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Chemically Recyclable Unnatural (1→6)-Polysaccharides from Cellulose-Derived Levoglucosenone and Dihydrolevoglucosenone

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KEYWORDS: biomass valorization; cationic ring-opening polymerization; organocatalysts; polysaccharides; chemical recycling

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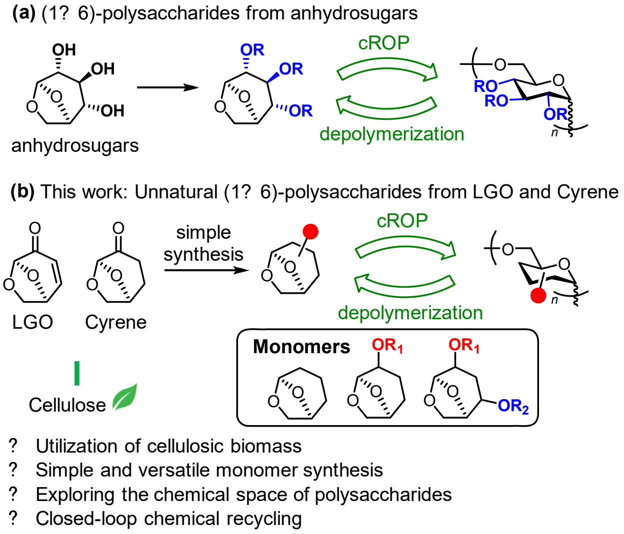
ABSTRACT: Unnatural polysaccharide analogs and their biological activities and material properties have attracted considerable research interest. However, these efforts often encounter challenges, especially those related to synthetic complexity and scalability. Here, we report a chemical synthesis of unnatural (1→6)-polysaccharides using levoglucosenone (LGO) and dihydrolevoglucosenone (Cyrene™), which are derived from cellulose. Using a versatile monomer synthesis from LGO and Cyrene and cationic ring-opening polymerization, (1→6)-polysaccharides with various tailored substituent patterns are obtained. Additionally, environmentally benign and easy-to-handle organic Brønsted acid catalysts are investigated. This study demonstrates well-controlled first-order polymerization kinetics for the reactive (1*S*,5*R*)-6,8-dioxabicyclo[3,2,1]octane (DBO) monomer. The synthesized (1→6)-polysaccharides exhibit high thermal stability and form amorphous solids under ambient conditions, which could be processed into highly transparent self-standing films. Additionally, these polymers exhibit excellent closed-loop chemical recyclability. This study provides an important approach to explore the chemical spaces of unnatural polysaccharides and contributes to the development of sustainable polymer materials from abundant biomass resources.

The use of biomass for sustainable polymer material production is widely recognized as a crucial approach to address the global challenges posed by plastic waste and the depletion of fossil fuel resources. Polysaccharides, which are one of the most abundant biomass resources on Earth, hold significant promise.[1,2] In addition to their natural abundance, the intriguing structural features of polysaccharides further enhance their applications.[3,4] Each pyranose or furanose monomer exhibits numerous substitution patterns coupled with regio- and stereoselectivities of the glycosidic linkages. These features result in a vast array of structural variations in homopolysaccharides, not to mention the complexities of heteropolysaccharides. Furthermore, the presence of acid-labile glycosidic linkages, also known as acetal moieties, facilitates easy decomposition and chemical recycling.[5–9] Therefore, exploring the structure-property relationship and fully harnessing the unique features of polysaccharides for sustainable polymer material development is an attractive avenue.

Among naturally abundant polysaccharides, cellulose has been extensively studied and utilized since the mid-1800s, leading to the production of commercial products such as nitrocellulose and cellulose acetate. For polysaccharides with low natural abundance, enzymatic[10,11] and chemical[12,13] syntheses have been explored as viable alternatives. Chemical polymerization using anhydrosugars via cationic ring-opening polymerization (cROP) has been extensively studied since the 1960s.[14–17] Recently, well-controlled polymerization techniques have been developed for these monomers, marking significant progress in this field (**Scheme 1a**).[6,18]

Scheme 1. Research background and this work.



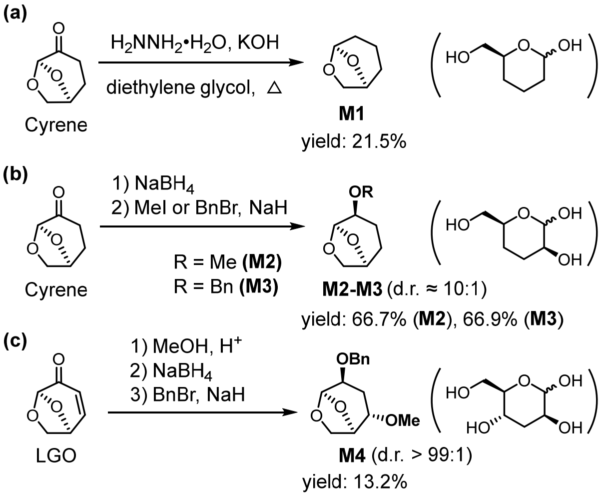
The chemical synthesis of unnatural polysaccharide analogs and investigations of their biological activities have been enduring research topics.[19] To date, several attempts have been made in which multi-step monomer syntheses were involved.[20–22] However, the exploration of their structure-material property relationships for novel sustainable polymer development is equally intriguing if a practical synthetic approach can be established, ideally from biomass resources.

Levoglucosenone (LGO), a compound characterized by its bicyclic acetal structure and *α,β*-unsaturated ketone moiety, is obtained through the pyrolysis of cellulose.[23] The reduction of the C=C double bond of LGO via hydrogenation produces dihydrolevoglucosenone, also known as Cyrene™.[24] The successful large-scale production of LGO and Cyrene by Circa Group Ltd. has led to extensive investigations into their applications. LGO is an important optically pure starting material for the chemical synthesis of pharmaceuticals.[25,26] And Cyrene is an environmentally friendly solvent.[24,27–29] Recently, the use of LGO and Cyrene in the synthesis of polymeric materials has gained attention.[30–36] However, in most reported cases, the bicyclic acetal moiety is not used to construct the polymer main chain. Notably, Schlaad and co-workers reported the cROP of LGO-derived levoglucosenyl methyl ether, which could be transformed into (1→6)-polysaccharide derivatives via post-polymerization modification.[37]

Building on these prior studies, we proposed the synthesis of unnatural (1→6)-polysaccharides from LGO and Cyrene (**Scheme 1b**). Leveraging the diverse organic reaction transformations of ketone and *α,β*-unsaturated ketone functional groups, followed by cROP of the bicyclic acetal, this approach offers a straightforward route to a variety of (1→6)-polysaccharides with minimal synthetic steps. Importantly, because LGO and Cyrene are optically pure compounds derived from cellulose, this method enables the synthesis of optically active (1→6)-polysaccharides from naturally abundant biomass.

The investigation commenced with monomer synthesis from Cyrene and LGO. In this study, three types of monomers for unnatural (1→6)-polysaccharides were synthesized: the monomer without side-chain substitution, the monomer with a single substitution, and the monomer with two different substitutions. 6,8-Dioxabicyclo[3.2.1]octane (6,8-DBO) possesses the core structure of a (1→6)-anhydrosugar but lacks any substitution on the side chain. Over the past few decades, this monomer has been widely used as a model monomer to study the fundamental polymerization chemistry of anhydrosugars. Racemic 6,8-DBO is typically synthesized from acrolein dimer via a two-step process.[38] However, obtaining optically pure (+)-(1*R*,5*S*)-6,8-DBO requires a much longer synthesis route, including a chiral resolution step using a chiral amine auxiliary, as reported by Okada and co-workers.[39] In this study, Cyrene was employed as the starting material for the synthesis of (–)-(1*S*,5*R*)-6,8-DBO (**M1**) via the classical Wolff-Kishner reduction (**Scheme 2a**). The nuclear magnetic resonance (NMR) spectra of **M1** were identical to those reported in the literature.[40] Notably, the optical rotation of **M1** was measured to be $[\alpha]_D^{20}$ = –116.6° (*c* 0.10, *n*-hexane), a value almost identical to the reported one for (1*R*,5*S*)-6,8-DBO ($[\alpha]_D^{20}$ = +111.4°, *c* 0.75, *n*-hexane), although with the opposite sign.[39] Thus, optically pure (–)-(1*S*,5*R*)-6,8-DBO (**M1**) was successfully synthesized from cellulose-derived Cyrene in a single step for the first time.

Scheme 2. Monomer synthesis (The corresponding sugar structures of synthesized "anhydrosugar" monomers are indicated in parentheses).

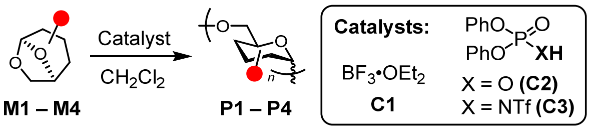


The synthesis of both mono- and di-substituted monomers followed straightforward procedures. The mono-substituted monomers **M2** and **M3** (d.r. ≈ 10:1) were obtained by reducing the carbonyl group of Cyrene, followed by Williamson ether synthesis (**Scheme 2b**).[41,42] The di-substituted monomer **M4** (d.r. > 99:1) was easily synthesized through 1,4-addition to the *α,β*-unsaturated ketone of LGO, followed by the aforementioned process (**Scheme 2c**).[43–45] Importantly, this simple three-step synthetic route for **M4** allowed the introduction of two different substituents in a convenient and practical manner, which is challenging to achieve using naturally available anhydrosugars via side-chain modifications. Notably, these monomers, **M1**–**M4**, can be considered as "anhydrosugar derivatives," and their corresponding sugar structures (indicated in parentheses in **Scheme 2**) have not been identified in nature.[46–48]

After successful synthesis of the monomers, polymerization was performed. In previous reports, the cROP of 6,8-DBO and 1,6-anhydrosugar derivatives typically involved strong Lewis or Brønsted acid catalysts such as PF_5, $BF_3·OEt_2$, ZnI_2, and TfOH. To validate the polymerizability of **M1**, which was synthesized using a newly developed route, the cROP of **M1** was initially conducted with the Lewis acid catalyst $BF_3·OEt_2$ (**C1**) at an $[\mathbf{M1}]_0/[\mathrm{cat.}]_0$ ratio of 100/1 in CH_2Cl_2 at 0 °C, with an initial monomer concentration ($[\mathbf{M1}]_0$) of 4.0 *M* (run 1 in **Table 1**). After 8 h of polymerization, the conversion of **M1** reached 77%. The molecular weight was measured to be 6.3 kDa by size exclusion chromatography (SEC) with a dispersity index (*Đ*) of 1.43. After confirmation of its polymerizability, more user-friendly, environmentally benign organic Brønsted acid catalysts were investigated. Diphenyl phosphate (**C2**), an organic acid catalyst with moderate acidity, has been reported to be an efficient catalyst for the ring-opening polymerization (ROP) of various cyclic monomers, even under ambient conditions.[49–51] However, the polymerization of **M1** by **C2** at room temperature did not proceed efficiently. Only 9% of **M1** was converted after 168 h and oligomers were obtained ($M_{\mathrm{n,\,SEC}}$ < 1.0 kDa, run 2 in **Table 1**). To enhance the catalytic efficiency, diphenyl *N*-triflyl phosphoramide (**C3**), which is approximately seven orders of magnitude higher in acidity than **C2**, was examined (run 3 in **Table 1**)[52]. At room temperature, the conversion of **M1** reached 73% within 5 h, although only oligomers were obtained. We suspected that the oligomers might have resulted from acid-catalyzed decomposition of the polyacetal (**P1**) formed during polymerization due to the lack of proper quenching of the acid catalyst and absence of protection for chain-end functionalities such as hydroxyl or hemiacetal groups. To our delight, when the reaction was quenched with Ac_2O in pyridine with a catalytic amount of 4-dimethylaminopyridine (DMAP), **P1** with $M_{\mathrm{n,SEC}}$ = 7.0 kDa and *Đ* = 1.46 was obtained (run 4 in **Table 1**). In the ^{1}H NMR spectrum of purified **P1**, the α/β stereoselectivity was determined to be 71/29 from the ^{1}H signal corresponding to the anomeric position. Compared to previous reports using $BF_3{\cdot}OEt_2$, especially at low temperatures, the α/β selectivity was not high under this condition. A peak corresponding to the acetyl groups at the chain ends was observed in the ^{1}H NMR spectrum (**Figure 1a**). Assuming complete chain-end functionalization by the acetyl group, the NMR-based molecular weight ($M_{\mathrm{n,NMR}}$) was calculated to be 6.8 kDa, which closely matched the value of $M_{\mathrm{n,SEC}}$. Nearly perfect chain-end functionalization was confirmed by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) analysis of **P1** (**Figure 1b, 1c**). Notably, a trace amount of cyclic oligomers was also observed in the low molecular weight portion of **P1** (**Table 1**, run 4), which was usually removed during the purification process (**Figure S14, S15**).

Next, the effects of monomer/catalyst ratio and polymerization temperature were investigated. Increasing the $[\mathbf{M1}]_0/[\mathrm{cat}]_0$ ratio to 300/1 resulted in a decrease in the polymerization rate, but the $M_{\mathrm{n,SEC}}$ value of **P1** increased to 12.2 kDa with a similar dispersity (*Đ* = 1.46, run 5 in **Table 1**, and **Figure 1d**). Lowering the polymerization temperature to 0 °C with an $[\mathbf{M1}]_0/[\mathrm{cat.}]_0$ ratio at 100/1 and, the polymerization became slower than the one at room temperature (run 6 in **Table 1**). And the obtained **P1** had similar molecular weight and dispersity as the one in run 5, **Table 1**. Further decreasing the polymerization temperature to –20 °C with an $[\mathbf{M1}]_0/[\mathrm{cat.}]_0$ ratio of 175/1, the polymerization rate became even lower, and the monomer conversion reached 80% after 360 h (run 7 in **Table 1**). The low polymerization rate provided us with a platform to monitor the polymerization kinetics using ^{1}H NMR and SEC. In the SEC analysis, a clear shift in the SEC trace to a higher molecular weight was observed with increasing reaction time (**Figure 1e**). The SEC molecular weight increased proportionally to the monomer conversion and *Đ* remained approximately 1.5 (**Figure 1f**). The time-$\ln([M]_0/[M]_t)$ plot exhibited a linear relationship, indicating that polymerization followed first-order kinetics with respect to the monomer (**Figure 1g**). After confirming the well-controlled polymerization of **M1** using catalyst **C3**, the synthesis of telechelic **P1** was attempted using propargyl alcohol as the chain transfer agent (CTA, run 8 in **Table 1**). Polymerization was performed at an $[\mathbf{M1}]_0/[\mathrm{CTA}]_0/[\mathbf{C3}]_0$ ratio of 100/1/1 in CH_2Cl_2 at room temperature. After 10 h, the conversion of **M1** reached 80%. Upon quenching the polymerization with Ac_2O, **P1** was obtained with $M_{\mathrm{n,SEC}}$ = 6.8 kDa and *Đ* = 1.46. Analysis of the ^{1}H NMR spectrum of **P1** revealed that approximately 70% of the polymers exhibited the desired telechelic structure characterized by a propargyl group at the reducing end and an acetyl group at

Table 1. Cationic ring-opening polymerization of **M1–M4**.[a]



run	cat.	M	$[M]_0$ /$[\mathrm{cat.}]_0$	temp. (°C)	time (h)	conv.[b] (%)	$M_{\mathrm{n,\,NMR}}$[c] (kDa)	$M_{\mathrm{n,\,SEC}}$[d] (kDa)	*Đ*[d]
1[e]	**C1**	**M1**	100/1	0	8	77	-[f]	6.3	1.43
2	**C2**	**M1**	100/1	r.t.	168	9	-[f]	<1.0	-[f]
3[g]	**C3**	**M1**	100/1	r.t.	5	73	-[f]	<1.0	-[f]
4[h]	**C3**	**M1**	100/1	r.t.	4	77	6.8	7.0	1.46
5[h]	**C3**	**M1**	300/1	r.t.	26	81	16.1	12.2	1.50
6[h]	**C3**	**M1**	100/1	0	32	74	17.3	12.0	1.58
7[h, i]	**C3**	**M1**	175/1	–20	360	80	19.7	14.0	1.46
8[h, j]	**C3**	**M1**	100/1	r.t.	10	80	7.6	6.8	1.46
9	**C3**	**M2**	100/1	r.t.	48	<1	-[f]	-[f]	-[f]
10[e]	**C1**	**M2**	10/1	0	8	55	-[f]	28.8	1.58
11[e]	**C1**	**M3**	10/1	0	12	80	-[f]	11.5	1.70
12[e]	**C1**	**M4**	10/1	0	12	87	-[f]	43.8	1.77

[a] Polymerization conditions: argon atmosphere in CH_2Cl_2; $[M]_0$ = 4.0 *M*. [b] Determined by ^{1}H NMR using mesitylene as an internal standard. [c] Determined by ^{1}H NMR spectroscopy of the obtained polymers. [d] Determined by SEC in tetrahydrofuran (THF) calibrated using a polystyrene standard. In runs 2 and 3, the reaction mixture was used. In other cases, isolated samples were measured. [e] Quenched with triethylamine (5 equiv.). [f] Not determined. [g] Diluted with $CHCl_3$ after polymerization. [h] Quenched with a mixture of acetic anhydride (5 equiv.), pyridine (5 equiv.), and 4-dimethylaminopyridine (2 equiv.) [i] 2.5 g scale [j] Propargyl alcohol (1 equiv.) was used as the chain transfer agent. Abbreviation: room temperature (r.t.).

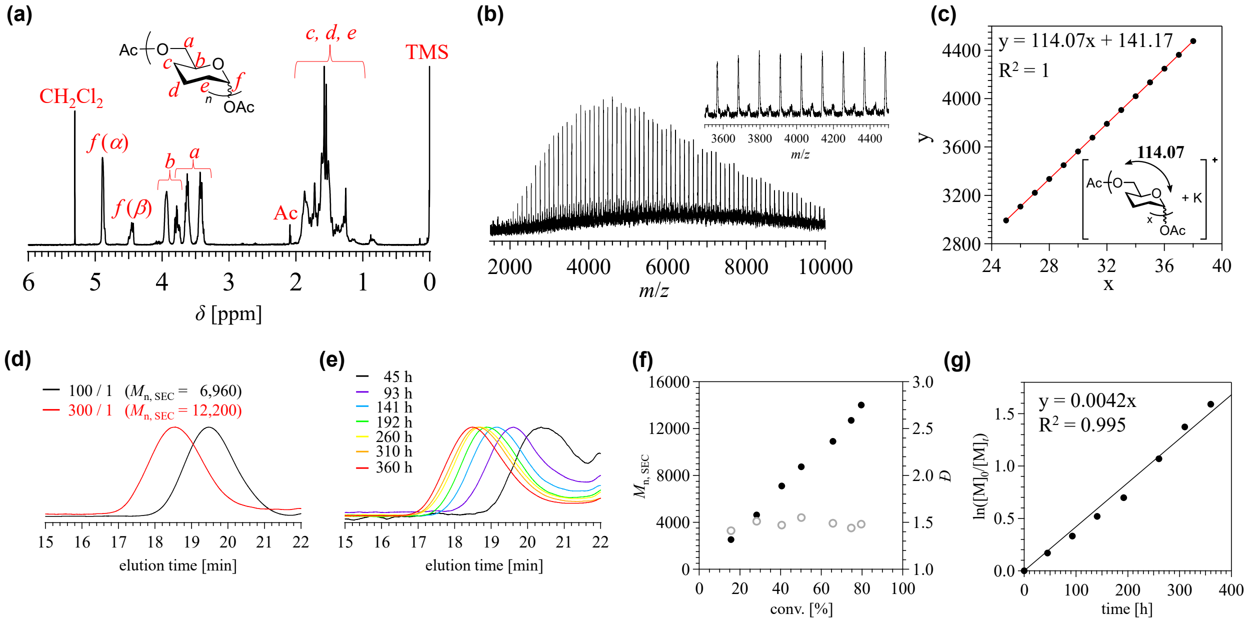


Figure 1. ^{1}H NMR (a) and MALDI-TOF MS spectra (b) of **P1** (run 4 in **Table 1**). (c) linearly fitted plot of m/z values (y) vs the number of **P1** repeat units (x). SEC traces of **P1** (runs 4 and 5, **Table 1**) (d), and the reaction mixture at different reaction time of run 7 in **Table 1** (e) (eluent, THF; flow rate, 1.0 mL min^{-1}; polystyrene standard). Conversion–$M_{\mathrm{n,SEC}}$ / $Đ$ plot (f) and Time-ln([M]$_0$/[M]$_t$) plot (g) of run 7 in **Table 1**.

the non-reducing end (**Figure S18**). Although the chain-end fidelity requires improvement, the successful introduction of the propargyl group opens avenues for further chain-end modifications, for instance, using azide-alkyne cycloaddition. The well-controlled polymerization of **M1** using catalyst **C3** could probably be attributed to the suitable acidity of **C3** and the dual activation mechanism (**Scheme S7–S10**).

After using **M1** as a model monomer to study polymerization, the polymerization behavior of the other synthesized monomers (**M2–M4**) was investigated. A single substitution was introduced at the 2-position in **M2**, and the cROP of **M2** was conducted with **C3** as the catalyst in CH_2Cl_2 at room temperature. However, no conversion of **M2** was observed after 48 h (run 9 in **Table 1**). This result indicates a significant difference in the reactivity between **M1**, the unsubstituted monomer, and **M2**, the single-substituted monomer. Schlaad and co-workers reported a similar cROP study of LGO-derived levoglucosenyl methyl ether using $BF_3{\cdot}OEt_2$ (**C1**) as the catalyst and a high monomer/catalyst ratio, such as 10/1.[37] Subsequent runs also used a ratio of 10/1 at 0 °C, and the conversion of **M2** increased to 55% after 8 h and then plateaued. This result indicates that 55% was presumably the theoretically highest conversion governed by thermal dynamics. After quenching the reaction by adding an excess amount of triethylamine, $M_{\mathrm{n,SEC}}$ was 28.8 kDa with $Đ$ = 1.58 (run 10 in **Table 1**). **M3** and **M4** were polymerized under the same conditions (runs 11 and 12 in **Table 1**). After 12 h, the conversion of **M3** reached 80% with $M_{\mathrm{n,SEC}}$ = 11.5 kDa and $Đ$ = 1.70. A similar amount of **M4** was consumed after 12 h (87%), and the obtained product had a higher molecular weight than that of **P2** and **P3**, $M_{\mathrm{n,SEC}}$ = 43.8 kDa with $Đ$ = 1.77. The α/β stereoselectivity of **P2–P4** was investigated using ^{1}H NMR analysis, and the α selectivities of **P2**, **P3**, and **P4** were 95%, 96%, and >99%, respectively (**Figure S19, S23, S27**). These results indicate that the substitutions significantly affect the monomer conversion and stereoselectivity of the polymerization.[53,54]

Free hydroxy groups on polysaccharides may be important for their biological activities. The benzyl group on **P4** was deprotected via hydrogenation using a 9 wt% Pd/C catalyst. Complete conversion of the benzyl groups was achieved after 12 h at room temperature, as confirmed by NMR, fourier transform infrared (FT-IR), and SEC measurements (**Figure 2 and Figure S31–S34**). Therefore, the versatile monomer synthesis protocol coupled with an appropriate deprotection reaction after cROP offers a powerful approach for manipulating the substituent positions and patterns of the hydroxy groups on (1→6)-polysaccharides.

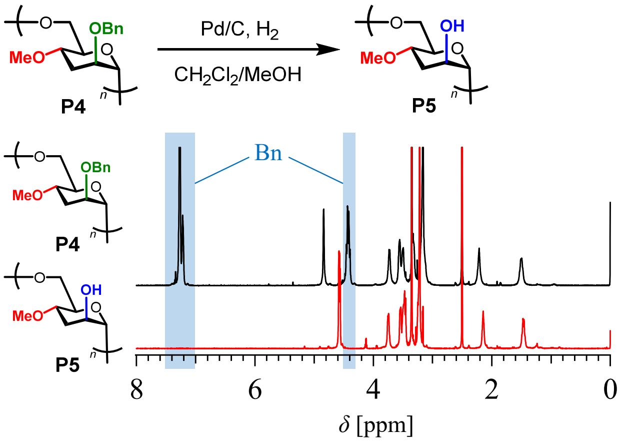


Figure 2. Debenzylation of **P4** (run 12 in **Table 1**).

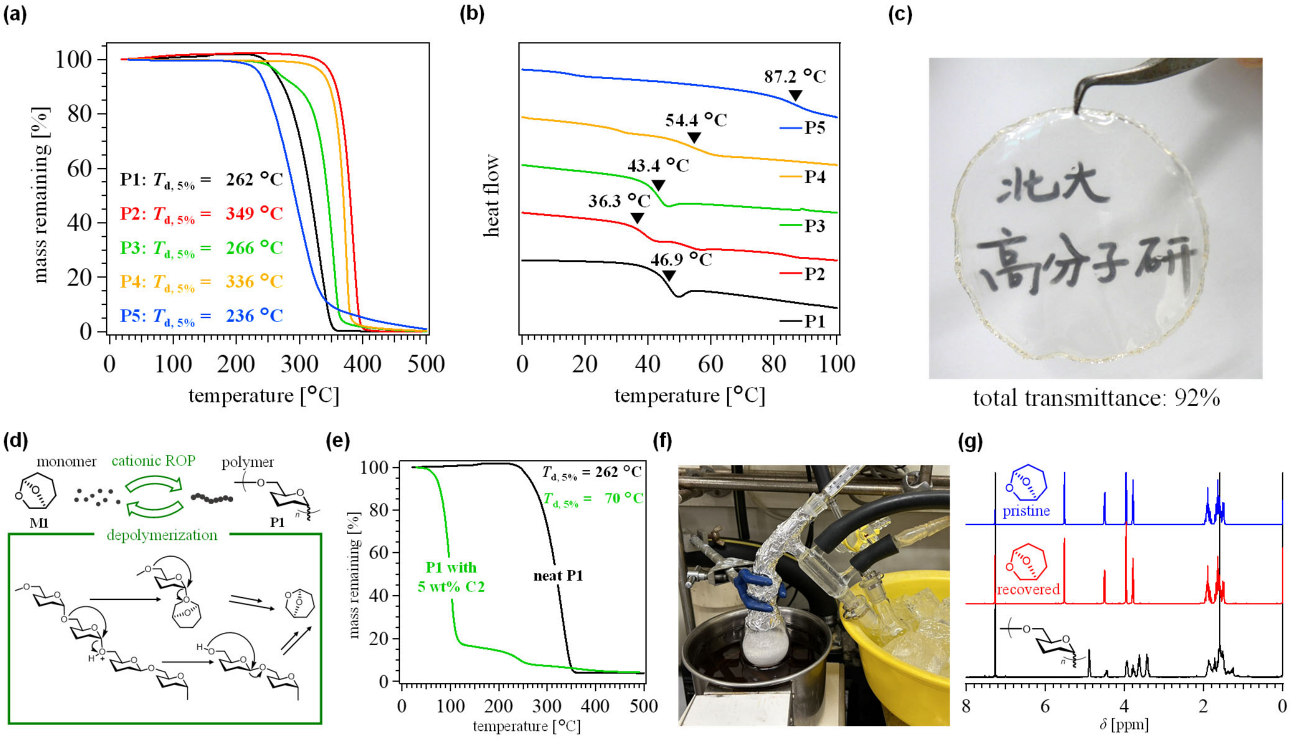


Figure 3. (a) TGA curves of **P1**–**P5**. (b) DSC curves of the second heating process of **P1**–**P5**. (c) The picture of the **P1** film. (d) Proposed depolymerization mechanism of **P1**. (e) TGA curves of neat **P1** (black) and **P1** with 5 wt% **C2** (green). (f) Depolymerization of **P1** by distillation. (g) ^{1}H NMR spectra of **M1** (blue), recovered product (red), and **P1** (black) in $CDCl_3$ (400 MHz). **P1, P2, P3, and P4** were obtained from runs 7, 10, 11, and 12, respectively, in **Table 1**.

Next, the material properties of **P1**–**P5** were evaluated. First, the thermal stability was examined by thermogravimetric analysis (TGA). As shown in **Figure 3a**, **P5** had the lowest thermal stability with a 5% weight loss temperature ($T_{d, 5\%}$) at 236 °C. For **P1**–**P4**, $T_{d, 5\%}$ exceeded 260 °C. In particular, the $T_{d, 5\%}$ values of **P2** and **P4** were 349 °C and 336 °C, respectively, which are much higher presumably due to their higher molecular weights than those of the other polymers (runs 10 and 12 in **Table 1**). Differential scanning calorimetry (DSC) analysis of **P1**–**P5** was conducted (**Figure 3b**). The glass transition temperature (T_g) of **P1** was 46.9 °C. The T_g values of **P2**, **P3**, and **P4** were 36.3 °C, 43.4 °C, and 54.4 °C, respectively. The T_g value increased as the bulkiness and number of substituents on the side chains increased in the case of (1→6)-polysaccharides with alkoxy side chains. The T_g value of **P5** was 87.2 °C, which is higher than that of **P4**, presumably due to the formation of hydrogen bonds by the hydroxy group. Notably, none of the DSC measurements for **P1**–**P5** exhibited a clear melting point. The absence of sharp crystalline peaks in the powder X-ray diffraction (PXRD) pattern also indicated their amorphous nature (**Figure S36**–**S38**). In general, amorphous polymers usually are more transparent than semi-crystalline polymers. When **P1** was solvent-cast to form a film, a freestanding film with high transparency was obtained (**Figure 3c**). The total transmittance of **P1** was measured to be 92%, which is at the same level with poly (methyl methacrylate) (**Table S1**). The natural (1→6)-polysaccharides reported by Niu and coworkers demonstrated a similar tendency, with most substituted (1→6)-glucans being amorphous and their T_g highly dependent on the side chain structures. However, the trimethoxy-substituted α-(1→6)-glucan is a semi-crystalline polymer with a melting point at 284 °C.[6] The difference between trimethoxy substituted α-(1→6)-glucan from **P2** and **P4**, which also contain methoxy groups, could be attributed to the different numbers of substituents (**P2, P4**), imperfect stereoselectivity (**P2**), and the presence of different substituents in single monomer units (**P4**).

Closed-loop recyclability is an important factor for the sustainability of polymer materials. Therefore, it would be ideal if the newly synthesized cellulose-derived unnatural (1→6)-polysaccharides could be chemically recycled back to the monomers to complete closed-loop cycles.

Thermodynamic parameters for the cROP of **M1** have been reported to be $\Delta H°$ = –17.5 kJ mol^{-1} and $\Delta S°$ = –59.4 J mol^{-1} K^{-1}, which indicates the ceiling temperature (T_c) = 21 °C when $[M]_{eq.}$ = 1 *M*.[55] Moreover, chemical recycling of (1→6)-polysaccharides was demonstrated by Niu and coworkers.[6] Therefore, the chemical recycling of the newly synthesized (1→6)-polysaccharide is promising (**Figure 3d**). First, TGA was conducted for the polymer samples (**P1**–**P4**) with Brønsted acid catalyst (5 wt% of **C2**). In all cases, the $T_{d, 5\%}$ value decreased dramatically, indicating acid-catalyzed depolymerization (**Figure 3e Figure S39**–**S41**). Subsequently, the depolymerization of **P1**–**P4** back to their corresponding monomers was confirmed by ^{1}H NMR analysis (**Figure S42**–**S45**). The depolymerization reactions were generally clean, and nearly quantitative yields were obtained according to calculations from the NMR analysis. For **P1**, depolymerization was conducted on a 1.86-gram scale, and monomer **M1** was isolated via distillation. This reaction resulted in pure **M1** in a reasonable yield of 60.2% considering the reaction scale (**Figure 3f, 3g**). Additionally, sublimation was employed to isolate **M1** from depolymerized **P1** (**Figure S46**). The optical rotation of the recovered **M1** was measured to be $[\alpha]_D^{20} = -112.4$ (*c* 0.10, *n*-hexane), which is almost identical to the pristine **M1**. It indicated that no racemization occurred during the polymerization and depolymerization. Polymerization using recovered **M1** gave almost the same result as the one using pristine **M1** (**Scheme S13).** Notably, thermal depolymerization of **P1** without a catalyst could also afford **M1** however with complex byproducts generated at the high temperature (**Figure S47**).

In conclusion, we have demonstrated a synthetic system to produce unnatural (1→6)-polysaccharides using cellulose-derived LGO and Cyrene. A straightforward, versatile monomer synthesis method has been developed by harnessing the unique structural features of LGO and Cyrene. An efficient cROP protocol for constructing (1→6)-polysaccharides with various tailored substituent patterns that are challenging to achieve using other synthetic methods was demonstrated. This approach enables the exploration of the uninvestigated chemical spaces of polysaccharide structures and study of their structure-property relationships. Furthermore, the synthesized (1→6)-polysaccharides exhibited excellent chemical recyclability. Ongoing research efforts include enhancing the controllability of chain-end functionality, reducing polydispersity, and improving the *α*/*β* selectivity. The results of these studies will be reported in due course.

ASSOCIATED CONTENT

Supporting Information.

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

General information, experimental procedures, NMR spectra, SEC traces, FT-IR, HRMS, optical rotation, PXRD, and discussion of some experiment results.

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Notes

The authors declare no competing financial interest.

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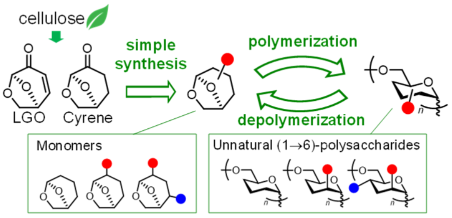

- ✓ Utilization of cellulosic biomass
- ✓ Simple and versatile monomer synthesis
- ✓ Exploring the chemical space of polysaccharides
- ✓ Closed-loop chemical recycling