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Achieving molecular weight distribution shape control and broad dispersities using RAFT polymerizations†

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Reversible addition–fragmentation chain-transfer (RAFT) polymerizations are one of the most versatile and powerful polymerization techniques for the synthesis of complex macromolecular architectures. While RAFT polymerizations often give polymers with narrow molecular weight distributions (MWDs), commodity plastics often have broad MWDs to give targeted properties and processability. Thus, new methods to precisely control both MWD breadth and shape are essential for fine-tuning polymer properties for next generation materials. Herein, we report a simple method for controlling polymer MWD features in thermally activated radical RAFT and redox activated cationic RAFT polymerizations by means of metered additions of chain transfer agents.

Introduction

Radical reversible addition–fragmentation chain-transfer (RAFT) polymerization is a versatile technique providing facile access to a wide range of polymers with predictable number average molecular weights (M_ns) and narrow molecular weight distributions (MWDs).[1–4] The scalability and commercial availability of dithiocarbonyl chain transfer agents (CTAs) renders RAFT polymerization a highly attractive technique for industrial applications.[1,5,6] Furthermore, a significant advantage of these processes is their tolerance to water, making them compatible with a variety of aqueous-phase reaction conditions including emulsion,[7] mini-emulsion,[8] and suspension[9] polymerizations. While it is valuable to generate polymers with narrow MWDs, it is often the case that polymers with broader MWDs are easier to process and are thus used in industrial settings.[10] More importantly, precise control of the breadth and shape[11,12] of a polymer's MWD can provide valuable handles for targeting desired physical properties and block copolymer morphology.[13]

Synthetic methods to control the entire MWD—both the breadth (dispersity, $Đ$) and shape—is a challenge that has recently attracted significant interest. As such, a variety of strategies for controlling a polymer's MWD have been developed.[14–38] In particular, several methods have focused on manipulating MWDs in RAFT polymerizations.[39–45] Boyer and co-workers employed a continuous flow PET-RAFT process in which adjusting pump flow rates over time led to control over a polymer's MWD.[39,44,46] Similarly, Junkers and co-workers were able to achieve broadened MWDs using radical RAFT polymerizations through automated continuous flow processes.[40,41] Recently, in a separate approach, Anastasaki and coworkers took advantage of two RAFT agents with different activities to afford MWDs over a broad range of $Đ$s.[42,43]

Our group has developed a method to deterministically control the shape and breadth of the MWD in a variety of polymerization systems (Scheme 1a).[13,47–55] This method utilizes metered additions of initiating species in controlled polymerizations to temporally regulate chain formation, and therefore, the final distribution of chain lengths. Previously, we have applied this method to anionic, nitroxide-mediated, and atom transfer radical polymerizations in which we could meter in an initiator into a solution of monomer.[13,47–54] In 2020, we also showed that we could apply this method to the polymerization of ethylene in which a co-initiator was required to activate a titanium phenoxyimine catalyst as it was being metered into the batch polymerization.[55] We envisaged that we could extend this method to thermally activated radical RAFT polymerizations in which a CTA could be metered into a solution of monomer and initiator (Scheme 1b). It is important to point out that this system would differ from our previous studies because the CTA does not act as the initiating species itself. Instead, addition of an active polymer chain to the CTA affords a stabilized dithiocarbonyl radical which, upon fragmentation, can generate new propagating chains. As the CTA is added over time into the ongoing polymerization process, new chains are

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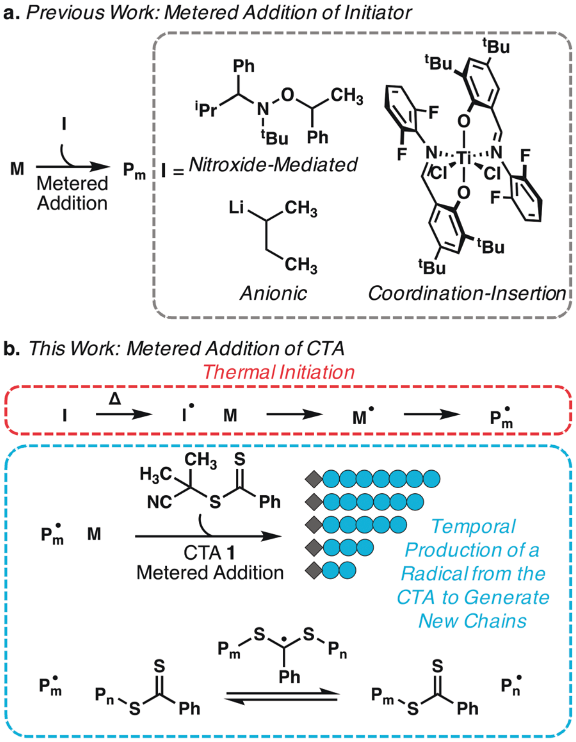


Scheme 1 (a) Controlling MWD shapes in polymerizations with a single initiating species. (b) Controlling MWD shapes in radical RAFT wherein the CTA, rather than the radical source, is metered in over time.

produced such that the polymer chain composition can be tailored. Furthermore, the retardation effects often seen in radical RAFT polymerizations using dithiobenzoate RAFT agents[56] provides an additional challenge, as the concentration of CTA is changed over time throughout the course of the reaction. Nonetheless, addition of the CTA over time will be able to control the polymerization by providing an equilibrium that minimizes the number of propagating radicals in solution.

Herein, we report a simple method for controlling both MWD shape and breadth in thermally activated radical RAFT polymerization by means of metered additions of the CTA. Using this method, we were able to produce polymers with dispersities as high as 6.2—the highest dispersity of any polymer synthesized using a metered addition of initiator previously reported by our group—and demonstrate their high chain-end fidelity by the synthesis of a diblock copolymer. Furthermore, we show that this general concept can be applied to redox activated cationic RAFT polymerization, producing polyvinyl ethers with controlled MWD features. We anticipate that this methodology will provide the early foundation for controlling MWD shape in industrially pertinent RAFT polymerizations.

Results and discussion

We began our investigation with the metered addition of CTA into the radical RAFT polymerization of methyl methacrylate (MMA) initiated by azobisisobutyronitile (AIBN) (Fig. 1). We chose 2-cyano-2-propyl benzodithioate (CTA **1**) as our CTA as it provides excellent control in radical RAFT polymerizations of MMA, giving samples with narrow Đ values and the ability to target M_n by changing the ratio of CTA to monomer. As a control sample, we heated a reaction with MMA, **1**, and 0.2 mol% of AIBN in toluene to 90 °C and monitored the reaction using ^{1}H NMR over the course of 6.5 h before quenching. As expected, a polymer with a narrow dispersity (Đ = 1.17) and good matching between experimental and theoretical M_n (M_n^exp = 10.3 kg mol^{-1}, M_n^theo = 11.9 kg mol^{-1}) was achieved with 60% monomer conversion as determined by ^{1}H NMR (Fig. 1, entry 1 and Table S9†).

We next proceeded with the metered addition of CTA **1** using various constant rates of addition (Fig. 1a–d, entries 2–5). To target the same M_n as in the control sample, the total molar concentrations of monomer, AIBN and CTA were held constant in all reactions. To achieve similar levels of conversion, all reactions were quenched after ~6 h (see Table S9† for details). Using a 0.5 h constant rate of addition and stopping the polymerization at ~60% conversion of MMA, we obtained PMMA with M_n^exp = 10.4 kg mol^{-1} and a broadened MWD, with Đ = 2.04 (Fig. 1a, entry 2). Based off our previous studies, a constant rate of addition provides a MWD with tailing toward low molar mass chains, a shift in the peak molecular weight (M_p) toward high molar mass chains, and an asymmetry factor greater than 1.0 (A_s > 1.0). In this case, we observed the opposite in which there was tailing toward higher molar mass PMMA chains with M_p shifted toward lower molar mass PMMA chains. The inability to control the MWD shape with short addition times could be the result of the induction time often observed with dithiobenzoate RAFT agents.[56] However, we found that increasing the addition time from 0.5 h to 1 h resulted in a polymer with a similar Đ but with A_s = 1.28 (Fig. 1a, entry 3). Under similar reaction conditions but using a 2 h addition time, the MWD was broadened even more to a Đ = 2.87 with an A_s of 1.46 (Fig. 1a, entry 4). Increasing the addition time of CTA **1** to 2.5 h afforded a 12.0 kg mol^{-1} polymer with Đ = 3.51 and A_s = 1.47 (Fig. 1a, entry 5). In each case, we observed good matching between M_n^theo and M_n^exp, indicating a controlled process. Increasing the addition time above 2.5 h did not result in any increase in Đ (Fig. S1†), giving this method a maximum Đ of ~3.5 for this molar mass. It is important to note that these polymers have monomodal MWDs, indicating that even at low CTA concentrations in the beginning of the reaction, polymer chains still enter the RAFT equilibrium such that uncontrolled free-radical polymerization is supressed. Furthermore, we found that Đ increases linearly with the addition time of CTA **1**, demonstrating the predictability of this method (Fig. 1d).

To further probe the extent to which MWD shape can be tailored in thermally activated radical RAFT, we set out to produce PMMA with the opposite MWD shape skewed to higher molar mass (A_s < 1.0). Interestingly, an exponentially increasing rate of CTA **1** addition results in a bimodal distribution (Fig. S2†). We posit that this is due to an insufficient

a.

Entry		Addition Time (h)	M_n^{theo} (kg/mol)[a]	M_n^{exp} (kg/mol)[b]	A_s[c]	Đ[c]
1	—	0	11.9	10.3	1.53	1.17
2	—	0.5	12.5	10.4	0.55	2.04
3	—	1.0	12.1	9.8	1.28	2.03
4	—	2.0	10.3	13.0	1.46	2.87
5	—	2.5	12.3	12.0	1.47	3.51

e.

Entry		Addition Time (h)	M_n^{theo} (kg/mol)[a]	M_n^{exp} (kg/mol)[b]	A_s[c]	Đ[c]
1	—	0	11.9	10.3	1.53	1.17
6	—	0.25	11.8	10.3	0.68	2.07
7	—	0.50	11.8	10.1	0.37	2.61
8	—	1.0	11.3	11.1	0.35	3.52
9	—	1.1	10.9	7.3	0.43	5.51
10	—	1.25	11.1	7.7	0.69	6.23

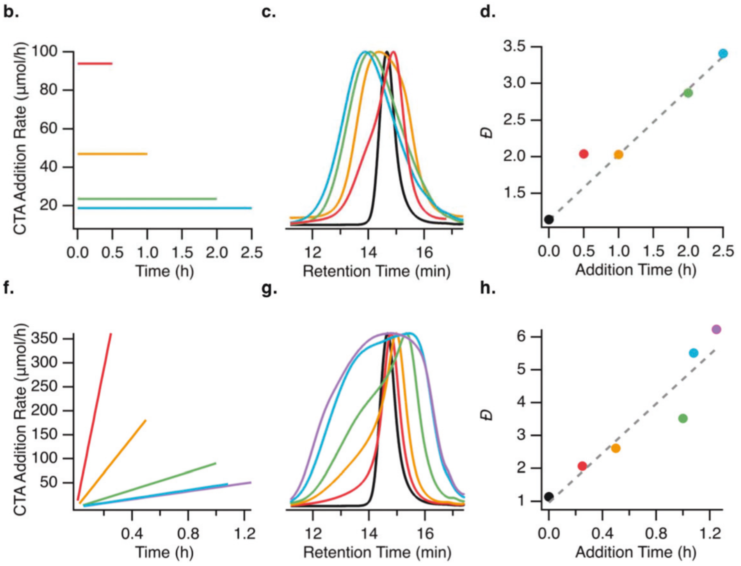


Fig. 1 Controlling MWDs in radical RAFT polymerization using (a–d) constant or (e–h) linearly increasing rates of CTA **1** addition. [a] Determined from ^{1}H NMR conversions. [b] Calculated from light scattering (LS) GPC data using a d*n*/d*c* of 0.0812. [c] Calculated from refractive index (RI) GPC relative to PS standards. All reactions were heated to 90 °C and the metered addition of CTA **1** was started when the vial was warm to touch. Reactions were run to ~60% conversion (~6 h, see Table S9† for details). Stock solutions of CTA **1** and AIBN in toluene were prepared such that [CTA **1**] = 0.07 M and [AIBN] = 0.01 M. Reaction equivalents MMA : CTA **1** : AIBN = 199 : 1 : 0.2.

concentration of CTA relative to AIBN in the beginning of the reaction such that uncontrolled free-radical polymerization of MMA dominates. To circumvent this issue, we moved to linearly increasing rates of initiator addition to eliminate any significant period of time that the reaction was allowed to stir with very low concentrations of CTA. In support of this hypothesis, we found that linearly increasing rates of addition of CTA **1** afforded PMMA with broadened MWDs and tailing toward higher molar mass chains (Fig. 1e–h, entries 6–10). Varying the addition time between 0.25 h to 1.0 h enabled the production of PMMA with the desired MWD shape, good matching between M_n^{theo} and M_n^{exp}, and with Đs between 2.07 and 3.52 (entries 6–8). We were additionally able to produce PMMA with extremely broad MWDs and with tailing toward high molar mass chains. Increasing the addition time beyond 1 h using a linearly increasing rate of addition afforded PMMA with Đs as high as 6.23 while maintaining the overall desired MWD shape and reasonably good matching between theoretical and experimental molecular weights (entries 9 and 10). As with our results from the constant rates of addition, we found that Đ increases linearly with the addition time of CTA **1** (Fig. 1h). These results demonstrate our ability to efficiently control MWD shapes in thermally activated radical RAFT polymerizations *via* metered additions of a CTA. Interestingly, the addition of CTA in these radical RAFT processes has allowed us to control MWD shapes at Đ values of >2, which is complementary to our previously reported methods for controlling MWD shapes at lower values of Đ using anionic, nitroxide-mediated, or coordination–insertion polymerization.

An advantage of RAFT polymerization is its utility in the production of well-defined block copolymers, which is enabled by the high chain-end fidelity (chains terminated with the dithiobenzoate chain end). To evaluate chain-end fidelity in our polymers with broadened distributions, we chain extended a disperse PMMA (PMMA$_{broad}$, Đ = 3.51, A_s = 1.47) macro-CTA with benzyl methacrylate (BMA) (Fig. 2a). The chain extension yielded a monomodal diblock with an M_n of 39.1 kg mol^{-1} and a Đ of 1.55 (Fig. 2b). The clean shift in M_p and the good match-

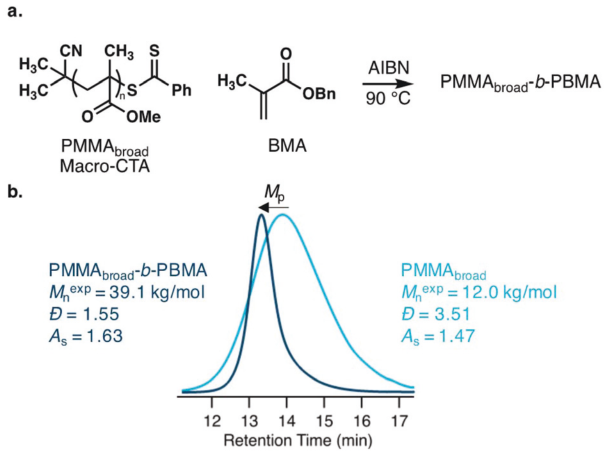
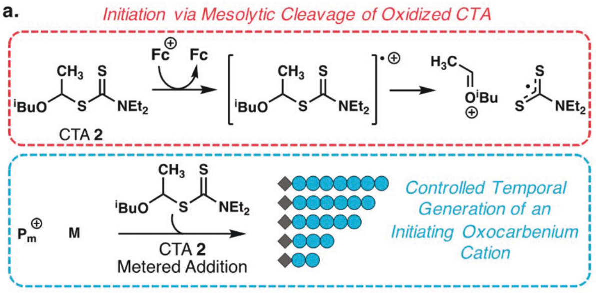


Fig. 2 Assessing chain-end fidelity of PMMA$_{broad}$ through use as a macro-CTA for chain extension with benzyl methacrylate. For PMMA$_{broad}$-*b*-PBMA, M_n was determined from ^{1}H NMR conversion. Đ and A_s were calculated from RI GPC relative to PS standards. Reaction was run for 5 h (~43% conversion of BMA). Stock solutions of the macro-CTA and AIBN in toluene were prepared such that [macro-CTA] = 0.015 M and [AIBN] = 0.0125 M. Reaction equivalents BMA : macro-CTA : AIBN = 342 : 1 : 0.2.

ing between theoretical and experimental molecular weights for the diblock copolymer (M_n^theo = 37.8 kg mol^{-1}, M_n^exp = 39.1 kg mol^{-1}) demonstrated excellent chain end fidelity in our polymers (Fig. S3†).

Inspired by these results, we posited that a similar strategy could be employed in the redox activated cationic RAFT polymerization, which uses ferrocenium tetrafluoroborate ($FcBF_4$) as a mild chemical oxidant. In this mechanism, $FcBF_4$ oxidizes CTA **2** to the radical cation, which subsequently undergoes mesolytic cleavage to form a stabilized dithiocarbonyl radical and an oxocarbenium cation which initiates polymerization of isobutyl vinyl ether (IBVE) (Fig. 3a). Thus, metered addition of CTA **2** should enable control over the resulting polymer MWD features. However, it is important to note that unlike in thermally activated radical RAFT where chain initiation by AIBN is independent of the CTA concentration, in this cationic RAFT mechanism, initiation is dependent on the CTA concentration as initiation occurs through direct oxidation of the CTA by $FcBF_4$. By metering in CTA over time, the concentration of CTA, and therefore initiation kinetics, changes over time. We anticipated that gaining control over MWD features would be inherently more challenging in this particular cationic RAFT system than in thermally activated radical RAFT polymerization. Further complicating the task, uncontrolled generation of new chains can occur in these polymerizations by direct monomer oxidation.



b.

Entry		Addition Time (h)	M_n^theo (kg/mol)[a]	M_n^exp (kg/mol)[b]	A_s[c]	$Đ$[c]
11	—	0	10.0	12.7	1.35	1.22
12	—	1.0	9.0	11.1	1.32	1.29
13	—	1.5	10.0	12.9	1.70	1.78
14	—	2.0	10.0	11.3	2.20	1.98

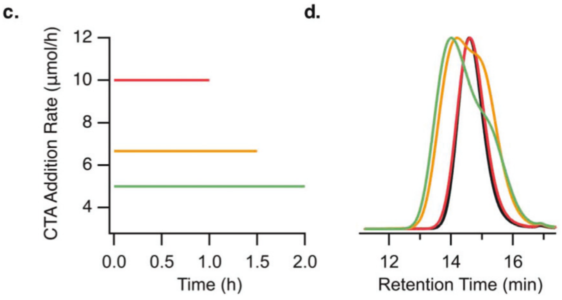


Fig. 3 Controlling MWDs in redox activated cationic RAFT polymerization of IBVE. [a] Determined from ^1H NMR conversions. [b] Calculated from LS GPC data using a d*n*/d*c* of 0.0381. [c] Calculated from RI GPC relative to PS standards. Reactions were run to ~100% conversion (~5 h). Stock solutions of CTA **2** and ferrocenium in dichloromethane were prepared such that [CTA **2**] = 0.02 M and [$FcBF_4$] = 2 mM. Reaction equivalents IBVE : CTA **2** : $FcBF_4$ = 100 : 1 : 0.0002.

As a proof of concept, a constant rate of CTA **2** addition afforded PIBVE with good matching between M_n^theo and M_n^exp, and with broadened MWDs tailing toward low molar mass chains (Fig. 3b–d). However, using either linearly or exponentially increasing rates of CTA **2** addition, we were unable to access monomodal distributions of the opposite MWD shape. Instead, we observed bimodal distributions in both cases (Fig. S4†). We expect that the concentration of CTA in the beginning of the reaction is too low using these addition profiles, such that direct monomer oxidation and uncontrolled cationic polymerization occurs before sufficient CTA is introduced into the reaction. Future studies will investigate the efficacy of our method in other cationic polymerizations wherein initiation is not influenced by CTA concentration. However, this is still an excellent method to broaden MWDs in the cationic polymerization of vinyl ethers.

Conclusions

Our results show that metered additions of chain transfer agents can be used to deterministically control polymer MWD breadth and shape in RAFT polymerizations. Using this strategy, we were able to produce well-defined polymers with tailored MWDs and dispersities as high as 6.2 in thermally activated radical RAFT polymerizations. High chain-end fidelity was demonstrated by the synthesis of a diblock copolymer *via* chain extension of a $PMMA_\text{broad}$ macro-CTA. We suspect that we can also achieve MWD shape control in radical RAFT by metering in a combination of AIBN and CTA, which is something our lab will pursue in future studies. Furthermore, preliminary studies revealed that this general strategy could be extended to a redox activated cationic RAFT polymerization. Additional studies will investigate the effect of metered CTA additions in cationic RAFT polymerizations in which initiation is independent of the CTA. We anticipate that our results will open the door for controlling MWD features in industrially-attractive RAFT polymerizations.

Conflicts of interest

There are no conflicts to declare.

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References

1 S. Perrier, *Macromolecules*, 2017, **50**, 7433–7447.

2 C. Barner-Kowollik, *Handbook of RAFT Polymerization*, Wiley-VCH Verlag, Weinheim, 2008.

3 G. Moad, E. Rizzardo and S. H. Thang, *Chem. – Asian J.*, 2013, **8**, 1634–1644.

4 X. Tian, J. Ding, B. Zhang, F. Qiu, X. Zhuang and Y. Chen, *Polymers*, 2018, **10**, 318.

5 M. Destarac, *Macromol. React. Eng.*, 2010, **4**, 165–179.

6 N. Micic, A. Young, J. Rosselgong and C. H. Hornung, *Processes*, 2014, **2**, 58–70.

7 For select examples, see: (*a*) C. J. Ferguson, R. J. Hughes, B. T. T. Pham, B. S. Hawkett, R. G. Gilbert, A. K. Serelis and C. H. Such, *Macromolecules*, 2002, **35**, 9243–9245; (*b*) S. W. Prescott, M. J. Ballard, E. Rizzardo and R. G. Gilbert, *Aust. J. Chem.*, 2002, **55**, 415–424; (*c*) J. Zhou, H. Yao and J. Ma, *Polym. Chem.*, 2018, **9**, 2532–2561; (*d*) N. G. Engelis, A. Anastasaki, G. Nurumbetov, N. P. Truong, V. Nikolaou, A. Shegiwal, M. R. Whittaker, T. P. Davis and D. M. Haddleton, *Nat. Chem.*, 2017, **9**, 171–178.

8 For select examples, see: (*a*) J. Jiang, W. J. Wang, B. G. Li and S. Zhu, *Ind. Eng. Chem. Res.*, 2019, **58**, 18997–19008; (*b*) Y. Luo, R. Wang, L. Yang, B. Yu, B. Li and S. Zhu, *Macromolecules*, 2006, **39**, 1328–1337; (*c*) X. Li, W.-J. Wang, F. Weng and B.-G. Li, *Ind. Eng. Chem. Res.*, 2014, **53**, 7321–7332.

9 For select examples, see: (*a*) H. Bouhamed, S. Boufi and A. Magnin, *J. Colloid Interface Sci.*, 2007, **312**, 279–291; (*b*) W. Zhang, B. Charleux and P. Cassagnau, *Macromolecules*, 2012, **45**, 5273–5280; (*c*) J. D. Biasutti, T. P. Davis, F. P. Lucien and J. P. A. Heuts, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 2001–2012; (*d*) Y. Zhang, J. Ding and S. Gong, *J. Appl. Polym. Sci.*, 2013, **128**, 2927–2932.

10 M. Stürzel, S. Mihan and R. Mülhaupt, *Chem. Rev.*, 2016, **116**, 1398–1433.

11 S. S. Rane and P. Choi, *Chem. Mater.*, 2005, **17**, 926.

12 S. Harrisson, *Polym. Chem.*, 2018, **9**, 1366–1370.

13 D. T. Gentekos, R. J. Sifri and B. P. Fors, *Nat. Rev. Mater.*, 2019, **4**, 761–774.

14 R. L. Laurence and G. Vasudevan, *Ind. Eng. Chem. Process Des. Dev.*, 1968, **7**, 427–433.

15 D. A. Couso, L. M. Alassia and G. R. Meira, *J. Appl. Polym. Sci.*, 1985, **30**, 3249–3265.

16 K.-I. Seno, S. Kanaoka and S. Aoshima, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 2212–2221.

17 P. D. Hustad, G. R. Marchand, E. I. Garcia-Meitin, P. L. Roberts and J. D. Weinhold, *Macromolecules*, 2009, **42**, 3788–3794.

18 J. M. Widin, A. K. Schmitt, K. Im, A. L. Schmitt and M. K. Mahanthappa, *Macromolecules*, 2010, **43**, 7913–7915.

19 A. Plichta, M. Zhong, W. Li, A. M. Elsen and K. Matyjaszewski, *Macromol. Chem. Phys.*, 2012, **213**, 2659–2668.

20 J. M. Widin, A. K. Schmitt, A. L. Schmitt, K. Im and M. K. Mahanthappa, *J. Am. Chem. Soc.*, 2012, **134**, 3834–3844.

21 A. K. Schmitt and M. K. Mahanthappa, *Macromolecules*, 2014, **47**, 4346–4356.

22 D. Liu, A. D. Sponza, D. Yang and M. Chiu, *Angew. Chem., Int. Ed.*, 2019, **58**, 16210–16216.

23 R. Whitfield, N. P. Truong, D. Messmer, K. Parkatzidis, M. Rolland and A. Anastasaki, *Chem. Sci.*, 2019, **10**, 8724–8734.

24 R. Whitfield, K. Parkatzidis, M. Rolland, N. P. Truong and A. Anastasaki, *Angew. Chem., Int. Ed.*, 2019, **58**, 13323–13328.

25 T. T. Wang, Y. Y. Wu, Z. H. Luo and Y. N. Zhou, *Macromolecules*, 2020, **53**, 10813–10822.

26 L. M. Alassia, D. A. Couso and G. R. Meira, *J. Appl. Polym. Sci.*, 1988, **36**, 481–494.

27 T. Junkers and J. H. Vrijsen, *Eur. Polym. J.*, 2020, **134**, 109834.

28 D. J. Walsh, D. A. Schinski, R. A. Schneider and D. Guironnet, *Nat. Commun.*, 2020, **11**, 3094.

29 H. Liu, Y. H. Xue, Y. L. Zhu, F. L. Gu and Z. Y. Lu, *Macromolecules*, 2020, **53**, 6409–6419.

30 T. Junkers, *Macromol. Chem. Phys.*, 2020, **221**, 2000234.

31 M. Rolland, N. P. Truong, R. Whitfield and A. Anastasaki, *ACS Macro Lett.*, 2020, **9**, 459–463.

32 W. Fischer, K. Knoll, W. Loth, V. Warzelhan, A. Deffieux, P. Desbois, M. Fontanille, S. Lätsch, C. Schade and H. Gausepohl, US6444762B1, 1997.

33 D. Bendejacq, V. Ponsinet, M. Joanicot, Y. L. Loo and R. A. Register, *Macromolecules*, 2002, **35**, 6645–6649.

34 E. Farkas, Z. G. Meszena and A. F. Johnson, *Ind. Eng. Chem. Res.*, 2004, **43**, 7356–7360.

35 N. A. Lynd and M. A. Hillmyer, *Macromolecules*, 2005, **38**, 8803–8810.

36 N. A. Lynd and M. A. Hillmyer, *Macromolecules*, 2007, **40**, 8050–8055.

37 A. J. Meuler, C. J. Ellison, C. M. Evans, M. A. Hillmyer and F. S. Bates, *Macromolecules*, 2007, **40**, 7072–7074.

38 J. Listak, W. Jakubowski, L. Mueller, A. Plichta, K. Matyjaszewski and M. R. Bockstaller, *Macromolecules*, 2008, **41**, 5919–5927.

39 N. Corrigan, A. Almasri, W. Taillades, J. Xu and C. Boyer, *Macromolecules*, 2017, **50**, 8438–8448.

40 M. Rubens and T. Junkers, *Polym. Chem.*, 2019, **10**, 5721–5725.

41 M. Rubens and T. Junkers, *Polym. Chem.*, 2019, **10**, 6315–6323.

42 R. Whitfield, K. Parkatzidis, N. P. Truong, T. Junkers and A. Anastasaki, *Chem*, 2020, **6**, 1340–1352.

43 K. Parkatzidis, N. P. Truong, M. N. Antonopoulou, R. Whitfield, D. Konkolewicz and A. Anastasaki, *Polym. Chem.*, 2020, **11**, 4968–4972.

44 K. Liu, N. Corrigan, A. Postma, G. Moad and C. Boyer, *Macromolecules*, 2020, **53**, 8867–8882.

45 K. Parkatzidis, H. Suk Wang, N. P. Truong and A. Anastasaki, *Chem*, 2020, **6**, 1575–1588.

46 N. Corrigan, R. Manahan, Z. T. Lew, J. Yeow, J. Xu and C. Boyer, *Macromolecules*, 2018, **51**, 4553–4563.

47 D. T. Gentekos and B. P. Fors, *ACS Macro Lett.*, 2018, **7**, 677–682.

48 D. T. Gentekos, J. Jia, E. S. Tirado, K. P. Barteau, D.-M. Smilgies, R. A. DiStasio and B. P. Fors, *J. Am. Chem. Soc.*, 2018, **140**, 4639–4648.

49 S. I. Rosenbloom, D. T. Gentekos, M. N. Silberstein and B. P. Fors, *Chem. Sci.*, 2020, **11**, 1361–1367.

50 V. Kottisch, D. T. Gentekos and B. P. Fors, *ACS Macro Lett.*, 2016, **5**, 796–800.

51 S. Domanskyi, D. T. Gentekos, V. Privman and B. P. Fors, *Polym. Chem.*, 2020, **11**, 326–336.

52 S. I. Rosenbloom and B. P. Fors, *Macromolecules*, 2020, 7479–7486.

53 M. Nadgorny, D. T. Gentekos, Z. Xiao, S. P. Singleton, B. P. Fors and L. A. Connal, *Macromol. Rapid Commun.*, 2017, **38**, 1700352.

54 D. T. Gentekos, L. N. Dupuis and B. P. Fors, *J. Am. Chem. Soc.*, 2016, **138**, 1848.

55 R. J. Sifri, O. Padilla-Veíez, G. W. Coates and B. P. Fors, *J. Am. Chem. Soc.*, 2020, **142**, 1443–1448.

56 C. Barner-kowollik, M. Buback, B. Charleux, M. L. Coote, M. Drache, T. Fukuda, A. Goto, B. Klumperman, A. B. Lowe, J. B. Mcleary, G. Moad, M. J. Monteiro, R. D. Sanderson, M. P. Tonge, P. Vana and P. Marie, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 5809–5831.