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Metallocene-Containing Homopolymers and Heterobimetallic Block Copolymers via Photoinduced RAFT Polymerization

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Abstract

We report the synthesis of cationic cobaltocenium and neutral ferrocene containing homopolymers mediated by photoinduced reversible addition-fragmentation chain transfer (RAFT) polymerization with a photocatalyst fac-[Ir(ppy)₃]. The homopolymers were further used as macromolecular chain transfer agents to synthesize diblock copolymers via chain extension. Controlled/“living” feature of photoinduced RAFT polymerization was confirmed by kinetic studies even without prior deoxygenation. A light switch between ON and OFF provided a spatiotemporal control of polymerization.

Metallopolymers, with metal centers incorporated into organic polymeric frameworks, have received significant attention over the past decades.¹ Among metallopolymers, metallocene-containing polymers show great potential in optical, magnetic, catalytic, electrochemical, and biomedical applications due to the physicochemical and processing advantages of organic polymers with the unique sandwich structures and multifunctionality of metallocenes.² Ferrocene is the most common metallocene for building metallopolymers. A variety of polymerization methods have been used since the first ferrocene-containing polymers were obtained by free radical polymerization of vinyl ferrocene in 1967.³ In comparison, due to the inherent stability of 18-electron species, 19-e cobaltocene can lose one electron easily to form the much more stable 18-e cobaltocenium cation. Besides some advantageous properties such as high chemical stability, the isoelectronic cobaltocenium monomers and polymers show high solubility in water with the use of hydrophilic

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counterion, which could be more beneficial for applications in green chemistry and biomedical areas.⁴

Controlled/"living" radical polymerizations (CRPs) have given notable impetus to the development of polymer science, offering new opportunities to synthesize novel polymers with diverse compositions, precise molecular weight, low dispersity, and well-defined structures.⁵ In recent years, external stimuli-induced CRPs have received significant interest due to their unique ability to switch polymerization between "On" and "Off" states, providing the capability to temporally and spatially control chemical reactivity. So far, light, electricity, mechanical force, and chemical redox triggers have been effectively used as external stimuli to exert control over CRPs.⁶ Among these stimuli, light is considered the most attractive regulator because of its low cost, relative ease of operation, and eco-friendly characteristics, just like photosynthesis in the plants converting solar energy into various biological macromolecules.⁷ For instance, Hawker, Matyjaszewski, Miyake, and others demonstrated novel metal-free atom transfer radical polymerization (ATRP) mediated by light and catalyzed by organic-based photoredox catalysts to polymerize vinyl monomers.⁸ Yoshida reported nitroxide-mediated photopolymerization (photo-NMP) accelerated by redox-active additives such as iodonium salts with 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) as a photoinitiator.⁹ The Boyer group envisioned a versatile photoinduced electron transfer (PET) reversible addition-fragmentation chain transfer (RAFT) polymerization that could be regulated at ultralow concentrations of photocatalyst tris[2-phenylpyridinato-C²,N]iridium(III) (fac-[Ir(ppy)₃]) under blue light.¹⁰ Shortly after organocatalytic RAFT polymerization could be also activated by conventional photoinitiators through the iniferter mechanism, as reported by Johnson et al. and others^{7a,11} Junkers and co-workers further reported continuous microflow photo-RAFT polymerization by conventional radical photoinitiators.¹²

Although there have been great achievements in photo-induced CRPs, metallocopolymers, especially metallocene-containing polymers, have not yet been synthesized by photo-induced CRPs. This may have been partially due to the high chemical stability of metallocene monomers, particularly cationic cobaltocenium. Most recently, our group and others prepared a series of cobaltocenium monomers that could serve as substrates to synthesize different kinds of metallocene-containing polymers via CRPs and other polymerization methods.^{2b,4d,g,13} Herein, we report the use of the photo-induced RAFT technique to prepare side-chain metallocene (including cobaltocenium and ferrocene) containing homopolymers and diblock copolymers. Results on kinetic studies demonstrated that the photoinduced RAFT processes of metallocene could be effectively controlled even without prior deoxygenation.

First, we carried out photoinduced RAFT polymerization of cobaltocenium-containing monomer, 2-cobaltocenium amidoethyl methacrylate hexafluorophosphate (CoAEMA), with fac-[Ir(ppy)₃] as photocatalyst, (dodecylthiocarbonothioylthio)-2-methylpropionic acid (DTPA) as chain transfer agent (CTA), and a 4.8 W blue LED light ($\lambda = 430$ nm) as a visible light source in DMF solution at room temperature (Scheme 1a and Figure S1). The photocatalyst fac-[Ir(ppy)₃] could be stimulated to form an excited species [Ir(III)*] under blue light irradiation and to reduce the thiocarbonylthio compound via a PET process.^{10c} We

found the cobaltocenium monomer successfully underwent polymerization at a low rate. The effects of RAFT agents, solvents, and additive amounts of photocatalyst on the polymerization rate were further studied. As we can see from Table 1, the increase in the amount of catalyst could slightly increase the rate of polymerization (No. 1–3). Compared to DMF and acetonitrile, DMSO produced the highest polymerization rate for the photoinduced RAFT processes (No. 3–5), which was consistent with previous reports.^{10c} Compared to cumyl dithiobenzoate (CDB), DTPA was a better CTA for the polymerization of cobaltocenium monomer (No. 6, 7). However, almost all reactions showed conversion <20% after 24 h at room temperature. The temperature might be too low to induce polymerization of the cobaltocenium monomer. To improve the reaction rate, we increased the temperature to 60 °C and 90 °C and achieved much higher conversion (43% conversion at 60 °C and 64% conversion at 90 °C).

Figure 1a and 1b showed ¹H NMR spectra of the CoAEMA monomer and its homopolymer PCoAEMA prepared with DTPA as CTA at 90 °C after 24 h. In comparison with the monomer, the vinyl proton signals from the methacrylate double bond at ~6.10 and ~5.70 ppm disappeared in polymers. Meanwhile, the peaks at ~6.25, ~5.90, and ~5.80 ppm corresponding to the cyclopentadienyl (Cp) rings of the cobaltocenium unit remained intact, and new broad peaks at 0.50–1.50 ppm from the protons of polymer backbone appeared, indicating the successful polymerization of the cobaltocenium monomer. Due to the strong electrostatic interaction between the stationary phase of microstyragel columns and cationic cobaltocenium moieties, it was very challenging to get the GPC signal of cobaltocenium-containing polymers. We calculated the molecular weight by NMR conversion (Figure S2), which was determined to be at 31 000 g/mol (No. 9 in Table 1). Similarly, the polymer prepared with CDB as RAFT agent at 90 °C has lower molecular weight (25 000 g/mol, No. 11 in Table 1, ¹H NMR spectra in Figure S3).

The kinetic studies of the CoAEMA monomer using DTPA as CTA were investigated via NMR conversion under continuous blue light irradiation at 90 °C. As expected, the polymerization showed an excellent controlled/“living” polymerization process, giving a linear plot of $\ln([M]_0/[M]_t)$ versus exposure time (Figure 1c). Subsequently, another identical reaction mixture was exposed to an alternating light “ON” and “OFF” environment. The light switch between ON and OFF resulted in reversible activation and deactivation of the polymerization (Figure 1d). Reaction proceeded when the light was turned on, and stopped when the light was turned off. This can be attributed to the rapid deactivation of photocatalyst in the absence of light. Most importantly, the cycle could be repeated several times, and $\ln([M]_0/[M]_t)$ still showed a good linear relationship with the time of exposure (Figure 1e), demonstrating a temporally controlled process.

Oxygen is considered as a vigorous radical scavenger and poses a threat to various free radical and living radical polymerizations. Thus, the deoxygenation via freeze-pump-thaw cycles or degas with nitrogen is commonly required before polymerization. Here, we tried to directly carry out photoinduced RAFT polymerization of the cobaltocenium monomer without prior deoxygenation. As shown in Figure 1f, after a long inhibition period of 5 h due to the reduction of oxygen by the photocatalyst, the semilogarithmic plot exhibited a linear relationship between $\ln([M]_0/[M]_t)$ and reaction time, indicating the well-controlled living

polymerization process. Polymerization rate was a little slower than that of the degassed reaction.

Based on the above results, we decided to investigate photoinduced RAFT polymerization of neutral ferrocene-containing monomers. We initially attempted to polymerize ferrocenylmethyl methacrylate (FeMMA) monomer but were not successful despite that despite that the temperature was increased to 90 °C (No. 12 in Table 1). It might be possible that the methylene group in α -position to the ferrocene unit in FeMMA was activated toward H-abstraction by a radical and gave rise to side reactions of chain transfer.^{3d} We then synthesized another ferrocene monomer without α -hydrogen: 2-(methacryloyloxy)ethyl ferrocenecarboxylate (MAEFe). As shown in the ¹H NMR spectrum of MAEFe, protons of Cp rings can be found at ~4.7, ~4.4, and ~4.2 ppm, and the peaks at ~6.0 and ~5.5 ppm were assigned to two vinyl protons from the methacrylate double bond (Figure 2a). We found MAEFe could be polymerized successfully by photoinduced RAFT at room temperature (No. 13 in Table 1). Similar to the cobaltocenium monomer, higher conversion of the ferrocene monomer was achieved when higher temperature was applied. For the polymer of MAEFe the peaks of the vinyl protons from methacrylate disappeared, and some new broad peaks at 0.80–2.00 ppm from the polymer backbone were observed in the ¹H NMR spectrum of homopolymer PMAEFe (Figure 2b), confirming the successful polymerization of MAEFe.

Similar to kinetic observations for the cobaltocenium monomer polymerization, the linear dependence of $\ln[M]_0/[M]_t$ versus time confirmed the controlled character of MAEFe polymerization conducted under blue light irradiation at 60 °C (Figure 2c). The clear shift of the GPC curves toward lower elution time was observed, corresponding to higher conversion and higher molecular weight (Figure S4). The plot of $M_{n, GPC}$ versus conversion gave a good linear relationship and exhibited the first-order kinetics of living polymerization (Figure 2d), although the molecular weight was slightly high at the initial stage. Moreover, alternate switch on and off light could similarly cause reversible activation or deactivation of the reaction to effectively control MAEFe polymerization (Figure 2e). Additional kinetic analysis of MAEFe polymerization in the presence of air further revealed MAEFe could be well photoinduced polymerized with controlled/living properties (Figure 2f).

Having successfully prepared homopolymers of cobaltocenium and ferrocene monomers via photoinduced RAFT polymerization, we further carried out the chain extension to demonstrate the controlled living nature of polymerization and end-group fidelity. First, chain extension of PMAEFe polymer was carried out using MMA as monomer to yield PMAEFe-*b*-PMMA diblock copolymer. The increasing integration of peaks at 1.80–2.20 and 0.80–1.00 ppm in the ¹H NMR spectrum of PMAEFe-*b*-PMMA indicated that MMA monomer was polymerized into the diblock copolymer (Figure 3a). GPC revealed that the molecular weight of PMAEFe-*b*-PMMA increased to 31 000 g/mol from the starting PMAEFe-macroinitiator with 7000 g/mol (Figure 3b). There was a small tailing in the homopolymer regime, and the molecular weight distribution was wider (from 1.14 to 1.62), indicating the loss of activity of some macroinitiator. The kinetic plot (Figure 3c) showed a good controlled/living character with a linear relationship between $\ln([M]_0/[M])$ and exposure time under the continuous irradiation of light. The PMAEFe-*b*-PMMA diblock

copolymers could be also spatiotemporally controlled via repeated switching “ON” and “OFF” of light (Figure 3d) in a similar fashion to the homopolymers.

Finally, we used a cobaltocenium-containing homopolymer as macro-CTA and MAEFe as a chain-extension monomer to prepare heterobimetallic diblock copolymers PCoAEMA-*b*-PMAEFe via photoinduced RAFT polymerization (Scheme 1b). As shown in the ¹H NMR spectrum of PCoAEMA-*b*-PMAEFe diblock copolymers (Figure 4a), chemical shifts at 5.70–6.30 ppm of Cp protons from cobaltocenium and peaks at 4.30–4.80 ppm assigned to Cp protons from ferrocene verified the successful block copolymerization. The block ratio of PCoAEMA:PMAEFe in copolymers was about 50:120, calculated by integration of relevant Cp proton signals. Similar light-responsive deactivation behaviors were also observed when the reaction was in the state of darkness (Figure 4b).

Block copolymers with different segment solubility can self-assemble into well-defined nanostructured micelles. Based on different solubility of PCoAEMA and PMAEFe blocks in DMF and MeCN (DMF is a good solvent for both blocks and MeCN only for cobaltocenium block), the self-assembly of PCoAEMA-*b*-PMAEFe diblock copolymers in the mixed solvents of DMF/MeCN (v/v: 1:3) was further monitored by transmission electron microscopy (TEM) and dynamic light scattering (DLS). As shown in Figure 4c, TEM image of PCoAEMA-*b*-PMAEFe dispersions indicated the formation of spherical micelles. The diameter was about 50 nm. The DLS measurement (Figure 4d) showed that the PCoAEMA-*b*-PMAEFe nanomicelles could be slightly swollen in solution and resulted in a larger hydrodynamic diameter of 70 nm.

In conclusion, this work demonstrated utilization of photoinduced RAFT polymerization for the preparation of side-chain metallocene-containing polymers using fac-[Ir(ppy)₃] as a photocatalyst under low intensity blue light. Compared with cationic cobaltocenium-containing monomer, neutral ferrocene-containing monomer showed faster polymerization and higher reactivity. Kinetic studies confirmed the controlled/living feature of such photoinduced RAFT polymerization for both cobaltocenium and ferrocene monomers even without prior deoxygenation. Metallocene-containing homo-polymers were further used as macro-CTAs to synthesize block copolymers. Importantly, all polymerizations could be spatiotemporally controlled by switching the light ON and OFF. Furthermore, amphiphilic heterobimetallic block copolymer PCoAEMA-*b*-PMAEFe could self-assemble to form spherical micelles in selected mixed solvents.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

1. (a) Yan Y, Zhang J, Ren L, Tang C. *Chem Soc Rev.* 2016; 45:5232–5263. [PubMed: 26910408] (b) Eloi JC, Chabanne L, Whittell GR, Manners I. *Mater Today.* 2008; 11:28, 36.(c) Hardy CG, Zhang J, Yan Y, Ren L, Tang C. *Prog Polym Sci.* 2014; 39:1742–1796.(d) Stanley JM, Holliday B. *J Coord Chem Rev.* 2012; 256:1520–1530.(e) Whittell GR, Hager MD, Schubert US, Manners I. *Nat Mater.* 2011; 10:176–188. [PubMed: 21336298] (f) Zhang KY, Liu S, Zhao Q, Huang W. *Coord Chem Rev.* 2016; 319:180–195.(g) Whittell GR, Manners I. *Adv Mater.* 2007; 19:3439–3468.(h) Lanigan N, Wang X. *Chem Commun.* 2013; 49:8133–8144.
2. (a) Alkan A, Wurm FR. *Macromol Rapid Commun.* 2016; 37:1482–1493. [PubMed: 27492968] (b) Gu H, Ciganda R, Gatard S, Lu F, Zhao P, Ruiz J, Astruc D. *J Organomet Chem.* 2016; 813:95–102. (c) Hardy CG, Ren L, Zhang J, Tang C. *Isr J Chem.* 2012; 52:230–245.(d) Vorotyntsev MA, Vasilyeva SV. *Adv Colloid Interface Sci.* 2008; 139:97–149. [PubMed: 18358450] (e) Williams KA, Boydston AJ, Bielawski CW. *Chem Soc Rev.* 2007; 36:729–744. [PubMed: 17471398]
3. (a) Pietschnig R. *Chem Soc Rev.* 2016; 45:5216–5231. [PubMed: 27156979] (b) Alkan A, Natalello A, Wagner M, Frey H, Wurm FR. *Macromolecules.* 2014; 47:2242–2249.(c) Baldwin MG, Johnson KE. *J Polym Sci Part A-1: Polym Chem.* 1967; 5:2091–2098.(d) Herfurth C, Voll D, Buller J, Weiss J, Barner-Kowollik C, Laschewsky A. *J Polym Sci Part A: Polym Chem.* 2012; 50:108–118.(e) Hmyene M, Yassar A, Escorne M, Percheron-Guegan A, Garnier F. *Adv Mater.* 1994; 6:564–568.(f) Hudson RDA. *J Organomet Chem.* 2001:637–639. 47–69.(g) Gallei M. *Macromol Chem Phys.* 2014; 215:699–704.
4. (a) Cuadrado I, Casado CM, Lobete F, Alonso B, Gonzalez B, Losada J, Amador U. *Organometallics.* 1999; 18:4960–4969.(b) Noor F, Wustholz A, Kinscherf R, Metzler-Nolte N. *Angew Chem Int Ed.* 2005; 44:2429–2432.(c) Rogers EI, Silvester DS, Poole DL, Aldous L, Hardacre C, Compton RG. *J Phys Chem C.* 2008; 112:2729–2735.(d) Vanicek S, Kopacka H, Wurst K, Muller T, Schottenberger H, Bildstein B. *Organometallics.* 2014; 33:1152–1156.(e) Wei J, Ren L, Tang C, Su Z. *Polym Chem.* 2014; 5:6480–6488.(f) Zhang J, Chen YP, Miller KP, Ganewatta MS, Bam M, Yan Y, Nagarkatti M, Decho AW, Tang C. *J Am Chem Soc.* 2014; 136:4873–4876. [PubMed: 24628053] (g) Zhang J, Yan J, Pageni P, Yan Y, Wirth A, Chen YP, Qiao Y, Wang Q, Decho AW, Tang C. *Sci Rep.* 2015; 5:11914. [PubMed: 26202475] (h) Hadadpour M, Gwyther J, Manners I, Ragogna PJ. *Chem Mater.* 2015; 27:3430–3440.(i) Mayer UF, Gilroy JB, O'Hare D, Manners I. *J Am Chem Soc.* 2009; 131:10382–10383. [PubMed: 19586050] (j) Gilroy JB, Patra SK, Mitchels JM, Winnik MA, Manners I. *Angew Chem Int Ed.* 2011; 50:5851–5855.
5. (a) Chiefari J, Chong Y, Ercole F, Krstina J, Jeffery J, Le TP, Mayadunne RT, Meijs GF, Moad CL, Moad G, et al. *Macromolecules.* 1998; 31:5559–5562.(b) Benoit D, Chaplinski V, Braslau R, Hawker CJ. *J Am Chem Soc.* 1999; 121:3904–3920.(c) Hawker CJ, Bosman AW, Harth E. *Chem Rev.* 2001; 101:3661–3688. [PubMed: 11740918] (d) Kamigaito M, Ando T, Sawamoto M. *Chem Rev.* 2001; 101:3689–3746. [PubMed: 11740919] (e) Moad G, Rizzardo E, Thang SH. *Aust J Chem.* 2005; 58:379–410.(f) Ouchi M, Terashima T, Sawamoto M. *Chem Rev.* 2009; 109:4963–5050. [PubMed: 19788190] (g) Matyjaszewski K. *Macromolecules.* 2012; 45:4015–4039.(h) Matyjaszewski K, Tsarevsky NV. *J Am Chem Soc.* 2014; 136:6513–6533. [PubMed: 24758377]
6. (a) Broderick EM, Guo N, Vogel CS, Xu C, Sutter Jr, Miller JT, Meyer K, Mehrkhodavandi P, Diaconescu PL. *J Am Chem Soc.* 2011; 133:9278–9281. [PubMed: 21604745] (b) Caruso MM, Davis DA, Shen Q, Odom SA, Sottos NR, White SR, Moore JS. *Chem Rev.* 2009; 109:5755–5798. [PubMed: 19827748] (c) Gregson CK, Gibson VC, Long NJ, Marshall EL, Oxford PJ, White AJ. *J Am Chem Soc.* 2006; 128:7410–7411. [PubMed: 16756273] (d) Leibfarth FA, Mattson KM, Fors BP, Collins HA, Hawker CJ. *Angew Chem Int Ed.* 2013; 52:199–210.(e) Magenau AJ, Strandwitz NC, Gennaro A, Matyjaszewski K. *Science.* 2011; 332:81–84. [PubMed: 21454784]
7. (a) Chen M, Zhong M, Johnson JA. *Chem Rev.* 2016; 116:10167. [PubMed: 26978484] (b) Fors BP, Hawker CJ. *Angew Chem Int Ed.* 2012; 51:8850–8853.(c) Fors BP, Poelma JE, Menyo MS, Robb MJ, Spokoyny DM, Kramer JW, Waite JH, Hawker CJ. *J Am Chem Soc.* 2013; 135:14106–14109. [PubMed: 24025201] (d) Trotta JT, Fors BP. *Synlett.* 2016; 27:702–713.(e) Xu J, Shanmugam S, Fu C, Aguey-Zinsou KF, Boyer C. *J Am Chem Soc.* 2016; 138:3094–3106. [PubMed: 26914442] (f) Yagci Y, Jockusch S, Turro NJ. *Macromolecules.* 2010; 43:6245–6260.
8. (a) Treat NJ, Sprafke H, Kramer JW, Clark PG, Barton BE, Read de Alaniz J, Fors BP, Hawker CJ. *J Am Chem Soc.* 2014; 136:16096–16101. [PubMed: 25360628] (b) Treat NJ, Fors BP, Kramer JW,

- Christianson M, Chiu C-Y, Alaniz JRd, Hawker CJ. *ACS Macro Lett.* 2014;580–584.(c) Miyake GM, Theriot JC. *Macromolecules.* 2014; 47:8255–8261.(d) Pan X, Lamson M, Yan J, Matyjaszewski K. *ACS Macro Lett.* 2015; 4:192–196.(e) Liu X, Zhang L, Cheng Z, Zhu X. *Polym Chem.* 2016; 7:689–700.(f) Theriot JC, Lim CH, Yang H, Ryan MD, Musgrave CB, Miyake GM. *Science.* 2016; 352:1082–1086. [PubMed: 27033549] (g) Yan J, Pan X, Schmitt M, Wang Z, Bockstaller MR, Matyjaszewski K. *ACS Macro Lett.* 2016; 5:661–665.(h) Wang J, Yuan L, Wang Z, Rahman MA, Huang Y, Zhu T, Wang R, Cheng J, Wang C, Chu F, Tang C. *Macromolecules.* 2016; 49:7709–7717.
9. (a) Yoshida E. *Colloid Polym Sci.* 2008; 286:1663–1666.(b) Yoshida E. *Colloid Polym Sci.* 2010; 288:1639–1643.(c) Yoshida E. *Polymers.* 2012; 4:1125–1156.
10. (a) Fu C, Xu J, Tao L, Boyer C. *ACS Macro Lett.* 2014; 3:633–638.(b) Shanmugam S, Boyer C. *J Am Chem Soc.* 2015; 137:9988–9999. [PubMed: 26171943] (c) Xu J, Jung K, Atme A, Shanmugam S, Boyer C. *J Am Chem Soc.* 2014; 136:5508–5519. [PubMed: 24689993]
11. (a) Pan X, Tasdelen MA, Laun J, Junkers T, Yagci Y, Matyjaszewski K. *Prog Polym Sci.* 2016; doi: 10.1016/j.progpolymsci.2016.06.005(b) Chen M, MacLeod MJ, Johnson JA. *ACS Macro Lett.* 2015; 4:566–569.
12. Wenn B, Junkers T. *Macromolecules.* 2016; 49:6888–6895.
13. (a) Ren L, Hardy CG, Tang C. *J Am Chem Soc.* 2010; 132:8874–8875. [PubMed: 20540580] (b) Ren L, Hardy CG, Tang S, Doxie DB, Hamidi N, Tang C. *Macromolecules.* 2010; 43:9304–9310. (c) Ren L, Zhang J, Bai X, Hardy CG, Shimizu KD, Tang C. *Chem Sci.* 2012; 3:580–583.(d) Ren L, Zhang J, Hardy CG, Doxie D, Fleming B, Tang C. *Macromolecules.* 2012; 45:2267–2275.(e) Yan Y, Zhang J, Qiao Y, Tang C. *Macromol Rapid Commun.* 2014; 35:254–259. [PubMed: 24023049] (f) Zhang J, Ren L, Hardy CG, Tang C. *Macromolecules.* 2012; 45:6857–6863.(g) Wang Y, Rapakousiou A, Astruc D. *Macromolecules.* 2014; 47:3767–3774.(h) Gu H, Ciganda R, Hernandez R, Castel P, Zhao P, Ruiz J, Astruc D. *Macromolecules.* 2015; 48:6071–6076.(i) Gu H, Ciganda R, Castel P, Ruiz J, Astruc D. *Macromolecules.* 2016; 49:4763–4773.(j) Vanicek S, Kopacka H, Wurst K, Muller T, Hassenruck C, Winter RF, Bildstein B. *Organometallics.* 2016; 35:2101–2109.(k) Ren L, Zhang J, Hardy CG, Ma S, Tang C. *Macromol Rapid Commun.* 2012; 33:510–516. [PubMed: 22252886] (l) Zhang J, Yan Y, Chance MW, Chen J, Hayat J, Ma S, Tang C. *Angew Chem Int Ed.* 2013; 52:13387–13391.(m) Gu H, Ciganda R, Hernandez R, Castel P, Zhao P, Ruiz J, Astruc D. *Macromol Rapid Commun.* 2016; 37:630–636. [PubMed: 26841204]

Figure 1. Photoinduced RAFT polymerization of CoAEMA using DTPA as CTA and fac-[Ir(ppy)₃] as photocatalyst under 4.8 W blue LED irradiation at 90 °C: ^1H NMR spectra of (a) cobaltocenium monomer CoAEMA and (b) cobaltocenium polymer PCoAEMA. (c) $\ln([M]_0/[M]_t)$ versus time under continuous light irradiation; (d) monomer conversion; and (e) $\ln([M]_0/[M]_t)$ versus time of exposure in the presence (“ON”) or in the absence (“OFF”) of light; (f) $\ln([M]_0/[M]_t)$ versus time in the presence of oxygen.

Figure 2.

Photoinduced polymerization of MAEFe using DTPA as CTA at 60 °C: ^1H NMR spectra of (a) ferrocene monomer MAEFe and (b) ferrocene polymer PMAEFe; (c) $\ln([M]_0/[M]_t)$ versus time and (d) M_n and M_w/M_n versus conversion; (e) monomer conversion in the presence (“ON”) or in the absence (“OFF”) of light; (f) $\ln([M]_0/[M]_t)$ versus time in the presence of oxygen.

Figure 3.

Photoinduced RAFT polymerization to prepare PMAEFe-*b*-PMMA diblock copolymer using PMAEFe as macro-CTA at 60 °C: (a) ^1H NMR spectrum of PMAEFe-*b*-PMMA; (b) GPC traces of PMAEFe macro-CTA ($M_n = 7000$ g/mol, $\text{PDI} = 1.12$) and PMAEFe-*b*-PMMA ($M_n = 31\,000$ g/mol, $\text{PDI} = 1.61$); (c) $\ln([M]_0/[M]_t)$ versus time under continuous light irradiation; (d) monomer conversion in the presence (“ON”) or in the absence (“OFF”) of light.

Figure 4.

Photoinduced RAFT polymerization to prepare heterobimetallic diblock copolymers PCoAEMA-*b*-PMAEFe using PCoAEMA as macro-CTA at 60 °C: (a) ^1H NMR spectrum of PCoAEMA-*b*-PMAEFe; (b) monomer conversion in the presence (“ON”) or in the absence (“OFF”) of light; (c) TEM image of PCoAEMA-*b*-PMAEFe micelles in DMF/MeCN (v/v: 1:3); (d) DLS results for the self-assembled PCoAEMA-*b*-PMAEFe in DMF/MeCN.

Scheme 1.

Synthesis of (a) PCoAEMA Homopolymer and (b) PCoAEMA-*b*-PMAEFe Heterobimetallic Diblock Copolymer by Photoinduced RAFT Polymerization

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Table 1
Preparation of Metallocene Homopolymers via Photoinduced RAFT Polymerization^a

entry	[M]: [CTA]: [Ir]	monomer	CTA	solvent	T (°C)	conv.	M _n
1	100:1:0.0001	CoAEMA	CDB	DMF	25	0.07	3400
2	100:1:0.001	CoAEMA	CDB	DMF	25	0.12	5800
3	100:1:0.01	CoAEMA	CDB	DMF	25	0.15	7300
4	100:1:0.01	CoAEMA	CDB	MeCN	25	0.13	6400
5	100:1:0.01	CoAEMA	CDB	DMSO	25	0.17	8300
6	100:1:0.01	CoAEMA	DTPA	DMF	25	0.19	9200
7	100:1:0.01	CoAEMA	DTPA	DMSO	25	0.22	10700
8	100:1:0.01	CoAEMA	DTPA	DMSO	60	0.43	21000
9	100:1:0.01	CoAEMA	DTPA	DMSO	90	0.64	31000
10	100:1:0.01	CoAEMA	CDB	DMSO	60	0.36	18000
11	100:1:0.01	CoAEMA	CDB	DMSO	90	0.51	25000
12	100:1:0.01	FeMMA	DTPA	DMSO	90	0	0
13	100:1:0.01	MAEFe	DTPA	DMSO	25	0.28	9500
14	100:1:0.01	MAEFe	DTPA	DMSO	90	0.74	25000
15	100:1:0.01	MAEFe	DTPA	DMSO	60	0.66	22000
16	300:1:0.01	MAEFe	DTPA	DMSO	60	0.57	58000

^a M_n calculated via NMR conversion of monomer; the reaction time was 24 h).