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Synthesis of poly(3-keto-D-glucal) via conjugate addition polymerization†

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The widespread environmental impact of petrochemical-derived plastics has spurred interest in renewable alternatives. Herein, we report the design, synthesis, and polymerization of a novel sugar-derived monomer, dimethyl acetal-3-keto-D-glucal, using conjugate addition polymerization (CAP) to yield poly(3-keto-D-glucal) after post-polymerization deprotection. The monomer, synthesized in two steps from D-glucal, features an α,β -unsaturated enone motif compatible with CAP. Systematic optimization of reaction parameters—including solvent, catalyst, temperature, concentration, and time—revealed that acetonitrile as the solvent and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the catalyst yielded polymers with molecular weights up to 1080 kDa and dispersities as low as 1.54. Post-polymerization deprotection under mild conditions afforded hydroxyl-functionalized polymers with enhanced thermal stability and water solubility. The glass transition temperatures were determined to be 41 °C and 60 °C for the hydrophobic and hydrophilic polymers, respectively. These findings establish glycals as promising renewable monomers and highlight conjugate addition polymerization as a versatile method for synthesizing high-performance sugar-based polymers, contributing to the growing field of sustainable materials.

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A. Introduction

Plastics are essential and contribute to an improved quality of life. Properties such as high strength, durability, and light weight make them suitable for a wide variety of applications.¹ Though plastics play an important role in modern consumer society, their widespread use raises critical challenges related to resource depletion, health, and environmental pollution.² Addressing these issues demands a comprehensive approach that balances convenience with the urgent need for sustainability.³ Most conventional plastics are derived from non-renewable, fossil fuel-based monomers,⁴ which not only take centuries to break down but often break down into microplastics that contaminate soil, affect marine life, and pollute waterways.⁵ Despite widespread awareness of the social and environmental impact of plastics, 99% of them are still synthesized from petrochemicals.⁶ Using renewable natural sources as a sustainable feedstock for polymeric materials, especially those that do not disrupt the food supply chain, will allow for many of these issues to be addressed.⁷

Many natural products have been used as building blocks for polymerization and have been well-documented in detailed

reviews.⁸ One well-studied classification of natural product-based monomers is sugars. They hold significant value due to their high functionality, extensive research backing, environmental friendliness, and strong potential for diverse end-of-life applications.⁹ For example, polymers that include pyranose or furanose structures exhibit notably high glass transition temperatures ($T_g = 87\text{--}233$ °C). The presence of hydroxy groups also broadens the possibilities for functionalizing these materials, as shown with post polymerization of poly(methyl 2,3-O-carbonyl- α -D-glucopyranoside).¹⁰ Additionally, scalable methods for synthesizing sugar-based polymers present a promising platform.¹¹ Although glycopolymers have been well studied,¹² advancements in backbone synthesis, especially the use of glycal, remain underexplored with only a few examples reported, such as vinyl copolymers,¹³ polycarbonates,¹⁴ and polysaccharides.²³ There are several key reasons that glycals have been used as a building block. Glycals are produced from readily available natural compounds like D-glucose, and are essential structural components in organic synthesis,¹⁴ due to the functional group-rich scaffold that provides chemical handles for reactions of these small molecules. Specifically, these notable sugar motifs consist of a cyclic enol ether with a double bond specifically located between carbons 1 and 2 of the pyran or furan rings, as well as primary and/or secondary hydroxyl groups. First identified and synthesized in 1913, they have quickly been developed into various derivatives used in the assembly of oligosaccharides and glycoconjugates.¹⁵

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Despite their functional richness, these small molecules have largely been overlooked in polymer science research, and possess untapped potential beyond their current use.

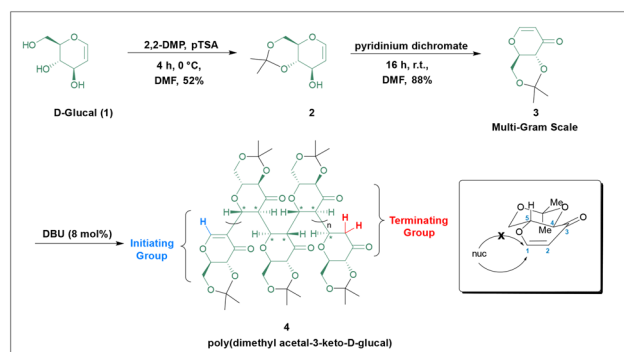
To facilitate the incorporation of these glycals into advanced polymeric backbones, we investigated conjugate addition polymerization (CAP). Conjugate addition polymerization involves a chain-growth process, where nucleophiles add to conjugated systems, this typically involves a diene and an electrophile. This method can be initiated by heat, light, or chemicals, producing materials like elastomers and thermoplastics that exhibit enhanced mechanical properties and thermal stability.¹⁶ The conjugate addition polymerization reaction has long been acknowledged as a versatile polymerization technique, adept at rapidly synthesizing macromolecules from a diverse array of monomers, including those with electron-poor olefins or nucleophiles.¹⁷ Recently, the successful polymerization of levoglucosenone (LGO), a sugar derivative, using CAP with 1,8-diazabicyclo[5.4.0]undec-7-en (DBU) as a catalyst was reported.¹⁸ This innovative and efficient one-step method transformed LGO into a high molecular weight polymer known as polycyrene, which demonstrated outstanding thermal stability and is chemically modifiable, and offers a potential alternative to petrochemically-derived materials. This groundbreaking study highlights the potential for employing various other sugar derivatives featuring an α , β -unsaturated motif, including glycals, within CAP frameworks.

Herein, we report the successful synthesis of poly(3-keto-D-glucal) from a derivative of D-glucal in an atom-efficient polymerization. The monomer was synthesized in two synthetic steps with a moderate yield. With the monomer in hand, the polymerization reaction was optimized by tuning solvent, catalyst, temperature, concentration, and time to achieve high molecular weights (5.8–1080 kDa) and moderate dispersity values ($D = 9.28$ – 1.54). Post-polymerization, the acetal protecting group was removed, which afforded the free hydroxyl groups. The thermal stability of these two polymers was high ($T_{d-5\%} = 183$ and 205 °C), and the protected and deprotected polymers showed a significant difference in T_g , 41 vs. 60 °C, respectively. Overall, this study builds upon the existing library of polymers synthesized by conjugate addition polymerization from bio-based starting materials

B. Results and discussion

Synthesis of poly(dimethyl acetal-3-keto-D-glucal)

The rationale behind this monomer design was to synthetically manipulate a sugar derivative to be used for CAP. For the reaction to proceed, it needed to have an α,β -unsaturated carbonyl and no functional groups that interfere with the polymerization. First, direct polymerization of 3-keto-D-glucal was attempted without the acetal protecting group, which resulted in some broadening in ^1H -NMR (Fig. S1†). However, characterizing the molecular weight by GPC was challenging due to the free hydroxyl groups. The next design of a CAP monomer was dimethyl acetal-3-keto-D-glucal (3), previously synthesized in



Scheme 1 Synthesis of CAP monomer (3) and its polymerization with DBU to form poly(dimethyl acetal-3-keto-D-glucal) (4). *Newly generated stereocenter showing anti-stereochemistry between the α - and β -positions of the carbonyl, showing preferred conformations based on steric analysis. Note: three repeat units are drawn out for clarity of the stereochemical outcome.

two steps, *en route* to trichothecenes,¹⁹ was synthesized as white crystalline needles. Poly(dimethyl acetal-3-keto-D-glucal) (4) was initially synthesized using DBU (8 mol%) as the catalyst in dioxane (4.5M) over 16 h at 60 °C as shown in Scheme 1, conditions that were similar to the CAP of levoglucosenone by Connal and coworkers.²⁰ The polymerization of the enone (3) resulted in the formation of a dark brown colored material (Fig. 1A and B), which was initially precipitated in water, followed by ether from DCM (Fig. 1C) that, upon filtering and

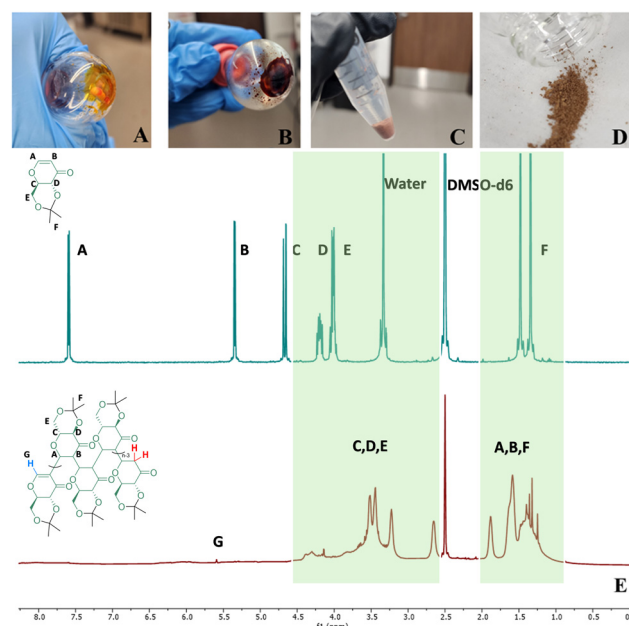


Fig. 1 Synthesis of poly(dimethyl acetal-3-keto-D-glucal) with DBU. Photos of (A) reaction at 1 h, (B) reaction at 16 h, (C) precipitation in water, followed by ether precipitation from DCM, and (D) tan precipitate obtained after drying. The characterization was performed and shown in (E) is the stacked NMR spectra of CAP monomer and poly(dimethyl acetal-3-keto-D-glucal). Note: Stereochemistry not shown for clarity.

drying, afforded a tan-colored precipitate (Fig. 1D). The polymer was characterized to be poly(dimethyl acetal-3-keto-D-glucal) through several methods. Upon subjecting the resulting initial polymerization to size exclusion chromatography gave $M_n = 6.4$ kDa and $D = 6.32$ (Fig. S8†). The chemical integration for the synthesized polymer was also confirmed by ^1H NMR spectroscopy, demonstrating the broadening of peaks for the observed polymer compared to the CAP monomer (Fig. 1E). It was also observed that running the reaction under N_2 or air gave similar results, and no significant difference was noted.

Investigation of various solvents for the polymerization of poly (dimethyl acetal-3-keto-D-glucal) (4)

For the synthesis of poly (dimethyl acetal-3-keto-D-glucal), solvent screening was limited to polar aprotic solvents because protic solvents would terminate the polymerization. Therefore, a solvent needed to be identified that enhanced mixing and solubility, thereby improving the molecular weight and dispersity of the polymer. Keeping all the other conditions constant from the initial screening (4.5M, DBU loading 8 mol%, 16 h, 60 °C), initial experiments were performed in dioxane, having a slightly similar structure to the enone (3); it was assumed it would give the best result. However, after a short polymerization time, the polymer became insoluble in dioxane and resulted in the lowest molecular weight (Table 1, entry 1). Similarly, the polymer was slightly soluble in acetone, giving it a lower molecular weight (Table 1, entry 2). The polymer was soluble in THF, acetonitrile, and DMF for the duration of the entire polymerization and resulted in similar molecular weights and dispersity values (Table 1, entries 3–5). Acetonitrile was chosen to explore further when changing other parameters because THF has a lower boiling point, which could limit the usage of higher temperatures, and DMF is highly toxic and challenging to remove during the workup, which could limit the utility of the resultant polymer.

Screening the reactivity of different bases for the polymerization of poly (dimethyl acetal-3-keto-D-glucal) (4)

Enone (3) was treated with various common nitrogen bases to investigate its potential for initiating the polymerization. Initial experiments using pyridine and triethylamine at room temperature resulted in no observable reaction (Table 2,

Table 1 Solvent screen for the effect on molecular weight (M_n) and dispersity (D) in the synthesis of poly (dimethyl acetal-3-keto-D-glucal)

Entry ^a	Solvent	M_n (kDa) ^b	M_w (kDa)	D	Recovery (%)
1	Acetone	6.7	52.0	7.80	17
2	CH_3CN	22.6	83.8	3.71	21
3	DMF	23.3	80.7	3.47	11
4	Dioxane	6.4	40.4	6.32	19
5	THF	10.5	97.2	9.28	20

^a All reactions done using 8 mol% DBU catalyst loading, 4.5M at 60 °C for 16 h. ^b Molecular weights were found using the dn/dc value calculated with the batch dn/dc method for polymer (ESI S34†).

Table 2 Base screening for the effect on molecular weight (M_n) and dispersity (D) in the synthesis of poly (dimethyl acetal-3-keto-D-glucal)

Entry ^{a,b}	Base/catalyst	M_n (kDa) ^c	M_w (kDa)	D	Recovery (%)
1	Pyridine	NR	NR	NR	NR
2	Triethylamine	NR	NR	NR	NR
3	DABCO	NR	NR	NR	NR
4	TBD ^a	5.8	36.0	6.32	13
5	DBU ^a	22.6	83.8	3.71	21

NR = no reaction. ^a All reactions done using 8 mol% catalyst, 4.5M, at r.t., in acetonitrile for 16 h. ^b Reaction done at 60 °C. ^c Molecular weights were found using the dn/dc value calculated with batch dn/dc method for polymer (ESI S34†).

entries 1 and 2). Thin-layer chromatography (TLC) analysis confirmed the presence of only the monomer. Subsequent treatment with 1,4-diazabicyclo [2.2.2] octane (DABCO), a base commonly employed as a catalyst in the Morita-Baylis-Hillman (MBH) reaction,²¹ similarly showed no polymerization at ambient conditions (Table 2, entry 3). However, upon heating to 60 °C, the reaction mixture developed a dark brown coloration. TLC analysis at this stage revealed multiple spots, suggesting the formation of oligomers of varying sizes. However, fast initiation was the goal; therefore, other bases were tested.

Next, bulky bases were tested as the initiator. Treatment with 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD), a guanidine base with a reactivity profile similar to DBU, yielded more promising results (Table 2, entry 4). At room temperature, TLC monitoring indicated partial polymerization, evidenced by the disappearance of the monomer and the appearance of new polymer-related spots. The aqueous layer was isolated and analyzed by NMR, which showed characteristic signals for protonated TBD, consistent with those observed for protonated DBU (Fig. S33 and S34†). Reaction with TBD was heated to have the same conditions as done with DBU to compare, and upon characterization by SEC, the result was an $M_n = 5.8$ kDa. Despite TBD's ability to initiate polymerization under similar conditions as DBU, its use was not pursued further due to slower initiation—likely attributed to increased steric hindrance—and its cost, which is approximately four times higher than that of DBU at the time of writing this manuscript. The DBU reaction resulted in a doubling of the molecular weight compared to TBD (Table 2, entry 5). Therefore, it was used for all future studies.

Identifying additional reaction conditions for the polymerization of poly (dimethyl acetal-3-keto-D-glucal) (4)

After identifying a suitable solvent and screening the bases, further exploration of conditions for the optimization of poly (dimethyl acetal-3-keto-D-glucal), the variations in the monomer concentration of the reaction were tested while keeping the DBU loading at 8 mol%. The outcomes of these experiments are shown in Table 3. Increasing the time initially at the concentration of 4.5M led to an increase in molecular

Table 3 Investigation of various reaction conditions on molecular (M_n) and dispersity (D) and recovery of poly (dimethyl acetal-3-keto-D-glucal)

Entry ^a	Concentration (M)	Time (h)	M_n (kDa) ^c	M_w (kDa)	D	Recovery (%)
1	4.5	24	27	144	5.26	25
2	4.5	48	117	446	3.81	31
3	4.5	72	148	466	3.14	34
4	2.25	24	14	53	3.78	21
5	2.25	48	57	223	3.91	37
6	2.25	72	176	544	3.07	49
7	1.12	24	19	58	2.96	23
8	1.12	48	98	301	3.06	36
9	1.12	72	241	688	2.85	55
10	0.65	24	18	67	3.67	27
11	0.65	48	106	320	3.01	39
12	0.65	72	443	981	2.21	58
13	0.65	96	491	898	1.82	47
14	0.65	144	477	751	1.57	44
15 ^b	0.65	22	1080	1673	1.54	71

^a All reactions done using 8 mol% catalyst, at 60 °C, in acetonitrile. ^b Reaction done at 80 °C. ^c Molecular weights were found using the dn/dc value calculated with a batch dn/dc method for polymer (ESI S34†).

weight (M_n) from 27 kDa to 117 to 148 kDa at 24, 48, and 72 h, respectively (Table 3, entries 1–3). This can be attributed to the condensation polymerization mechanism leading to a higher molecular weight. The effect on molecular weight was examined when changing different concentrations. Initially, it was observed that the molecular weight decreased as the concentration decreased. When the concentration was halved, the M_n increased to 176 kDa (Table 3, entry 6), and when the concentration decreased to 0.65M, the M_n increased to 443 kDa (Table 3, entry 12). At 72 h, it was observed that with the increase in time and decrease in concentration, the molecular weight increased, as well as obtaining a lower dispersity (Table 3, entries 6, 9 and 12), which is likely due to the insolubility of the polymer at higher concentrations, which was observed during the polymerization as a solid crashing out. At longer reaction times, there was little increase in molecular weight at 96 h (Table 3, entry 13) and a decrease in molecular weight at 144 h due to the insolubility of a fraction of the polymer. When the temperature increased, and the reaction was conducted for a shorter time, it resulted in a M_n = 1080 kDa with a low dispersity (D = 1.54) in 22 h (Table 3, entry 15). It is worth noting that temperatures higher than 80 °C for longer than 22 h at 0.65M gave insoluble products that could not be characterized. Overall, changing parameters such as concentration, time, and temperature resulted in drastic changes in molecular weight with optimized conditions, resulting in polymers with greater than 1000 kDa.

The effect of catalyst loading was also examined while maintaining constant temperature, time, and concentration (60 °C for 72 hours at 0.65M). Polymerizations were carried out with 4 and 2 mol% DBU loading. The results in (Table 4, entries 1–3) show that as the catalyst loading decreased, the molecular weight (M_n) dropped from 443 kDa to 52 kDa between 8–2 mol%. This decrease can be attributed to fewer initiation events, leading to polymers that incorporate fewer monomer units and thus result in a lower average molecular weight.

Table 4 Impact of catalyst loading on molecular weight (M_n) of poly (dimethyl acetal-3-keto-D-glucal)

Entry	Catalyst (mol%)	M_n (kDa) ^b	D	Recovery (%) ^a
1	8	443	2.21	58
2	4	112	2.68	27
3	2	52	3.22	21

^a All reactions were precipitated in water, followed by precipitation in ether. ^b Molecular weights were found using the dn/dc value calculated with the batch dn/dc method for polymer (ESI S34†).

Polymer recovery was evaluated through a two-step precipitation process: initially into water from the cooled reaction mixture, followed by precipitation into diethyl ether from dichloromethane (DCM). At a constant reaction time of 72 hours, a decrease in reaction concentration increased polymer recovery from 34% to 58% (Table 5, entries 1–4). In contrast, extending the reaction time beyond 72 hours (Table 5, entry 5) led to a decline in recovery, likely due to the formation of high-molecular-weight, insoluble polymeric fragments. Keeping the concentration the same and increasing the temperature to 80 °C at reduced time 22 h gave an increase in recovery up to 71% (Table 5, entry 6). The SEC trace of the

Table 5 Impact of reaction time on the recovery of poly (dimethyl acetal-3-keto-D-glucal)

Entry ^{a,b}	Concentration (M)	Time (h)	Recovery (%) ^c
1	4.5	72	34
2	2.25	72	49
3	1.25	72	55
4	0.65	72	58
5	0.65	144	44
6 ^b	0.65	22	71

^a All reactions done using 8 mol% catalyst, at 60 °C, in acetonitrile. ^b Reaction performed at 80 °C. ^c All reactions were precipitated in water, followed by precipitation in ether.

Table 6 TGA and DSC results for the obtained polymeric material poly(3-keto-D-glucal), and the protected derivative

Polymer	TGA ^a		DSC ^b		
	<i>T</i> _{d-5%} (°C)	Derivative (°C)	<i>T</i> _g (°C)	<i>H</i> _{relax} (J g ⁻¹)	<i>C</i> _p (J g ⁻¹ °C ⁻¹)
Poly (dimethyl acetal 3-keto-D-glucal)	183	213	41	0.31	17.9
Poly(3-keto-D-glucal)	205	236	60	0.24	4.6

^a TGA data was collected from 0–700 °C. ^b DSC data was collected at 3rd cycle from 0–150 °C.

difference was the broad -OH peak at 3350 cm⁻¹ for poly(3-keto-D-glucal) (5), indicating the deprotection. The sharp carbonyl peak at 1720 cm⁻¹ was retained in poly(3-keto-D-glucal), indicating the backbone structure did not change under deprotection conditions. Poly(3-keto-D-glucal) (5) was also characterized by ¹H NMR (Fig. S37†), which showed some reduction in the region of the peaks of the dimethyl acetal, due to deprotection. However, the polymer backbone appeared in the same region, and ¹H NMR was inconclusive.

Thermal properties and stability comparison of poly (dimethyl acetal-3-keto-D-glucal) with poly(3-keto-D-glucal)

Based on the structures of poly (dimethyl acetal-3-keto-D-glucal) (4) and poly(3-keto-D-glucal) (5), it was expected that the physical properties would be different; therefore, broad characterization was required. Beginning with thermal characterization, thermogravimetric analysis (TGA) was used to measure the degradation temperature (*T*_{d-5%}) (Table 6). Poly (dimethyl acetal-3-keto-D-glucal) (4) showed good thermal stability, having a *T*_{d-5%} at 183 °C, and when reported at the derivative, it is 213 °C. Deprotected poly(3-keto-D-glucal) (5) showed *T*_{d-5%} at 205 °C, and when reported at the derivative, it is 236 °C. This increase in thermal stability is attributed to the free hydroxyl groups on 5, which can promote hydrogen bonding interactions between polymer chains that will not occur with the protected dimethyl acetate on poly (dimethyl acetal-3-keto-D-glucal) (4). The differential scanning calorimetry (DSC) data also showed a similar trend. The glass transition temperature for the protected poly (dimethyl acetal-3-keto-D-glucal) (4) occurred at *T*_g = 41 °C, while poly(3-keto-D-glucal) (5) showed a glass transition temperature at *T*_g = 60 °C. The increase in glass transition temperature is due to the formation of hydrogen bonding, which occurs upon deprotection of the dimethyl acetal so that the neighboring polymer chains increase the polymers' intermolecular interactions and, therefore, increase the *T*_g. The heat capacity (*C*_p) is influenced by the molecular structure and interactions between the chains for the protected polymer, poly (dimethyl acetal-3-keto-D-glucal). The *C*_p is more than 4 times higher than poly(3-keto-D-glucal) (5), which possibly could be due to poly (dimethyl acetal-3-keto-D-glucal) (4) having a cyclic, protected side group restricting the chain mobility, and more energy would be required to undergo a phase transition. Alternatively, the free hydroxyl group would form hydrogen bonding for poly(3-keto-D-glucal) (5) and therefore would lead to a more rigid structure that would potentially decrease the chain mobility, lowering

the heat capacity as less energy would be needed to increase the temperature for this system. The structural variations between the protected and the deprotected polymers gave rise to variations in their thermal properties.

Attempts to form bulk materials for further characterization

To enhance the utility of the 3-keto-D-glucal polymers and their hydrophobic derivatives, significant efforts were made to develop structurally relevant materials. To improve the utility of this polymerization poly(dimethyl acetal 3-keto-D-glucal) (4) was heat cured at 120 °C for 16 h to form bars (Fig. 3), which were matte black and non-glassy, however, these bars were very brittle and therefore no relevant mechanical analysis could be done, other attempts to make bars included heat press under pressure with 120 °C heat curing, solvent casting and evaporation of solvent followed with heat which yield the same results as above and the bars that did form were quite brittle. The same attempts were made to make bulk materials from poly(3-keto-D-glucal); however, these materials did not form bars. To further probe why these high molecular weight polymers were not able to be processed into a structural material, powder X-ray diffractometer data were collected. Both the protected and deprotected polymers were found to be primarily amorphous, with 0.48% and 1.53% crystallinity, respectively (Fig. S46 and S47†). The lack of crystallinity is one explanation for the lack of mechanical properties for the synthesized polymers.

C. Conclusions

In conclusion, we successfully present the synthesis of poly (dimethyl acetal 3-keto-D-glucal) using conjugate addition polymerization from the biobased starting material, D-glucal. The resultant polymer showcased a favorable thermal stability at *T*_{d-5%} = 183 °C as well as a *T*_g = 41 °C. The optimization of the synthetic conditions resulted in very high molecular weights up to (*M*_n = 1080 kDa) with 71% recovery. The protected polymer was transformed using mild acidic conditions into poly(3-keto-D-glucal) that, unlike its precursor, is water soluble. Due to intermolecular hydrogen bonding, the deprotected polymer showed improved thermal stability with a *T*_{d-5%} = 205 °C and a *T*_g = 60 °C. This deprotected polymer is rich in functional groups and provides avenues for post-polymerization, including selective reactions at the primary or secondary alcohol, which can be further explored for advanced applications using conjugate addition polymerization.

Author contributions

S.L.K. conceptualized the project and interpreted data. M.M.S., M.K.F., and L.P.B. synthesized the monomers and polymers. M.M.S. performed the characterization of the polymers.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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