such catalysts, due to the strong electron donicity of NHC.

A series of air-stable FeX₃(NHC) complexes were synthesized according to reported literature procedures.¹⁸ Complexes of FeX₃ (X = Cl or Br) with 1 equiv of either 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IDipp) or 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene (HIDipp) were prepared: FeCl₃(IDipp) (I–Cl), FeCl₃(HIDipp) (H–Cl), FeBr₃(IDipp) (I–Br), and FeBr₃(HIDipp) (H–Br) (Figure 1). The compounds are in a high-spin iron(III) state, which is necessary for Fe-catalyzed ATRP.^{5d,f,18,19} In addition, the synthesized

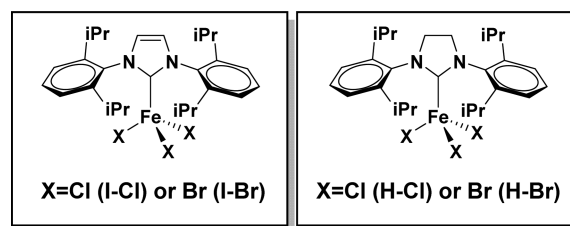


Figure 1. Structures of FeX₃(NHC) catalysts.

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catalysts are nonhygroscopic and easier to handle (FeX_3 are hygroscopic).

The four $\text{FeX}_3(\text{NHC})$ complexes were analyzed by electrochemical methods (cyclic voltammetry, CV). Catalysts with more negative half-wave potential ($E_{1/2}$) indicate that more reducing properties and faster polymerizations can be observed under normal ATRP conditions when using more reducing catalyst complexes (with more negative $E_{1/2}$).^{1b,20} The $E_{1/2}$ values for the series of $\text{FeX}_3(\text{NHC})$ s were measured, and the results showed -0.48 (I-Cl), -0.48 (H-Cl), -0.36 (I-Br), and -0.35 (H-Br) V (versus $\text{Fc}^{0/+}$). All of the CV spectra showed a single reversible redox peak ($\Delta E = 0.07$ V, Figure S1, Supporting Information). The chloride complexes, I-Cl and H-Cl, showed more negative $E_{1/2}$ values. Complexes with all of the NHC ligands showed more negative $E_{1/2}$ values than $\text{FeCl}_3/\text{Cl}^-$ or $\text{FeBr}_3/\text{Br}^-$ (-0.41 and -0.21 V vs $\text{Fc}^{0/+}$, respectively, Figure S1, Supporting Information), indicating NHCs are strongly electron donating. Dissociation of NHCs from $\text{FeX}_3(\text{NHC})$ complexes was not observed during CV measurements (single redox peak).²¹ No significant difference was observed between unsaturated and saturated $\text{FeX}_3(\text{NHC})$ complexes.

ICAR ATRP of methyl methacrylate (MMA) was carried out with 50 ppm of catalyst complexes (Table 1) to investigate

Table 1. Summary of ICAR ATRP of MMA with 50 ppm of Catalysts

entry	catalysts	conv. ^c (%)	$M_{n,\text{GPC}}^d$	$M_{n,\text{th}}$	M_w/M_n^c
1 ^a	I-Cl	65	13100	13300	1.45
2 ^a	H-Cl	65	13000	13300	1.40
3 ^a	I-Br	63	12600	12900	1.23
4 ^a	H-Br	64	12900	13000	1.20
5 ^b	I-Cl/TBACl	38	10900	7800	1.75
6 ^b	I-Br/TBABr	45	9200	9300	1.39

^a $[\text{MMA}]/[\text{EBrPA}]/[\text{Cat.}]/[\text{AIBN}] = 200/1/0.01/0.2$; $[\text{MMA}] = 4.7$ M in 50% (v/v) anisole at 60 °C for 24 h. ^b $[\text{MMA}]/[\text{EBrPA}]/[\text{Cat.}]/[\text{TBAX}]/[\text{AIBN}] = 200/1/0.01/0.02/0.2$; $[\text{MMA}] = 4.7$ M in 50% (v/v) anisole at 60 °C for 24 h. ^cConversion measured by GC. ^d M_n and M_w/M_n based on GPC with polyMMA standards in THF.

their catalytic activities. The polymerizations were conducted in 50% anisole at 60 °C with the ratio of $[\text{MMA}]/[\text{EBrPA}]/[\text{Cat.}]/[\text{AIBN}] = 200/1/0.01/0.2$ (EBrPA: ethyl 2-bromo-2-phenylacetate). Table 1 lists the results of ICAR ATRPs of MMA. Good control and high activity over the polymerization

were observed with $\text{FeX}_3(\text{NHC})$ s catalysts. Polymerization with FeX_3/X^- showed lower activity and broader MWD (Table S1, Supporting Information).

ICAR ATRP with I-Cl and H-Cl resulted in ~65% monomer conversions after 24 h, and the number-average molecular weight (M_n) of the final products matched to the theoretical value but relatively broad molecular weight distributions ($M_w/M_n = 1.45$ and 1.40, respectively), probably caused by less efficient deactivation by I-Cl and H-Cl (Table 1, entries 1 and 2). This can be especially noticed at lower conversion when molecular weights were significantly higher than theoretical values (Figure 2A). On the other hand, ICAR ATRP of MMA with Br derivatives (I-Br or H-Br) showed a similar rate of polymerization (R_p) but exhibited better polymerization control as compared to Cl derivatives (Figure 2 and Figure S2, Supporting Information). $M_{n,\text{GPC}}$ values were much closer to the theoretical values, and more uniform polymers were synthesized ($M_w/M_n = 1.23$ and 1.20, respectively; Table 1, entries 3 and 4) under the same reaction conditions (conversion = ~64%, after 24 h). The best control of MMA polymerization was attained with H-Br. FeX_3 with extra halide using tetrabutylammonium halide (TBAX, with X = Cl or Br) and triphenylphosphine (PPh_3) showed lower activity and controllability than $\text{Fe}(\text{NHC})$ s, presumably due to the strong electron donicity of the carbene ligands and higher stability of $\text{FeX}_3(\text{NHC})$ s (Table S1, Supporting Information).

All complexes exhibited the similar R_p , although Cl derivatives have more negative $E_{1/2}$ than Br ones. This is because R_p in ICAR ATRP is determined by the rate of decomposition of the azo-initiator (AIBN) and noted by the catalyst activity.²² However, the catalyst affects M_w/M_n values via rate of deactivation (defined by both rate constant of deactivation and equilibrium constant, i.e., concentration of deactivator). Slightly curved first-order kinetic plots were observed at higher monomer conversions (>50%) due to a decreased amount of the thermally decomposed AIBN (Figure 2B and Figure S2, Supporting Information).

ICAR ATRPs with I-Cl and I-Br were also carried out in the presence of additional halide anions, i.e., 2 equiv of TBAX. The presence of halide anions could affect the catalytic activity of FeX_3 for either ATRP or ATRA due to the formation of FeX_4^- .^{13e,f,21} However, no improvement was observed under ICAR ATRP with salts for either I-Cl or I-Br, due to sufficiently strong complexation of NHC with the Fe moiety. In the case of $\text{FeX}_3(\text{NHC})$ s, CV measurements (for example, I-Br) showed no additional peaks and no $E_{1/2}$ changes after

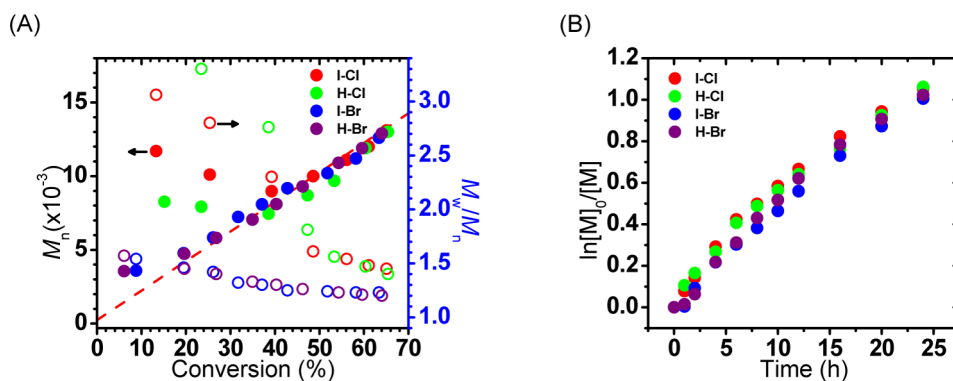


Figure 2. (A) Plot of M_n and M_w/M_n vs conversion; (B) kinetic plots of $\ln([M]_0/[M])$ vs time with iron complexes; reaction conditions: $[\text{MMA}]/[\text{EBrPA}]/[\text{Cat.}]/[\text{AIBN}] = 200/1/0.01/0.2$, $[\text{MMA}] = 4.7$ M in 50% (v/v) anisole at 60 °C for 24 h.

addition of TBAX (Figure S3, Supporting Information). ICAR ATRP of MMA with I–Br in the presence of 2 equiv of X^- showed slower polymerization, and conversion of 45% was reached after 24 h with higher M_w/M_n (1.39) (Table 1, entries 5 and 6).

ICAR ATRP of St was also carried out to determine the catalytic activity of $FeX_3(NHC)$ complexes with a less reactive monomer (Table 2). Monomer conversions reached about 53%

Table 2. Summary of ICAR ATRP of St with 50 ppm of Catalysts^a

entry	catalysts	conv. ^b (%)	$M_{n,GPC}^c$	$M_{n,th}$	M_w/M_n^b
1	I–Cl	53	9500	11300	1.24
2	H–Cl	56	9600	11800	1.29
3	I–Br	52	9000	11000	1.13
4	H–Br	53	9500	11400	1.19

^a $[St]/[EBrPA]/[Cat.]/[AIBN] = 200/1/0.01/0.2$; $[St] = 4.4$ M in 50% (v/v) anisole at 60 °C for 72 h. ^bConversion measured by GC. ^c M_n and M_w/M_n based on GPC with polySt standards in THF.

and 56% after 72 h for I–Cl and H–Cl. According to GPC analysis, molecular weights were $M_n = 9500$ and 9600 and $M_w/M_n = 1.24$ and 1.29 , respectively (Table 2, entries 1 and 2). Polymers formed with the Br derivatives (I–Br and H–Br) showed lower M_w/M_n values of 1.13 and 1.19, for I–Br and H–Br, respectively (Table 2, entries 3 and 4) and better control than FeX_3 (Table S2, Supporting Information). Complexes with unsaturated NHCs showed slightly better control than with saturated ones, in contrast to polymerization of MMA. As shown in Figure 3A, polymerization of styrene (St) using $FeX_3(NHC)$ s was successful, providing polymers characterized by a linear relationship between M_n and conversion and a narrow molecular weight distribution. Similar to MMA polymerization, no significant differences in R_p were observed (radical concentration is determined by decomposition of AIBN) (Figure 3B and Figure S4, Supporting Information). Polymerizations were slower than for MMA due to lower values of propagation rate constants.

In summary, ICAR ATRPs of MMA and St were successfully carried out at low catalysts loading (50 ppm $FeX_3(NHC)$ s). The prepared complexes showed higher activity and better control for ICAR ATRP than FeX_3 , $FeX_3/TBAX$, or FeX_3/PPh_3 , presumably due to the strong electron donicity of the carbene ligands and stability of $FeX_3(NHC)$ s. Br derivatives

exhibited better efficient activation than Cl derivatives, and the best control can be achieved by using I–Br and H–Br catalysts.

■ ASSOCIATED CONTENT

Supporting Information

Materials, synthetic procedures, instrumentation, schemes, and supporting experimental results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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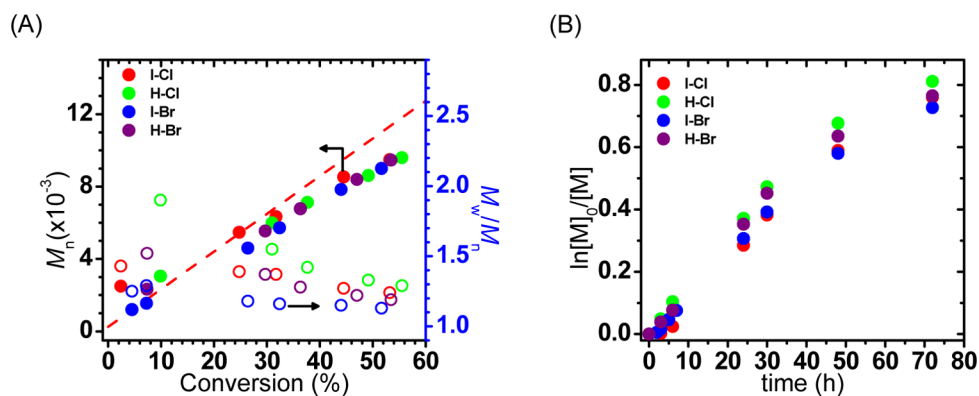


Figure 3. (A) Plot of M_n and M_w/M_n vs conversion; (B) kinetic plots of $\ln([M]_0/[M])$ vs time; reaction conditions: $[St]/[EBrPA]/[Cat.]/[AIBN] = 200/1/0.01/0.2$; $[St] = 4.4$ M in 50% (v/v) anisole at 60 °C for 72 h.

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