Controlled Cationic Polymerization: Single-Component Initiation Under Ambient Conditions

Veronika Kottisch, Jacob O'Leary, Quentin Michaudel, Erin E. Stache, Tristan H. Lambert*, and Brett P. Fors*

Cornell University, Ithaca, New York 14853, United States

Supporting Information Placeholder

ABSTRACT: Cationic polymerizations provide a valuable strategy for preparing macromolecules with excellent control but are inherently sensitive to impurities and commonly require rigorous reagent purification, low temperatures, and strictly anhydrous reaction conditions. By using pentacarbomethoxycyclopentadiene (PCCP) as the single-component initiating organic acid, we found that a diverse library of vinyl ethers can be controllably polymerized under ambient conditions. Additionally, excellent chain-end fidelity is maintained even without rigorous monomer purification. We hypothesize that a tight ion complex between the PCCP anion and the oxocarbenium ion chain end prevents chain-transfer events and enables a polymerization with living characteristics. Furthermore, terminating the polymerization with functional nucleophiles allows for chain-end functionalization in high yields.

Living ionic polymerizations are a powerful class of reactions that enable the synthesis of macromolecules with exquisite levels of control.[1,2] However, the utility of these processes is limited because of their sensitivity to impurities and requirement of stringent reaction conditions. Specifically, controlled cationic polymerizations have to be run at low temperatures under highly inert atmospheres and require the use of monomers, solvents, and catalysts that have been rigorously purified.[2–14] These requirements inhibit the broader scientific community from fully taking advantage of these polymerizations to make well-defined polymeric materials for a variety of applications.

Over the past several years multiple research groups have reported cationic polymerization methods that use a single component initiating species to make these processes more user-friendly; however, these reactions still mostly require low temperatures, inert atmospheres, and highly purified reagents.[15–18] Additionally, there have been a small number of methods published that can be run open to air or at elevated temperatures.[19] Unfortunately, these polymerizations open to air are not well controlled or afford only low molecular weights resulting from termination events.[20–21] On this basis, the development of a controlled cationic polymerization that can be run at ambient temperature without the need for purified reagents and the use of an inert atmosphere remains a grand challenge.

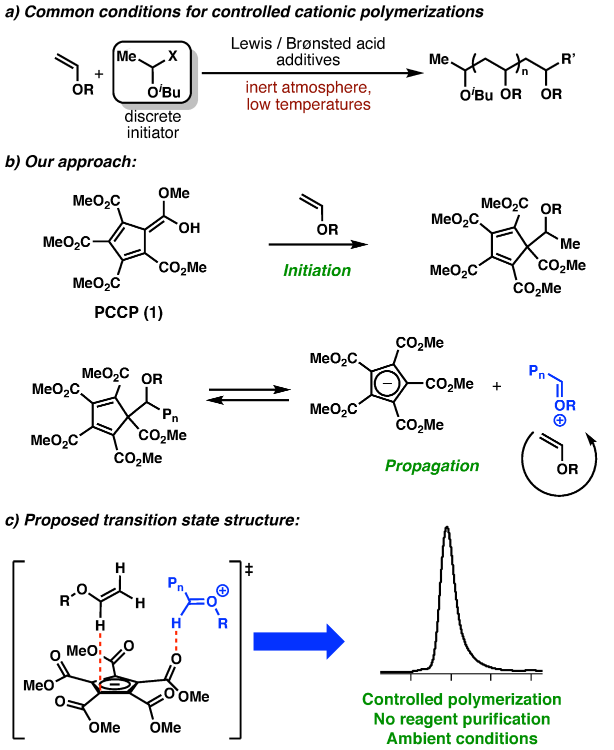


Figure 1. a) Typical reaction conditions of cationic polymerizations. b) PCCP is used in this work to controllably polymerize vinyl ethers. c) Key H–bonding interactions lead to a controlled polymerization with narrow molecular weight distributions.

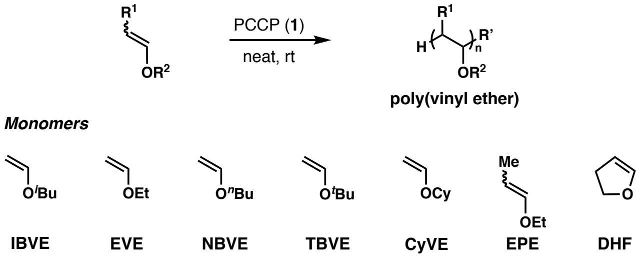
To overcome the limitations described above, we sought a cationic polymerization system where both the identity of the active chain-end and the mechanism of monomer addition were distinct from current systems. Specifically, we hypothesized that a process where the cationic chain end would tightly interact with a well-chosen counteranion would allow room temperature propagation, as well as selective addition of the monomer over nucleophilic impurities to circumvent termination and chain-transfer events.

With this in mind, our attention was drawn to electron-deficient cyclopentadienes, such as 1,2,3,4,5-pentacarobomethoxycyclopentadiene (PCCP, **1**). This bench-stable, easily handled solid has an exceptionally low pKa [22,23] and can be readily synthesized on scale from inexpensive, commercially available starting materials. One of our research groups (T.H.L.) has recently leveraged the unique reactivity of these cyclopentadienes for small molecule transformations.[24–26] Of particular relevance, we reported that PCCP-oxocarbenium complexes react with vinyl ethers. In collaboration with Vetticatt and co-workers, we found that this transformation proceeds via a transition state that involves non-covalent interactions between key reactant C–H bonds with both the cyclopentadienyl ring and carbonyl oxygens of the anion.[25] In regard to the current work, we hypothesized that this mechanism would enable cationic polymerization, in which selective addition of vinyl ethers over other nucleophilic impurities to a propagating oxocarbenium ion chain end would prevent termination and chain transfer events (Figure 1). Specifically, we propose that the propagating chain end would exist as an equilibrium between the cyclopentadienyl-oxocarbenium salt **2** and the covalent species **3** (Figure 1b), and that addition of monomers to **2** would occur via the transition state depicted in Figure 1c.[25,26] Given the reactive nature of the oxocarbenium ion, we speculate that the chain end would exist primarily in the covalent form and provide controlled polymerization at ambient temperature. This proposed mechanism would eliminate the need for highly purified reagents, an inert atmosphere in order to exclude moisture, and low temperature conditions.

To test this hypothesis, we first examined the polymerization of isobutyl vinyl ether (IBVE) in the presence of PCCP. Importantly, all of the reactions were run open to air at room temperature. IBVE was simply passed through a plug of alumina to remove the KOH inhibitor prior to the reaction and was used without further purification. We envisioned that **1** would efficiently initiate polymerization through the protonation of IBVE (Figure 1b); acids with comparable pKa values have been shown to readily protonate vinyl ethers to form Markovnikov adducts.[10] Stirring **1** with 50 equivalents of IBVE led to complete consumption of the monomer after 16 hours to give a 5.1 kg/mol polymer with a narrow dispersity ($Đ$) of 1.1 (Table 1, entry 1). Importantly, the experimental number average molar mass (M_n) matched well with the theoretical value (M_n(theo) = 5.0 kg/mol), suggesting that each molecule of **1** is initiating a polymer chain. The narrow $Đ$ value demonstrates that initiation with **1** through protonation of the IBVE is highly efficient (Figure 1b). Additionally, these data together provides strong evidence that termination and chain transfer events are not playing a major role in this reaction. Moreover, the relatively slow rate of polymerization and excellent control observed implies a strong interaction between the cyclopentadienyl anion and the oxocarbenium ion chain end, either as a tight ion pair or a dynamic covalent bond.[27] It is worth noting that the polymerization can be performed in a variety of solvents, including hexanes, toluene, and DCM. The reaction rate is slightly higher in DCM, but proceeds with a minor loss of control (See supporting information).[28]

To further probe the control in this system, we varied the ratio of **1** to IBVE and targeted polymers with higher molar mass. In all cases, polymers with narrow Đ values were obtained and the experimental M_ns were slightly lower than theoretical values but still in good agreement (Table 1, entries 2 and 3). These results suggest that, if chain transfer occurs, it has minimal effect on the polymerization process. When these same reactions were run under inert atmospheres with highly purified IBVE, almost identical results were obtained (see supporting information for details). This practical and robust new method eliminates the need for tedious purifications and the use of highly specialized moisture-free techniques. Targeting M_ns above 20 kg/mol with IBVE leads to increased chain transfer and lower experimental molar masses under both moisture-free and ambient conditions.

Table 1. Cationic polymerization of vinyl ethers promoted by 1.



Entry[a]	Monomer	Time (h)	M_n theo (kg/mol)	M_n exp (kg/mol)	$Đ$
1	IBVE	16	5.0	5.1	1.11
2	IBVE	16	9.3	7.2	1.27
3	IBVE	16	23.0	18.1	1.15
4	EVE	3	3.4	2.5	1.06
5	EVE	5	6.6	6.5	1.08
6	EVE	20	13.5	12.8	1.06
7	NBVE	6	8.9	7.3	1.13
8	TBVE	0.1	8.1	6.2	1.25
9	CyVE	0.1	11.2	10.5	1.27
10[b]	EPE	6	4.0	5.4	1.24
11[c]	DHF	5	33.6	34.1	1.20
12[c,d]	DHF	3.5	44.9	49.9	1.33

[a]Vinyl ether (50–1300 equiv, filtered through basic alumina) and **1** (1 equiv, 0.014 mmol) were stirred under ambient atmosphere at room temperature unless otherwise noted; [b]performed at 0 °C; [c]performed under nitrogen atmosphere with distilled DHF; [d]diluted with equal volume of DCM.

We further investigated the scope of these polymerizations using a diverse array of vinyl ether monomers. Ethyl vinyl ether (EVE) polymerized at a slightly faster rate than IBVE and gave polymers with $Đ$ values of <1.1 and excellent control over the M_n (Table 1, entries 4–6). The linear congener of IBVE, *n*-butyl vinyl ether (NBVE), also polymerized under our standard conditions to yield a well-defined material with a narrow $Đ$ of 1.13 (Table 1, entry 7). Additionally, more sterically challenging monomers such as *tert*-butyl vinyl ether (TBVE) and cyclohexyl vinyl ether (CyVE) polymerized within minutes in a controlled fashion (Table 1, entries 8 and 9); we postulated that the increased size of the monomers weakens the interaction between the cyclopentadienyl anion and the oxocarbenium ion and, therefore, results in an accelerated rate.

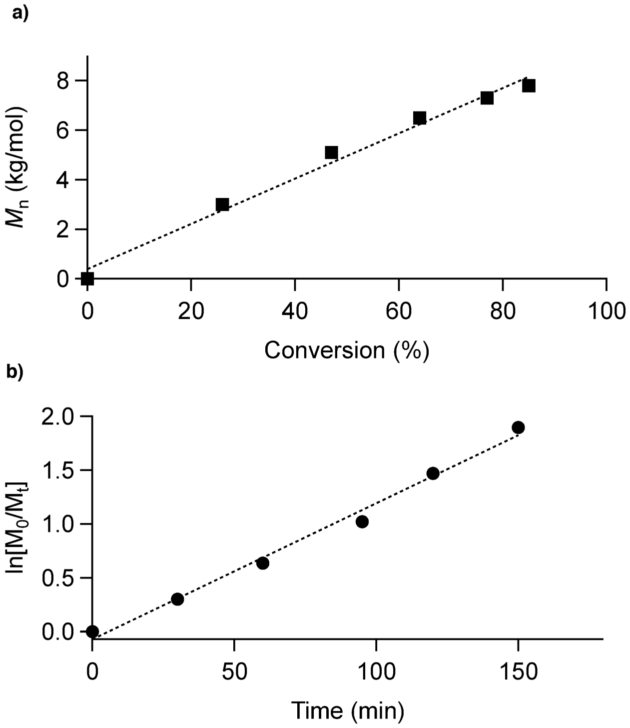


Figure 2. a) The molecular weight of poly(IBVE) grows linearly with conversion. b) A linear relationship of the change in monomer concentration with time indicates constant cation concentration throughout the polymerization of IBVE with **1**.

1,2-Disubstituted vinyl ethers that are more recalcitrant to controlled polymerization also polymerized in a controlled fashion using **1** as an initiator, but modified conditions were required.[29,30] Under our standard conditions, ethyl-1-propenyl ether (EPE) only gave oligomerization. We posited that this could be due to a lower ceiling temperature of the poly(EPE). In support of this hypothesis, controlled polymerization was observed when the reaction was performed at 0 °C (Table 1, entry 10); it is worth noting the EPE reactions were still performed open to the air with unpurified monomer. Additionally, dihydrofuran (DHF), which is an interesting monomer because poly(DHF) has a high glass transition temperature of 126 °C,[30] polymerized under the standard conditions; however, the experimental M_n values of the formed polymer were lower than predicted and the molecular weight distributions were broad. We found that purification of the monomer and running the reaction under an inert atmosphere had a large influence in this case and led to a controlled polymerization process (Table 1, entries 11 and 12). These results indicate that the polymerization of DHF is much more sensitive to nucleophilic impurities than other monomers we have tested. We reasoned that this change in reactivity could be caused by a weakening of the interaction between the PCCP anion and the oxocarbenium ion, which we believe is responsible for the selectivity of vinyl ether addition over other nucleophiles.[31]

Next, we investigated the kinetics of the polymerization of IBVE initiated by **1**. When monitoring the reaction, we observed that M_n grew linearly with conversion, demonstrating that this polymerization was proceeding through a chain growth process (Figure 2a). Additionally, plotting the natural log of monomer depletion versus time showed a linear relationship (Figure 2b). This result demonstrated that the polymerization showcases well-behaved first order kinetics and that the cation concentration remains constant throughout the polymerization, further supporting our hypothesis that termination was not playing a major role in these reactions.

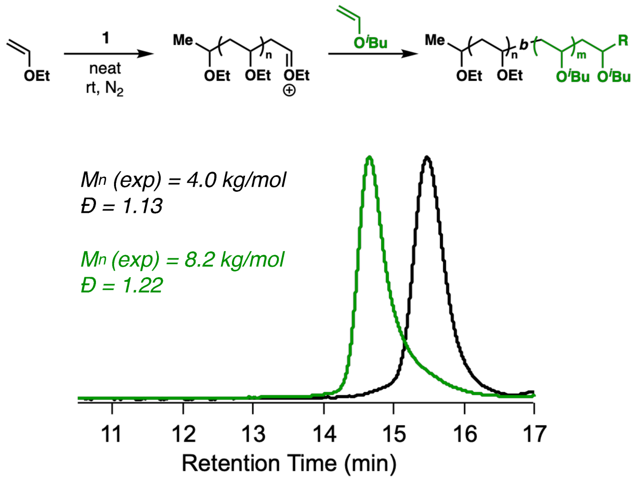


Figure 3. Synthesis of diblock copolymer demonstrates good chain-end fidelity.

The living characteristics and the chain-end fidelity of this reaction, were subsequently probed through the synthesis of diblock copolymers. In our initial studies we used purified monomers and an N_2 atmosphere. For the first block we grew a 4.0 kg/mol poly(EVE) and then after >95% conversion added IBVE to furnish a well-defined 8.2 kg/mol poly(EVE-*b*-IBVE) diblock polymer. The size exclusion chromatography trace of the polymer after chain extension showed a clear shift to higher molecular weights, while maintaining a narrow *Đ* of 1.2 (Figure 3). It should be noted that when the reaction was allowed to sit at full conversion before the addition of the second monomer, termination events started to occur. Additionally, we found that when these same experiments were run with unpurified monomers and open to the air, some termination was observed at high conversion (see supporting information for details). Interestingly, in these cases if the second monomer was added before the first block reached 85% conversion efficient chain extension was observed with little to no termination to yield a tapered diblock copolymer. These results suggested that termination reactions with nucleophilic impurities started to become competitive when the reactions reach high conversion.

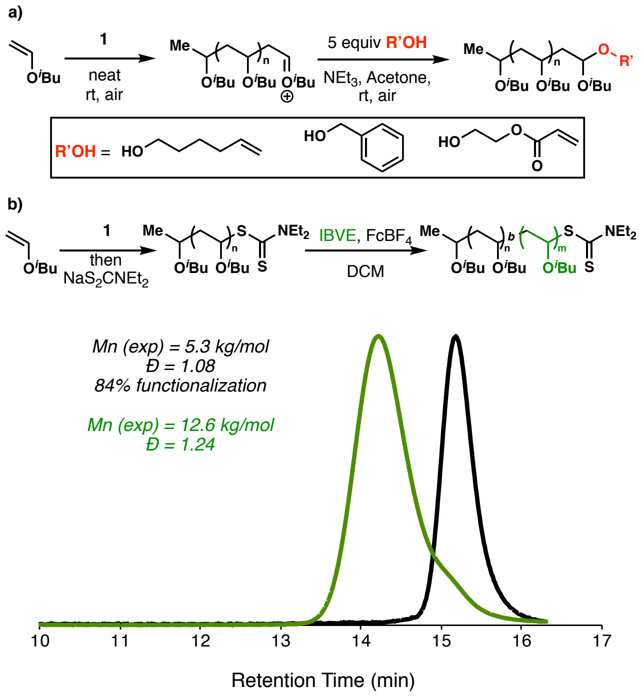


Figure 4. *In situ* chain-end functionalization of poly(IBVE) by quenching the polymerization a) with functional alcohols; b) with a dithiocarbamate salt, followed by chain extension with IBVE using ferrocenium tetrafluoroborate as the initiator.

To fully take advantage of these operationally simple polymerizations we looked to chain-end functionalize our polymers by quenching the propagating oxocarbenium ion with alcohols following full conversion of the monomer. Addition of 5 equivalents of various alcohols and triethylamine to poly(IBVE) gave polymers with >95% of the desired acetals (Figure 4a). Additionally, we demonstrated that the oxocarbenium chain ends could efficiently be trapped with a dithiocarbamate salt to generate a poly(IBVE) macroinitiator, which provides an access to multiblock material via chain extension (Figure 4b).[7,13,32–34] Accordingly, using ferrocenium trifluoroborate ($FcBF_4$) as a chemical mediator as described in our previous study, poly(IBVE) was efficiently chain extended via a cationic reversible-addition-fragmentation chain-transfer (RAFT) polymerization to provide poly(IBVE-*b*-IBVE) with excellent control. These results clearly demonstrate that we can effectively manipulate our chain ends after polymerization, as well as chain extend with other polymerization methods to make functional materials.

In conclusion, we have developed a novel single-component acid-mediated polymerization of a variety of vinyl ethers under mild conditions. The polymerization is initiated by PCCP and controlled by the tight ion pair of the cyclopentadienyl anion and propagating cation. This interaction allows for good chain-end fidelity and the synthesis of block copolymers. Interestingly, the polymerization proceeds even under ambient atmosphere and does not require rigorous purification. We imagine that this method will induce a shift in how the sensitivity of cationic polymerizations is conceptualized by the polymer community.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

General experimental considerations, experimental procedures, and additional supporting data (PDF).

AUTHOR INFORMATION

Corresponding Author

Brett P. Fors: bpf46@cornell.edu

Tristan H. Lambert: Tristan.lambert@cornell.edu

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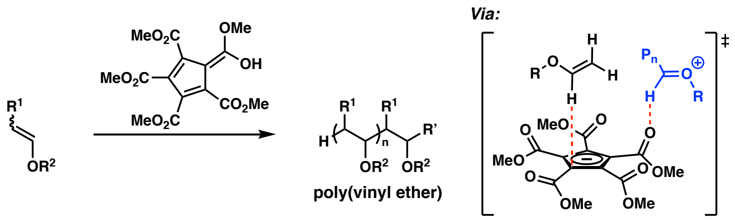

·ambient conditions ·no reagent purification ·broad monomer scope

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