Accelerating cationic polymerizations with a hydrogen bond donor

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ABSTRACT: Photoacid generators (PAGs) have facilitated a number of technology breakthroughs in the electronic, coating, and additive manufacturing industries. Traditionally, PAGs that contain weakly coordinating anions, such as PF_6^-, generate Brønsted superacids under UV irradiation for rapid cationic polymerizations. However, PAGs with strongly coordinating anions remain under-utilized as they form weak acids that are inefficient or even incapable of initiating polymerization. To expand the scope of potential counteranions in PAGs, we leveraged a thiophosphoramide hydrogen bond donor (HBD) to catalyze photoinitiated cationic polymerizations from diphenyliodonium PAGs. Through the formation of hydrogen bonds between the HBD and PAG counteranion, acceleration of the polymerization rate was observed for a range of non-coordinating and coordinating anions. The effect of the HBD on the polymerization kinetics was investigated by ^{1}H–NMR titrations and geometry optimizations. Extending HBD catalysis beyond photopolymerizations, addition of HBD also enabled hydrochloric acid to initiate controlled reversible addition–fragmentation chain transfer (RAFT) polymerization under ambient conditions. With the versatility of HBD, there is potential to access initiation systems that were previously believed to be impractical for cationic polymerization.

1. Introduction

Photoacid generators (PAGs) are a class of light-sensitive molecules that generate acids upon light exposure, inducing photoinitiated cationic polymerizations.[1-4] The development of PAGs has enabled advances in numerous applications such as photolithography, photocurable coatings and adhesives, and 3D printing.[5-7] To achieve efficient polymerizations on time scales for manufacturing, most ionic PAGs contain non-coordinating anions that form Brønsted superacids.[7-11] Specifically, Crivello and Lam were the first to employ diphenyliodonium salts with weakly coordinating anions (SbF_6^-, PF_6^-, etc) for such applications.[11,12] Under ultraviolet (UV) irradiation, strong acids ($HSbF_6$, HPF_6, etc) are formed from the photolysis of the diphenyliodonium, initiating cationic polymerization (Figure 1). While superacids facilitate rapid polymerization, the utilization of fluorine-containing PAGs poses potential health hazards that can limit their applications.[13-15] PAGs with coordinating anions (*e.g.,* Cl^-) are often more benign but not commonly used, as they generate weak acids (*e.g.,* HCl) that form monomer–acid adducts with equilibria that lie primarily towards the covalent dormant state. With a lack of ionization at the chain end, propagation is infrequent, leading to polymerizations too slow for practical applications.

In response to this challenge, research has examined the use of diphenyliodonium halides to initiate cationic polymerization from the acids formed by UV irradiation (Figure 1). The Mah group employed zinc halides to impart livingness to the polymerization of isobutyl vinyl ether when initiated by diphenyliodonium halides.[16,17] Leveraging the reversible cleavage of carbon–iodine bonds, Aoshima and co-workers utilized hydroiodic acid generated from UV irradiation of diphenyliodonium salts to control the polymerization of isopropyl vinyl ether.[18] While these systems contain diphenyliodonium PAGs with non-fluorinated anions, the polymerizations require low temperatures, inert atmospheres, volatile solvents, and lengthy reaction times—conditions that can hinder application. Thus, we aimed to identify a catalyst that could accelerate photoinitiated cationic polymerizations using non-fluorinated diphenyliodonium salts under mild reaction conditions.

Hydrogen bond donors (HBDs) have been extensively studied for small molecule synthesis.[19-22] Applying this chemistry to polymer science, HBDs have recently been utilized in the catalysis of cationic polymerizations under mild conditions, such as with thiophosphoramides employed in our groups and selenocyclodiphosph(V)azanes used by Tao and coworkers.[23-27] In our report, a bench-stable organic acid 1,2,3,4,5–pentacarbomethoxycyclopentadiene (PCCP) afforded controlled polymerization of vinyl ethers under ambient conditions.[23] In our proposed model, the addition of HBDs lowered the basicity and thus nucleophilicity of the PCCP anion, reducing its affinity for the cationic chain end and accelerating polymerization.[24] As depicted in Figure 1, the thiophosphoramide HBD afforded both rapid kinetics as well as controlled polymerization. When this work was adapted to a cationic reversible addition–fragmentation chain transfer (RAFT) polymerization, the addition of HBD was also critical for achieving high conversions while retaining moisture tolerance.[25] This HBD has also been shown to coordinate to a variety of other anions and improve systems ranging from ion recognition for transport to ionic Diels-Alder reactions.[28,29]

Influenced by these studies, we speculated that the addition of HBD to cationic polymerizations with coordinating anions would diminish the ion affinity to the propagating chain ends, accelerating the polymerization rate. Herein, we confirm this hypothesis by accelerating not only photopolymerizations initiated by PAGs containing both weakly and strongly coordinating anions, but also Brønsted acid-initiated RAFT polymerizations under ambient conditions. Importantly, the high stability of the $-CF_3$ groups on the HBD reduces the likelihood of hazardous byproducts in the polymerization. Thus, this work demonstrates that HBD catalysis is broadly applicable to a variety of cationic polymerization methods, with potential applications from fluorine-free photoinitiation to user

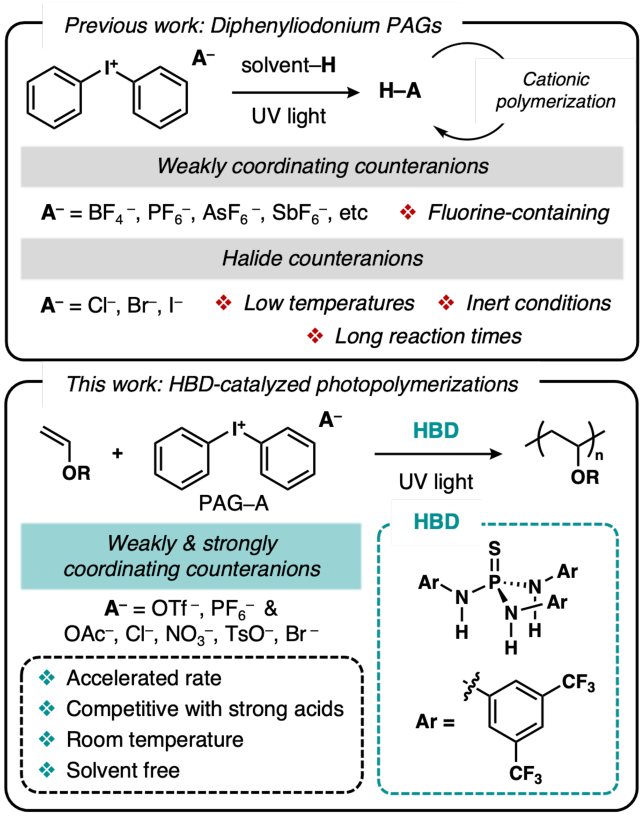

Figure 1. In previous work, diphenyliodonium photoacid generators (PAGs) have been utilized with non-coordinating anions to initiate rapid cationic polymerization under UV irradiation. Fluorine-free PAGs have been leveraged to impart control on photopolymerizations at low temperatures with long reactions times. In this work, we demonstrate that ability of a thiophosphoramide hydrogen bond donor (HBD) to catalyze polymerization from PAGs with a range of weakly to strongly coordinating anions under tolerant conditions with competitive rates.

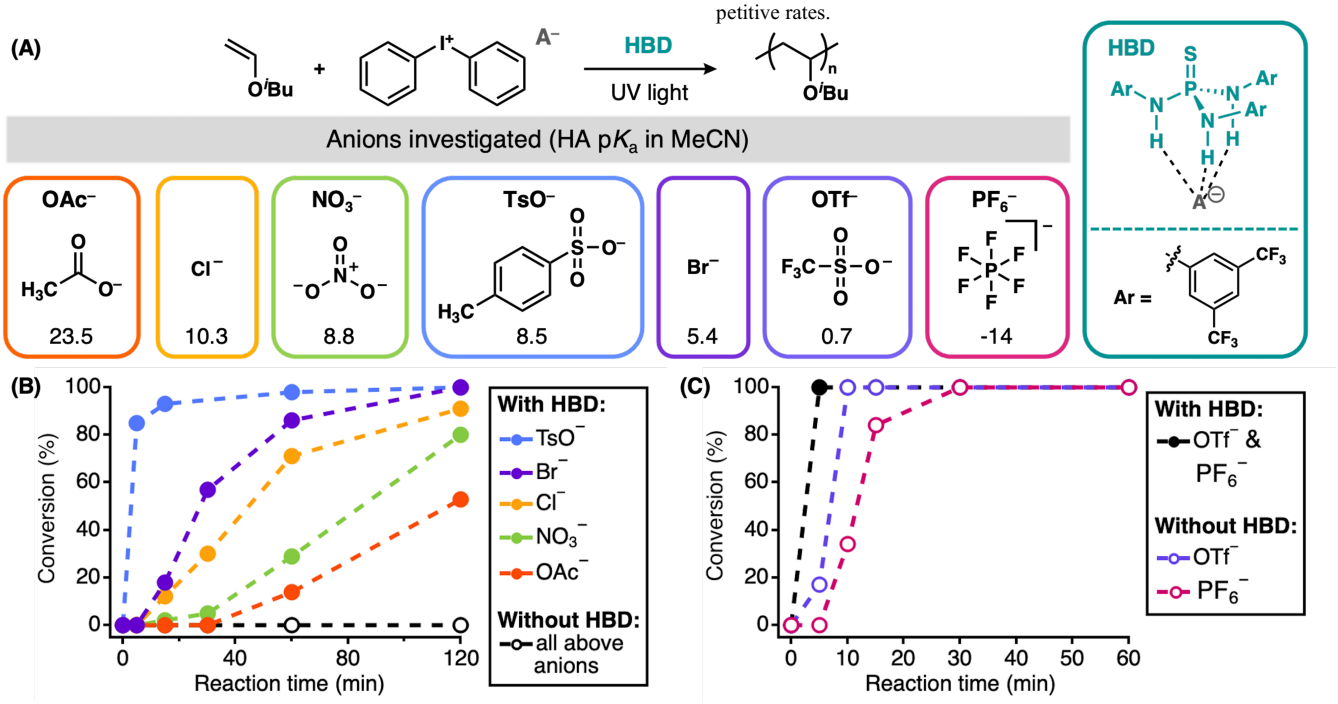

Figure 2. (A) The photopolymerization kinetics with and without HBD for PAGs containing a range of anions were investigated (200 equiv isobutyl vinyl ether (IBVE), 1 equiv PAG–A, 0 or 1 equiv HBD). These anions include: acetate (OAc^-), chloride (Cl^-), nitrate (NO_3^-), tosylate (TsO^-), bromide (Br^-), triflate (OTf^-), and hexafluorophosphate (PF_6^-), with their structures and pK_as in acetonitrile (MeCN) given. (B) Without HBD, the more strongly coordinating anions (OAc^-, Cl^-, NO_3^-, TsO^-, Br^-) did not polymerize (black open circles). Upon the addition of HBD, all of the anions experienced initiation within 60 minutes. (C) Only PAG–OTf and PAG–PF_6 resulted in polymerization without HBD. Even so, these weakly coordinating anions still saw accelerated rates with the addition of HBD.

friendly controlled polymerizations.

2. Results and discussion

To test the HBD catalysis, we initially utilized a diphenyliodonium PAG with a chloride counteranion (PAG–Cl), as the HCl generated has a similar pK_a but very different structure to PCCP. As a control, 200 equiv of isobutyl vinyl ether (IBVE) was added to 1 equiv of PAG–Cl in the absence of solvent and irradiated with 300 nm UV light. No polymerization was observed after 120 minutes of light irradiation, indicating that the HCl generated by PAG–Cl was insufficient to polymerize IBVE. However, adding 1 equiv of the thiophosphoramide HBD relative to the PAG led to a 91% IBVE monomer conversion after 120 min of light irradiation (Figure 2B, yellow trace). As in our previous report, we propose that this catalysis is a result of HBD coordination to the chloride anion, which facilitates ionization to form a cationic chain end for propagation.[24]

To test the anion versatility of the HBD, we selected commercially available diphenyliodonium PAGs that result in conjugate acids with a breadth of pK_as including: hexafluorophosphate (PF_6^-), triflate (OTf^-), bromide (Br^-), tosylate (TsO^-), nitrate (NO_3^-), and acetate (OAc^-) (Figure 2A). After exposure to UV light without HBD, neat IBVE reached full conversion in under 30 minutes for PAG–PF_6 and PAG–OTf, while the other PAGs were unable to initiate polymerization after 120 minutes (Figure 2B-C, open circles). For the anions unable to initiate, we probed the effects of 1 equiv of HBD relative to PAG on the polymerization kinetics. The addition of HBD enabled initiation in under 60 minutes, with the polymerization rates trending as $TsO^- > Br^- > Cl^- > NO_3^- > OAc^-$ (Figure 2B, closed circles). HBD also led to faster rates of polymerization for PAG–PF_6 and PAG–OTf, which are known for their rapid photoinitiation (Figure 2C, closed circles). The hexafluoroantimonate anion (SbF_6^-) was also tested in the form of a p-(octyloxyphenyl)phenyliodonium salt, which also demonstrated faster kinetics upon the addition of 1 equiv HBD (Figure S17). Interestingly, the polymerization using PAG–TsO and HBD achieved similar kinetics as the polymerizations of PAG–OTf and PAG–PF_6 without HBD, demonstrating the ability of HBD catalysis to achieve competitive rates with current photoinitiation standards.

In general, the polymerization kinetics with HBD correlate with the acidity of the Brønsted acids generated from the PAGs.[30,31] Acids with lower pK_a values in acetonitrile (MeCN) resulted in faster polymerization rates. However, based solely on pK_a, both PAG–Br and PAG–NO_3 saw less rate acceleration from HBD than predicted. To investigate the reasons behind these trends, ^{1}H–NMR titrations were performed with HBD as the host and increasing amounts of anion in the form of their tetrabutylammonium (TBA) salts (Figure 3A). The amine protons on the HBD were tracked as the signal moved downfield with increasing anion concentration. The more strongly coordinating anions reached saturation with approximately 1 equiv of TBA salt with respect to HBD, indicating that there is 1:1 binding of the anion to the hydrogen bond donor (Figure 3A). Titrations with OAc^- were unsuccessful as the N–H signal broadened into the baseline, which has previously been reported as being due to deprotonation instead of binding (Figure S19).[28] The relatively large induction period for the polymerization of PAG–OAc and HBD may be due to similar unproductive pathways that stall polymerization until sufficient acid is produced. In contrast, the weakly coordinating anion PF_6^- continued to shift downfield even after the addition of 7 equivalents of TBA salt relative to HBD, indicating that the system was still not fully saturated at large excess.

Utilizing the titration experiments for TsO^-, Br^-, Cl^-, and NO_3^-, the binding constants (K_{eq}) were approximated by fitting the data to the equation for 1:1 binding (Equation S1 and Figure S25-28). The resulting fits gave K_{eq}s in the order of $TsO^- \cong NO_3^- > Br^- \cong Cl^-$. From these approximations, TsO^- binds more strongly to the HBD than Br^- and Cl^-, likely increasing ionization at the chain end and allowing for higher rates of propagation. As Br^- and Cl^- have similar binding constants for HBD, the similar reaction kinetics also align with the titration data, despite the differences in their pK_as.

However, the titration data alone is unable to explain the experimental differences between PAG–OTs and PAG–NO_3. Despite nitric acid and tosic acid having similar pK_as and their anions having similar K_{eq}s with HBD, the PAG–NO_3 polymerization was significantly slower. The PAG–NO_3 polymerization reached only 80% conversion after 2 hours, whereas the PAG–OTs achieved 85% conversion after 5 minutes of light irradiation. One alternative explanation for the disparity in kinetics could arise from the differences in their geometries.

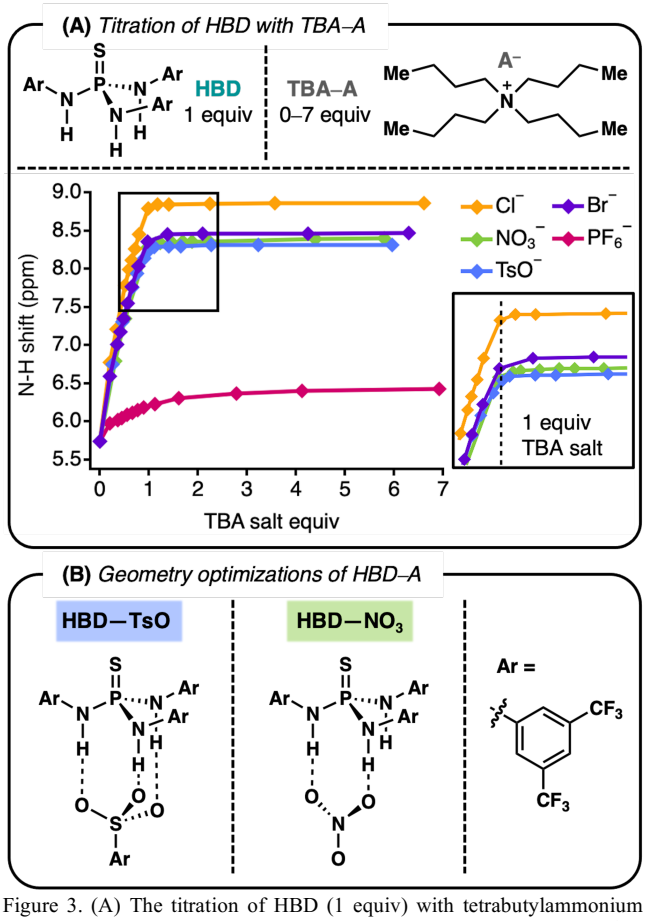

Figure 3. (A) The titration of HBD (1 equiv) with tetrabutylammonium (TBA) –Cl, –NO_3, –TsO, –Br, and –PF_6 (0–7 equiv) was tracked by ^{1}H-NMR. The N–H protons on the HBD shifted downfield with increased TBA salt concentration. The data collected for TBA–Cl, –NO_3, –TsO, and –Br fit the model for 1:1 binding with HBD, while TBA–PF_6 continued to shift the N–H signal downfield even at large excess. (B) Geometry optimizations with density functional theory for the HBD–TsO complex resulted in three H–bonds, while the HBD–NO_3 complex was predicted to contain only two H–bonds.

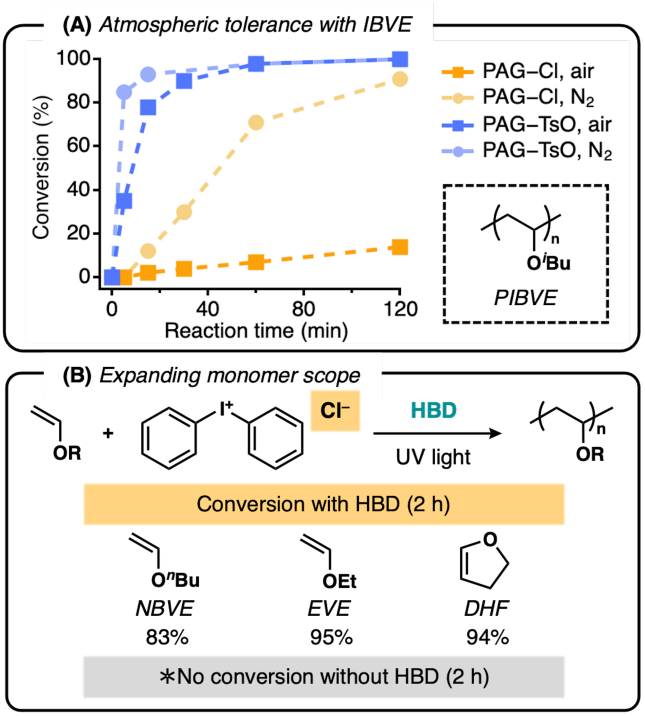

Figure 4. (A) With HBD, the photopolymerizations still occur in air. PAG–TsO demonstrated a small reduction in rate and thus a high tolerance to ambient conditions. With slower kinetics to begin with, the polymerization of PAG–Cl under air experienced a more significant reduction in rate. (B) Both alkyl and cyclic vinyl ethers were polymerized with PAG–Cl and HBD, reaching high conversions in 2 h. These include n-butyl vinyl ether (NBVE), ethyl vinyl ether (EVE), and 2,3-dihydrofuran (DHF).

The pseudo-tetrahedral geometry of the sulfate group on TsO^- may allow for more favorable coordination to the tetrahedral shape of the HBD, compared to the trigonal planar geometry of NO_3^-.

Density functional theory (DFT) was utilized to generate optimized geometries for binding between the HBD and the anions. The optimized geometry for TsO^- corresponded to the oxygens of the sulfate group on TsO^- hydrogen bonding to all three of the hydrogens of the amines on the HBD. However, the optimized geometry between the nitrate anion and HBD resulted in only two hydrogen bonds between the oxygens on NO_3^- and the hydrogens of the N–Hs on the HBD (Figure 3B). As we have previously shown, the ability to coordinate to all three sites on the HBD increases the rate of polymerization compared to binding to just two sites.[24] From these optimizations, we concluded that the geometry mismatch between NO_3^- and HBD is likely the cause of its reduced polymerizations rates. From these binding studies, we found that HBD is broadly applicable to a variety of counteranions, with the degree of rate acceleration impacted by acidity and geometry.

To further demonstrate the feasibility of HBD catalysis, the polymerizations were performed neat with exposure to air (Figure 4A). Once again, PAG–TsO with 1 equiv of HBD displayed the fastest kinetics, achieving 90% conversion after 30 min. Despite reacting under ambient conditions, the polymerization still reached full conversion within 2 hours. However, when PAG–Cl was polymerized with 1 equiv of HBD under air, a major reduction in polymerization rate was observed, reaching only 14% conversion after 2 hours. The dramatic decrease in kinetics for PAG–Cl is likely due to the slower kinetics originally observed under nitrogen, enabling chain-end quenching due to moisture. As PAG–TsO with HBD still provides reasonable kinetics under air, these results exemplify the ability of HBD to catalyze cationic polymerizations that were previously difficult to access.

Examining the tolerance of the photoinitiated polymerizations further, the storage stability of the resins was investigated under air over 3 days. Amber vials of uninhibited IBVE, PAG–TsO, and HBD were stored at 20 °C (room temperature), 4 °C (in the fridge), and −18 °C (in the freezer) under air. After 3 days, no polymerization was observed by ^{1}H–NMR for any of the conditions, demonstrating the stability of the resins over multiple days, even at room temperature (Figure S36). To ensure polymerization was still possible, the resins were transferred to quartz tubes with dichloromethane and irradiated with 300 nm lights under ambient conditions (Figure S37). In all cases, high conversions (>97%) of IBVE to polymer were achieved within 1 hour, indicating that the resins were still viable after storage in a range of conditions.

A variety of vinyl ethers were studied to show the monomer scope of HBD-catalyzed cationic polymerizations in the absence of solvent: *n*-butyl vinyl ether (NBVE), ethyl vinyl ether (EVE), and 2,3-dihydrofuran (DHF). PAG–Cl was utilized to explore the boundaries of the weaker acids generated in this system. Without HBD, no polymerization was observed for these vinyl ethers using PAG–Cl. EVE did undergo monomer decomposition as a result of acid-catalyzed hydrolysis to form acetaldehyde and acetals (Figure S38). Upon the addition of 1 equiv of HBD, all monomers achieved high conversions after 120 minutes. Importantly, for EVE in the presence of HBD, most of the monomer conversion was to polymer, with very little degradation products observed by ^{1}H–NMR (Figure S42). DHF exhibited the greatest rate increase, achieving almost full conversion after 30 minutes (88% conversion). These additional monomers expand the range of achievable physical properties of the resulting polymers with reported glass transition temperature ranging from −50 °C to 135 °C.[32,33]

As the HBD was adapted to PAGs that generated acids of various pK_as, we hypothesized that the HBD could catalyze Brønsted acid-initiated polymerizations outside of PCCP, such as those initiated by hydrochloric acid (HCl). Very few examples of HCl-initiated cationic polymerizations are reported in literature. Sugihara and co-workers demonstrated that HCl•Et_2O is capable of initiating controlled cationic polymerization at 0 °C, under nitrogen with rigorously dried reagents.[34-36] They adapted this system to initiate cationic RAFT polymerization, requiring similarly dry and cold conditions.[37-39] Recently, our groups reported the PCCP-initiated, HBD-catalyzed cationic RAFT polymerization of vinyl ethers that was performed at room temperature, under air, and without reagent purification.[25]

Influenced by these reports, we aimed to initiate cationic RAFT polymerizations with HCl under ambient conditions through HBD catalysis. To test this hypothesis, 1 equiv of HCl in ether was added to 150 equiv of distilled IBVE in a nitrogen glove box to mirror literature conditions but at room temperature. No polymerization was observed by ^{1}H-NMR, although there was decomposition of IBVE to acetal side products (Figure S49). Upon the addition of 0.5 equiv of HBD under the same conditions, the reaction reached full conversion after 3.5 hours, yielding polymers with a bimodal distribution (Figure

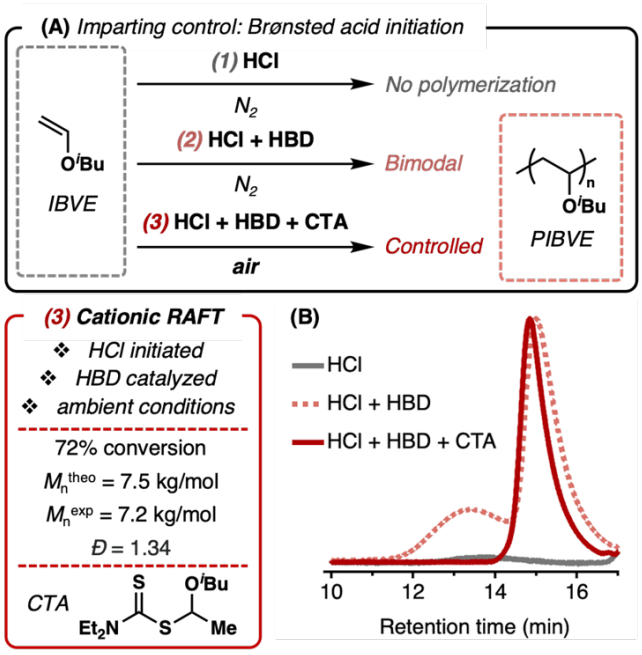

Figure 5. (A) (1) No polymerization was observed with IBVE and HCl, at room temperature under nitrogen. (2) Upon the addition of HBD to these conditions, the resulting polymer had a bimodal distribution, indicating initiation but not control. (3) A chain transfer agent (CTA) was added to impart control through a reversible addition–fragmentation chain transfer (RAFT) mechanism. Due to the addition of HBD, HCl-initiated cationic RAFT was performed at room temperature, without monomer purification, and under air. (B) The resulting polymer from this HBD catalyzed RAFT had matching theoretical and experimental molecular weights and a relatively low dispersity, as confirmed by gel permeation chromatography.

5B). To impart control, 1 equiv of a dithiocarbamate RAFT chain transfer agent (CTA) was added, and the amount of HCl was dropped to 0.5 equiv to match that of the HBD. To test the tolerance, this polymerization was performed under air, neat without monomer purification, and at room temperature. After 4 hours, 72% conversion of IBVE was observed, resulting in polymer with a dispersity of 1.34 and an experimental M_n = 7.2 kg/mol, matching the theoretical M_n = 7.5 kg/mol (Figure 5B). When no HBD was added under the same reaction conditions, no polymerization was seen after 2 days, with 12% conversion to degradation products (Figure S51). These results suggest that HBD will catalyze various methods of solvent-free cationic polymerizations, accessing counteranions and conditions that were previously difficult to achieve.

3. Conclusions

In summary, we demonstrate HBD can be used as a general catalyst for various cationic polymerization methods with a wide range of counteranions. We present the HBD-catalyzed photopolymerizations of vinyl ethers using PAG counteranions that were previously unable to initiate vinyl ethers in reasonable time scales. The accelerated polymerization rates were enabled by the formation of hydrogen bonding between the HBD and PAG anion, thus reducing the anion's affinity to the growing cationic polymer chain end. The acceleration was primarily dictated by the pK_a of the resulting conjugate acid, with exceptions investigated by ^{1}H–NMR titrations and DFT geometry optimizations. By expanding these reaction conditions to different monomers and atmospheres, we hope to increase the feasibility of this method for the fabrication of polymeric materials with tunable physical properties. Furthermore, through HBD catalysis, HCl-initiated cationic RAFT polymerization was performed without monomer purification, under air, and at room temperature. Therefore, these initial results suggest that HBD catalysis is able to accelerate a variety of cationic polymerizations, improving the feasibility of current initiation methods, as well as expanding the scope of possible initiators.

CRediT authorship contribution statement

Shelby L Shankel: conceptualization, investigation, visualization, writing original draft, review and editing. **Yuting Ma**: conceptualization, investigation, writing original draft, review and editing. **Jesse A. Spivey**: formal analysis, software. **Leila Filien**: investigation. **Tristan H. Lambert**: conceptualization, funding acquisition, resources, review and editing. **Brett P. Fors**: conceptualization, funding acquisition, resources, review and editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online.

Materials, instrumentation, experimental procedures, ^{1}H-NMR spectra for small molecule synthesis and polymerizations, fittings for titration data, coordinates for optimized geometries

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