ACS Macro Letters
Letter
Cite This: ACS Macro Lett. 2019, 8, 1110−1114
pubs.acs.org/macroletters

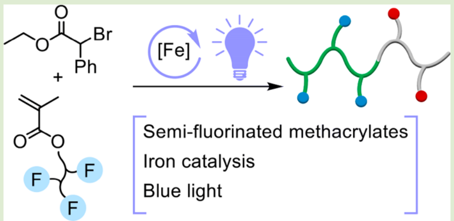
Iron-Catalyzed Atom Transfer Radical Polymerization of Semifluorinated Methacrylates

Sajjad Dadashi-Silab and Krzysztof Matyjaszewski*

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, United States

Supporting Information

ABSTRACT: Fluorinated polymers are an important class of functional materials that exhibit unique properties such as high chemical resistance, thermal stability, and low surface energy. Atom transfer radical polymerization (ATRP) of semifluorinated monomers catalyzed by copper catalysts often requires development of special conditions to control the polymerization and prevent side reactions such as base-catalyzed transesterification between the fluoro-containing monomers and solvents. In this paper, photoinduced iron-catalyzed ATRP was applied to the polymerization of a variety of semifluorinated methacrylate monomers. Polymerizations were initiated by photochemical generation of the Fe catalyst activator under blue light irradiation, enabling temporal control over the growth of polymer chains, and were well-controlled in various solvents, including fluorinated and nonfluorinated solvents, without undergoing any side reactions. Moreover, in situ chain extension and block copolymerization experiments demonstrated the preservation of chain end functionality, enabling facile synthesis of well-controlled block copolymers.



Fluorinated polymers possess distinct chemical and physical properties compared to their hydrogenated analogues.[1,2] These materials are highly hydrophobic in nature and exhibit excellent chemical and thermal stability and low refractive indices. In particular, the low surface energy of fluorinated materials, imparted by the unique properties of the C−F bond, makes these polymers suitable for a wide range of applications including fabrication of low friction, low adhesion, and low energy surfaces and many other areas.[3−5]

Use of reversible deactivation radical polymerization (RDRP) techniques gives access to the synthesis of well-defined, fluorine-containing functional polymeric materials.[6−11] However, atom transfer radical polymerization (ATRP)[12,13] of semifluorinated monomers has often been challenging and has required development of special reaction conditions to control the polymerization. For example, previous studies have reported that semifluorinated ligands[14] or solvents were required to both solubilize the catalytic systems and control the polymerization. Furthermore, a transesterification reaction between the fluorinated monomers and solvents may be promoted in the presence of nitrogen-containing ligands that can also act as a base to catalyze this reaction. Consequently, in the presence of monomers and protic solvents bearing different fluorinated alkyl chains, the transesterification reaction resulted in inhomogeneity along the polymer chains and therefore loss of control over molecular weight.

Conducting polymerizations under acidic conditions was reported to suppress the base-catalyzed transesterification reaction of fluorinated monomers and solvents by the ligand.[15] Moreover, in a recent study, a tertiary fluorinated alcohol was shown to act as a suitable solvent, which in contrast to primary or secondary fluorinated alcohols did not undergo a transesterification reaction with the monomer.[16] Therefore, photoinduced ATRP of semifluorinated monomers was controlled by generation of the activator Cu catalyst under UV light irradiation. However, developing new polymerization platforms that do not require special solvents or reaction conditions and are also operational under mild, environmentally friendly conditions would be advantageous in many aspects.

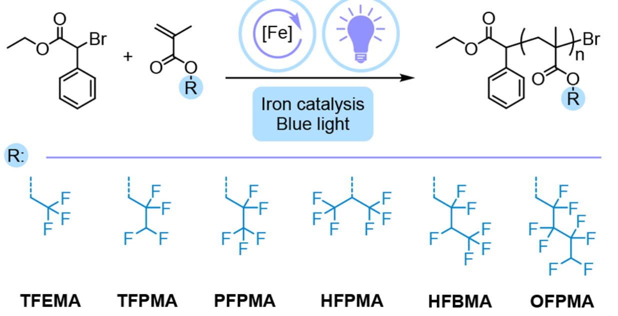
In this study, we sought to address this challenge by developing Fe-catalyzed ATRP and also expand its utility to include polymerization of functional monomers including semifluorinated methacrylates. Fe-based complexes are a robust and efficient class of ATRP catalysis for polymerization of various monomers with high efficiency.[17−31] Notably, Fe is an abundant metal, has low toxicity, and has important biological and chemical functions that make it suitable for mediating various chemical transformations.[32] In Fe-catalyzed ATRP, control over the growth of polymer chains is established via a redox process between Fe^{II} and $X{-}Fe^{III}$ (X: Br or Cl) complexes that act as activator and deactivator species, respectively.[33,34] Furthermore, the interaction of the propagating radicals with Fe^{II} complexes may contribute to impart control over polymerization through an organometallic-mediated radical polymerization pathway.[35] Recent studies have shown that Fe-catalyzed ATRP can be initiated and controlled by external stimuli including visible light and performed in simple catalytic platforms even without the need for use of special ligands or other reagents.[36−40]

Received: July 27, 2019
Accepted: August 14, 2019
Published: August 16, 2019

DOI: 10.1021/acsmacrolett.9b00579
ACS Macro Lett. 2019, 8, 1110−1114

In this paper, Fe-catalyzed ATRP was applied to the polymerization of semifluorinated methacrylate monomers. Importantly, this Fe-based catalytic system was mediated under blue light irradiation and resulted in controlling the polymerization of different semifluorinated monomers in the presence of fluorinated or nonfluorinated solvents (Scheme 1).

Scheme 1. Polymerization of Semifluorinated Methacrylate Monomers by Photoinduced Fe-Catalyzed ATRP



The efficiency of Fe-catalyzed ATRP was initially demonstrated by the polymerization of 2,2,2-trifluoroethyl methacrylate (TFEMA) in a variety of solvents that resulted in well-controlled polymerizations (Table 1). The polymerizations were conducted using iron(III) bromide ($FeBr_3$) catalyst in the presence of tetrabutylammonium bromide (TBABr),[41,42] and ethyl α-bromophenylacetate (EBPA) as the initiator and irradiated under blue light (465 nm) for 24 h. The generation of $FeBr_2$ activator catalyst was triggered under blue light. The Fe catalyst was only partially soluble in polymerizations run in toluene as a solvent, and that resulted in poor control over the polymerization of TFEMA (entry 1, Table 1).

Table 1. Results of Fe-Catalyzed ATRP of TFEMA in Different Solvents[a]

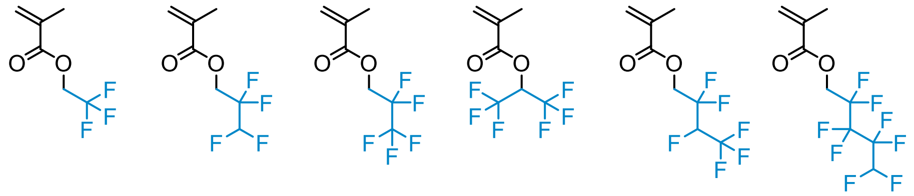
entry	solvent	conv. (%)	$M_{n,th}$	M_n	$Đ$
1	toluene	91	7900	6500	2.31
2	DMF	94	8200	11100	1.78
3	anisole	94	8200	8600	1.17
4	MeCN	92	8000	8300	1.21
5	TFE[b]	90	7800	7900	1.16

[a]Reactions conditions: $[TFEMA]/[EBPA]/[FeBr_3]/[TBABr] = 50/1/0.04/0.08$ in 50 vol % solvent, irradiated under blue light (465 nm, 12 mW/cm^2) for 24 h. [b]10 vol % anisole was used to dissolve the catalyst (TFE/anisole = 9/1).

In the presence of *N*,*N*-dimethylformamide (DMF), the polymerization reached high monomer conversion but showed a relatively high dispersity ($Đ$) of 1.78 (entry 2, Table 1). However, use of anisole, acetonitrile (MeCN), or 2,2,2-trifluoroethanol (TFE) as solvent resulted in well-controlled polymerizations reaching high monomer conversions (>90%), providing low $Đ$ and molecular weights that were in agreement with theoretical values (entries 3−5, Table 1).

Synthesis of polymers targeting different degrees of polymerization (DP) was also performed. As shown in Table S1 and Figure S2, polymerization of TFEMA can be controlled while targeting DPs in the 25−400 range, reaching high monomer conversion under blue light irradiation. At higher DPs (200 and 400), molecular weights appeared to be lower than theoretical values, which might be a result of the formation of new initiating chains due to photoreduction of the $FeBr_3$ species.[38,40]

Fe-catalyzed ATRP was successful in controlling the polymerization of various semifluorinated methacrylates. Monomers containing 3−8 fluorine atoms include TFEMA, tetrafluoropropyl methacrylate (TFPMA), pentafluoropropyl methacrylate (PFPMA), hexafluoroisopropyl methacrylate (HFPMA), hexafluorobutyl methacrylate (HFBMA), and octafluoropentyl methacrylate (OFPMA). The monomers were successfully polymerized by photoinduced Fe-catalyzed ATRP reaching high monomer conversions (>90%) and displaying molecular weights close to theoretical values with low $Đ$ (Figure 1). Size exclusion chromatography (SEC) traces of these polymers presented in Figure S3 show a narrow, monomodal distribution of molecular weights. SEC measurements were performed using THF or DMF as an eluent. Polymers containing 4 or less fluorine atoms per monomer unit showed a positive peak in THF, while polymers with more than 4 fluorine atoms per repeat unit showed negative signals in the SEC measurements in THF or DMF, due to their lower refractive index than the eluent ($n_{THF} = 1.404$, $n_{DMF} = 1.427$). Interestingly, analysis of PHFBMA and POFPMA in DMF SEC gave molecular weights in agreement with the theoretical



Monomer	TFEMA	TFPMA	PFPMA	HFPMA	HFBMA	OFPMA
Conv. (%)	90	91	92	70	95	94
$M_{n,th}$	7800	9400	10200	8500	11900	14100
M_n	7900	10000	9900	7700	11400	12800
$Đ$	1.16	1.17	1.19	1.22	1.16	1.17

Figure 1. Results of Fe-catalyzed ATRP of methacrylate monomers containing different fluoroalkyl groups. Reaction conditions: $[M]/[EBPA]/[FeBr_3]/[TBABr] = 50/1/0.04/0.08$ in 50 vol % solvent (TFE/anisole = 9/1), irradiated under blue LEDs for 24 h.

DOI: 10.1021/acsmacrolett.9b00579
ACS Macro Lett. 2019, 8, 1110−1114

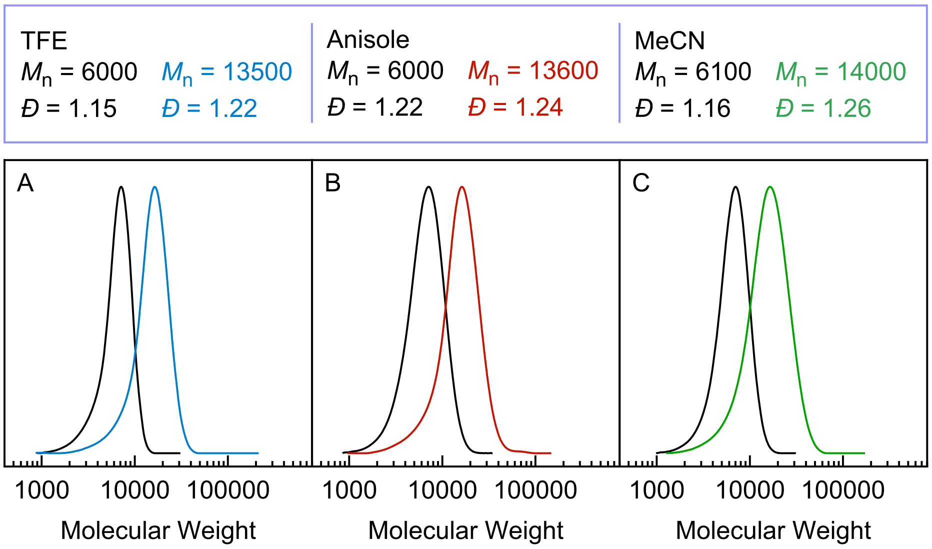


Figure 2. SEC traces of in situ chain extension of PTFEMA in different solvents showing high chain end functionality in Fe-catalyzed photoinduced ATRP. Reaction conditions for the first block: [TFEMA]/[EBPA]/[$FeBr_3$]/[TBABr] = 33/1/0.04/0.08, in 50 vol % solvent irradiated under blue light (465 nm, 12 mW/cm^2) for 24 h. A degassed solution of TFEMA in respective solvents was added, and reactions were allowed to run for 24 h under blue light.

values, whereas the THF SEC gave molecular weights lower than expected values for these samples. Moreover, polymerization of these monomers was successfully conducted and controlled in different solvents (Table S2).

Chain extension experiments performed upon sequential addition of the monomer demonstrated high chain end functionality obtained in the polymerizations conducted in different solvents. Polymerization of TFEMA was initially performed in the presence of TFE, anisole, or MeCN as solvents. Upon completion of the polymerizations, a second batch of TFEMA monomer in respective solvents was added, and the reactions were allowed to continue polymerization under blue light irradiation. SEC results showed a shift toward higher molecular weights, indicating a successful chain extension that resulted in well-defined polymer chains with low $Đ$ and monomodal molecular weight distributions in all solvents (Figure 2).

Furthermore, in situ block copolymerization experiments were successfully performed upon sequential addition of monomers to synthesize well-defined block copolymers. For example, TFEMA was polymerized to high monomer conversion in TFE solvent (>90%, M_n = 8200, $Đ$ = 1.18), and subsequently a degassed solution of TFPMA in TFE was injected into the reaction. Irradiation of the solution resulted in increasing the molecular weight of the polymer to 22 000 with a $Đ$ of 1.33 (Figure 3A). Similarly, block copolymerization with butyl methacrylate (BMA) resulted in a well-controlled block copolymer (M_n = 19 000, $Đ$ = 1.34) containing fluorinated and nonfluorinated segments (Figure 3B). SEC results showed a shift to higher molecular weights while retaining narrow, monomodal molecular weight distributions as presented in Figure 3.

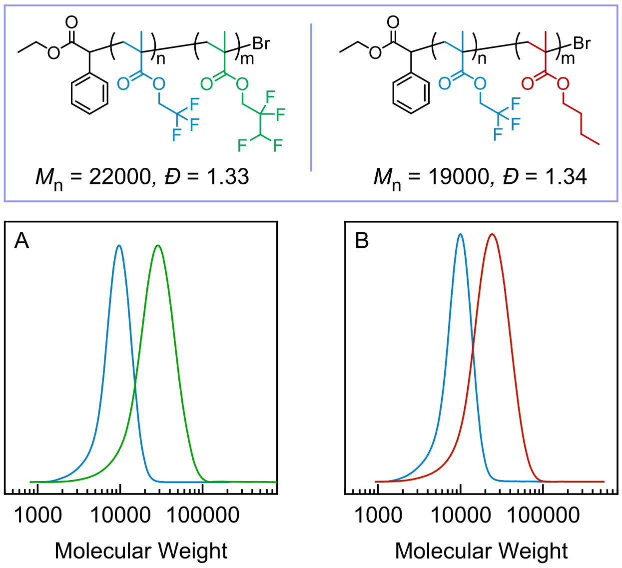


Figure 3. Block copolymers synthesized by in situ chain extension upon sequential addition of monomers in Fe-catalyzed ATRP.

Temporal control was successfully demonstrated in Fe-catalyzed ATRP of TFEMA by switching the light on/off. Irradiation of the reaction under blue light started the polymerization by generation of the Fe^{II} activator. Removal of the light significantly decreased the rate of the polymerization with only minimal monomer conversion observed in the dark periods. Therefore, the polymerization was successfully switched multiple times between on and off states upon applying or removal of the light (Figure 4). Importantly, control over the polymerization was maintained throughout temporal control with molecular weights in agreement with theoretical values and polymers showing low $Đ < 1.2$. Moreover, keeping the polymerization in the dark for longer times showed minimal chain growth only in the early stages, and the polymerization stopped afterward (Figure S5). Re-exposing the reaction to light restarted the polymerization as a result of the photochemical generation of Fe^{II} activator catalyst. These observations suggest that the Fe^{II} activator was present in very low concentrations and was quickly consumed as a result of radical termination, and consequently polymerizations stopped in the dark.[43] Accordingly, decreasing the concentration of the catalyst from 4 to 2 mol % (with respect to initiator) resulted in perfect temporal control with

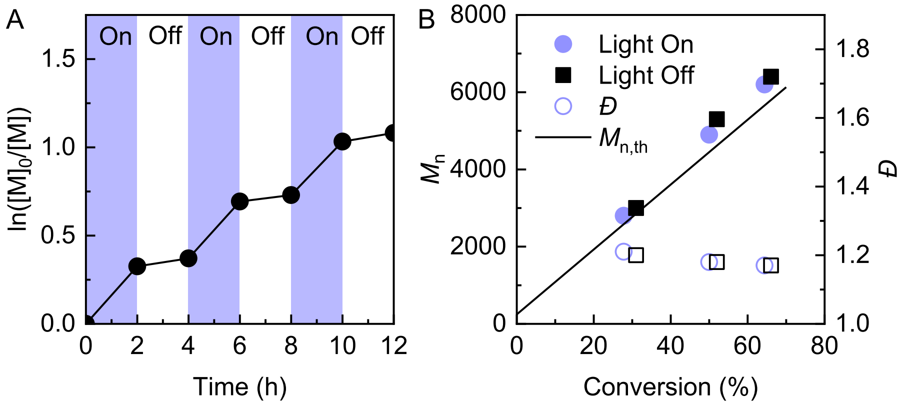


Figure 4. Temporal control in photoinduced Fe-catalyzed ATRP of TFEMA. (A) Kinetics of temporal control and (B) number-average molecular weight (M_n, solid points) and dispersity ($Đ$, open points) as a function of monomer conversion. Reaction conditions: [TFEMA]/[EBPA]/[$FeBr_3$]/[TBABr] = 50/1/0.04/0.08 in 50 vol % solvent (TFE/anisole = 9/1).

no monomer conversion in the off periods (Figures S4 and S5). These results verify a well-controlled polymerization catalyzed by Fe that can be photochemically controlled to mediate the growth of polymer chains in a temporal manner.

The versatility of the Fe-based catalytic system allowed for use of different solvents from fluorinated to nonfluorinated solvents for the polymerization of semifluorinated monomers. Importantly, no side reactions were observed when using a semifluorinated monomer in the presence of a fluorinated solvent, each bearing different fluoroalkyl groups. In Cu-catalyzed ATRP systems, amine-based ligands may induce a base-catalyzed transesterification reaction between the fluorinated monomer and solvent. Therefore, special reaction conditions or special solvents were required to control the polymerization and prevent such side reactions.[16] However, under Fe-catalyzed ATRP conditions, polymerizations were well-controlled in a variety of fluorinated and traditional solvents without undergoing any side reactions. A control experiment using PFPMA monomer and TFE solvent was performed to further demonstrate the lack of side reactions between the monomer and solvent in the presence of $FeBr_3$/TBABr. NMR analysis of the solution showed no change in the respective shifts of the reagents after 24 h, indicating that no transesterification reaction was promoted between the fluorinated monomer and solvent under Fe-catalyzed ATRP conditions, as presented in Figure S6. Therefore, different semifluorinated monomers were successfully polymerized using TFE or other solvents.

In summary, ATRP of semifluorinated methacrylate monomers was successfully initiated and controlled by Fe catalysis under visible-light irradiation. The versatility of the Fe catalyst allowed the polymerizations to be carried out in a variety of solvents without any side reactions. In situ chain extension and block copolymerization experiments proved the preservation of chain end functionality, allowing the synthesis of well-defined block copolymers.

Fe is a ubiquitous and environmentally friendly catalyst that can be photochemically activated under visible-light irradiation and provides a green catalytic approach for catalyzing ATRP processes. Future studies will focus on developing new Fe-based catalysts and study their catalytic efficiency in the polymerization of various functional monomers and the architecture of polymeric materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.9b00579.

Experimental procedure, detailed polymerization results, and SEC traces (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: km3b@andrew.cmu.edu (K.M.).

ORCID

Sajjad Dadashi-Silab: 0000-0002-4285-5846
Krzysztof Matyjaszewski: 0000-0003-1960-3402

Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Support from the NSF (CHE 1707490) is gratefully acknowledged. NMR instrumentation at Carnegie Mellon University was partially supported by the NSF (CHE-0130903, CHE-1039870, and CHE-1726525).

■ REFERENCES

(1) Yao, W.; Li, Y.; Huang, X. Fluorinated poly(meth)acrylate: Synthesis and properties. *Polymer* **2014**, *55*, 6197.

(2) Vitale, A.; Bongiovanni, R.; Ameduri, B. Fluorinated Oligomers and Polymers in Photopolymerization. *Chem. Rev.* **2015**, *115*, 8835.

(3) Babudri, F.; Farinola, G. M.; Naso, F.; Ragni, R. Fluorinated organic materials for electronic and optoelectronic applications: the role of the fluorine atom. *Chem. Commun.* **2007**, 1003.

(4) Ameduri, B. Fluoropolymers: The Right Material for the Right Applications. *Chem. - Eur. J.* **2018**, *24*, 18830.

(5) Cuthbert, J.; Martinez, M. R.; Sun, M.; Flum, J.; Li, L.; Olszewski, M.; Wang, Z.; Kowalewski, T.; Matyjaszewski, K. Non-Tacky Fluorinated and Elastomeric STEM Networks. *Macromol. Rapid Commun.* **2019**, *40*, 1800876.

(6) Hirao, A.; Sugiyama, K.; Yokoyama, H. Precise synthesis and surface structures of architectural per- and semifluorinated polymers with well-defined structures. *Prog. Polym. Sci.* **2007**, *32*, 1393.

(7) Bruno, A. Controlled Radical (Co)polymerization of Fluoromonomers. *Macromolecules* **2010**, *43*, 10163.
(8) Yang, Q.; Guerre, M.; Ladmiral, V.; Ameduri, B. Thermal and photo-RAFT polymerization of 2,2,2-trifluoroethyl α-fluoroacrylate. *Polym. Chem.* **2018**, *9*, 3388.
(9) Gong, H.; Zhao, Y.; Shen, X.; Lin, J.; Chen, M. Organocatalyzed Photocontrolled Radical Polymerization of Semifluorinated (Meth)-acrylates Driven by Visible Light. *Angew. Chem., Int. Ed.* **2018**, *57*, 333.
(10) Anastasaki, A.; Oschmann, B.; Willenbacher, J.; Melker, A.; Van Son, M. H. C.; Truong, N. P.; Schulze, M. W.; Discekici, E. H.; McGrath, A. J.; Davis, T. P.; Bates, C. M.; Hawker, C. J. One-Pot Synthesis of ABCDE Multiblock Copolymers with Hydrophobic, Hydrophilic, and Semi-Fluorinated Segments. *Angew. Chem., Int. Ed.* **2017**, *56*, 14483.
(11) Whitfield, R.; Parkatzidis, K.; Rolland, M.; Truong, N. P.; Anastasaki, A. Tuning Dispersity by Photoinduced Atom Transfer Radical Polymerisation: Monomodal Distributions with ppm Copper Concentration. *Angew. Chem., Int. Ed.* **2019**, DOI: 10.1002/anie.201906471.
(12) Wang, J.-S.; Matyjaszewski, K. Controlled/"living" radical polymerization. atom transfer radical polymerization in the presence of transition-metal complexes. *J. Am. Chem. Soc.* **1995**, *117*, 5614.
(13) Matyjaszewski, K.; Xia, J. Atom Transfer Radical Polymerization. *Chem. Rev.* **2001**, *101*, 2921.
(14) Xia, J.; Johnson, T.; Gaynor, S. G.; Matyjaszewski, K.; DeSimone, J. Atom Transfer Radical Polymerization in Supercritical Carbon Dioxide. *Macromolecules* **1999**, *32*, 4802.
(15) Samanta, S. R.; Cai, R.; Percec, V. SET-LRP of semifluorinated acrylates and methacrylates. *Polym. Chem.* **2014**, *5*, 5479.
(16) Discekici, E. H.; Anastasaki, A.; Kaminker, R.; Willenbacher, J.; Truong, N. P.; Fleischmann, C.; Oschmann, B.; Lunn, D. J.; Read de Alaniz, J.; Davis, T. P.; Bates, C. M.; Hawker, C. J. Light-Mediated Atom Transfer Radical Polymerization of Semi-Fluorinated (Meth)-acrylates: Facile Access to Functional Materials. *J. Am. Chem. Soc.* **2017**, *139*, 5939.
(17) Poli, R.; Allan, L. E. N.; Shaver, M. P. Iron-mediated reversible deactivation controlled radical polymerization. *Prog. Polym. Sci.* **2014**, *39*, 1827.
(18) Xue, Z.; He, D.; Xie, X. Iron-catalyzed atom transfer radical polymerization. *Polym. Chem.* **2015**, *6*, 1660.
(19) Matyjaszewski, K.; Wei, M.; Xia, J.; McDermott, N. E. Controlled/"Living" Radical Polymerization of Styrene and Methyl Methacrylate Catalyzed by Iron Complexes. *Macromolecules* **1997**, *30*, 8161.
(20) Ando, T.; Kamigaito, M.; Sawamoto, M. Iron(II) Chloride Complex for Living Radical Polymerization of Methyl Methacrylate. *Macromolecules* **1997**, *30*, 4507.
(21) Xue, Z.; Linh, N. T. B.; Noh, S. K.; Lyoo, W. S. Phosphorus-Containing Ligands for Iron(III)-Catalyzed Atom Transfer Radical Polymerization. *Angew. Chem., Int. Ed.* **2008**, *47*, 6426.
(22) Wang, Y.; Zhang, Y.; Parker, B.; Matyjaszewski, K. ATRP of MMA with ppm Levels of Iron Catalyst. *Macromolecules* **2011**, *44*, 4022.
(23) Simakova, A.; Mackenzie, M.; Averick, S. E.; Park, S.; Matyjaszewski, K. Bioinspired Iron-Based Catalyst for Atom Transfer Radical Polymerization. *Angew. Chem., Int. Ed.* **2013**, *52*, 12148.
(24) Nishizawa, K.; Ouchi, M.; Sawamoto, M. Phosphine−Ligand Decoration toward Active and Robust Iron Catalysts in LRP. *Macromolecules* **2013**, *46*, 3342.
(25) Allan, L. E. N.; MacDonald, J. P.; Nichol, G. S.; Shaver, M. P. Single Component Iron Catalysts for Atom Transfer and Organometallic Mediated Radical Polymerizations: Mechanistic Studies and Reaction Scope. *Macromolecules* **2014**, *47*, 1249.
(26) Poli, R.; Shaver, M. P. ATRP/OMRP/CCT Interplay in Styrene Polymerization Mediated by Iron(II) Complexes: A DFT Study of the α-Diimine System. *Chem. - Eur. J.* **2014**, *20*, 17530.
(27) Schroeder, H.; Matyjaszewski, K.; Buback, M. Kinetics of Fe-Mediated ATRP with Triarylphosphines. *Macromolecules* **2015**, *48*, 4431.
(28) Poli, R.; Shaver, M. P. Atom Transfer Radical Polymerization (ATRP) and Organometallic Mediated Radical Polymerization (OMRP) of Styrene Mediated by Diaminobis(phenolato)iron(II) Complexes: A DFT Study. *Inorg. Chem.* **2014**, *53*, 7580.
(29) Telitel, S.; Dumur, F.; Campolo, D.; Poly, J.; Gigmes, D.; Pierre Fouassier, J.; Lalevée, J. Iron complexes as potential photocatalysts for controlled radical photopolymerizations: A tool for modifications and patterning of surfaces. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, *54*, 702.
(30) Schroeder, H.; Buback, M.; Shaver, M. P. Kinetics of Amine−Bis(phenolate) Iron-Mediated ATRP Up to High Pressure. *Macromolecules* **2015**, *48*, 6114.
(31) Fu, L.; Simakova, A.; Fantin, M.; Wang, Y.; Matyjaszewski, K. Direct ATRP of Methacrylic Acid with Iron-Porphyrin Based Catalysts. *ACS Macro Lett.* **2018**, *7*, 26.
(32) Bauer, I.; Knölker, H.-J. Iron Catalysis in Organic Synthesis. *Chem. Rev.* **2015**, *115*, 3170.
(33) Matyjaszewski, K. Atom Transfer Radical Polymerization (ATRP): Current Status and Future Perspectives. *Macromolecules* **2012**, *45*, 4015.
(34) di Lena, F.; Matyjaszewski, K. Transition metal catalysts for controlled radical polymerization. *Prog. Polym. Sci.* **2010**, *35*, 959.
(35) Coward, D. L.; Lake, B. R. M.; Shaver, M. P. Understanding Organometallic-Mediated Radical Polymerization with an Iron(II) Amine−Bis(phenolate). *Organometallics* **2017**, *36*, 3322.
(36) Wang, Y.; Matyjaszewski, K. ATRP of MMA in Polar Solvents Catalyzed by FeBr2 without Additional Ligand. *Macromolecules* **2010**, *43*, 4003.
(37) Khan, M. Y.; Chen, X.; Lee, S. W.; Noh, S. K. Development of New Atom Transfer Radical Polymerization System by Iron (III)-Metal Salts Without Using any External Initiator and Reducing Agent. *Macromol. Rapid Commun.* **2013**, *34*, 1225.
(38) Pan, X.; Malhotra, N.; Zhang, J.; Matyjaszewski, K. Photoinduced Fe-Based Atom Transfer Radical Polymerization in the Absence of Additional Ligands, Reducing Agents, and Radical Initiators. *Macromolecules* **2015**, *48*, 6948.
(39) Pan, X.; Malhotra, N.; Dadashi-Silab, S.; Matyjaszewski, K. A Simplified Fe-Based PhotoATRP Using Only Monomers and Solvent. *Macromol. Rapid Commun.* **2017**, *38*, 1600651.
(40) Dadashi-Silab, S.; Pan, X.; Matyjaszewski, K. Photoinduced Iron-Catalyzed Atom Transfer Radical Polymerization with ppm Levels of Iron Catalyst under Blue Light Irradiation. *Macromolecules* **2017**, *50*, 7967.
(41) Teodorescu, M.; Gaynor, S. G.; Matyjaszewski, K. Halide Anions as Ligands in Iron-Mediated Atom Transfer Radical Polymerization. *Macromolecules* **2000**, *33*, 2335.
(42) Wang, J.; Han, J.; Xie, X.; Xue, Z.; Fliedel, C.; Poli, R. FeBr2-Catalyzed Bulk ATRP Promoted by Simple Inorganic Salts. *Macromolecules* **2019**, *52*, 5366.
(43) Dadashi-Silab, S.; Matyjaszewski, K. Temporal Control in Atom Transfer Radical Polymerization Using Zerovalent Metals. *Macromolecules* **2018**, *51*, 4250.