

Polar Thermoplastics with Tunable Physical Properties Enabled by the Stereoselective Copolymerization of Vinyl Ethers

Aaron J. Teator,¹ Travis P. Varner,¹ Paige E. Jacky,¹ Karolina A. Sheyko, and Frank A. Leibfarth^{1*}

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, United States

Supporting Information

ABSTRACT: A series of isotactic, semicrystalline vinyl ether copolymers (up to 94% *meso* diads) were synthesized using a chiral BINOL-based phosphoric acid in combination with a titanium Lewis acid. This stereoselective cationic polymerization enabled the systematic tuning of both glass transition (T_g) and melting temperature (T_m) in copolymers derived from alkyl vinyl ethers (i.e., ethyl, butyl, isobutyl). Additionally, a vinyl ether comonomer bearing an acyl-protected alcohol was utilized as a platform for postfunctionalization. Copolymers containing the masked alcohols were shown to undergo deprotection and subsequent coupling with a desired acid chloride. Collectively, these results highlight the diverse material properties and expanded chemical space accessible through stereoselective cationic polymerization mediated by a chiral anion.



Vinyl ethers represent an abundant and underutilized chemical feedstock for the production of high-value polymers. The range of commercially available vinyl ether monomers enables the preparation of materials that offer a diverse array of functionality. The rich history of methodology development for cationic polymerization has resulted in multiple complementary approaches for the homo- and copolymerization of vinyl ethers.^{1–6} Poly(vinyl ether)s (PVEs), however, typically display low glass transition temperatures ($T_g < -20$ °C) and are amorphous viscoelastic fluids at room temperature.⁷ Thus, the majority of these polymers exhibit nearly identical thermomechanical properties at common operating temperatures that are independent of side chain identity.⁸

One frequently utilized strategy for tuning material properties is copolymerization, whereby two or more constituent monomers are combined into a single copolymer in order to achieve the synergistic combination of properties represented by the individual homopolymers.⁹ Previous approaches toward modulating the physical properties of PVEs through copolymerization have focused on influencing either the thermomechanical or interfacial properties through the incorporation of a functional comonomer (Figure 1). For example, the incorporation of octadecyl vinyl ether (ODVE) into PVE copolymers has been investigated to impart semicrystalline properties into atactic materials driven by crystallization of the ODVE side chains. When copolymerized with isobutyl vinyl ether (iBVE), this approach yielded materials with tunable melting temperatures up to a maximum T_m of 43 °C.¹⁰ Copolymerization of ODVE with the water-soluble monomer methoxy ethyl vinyl ether (MOVE) resulted in materials which form hydrogels cross-linked by semicrystalline ODVE-rich phases.^{11–13} Similarly, Kennemur and co-workers recently copolymerized iBVE with a rigid, isosorbide-

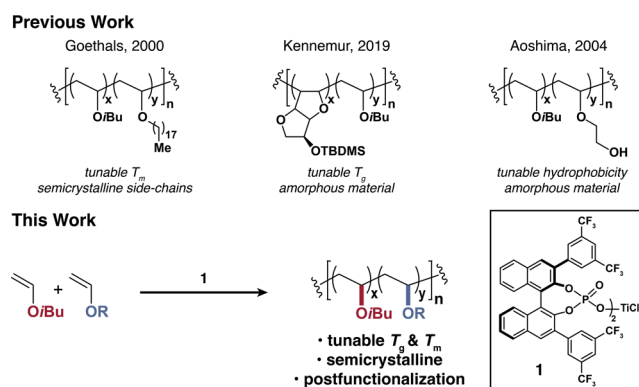


Figure 1. Stereoselective cationic polymerization using **1** enables the preparation of polar, semicrystalline thermoplastics with tunable thermal properties.

derived vinyl ether monomer in order to modulate the T_g of the resulting PVE copolymers over a 25 °C range.¹⁴ Aoshima and co-workers sought to influence the relative hydrophobicity of PVEs by copolymerizing a *tert*-butyldimethylsilyl (TBDMS)-protected hydroxyethyl vinyl ether comonomer with iBVE.¹⁵ Upon deprotection to reveal an alcohol-functional comonomer, the relative incorporation of a hydrophilic comonomer enabled rational tuning of the aqueous lower critical solution temperature (LCST). These examples, and others,^{16–22} highlight the challenge of preparing PVE copolymers that simultaneously exhibit high-value functionality and desirable thermomechanical properties.

Received: October 14, 2019

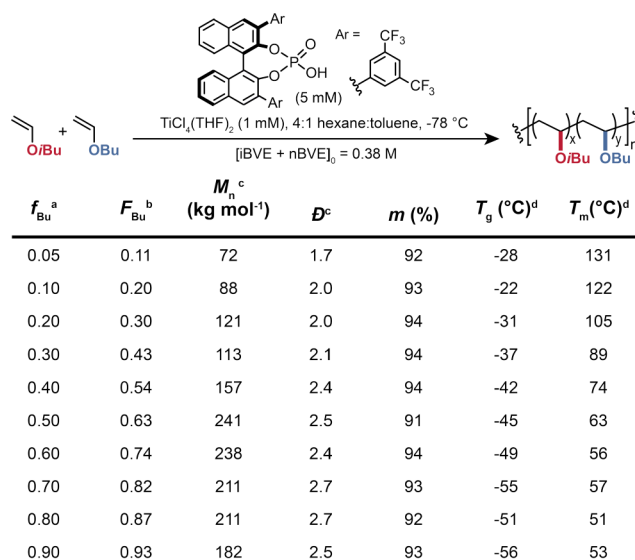
Accepted: November 12, 2019

Published: November 15, 2019

Despite the previous approaches toward the production of functional atactic PVE copolymers, the amorphous nature of these materials inherently limits the diversity of their thermomechanical properties. In contrast, polyolefins represent a high-volume and versatile class of semicrystalline thermoplastics. The incorporation of polar groups into polyolefins through copolymerization has been a long-standing challenge. Attempts to incorporate Lewis basic functionality into polyolefins using early transition metal complexes lead to catalyst poisoning and invariably limit the degree of comonomer incorporation accessible through coordination–insertion mechanisms.²³ Although late transition metal catalysts have been developed to combat this limitation,^{24–27} the requisite activity, structural control, or stereocontrol for translation has not been demonstrated to date. The copolymerization of vinyl monomers to achieve semicrystalline thermoplastics with tunable thermomechanical and interfacial properties, therefore, remains an outstanding challenge.²⁸

Recently, we reported a general method for the stereoselective cationic homopolymerization of vinyl ethers to achieve polar, semicrystalline thermoplastics that demonstrated adhesion properties over an order of magnitude greater than polyolefins.²⁹ This method utilizes a 1,1'-bi-2-naphthol (BINOL)-based phosphoric acid in combination with a titanium Lewis acid (**1**) to achieve isotactic PVEs with high degrees of stereoselectivity (up to 93% *meso* diads). The identity of the alkyl side-chain functionality had a distinct impact on the thermal properties of the obtained polymers. Isotactic PVEs bearing linear alkyl substituents (e.g., ethyl, propyl, butyl) exhibited T_m 's that ranged from 65 to 76 °C, while those with branched side chains (e.g., isopropyl, isobutyl) featured T_m 's that ranged from 138 to 152 °C. We envisioned leveraging this disparity of thermal properties between linear and branched vinyl ether substituents to prepare semicrystalline thermoplastics with tunable thermomechanical and interfacial properties. Herein, we present a systematic evaluation of stereoselective vinyl ether copolymerization using catalyst **1**. We demonstrate the generality of this catalyst through the stereoselective statistical copolymerization of alkyl vinyl ether monomers. The introduction of comonomers does not influence the stereoselectivity of catalyst **1** and enables the realization of semicrystalline thermoplastics derived from polar vinyl monomers with tunable thermal properties. Furthermore, the functional group tolerance of **1** is exploited to access polar thermoplastics with rationally designed functionality.

Considering the disparate thermal properties exhibited by isotactic PVEs bearing linear and branched alkyl substituents, we chose to first explore the copolymerization of butyl vinyl ether (nBVE) with iBVE (Figure 2). Addition of a prechilled solution of **1** to a mixture of nBVE and iBVE at –78 °C resulted in efficient copolymerization that produced high molecular weight materials ($M_n > 70 \text{ kg mol}^{-1}$) via an uncontrolled chain-growth polymerization. In order to tune the ultimate incorporation of nBVE in the resulting copolymers, reactions were performed using a variety of molar feed ratios of nBVE (f_{Bu}) relative to iBVE. As shown in Figure 3A, distinct ¹H NMR resonances were observed for iBVE (δ 3.25–2.05 ppm, CDCl₃) and nBVE (δ 1.40–1.30 ppm, CDCl₃) repeat units, which were integrated relative to each other in order to determine the mole fraction of nBVE (F_{Bu}). Analysis of the ¹³C NMR enabled the determination of stereoselectivity by comparing the integration of the region corresponding to the



^a mole fraction of nBVE in the monomer feed. ^b mole fraction of nBVE in copolymer determined by ¹H NMR integration. ^c M_n indicates the number average molecular weight of the polymer. Dispersity was calculated according to $D = M_w/M_n$, where M_w is the weight average molecular weight. ^d T_g and T_m obtained from a second heating scan (10 °C/min) after the thermal history was removed.

Figure 2. Reaction scheme depicting the stereoselective copolymerization of iBVE and nBVE using **1** and a summary of copolymerization experiments.

racemo diads (δ 42.0–41.0 ppm, CDCl₃) to the region corresponding to the *meso* diads (δ 40.4–39.2 ppm, CDCl₃) (Figure 3B). Catalyst **1** enabled the preparation of poly(iBVE-co-nBVE) with high degrees of isotacticity (91–94% *meso* diads) for all copolymer compositions, demonstrating the generality of **1** for stereoselective copolymerization of multiple alkyl vinyl ethers. This substrate tolerance represents an improvement over previous work where stereoselectivity was sensitive to even slight changes in monomer structure.^{30,31}

Next, we sought to investigate the relationship between f_{Bu} and F_{Bu} through kinetic analysis. Although values of F_{Bu} did not scale proportionally to f_{Bu} , increasing f_{Bu} resulted in increased F_{Bu} which enabled the preparation of copolymers with predetermined F_{Bu} values. In order to gain a deeper understanding of the reaction, a series of copolymerizations where $f_{\text{Bu}} = 0.50$ were quenched at various time points to evaluate reaction kinetics. As shown in Figure 4, iBVE was consumed at a slower rate ($k_{\text{obs}} = 4.4 \times 10^{-4} \text{ s}^{-1}$) relative to the consumption of nBVE ($k_{\text{obs}} = 7.8 \times 10^{-4} \text{ s}^{-1}$) throughout the copolymerization. Previous explorations of vinyl ether copolymerization, in particular those initiated by trifluoromethanesulfonic acid or boron trifluoride diethyl etherate, observed the opposite reactivity trend, whereby the more sterically hindered comonomer was consistently incorporated at a faster rate.^{32,33} The catalyst-controlled stereoselectivity exhibited in polymerizations mediated by **1** suggests a close interaction between the chiral anion and the propagating chain end, which we hypothesize to be interrupted by sterically demanding side chains. The relatively slow rate of iBVE consumption observed during copolymerization with nBVE is thus likely related to an adverse steric interaction between iBVE and **1**. Comonomer consumption plateaus at a combined monomer conversion of ~65% after 30 min (Figure S14) which, combined with the aforementioned rates, is consistent with the observed F_{Bu} values.

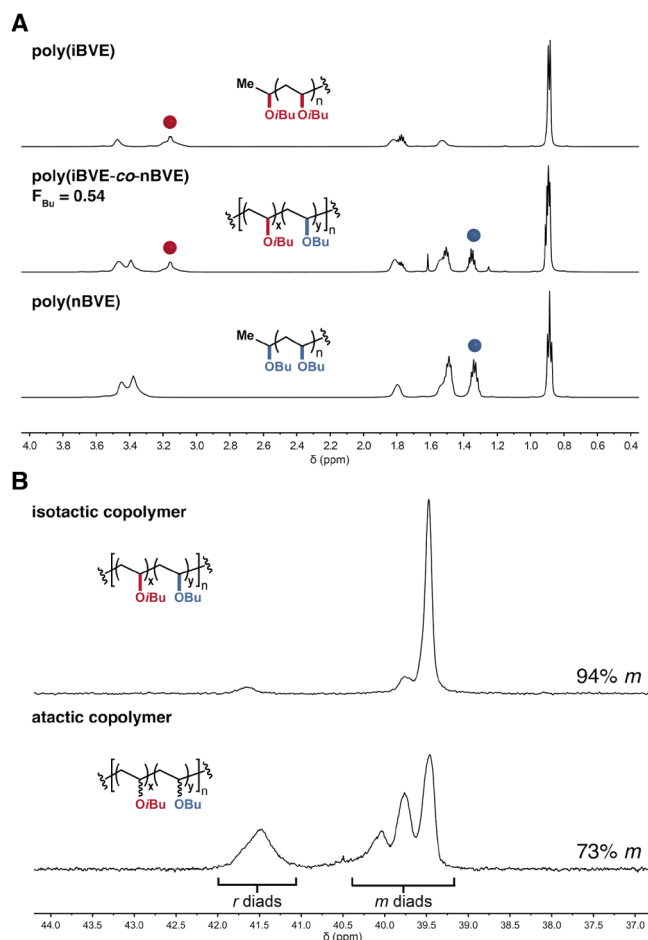


Figure 3. (A) ^1H NMR (CDCl_3) spectra of poly(iBVE) (top), poly(iBVE-co-nBVE) (middle), and poly(nBVE) (bottom) highlighting the distinct resonances observed for iBVE (red sphere) and nBVE (blue sphere) repeat units. (B) Observed differences of the backbone methylene ^{13}C NMR (CDCl_3) resonances in an isotactic poly(iBVE-co-nBVE) made using **1** and an atactic poly(iBVE-co-nBVE) made using trifluoromethanesulfonic acid.

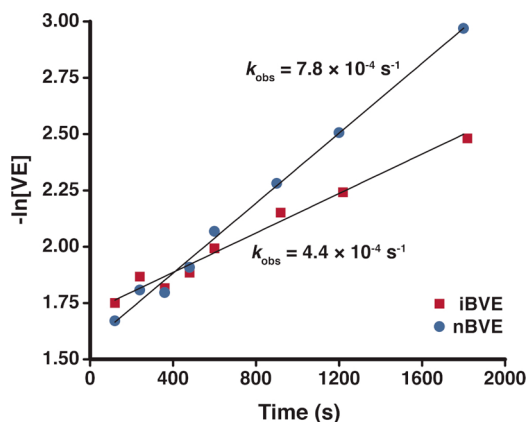


Figure 4. Plot of $-\ln[\text{VE}]$ versus time of the copolymerization of iBVE and nBVE. Conversions of iBVE (■) and nBVE (●) monitored independently by ^1H NMR (CDCl_3). VE = vinyl ether. $[\text{iBVE}]_0 = 0.19 \text{ M}$. $[\text{nBVE}]_0 = 0.19 \text{ M}$.

Each of the obtained poly(iBVE-co-nBVE) samples were semicrystalline thermoplastics at room temperature. As shown in Figure 5, differential scanning calorimetry (DSC) analysis at

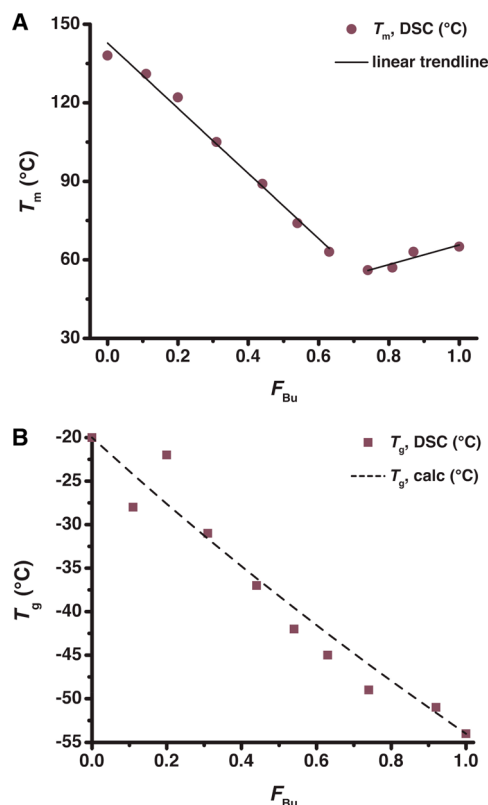


Figure 5. (A) Plot of T_m obtained by DSC as a function of molar incorporation of nBVE (F_{Bu}). Solid lines highlight observed trends. (B) Plot of T_g obtained by DSC as a function of F_{Bu} . Dashed line indicates T_g values predicted using the Fox equation.

a scan rate of $10 \text{ }^\circ\text{C}/\text{min}$ with data taken from the second heating cycle revealed the copolymers exhibited T_g and T_m values that span the range between those of poly(iBVE) ($T_g = -20 \text{ }^\circ\text{C}$, $T_m = 138 \text{ }^\circ\text{C}$) and poly(nBVE) ($T_g = -53 \text{ }^\circ\text{C}$, $T_m = 65 \text{ }^\circ\text{C}$). The T_g values observed by DSC scale with F_{Bu} as predicted by the Fox equation^{34,35} (Figure 5B) and remain well below room temperature. The apparent T_m values decrease linearly with increasing F_{Bu} as expected but reach an inflection point at approximately $F_{\text{Bu}} = 0.7$, which we hypothesize is due to a switch in the composition of the crystalline regions from iBVE repeat units to nBVE repeat units. Accordingly, as incorporation of nBVE increases from this point (i.e., $F_{\text{Bu}} > 0.7$) a slight increase in T_m is observed, likely resulting from decreasing contributions from iBVE “defects” within the nBVE crystalline phase. Regardless, the observed trends afford the ability to rationally tune both T_g and T_m by selecting the appropriate f_{Bu} and highlight the general utility of vinyl ether copolymerizations facilitated by **1**.

In an effort to explore the substrate scope of this methodology, we next performed a series of copolymerizations using ethyl vinyl ether (EVE) as a comonomer with iBVE. Similar to the iBVE/nBVE comonomer pair, utilizing a variety of EVE molar feed ratios (f_{Et}) resulted in isotactic copolymers (91–93% *meso* diads) with tunable degrees of EVE incorporation (F_{Et}) (Table S1). The obtained F_{Et} values were again consistently higher than f_{Et} likely due to a kinetic phenomenon similar to that described above. The T_g values exhibited by poly(iBVE-co-EVE) decreased as expected with increasing F_{Et} but appeared to plateau at $T_g = -37 \text{ }^\circ\text{C}$ when $F_{\text{Et}} \geq 0.5$. Similarly, the observed T_m values decreased linearly with

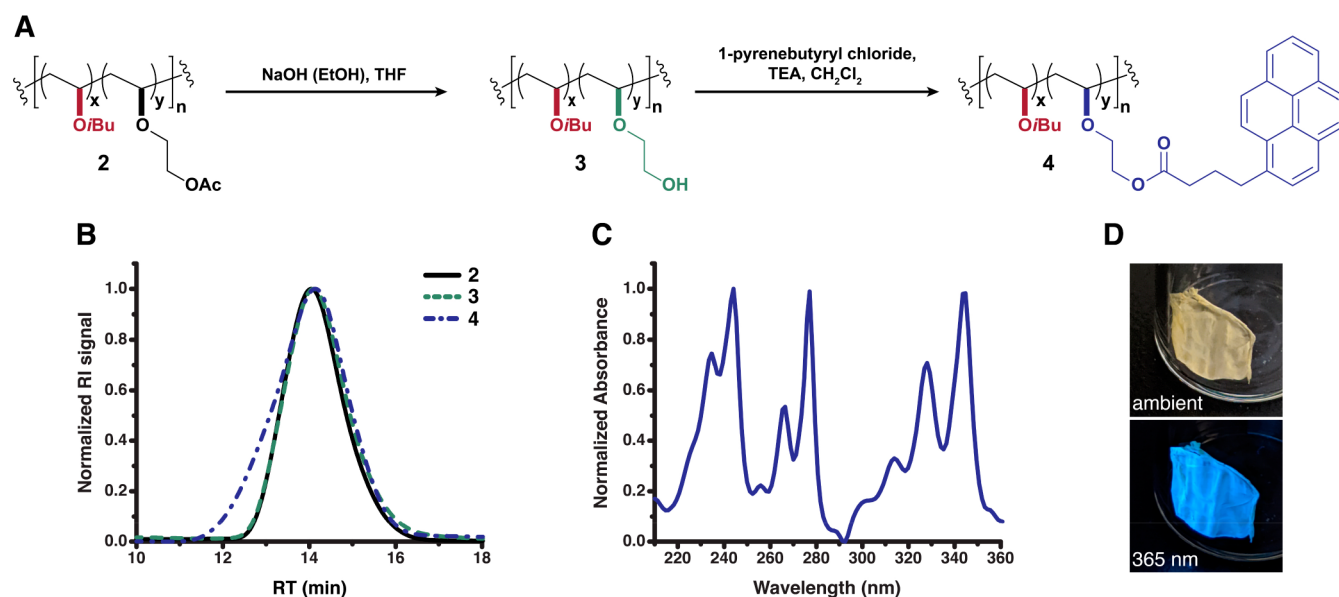


Figure 6. (A) Reaction scheme depicting deprotection of copolymer 2 and postfunctionalization of 3 to generate 4. (B) Overlay of GPC traces before and after each step depicted in A. (C) Photodiode array (PDA) trace at 13.9 min retention time (RT) confirming the structure of 4. (D) Visual representation (photo) highlighting the solid-state fluorescence of 4 observed under 365 nm irradiation.

increasing F_{Et} from 138 °C until plateauing at ~40 °C when $F_{Et} \geq 0.5$. No T_m was reliably observed in the second heating cycle by DSC when $F_{Et} \geq 0.3$, although these materials crystallized slowly at room temperature and exhibited obvious first-order transitions in the first heating cycle.

Having demonstrated that the stereoselective copolymerization of nBVE or EVE with iBVE resulted in semicrystalline thermoplastic materials with modular T_g and T_m values, we next explored the diversity of functionality that can be incorporated into PVE copolymers. We prepared a copolymer using acyl-protected ethylene glycol vinyl ether (AcVE) as a comonomer with iBVE (2, Figure 6A). Using a molar feed ratio (f_{Ac}) of 0.05 we achieved a high molecular weight ($M_n = 41 \text{ kg mol}^{-1}$) copolymer with a 6.5% incorporation of AcVE ($F_{Ac} = 0.065$) and 90% *meso* diads. At this degree of incorporation, the material remained a high-melting thermoplastic with a T_g of −26 °C and a T_m of 124 °C. Deprotection of the acyl functional group in 2 using NaOH efficiently yielded copolymer 3 which features repeat units containing free hydroxyl groups. As shown in Figure 6B, the gel permeation chromatography (GPC) traces for 2 and 3 closely overlap indicating the reaction proceeds without appreciable byproduct formation. Subsequent coupling with 1-pyrenebutyryl chloride yielded pyrene-appended copolymer 4, as evidenced by ¹H and ¹³C NMR as well as GPC in conjunction with a photodiode array (PDA) detector (Figure 6C). This material exhibited a slightly increased T_g of −16 °C relative to 2 and remained a high-melting thermoplastic with a T_m of 126 °C, but was now fluorescent under UV irradiation.

In summary, we have leveraged the stereoselective cationic polymerization facilitated by catalyst 1 to prepare a series of isotactic vinyl ether-based copolymers. Through judicious choice of comonomer pairs, both the T_m and T_g of the resulting materials can be rationally tuned by modulating the relative incorporation of each comonomer. Furthermore, vinyl ethers which contain masked hydroxyl functionality were shown to be competent comonomers for further diversification and were utilized to append a fluorescent pyrene-derived

functional group. The ability to copolymerize heteroatom-containing comonomers as well as perform multiple post-functionalization reactions without sacrificing the stereochemistry and desirable thermal properties of the homopolymers represents a practical approach toward polar, high-performance thermoplastics and will lead to isotactic PVEs with a multitude of functionality.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.9b00802.

Experimental details, supplementary text, and additional figures S1–S28 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: frankl@email.unc.edu.

ORCID

Aaron J. Teator: 0000-0003-4890-2487

Travis P. Varner: 0000-0003-1320-6262

Paige E. Jacky: 0000-0003-2375-4107

Frank A. Leibfarth: 0000-0001-7737-0331

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the National Science Foundation under the CAREER award (CHE-1847362).

■ REFERENCES

- (1) Aoshima, S.; Kanaoka, S. A Renaissance in Living Cationic Polymerization. *Chem. Rev.* **2009**, *109*, 5245–5287.
- (2) Uchiyama, M.; Satoh, K.; Kamigaito, M. Cationic RAFT Polymerization Using Ppm Concentrations of Organic Acid. *Angew. Chem., Int. Ed.* **2015**, *54*, 1924–1928.

- (3) Kottisch, V.; Michaudel, Q.; Fors, B. P. Photocontrolled Interconversion of Cationic and Radical Polymerizations. *J. Am. Chem. Soc.* **2017**, *139*, 10665–10668.
- (4) Kottisch, V.; O'Leary, J.; Michaudel, Q.; Stache, E. E.; Lambert, T. H.; Fors, B. P. Controlled Cationic Polymerization: Single-Component Initiation under Ambient Conditions. *J. Am. Chem. Soc.* **2019**, *141*, 10605–10609.
- (5) Prasher, A.; Hu, H.; Tanaka, J.; Nicewicz, D. A.; You, W. Alcohol Mediated Degenerate Chain Transfer Controlled Cationic Polymerisation of *Para*-Alkoxyethylene. *Polym. Chem.* **2019**, *10*, 4126–4133.
- (6) Kamigaito, M.; Satoh, K.; Uchiyama, M. Degenerative Chain-transfer Process: Controlling All Chain-growth Polymerizations and Enabling Novel Monomer Sequences. *J. Polym. Sci., Part A: Polym. Chem.* **2019**, *57*, 243–254.
- (7) Schröder, G. Poly(Vinyl Ethers). *Ullmann's Encycl. Ind. Chem.* **2000**, *28*, 481–485.
- (8) Fishbein, L.; Crowe, B. F. The Relation of Structure to Some Physical and Mechanical Properties of Poly(Vinyl Alkyl Ethers). *Makromol. Chem.* **1961**, *48*, 221–228.
- (9) Dube, M. A.; Saldivar-Guerra, E.; Capata-Gonzalez, I. Copolymerization. *Handb. Polym. Synth. Charact. Process.* **2013**, 105–125.
- (10) Zhang, X.; Reyntjens, W.; Goethals, E. J. Living Copolymerization of Octadecyl Vinyl Ether with Isobutyl Vinyl Ether: Copolymerization Parameters and Crystallization Behaviour of the Copolymers. *Polym. Int.* **2000**, *49*, 277–280.
- (11) Yoshida, T.; Seno, K.-I.; Kanaoka, S.; Aoshima, S. Stimuli-Responsive Reversible Physical Networks. I. Synthesis and Physical Network Properties of Amphiphilic Block and Random Copolymers with Long Alkyl Chains by Living Cationic Polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1155–1165.
- (12) Yoshida, T.; Kanaoka, S.; Watanabe, H.; Aoshima, S. Stimuli-Responsive Reversible Physical Networks. II. Design and Properties of Homogeneous Physical Networks Consisting of Periodic Copolymers Synthesized by Living Cationic Polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 2712–2722.
- (13) Sugihara, S.; Kanaoka, S.; Aoshima, S. Double Thermosensitive Diblock Copolymers of Vinyl Ethers with Pendant Oxyethylene Groups: Unique Physical Gelation. *Macromolecules* **2005**, *38*, 1919–1927.
- (14) Kieber, R. J.; Ozkardes, C.; Sanchez, N.; Kennemur, J. G. Cationic Copolymerization of Isosorbide towards Value-Added Poly(Vinyl Ethers). *Polym. Chem.* **2019**, *10*, 3514.
- (15) Sugihara, S.; Kanaoka, S.; Aoshima, S. Thermosensitive Random Copolymers of Hydrophilic and Hydrophobic Monomers Obtained by Living Cationic Copolymerization. *Macromolecules* **2004**, *37*, 1711–1719.
- (16) Yoshida, T.; Doi, M.; Kanaoka, S.; Aoshima, S. Polymer Surface Modification Using Diblock Copolymers Containing Azobenzene. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5704–5709.
- (17) Ida, S.; Ouchi, M.; Sawamoto, M. Living Cationic Polymerization of an Azide-Containing Vinyl Ether toward Addressable Functionalization of Polymers. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 1449–1455.
- (18) Yoshida, T.; Kanaoka, S.; Aoshima, S. Photo-Responsive Copolymers with Azobenzene Side Groups Synthesized by Living Cationic Polymerization: Efficient Amplification of Photosensitivity in Aqueous Photo-Switching System. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5337–5342.
- (19) Shibata, T.; Kanaoka, S.; Aoshima, S. Quantitative Synthesis of Star-Shaped Poly(Vinyl Ether)s with a Narrow Molecular Weight Distribution by Living Cationic Polymerization. *J. Am. Chem. Soc.* **2006**, *128*, 7497–7504.
- (20) Yoshida, T.; Kanaoka, S.; Aoshima, S. Photosensitive Copolymers with Various Types of Azobenzene Side Groups Synthesized by Living Cationic Polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4292–4297.
- (21) Goethals, E. J.; Reyntjens, W.; Lievens, S. Poly(Vinyl Ethers) as Building Blocks for New Materials. *Macromol. Symp.* **1998**, *132*, 57–64.
- (22) Kwon, S.; Lee, Y.; Mah, S. Living Cationic Polymerization of Vinyl Ethers in the Presence of Iodomethyl Methyl Ether and Zinc Iodide. *Fibers Polym.* **2001**, *2*, 9–12.
- (23) Ittel, S. D.; Johnson, L. K.; Brookhart, M. Late-Metal Catalysts for Ethylene Homo- and Copolymerization. *Chem. Rev.* **2000**, *100*, 1169–1203.
- (24) Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M. Living Alkene Polymerization: New Methods for the Precision Synthesis of Polyolefins. *Prog. Polym. Sci.* **2007**, *32*, 30–92.
- (25) Nakamura, A.; Anselment, T. M. J.; Clavierie, J.; Goodall, B.; Jordan, R. F.; Mecking, S.; Rieger, B.; Sen, A.; Van Leeuwen, P. W. N. M.; Nozaki, K. Ortho-Phosphinobenzenesulfonate: A Superb Ligand for Palladium-Catalyzed Coordination-Insertion Copolymerization of Polar Vinyl Monomers. *Acc. Chem. Res.* **2013**, *46*, 1438–1449.
- (26) Franssen, N. M. G.; Reek, J. N. H.; de Bruin, B. Synthesis of Functional 'Polyolefins': State of the Art and Remaining Challenges. *Chem. Soc. Rev.* **2013**, *42*, 5809–5832.
- (27) Chen, E. Y.-X. Coordination Polymerization of Polar Vinyl Monomers by Single-Site Metal Catalysts. *Chem. Rev.* **2009**, *109*, 5157–5214.
- (28) Worch, J. C.; Prydderch, H.; Jimaja, S.; Bexis, P.; Becker, M. L.; Dove, A. P. Stereochemical Enhancement of Polymer Properties. *Nat. Rev. Chem.* **2019**, *3*, 514.
- (29) Teator, A. J.; Leibfarth, F. A. Catalyst-Controlled Stereoselective Cationic Polymerization of Vinyl Ethers. *Science* **2019**, *363*, 1439–1443.
- (30) Ouchi, M.; Kamigaito, M.; Sawamoto, M. Stereoregulation in Cationic Polymerization by Designed Lewis Acids I: Highly Isotactic Poly(isobutyl vinyl ether) with Titanium-based Lewis Acids. *Macromolecules* **1999**, *32*, 6407–6411.
- (31) Ouchi, M.; Kamigaito, M.; Sawamoto, M. Stereoregulation in Cationic Polymerization by Designed Lewis Acids II: Effects of Alkyl Vinyl Ether Structure. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1060–1066.
- (32) Yuki, H.; Hatada, K.; Nagata, K.; Emura, T. Reactivities and ¹³C NMR Spectra of Alkyl Vinyl Ethers. *Polym. J.* **1970**, *1*, 269–270.
- (33) Higashimura, T.; Masamoto, J.; Okamura, S. Cationic Copolymerization of Vinyl Ethers Catalyzed by BF₃•(OC₂H₅)₂. *Kobunshi Kagaku* **1968**, *25*, 702–707.
- (34) Fox, T. G.; Flory, P. J. The Glass Temperature and Related Properties of Polystyrene. Influence of Molecular Weight. *J. Polym. Sci.* **1954**, *14*, 315–319.
- (35) Fox, T. G.; Flory, P. J. Second-Order Transition Temperatures and Related Properties of Polystyrene. I. Influence of Molecular Weight. *J. Appl. Phys.* **1950**, *21*, 581–591.