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Moisture tolerant cationic RAFT polymerization of vinyl ethers

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Moisture tolerant cationic RAFT polymerization of vinyl ethers

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Cationic reversible addition—fragmentation chain transfer (RAFT) polymerizations have permitted the controlled polymerization of vinyl ethers and select styrenics with predictable molar masses and easily modified thiocarbonylthio chain ends. However, most cationic RAFT systems require inert reaction conditions with highly purified reagents and low temperatures. Our groups recently developed a living cationic polymerization that does not require these rigorous conditions by utilizing a strong organic acid (pentacarbomethoxycyclopentadiene (PCCP)) and a hydrogen bond donor. By combining our PCCP acid promoted polymerization with a chain transfer agent, we have designed a tolerant cationic RAFT system that can be performed neat, open to the air, and at room temperature. Additionally, this system allows us to utilize catalytic amounts of the PCCP acid to furnish polymers with chain end functionality that can be easily isolated and further manipulated to make functional materials.

Introduction

Reversible addition–fragmentation chain–transfer (RAFT) polymerizations provide controlled polymerization through a degenerate chain–transfer mechanism.[1,2] Traditionally a radical process, the first report of cationic RAFT polymerization by Kamigaito in 2015 utilized thiocarbonylthio chain-transfer agents (CTAs) and a Brønsted acid initiator to controllably polymerize vinyl ethers and electron-rich styrenics with stable chain ends.[3] Since then, further work has expanded the scope of cationic degenerate chain transfer polymerizations, such as the discovery of alternate CTAs (*i.e.*, thioethers, alcohols, and phosphoric/phosphinic acids).[4–8] In addition to the use of strong acids for initiation,[3,9,10] cationic RAFT can also be initiated by the combination of alkyl chlorides with a variety of Lewis acids, as well as through the oxidation of the CTA chemically, photochemically, and electrochemically.[5,11–16] With the diversity of strategies for cationic RAFT continuing to grow, the method has been utilized to make complex polymer architectures, as well as intricate compositions through mechanistic interconversion to radical polymerization.[3,9,12,17–21] Despite these advancements, such techniques often require highly purified monomers and solvents, inert atmospheres, and low temperatures to prevent unwanted chain transfer and termination events.

As conventional "living" cationic polymerizations (LCPs) involve similar requirements, recent work has focused on simplifying the reaction conditions and expanding the utility of the resulting polymers.[22] For example, in 2019, Pan, Zhang, Zhu, and co-workers utilized an *in situ* generated manganese catalyst

(Mn(CO)$_5$Br) for the controlled cationic polymerization of vinyl ethers at 0 °C without rigorous purification of reagents.[23] Simplifying the reaction conditions even further, Perrier, Zhu, and co-workers adapted the manganese-catalysed system to cationic RAFT that was performed at room temperature and without degassing, demonstrating a tolerance to water.[24,25] Utilizing the same Mn(CO)$_5$Br catalyst, Li, Zhu, and co-workers incorporated electrophilic selenium reagents as initiators to achieve controlled cationic polymerization under ambient conditions.[26] To accomplish the same ease of use, they also recently leveraged selenonium cations as Lewis acids to promote initiation and propagation in cationic RAFT, despite the presence of water.[27]
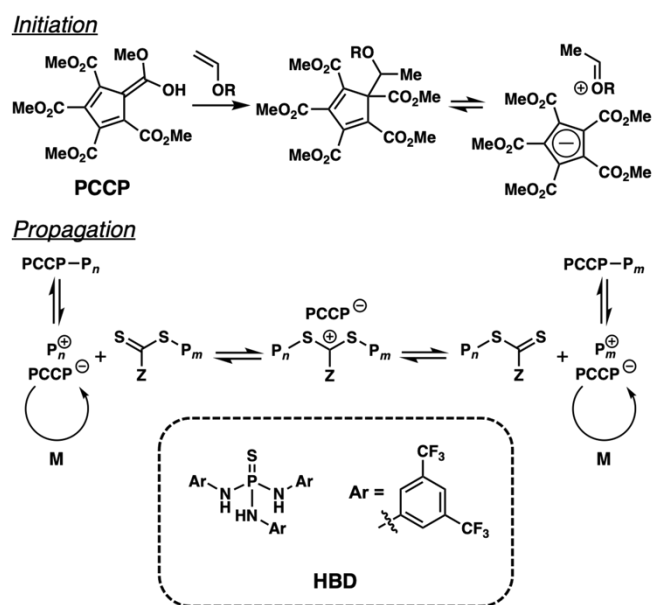

Figure 1. Proposed initiation and propagation for degenerate chain transfer with PCCP.

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Similarly, we recently developed a method of "living" cationic polymerization that can be performed open to the air, at room temperature, and without the need for rigorous purification of monomers.[28] The initial system initiated controlled polymerization of vinyl ethers with 1,2,3,4,5-pentacarbomethoxycyclopentadiene (PCCP), an acid with an unusually low pK_a for a carbon acid due to the additive effects of induction, resonance, and aromaticity.[29,30] Despite its high acidity, PCCP is a bench-stable, inexpensive solid that is easy to handle. Initiation occurred when PCCP protonated a vinyl ether to reveal a propagating oxocarbenium ion with the PCCP as the counteranion. We have proposed that this ion pair is in equilibrium with a dormant covalent adduct, which reduced the number of propagating chain ends. This equilibrium, combined with the interaction of the PCCP anion and cationic chain end, reduced deleterious reactions with nucleophiles and, hence, prevented the need for air-free conditions and rigorous purification of the reagents. However, as the degree of polymerization increased, molecular weights were lower and distributions were broader than predicted. We hypothesized that these effects were due to irreversible chain transfer caused by the PCCP anion deprotonating alpha to the oxocarbenium ion, leading to termination of the chain and protonation of the PCCP, which could then initiate a new polymer. To address this challenge, a hydrogen bond donor (HBD) was added to decrease the basicity of the PCCP anion to prevent this undesired elimination and reformation of the PCCP acid. As predicted, a thiophosphoramide HBD resulted in faster polymerizations with higher molecular weights, while still maintaining tolerance to atmospheric conditions.[31]

We envisioned that these benefits could be adapted to cationic RAFT by utilizing small amounts of PCCP acid and HBD for initiation, along with a dithiocarbonyl CTA (Figure 1). In this design, the PCCP acid would act as the cationogen and counter ion to propagating chain ends, and the HBD would reduce termination and subsequent chain transfer, as with our previous system. However, by adding the capabilities of cationic RAFT, the CTA would provide an additional level of control by allowing for degenerate chain transfer through the thiocarbonylthio functional group. Therefore, with the combination of these techniques, we posited that chain end protection would be particularly robust and, hence, tolerant of nucleophiles, especially water, that often cause termination. As a result, this strategy would circumvent the rigorous purification of reagents and the use of an inert atmosphere previously common to cationic RAFT, while still providing the benefits of the thiocarbonylthio CTA, such as catalytic amounts of initiator and high chain end fidelity. Herein, we report the realization of this idea for the moisture tolerant cationic RAFT polymerization of vinyl ethers.

Results and discussion

We began our investigation of this proposed system by combining isobutyl vinyl ether (IBVE) and the dithiocarbamate CTA with varying amounts of PCCP and HBD. Addition of 0.025 mol% of both PCCP and HBD led to a 16.0 kg/mol polymer with

Table 1. Polymerizations with varying monomer feed ratios afforded polymers with expected molar masses and narrow distributions. Control experiments showed the necessity for both PCCP and HBD but not for a nitrogen atmosphere or rigorous monomer purification.

Entry[a]	IBVE:PCCP:HBD	Time (h)	M_n^{theo} (kg/mol)	M_n^{exp} (kg/mol)	Đ
1[b]	200:0.05:0.05	4	14.1	16.0	1.17
2[b]	200:0.05:0	26	1.6	2.0	1.67
3[b]	200:0:1	26	0	-	-
4[b,c]	200:0.05:0.05	5	15.7	17.2	1.17
5	200:0.05:0.05	3.5	15.9	18.6	1.11
6	300:0.075:0.075	3.5	21.9	23.5	1.22
7	400:0.1:0.1	3.5	29.0	26.7	1.26
8	600:0.15:0.15	3.5	43.0	35.7	1.31
9	800:0.2:0.2	3.5	51.7	46.6	1.27
10	1200:0.3:0.3	3.5	68.6	47.8	1.38

[a]IBVE (200—1200 equiv, 5.6 mmol, filtered through basic alumina) was added to CTA (1 equiv), PCCP, and HBD and stirred under ambient atmosphere at room temperature unless otherwise noted. [b]Performed under nitrogen atmosphere. [c]Performed with distilled monomer.

a dispersity (Đ) of 1.17 in 4 h, and excellent agreement between theoretical and experimental molar masses was observed (Table 1, entry 1). Removal of the HBD under identical conditions resulted in a significantly slower reaction rate, reaching only 7% conversion after 26 h (Table 1, entry 2). This result demonstrated that the HBD was critical for these polymerizations. As expected, when the PCCP was removed from the polymerization, no initiation was seen (Table 1, entry 3). Lowering the PCCP and HBD equivalents to 0.013 mol% resulted in increased reaction times and broadened Đs, while increasing the two reagents to 0.050 mol% showed no significant improvements over the reaction with 0.025 mol% of each (Table S1). Use of dichloromethane (DCM) as a solvent led to slightly higher conversions but similar or increased Đs (Table S2 and S3). This broadening of distributions was also observed in polymerizations initiated solely by PCCP when various solvents, including DCM, were added.[28,32]

These initial reactions were run under an inert atmosphere of N_2 with unpurified monomer. When the optimized conditions were used with distilled monomer, no difference in the resultant polymer was observed, illustrating that monomer purification was unnecessary (Table 1, entry 4). More importantly, when the same reaction was run with unpurified monomer and open to the air, identical levels of control were observed (Table 1, entry 5). This result suggests that the user-friendly benefits of our initial PCCP based cationic polymerizations translated to this new RAFT system. To further explore this method, these conditions were applied to a variety of monomer to CTA ratios at room temperature under ambient conditions. In all cases, very little to no decomposition of IBVE to acetaldehyde and isobutanol was observed even though
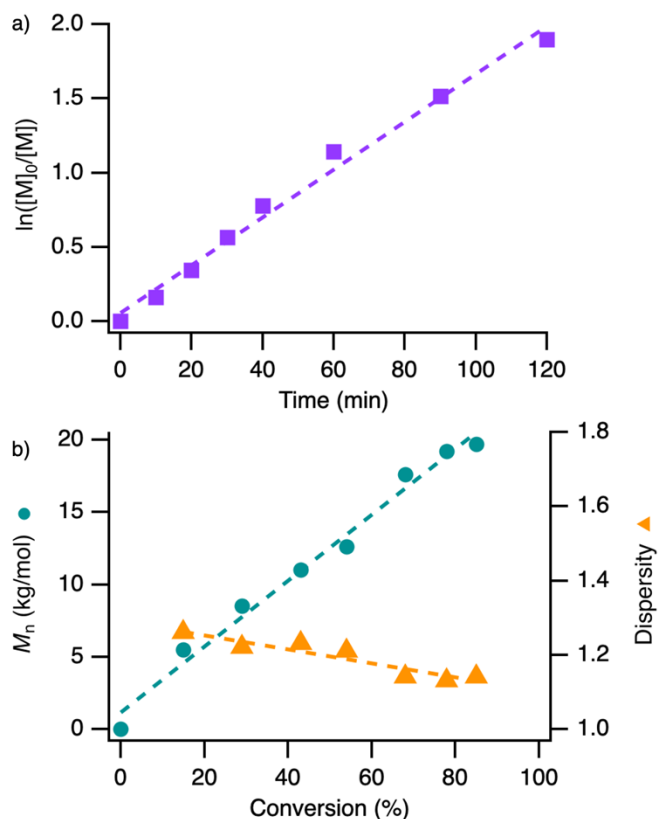
Figure 2. a) Semilogarithmic plot showed first order kinetics, indicating a constant concentration of propagating cations throughout the polymerization. b) Molecular weight increased linearly, and dispersity decreased with increased conversion. Hence, kinetic analysis suggested that the polymerization has living characteristics.

Table 2. Controlled polymerization of cyclic and acyclic vinyl ethers accessible with PCCP initiated RAFT.

Entry[a]	Monomer	HBD equiv	Time (h)	M_n^{theo} (kg/mol)	M_n^{exp} (kg/mol)	Đ
1	EVE	0.15	16	12.9	12.2	1.11
2	Cl-EVE	0.30	41	11.4	10.9	1.25
3[b]	DHF	0.05	22	11.4	8.5	1.24
4[b]	TBVE	0.05	18	10.9	9.5	1.78
5[b,c]	CyVE	0.05	3	24.2	17.6	1.68

[a]Vinyl ether (200 equiv, 5.6 mmol, filtered through basic alumina), CTA (1 equiv, 0.028 mmol), PCCP (0.05 equiv, 0.0014 mmol), and HBD were stirred under ambient atmosphere at room temperature unless otherwise noted. [b]Performed with 1:2 of DCM:VE by volume. [c]Performed at 0 ºC.

these reactions were run open to the air. Polymers with $M_{n,theo}$ below 50 kg/mol exhibited low Đs and good matching with $M_{n,exp}$ (Table 1, entries 5-8). The control over the predicted molar masses suggests that each dithiocarbamate CTA generated a single polymer chain, while the narrow Đs indicate that initiation was relatively fast. Both of these observations indicate a polymerization with living characteristics.[33]

However, as the amount of monomer increased past 800 equivalents relative to the CTA, the experimental molar mass remained around 50 kg/mol, despite theoretical molecular weights increasing (Table 1, entries 9 and 10). When more HBD was added in an attempt to reduce possible chain transfer events, the polymerization was faster but little effect on the experimental molecular weight and dispersity was observed (Table S4, entries 1-3). This trend was consistent at lower molecular weights as well, in which an increase in HBD had little effect on the results (Table S1, entries 3-5). Upon the addition of both more PCCP and HBD, no improvement in molecular weight nor dispersity was observed (Table S4, entries 4-6). A potential reason for this is that the ratio of monomer to PCCP remained constant, so as equivalents of monomer increased to achieve larger molecular weights, the ratio of PCCP to CTA also increased. Therefore, the PCCP mechanism, which displayed less control at room temperature,[31] may compete with the RAFT mechanism to prevent larger M_ns.

It is worth reemphasizing that the trends in molecular weight and dispersity were consistent regardless of atmosphere or purification method (Table S5). The polymerizations performed under air with unpurified monomer produced similar results to those done under a nitrogen atmosphere with distilled monomer. The similarity of the results suggested that the chain end was sufficiently protected, as an increase in nucleophiles that could have caused unwanted termination actually had little effect on the polymerization results. To confirm that this polymerization technique still had living characteristics with impurities present, despite the low equivalents of PCCP and HBD, the reaction was monitored up to 85% conversion by ^{1}H-NMR and GPC. When the conversion was plotted in a semilogarithmic plot, a linear trend was observed, suggesting first order kinetics with respect to monomer conversion and, thus, that the concentration of active chain ends remained constant throughout the polymerization (Figure 2a). Furthermore, as conversion increased, the average M_n increased linearly and the Đ decreased (Figure 2b). At 85% conversion, the reaction became too viscous to continue sampling. As a result, kinetics were also performed with the addition of DCM, up to 95% conversion (Figure S7). While the polymerization was slightly slower with DCM, the semilogarithmic plot still displayed first order kinetics, and the molecular weights were predictable with correspondingly narrow distributions. Overall, this data is consistent with the criteria for a polymerization with living characteristics.[34]

This system also enabled the polymerization of many vinyl ethers under ambient conditions, including ethyl vinyl ether (EVE), 2-chloroethyl vinyl ether (Cl-EVE), 2,3-dihydrofuran (DHF), *tert*-butyl vinyl ether (TBVE), and cyclohexyl vinyl ether (CyVE) (Table 2). For EVE and Cl-EVE, additional HBD was required to increase the rate of polymerization. In the case of DHF, TBVE, and CyVE, DCM was added to permit stirring at higher conversions due to the higher T_gs of the polymers. Polymerizations of CyVE also had to be cooled to 0 °C due to
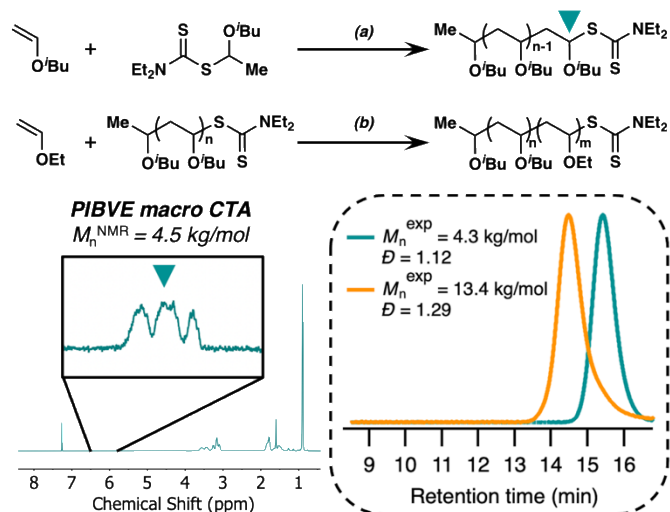
(a) IBVE (50 equiv, 5.6 mmol), CTA (1 equiv, 0.11 mmol), PCCP (0.013 equiv, 0.0014 mmol), HBD (0.013 equiv, 0.0014 mmol), air, room temp, 6 h.
(b) EVE (140 equiv, 3.5 mmol), PIBVE macro CTA (1 equiv, 0.025 mmol), PCCP (0.05 equiv, 0.0013 mmol), HBD (0.15 equiv, 0.0038 mmol), air, room temp, 6 h.

Figure 3. High chain end fidelity was demonstrated through ^{1}H-NMR analysis and chain extension with EVE under ambient conditions.
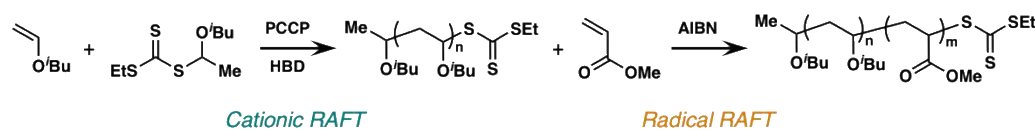
increased rate of polymerization. Polymerizations of these monomers performed under nitrogen did not improve the results, again demonstrating the robustness of the system (Table S6).

Chain end fidelity was probed by chain end analysis of precipitated PIBVE with ^{1}H-NMR, giving an $M_{n,NMR}$ that matched the $M_{n,exp}$ (Figure 3).[3] As a further demonstration of chain end fidelity, the chain extension of PEVE from precipitated PIBVE was performed, showing a clear shift to higher molar masses, while maintaining monomodal narrow distributions. Using ^{1}H-NMR analysis to calculate the degree of polymerization of the second block, the experimental M_n found from this method matched the theoretical M_n from conversion (Figure S10). When compared to chain extensions done under nitrogen both sequentially in one-pot (Figure S8) and stepwise after

precipitation (Figure S9), the results agreed with the diblock synthesized under ambient conditions. The ability to chain extend, combined with the data from ^{1}H-NMR, demonstrates the high chain end fidelity of the thiocarbonylthio CTA that is expected from RAFT polymerizations.[1,2] Therefore, these results support the hypothesis that the chains are participating in a RAFT mechanism.
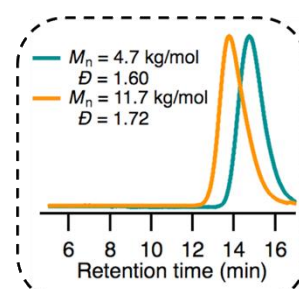
With this data, the versatility of the RAFT chain end was subsequently explored. Utilizing a trithiocarbonate CTA amenable to cationic and radical RAFT, PIBVE was polymerized to nearly full conversion and then chain extended with methyl acrylate (MA) both in situ (Figure 4a) and stepwise after precipitation (Figure S12). The slight loss of control in these blocks is due to the use of the trithiocarbonate CTA, which has been shown to lead to higher dispersities in cationic RAFT than the dithiocarbamate CTA.[3] However, when the dithiocarbamate CTA was attempted for use in the mechanistic interconversion, no radical chain extension was seen (Figure S13). Thus, the trithiocarbonate CTA was chosen for its ability to participate in both cationic and radical RAFT, despite the slightly broader distribution. In addition to interconversion between RAFT mechanisms, the identity of the chain end can also be altered with post-polymerization modifications to access broader applications. For example, by terminating the polymerization with 2-hydroxyethyl acrylate and ferrocenium tetrafluoroborate (FcBF$_4$), the chain end was oxidized and then quenched by the alcohol to give the desired acetal chain end with an acrylate functionality (Figure 4b). With the presence of the alkene confirmed by ^{1}H-NMR, the acrylate could potentially be used in the radical polymerization of more complex architectures, such as bottle brushes. With multiple ways to combine the cationic and radical mechanisms, this method further widens the potential materials and, thus, applications that can be synthesized with RAFT polymerizations.
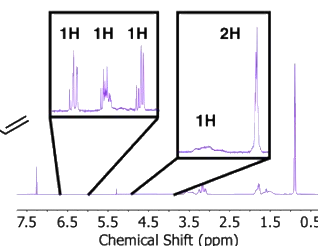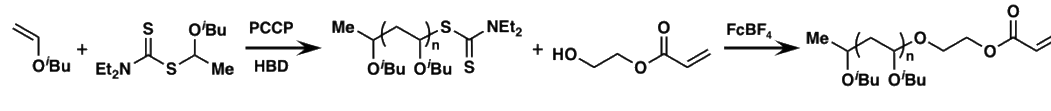

Figure 4. Through a) chain extension with methyl acrylate and b) post-polymerization functionalization to install an acrylate, cationic and radical RAFT can be combined to access a variety of polymer compositions and architectures.

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Table 3. The polymerization showed a tolerance of up to 800 equivalents of water relative to PCCP.

Entry[a]	$[H_2O]_0/[PCCP]_0$	Time (h)	M_n^{theo} (kg/mol)	M_n^{exp} (kg/mol)	Đ
1	40	8	8.8	9.8	1.19
2	200	24	9.1	7.6	1.14
3	400	69	6.8	6.4	1.11
4	600	69	3.8	2.7	1.20
5	800	72	3.8	1.1	1.30

[a]IBVE (100 equiv, 5.6 mmol, filtered through basic alumina) and deionized water (40-800 equiv) were added to CTA (1 equiv, 0.056 mmol), PCCP (0.025 equiv, 0.0014 mmol), and HBD (0.075 equiv, 0.0042 mmol) and stirred under ambient atmosphere at room temperature.

As shown above, this polymerization technique is tolerant to ambient conditions, foregoing the need for rigorous purification of reagents and purging with inert gases. To test the limits of the water tolerance of the system, water was intentionally added to the reactions, along with additional HBD to increase the slowed reaction rates (Table 3). As expected, as more water was added, more conversion of IBVE to side products was observed. However, accounting for the monomer consumed in the water degradation pathway, the experimental and theoretical molecular weights agreed, accompanied by narrow distributions (Figure S14-S18). When calculated by the same method as Perrier, Zhu, and co-workers, these trends remained true up to 800 equivalents of water relative to the PCCP initiator, or 20 equivalents relative to the dithiocarbamate CTA.[24]

In an effort to further understand the mechanism of this water tolerance, a polymerization with 100 equivalents of additional water was monitored over 7 hours (Figure S20). Within 2 hours, only 8% conversion to PIBVE and 5% conversion to the acetal side product was observed, as compared to the 86% conversion to polymer of a control set up without water (Figure S22). After this time though, the acetal formation reached a peak of 7%, and the polymerization proceeded. Analysing the data after this initial period, the theoretical and experimental molecular weights matched, with narrow dispersities, and the semilogarithmic plot demonstrated first order behaviour (Figure S21). Therefore, we propose that the water is consumed first to produce acetaldehyde and an acetal, resulting in an inhibition period. While the formation of these side products does slow the polymerization rate, they do not appear to affect the control of this technique, as it retains first order kinetics and results in polymers with predictable M_ns and low Đs.

Conclusions

In conclusion, we report a new tolerant cationic RAFT polymerization with bench-stable, easy-to-handle reagents. As a result, these polymerizations can be performed under atmospheric conditions with facile purification of monomer, significantly simplifying the polymerization set up. The system has been shown to be applicable to acyclic and cyclic monomers

with some adjustments to conditions. Despite the nucleophilic impurities present, the thiocarbonylthio chain ends from the RAFT process remain intact, enabling chain extension or post-polymerization modification.[35] We propose that this tolerance to impurities is due to the complex formed between the HBD, PCCP anion, and oxocarbenium ion that afforded similar tolerance in previous systems, preventing deleterious reactions with nucleophiles. Importantly, the amounts of PCCP and HBD needed to realize this tolerance are much lower than previous systems due to the control imparted by the RAFT process, allowing for the reactions to be performed at room temperature while still maintaining low concentrations of actively propagating chain ends. This method provides a simple and easily accessible technique for synthesizing polymers through cationic RAFT, which provides promise for using the technique in larger, industrial scale applications.

Author Contributions

SLS - formal analysis, investigation, writing original draft. THL - funding acquisition, resources. BPF - funding acquisition, resources. All authors - conceptualization, review, and editing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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