Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Effect of Halogen and Solvent on Iron-Catalyzed Atom Transfer Radical Polymerization

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EXPERIMENTAL

Materials

Methyl methacrylate (MMA, Sigma-Aldrich, 99%), 2,2,2-trifluoroethyl methacrylate (TFEMA, TCI, 98%), and benzyl methacrylate (BzMA, TCI, > 98%) were purified by passing through a column of basic alumina. Azobisisobutyronitrile (AIBN, Sigma-Aldrich, 98%) was recrystallized in methanol before use. Iron(III) bromide ($FeBr_3$, Alfa Aesar, 98%), iron(III) chloride ($FeCl_3$, Sigma-Aldrich, 97%), tetrabutylammonium bromide (TBABr, Sigma-Aldrich, 98%), tetrabutylammonium chloride (TBACl, Sigma-Aldrich, > 97%), ethyl α-bromophenylacetate (EBPA, Sigma-Aldrich, 97%), ethyl α-chlorophenylacetate (ECPA, Sigma-Aldrich, 97%), anisole, and acetonitrile (MeCN) were used as received.

Instrumentation

^1H nuclear magnetic resonance (^1H NMR) measurements were performed on a Bruker Avance™ III 500 MHz spectrometer. UV-vis spectra were recorded using an Agilent 8453 spectrophotometer. Electrochemical measurements were performed in a six-neck electrochemical cell, connected to an Autolab PGSTAT100N potentiostat/galvanostat, run by a PC with NOVA 2.1 software (Metrohm USA). The cell was equipped with a three-electrode system. The counter electrode was a Platinum foil, the reference electrode was a home-made Ag|AgI|0.1 M n-Bu_4NI in DMF), whereas the working electrode was a glassy carbon tip (Metrohm, 3 mm diameter). The glassy carbon electrode was cleaned before each experiment with a 0.25 mm diamond paste and rinsed by ultrasonication with ethanol. The ferrocenium/ferrocene redox couple was used as the internal standard to convert all potentials to the aqueous saturated calomel electrode (SCE).

Molecular weight and dispersity of the polymers were measured by gel permeation chromatography (GPC). The GPC instrument used a Waters 515 pump and a Waters 2414 differential refractometer using PSS columns (SDV 10^5, 10^3, and 500 Å) with tetrahydrofuran as the eluent at 35 °C and a flow rate of 1 mL min^{-1}. Linear poly(methyl methacrylate) standards were used for calibration. UV-Vis measurements were performed using an Agilent 8453 spectrophotometer. Blue (465 nm, 12 mW/cm^2) and violet (400 nm, 10 mW/cm^2) LEDs purchased from AspectLED and mounted inside a glass container. A cooling fan was placed on top to maintain reactions at room temperature.

General procedure for iron-catalyzed ICAR ATRP of MMA

To a 2-dram reaction vial, AIBN (6.17 mg, 37.6 mmol) was added, and the vial equipped with a stir bar and sealed with a rubber septum was subjected to vacuum and backfilling with nitrogen for five times. Purified monomer and anisole were degassed by sparging with nitrogen in separate containers for 30 min. Anisole (1 mL) was added to the reaction vial followed by injection of a stock solution of $FeBr_3$ and TBABr (50 µL of the stock solution at a concentration of 75.2 mM; $FeBr_3$ = 1.11, 3.76 µmol, 0.04 equiv.; TBABr = 1.21 mg, 3.76 µmol, 0.04 equiv.) under nitrogen. MMA (1 mL, 9.4 mmol, 100 equiv.) and EBPA (16.4 µL, 94 µmol, 1 equiv.) were injected into the reaction vial and the solution was further degassed with nitrogen for ~5 min. The reaction vial was placed in pre-heated oil bath at 65 °C. Samples were taken and analyzed by NMR and GPC to determine monomer conversion and molecular weight properties.

General procedure for iron-catalyzed photoinduced ATRP of MMA

A 2-dram reaction vial equipped with a stir bar and sealed with a rubber septum was subjected to vacuum and backfilling with nitrogen for five times. Purified monomer and anisole were degassed by sparging with nitrogen in separate containers for 30 min. Anisole (1 mL) was added to the reaction vial followed by injection of a stock solution of $FeBr_3$ and TBABr (50 µL of the stock solution at a concentration of 75.2 mM; $FeBr_3$ = 1.11, 3.76 µmol, 0.04 equiv.; TBABr = 1.21 mg, 3.76 µmol, 0.04 equiv.) under nitrogen. MMA (1 mL, 9.4 mmol, 100 equiv.) and EBPA (16.4 µL, 94 µmol, 1 equiv.) were injected into the reaction vial and the solution was further degassed with nitrogen for ~5 min. The reaction vial was irradiated in either blue or violet LED photoreactors with a cooling fan on top to maintain the reactions at room temperature. Samples were taken and analyzed by NMR and GPC to determine monomer conversion and molecular weight properties.

General procedure for synthesis of block copolymers by iron-catalyzed ICAR ATRP

To a 20-mL reaction vial, AIBN (30.85 mg, 188 mmol) was added, and the vial equipped with a stir bar and sealed with a rubber septum was subjected to vacuum and backfilling with nitrogen for five times. Purified monomer and anisole were degassed by sparging with nitrogen in separate containers for 30 min. Anisole (5 mL) was added to the reaction vial followed by injection of a stock solution of $FeBr_3$ and TBABr in anisole ($FeBr_3$ = 5.55, 18.8 µmol, 0.04 equiv.; TBABr = 6.05 mg, 18.8 µmol, 0.04 equiv.) under nitrogen. MMA (5 mL, 47 mmol, 100 equiv.) and EBPA

(82 μL, 94 μmol, 1 equiv.) were injected into the reaction vial and the solution was further degassed with nitrogen for ~5 min. The reaction vial was placed in pre-heated oil bath at 65 °C. The reaction was stopped after 6 h. The reaction mixture was diluted with acetone and the catalyst was separated by passing through a column of basic alumina. Excess solvent was evaporated and the PMMA-Br macroinitiator was precipitated in cold methanol. The macroinitiator was separated by filtration and dried in vacuum (M_n = 8700, $Đ$ = 1.13). The PMMA-Br macroinitiator was used in block copolymerization using BzMA monomer following similar conditions and the general procedure.

Electrochemical analysis of the iron catalysts:

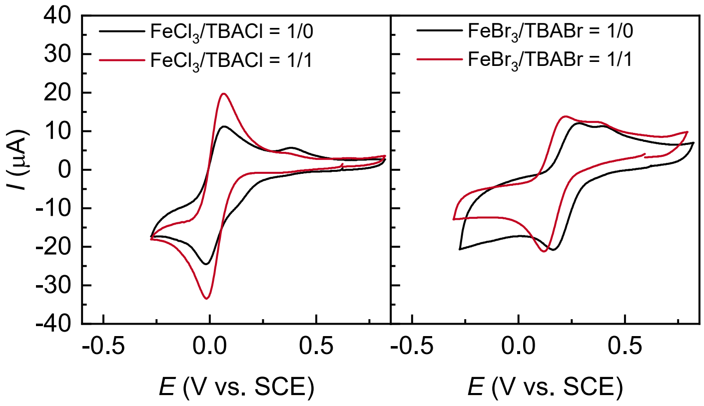


Figure S1. Cyclic voltammetry of iron species. FeX_3/TBAX 1/0 and 1/1 in MeCN at a scan rate of 100 mV s^{-1}, $[FeX_3]$ = 1 mM.

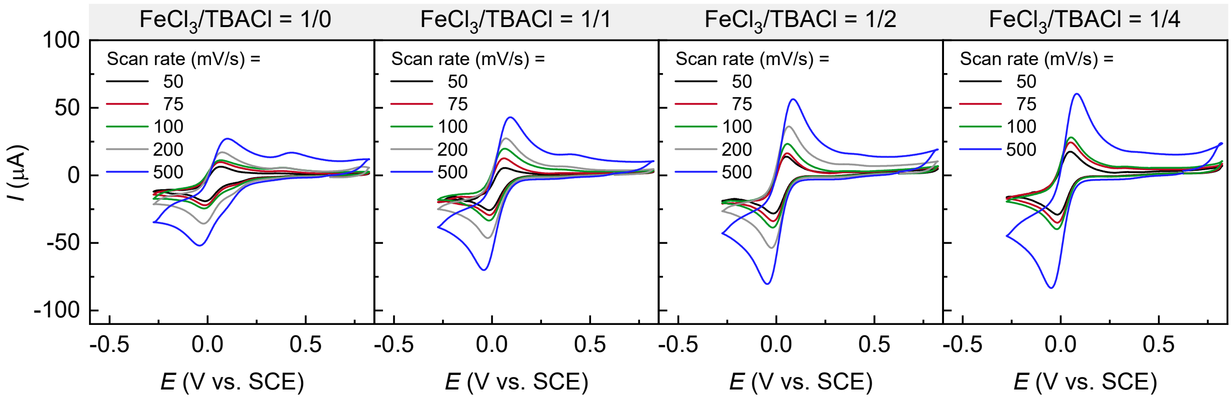


Figure S2. Cyclic voltammetry of $FeCl_3$ titrated with different ratios of TBACl as a ligand in MeCN. $[FeCl_3]$ = 1 mM with $TEABF_4$ (0.1 M) as a supporting electrolyte.

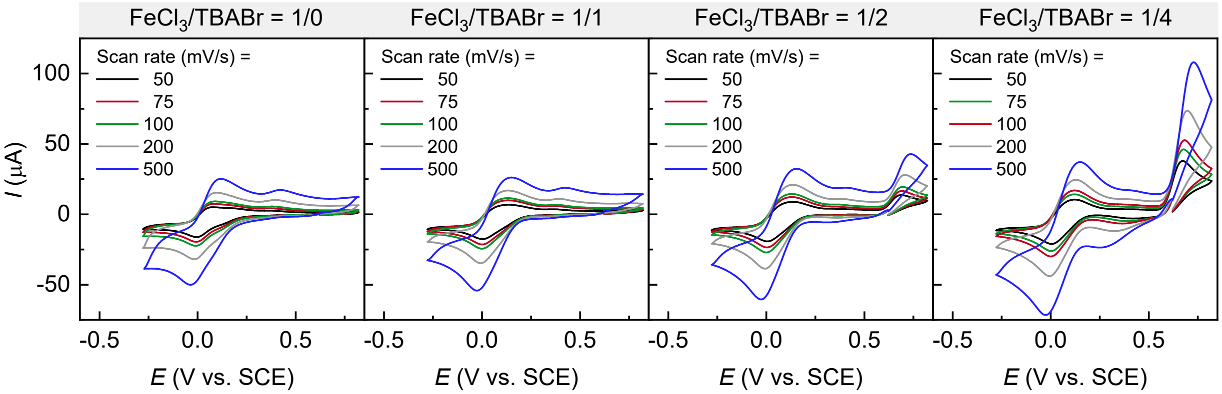


Figure S3. Cyclic voltammetry of $FeCl_3$ titrated with different ratios of TBABr as a ligand in MeCN. $[FeCl_3]$ = 1 mM with $TEABF_4$ (0.1 M) as a supporting electrolyte.

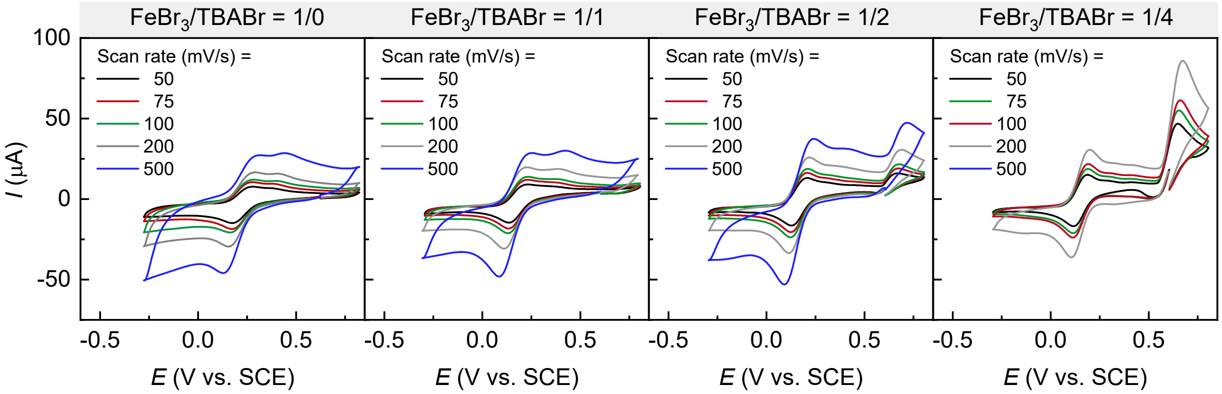


Figure S4. Cyclic voltammetry of $FeBr_3$ titrated with different ratios of TBABr as a ligand in MeCN. $[FeBr_3]$ = 1 mM with $TEABF_4$ (0.1 M) as a supporting electrolyte.

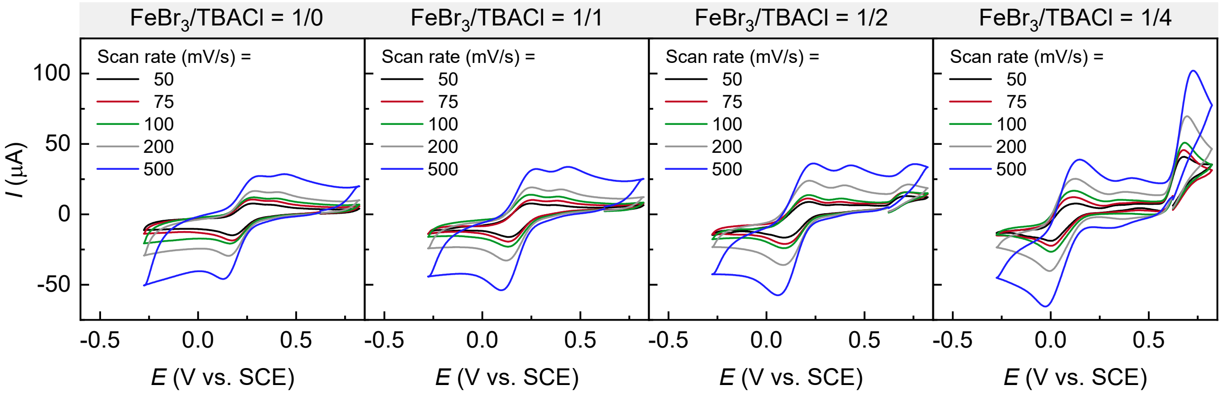
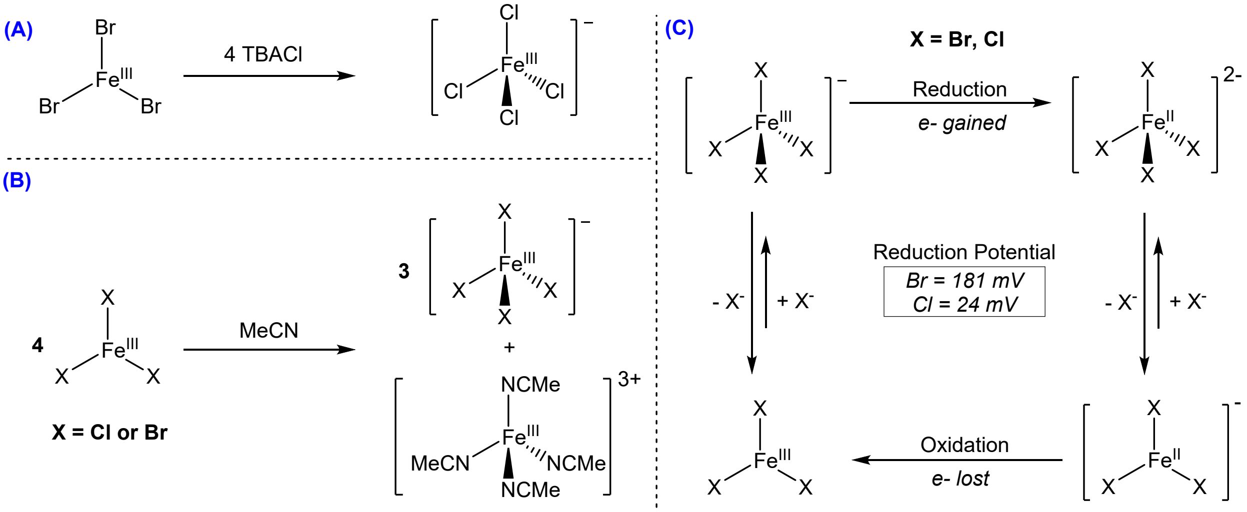


Figure S5. Cyclic voltammetry of $FeBr_3$ titrated with different ratios of TBACl as a ligand in MeCN. $[FeBr_3]$ = 1 mM with $TEABF_4$ (0.1 M) as a supporting electrolyte.



Scheme S1. (A) Formation of the anionic $FeCl_4^-$ upon addition of TBACl to $FeBr_3$, showing dispalcement of Br^- with Cl^- ligands (tetrabutylammonium counter-cations are not shown). (B) Schematic representation of the disproportionation of FeX_3 in MeCN to form the anionic FeX_4^- and the cationic $Fe(MeCN)_4^{3+}$ species. (C) Summary of the electrochemical analysis of Fe salts in MeCN (FeX_3/TBAX = 1/1).

Table S1. Half-wave reduction potential of iron species in the presence of different ratios of halide anions. [a]

FeX_3/TBAX	$E^{\Theta}_{1/2}$(mV vs. SCE)			
	$FeCl_3$/TBACl	$FeCl_3$/TBABr	$FeBr_3$/TBABr	$FeBr_3$/TBACl
1/0	29	30	200	200
1/1	24	66	181	188
1/2	20	65	166	150
1/4	16	60	151	59

[a] [FeX_3] = 1 mM, [$TEABF_4$] = 0.1 M used as a supporting electrolyte in MeCN (total volume = 15 mL).

Effect of MeCN as a solvent in iron-catalyzed ATRP of MMA:

UV-Vis results

Addition of MeCN to a solution of $FeBr_3$ in anisole resulted in a progressive change in the UV-Vis spectra of the solution showing absorption peaks at ~390 and ~470 nm that resemble formation of anionic iron species upon addition of MeCN (1-10 vol% with respect to anisole) (Figure S1).

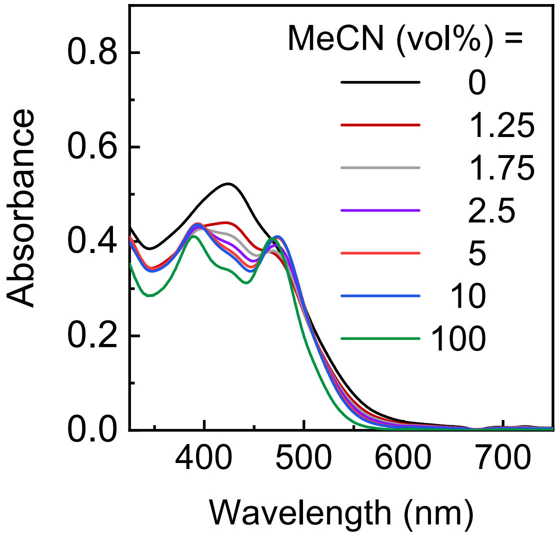


Figure S6. UV-Vis spectra of $FeBr_3$ in anisole upon increasingly addition of MeCN. The changes in the spectra are attributed to the generation of anionic iron species upon addition of MeCN. $[FeBr_3]$ = 0.1 mM. In 1.25 vol%, $[MeCN]/[FeBr_3]$ = 2400.

Iron-catalyzed ATRP of MMA showed an increase in dispersity of polymers by increasing the volume ratio of MeCN with respect to anisole as the solvent (Table S1). These results confirm the importance of the polarity of the reaction medium to obtain well-controlled polymerizations in iron-catalyzed ATRP.

Table S2. Results of iron-catalyzed ICAR ATRP of MMA with varying ratios of anisole and MeCN solvents [a]

Entry	MeCN (vol%)	Conversion (%)	$M_{n,th}$	M_n	$Đ$
1	0	96	9800	9400	1.18
2	25	97	10000	8900	1.24
3	50	93	9600	8700	1.28
4	75	95	9800	9600	1.36
5	100	92	9500	9500	1.69

[a] Reaction conditions: [MMA]/[EBPA]/[$FeBr_3$]/[TBABr]/[AIBN] = 100/1/0.04/0.04/0.4 in 50 vol% solvent (MeCN/anisole = 0-100%) at 65 °C for 18 h.

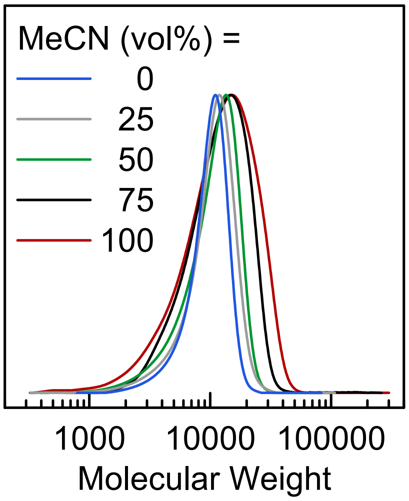


Figure S7. GPC traces of PMMA synthesizedd in iron-catalyzed ATRP with varying ratios of MeCN and anisole as the solvent. Increasing the volume ratio of MeCN resulted in broadening the molecular weight distribution of the polymers. Reaction conditions: [MMA]/[EBPA]/[$FeBr_3$]/[TBABr]/[AIBN] = 100/1/0.04/0.04/0.4 in 50 vol% solvent (MeCN/anisole = 0-100%) at 65 °C for 18 h.

Iron-catalyzed ATRP of 2,2,2-trifluoroethyl methacrylate (TFEMA) in MeCN:

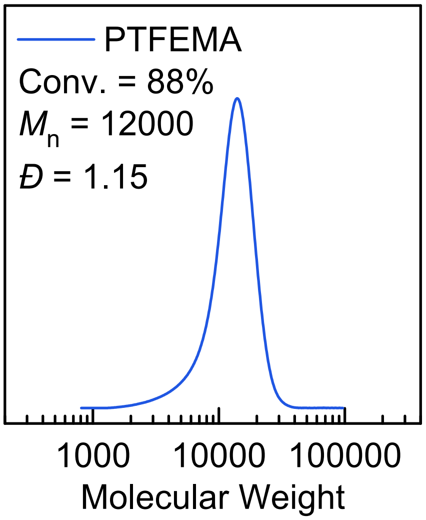


Figure S8. GPC traces of PTFEMA synthesized in iron-catalyzed ATRP in MeCN showing well-controlled properties achieved in a relatively low polar medium containing MeCN solvent impaprted by the hydrophobic nature the semi-fluorinated monomer. Reaction conditions: [TFEMA]/[EBPA]/[$FeBr_3$]/[TBABr]/[AIBN] = 100/1/0.04/0.04/0.4 in MeCN (50 vol%) at 65 °C.

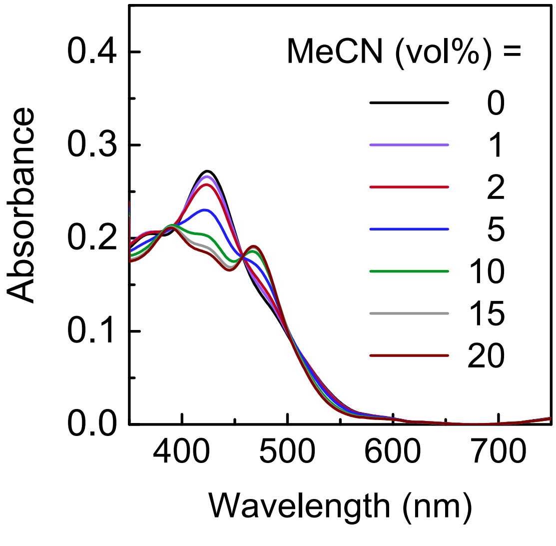


Figure S9. UV-Vis spectra of $FeBr_3$ in TFEMA upon increasingly addition of MeCN. The changes in the spectra are attributed to the generation of the anionic iron species upon addition of MeCN.

Kinetics of iron-catalyzed ATRP of MMA with Br vs. Cl:

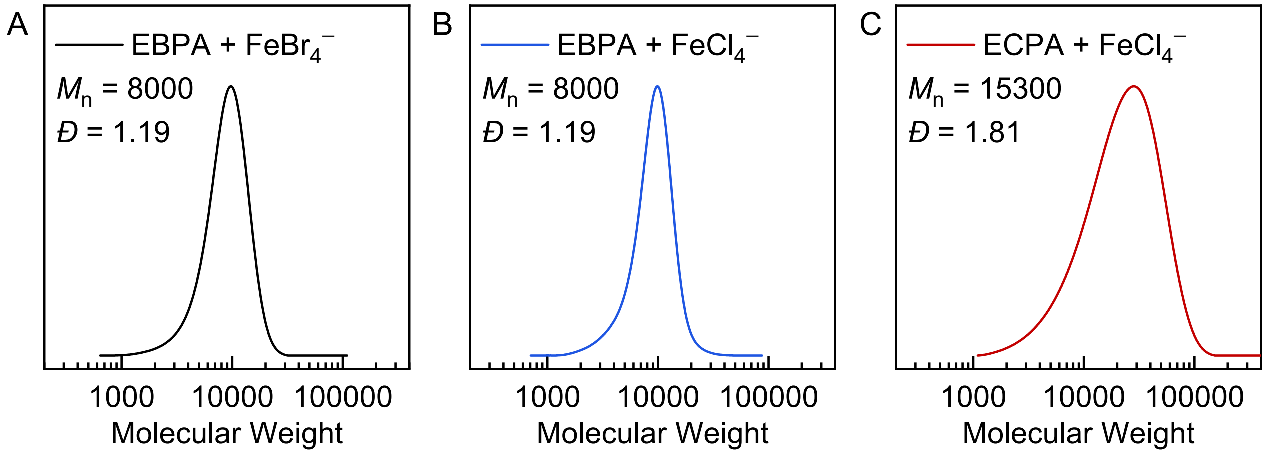


Figure S10. GPC traces of PMMA obtained in iron-catalyzed ATRP with Br or Cl-based initiating systems. Reaction conditions: [MMA]/[EXPA]/[FeX$_3$]/[TBAX]/[AIBN] = 100/1/0.04/0.04/0.4 (X = Br or Cl) in anisole (50 vol%) at 65 °C (full polymerization data are presented in Figure 3, main text).

Effect of the catalyst concentration:

Iron-catalyzed ATRP of MMA using different concentrations of $FeBr_3$/TBABr in anisole showed polymers with well-controlled molecular weights. Increasing the concentration of the catalyst from 100 to 200 and 400 ppm led to a decrease in the dispersity of the resulting polymers.

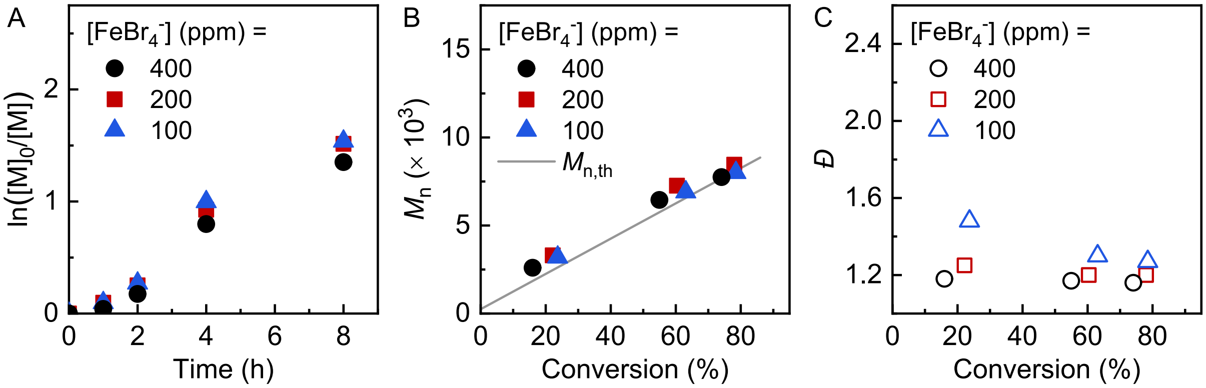


Figure S11. Results of polymerization of MMA using different concentration of the iron catalyst. (A) Kinetics of the polymerization, (B) molecular weight and (C) dispersity of the resulting polymers as a function of monomer conversion. Reaction conditions: [MMA]/[EBPA]/[$FeBr_3$]/[TBABr]/[AIBN] = 100/1/x/x/0.4 (x = 0.01, 0.02, or 0.04 equiv. corresponding to 100, 200, or 400 ppm with respect to monomer, respectively) in anisole (50 vol%) at 65 °C.

Kinetics of the ICAR ATRP of MMA in MeCN:

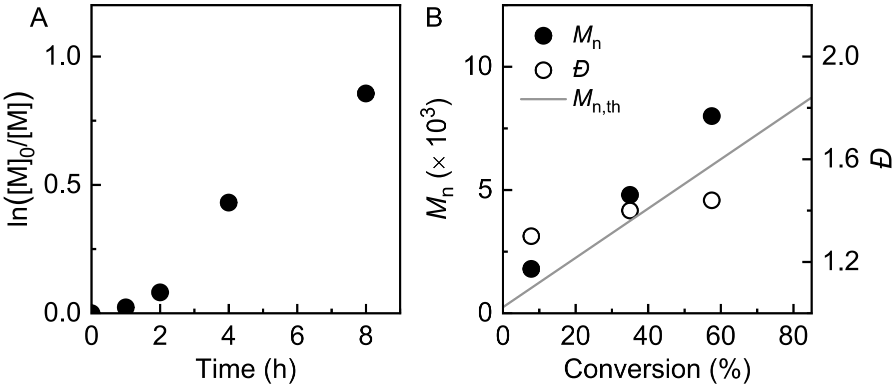


Figure S12. Kinetics of iron-catalyzed ICAR-ATRP of MMA in MeCN. Reaction conditions: [MMA]/[EBPA]/[$FeBr_3$]/[TBABr]/[AIBN] = 100/1/0.04/0.04/0.4 in MeCN (50 vol%) at 65 °C.