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Ring-Opening Metathesis Polymerization of Unsaturated Carbohydrate Derivatives: Levoglucosenyl Alkyl Ethers

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exhibit Schulz–Flory-type molar mass distributions and are thermoplastic materials with rather low glass transition temperatures in the range of 43-0 °C depending on the length of the alkyl substituent. Kinetic studies revealed that the polymerization proceeded rapidly to a steady state with a certain minimum monomer concentration threshold. When the steady state was reached, just about half of the [Ru] catalyst had been effective to initiate the polymerization, indicating that the initiation step was a slow process. The remaining catalyst was still active and did no longer react with monomers but with in-chain double bonds, cutting the formed polymer chains into shorter fragments. In the long term, all catalyst was consumed and propagating [Ru] chain ends were deactivated by the elimination of [Ru] from the chain ends to form inactive chains with terminal aldehyde groups.

■ INTRODUCTION

The demands for sustainable polymers are growing with the ever-increasing concerns of the environmental impact of a fossil-resource-based economy.¹⁻³ Biomass-derived polymers have the potential to overcome various concerns of crude oilderived polymers, such as limited availability, biocompatibility, and degradability issues. Among the renewable sources, which are explored for the synthesis of biobased polymers, cellulose is the most abundant one on earth and therefore highly attractive as a nonedible feedstock.^{4,5} An interesting unsaturated bicyclic carbohydrate molecule produced from (waste) cellulose feedstock in just one step is levoglucosenone (compound 1 in Scheme 1), which nowadays is made available in larger quantities by the Circa Group Ltd., Australia, and which can be easily reduced to levoglucosenol (2a). While the polymerization of levoglucosenone failed, we have recently succeeded to polymerize levoglucosenol by ring-opening olefin metathesis polymerization (ROMP).⁶ Polymerization of any carbohydrate derivatives by ROMP, taking advantage of unsaturated carbohydrate heterocycles, was unreported prior to this, albeit metathesis polymerization has been known for decades⁷⁻⁹ and applied to even functional monomers, including carbohydratefunctionalized norbornenes¹⁰ or norbornene derivatives of levoglucosenone.^{11,12} A reason for this might be the combination of lacking ring strain in common unsaturated carbohydrate derivatives, such as glycals or glycosyl derivatives, and the high density of oxygen-containing moieties that may

dihydrolevoglucosenone (Cyrene), and ethyl acetate. The

prepared polyacetals with degrees of polymerization of ~100

interfere with the catalyst. Following an alternative strategy, carbohydrate monomers derived in four steps from glucose and galactose, consisting of endocyclic alkene and terminal alkyne moieties, were polymerized by a living cascade ene-yne metathesis approach.¹³

Solvent: Dioxane, DCM, 2-MeTHF, Cyrene, EtOAc

ROMP

The ROMP of levoglucosenol was demonstrated to produce high-molar mass polyacetals (3a), which exhibited thermoplastic behavior and were easily degradable by acid-catalyzed hydrolysis.⁶ So far, the ROMP of levoglucosenol was only successful with the mono-ortho-substituted N-heterocyclic carbene derivative of the second-generation Grubbs catalyst C793, while other ruthenium-based catalysts with sterically more demanding ligands were not effective.⁶ The polymerization exhibited a nonliving character, as seen by incomplete monomer conversions, nonlinear correlations between polymer molar mass and conversion, and Schulz–Flory-type polymer molar mass distributions. The polyacetals formed were chiral but amorphous materials, supposedly due to a statistical distribution of sequence isomers along the polymer chain,

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© 2021 The Authors. Published by American Chemical Society Scheme 1. Synthesis and Subsequent ROMP of Levoglucosenol 2a (R = H) and Levoglucosenyl Alkyl Ethers 2b-f (R = Methyl, Ethyl, *n*-Propyl, Isopropyl, and *n*-Butyl) Using the Catalyst C793 in Different Solvents to Yield the Polyacetals 3a-f (Simplified Structure, Different Sequence Isomers Are Not Shown); (a) NaBH₄, H₂O, (b) (i) NaH, THF, (ii) Alkyl Iodide, THF, and (c) C793, 1,4-Dioxane or Other Solvent, Room Temperature



suggesting a low regioselectivity of the catalyst system. Notwithstanding the current limitations, the successful production of levoglucosenol-based polyacetals has opened a new field of thermoplastic polymer materials with a highly sustainable property profile.

In this work, we explore other bicyclic monomers based on levoglucosenol, namely, levoglucosenyl alkyl ethers (2b-f,alkyl = methyl, ethyl, *n*-propyl, isopropyl, and *n*-butyl), and also "green" solvents for the polymerization *via* ROMP (see Scheme 1). We show that, as for levoglucosenol, specifically the catalyst C793 enables a polymerization of the levoglucosenyl alkyl ethers to afford thermoplastic polyacetals (3b-f)with tunable glass transition temperatures. In analogy to levoglucosenol, the ROMP of the new monomers also showed the features of a nonliving polymerization. To clarify the scope and current limits of the synthesis of levoglucosenol-based polymers, we exemplarily explored the kinetics and mechanism of the ROMP of levoglucosenyl methyl ether in more detail.

EXPERIMENTAL SECTION

Chemicals. Levoglucosenone (CAS number 37112-31-5, 99.3% purity) and dihydrolevoglucosenone (Cyrene, 99.5%) were provided by Circa Group Ltd, Australia. Sodium borohydride (98%), iodomethane (99%), iodoethane (99%), 1-iodopropane (99%), 1bromobutane (99%), tetrabutylammonium iodide (98%), ethyl vinyl ether (99%), 1,4-dioxane (99.8%, anhydrous), 2-methyltetrahydrofuran (2-MeTHF, 99%, anhydrous), and ethyl acetate (99.8%, anhydrous) were purchased from Acros Chemicals. Grubbs catalyst C793 [1,3-bis-(2-methylphenyl)-2-imidazolidinylidene]-dichloro-(benzylidene)-(tricyclohexylphosphine)ruthenium(II) (CAS number 927429-60-5), 2-iodopropane (99%), and tetrahydrofuran (THF, 99.5% anhydrous) were purchased from Sigma-Aldrich. Dichloromethane (DCM, analytical grade), methanol (analytical grade), and cyclohexane (analytical grade) were purchased from Fischer Scientific. Chloroform-d (99.8% D) and 1,4-dioxane d₈ (99% D) were purchased from Deutero GmbH and Eurisotop, respectively.

Levoglucosenol 2a was synthesized by the reduction of levoglucosenone 1 with sodium borohydride.⁶ The levoglucosenyl alkyl ethers 2b-f were synthesized by the alkylation of 2a with the respective alkyl iodides,¹⁴ see the Supporting Information.

Analytical Instrumentation. Nuclear magnetic resonance (NMR) spectra were recorded with Bruker AVANCE Neo 400

MHz, Bruker AVANCE 500 MHz, or Bruker AVANCE III 600 MHz spectrometers at room temperature. Samples were prepared in CDCl_3 or 1,4-dioxane- d_8 [hexamethyldisilane (HMD) was added as the internal standard]. ¹H NMR signals were referenced to the solvent peak at δ 7.26 ppm (CDCl₃), δ 3.53 ppm (1,4-dioxane- d_8), or δ 0 ppm (HMD).

Size exclusion chromatography (SEC) with simultaneous UV and RI detection was performed with THF as the eluent (a flow rate of 0.5 mL·min⁻¹) at room temperature. The stationary phase was a 300 × 8 mm² PSS SDV linear M column (3 μ m particle size, molar mass range 10²-10⁶ Da). Solutions containing ~0.15 wt % polymers were filtered through 0.45 μ m PTFE filters; the injected volume was 100 μ L. Polystyrene standards (PSS, Mainz, Germany) were used for calibration.

Thermogravimetric analysis (TGA) was performed with a Mettler Toledo TGA/SDTA851 in a temperature range from 25 to 900 $^{\circ}$ C at a heating rate of 10 $^{\circ}$ C min⁻¹ under a continuous nitrogen flow of 20 mL min⁻¹.

Differential scanning calorimetry (DSC) was measured on a Mettler Toledo DSC822e in a temperature range from -80 to 150 °C under a continuous nitrogen flow of 20 mL min⁻¹. Glass transition temperatures were determined from the third heating curves at a heating rate of 30 °C min⁻¹.

RESULTS AND DISCUSSION

As reported previously,⁶ the ROMP of levoglucosenol 2a was only successful with the mono-ortho-substituted N-heterocyclic carbene derivative of the second-generation Grubbs catalyst C793 (Scheme 1). Preferably, the polymerization was conducted in 1,4-dioxane solution owing to the poor solubility of the poly(levoglucosenol) 3a in other solvents typically employed for olefin metathesis, such as DCM or toluene, at room temperature. While the polymerization of 2a proceeded rapidly within the first 30 min, it leveled off thereafter at a maximum monomer conversion of $\sim 60\%$ (Figure 1A). Furthermore, polymer 3a exhibited a Schulz-Flory-type molar mass distribution with a dispersity of around 2 (Figure 1C). These features demonstrated the nonliving character of the polymerization system. The polymerization kinetics might indicate that the reaction takes place under thermodynamic and not under kinetic control as is characteristic for most chain-growth polymerizations. Alternatively, it could indicate



Figure 1. (A) Time-conversion plot for the ROMP of levoglucosenol **2a** in 1,4-dioxane ($[2a]_0 = 4$ mmol per mL solvent, $[2a]_0/[C793]_0 = 100$, room temperature; monomer conversions were determined by the ¹H NMR analysis of crude reaction solutions after quenching with ethyl vinyl ether); the line is to guide the eye. (B) Evolution of the apparent number-average degrees of polymerization and dispersity indices (numbers in parentheses), as determined by SEC (eluent: NMP) with polystyrene calibration, as a function of monomer conversion. The theoretical degree of polymerization (dashed line) is calculated by ($[2]_0/[C793]_0$) × monomer conversion, as it would be expected for a living chain-growth polymerization. (C) SEC-RI trace of polymer **3a** obtained after a reaction time of 24 h. Data are taken from ref 6 and replotted to compare with the polymerizations of levoglucosenyl alkyl ethers **2b**–f.

the occurrence of unimolecular termination reactions, whereby the maximum monomer conversion would be determined by the relative apparent rate constant of propagation to termination (see below). The apparent number-average molar masses or degrees of polymerization of 3a, as determined by SEC with polystyrene calibration, were found to be up to ~10 times larger than the theoretical values and did not correlate linearly with the monomer conversion (Figure 1B). These observations possibly indicate an incomplete and/ or slow initiation of growing chains by the catalyst in combination with termination and/or back-biting reactions.

Applying the same conditions as for 2a (see the caption in Figure 1), the levoglucosenyl alkyl ethers 2b-f, which were synthesized by the straightforward alkylation of levoglucosenol 2a with alkyl iodides (see the Supporting Information), were polymerized with C793 in the 1,4-dioxane solution to give the corresponding poly(levoglucosenyl alkyl ether)s 3b-f (Figure 2). The molecular structures of the produced polyacetals 3b-f were confirmed by ¹H, ¹³C, and 2D NMR spectroscopy (see the Supporting Information). Unlike the parent polymer 3a, the polymers 3b-f exhibited an enhanced solubility and were soluble not only in 1,4-dioxane but also in DCM, which is a preferred solvent for metathesis reactions, as well as in a number of polar aprotic "green" solvents, such as 2-MeTHF, dihydrolevoglucosenone (Cyrene), or ethyl acetate (Scheme 1). The polymerization of exemplarily 2b could be performed



Figure 2. ROMP of levoglucosenyl alkyl ethers **2b**-**f** in 1,4-dioxane at room temperature ($[2b-f]_0 = 4$ mmol per mL solvent, $[2b-f]_0/[C793]_0 = 100$): (A) time-conversion plots [monomer conversions were determined by ¹H NMR analysis (solvent: CDCl₃) of crude reaction solutions after quenching with ethyl vinyl ether] (lines are to guide the eye) and (B) evolution of the apparent number-average degrees of polymerization, as determined by SEC (eluent: THF) with polystyrene calibration, as a function of monomer conversion. The dashed line indicates the theoretical degrees of polymerization as calculated for a living chain-growth polymerization. (C) SEC-RI traces of precipitated polymers 3b-f obtained after a reaction time of 24 h.

successfully in all these solvents (Figure 3). Evidently, all the polymerizations of 2b-f in 1,4-dioxane and of 2b in the various solvents followed virtually the same general kinetics, which are very similar to that of 2a (Figure 1). The polymerizations reached maximum monomer conversion thresholds of about 70–80% within about 60–120 min. The polymerization rates decreased slightly with an increase in the size of the alkyl ether substituent of the monomers 2b-f but were virtually unaffected by the selected solvent. In all cases, the apparent degrees of polymerization were larger than theoretically expected and nonlinearly correlated with the monomer conversion. The final polymers 3b-f exhibited Schulz–Flory-type molar mass distributions ($D \sim 2$) similar to that observed for 3a.

The poly(levoglucosenyl alkyl ether)s **3b**-f are thermally stable up to 240–285 °C, as determined by TGA, and are amorphous with glass transition temperatures in the range of $T_g \sim 43$ to 0 °C, as determined by DSC (see the Supporting Information). As expected, the glass transition temperatures of **3b**-f are lower than that of poly(levoglucosenol) **3a** ($T_g \sim 100$ °C)⁶ and they continuously decrease with an increase in the length of the *n*-alkyl substituent, that is, $T_g \sim 43$ °C for **3b** (R = methyl), 32 °C for **3c** (ethyl), 8 °C for **3d** (*n*-propyl), and 0 °C for **3f** (*n*-butyl). The glass transition temperature of **3e** (isopropyl) is $T_g \sim 35$ °C and thus considerably higher than that of **3d**, which might be attributed to a reduced flexibility of the polymer chain. Notably, this behavior is analogous to that of poly(alkyl styrene)s or poly[alkyl (meth)acrylate]s.¹⁵



Figure 3. ROMP of levoglucosenyl methyl ether **2b** in different solvents (1,4-dioxane, DCM, 2-MeTHF, Cyrene, and ethyl acetate) at room temperature ([**2b**]₀ = 4 mmol per mL solvent, [**2b**]₀/[C793]₀ = 100): (A) time-conversion plots [monomer conversions were determined by ¹H NMR analysis (solvent: CDCl₃) of crude reaction solutions after quenching with ethyl vinyl ether] (lines are to guide the eye) and (B) evolution of the apparent number-average degrees of polymerization, as determined by SEC (eluent: THF) with polystyrene calibration, as a function of monomer conversion. The dashed line indicates the theoretical degrees of polymerization as calculated for a living chain-growth polymerization. (C) SEC-RI traces of precipitated polymer **3b** obtained after a reaction time of 24 h.

Kinetic and Mechanistic Study. Remarkably, all polymerizations of 2a-f in various solvents showed very similar features. We therefore chose to examine the kinetics of the polymerization of 2b with C793 in 1,4-dioxane, as a representative example, in more detail by ¹H NMR spectroscopy. Kinetic experiments for different monomer and catalyst concentrations were performed *in situ* in NMR tubes at room temperature using the solvent 1,4-dioxane- d_8 . An exemplary ¹H NMR spectrum of a mixture of **2b**/C793 recorded at an intermediate reaction time is shown in Figure 4 (see also the Supporting Information). Monomer conversions were determined by considering the integrals of characteristic olefinic proton signals of the monomer **2b** (δ 6.0 ppm, 1H, and 5.6 ppm, 1H) and of the polymer **3b** (δ 5.7 ppm, 2H). Numberaverage degrees of the polymerization of **3b** were calculated by end-group analysis from the relative signal intensities of the phenyl group (δ 7.4 ppm, 2H) at the α -chain end and of the olefin protons of the repeat units. The [Ru]=C<u>H</u>-phenyl signal of the catalyst was observed at δ 19.1 ppm (see the ¹H NMR spectrum of the catalyst in the Supporting Information). Multiple signals were detected at δ 18.5–16.5 ppm, which were attributed to active [Ru]=CH chain ends.

The time-conversion plots (Figure 5A,E) obtained for different monomer (2b) and catalyst (C793) concentrations showed the characteristic features of initial fast monomer consumption, which leveled off after ~100 min approaching a maximum monomer conversion. The value of the maximum monomer conversion depended on the initial monomer concentration (Figure 5A) but was independent of the catalyst concentration (Figure 5E). These findings exclude unimolecular termination reactions as a possible explanation for this kinetic behavior, for which it is expected that the maximum monomer conversion correlates with the catalyst concentration but not with the monomer concentration. The results rather suggest that the polymerization proceeded rapidly to a steady state when having reached a certain threshold value of the minimum residual monomer concentration. This steady state could possibly be explained in terms of a reversible polymerization system with a low ceiling concentration or temperature, in which polymerization and depolymerization occur at the same rates. If so, the treatment of an isolated polymer 3b with the catalyst should result in a cleavage and activation of polymer chains and, at a sufficiently low polymer concentration, reformation of the cyclic monomer 2b. Indeed, this was observed for a mixture of **3b** (0.07 mmol monomer) and C793 (0.014 mmol) in 1,4-dioxane- d_8 (0.5 mL) by analysis with ¹H NMR spectroscopy and SEC (see the Supporting Information).



Figure 4. ¹H NMR spectrum (400 MHz) of the polymerization mixture of 2b (2 mmol)/C793 (0.4 mmol) in 1,4-dioxane- d_8 (0.5 mL) after a reaction time of 90 min at room temperature. [Signal at δ 0.0 ppm originates from hexamethyldisilane (HMD) as the internal standard.]



Figure 5. ROMP of levoglucosenyl methyl ether **2b** with C793 in 1,4-dioxane- d_8 at room temperature for different monomer (A–D) and catalyst concentrations (E–H): (A,E) time-conversion plots (monomer conversions were determined by ¹H NMR analysis), (B,F) consumption of the catalyst with time, as determined by the depletion of the ¹H NMR signal of the catalyst at δ = 19.1 ppm, (C,G) evolution of the number-average degree of polymerization, as determined by ¹H NMR end-group analysis, as a function of monomer conversion (the theoretical degrees of polymerization, as calculated for a living chain-growth polymerization, are indicated by dashed lines in the respective colors), and (D,H) SEC-RI traces of the crude polymer **3b** produced at the end of the kinetic experiments (the peak at 11.8 mL is from the catalyst).

According to the evolution of the [Ru]=CH signal with time, the rate at which the catalyst was consumed to initiate the polymerization of 2b was comparatively slow with a halfvalue period of 100-500 min (Figure 5B,F). The rate of initiation depended on both the initial monomer and catalyst concentrations: it was the faster, the higher was the monomer concentration (Figure 5B), and the lower was the catalyst concentration (Figure 5F). Amazingly, only about half of the catalyst had been used for the initiation of chains when the polymerization came to a stop at the maximum monomer conversion. The remaining catalyst was still reactive and was slowly consumed, however, without noticeable consumption of monomer. These findings further support our earlier hypothesis (see above) that the polymerizations reached steady-state conditions. Supposedly, if no more with the monomer, the catalyst then reacted with the in-chain double bonds of the produced polymer, resulting in a cleavage of chains into smaller fragments, thus equilibrating the molar mass distribution. Notably, smaller polymer fragments could also be produced by inter- or intramolecular equilibration reactions of the active [Ru] chain ends with in-chain double bonds. An intermolecular exchange reaction between two active chains produces two chains with different lengths but the same end groups, while an intramolecular back-biting releases an active linear chain and an inactive macrocycle lacking the benzylidene end group. However, the reaction of the catalyst with an in-chain double bond of a macrocycle would lead to a regeneration of an active linear chain carrying benzylidene and [Ru] end groups.

The slow initiation and the fragmentation processes must both be reflected in the evolution of the number-average degree of polymerization with monomer conversion (Figure 5C,G). The degrees of polymerization, as determined by ¹H NMR end-group analyses, were much higher than those calculated for a living process by $([2b]_0/[C793]_0) \times monomer$ conversion because the actual concentration of actively growing polymer chains was substantially lower than the nominal catalyst concentration. With the ongoing reaction time and continuous reaction of the catalyst with either monomers (chain growth) or polymers (e.g., by the cleavage of a linear chain or opening of a macrocycle), the average degree of polymerization decreased. Finally, that is, at full consumption of the catalyst, it matched the theoretical value (based on the assumption that all chains carry one benzylidene end group). According to SEC analysis (Figure 5D,H), the polymer 3b produced at the end of the kinetic experiments exhibited the expected monomodal Schulz-Flory-type molar mass distributions with a dispersity of $D \sim 2$.

The main features of the polymerization mechanism, as revealed by the kinetic studies, are summarized in Scheme 2. The initial formation of propagating [Ru] chains from **2b** and C793 is a slow process, but once initiated, the polymerization proceeds rapidly to a steady state with a certain minimum monomer concentration threshold. Yet, the remaining catalyst is still reactive and does not further react with the monomer but with in-chain double bonds to cut polymer chains into shorter fragments. The finally obtained polymer **3b** exhibits the

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Scheme 2. Proposed Simplified Reaction Scheme for the ROMP of 2b and Cleavage of Polymer Chains by the Reaction of In-Chain Double Bonds with the Catalyst $C793^a$



^{*a*}Note: the addition of the catalyst or active chain end to the monomer or in-chain double bond can produce two regioisomers and here, only the tentatively preferred one is shown.

theoretically expected degree of polymerization and a Schulz– Flory-type molar mass distribution.

In order to assess the long-term activity of [Ru]-alkylidene chain ends, we added a second monomer batch (either **2b**, norbornene, or cyclooctene) to a polymerization mixture after all catalysts had been consumed. In these experiments, however, we did not detect an increase of molar mass or a change in the molar mass distribution (data not shown), suggesting that all [Ru] species were deactivated at this point.

The deactivation of [Ru] chain ends could also be recognized in the ¹H NMR spectra taken during the polymerization of 2b at high catalyst loading (2b 1 mmol/ C793 0.04 mmol; blue curve in Figure 5E), which are shown in Figure 6. Three proton signals were initially detected at δ 16.5-18.5 ppm, which could be attributed to different propagating [Ru]-alkylidene species. These proton signals started to disappear after the steady state of the polymerization had been reached (after about 100 min) and were no longer detected at >1200 min. Intriguingly, parallel to the disappearance of the [Ru]-alkylidene signals, three sets of proton signals showed up at δ 9.2–9.8 ppm, a range which is very characteristic for the carbonyl protons of aldehyde groups. For very high catalyst loading, that is, $[2b]_0/[C793]_0 = 5$, and thus higher amount of chain ends, the presence of aldehyde groups could be clearly confirmed by ¹H-¹³C HSQC NMR spectroscopy showing a direct correlation between proton signals at δ 9.2–9.8 ppm and carbonyl signals at δ 187–190 ppm (see the Supporting Information). By the integration of the proton signals [Ru]=CH- (t = 5 min) and -CHO (t = 5 min) 2828 min) (Figure 6), it can be estimated that at least 75% of the active chain ends were transformed into aldehydes. Hence, transformation of the [Ru]-active chain end into an aldehyde seems to be the predominant deactivation pathway, notwith-



Figure 6. ¹H NMR spectra (400 MHz), selected regions of 9–10 and 17–20 ppm, taken during the polymerization of **2b** (1 mmol) with C793 (0.04 mmol) in 1,4-dioxane- d_8 (0.5 mL) at room temperature (corresponding to the blue curve in Figure 5E).

standing that other (however not yet identified) pathways cannot be safely excluded.

As reported in the literature, catalyst deactivation may occur from the resting state of the catalyst, for instance, through thermal dimerization¹⁶ or by reaction with water,¹⁷ alcohols, or oxygen.¹⁸⁻²⁰ These catalyst deactivation pathways have in common that [Ru]-hydride species are formed.²¹ These, in their turn, may catalyze an isomerization of double bonds.²² A possible catalyst deactivation pathway, which has been exclusively observed for second-generation catalysts with sterically less hindered N-aryl substituents such as the C793 catalyst used here, involves an activation of the ortho-C-H bond of the N-aryl substituent and transfer of the benzylidene ligand to the N-aryl substituent.²⁴⁻²⁶ The [Ru] complexes resulting from this decomposition pathway are catalytically inactive because the [Ru]-alkylidene unit is irreversibly lost. Alternative catalyst deactivation mechanisms have been proposed starting from the metallacyclobutane intermediate of the catalytic cycle, which can be attacked by bases²⁷ or may undergo β -hydride elimination.²⁸

Based on these considerations, we tentatively propose the [Ru]–alkylidene deactivation pathways outlined in Scheme 3 to rationalize the observed chain growth termination. In their catalytically active state, [Ru]–alkylidenes are 14-electron complexes and therefore highly Lewis acidic (pathway A). This inherent Lewis acidity has earlier been proposed as a trigger mechanism for a semipinacol rearrangement following a cross metathesis reaction.²⁹ Coordination of the Lewis acid to the acetal oxygen atom in the β -position to [Ru] facilitates the

Scheme 3. Proposed Reaction Pathways for the Deactivation of [Ru]-Alkylidene Chain Ends *via* Lewis Acid-Assisted Hydrolysis of the Terminal Acetal (Pathway A) or β -Hydride Elimination/Reductive Elimination and Acetal Hydrolysis (Pathway B)



nucleophilic attack of water (traces of water in the reaction mixture or from moisture), yielding a hemiacetal. From this hemiacetal, a [Ru]-carbene diol is rapidly cleaved off, furnishing the polymer chain with an aldehyde group at the former [Ru]-alkylidene terminus. The released [Ru]-carbene diol species should further decompose, for instance, through β hydride elimination and reductive elimination, under the formation of a [Ru]-H complex and hydroxyacetone. As mentioned before, the released [Ru]-H complex may catalyze double-bond isomerization, which could lead to the formation of a conjugated aldehyde end group. Alternatively, the [Ru]alkylidene species may undergo β -hydride elimination in competition to chain propagation (pathway B). The resulting [Ru]-hydride species may then undergo reductive elimination of an inactive [Ru] species and formation of an enol ether. This enol ether should be easily hydrolyzed in the presence of the Lewis acidic [Ru] fragments to furnish an aldehydeterminated polymer (same as before) and hydroxyacetone as a byproduct. Such a catalyst deactivation mechanism has earlier been proposed for olefin metathesis reactions with allyl alcohols.^{30,31} In any case, although deactivation or termination of the propagating [Ru] chains occurred, this was responsible for neither the incomplete monomer conversions nor the broad molar mass distributions.

The deactivation of [Ru]–alkylidene chain ends resulting in the formation of terminated chains with aldehyde end groups is ascertained; however, it is not clear by which pathway A or B. Pathway A (tentatively favored) offers the possibility that the [Ru] chain ends remain active when the polymerization is performed under rigorously water-free conditions. Following pathway B, the deactivation would occur even in the complete absence of water or moisture.

CONCLUSIONS

A series of levoglucosenyl alkyl ethers 2b-f were synthesized and polymerized by ROMP using the Grubbs catalyst C793. Polymerizations could be successfully performed not only in conventional solvents such as 1,4-dioxane and DCM but also in polar aprotic "green" solvents such as 2-MeTHF, Cyrene, and ethyl acetate. All produced polyacetals had apparent degrees of polymerization of ~100 and broad Schulz–Florytype molar mass distributions with a dispersity of ~2. They were amorphous and showed thermoplastic behavior. Their glass transition temperatures could be modulated by the choice of the alkyl substituent, continuously decreasing from 100 to 0 °C with an increase in the length of the substituent for polymers 3a-f. These findings demonstrate the high potential of levoglucosenol-based polymers as sustainable plastic materials.

Until now, the polymerizations of 2a and 2b-f were limited to the use of the catalyst C793, showing nonliving character. While the propagation step is quite fast, the initiation of the polymerization is comparatively slow. Apparently, the polymerization reaches rapidly a steady state at monomer conversions of 60–80% before the catalyst has been reacted completely. The residual catalyst then does not react with monomers but with in-chain double bonds, thus cutting the formed polymer chains into fragments and equilibrating the molar mass distribution. Finally, the polymers exhibit the expected molar mass with a Schulz–Flory-type molar mass distribution. In the long term, all propagating [Ru] chains are deactivated by the elimination of the [Ru] from the chain ends under the formation of inactive chains with terminal aldehyde groups.

Future investigations will be devoted to a deeper analysis of the polymerization mechanism including the identification and fate of the propagating [Ru] species. The ultimate goals are to accelerate the initiation step (*i.e.*, the reaction of the catalyst with the monomer) and to prevent deactivation of [Ru] chain ends, which would enable the synthesis of block copolymers or of even more complex polymer architectures. Furthermore, a detailed analysis of the polymer microstructures, that is, distribution of regioisomers and cis/trans ratio of in-chain double bonds, is on the way.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c02821.

Procedures for the synthesis of monomers 2b-f and polymerization reactions; ¹H NMR spectrum of catalyst C793; ¹H, ¹³C NMR, and ESI-MS spectra for 2b-f; ¹H, ¹³C, ¹H-¹H COSY, and ¹H-¹³C HSQC spectra and TGA/DSC curves for polymers 3b-f; ¹H NMR spectra and SEC traces for the polymerizations of 2b-f in 1,4dioxane and for 2b in DCM, 2-MeTHF, Cyrene, and ethyl acetate; ¹H NMR spectra for *in situ* kinetic experiments for the polymerization of 2b in 1,4-dioxane d_{8} ; ¹H-¹³C HSQC spectrum of a crude reaction mixture 2b/C793 at high catalyst loading for the identification of terminal aldehyde groups; and ¹H NMR spectra and SEC traces for the degradation of polymer 3b with C793 (PDF)

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Notes

The authors declare no competing financial interest.

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