

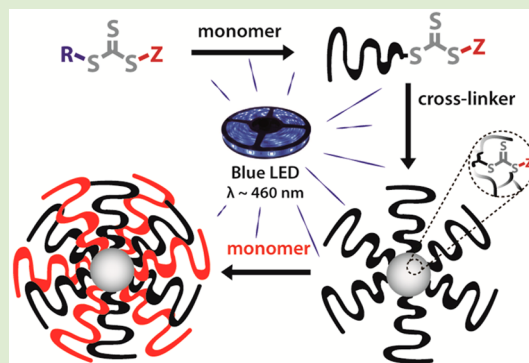
Controlled Formation of Star Polymer Nanoparticles via Visible Light Photopolymerization

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Supporting Information

ABSTRACT: A recently developed visible light mediated photocontrolled radical polymerization technique using trithiocarbonates (i.e., conventional RAFT agents) as the sole control agent in the absence of additional photoinitiators or catalysts is utilized for the synthesis of core cross-linked star (CCS) polymer nanoparticles. The attractive features of this photopolymerization system, including high end-group fidelity at (near) complete monomer conversion, are exploited to facilitate a high-yielding, one-pot pathway toward well-defined star polymer products. Moreover, reinitiation of the photoactive trithiocarbonate moieties from within the star core is demonstrated to form (pseudo)miktoarm stars via an “in–out” approach, showing extremely high initiation efficiency (95%).



The synthesis of star polymer nanoparticles via the “arm-first” approach, whereby a macroinitiator is chain-extended in the presence of a di- or multivinyl agent (i.e., cross-linker), continues to be an active field of research.^{1–15} Various techniques have been employed to generate these nanoparticles, commonly defined as core cross-linked star (CCS) polymers, however, their synthesis via reversible deactivation radical polymerization (RDRP) is arguably the most convenient and versatile approach.¹ Until relatively recently, the synthesis of CCS polymers via the arm-first approach had suffered from significant limitations with regards to star conversion efficiency. This has been ascribed to loss of the active, or “living”, linear polymer end-group as well as steric congestion around the star core during the cross-linking step. To improve star conversion, the synthesis of linear precursors was often stopped at low monomer conversions to preserve the end-group fidelity; however, this requires an intermediate purification step to remove unreacted monomers prior to addition of a cross-linker, which is undesirable. Improvements in RDRP technologies to increase the chemical fidelity and/or manipulate the radical concentration to minimize termination events have been utilized to improve star yields, with metal-catalyzed RDRPs now demonstrated to form CCS polymers in almost quantitative yield^{16,17} and in some cases with no intermediate purification of the linear precursor required.^{18–20}

In contrast, forming CCS polymers via the arm-first approach using reversible addition–fragmentation chain transfer (RAFT) polymerization has been challenging, where low star yields and poorly defined star products are common despite the intensive interest in developing pathways toward CCS polymers via this technique.^{21,22} These challenges can be overcome by using a

cross-linker of poor solubility in the chosen reaction solvent²³ due to preassembly of the linear species into star-like structures during the early stages of cross-linking resulting in improved star yields and dispersities.^{9,24–26} However, in these systems, careful consideration of each component’s solubility is required to ensure a successful synthesis. Thus, there exists a need for the development of new synthetic strategies capable of producing well-defined CCS polymers in high yields using metal-free RDRP techniques.

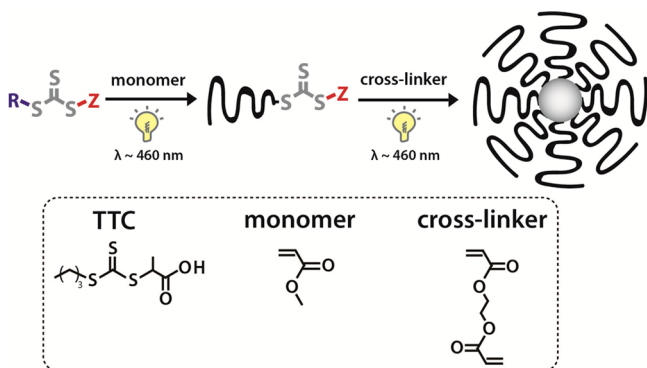
Photoactivated RDRP processes^{27–31} have received a great deal of interest of late as a result of their inherent spatiotemporal control, allowing access to unique materials and structures.^{32,33} We recently developed a novel photocontrolled radical polymerization (PRP) method wherein visible light irradiation of trithiocarbonates (TTCs) (i.e., traditional chain transfer reagents used in RAFT polymerization) is used to induce a controlled polymerization process (Scheme 1).³⁴ A similar system was also reported by Boyer et al.³⁵ The polymerization proceeds solely using TTCs as the control agent and in the absence of any additional radical initiator or catalyst that may compromise the integrity of the microstructural features of a polymer chain.³⁶ With this PRP approach, high molecular weight polyacrylates and polyacrylamides with excellent chain-end fidelity (>99%) were attained even at (near) complete monomer conversion. Taking advantage of the efficiency and versatility of this PRP technique, we herein demonstrate the synthesis of CCS polymers with

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Scheme 1. Photocontrolled Radical Polymerization (PRP) in the Sole Presence of a Trithiocarbonate (TTC) under Visible Light (~ 460 nm)^a



^aInitial polymerization of monomer generates a linear macroinitiator which is followed by sequential addition of a cross-linking reagent to generate in situ core cross-linked star (CCS) polymer nanoparticles.

high macroinitiator-to-star conversion (>95%) via a one-pot, two-step approach (Scheme 1). Retention of the active TTC chain-end following star formation is then demonstrated by performing an “in–out” chain extension, where ca. 95% reinitiation efficiency from the core-embedded TTC groups was attained, as indicated by kinetic analysis. The efficiency of forming CCS polymer nanoparticles using the described system indicates that it can potentially be applied for other controlled cross-linking reactions to generate various architectures such as hydro- and cryogels as well as surface coatings.

To demonstrate the formation of CCS polymers via the visible light PRP, methyl acrylate (MA) and 2-(((butylthio)carbonothioyl)thio)propanoic acid (BCTP) were chosen as the model monomer and TTC, respectively. For example, MA (0.5 mL, 80 equiv) and BCTP (16.5 mg, 1 equiv) were first dissolved in DMSO (50% v/v with respect to monomer) and the reaction mixture was thoroughly degassed and then placed in a homemade photoreactor (see Figure S1, Supporting Information (SI)). The light source was turned on to mark the start of the reaction. After 16–24 h, an aliquot was extracted via degassed syringe to monitor the monomer conversion by ¹H NMR spectroscopy and linear polymer formation via GPC analysis. When high monomer conversions were reached ($\geq 95\%$), a solution of divinyl cross-linker (i.e., ethylene glycol diacrylate (EGDA), 10 equiv) in DMSO (8:1 v/w ratio of solvent to linear polymer species) was added and the new reaction mixture containing linear poly(methyl acrylate) (PMA) macroinitiator (MI) and EGDA was again degassed. The light source was then turned on to initiate the cross-linking reaction. Samples were withdrawn periodically under an argon blanket to monitor monomer consumption by ¹H NMR and star polymer formation by GPC analysis.

The polymerization to form linear PMA MIs was well controlled, where polymers of low dispersity ($\mathcal{D} \leq 1.25$) were obtained within 24 h of irradiation when the targeted degree of polymerization (DP_n) for the linear species was ≤ 80 (Table S1, SI). However, a longer irradiation time (48 h) was required for targeted DP_n of 120. The long reaction time is undesirable, however, improvements in the rate may be foreseen by increasing the irradiation intensity or changing the irradiated cross-sectional area, as has been demonstrated in related works.^{37,38} Nonetheless, the dispersity of the higher molecular

weight linear PMA remained low ($\mathcal{D} = 1.21$). ¹H NMR spectroscopy of all MI crude reaction mixtures prior to the cross-linking step showed high monomer conversions ($\geq 95\%$), thus confirming that the actual DP_n values are close to the targeted values.³⁴ On the basis of our group's experience in generating CCS polymers,¹⁸ we initially investigated the CCS formation process via our PRP system using PMA MI with DP_n of 80 and at a cross-linker-to-macroinitiator molar ratio ($[XL]/[MI]$) of 10:1. Indeed, under this condition, well-defined PMA CCS with number-averaged molecular weight (M_n) of 149300 g mol⁻¹, $\mathcal{D} = 1.41$, and a calculated arm number (N_{arm}) of 28 was attained, as determined by GPC-multiangle laser light scattering (MALLS) analysis. Furthermore, the GPC differential refractive index (DRI) chromatograms revealed high macroinitiator-to-star conversion (94%, Figure 1b), demonstrating that star polymer nanoparticles can be formed efficiently under the current PRP system.

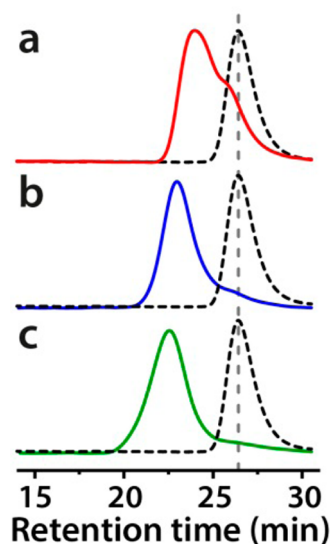


Figure 1. GPC differential refractive index (DRI) chromatograms of PMA MI (with DP_n of 80) and the CCS polymers formed at various $[XL]/[MI]$ molar ratio of (a) 5:1, (b) 10:1, and (c) 15:1.

Parameters thought to affect the star formation process were then investigated further to ascertain the optimal conditions for forming star polymers via PRP. First, the influence of the amount of added cross-linker (EGDA) was investigated by varying the $[XL]/[MI]$. As shown in Figure 1, at the lowest $[XL]/[MI]$ of 5:1, inefficient macroinitiator-to-star conversion was observed (<60%) where significant amounts of linear MI (and partially chain-extended polymer) remain unincorporated into the star structure after 24 h of irradiation (Figure 1a). The suboptimal star conversion observed is thought to be due to the formation of stars with small, highly shielded cores that cannot be accessed by unincorporated (but still active) linear MIs due to steric hindrance, thus limiting the star conversion efficiency. The M_n of the ill-defined star is 34430 g mol⁻¹, with $\mathcal{D} = 1.59$ and $N_{arm} = 7$. In contrast, both of the higher $[XL]/[MI]$ ratios investigated (10:1 and 15:1) show high star conversions (94% and 96%, respectively) and higher molecular weight stars ($M_n = 149300$ g mol⁻¹ and 268800 g mol⁻¹, respectively) with high arm numbers ($N_{arm} = 28$ and $N_{arm} = 56$) after 24 h of irradiation (Figure 1b,c). GPC analysis after a further 24 h irradiation (i.e., total irradiation time = 48 h) showed minimal

change for both CCS polymers formed with the higher $[XL]/[MI]$ ratio, indicating the star formation process had gone to completion (Figure S2, SI). Stars formed with the highest $[XL]/[MI]$ ratio investigated (15:1) showed a slightly broader dispersity value compared to those formed with $[XL]/[MI] = 10:1$ ($\bar{D} = 1.75$ vs 1.41), suggesting that a $[XL]/[MI]$ ratio of 10 gave star products of a narrower size distribution with similar star conversion efficiency. Meanwhile, ^1H NMR analysis (Figure S3, SI) revealed that resonances corresponding to the vinyl groups of cross-linker EGDA (and residual MA from the MI synthesis step) were almost undetectable ($<1\%$), indicating that all the double bonds had been reacted. The hydrodynamic diameter (D_h) of the CCS polymers in THF was also measured via DLS, and it was observed that the D_h of the CCS nanoparticles increased from 10 to 23 nm with increasing $[XL]/[MI]$ ratio (Figure 2).

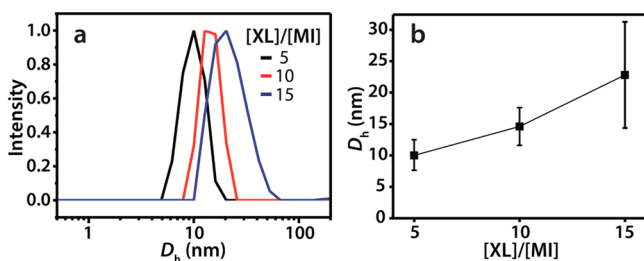


Figure 2. DLS analysis of PMA CCS polymers in THF formed at various $[XL]/[MI]$ molar ratio (fixed MI DP_n of 80): (a) overlay of DLS plots, and (b) peak D_h value increases with increasing $[XL]/[MI]$.

Next, the dependence of star formation on the chain length of the linear MI was investigated using MIs of different DP_n values (i.e., 60, 80, and 120). The $[XL]/[MI]$ was fixed at 10:1 for these experiments, as this ratio was shown to be sufficient to produce high star conversion. The results of these experiments illustrate that when the MI chain length is short (i.e., $DP_n = 60$, $M_n = 4040 \text{ g mol}^{-1}$), the reactive core cannot be shielded effectively to prevent star–star coupling reactions, leading to the formation of high molecular weight multistars. This is shown by the bimodal peak distribution in the GPC DRI chromatogram (Figure 3a) and the DLS distribution (Figure S5, SI). PMA MI with $DP_n = 80$ ($M_n = 6000 \text{ g mol}^{-1}$) shows the most optimal star conversion efficiency among the chain lengths investigated in this study (Figure 3b). Increasing the MI chain length to $DP_n = 120$ ($M_n = 10220 \text{ g mol}^{-1}$, Figure 3c) did not result in star–star coupling, however, the star conversion is not optimal (89%). In this case, stars formed during the initial period of the cross-linking step are strongly shielded by the long linear arms, thus hindering the addition of further MIs into the star structure. The D_h measured via DLS for CCS made from PMA MI with $DP_n = 120$ was 18.2 nm, which is slightly larger than when the DP_n of the MI is 80 (14.6 nm) but not as large as stars formed with a higher $[XL]/[MI]$ ratio of 15:1 (22.8 nm).

Assuming the TTC functionality was embedded in the core following CCS formation, we next investigated whether it was still active (or “living”) by adding fresh monomer solution to the reaction mixture and subjecting the polymerizable medium to further visible light irradiation. Analogous to the synthesis of block copolymers in situ, this should effect a chain extension from within the core of the CCS polymer. This approach,

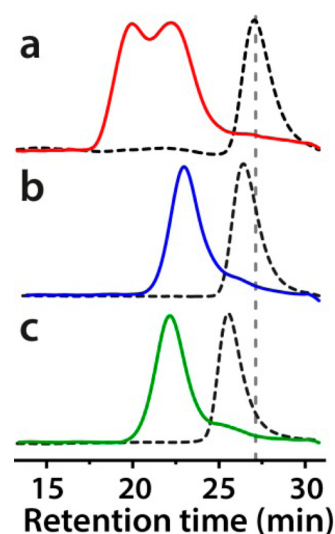


Figure 3. GPC DRI traces of PMA MIs of different DP_n values and their corresponding CCS polymers formed at $[XL]/[MI] = 10:1$. For (a), (b), and (c), the DP_n values are 60, 80, and 120, respectively.

known as the “in–out” method, can be used to generate additional arms for each star as well as hetero/miktoarm stars when different monomers are employed.^{2,39,40} A number of factors can affect the initiation efficiency from the initiating moieties embedded in the star core, including the initial arm length, the cross-linking density of the core, and the chemical compatibility of the second monomer to the preformed stars.⁴⁰ Additionally, for polymerization reactions requiring catalyst complexes or additional radical initiators, diffusion to the initiating site can be restricted, thereby limiting the efficiency of reinitiation. In the present system, given the complete absence of catalysts or initiators, the latter limitation is circumvented and diffusion of the monomer to the initiating sites is the only requirement for polymerization to occur. A schematic of this approach is shown in Figure 4a. Here, we demonstrate the feasibility of this in–out technique using the same model monomer (i.e., methyl acrylate) that was employed for the initial synthesis of the PMA MI ($DP_n = 80$) and the formed CCS thereof (CCS-6, Table 1) to generate a pseudo-miktoarm star polymer (CCS-7). GPC DRI and DLS traces in Figure 4b and Figure S6 reveal clear shifts toward higher molecular weight species and a larger D_h value (22.1 vs 14.3 nm), respectively, upon further addition of fresh monomer after the initial CCS formation step, thus confirming that the core-localized TTC moieties are still active and can induce subsequent PRP. Kinetic investigations were performed in order to quantitatively determine the initiation efficiency (IE) of the CCS polymer.⁴⁰ Namely, a control reaction with identical TTC and monomer concentration was performed simultaneously, and the kinetics were compared (Figure S7, SI). The rate of polymerization is assumed to be proportional to the number or active (i.e., TTC-containing) chain-ends, while the IE of the small molecule TTC is assumed to be 100%. Therefore, the IE_{star} can be defined as the ratio between the apparent rate constant for the CCS-initiated polymerization and the native TTC-initiated polymerization (i.e., $k_{\text{ap,star}}/k_{\text{ap,control}}$). Using this approach, the IE_{star} of the PMA CCS polymer is determined to be 95%, indicating extremely high reinitiation from core-embedded TTC moieties. The monomer conversion was assessed to be 89% by ^1H NMR analysis after 24 h of irradiation. The value for

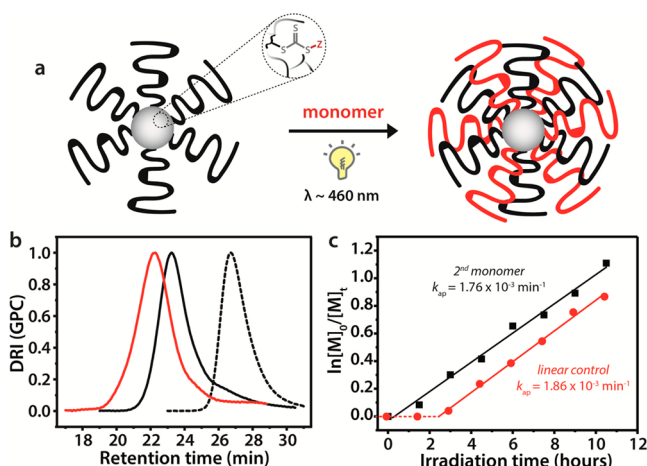


Figure 4. “Living” core CCS polymers are chain extended upon the addition of fresh monomer to generate pseudo-miktoarm stars via an “in–out” approach: (a) schematic illustrating the active TTC moiety in the CCS core and the reactivation to generate pseudo-miktoarm stars; (b) GPC DRI chromatograms of the PMA MI (dotted), CCS (black), and pseudo-miktoarm CCS (red) following sequential monomer/cross-linker/monomer additions in one pot; (c) kinetics of monomer conversion during in–out chain extension compared to control synthesis of linear PMA. Comparison of apparent rate constants gives $IE_{\text{star}} = 95\%$, indicating high TTC retention within the CCS core.

N_{arm} of CCS-7 can be calculated using the observed IE_{star} and the N_{arm} value of the star MI (CCS-6), as illustrated in eq 1.⁴¹

$$N_{\text{arm, total}} = (IE_{\text{star}} \times N_{\text{arm, CCS-MI}}) + N_{\text{arm, CCS-MI}} \quad (1)$$

This generates a theoretical N_{arm} value for CCS-7 of 60. Moreover, the high value of IE_{star} indicates that the formed additional arms should be similar in length to the initially formed star arms (as the same DP_n was targeted for each step). Interestingly, the chain-extension initiated by the CCS polymer displayed a shorter induction delay compared to the linear control (Figure 4c). This will be the subject of further investigation in a future study. The high end-group fidelity demonstrated by this in–out experiment (even after multiple polymerization steps) strongly suggests that star core functionalization via coupling chemistries for the attachment of functional small molecules or drugs may be readily achieved, or alternatively after following the in–out procedure, new functional groups can be introduced at the star periphery.

Table 1. Characterization Data for CCS Polymer Nanoparticles Synthesized in This Study

entry	sample name	MI DP_n	[XL]/[MI]	M_w (g mol ⁻¹) ^a	\bar{D} ^a	N_{arm} ^b	star conv (%) ^c	D_h (nm) ^d
1	CCS-1	80	5	54740	1.59	7	<60	10.0
2	CCS-2	80	10	210510	1.41	28	94	14.6
3	CCS-3	80	15	470400	1.75	56	96	22.8
4	CCS-4	60	10	3845400	1.94	722	95	16.5/66.7 ^e
5	CCS-5	120	10	380360	1.48	31	89	18.2
6	CCS-6	80	10	181040	1.41	31	96	14.3
7	CCS-7	80 ^f		430860	1.67	60 ^g	96	27.8

^aMolecular weights and dispersities determined via GPC equipped with multiangle laser light scattering (MALLS) detector using ASTRA software from Wyatt Technology. ^bCalculated using equations described in the literature (see Supporting Information). ^cApproximated by chromatogram area analysis of MI and CCS peaks fitted as Gaussian. ^dMeasured via DLS at sample concentration of ca. 1 mg mL⁻¹ in THF. ^eBimodal distribution observed. ^fAdditional monomer equivalents per TTC moiety for “in–out” experiment. ^gCalculated using kinetic arguments to assess the initiation efficiency of the star MI CCS-6 (vide infra).

In conclusion, this study demonstrates the efficient synthesis of CCS polymer nanoparticles via a one-pot approach under visible light irradiation utilizing TTCs (i.e., typical RAFT agents) in a simple photocontrolled radical polymerization system. The integrity of the chain ends observed for the linear macroinitiators was retained in the final star structure, as evidenced by the efficient reinitiation from core-localized TTC moieties to generate pseudo-miktoarm stars of roughly twice the molecular weight of the original CCS. The high retention of TTC groups in the star core potentially provides an avenue for postfunctionalization reactions using other coupling chemistries to afford multifunctional nanoparticles for targeted applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00530.

Additional experimental and characterization data including equations for the calculation of N_{arm} , light source emission characterization, ¹H NMR spectra of reaction mixtures, and DLS plots of the various synthesized CCS nanoparticle products (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- Blencowe, A.; Tan, J. F.; Goh, T. K.; Qiao, G. G. *Polymer* **2009**, *50*, 5–32.
- Gao, H.; Matyjaszewski, K. *Prog. Polym. Sci.* **2009**, *34*, 317–350.
- Koda, Y.; Terashima, T.; Nomura, A.; Ouchi, M.; Sawamoto, M. *Macromolecules* **2011**, *44*, 4574–4578.
- Terashima, T.; Nomura, A.; Ito, M.; Ouchi, M.; Sawamoto, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 7892–7895.
- Koda, Y.; Terashima, T.; Sawamoto, M. *J. Am. Chem. Soc.* **2014**, *136*, 15742–15748.

- (6) Terashima, T. *Polymer J.* **2014**, 1–10.
- (7) Koda, Y.; Terashima, T.; Takenaka, M.; Sawamoto, M. *ACS Macro Lett.* **2015**, 4, 377–380.
- (8) Liu, J.; Duong, H.; Whittaker, M. R.; Davis, T. P.; Boyer, C. *Macromol. Rapid Commun.* **2012**, 33, 760–766.
- (9) Qiu, Q.; Liu, G.; An, Z. *Chem. Commun.* **2011**, 47, 12685–12687.
- (10) Chen, Q.; Cao, X.; Liu, H.; Zhou, W.; Qin, L.; An, Z. *Polym. Chem.* **2013**, 4, 4092–4102.
- (11) Chen, Q.; Cao, X.; Xu, Y.; An, Z. *Macromol. Rapid Commun.* **2013**, 34, 1507–1517.
- (12) Chen, Q.; Deng, X.; An, Z. *Macromol. Rapid Commun.* **2014**, 35, 1148–1152.
- (13) Chen, Q.; Xu, Y.; Cao, X.; Qin, L.; An, Z. *Polym. Chem.* **2014**, 5, 175–185.
- (14) Li, W.; Yu, Y.; Lamson, M.; Silverstein, M. S.; Tilton, R. D.; Matyjaszewski, K. *Macromolecules* **2012**, 45, 9419–9426.
- (15) Tucker, B. S.; Getchell, S. G.; Hill, M. R.; Sumerlin, B. S. *Polym. Chem.* **2015**, 6, 4258–4263.
- (16) Burdynska, J.; Cho, H. Y.; Mueller, L.; Matyjaszewski, K. *Macromolecules* **2010**, 43, 9227–9229.
- (17) Park, S.; Cho, H. Y.; Wegner, K. B.; Burdynska, J.; Magenau, A. J.; Paik, H.-j.; Jurga, S.; Matyjaszewski, K. *Macromolecules* **2013**, 46, 5856–5860.
- (18) Wong, E. H. H.; Blencowe, A.; Qiao, G. G. *Polym. Chem.* **2013**, 4, 4562–4565.
- (19) McKenzie, T. G.; Wong, E. H. H.; Fu, Q.; Lam, S. J.; Dunstan, D. E.; Qiao, G. G. *Macromolecules* **2014**, 47, 7869–7877.
- (20) Tan, S.; Wong, E. H. H.; Fu, Q.; Ren, J. M.; Sulistio, A.; Ladewig, K.; Blencowe, A.; Qiao, G. G. *Aust. J. Chem.* **2014**, 67, 173–178.
- (21) Barner-Kowollik, C.; Davis, T. P.; Stenzel, M. H. *Aust. J. Chem.* **2006**, 59, 719–727.
- (22) Wei, X.; Moad, G.; Muir, B. W.; Rizzardo, E.; Rosselgong, J.; Yang, W.; Thang, S. H. *Macromol. Rapid Commun.* **2014**, 35, 840–845.
- (23) Ferreira, J.; Syrett, J.; Whittaker, M.; Haddleton, D.; Davis, T. P.; Boyer, C. *Polym. Chem.* **2011**, 2, 1671–1677.
- (24) Zhang, C.; Miao, M.; Cao, X.; An, Z. *Polym. Chem.* **2012**, 3, 2656–2664.
- (25) Shi, X.; Miao, M.; An, Z. *Polym. Chem.* **2013**, 4, 1950–1959.
- (26) Cao, X.; Zhang, C.; Wu, S.; An, Z. *Polym. Chem.* **2014**, 5, 4277–4284.
- (27) Guillaneuf, Y.; Bertin, D.; Gigmès, D.; Versace, D.-L.; Lalevée, J.; Fouassier, J.-P. *Macromolecules* **2010**, 43, 2204–2212.
- (28) Fors, B. P.; Hawker, C. J. *Angew. Chem., Int. Ed.* **2012**, 51, 8850–8853.
- (29) Xu, J.; Jung, K.; Atme, A.; Shanmugam, S.; Boyer, C. *J. Am. Chem. Soc.* **2014**, 136, 5508–5519.
- (30) Konkolewicz, D.; Schröder, K.; Buback, J.; Bernhard, S.; Matyjaszewski, K. *ACS Macro Lett.* **2012**, 1, 1219–1223.
- (31) Ribelli, T. G.; Konkolewicz, D.; Bernhard, S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2014**, 136, 13303–13312.
- (32) Fors, B. P.; Poelma, J. E.; Menyo, M. S.; Robb, M. J.; Spokoyny, D. M.; Kramer, J. W.; Waite, J. H.; Hawker, C. J. *J. Am. Chem. Soc.* **2013**, 135, 14106–14109.
- (33) Poelma, J. E.; Fors, B. P.; Meyers, G. F.; Kramer, J. W.; Hawker, C. J. *Angew. Chem., Int. Ed.* **2013**, 52, 6844–6848.
- (34) McKenzie, T. G.; Fu, Q.; Wong, E. H. H.; Dunstan, D. E.; Qiao, G. G. *Macromolecules* **2015**, 48, 3864–3872.
- (35) Jiangtao, X.; Sivaprakash, S.; Nathaniel Alan, C.; Boyer, C. In *Controlled Radical Polymerization: Mechanisms*; American Chemical Society: Washington, DC, 2015; Vol. 1187, pp 247–267.
- (36) Vandenbergh, J.; Junkers, T. *Macromolecules* **2014**, 47, 5051–5059.
- (37) Zhou, H.; Johnson, J. A. *Angew. Chem.* **2013**, 125, 2291–2294.
- (38) Chen, M.; Johnson, J. A. *Chem. Commun.* **2015**, 51, 6742–6745.
- (39) Matyjaszewski, K. *Polym. Int.* **2003**, 52, 1559–1565.
- (40) Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, 39, 7216–7223.
- (41) Liu, P.; Ye, Z.; Wang, W.-J.; Li, B.-G. *Polym. Chem.* **2014**, 5, 5443–5452.