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Cationic copolymerization of isosorbide towards value-added poly(vinyl ethers)†

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Biomass-derived isosorbide (IS) was converted into a mono-glycal (*i.e.* vinyl ether) derivative (Gly-IS) to investigate its efficacy for cationic polymerization. While homopolymerization was unsuccessful, likely due to the steric demand near the propagating cationic site, copolymerization with isobutyl vinyl ether (IBVE) revealed great promise for the use of Gly-IS as a rigid and sustainable comonomer. Traditional cationic methods yielded copolymers with IBVE, but the incorporation of Gly-IS was hindered by the propensity for Lewis acids to catalyze a ring-opening reaction driven by aromatization to a chiral furan analog. This reaction was discovered to be significantly sequestered through the use of metal-free photoinitiated cationic copolymerization methods that are void of Lewis acid reagents, yielding a much higher incorporation of Gly-IS (up to 42 mol%) into the copolymer. The rigidity and chirality of the Gly-IS repeating unit was found to increase the glass transition temperature (T_g) up to 25 °C with 33 mol% incorporation at modest molar mass (10.4 kg mol^{-1}) while all copolymers displayed thermal stability up to 320 °C under inert atmosphere. Due to its chiral structure, specific optical rotation [α] of the copolymer also increased with incorporation of Gly-IS. Therefore, Gly-IS presents opportunity as a sustainable and value-added comonomer to modulate the properties of common poly(vinyl ether) systems.

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Introduction

Isosorbide (IS) is one of the US Department of Energy's (DOE) top biomass chemicals.[1] It is synthesized from a double dehydration of D-sorbitol which was produced from glucose on a scale of 1.7 Mton year^{-1} in 2011.[2,3] The chirality, rigidity, and diol functionality of IS make it an attractive renewable polymeric feedstock for inclusion with a variety of step-growth polymerization strategies.[3–9] IS containing polymers have been found to improve scratch resistance with superior optical properties while the rigidity imposed by the isohexide structure often leads to favorable thermal properties such as high glass transition temperatures (T_g).[2–4,10–12] The combination of these advantages has begun to reach industrial relevance. For example, Mitsubishi Chemical is now incorporating IS into commercial polycarbonates with improved performance for numerous applications.[13]

An intriguing aspect of IS is its chiral, three-dimensional structure, shown in Scheme 1. The 120° angle between the two fused tetrahydrofuran (THF) rings provides an *endo* and *exo* face which are each occupied by one of the alcohol substituents. The *endo* alcohol, located within the "V" of the fused rings, is more sterically encumbered than the *exo* alcohol. Furthermore, the *endo* alcohol has a higher nucleophilicity due to its proximity to the oxygens on the THF rings which allow for intramolecular hydrogen bonding.[3,4,14,15] The difference in reactivity and accessibility of the two alcohols has led to a number of synthetic reactions that preferentially derivatize one of the alcohols and allow access to asymmetric IS analogs.[2,16–21] In some cases, selective transformation of one IS alcohol provides derivatives amenable for chain-growth polymerization strategies although surprisingly few examples have been reported.[22–27] Drockenmuller and coworkers replaced one of the alcohols on IS, isomannide, and isoidide, with a terminal alkyne. After copper-(I)-catalyzed azide–alkyne cycloaddition, the resulting 1-vinyl-4-dianhydrohexitol-1,2,3-triazole monomers were polymerized by reversible-addition fragmentation transfer (RAFT) using a xanthate chain transfer agent (CTA).[22] Depending on the stereochemistry of the isohexide core, these materials displayed notable differences in solubility and T_g. Reineke and coworkers have reported AB diblock and ABA triblock polymers where the "A" block is comprised of polyacrylate or polymethacrylate with monoacetylated IS pendants.[23–25] The resulting materials, also synthesized by RAFT, were found to have favorable thermal, mechanical, and adhesive properties. The same group very recently reported a tricyclic ether derivative of IS which undergoes ring opening

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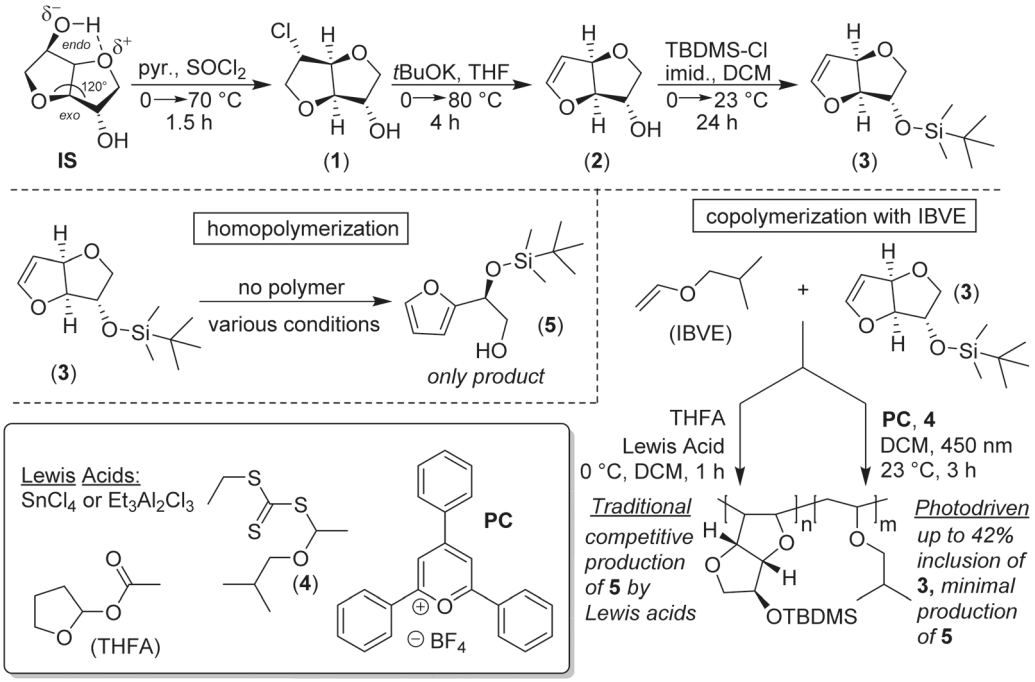


Scheme 1 Synthesis, cationic polymerization, and copolymerization of *tert*-butyldimethyl(((3*S*,3a*S*,6a*R*)-2,3,3a,6a-tetrahydrofuro[3,2-*b*]furan-3-yl) oxy)silane (**3**) under traditional living and photo-driven cationic polymerization conditions.

polymerization (ROP) into linear or cyclic polymers assisted by scandium triflate coordination.[26] Collectively, these reports illustrate the promise and potential utility for the use of IS in chain growth strategies.

We envisioned that selective elimination of one of the IS alcohols would produce a cyclic vinyl ether or glycal-functionalized IS derivative (**2**, **3** in Scheme 1) that may be susceptible to traditional cationic polymerization methods used for vinyl ethers. Commercial poly(vinyl ethers) (PVEs) are industrially useful as adhesives, coatings, and plasticizers, and are typically low glass transition temperature (T_g) materials.[28–30] Similarly, many PVEs synthesized from bio-derived sources have low T_g's.[31–35] Strategies to increase their glass transition temperature and/or alter material properties, especially through the use of sustainable comonomers, stands to expand the scope of PVEs for varying applications.[36] For example, Leibfarth and coworkers recently reported improved material and adhesion properties from highly isotactic PVEs produced by a bulky chiral counter-anion and a titanium catalyst.[37] Another potential means to alter the material properties is to increase the rigidity of the backbone through cyclic vinyl ethers. The resulting alicyclic polymers have already gained particular interest due to their favorable thermal properties, low dielectric constants, and high transparency.[38–40] One notable example is 2,3-dihydrofuran (DHF), a monocyclic version of **2** and **3** (Scheme 1), which has been found to undergo cationic polymerization with good control despite an increase in reactivity compared with linear vinyl ethers.[40–42] Within this report we investigate the efficacy for **3** to undergo cationic polymerization in homo- and copolymerizations utilizing living cationic conditions previously successful for DHF. We also investigate the propensity for cationic polymerization using recently reported photo-driven methods,[43,44] which offer a metal-free and potentially green alternative for producing PVEs.

Experimental

All chemicals were used as received unless otherwise stated. Carbon disulfide (>99.9% purified by redistillation), thionyl chloride (>99%), potassium *tert*-butoxide (*t*BuOK) (>98%), calcium hydride (≥90%, powder), sulfuric acid (95–98%), ammonia solution in methanol (2 M), acetic acid (≥99%), 2,3-dihydrofuran (DHF) (99%), and imidazole (99%) were obtained from Sigma-Aldrich. Ethyl acetate (≥99.5%), hexane (≥98.5%), dichloromethane (DCM) (≥99.5%), and methanol (≥99.8%) were obtained from EMD Millipore. Sodium sulfate (>99%), sodium chloride (>99%), and sodium bicarbonate (≥99.7%) were obtained from BDH. *tert*-Butyldimethylsilyl chloride (TBDMS-Cl) (>99%) was obtained from Oakwood Chemical. 2,4,6-Triphenylpyrylium tetrafluoroborate (97%) was obtained from Alfa Aesar. Isosorbide (IS) (>98%) and pyridinium *p*-toluenesulfonate (PTSA) (≥98%) were obtained from TCI. Silica gel, SiliaFlash P60 (40–63 μm), was obtained from SiliCycle. Sodium hydride (60% dispersion in mineral oil) was obtained from Acros Organics. Ethanethiol (97%) was obtained from Sigma-Aldrich and was distilled before use. Pyridine (>99%) was obtained from Sigma-Aldrich and was stored over 4 Å molecular sieves. Anhydrous diethyl ether (DEE) and tetrahydrofuran (THF) were obtained from a SG

Water USA Company solvent still where it was passed through two columns of neutral alumina then an in-line 2 μm filter. Dry toluene and DCM were also obtained from a SG Water USA Company solvent still where they were passed through two columns of neutral alumina then an in-line 2 μm filter, followed by distilling twice over CaH_2 prior to polymerizations. Chloroform-*d* ($CDCl_3$) (99.8%, Sigma-Aldrich) was stored over 4 Å molecular sieves. Isobutyl vinyl ether (IBVE) (99%, 0.1% KOH as a stabilizer) was obtained from Sigma-Aldrich and was distilled twice over CaH_2.

^{1}H and ^{13}C NMR experiments were conducted on a Bruker Advance III 600 MHz NMR. For polymer analysis, a pulse delay of 10 s was used for ^{1}H NMR to accommodate longer relaxation times and ensure accurate integration comparisons. Number average molar mass (M_n) and dispersity ($Đ$) were determined by an Agilent–Wyatt combination triple detection size exclusion chromatograph (SEC) containing 3 successive Agilent PL-gel Mixed C columns (THF mobile phase, 25 °C), an Agilent 1260 infinity series pump, degasser, autosampler, and thermostatted column chamber. The Wyatt triple detection unit hosts a MiniDawn TREOS 3-angle light scattering detector, Optilab TrEX refractive index detector, and a Viscostar II differential viscometer. The M_n and $Đ$ for each sample were determined by a 10-point universal calibration with narrow $Đ$ polystyrene standards ranging from 580 to 7 500 000 Da. Differential scanning calorimetry (DSC) was conducted on a TA Instruments model Q1000 with a model RCS 90 refrigerated cooling system accessory. Temperature was cooled to −60 °C at a rate of 10 °C min^{-1}, held isothermal for 2 min, then ramped to 100 °C, at a rate of 10 °C min^{-1}. The heat-cool cycle was then repeated, and thermal transitions were recorded upon the third heating. The LED (blue light ~450 nm) strip used was obtained from Amazing power (12 V, 3.65 W ft^{-1}). Thermogravimetric analysis (TGA) was performed on a TA Instruments model Q600 simultaneous DSC/TGA (SDT), under argon atmosphere. Samples were held isothermal at 100 °C for 10 min, then ramped to 600 °C at a rate of 10 °C min^{-1}. Purification of the RAFT agent (**4**) was conducted using a Biotage Isolera One system with accelerated chromatographic isolation (ACI) using SNAP cartridges with a silica stationary phase. All other columns were done with flash chromatography using a silica gel stationary phase obtained from SiliCycle. Optical rotation was performed at known concentrations between 10–15 mg mL^{-1} in DCM at 25 °C using a Jasco P-2000 polarimeter with a wavelength of 589 nm and quartz cells with a path length of either 1 dm or 1 cm. The glovebox used for some of the synthetic procedures was an MBraun UniLab system under dry nitrogen atmosphere (<5 ppm H_2O, <5 ppm O_2).

Synthesis

(3*S*,3a*R*,6*S*,6a*S*)-6-Chlorohexahydrofuro[3,2-*b*]furan-3-ol (1) was synthesized in accordance with literature[18] and is briefly described here.

Isosorbide (5.929 g, 40.6 mmol, 1 eq.) and pyridine (9.84 mL, 122 mmol, 3 eq.) were added to an oven-dried 50 mL round bottom flask (RBF) equipped with a magnetic stir bar. An oven-dried addition funnel was attached, and the mixture was cooled to 0 °C while purging with nitrogen. Thionyl chloride (6.5 mL, 89.3 mmol, 2.2 eq.) was added from the addition funnel to the reaction mixture dropwise over the course of ~30 min. Upon complete addition, the reaction mixture was heated to 70 °C for 1.5 h under nitrogen. The reaction mixture was then cooled to 0 °C, quenched with 10 mL of H_2O, stirred for 5 min, and transferred to a separatory funnel. The product was extracted using 30 mL brine and 30 mL ethyl acetate. The aqueous layer was then washed with ethyl acetate (30 mL) three times. The combined organic layers were dried over sodium sulfate then concentrated *en vacuo* to produce a crude brown solid (yield 71%). The crude product can be purified by recrystallization from anhydrous DEE to afford 3.147 g white solid (47% yield), however it was determined that crude **1** can be used in the next synthetic step without penalty to the yield of **2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.80 (s, 1H), 4.68 (s, 1H), 4.38 (s, 1H), 4.33 (s, 1H), 4.04 (s, 2H), 3.88 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 88.19, 87.58, 75.94, 75.56, 74.95, 60.62. NMR analysis is consistent with literature[18]

(3*S*,3a*R*,6a*R*)-2,3,3a,6a-Tetrahydrofuro[3,2-*b*]furan-3-ol (2) was synthesized following literature[18] with some modifications as described below.

In a glovebox, *t*BuOK (7.769 g, 69.2 mmol, 3 eq.) was added to an oven dried 100 mL RBF with a magnetic stir bar. The flask was capped, removed, and dry THF (25 mL) was added followed by cooling to 0 °C. After attachment of an addition funnel and reflux condenser, the setup was purged with N_2. The addition funnel was charged with **1** (3.799 g, 23.1 mmol, 1 eq.) dissolved in 10 mL dry THF followed by dropwise addition to the reaction flask. Following complete addition of **1**, the reaction was heated to 80 °C and stirred for 4 h under N_2. The mixture was cooled to 0 °C, quenched with 100 mL H_2O, diluted with 80 mL ethyl acetate, and transferred to a separatory funnel. The organic layer was collected, and the aqueous layer was washed three times with 80 mL ethyl acetate. The organic layers were combined and dried over Na_2SO_4, followed by concentration *en vacuo*. The crude product was then purified by column chromatography using a 95 : 5 DCM : MeOH mixture as the mobile phase (R_f = 0.30) to yield 2.051 g of **2** as a white solid (69% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 6.51 (s, 1H), 5.48 (s, 1H), 5.03 (s, 1H), 4.75 (s, 1H), 4.30 (s, 1H), 3.83 (s, 1H), 3.49 (s, 1H), 1.81 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 150.17, 99.90, 88.61, 83.86, 76.01, 70.01. NMR analysis is consistent with literature.[18]

***tert*-Butyldimethyl(((3*S*,3a*S*,6a*R*)-2,3,3a,6a-tetrahydrofuro[3,2-*b*]furan-3-yl)oxy)silane (3)** was synthesized following a previous procedure[45] and described below.

To a 100 mL RBF with a magnetic stir bar, **2** (1.302 g, 10.2 mmol, 1 eq.), imidazole (3.460 g, 50.8 mmol, 5 eq.), and dry DCM (50 mL) were added to a dry 100 mL RBF and magnetic stir bar. The solution was sparged with N_2 and cooled to 0 °C. TBDMS-Cl (4.615 g, 30.6 mmol, 3 eq.) was dissolved in 10 mL dry DCM and added dropwise using a syringe. The reac-

tion was gradually warmed to room temperature and stirred for 24 h under N_2. After filtering and washing the solids with DCM, the filtrate was collected in a separatory funnel and was washed with water (50 mL) twice. The organic layer was collected, dried over Na_2SO_4, then concentrated *en vacuo*. The resulting crude product was purified *via* column chromatography with 9 : 1 hexane : ethyl acetate as a mobile phase (R_f = 0.39), resulting in 1.717 g of **3** as a colorless oil (70% yield). The product was vacuum transferred from CaH_2 twice at 50 mTorr using a bath at 50 °C for complete drying. It was then stored in the glovebox at −20 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 6.48 (s, 1H), 5.43 (s, 1H), 5.04 (s, 1H), 4.65 (s, 1H), 4.28 (s, 1H), 3.72 (s, 1H), 3.45 (s, 1H), 0.90 (s, 9H), 0.12 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 149.48, 100.53, 89.79, 83.76, 76.95, 70.70, 25.95, 18.32, −4.63.

***S*-1-Isobutoxylethyl *S*′-ethyl trithiocarbonate (4)** was synthesized according to a previous procedure[43] and is described here.

NaH (1.000 g, 25.0 mmol, 1 eq.) was added to a dry RBF along with 10 mL anhydrous DEE. The mixture was cooled to 0 °C and purged with N_2. Ethanethiol (1.85 mL, 25 mmol, 1 eq.) was added dropwise using an addition funnel and the reaction was stirred at 23 °C for 10 min. The mixture was returned to 0 °C and CS_2 (1.65 mL, 27.5 mmol, 1.1 eq.) was added dropwise using the addition funnel. After complete addition, the reaction was returned to 23 °C and stirred for 2 h. The reaction was cooled to 0 °C and the IBVE-HCl adduct (see below) was added, after which the mixture was stirred at 23 °C for 2 h. Anhydrous DEE (10 mL) was used to dilute the reaction, which was then quenched with saturated $NaHCO_3$ solution (10 mL). The solution was added to a separatory funnel and the organic layer was collected. The aqueous layer was then washed twice with DEE (10 mL). The combined organic layers were then diluted with hexanes, washed with water (10 mL), brine (10 mL), then dried over Na_2SO_4. After filtration, the filtrate was collected and concentrated *en vacuo*. The crude mixture was purified with flash column chromatography in hexanes (R_f = 0.21). Further purification was done using a Biotage Isolera One system using hexane as an eluent. The product was concentrated to obtain **4** as a pure yellow oil. NMR analysis is consistent with literature.[43]

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 5.98 (s, 1H), 3.45 (s, 1H), 3.36 (s, 2H), 3.29 (s, 1H), 1.83 (s, 1H), 1.71 (s, 3H), 1.35 (s, 3H), 0.88 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 224.89, 89.09, 76.50, 31.06, 28.46, 22.95, 19.43, 13.12.

The IBVE-HCl adduct was synthesized *in situ* following literature examples.[46,47] IBVE (3.26 mL, 25 mmol) was added to a RBF with 25 mL anhydrous DEE. HCl gas was then bubbled into the IBVE solution for 30 min. The HCl (g) was generated by adding concentrated H_2SO_4 onto NaCl and was dried by passing through a plug of $CaCl_2$. The mixture was sparged with N_2 to remove excess HCl, and NMR spectroscopy confirmed complete conversion to the IBVE-HCl adduct (see Fig. S22†).

(*S*)-2-((*tert*-Butyldimethylsilyl)oxy)-2-(furan-2-yl)ethan-1-ol (5) was synthesized following previous procedures.[48]

In a 50 mL RBF with a magnetic stir bar, **3** (1.371 g, 5.67 mmol, 1 eq.) was dissolved in 20 mL anhydrous THF. Under a blanket of N_2, PTSA (35.5 mg, 0.14 mmol, 0.025 eq.) was added and the solution was heated to 50 °C and stirred for 30 min. The reaction was cooled to ambient and $NaHCO_3$ (47.5 mg, 0.57 mmol, 0.1 eq.) was added, followed by concentration *en vacuo*. The crude mixture was then purified with column chromatography using a hexane : ethyl acetate (8 : 2) mixture as the mobile phase (R_f = 0.32), resulting in **5** as a colorless oil (1.171 g, 85% yield). Product confirmed by ^{1}H NMR (Fig. S16†) in accordance to previous literature.[48]

2-Tetrahydrofuranyl acetate (THFA) initiator was synthesized according to literature.[40]

DHF (14.4 mL, 189 mmol, 1.5 eq.) and acetic acid (7.565 g, 126 mmol, 1 eq.) were added to a 100 mL RBF equipped with a reflux condenser. The mixture was heated to reflux for 3 h, and the collected product was fractionally distilled from CaH_2 twice (bp ∼60 °C at 10 mTorr) to afford 6.239 g colorless oil (38% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 6.27 (s, 1H), 4.04 (s, 1H), 3.91 (s, 1H), 2.02 (s, 7H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 170.65, 99.08, 69.00, 32.20, 23.00, 21.47.

Lewis acid initiated polymerization

Traditional living cationic polymerizations using Lewis acids were conducted following previous procedures[40] and is briefly described here.

In the glovebox, **3** (200 eq.) was added to an oven dry 10 mL RBF equipped with a magnetic stir bar. Stock initiator solution of THFA was prepared in anhydrous solvent (DCM or toluene) (79 mM), and 0.1 mL (7.9 μmol, 1 eq.) was added to the RBF along with 1.5 mL additional anhydrous solvent. The RBF was then removed from the glovebox, and the mixture was cooled to 0 °C. Lewis acid initiator, $SnCl_4$ or $Et_3Al_2Cl_3$, (5 eq.) was then added, and the reaction was stirred at 0 °C for between 1 and 24 h. The polymerization was then quenched with 2 mL prechilled NH_3 in MeOH (2 M), diluted in additional solvent, washed with water, and concentrated *en vacuo*.

Lewis acid initiated copolymerization

In the glovebox, IBVE and **3** were added in known quantities in varying ratios (300 eq. total) to an oven dry 10 mL RBF equipped with a magnetic stir bar. A stock initiator solution of THFA was then prepared in anhydrous DCM (79 mM), and 0.1 mL (7.9 μmol, 1 eq.) was then added to the RBF. The mixture was then diluted with anhydrous DCM (1.6 mL), removed from the glovebox, then cooled to 0 °C. $Et_3Al_2Cl_3$ (99 μL, 39.7 μmol, 5 eq.) was then added, and the reaction was stirred for 1 h. Upon quenching with 2 mL of NH_3 in MeOH (2 M), the solution was diluted in DCM, washed with water, then concentrated *en vacuo*. After redissolving in a small amount of DCM, the solution was precipitated in excess MeOH, and the solids were isolated and dried *en vacuo* at 100 °C for 48 h.

Photoinitiated copolymerizations of 3 and IBVE

Visible light-driven cationic polymerizations were carried out following previous procedures by Fors and coworkers[43,44] and

a representative procedure is described below. Homopolymerizations were carried out in an identical procedure, with no IBVE comonomer present.

In the glovebox, **4** (3.9 mg, 16.5 μmol, 1 eq.) was added to a 4 mL scintillation vial equipped with a magnetic stir bar. IBVE and **3** were then added using volumetric syringes at known quantities of varying ratios which totaled 300 molar equivalents to **4**. The photocatalyst (**PC**), 2,4,6-triphenylpyrylium tetrafluoroborate, (Scheme 1) solution was then prepared in anhydrous DCM (2 mM), and 0.093 mL (0.185 μmol, 0.01 eq.) was added into the vial, which was then sealed and removed from the glovebox. The vial was placed in a beaker that was encapsulated with the LED light strip affixed around the walls. It was also partially submerged in water to mitigate heat. After irradiation for 3 h, the reaction vial was removed and opened to air. The viscous mixture was then diluted in a small amount of DCM followed by precipitation in excess MeOH. After decanting, the solids were then dried within a vacuum oven at 100 °C for 48 h.

Results and discussion

The top of Scheme 1 outlines the synthetic transformations to selectively eliminate the *endo*-alcohol of IS. Hydrogen bonding of the *endo*-alcohol to oxygen within the IS scaffold enhances its nucleophilicity and allows increased selectivity (up to 70% yield) for reaction with thionyl chloride. Elimination of the resulting *exo*-chloride, **1**, using *t*BuOK produces the Gly-IS derivative, **2**, at ~70% yield following purification.[18] The remaining *exo*-alcohol on **2** was protected with TBDMS-Cl, producing **3** to prevent unwanted chain transfer or termination during the cationic polymerization. TBDMS was chosen due to its higher stability towards cationic polymerization over less bulky silyl protecting groups.[49] To examine the viability of cationic polymerization on **3**, we first attempted traditional cationic polymerizations using different Lewis acids ($SnCl_4$ or $Et_3Al_2Cl_3$) as an activator and 2-tetrahydrofuranyl acetate (THFA) as an initiator in DCM at 0 °C (Scheme 1).[36,40,50] These conditions were chosen due to their ability to successfully polymerize DHF in previous literature.[40] For every polymerization attempted, it was determined that no polymer had formed by SEC. Upon further investigation of the product by ^{1}H NMR (Fig. S17†) it was found that **3** instead underwent a near-quantitative ring opening and subsequent aromatization reaction to produce the chiral furan derivative, **5**, shown in Scheme 1. A survey of literature revealed precedence for this reaction under Brønsted–Lowry acid conditions through the mechanism described in Scheme S2.†[19,48] We further confirmed the susceptibility of **3** to this reaction using PTSA which proceeded with >99% conversion to **5** (Fig. S16†) and had an identical ^{1}H-NMR spectrum to the product produced by cationic homopolymerization with Lewis acids.[48]

We hypothesized that the large steric demand near the active cationic propagation site of **3** was significantly reducing the ceiling temperature (T_c) for this system, preventing homopropagation, and promoting the formation of **5** instead (Fig. S17†). Although **3** appears unable to propagate with itself under these conditions, we envisioned that copolymerizations using a less sterically hindered vinyl ether, such as IBVE, may allow the incorporation of **3** as a value-added comonomer within PVE derivatives. Furthermore, if copolymerization is viable and fast, the production of unwanted **5** may be kinetically disfavored. To test this, several copolymerizations were conducted using $Et_3Al_2Cl_3$ as an activator and THFA as an initiator (Scheme 1) with varying molar ratios of **3** (f_3) and IBVE incorporated into the feed, where $f_3 = [\mathbf{3}]_0 \times ([\mathbf{3}]_0 + [\mathrm{IBVE}]_0)^{-1}$, shown in Table 1. Following polymerization at 0 °C for 1 h, the reaction solution produced white polymer upon precipitation in MeOH. To determine if the polymer product was comprised of both **3** and IBVE repeating units, ^{1}H NMR analysis was performed to elucidate peaks associated with each comonomer. As shown in Fig. 1, distinct peaks from 4.5–5.0 ppm and 5.6–6.0 ppm are seen which increase in size with an increase in f_3 used in each copolymerization. These peaks were comparatively integrated to the peaks at ~3.0–3.8 ppm associated with the 3 hydrogen signals of IBVE and subtracted to account for the 2 overlapping hydrogen signals from **3**. The molar fraction of **3** repeating units within the copolymers (F_3) are provided in Table 1. A homopolymerization of IBVE (L0 in Fig. 1), was performed to elucidate only the proton signal resonances associated with IBVE repeating unit. The reported sample IDs in Table 1 and Fig. 1 are dictated by the type of initiating method (L for Lewis acid), followed by a number that corresponds to % mol fraction of **3** repeating units ($F_3 \times 100$). Analysis by SEC revealed that the number average molar mass ($M_{n,SEC}$) of each copolymer was significantly lower than theoretical ($M_{n,theo}$) determined from eqn (1)–(3), where n_x indicates moles of "x", M_x is that monomer's formula weight, and N_x is the degree of polymerization of either monomer. Full conversion of IBVE was observed by ^{1}H NMR of the crude copolymerization solutions, which is also known in literature to occur under similar conditions.[40,50] However, the theoretical molar mass calculation also assumes living conditions and therefore the disparity of our experimental molar mass is a good indication that a significant

Table 1 Copolymerizations of IBVE and **3** activated by $Et_3Al_2Cl_3$ and initiated by THFA in DCM at 0 °C for 1 h

Sample ID	f_3 [a]	F_3 [b]	F_3/f_3	$M_{n,theo}$ [c] (kg mol^{-1})	$M_{n,SEC}$ [d] (kg mol^{-1})	$Đ$ [d]	T_g [e] (°C)
L0	—	—	—	18.0	14.1	1.68	−17.8
L3	0.065	0.030	0.46	30.38	6.47	2.43	−15.1
L8	0.14	0.078	0.56	30.67	7.11	2.30	−12.4
L23	0.30	0.23	0.77	35.74	9.54	1.43	−1.03

[a] Mole fraction of **3** incorporated into the monomer feed with IBVE. [b] Mole fraction of **3** repeating units incorporated into the polymer determined *via* ^{1}H NMR analysis. [c] Calculated assuming 100% conversion of IBVE, with an adjustment for F_3 as described in eqn (1)–(3). [d] Determined from SEC (THF mobile phase) using conventional column calibration *vs.* narrow $Đ$ polystyrene standards. [e] Obtained by DSC from the third heating curve at a rate of 10 °C min^{-1}.

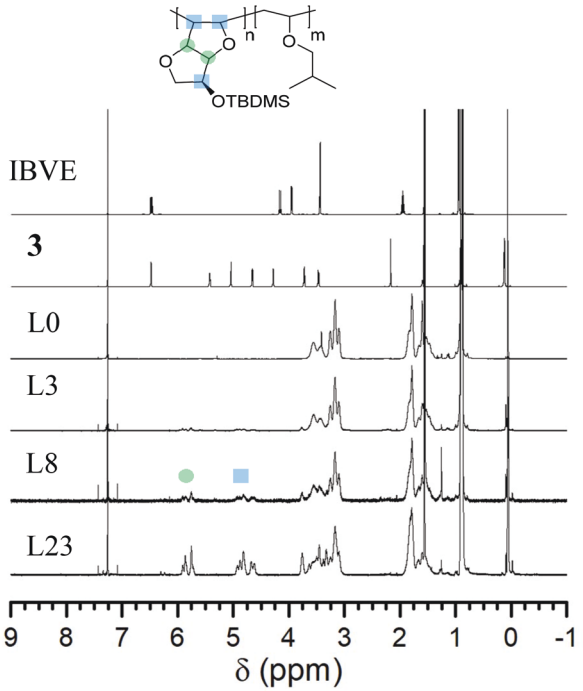


Fig. 1 ^{1}H NMR ($CDCl_3$, 600 MHz) overlay of IBVE (top), **3**, and subsequent copolymers in increasing content of **3** synthesized from $Et_3Al_2Cl_3$ and THFA in DCM at 0 °C.

amount of side reactions occurred. After each copolymerization, ^{1}H NMR of the crude polymerization product revealed a significant portion **5** had been produced even at low f_3 (Fig. S26†). This identifies why $F_3 \ll f_3$ in the resulting copolymer. On average only ~60% of **3** initially incorporated into the feed was found in the resulting copolymer ($F_3/f_3 \sim 0.6$), with appreciable variation between copolymerization attempts.

$$N_{\mathrm{IBVE}} = \frac{n_{\mathrm{IBVE}}}{n_{\mathrm{THFA}}} \quad (1)$$

$$F_{\mathrm{IBVE}} = \frac{N_{\mathrm{IBVE}}}{N_{\mathrm{IBVE}} + N_3} \quad (2)$$

$$M_{\mathrm{n,theo}} = M_{\mathrm{IBVE}} N_{\mathrm{IBVE}} + M_3 N_3 \quad (3)$$

Due to the propensity for Lewis acids to result in an appreciable formation of **5** even with the presence of IBVE comonomer, we envisioned that an alternative method for cationic polymerization, which is void of Lewis acids, may allow for increased incorporation of **3** and potentially sequester the formation of **5**. Recent work by Fors and coworkers has introduced an alternative method to perform living cationic polymerizations of vinyl ethers using a photo-initiated and photocontrolled RAFT mechanism.[43,44] This involves the visible-light excitation of a photocatalyst (**PC**), followed by single electron oxidation of a di- or trithiocarbonate RAFT degenerative chain transfer agent (CTA) and subsequent mesolytic cleavage to generate a propagating cation. The reversible nature of this mechanism with the stimulus of blue LED light (~450 nm) shows promise for facile control over cationic polymerizations under metal-free conditions.[43,44]

Homopolymerization of **3** was again attempted using the RAFT CTA, **4**, and 2,4,6-triphenylpyrylium tetrafluoroborate photocatalyst, **PC** (Scheme 1). Over the course of 3 h, no polymer and the formation of **5** occurred, which further supports the hypothesis that homopropagation of **3** is not viable. However, since the formation of **5** required longer reaction time, improved copolymerization with IBVE may be possible. To test this, a series of copolymerizations were performed using f_3 values ranging from 0.05 to 0.60 (Table 2). Polymer was successfully produced for each copolymerization attempt and ^{1}H NMR analysis (Fig. 2) revealed over 80% incorporation ($F_3/f_3 \times 100$) of **3** in every polymer with the exception of the highest feed attempt (~70%). Here we note for the sample IDs in Table 2, "P" stands for photoinitiated and the following number still represents % mol fraction of **3** repeating units ($F_3 \times 100$). Consistent with literature,[43,44] IBVE conversion for all copolymerizations was near-quantitative as evidenced by ^{1}H NMR analysis of the polymerization. This can be seen by the disappearance of the olefin peaks at $\delta \sim 3.94$ and 4.14 ppm in the crude ^{1}H NMR. Interestingly, samples P17, P26, P33, and P42 exhibited a consistent decrease in $M_{\mathrm{n,SEC}}$ when compared to $M_{\mathrm{n,theo}}$ even though IBVE conversion remains quantitative and the amount of successfully polymerized **3** remains consistent ($F_3/f_3 \approx 85\%$). Here we note that $M_{\mathrm{n,theo}}$ is still calculated in accordance with eqn (1)–(3) with the exception that n_{THFA} is replaced with $n_{\mathbf{4}}$ in eqn (1). Duplicate copolymerizations performed on P26 and P33 determined these low molar mass outcomes to also be consistent. Furthermore, ^{1}H NMR analysis of the crude reaction mixture of P33 showed near complete conversion (>99% conversion of IBVE, ~98% conversion of **3**) (Fig. S20†). Significant chain transfer events are a possible explanation for simultaneously seeing high monomer conversions and molar masses much lower than theoretical. The ^{1}H NMR spectra in Fig. 2 are of copolymer samples that have been cleaned from small molecule contaminants after

Table 2 Copolymers of IBVE and **3**

Sample ID	f_3 [a]	F_3 [b]	F_3/f_3	$M_{\mathrm{n,\,theo}}$ [c] (kg mol^{-1})	$M_{\mathrm{n,\,SEC}}$ [d] (kg mol^{-1})	$Đ$ [d]	T_g [e] (°C)
P0[f]	—	—	—	18.0	14.1	1.68	−17.8
P4	0.050	0.042	0.84	30.42	25.3	1.57	−11.4
P8	0.098	0.078	0.80	28.55	26.3	2.11	−11.1
P13	0.16	0.13	0.81	31.80	25.2	1.60	−10.3
P17	0.20	0.17	0.85	33.27	18.9	1.80	−5.2
P26	0.30	0.26	0.87	34.85	13.6	1.72	1.2
P33	0.40	0.33	0.83	48.69	10.4	1.65	6.6
P42	0.60	0.42	0.7	49.63	2.01	1.96	−11.4

[a] Mole fraction of **3** incorporated into the feed. [b] Mole fraction of **3** incorporated into the polymer determined by ^{1}H NMR analysis. [c] Calculated assuming 100% conversion of IBVE and adjusted for F_3 in accordance with eqn (1)–(3). [d] Determined from SEC (THF mobile phase) using conventional column calibration *vs.* narrow $Đ$ polystyrene standards. [e] Obtained from the third heating curve in DSC analysis at a rate of 10 °C min^{-1}. [f] P0 and L0 are the same IBVE homopolymer.

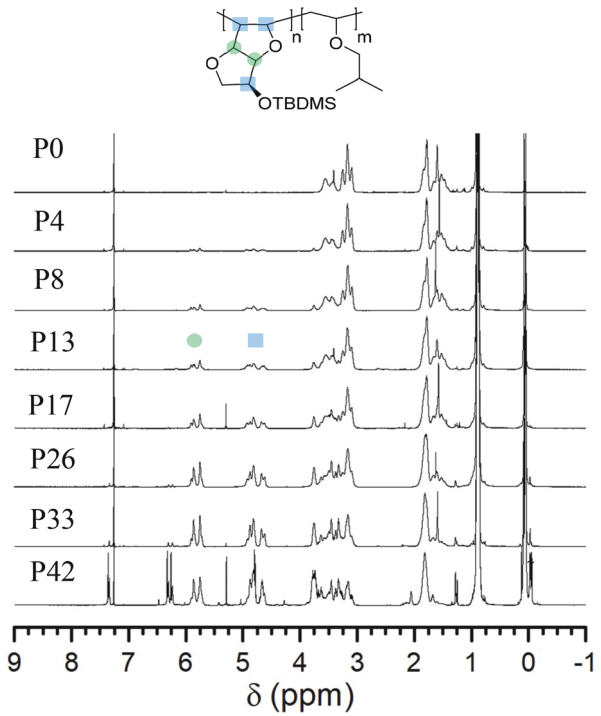
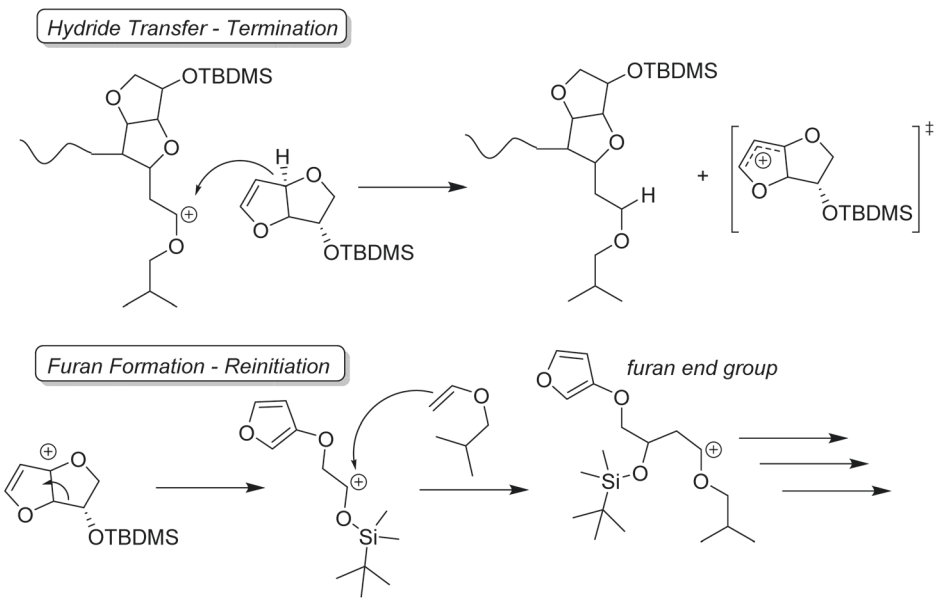


Fig. 2 ^{1}H NMR ($CDCl_3$, 600 MHz, 25 °C) stacked overlay of copolymers generated from photocontrolled cationic polymerization in Table 2.

precipitations in MeOH. Therefore, all the peaks within the spectra are reasonably assumed to be part of the copolymer chains. With this in mind, the appearance and increased size of new peaks at 6.24, 6.30, and 7.34 ppm for P26, P33, and especially P42 are indicative of new chemistries on the copolymers and provide valuable insight on the potential mechanism of chain transfer. Integration of the peaks at 6.24, 6.30, and 7.34 ppm reveals that they all correspond to the same number of hydrogens (Fig. S21†). Furthermore, the chemical shift of these three peaks are consistent with the three aromatic protons of a monosubstituted furan ring yet are shifted slightly upfield by ~0.02 ppm from the peaks observed for **5**. Collectively these observations suggest that chain transfer is occurring through an intermediate which is producing a furan ring and then reinitiating a new polymer chain. We have proposed a mechanism for this chain transfer process in Scheme 2.

DSC analysis was performed on each copolymer in Table 2 and the resulting thermograms are provided in Fig. 3a. The midpoint T_g values are also provided in Table 2. At the lowest **3** incorporation (F_3 = 0.042), a modest increase in T_g (−11.4 °C) is observed when compared to the T_g of IBVE homopolymer, (−17.8 °C). As the F_3 is increased, a slight increase in T_g is observed until $F_3 \approx 0.17$, after which there is a notable increase. At F_3 = 0.33, the T_g reaches 6.6 °C, almost 25 °C higher than pure IBVE. For P42, the T_g decreased to −11.2 °C (Table 2), however, we attribute this outcome to the extremely low molar mass (2.01 kg mol^{-1}) of this copolymer. Similar trends can be seen in the copolymers obtained from traditional Lewis acid-initiated systems, shown in Table 1 and Fig. S25,† where increasing **3** yields an increase in T_g. Thermal stability was measured by TGA analysis while heating to 600 °C at a rate of 10 °C min^{-1} and is shown in Fig. 4. P4 and P26 were tested and were found to have a T_d (5% mass loss) of 326 ± 5 °C, illustrating the independence of F_3 on T_d.

Due to the chirality of IS, polarimetry experiments conducted at 25 °C using 589 nm plane-polarized light were performed on each sample in Table 2 and are shown in Fig. 5. As expected, the absolute specific optical rotation, [α], observed



Scheme 2 Proposed chain transfer mechanism producing furan end groups.

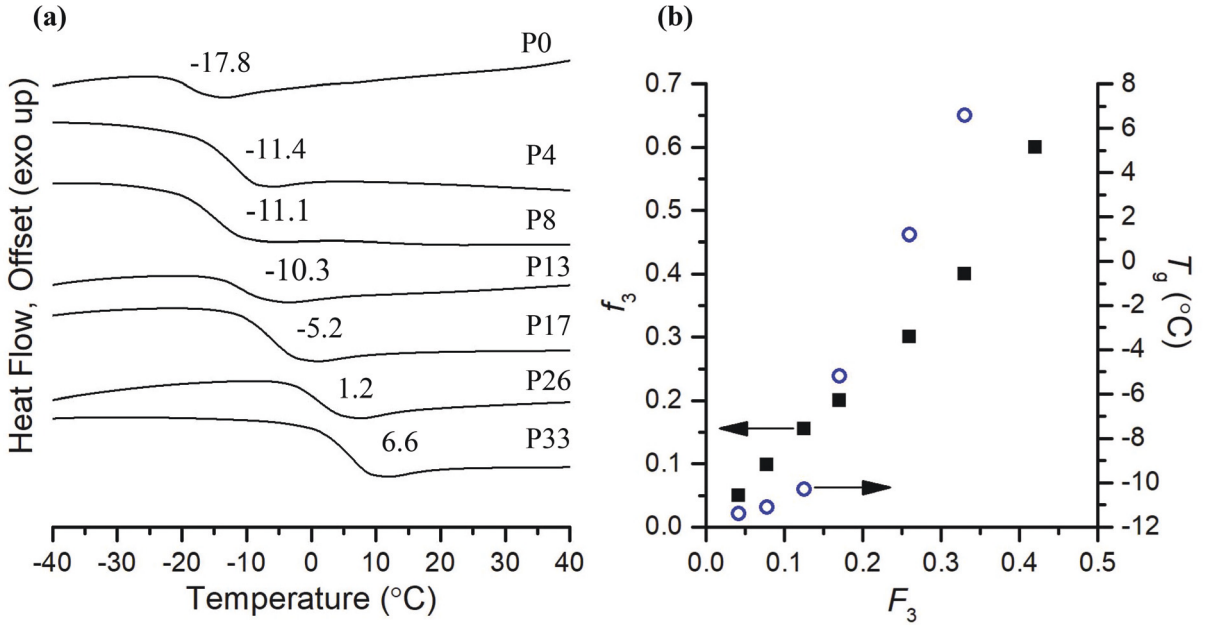


Fig. 3 (a) Offset DSC thermograms of copolymers (*exo* up) described in Table 2. Samples were cycled from −60 °C to 100 °C at a rate of 10 °C min^{-1}. Data shown was obtained from the third heating. (b) Plot of feed (f_3) (filled black squares) as a function of backbone incorporation (F_3). An alternate *y*-axis plots T_g values (open blue circles) as a function of F_3.

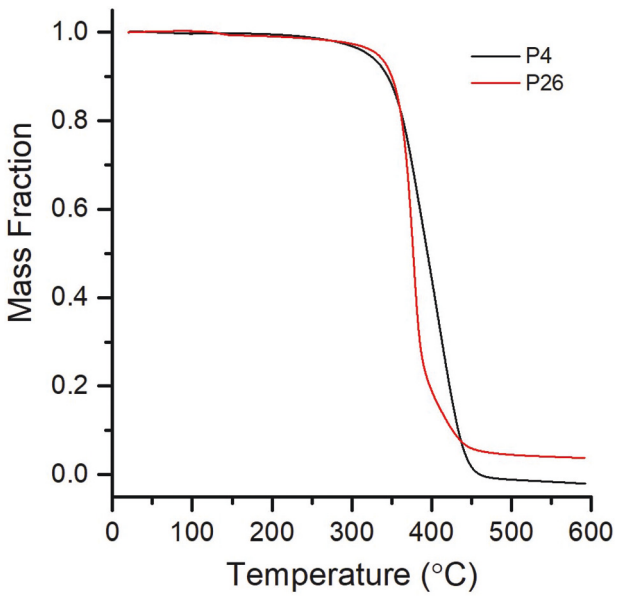


Fig. 4 TGA traces of P4 and P26, heating at a rate of 10 °C min^{-1} up to 600 °C under argon.

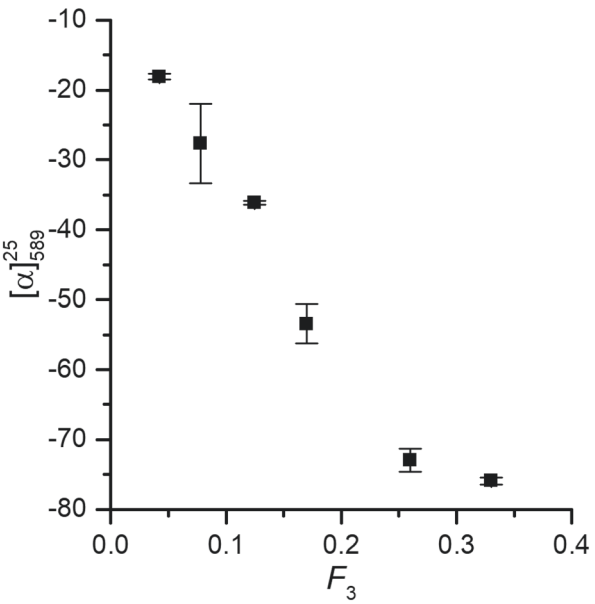


Fig. 5 Plot of F_3 *vs.* specific optical rotation [α] of each copolymer. Error bars represent the standard deviation of duplicate analyses performed on each copolymer sample.

for each copolymer increases (*i.e.* becomes a larger negative value) as a function of increased F_3 within the microstructure (Fig. 5). These [α] values were obtained by averaging duplicate analyses performed on each copolymer sample (Table S1†). By normalizing for F_3, these [α] values can be corrected to account only for the weight fraction (w) (eqn (S1)†) of the repeating units of **3** within the each copolymer to determine $[\alpha]_{P3} = [\alpha]w^{-1}$. These adjusted specific optical rotation values remain relatively consistent ($[\alpha]_{P3} = -159 \pm 20°$ mL g^{-1} dm^{-1}) when averaged over all copolymers (Table S1†), however they are considerably larger than the original monomer **3** ($[\alpha]_3 = -12.3°$ mL g^{-1} dm^{-1}). This increase can be attributed to the stereocenters produced by formation of alicyclic units on the copolymer microstructure.

Conclusion

This study investigates and confirms the cationic copolymerizability of **3**, an IS derivative containing a glycal functionality on one of the two fused rings. Although homopolymerization attempts were unsuccessful, copolymerizations with IBVE utilizing traditional cationic polymerization with Lewis acids and recently discovered photo-driven cationic methods successfully incorporated up to 42 mol% of **3** into the copolymer microstructure. Lewis acids are found to substantially promote a competing side-reaction with **3** that causes ring-opening and rearrangement to a chiral furan derivative, **5**, rather than polymerization. Photo-driven cationic polymerization initiated by a RAFT agent succeeds in promoting propagation over this rearrangement, however the occurrence of a chain transfer reaction increases with increasing amount of **3** in the monomer feed and ultimately limits high molar mass under these conditions. Due to the alicyclic repeating unit structure from **3**, the T_g of these copolymers increase by up to 25 °C with ~33 mol% of these units within the microstructure and these copolymers were found to be thermally stable up to ~330 °C under inert atmosphere. Polarimetry experiments showed an increase in specific optical rotation of the copolymer proportional to the mol fraction of chiral **3** repeating units in the copolymer. While further investigations are certainly necessary to optimize these copolymerizations, reduce side reactions, and potentially derivatize the TBDMS protected alcohol on **3**, this study confirms the efficacy of using these biomass-derived comonomers towards value-added PVEs where higher T_g values may be desired.

Conflicts of interest

There are no conflicts of interest to declare.

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