



Synthesis of optically inactive cellulose via cationic ring-opening polymerization

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Abstract Cellulose, which comprises D-glucose and L-glucose (D,L-cellulose), was synthesized from D-glucose (**1D**) and L-glucose (**1L**) via cationic ring-opening polymerization. Specifically, the ring-opening copolymerization of 3-*O*-benzyl-2,6-di-*O*-pivaloyl- β -D-glucopyranoside (**2D**) and 3-*O*-benzyl-2,6-di-*O*-pivaloyl- β -D-glucopyranoside (**2L**), synthesized from compounds **1D** and **1L**, respectively, in a 1:1 ratio, afforded 3-*O*-benzyl-2,6-di-*O*- β -D,L-glucopyranan (**3DL**) with a degree of polymerization (*DP_n*) of 28.5 (*M_w/M_n* = 1.90) in quantitative yield. The deprotection of compound **3DL** and subsequent acetylation proceeded smoothly to afford acetylated compound **4DL** with a *DP_n* of 18.6 (*M_w/M_n* = 2.08). The specific rotation of acetylated compound **4DL** was + 0.01°, suggesting that acetylated compound **4DL** was optically inactive cellulose triacetate. Furthermore, before acetylation, compound **4DL** was an optically inactive cellulose comprising an almost racemic mixture of D-glucose and L-glucose. Compound **4DL** was an amorphous polymer. This is the

first reported synthesis of optically inactive D,L-cellulose.

Keywords Chirality · Copolymer · D,L-cellulose · β -1,4-glucan · Optically inactivity

Introduction

Natural cellulose, which is the main constituent of plant cell wall, is a chiral homopolymer consisting of D-glucose (denoted as D-cellulose hereafter). This chirality is an important feature of high-value-added D-cellulose applications, such as chiral separation (Francotte 1994; Okamoto and Yashima 1998; D’Orazio et al. 2019; Chankvetadze 2020), chiral nematic D-cellulose liquid crystals (Nishio et al. 2016; Almedia et al. 2018), and D-cellulose-based organocatalysts for asymmetric synthesis (Ikai et al. 2011; Yasukawa et al. 2015; Ranaivoarimanana et al. 2019). Recently, an enantiomer of D-cellulose (denoted as L-cellulose hereafter) consisting of L-glucose was synthesized by our group using cationic ring-opening polymerization (Yagura et al. 2020). D-Cellulose and L-cellulose are crystalline and optically active polymers owing to their homochiral structures.

Poly (L-lactic acid) (PLLA) is a widely known alternative biodegradable chiral homopolymer (Rasal et al. 2010, Castro-Aguirre et al. 2016). PLLA has two

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stereoisomers, namely, poly (D-lactic acid) (PDLA) and poly (D,L-lactic acid) (PDLLA), the latter of which is a copolymer of L-lactic acid and D-lactic acid, which have also been well studied (Nampoothiri et al. 2010; Tsuji 2016). The structure and properties of PDLLA have been reported to be significantly different from those of PLLA and PDLA, as PDLLA is a diastereomer of PLLA or PDLA. For example, PDLLA with 15% L-lactic acid content is amorphous (Rasal et al. 2010). Therefore, cellulose consisting of D-glucose and L-glucose (denoted as D,L-cellulose hereafter) is expected to have a different structure and properties compared with D-cellulose. In particular, D,L-cellulose with a racemic mixture of D-glucose and L-glucose is expected to be an amorphous and optically inactive polymer owing to its racemic heterochiral structure. As the effect of D-cellulose chirality on its applications has not been well clarified, this optically inactive control sample is important for basic research on high-value-added applications of D-cellulose based on its chirality. However, to our knowledge, D,L-cellulose has not been found in nature or synthesized artificially. Our group has already reported the syntheses of D-cellulose (Nakatsubo et al. 1996; Kamitakahara et al. 1996; Adelwöhner et al. 2009) and L-cellulose (Yagura et al. 2020) using cationic ring-opening polymerization. Therefore, this study describes the synthesis of D,L-cellulose with a racemic mixture of D-glucose and L-glucose (D-glucose/L-glucose = 1:1) as an optically inactive cellulose via a synthetic route using cationic ring-opening polymerization, as shown in Scheme 1.

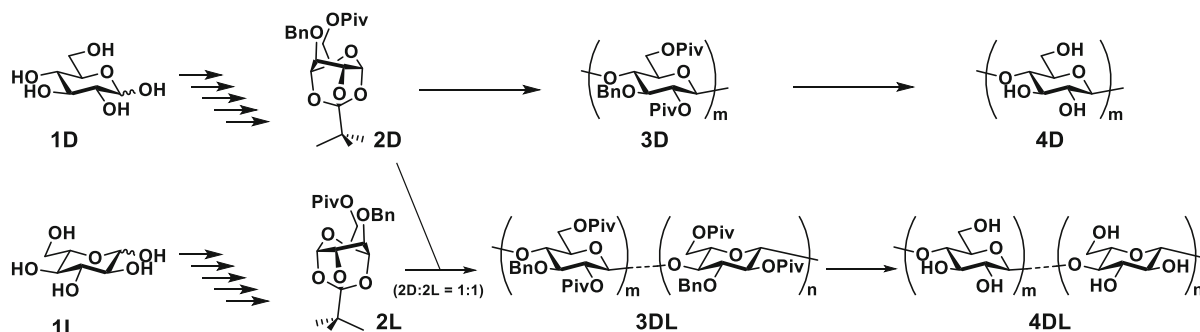
Experimental

Materials

D-glucose (**1D**) and L-glucose (**1L**) were purchased from Nacalai Tesque Inc. (Kyoto, Japan) and Tokyo Chemical Industry Co. (Tokyo, Japan), respectively, and were dried in a vacuum desiccator under high vacuum (less than 1 hPa) at 70 °C for 16 h before use. Compounds **2D** and **2L** were synthesized from compounds **1D** and **1L**, respectively, according to previous reports (Adelwöhner et al. 2009; Yagura et al. 2020). Powdered 4 Å molecular sieves were activated in a GTO-2000 glass tube oven (Sibata Scientific Technology Ltd, Tokyo, Japan) under high vacuum (less than 1 hPa) at 300 °C for 3 h and kept at 105 °C in an SA46 drying oven (Masuda Co., Osaka, Japan) before use. All other chemicals were purchased from Nacalai Tesque Inc. and FUJIFILM Wako Pure Chemical Co. (Osaka, Japan), and used without further purification unless otherwise noted.

Measurements

Specific rotations were determined using a JASCO P-2200 polarimeter (JASCO, Hachioji, Japan) as the average values of five measurements. ¹H and ¹³C NMR spectra were recorded on a Varian 500 NMR spectrometer (500 MHz, Agilent Technologies, Santa Clara, CA, USA) using tetramethylsilane (TMS) as an internal reference standard in CDCl₃ as solvent, unless otherwise stated. Chemical shifts (δ) and coupling constants (J) are reported in ppm (parts per million) and Hz, respectively. Fourier-transform infrared (FT-IR) spectra were recorded in KBr pellets using a Shimadzu IRPrestige-21 spectrophotometer



Scheme 1. Synthetic route for the preparation of D,L-cellulose (**4DL**) and D-cellulose (**4D**)

(Shimadzu, Kyoto, Japan). Gel permeation chromatography (GPC) was performed on a Shimadzu LC-10 system (Shimadzu) equipped with a Shimadzu UV-vis detector (SPD-10AVp) and a Shimadzu RI detector (RID-10A) under the following conditions: columns, Shodex K-802, K-802.5, and K-805 (Showa Denko K.K., Tokyo, Japan) arranged in series; eluent, CHCl₃; temperature, 40 °C; flow rate, 1.0 mL/min; standards, polystyrene standards (Showa Denko K.K.). X-ray diffractograms were recorded on a Rigaku RINT-Ultima IV diffractometer (Rigaku, Tokyo, Japan). Samples were annealed at 120 °C for 1 h and then at 210 °C for 10 min under high vacuum (less than 1 hPa) before X-ray diffraction using a Sibata GTO-2000 glass tube oven.

3-*O*-Benzyl-2,6-di-*O*-pivaloyl-(1 → 4)-β-D,L-glucopyranan (**3DL**).

Compound **2D** (100 mg, 0.24 mmol) and compound **2L** (100 mg, 0.24 mmol) were placed in a glass ampoule in a vacuum desiccator under high vacuum (less than 1 hPa) at room temperature for 16 h. Anhydrous CH₂Cl₂ (200 μL; distilled from P₂O₅) and BF₃–Et₂O (2.9 μL, 5 mol%) were added via syringe through the sealed cap of the glass ampoule. The reaction mixture was stirred under atmospheric pressure at 37 °C for 24 h, after which solidification was observed. After the reaction, the mixture was dissolved in EtOAc (20 mL). The organic layer was washed with distilled water, saturated aqueous NaHCO₃ solution, and brine, dried over anhydrous Na₂SO₄, and concentrated to afford compound **3DL** as a colorless solid in quantitative yield.

Compound **3DL**: $[\alpha]_D^{25} = -0.11^\circ$ ($c = 1.0$ in CDCl₃); $DP_n = 28.5$ ($M_w/M_n = 1.90$); ¹H NMR (CDCl₃) δ 7.32–7.20 (CH₂Ph), 4.95–3.17 (CH₂Ph, H-1, H-2, H-3, H-4, H-5, H-6a, H-6b), 1.29–0.99 (C(CH₃)₃); ¹³C NMR (CDCl₃) δ 178.0, 177.5, 177.3, 176.4 (C = O), 138.7, 137.3, 128.5, 128.4, 128.0, 127.8, 127.4, 127.3, 126.9, 126.8 (CH₂Ph), 100.0, 99.3 (C-1), 83.2, 80.5 (C-3), 76.7, 76.0 (C-5), 74.5 (CH₂-Ph), 73.2, 73.1 (C-4), 72.8, 72.2 (C-2), 63.6, 63.0, 62.5, 61.5 (C-6), 38.8, 38.7 (C(CH₃)₃), 27.2, 27.1, 27.0, 27.0 (C(CH₃)₃).

(1 → 4)-β-D,L-Glucopyranan (D,L-cellulose, 4DL)

Compound **3DL** (200 mg) was dissolved in THF/AcOH (5 mL; 1:1, v/v), and Pd(OH)₂ on charcoal (100 mg) was added. The reaction mixture was hydrogenated with vigorous stirring under H₂ at atmospheric pressure and room temperature for 24 h, filtered through Celite 535RVS (Nacalai Tesque Inc.), washing with THF, and concentrated azeotropically with EtOH to give the partially debenzylated product as a colorless solid. This product was subjected to further debenzylation under the same conditions three times to obtain the fully debenzylated product as a colorless solid. The product was dissolved in THF/MeOH (15 mL; 10:1, v/v) and 28% NaOMe in MeOH solution (0.2 mL) was added. The reaction mixture was stirred at 50 °C for 12 h and then neutralized with 1 M HCl aqueous solution. The resulting mixture was evaporated to remove THF and MeOH, dialyzed against distilled water using a Spectra/Por Dialysis Membrane (MWCO 100–500, Repligen Co., Waltham, MA, USA) for 4 days, changing the water every 12 h, and then freeze-dried to afford compound **4DL** (54.6 mg, 72.7% yield) as a colorless solid.

Compound **4DL**: FT-IR (KBr) ν 3404, 2903, 1634, 1558, 1373, 1362, 1154, 1069, 1026, 893 cm⁻¹.

Compound **4DL** was acetylated with Ac₂O/pyridine at 50 °C for 12 h, and subjected to specific rotation, GPC and ¹H/¹³C NMR measurements.

Acetylated compound **4DL**: $[\alpha]_D^{25} = +0.01^\circ$ ($c = 0.55$ in CDCl₃); $DP_n = 18.6$ ($M_w/M_n = 2.08$), ¹H NMR (CDCl₃) δ 5.07 (H-3), 4.81, 4.76 (H-2), 4.56 (H-1), 4.42 (H-1, H-6a), 4.04, 4.02 (H-6b), 3.73, 3.72 (H-4), 3.50 (H-5), 2.14, 2.10, 2.08, 2.01, 1.98, 1.95 (CH₃); ¹³C NMR (CDCl₃) δ 170.5, 170.4, 170.2, 169.8, 169.6, 169.3 (C=O), 100.5, 100.4 (C-1), 76.1, 74.8, 74.4, 73.7, 72.8, 72.3, 72.0, 71.9, 71.6, 71.3, 68.1, 67.7 (C-2, C-3, C-4, C-5), 62.8, 62.1, 61.5, 61.3 (C-6), 20.8 (× 2), 20.7, 20.6, 20.5, 20.5 (× 2) (CH₃).

Results and discussion

Cationic ring-opening copolymerization of glucose orthoester derivatives **2D** and **2L**.

Glucose orthoester derivatives **2D** and **2L** were synthesized from compounds **1D** and **1L**, respectively,

according to previous reports (Adelwöhrer et al. 2009; Yagura et al. 2020). The ring-opening copolymerization of compounds **2D** and **2L** in a 1:1 ratio was conducted to give compound **3DL** in quantitative yield. Compound **3D** was also prepared as a control by the ring-opening polymerization of compound **2D** in a previous paper. Figure 1 shows the ^1H and ^{13}C NMR spectra of compounds **3DL** and **3D**. Signals assigned to benzyl groups in the range of 7.20–7.32 ppm and pivaloyl groups in the range of 0.99–1.29 ppm were found in the ^1H NMR spectrum of compound **3DL**, and signals assigned to benzyl groups in the range of 127–139 ppm and pivaloyl groups around 39 and 27 ppm were found in the ^{13}C NMR spectrum of compound **3DL**. Signals derived from acetyl groups in the range of 0.99–1.29 ppm and benzyl groups in the range of 127–139 ppm of compound **3DL** were more complicated than the corresponded signals of compound **3D**. It might be heterochiral structure of compound **3DL**. Signals assigned to ring protons of anhydroglucose units (AGUs) and benzyl protons in the range of 3.17–4.95 ppm in the ^1H spectrum of compound **3DL** were more complicated than those of compound **3D**. Similar results were observed for the ^{13}C NMR spectra of compounds **3DL** and **3D**.

Figure 2 shows HSQC NMR spectra of the AGU ring proton region in compounds **3DL** and **3D**. All correlation signals derived from compound **3D** were observed, with new correlation signals observed in the NMR spectrum of compound **3DL**. For example, the correlation signal derived from C-1/H-1 at 100.0/

4.30 ppm, which corresponded to that from C-1/H-1 in compound **3D**, and a new correlation signal at 99.3/4.72 ppm were observed. The chemical shifts of both signals suggested that only β -bonds were formed in the polymerization. There are theoretically four types of glycosidic linkage, namely, those between D-glucose and D-glucose (D–D), L-glucose and L-glucose (L–L), D-glucose and L-glucose (D–L), and L-glucose and D-glucose (L–D). The former two are homochiral structure linkages, while the latter two are heterochiral structure linkages. In the ^1H and ^{13}C NMR spectra, signals derived from C-1 and H-1 in pseudo-disaccharides with a D–D linkage have been reported to appear at different positions to those of C-1 and H-1 in pseudo-disaccharides with a D–L linkage (Ogawa et al. 1991; Duus et al. 1994). The correlation signals derived from C-1/H-1 in compound **3D** (D–D linkages) and an enantiomer of compound **3D** (L–L linkages) have previously been reported to appear at the same position (Yagura et al. 2020). In the NMR spectrum of compound **3DL**, the correlation signal at 100.0/4.30 ppm was assigned to C-1/H-1 in the homochiral structure, while that at 99.3/4.72 ppm was assigned to C-1/H-1 in the heterochiral structure. The specific rotation of compound **3DL** was -0.11° . The results suggested that copolymerization proceeded smoothly to afford a β -glucopyranan derivative, with the composition ratio of compound **3DL** almost reflecting the ratio of compounds **2D** and **2L** used. The DP_n of compound **3DL** was 28.5 ($M_w/M_n = 1.90$).

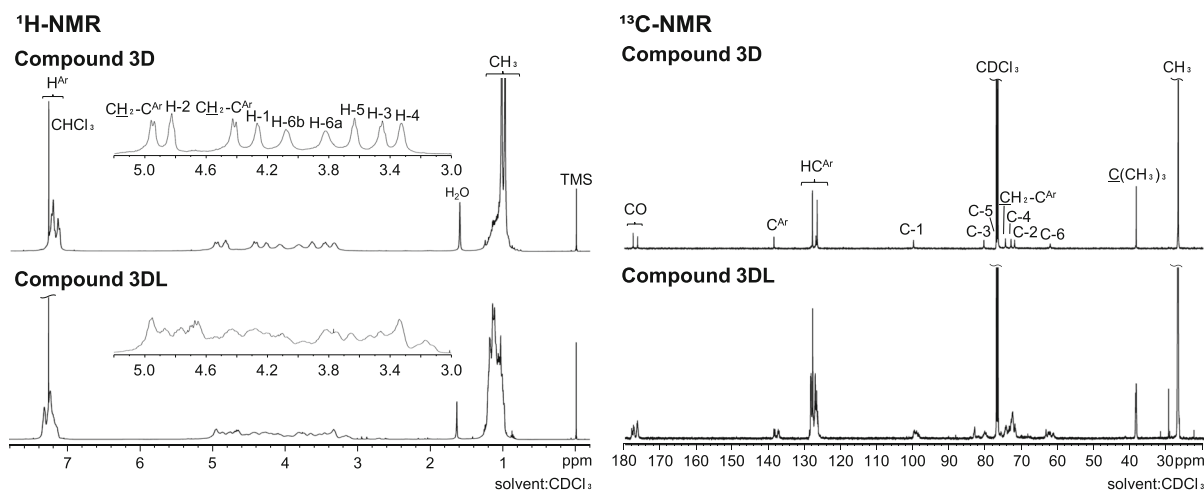
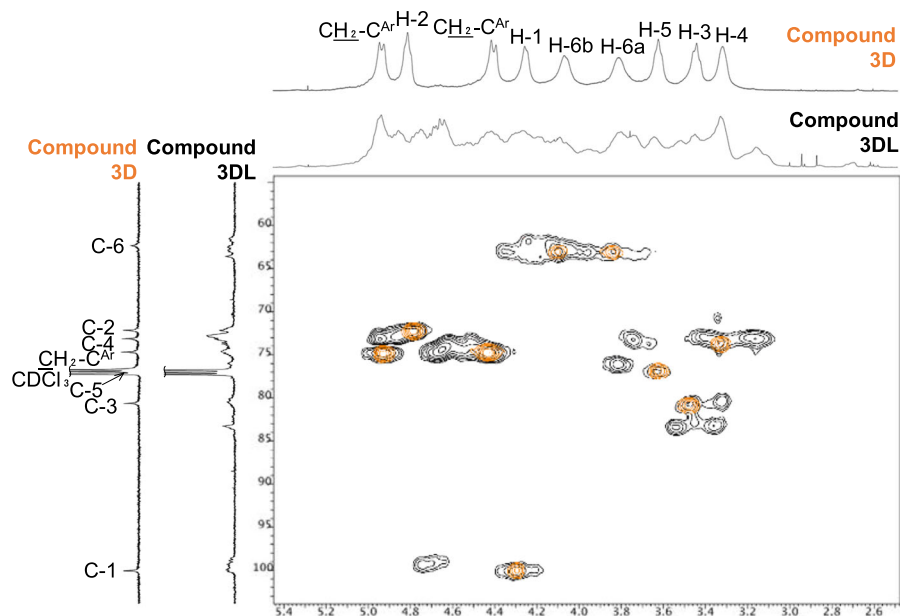


Fig. 1 ^1H and ^{13}C NMR spectra of compounds **3D** and **3DL**

Fig. 2 HSQC NMR spectra of compounds **3D** and **3DL**



Conversion of polymer **3DL** into (1 → 4)-β-D,L-glucopyranan (**4DL**).

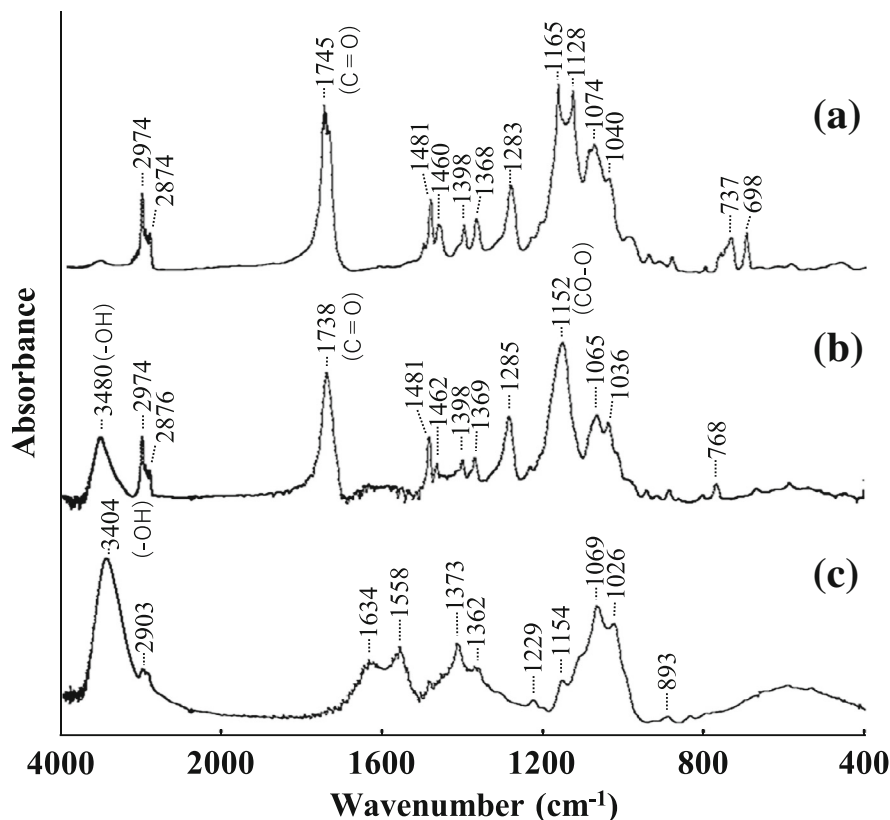
Compound **3DL** was deprotected according to a previously reported method (Yagura et al. 2020), affording compound **4DL** in 72.7% yield. Figure 3 shows the FT-IR spectra of compound **3DL**, the debenzylated product, and compound **4DL**. Bands attributed to benzyl groups at around 698 cm^{-1} and pivaloyl groups at around 1745 cm^{-1} had disappeared in the FT-IR spectrum of compound **4DL**. Furthermore, compound **4DL** was acetylated with Ac_2O /pyridine at 50 °C for 12 h to give fully acetylated compound **4DL** for characterization.

Figure 4 shows the ^1H and ^{13}C NMR spectra of acetylated compound **4DL**. Signals assigned to benzyl groups, in the range of 7.20–7.32 ppm and around 128 ppm, and to pivaloyl groups, in the range of 0.99–1.29 ppm and around 39 ppm, also disappeared in the ^1H and ^{13}C NMR spectra of acetylated compound **4DL**. These results suggested that the protecting groups in compound **3DL** were completely removed. Signals derived from acetyl groups around 2.0 ppm were complicated because of heterochiral structure.

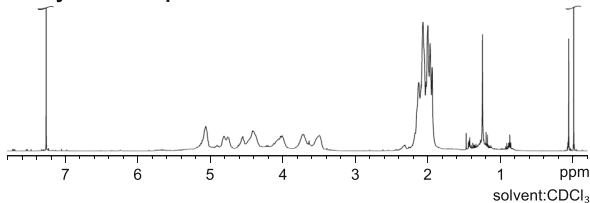
Figure 5 shows the HSQC NMR spectra of the AGU ring proton region in acetylated compounds **4D** and **4DL**. The signal pattern of acetylated compound **4DL** was simplified compared with that of compound **3DL**. This might be due to the bulky benzyl and

pivaloyl groups being substituted with small acetyl groups. All correlation signals derived from acetylated compound **4D** were observed, while new correlation signals were observed in the NMR spectrum of acetylated compound **4DL**. In particular, correlation signals derived from C-1/H-1 in compound **4DL** were observed at 100.5/4.42 ppm and 100.4/4.56 ppm. Correlation signals derived from C-1/H-1 in acetylated compound **4D** were observed at 100.5/4.41 ppm in Fig. 5a and in commercial cellulose triacetate (Yagura et al. 2020). The H-1 signals in pseudo-cellobiose octaacetate with D–D 1,4-linkages and D–L 1,4-linkages have been reported to be observed at 4.52 and 4.67 ppm, respectively (Ogawa et al. 1991). The correlation signal at 100.5/4.42 ppm was assigned to C-1/H-1 in a homochiral structure, while that at 100.4/4.56 ppm was assigned to C-1/H-1 in a heterochiral structure in the NMR spectrum of acetylated compound **4DL**. All correlation signals in the HSQC NMR spectrum of acetylated compound **4DL** were assigned by the comparison with HSQC NMR spectra of acetylated compound **4D** and acetylated compound **4DL** with D/L ratio of 9/1 (Figure S1) which will be published in detail elsewhere. The specific rotation and DP_n of acetylated compound **4DL** were + 0.01° and 18.6 ($M_w/M_n = 2.08$), respectively. These results suggested that before acetylation, compound **4DL** was a β-1,4-D,L-glucopyranan (D,L-cellulose) comprising

Fig. 3 FT-IR spectra of compound **3DL** (a); debenzylated **3DL** (b); compound **4DL** (c)



¹H-NMR
Acetylated compound **4DL**



¹³C-NMR
Acetylated compound **4DL**

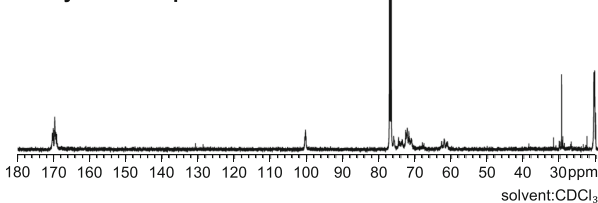


Fig. 4. ¹H and ¹³C NMR spectra of acetylated compound **4DL**

an almost racemic mixture of D-glucose and L-glucose, namely, optically inactive D,L-cellulose.

X-ray diffractograms of compounds **4DL** and **4D** are shown in Fig. 6. The diffractogram of compound **4DL** indicated an amorphous structure like that of PDLLA, although it was annealed before measurement. This was due to the heterochiral structure of compound **4DL**.

Conclusion

The ring-opening copolymerization of compounds **2D** and **2L** in a 1:1 ratio was conducted to give compound **3DL** with a *DP_n* of 28.5 (*M_w/M_n* = 1.90) in quantitative yield. Deprotection of compound **3DL** and subsequent acetylation proceeded smoothly to afford acetylated compound **4DL** with a *DP_n* of 18.6 (*M_w/M_n* = 2.08). The specific rotation of acetylated compound **4DL** was + 0.01°, suggesting that before acetylation, compound **4DL** was an optically inactive cellulose. Compound **4DL** was an amorphous

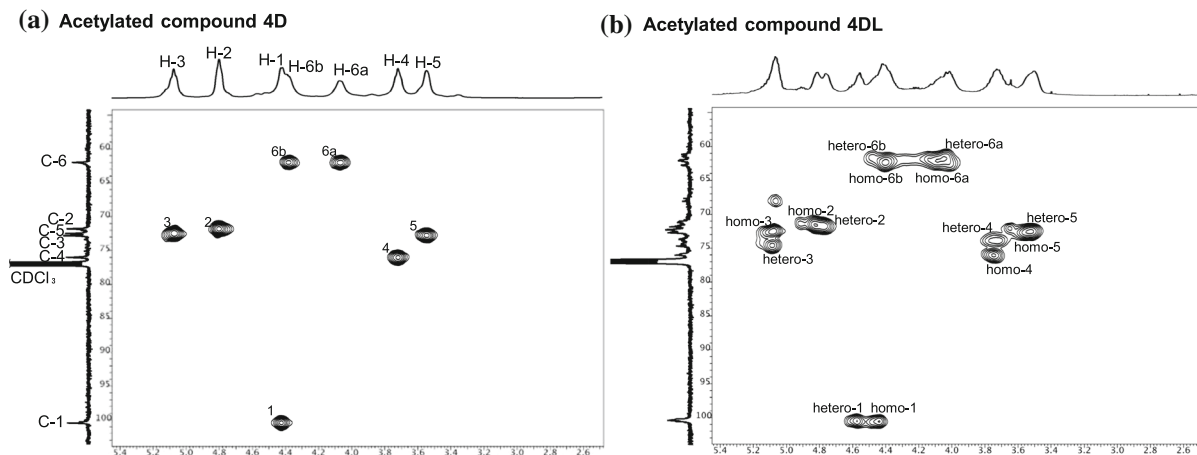
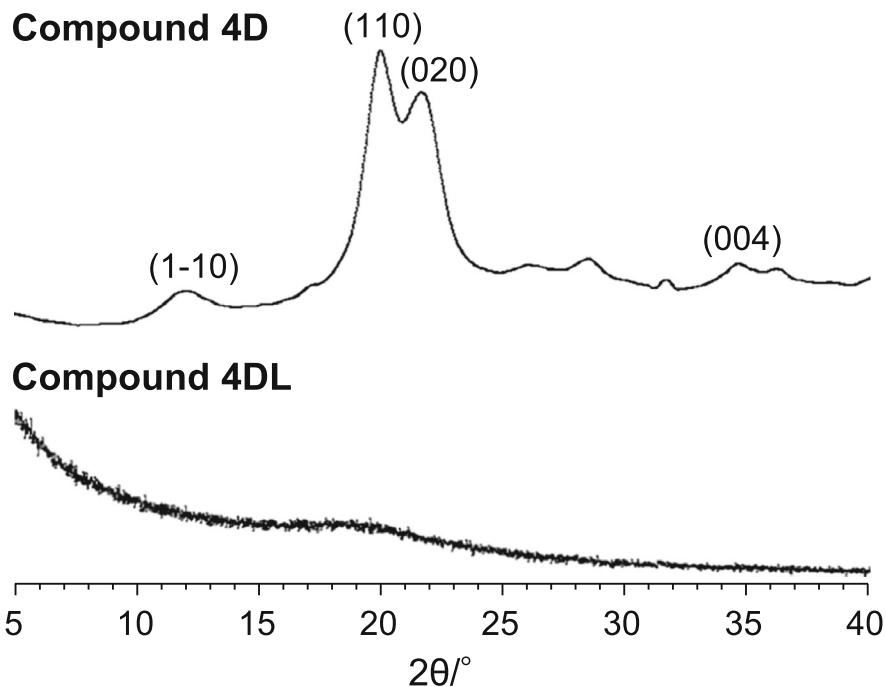


Fig. 5 HSQC NMR spectra of acetylated compounds **4D** and **4DL**

Fig. 6 X-ray diffractograms of compounds **4D** and **4DL**



polymer, as expected. This method for the synthesis of compound **4DL** with a D/L ratio of 1:1 could be applied to the synthesis of D,L-celluloses with various D/L ratios. D,L-celluloses are expected to provide future research opportunities regarding the chirality of D-cellulose.

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Declarations

Conflicts of interest The authors declare that they have no conflict of interest.

Human and Animal rights This is not research involving Human participants and Animals.

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