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Curdlan ester derivatives: Synthesis, structure, and properties

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ABSTRACT

A series of ester derivatives of curdlan, which is a β-(1 → 3)-D-glucan extracellularly produced by microorganism, with varying alkyl chain lengths (C2–C12) were synthesized by the heterogeneous reaction using trifluoroacetic anhydride. As a result, high-molecular-weight ($M_w \geq 6 \times 10^5$) and fully-acylated curdlan was obtained with relatively high yield (>70%). Thermal stability of curdlan was greatly improved by esterification. Crystallization was observed for curdlan esters with C2–C6 side chains. Both T_g (170 → 50 °C) and T_m (290 → 170 °C) of curdlan esters decreased with increasing the side-chain length. By the increase in the side-chain carbon number, curdlan esters showed lower Young's modulus and tensile strength, and larger elongation at break. Thus, material properties of curdlan esters can be controlled by changing the side-chain length. It was found that the increase of the side-chain length resulted in the decrease of crystallinity and the change of crystal structures.

1. Introduction

Curdlan is a homopolysaccharide extracellularly produced by microorganism such as *Alcaligenes faecalis* and is one of the β-(1 → 3)-D-glucans without branching (Harada, 1977; Harada, Misaki, & Saito, 1968; Harada, Terasaki, & Harada, 1993; McIntosh, Stone, & Stanisich, 2005; Paul, Morin, & Monsan, 1986; Sutherland, 1994). Curdlan is mainly used as a gum (thickener) in food field because this polysaccharide is thermo-gelable and nontoxic. It is said that the mechanism of crosslinking in the curdlan gel network is based on the triple helix formation and aggregation of triple helices (Dea, 1993). Depending on the preparation condition, curdlan forms three crystal modifications (forms I, II, and III). Curdlan form I consists of a right-handed 6/1 single helix with large amount of water (Okuyama et al., 1991). Curdlan forms II and III are the triple helical structures composed of right-handed 6/1 helices (Chuah, Sarko, Deslandes, & Marchessault, 1983; Deslandes, Marchessault, & Sarko, 1980). These two forms with triple helices are different in the degree of hydration and fiber repeats.

Chemical modification of polysaccharides such as esterification is an effective way to obtain thermoplastic polymeric materials (Edgar et al., 2001; Heinze & Liebert, 2001; Heinze & Liebert, 2004). In general, unmodified polysaccharides such as cellulose and starch show no thermoplasticity because of their strong intra- and inter-molecular hydrogen bonding. Esterification of hydroxyl groups of polysaccharides hinders their tendency to form hydrogen bonding network, resulting in an increase in hydrophobicity (i.e., solubility in organic solvents) and improvements in thermal and mechanical properties. It is well-known that polysaccharide esters exhibit widely varied structure and properties depending on the carbon number of the ester substituent, as seen in cellulose esters (Crepy, Miri, Joly, Martin, & Lefebvre, 2011; Malm, Mench, Kendall, & Hiatt, 1951a, 1951b; Morooka, Norimoto, Yamada, & Shiraishi, 1984; Sealey, Samaranayake, Todd, & Glasser, 1996), amylose esters (Fang, Fowler, Tomkinson, & Hill, 2002; Sagar & Merrill, 1995), konjac glucomannan esters (Enomoto-Rogers, Ohmomo, & Iwata, 2013; Enomoto-Rogers, Ohmomo, Takemura, & Iwata, 2014), xylan esters (Fundador, Enomoto-Rogers, Takemura, & Iwata, 2012a, 2012b), and so forth. Therefore, adjustment of the ester substituent length, i.e., the side-chain length is needed to obtain desired material properties.

As for curdlan derivatives, Okuyama et al. (1996) prepared curdlan triacetate and investigated its molecular and crystal structures. It was found that the helical conformation of curdlan triacetate is the right-handed single 6/1 helix, whose backbone conformation is the same as that of curdlan form I (Okuyama et al., 1991). However, as far as we know, the effect of the length of the ester substituent on structure and properties of curdlan esters has not been investigated and hence is still unclear. Since curdlan triacetate possesses highly crystalline nature (Okuyama et al., 1996), it can be said that fully-acylated curdlan esters have the potential to be bio-based crystalline thermoplastics as an alternative to

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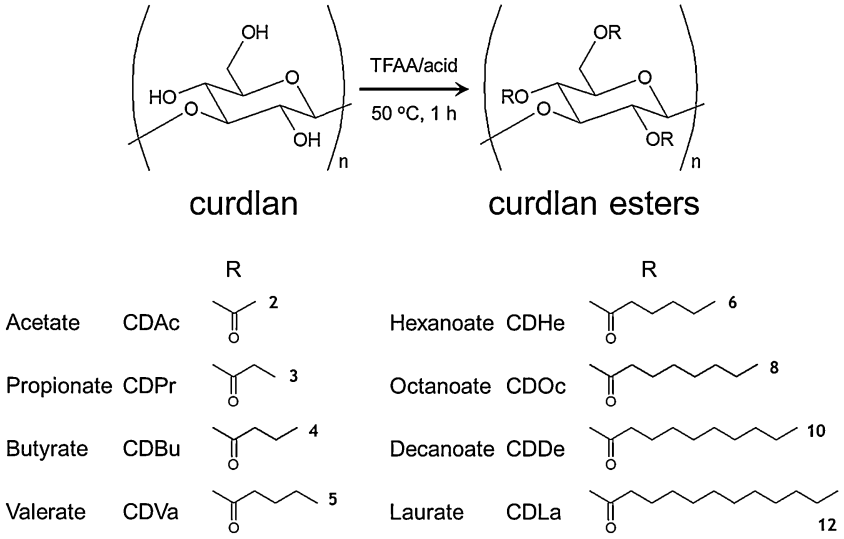

Scheme 1. Syntheses of curdlan esters. Abbreviations of curdlan esters are also shown. Each acyl group is labeled with the corresponding carbon number.

conventional petroleum-based plastics and are expected to be used as packaging materials in the form of films or fibers.

In this study, to elucidate the effect of the side-chain length on structure and properties of curdlan esters, a series of curdlan ester derivatives with varying alkyl chain lengths (C2–C12) were synthesized by the heterogeneous reaction and characterized by using NMR and gel permeation chromatography (GPC). Glass transition, crystallization, and melting behaviors as well as thermal degradation behaviors of curdlan esters were systematically investigated. Tensile mechanical properties of films of curdlan esters were also examined. Furthermore, crystallinity of curdlan esters was evaluated by using X-ray diffraction technique.

2. Materials and methods

2.1. Materials

Curdlan (Wako Pure Chemical Industries, Ltd.), trifluoroacetic anhydride (TFAA, 98%, Wako Pure Chemical Industries, Ltd.), carboxylic acids (acetic, propionic, butyric, valeric, hexanoic, octanoic, decanoic, and lauric acids), and all other reagents were used as received from commercial suppliers without further purification.

2.2. Esterification of curdlan

Curdlan (0.5 g) was dried in vacuo at 100 °C for 3 h before esterification. Esterification of curdlan (Scheme 1) was performed according to the acylation method of starch using TFAA (Yang & Montgomery, 2006). Pre-dried curdlan was added little by little to a pre-mixed solution of TFAA (20 mL) and carboxylic acid (10 g for lauric acid; 10 mL for others), which had been stirred at 50 °C for 5 min in a flask. The solution was stirred at 50 °C for 1.0 h. After cooling to room temperature, the solution was poured into 1 L of $NaHCO_3$ aqueous solution. The precipitate was filtered, washed with methanol until neutral, and dried in vacuo. The degree of substitution (DS) of ester groups for hydroxyl groups was calculated from the ratio of the peak area of the methyl protons in the ester group ([CH_3]) to that of the ring protons in the glucose unit ([ring-H]) in the ^{1}H NMR spectrum, as follows: DS = ([CH_3]/3)/([ring-H]/7).

Curdlan acetate (*CDAc*). ^{1}H NMR (500 MHz, CF_3COOD, δ, ppm): 2.23 (—CH_3), 3.87–5.22 (ring protons).

Curdlan propionate (*CDPr*). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 1.13 (—CH_3), 2.27–2.51 (—CH_2), 3.58–4.86 (ring protons).

Curdlan butyrate (*CDBu*). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 0.95 (—CH_3), 1.63 (—$CH_2CH_2CH_3$), 2.19–2.47 (—$CH_2CH_2CH_3$), 3.53–4.82 (ring protons).

Curdlan valerate (*CDVa*). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 0.92 (—CH_3), 1.31–1.42 (—$CH_2CH_2CH_2CH_3$), 1.58–1.75 (—$CH_2CH_2CH_2CH_3$), 2.25–2.45 (—$CH_2CH_2CH_2CH_3$), 3.53–4.82 (ring protons).

Curdlan hexanoate (*CDHe*). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 0.90 (—CH_3), 1.31 (—$CH_2CH_2CH_2CH_2CH_3$), 1.60 (—$CH_2CH_2CH_2CH_2CH_3$), 2.23–2.45 (—$CH_2CH_2CH_2CH_2CH_3$), 3.53–4.85 (ring protons).

Curdlan octanoate (*CDOc*). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 0.88 (—CH_3), 1.29 (—$CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 1.60 (—$CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 2.31 (—$CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 3.47–4.90 (ring protons).

Curdlan decanoate (*CDDe*). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 0.89 (—CH_3), 1.27 (—$CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 1.58 (—$CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 2.29 (—$CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 3.55–4.87 (ring protons).

Curdlan laurate (*CDLa*). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 0.88 (—CH_3), 1.26 (—$CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 1.58 (—$CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 2.31 (—$CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$), 3.47–4.90 (ring protons).

2.3. Nuclear magnetic resonance (NMR)

^{1}H NMR spectra were measured using a JNM-A500 FT-NMR system (500 MHz, JEOL Ltd.) at 25 °C. $CDCl_3$ was used as deuterated solvent for curdlan esters except for CDAc (CF_3COOD), where solution concentration was set to 10 mg/mL. Chemical shifts (δ in ppm) were referenced to the resonance of tetramethylsilane (TMS; $\delta = 0$) for $CDCl_3$ and referenced to an internal solvent resonance for CF_3COOD ($\delta = 11.50$).

2.4. Gel permeation chromatography (GPC)

Number- and weight-average molecular weights (M_n and M_w, respectively) and polydispersity indices (M_w/M_n) were determined by using a GPC system composed of a CBM-20A communications bus module, a DGU-20A3 degasser, an LC-6AD liquid chromatograph, an SIL-20AC HT auto sampler, an RID-10A refractive index detector, and a CTO-20A column oven (Shimadzu Corp.).

Chloroform was used as an eluent at a flow rate of 0.8 mL/min and the column oven was set to 40 °C. Polystyrene standards (Shodex® STANDARD SM-105, Showa Denko K.K.) were used to calibrate molecular weights.

2.5. Thermogravimetric analysis (TGA)

Thermal decomposition behaviors were investigated using a Thermo plus TG8120 (Rigaku Corp.) in the temperature range from room temperature to 500 °C at a heating rate of 20 °C/min under the nitrogen gas atmosphere. About 5 mg sample was packed in an aluminum pan.

2.6. Differential scanning calorimetry (DSC)

Glass transition, crystallization, and melting behaviors were examined using a DSC 8500 (PerkinElmer Co., Ltd.). About 1.5 mg sample packed in an aluminum pan was heated at a rate of 100 °C/min (20 °C/min for CDAc) from 30 °C to 250 °C (300 °C for CDAc) and held at 250 °C (300 °C for CDAc) for 30 s. After quenching to −70 °C at a cooling rate of 200 °C/min (30 s holding), the second heating scan was conducted to 250 °C (300 °C for CDAc) at a heating rate of 20 °C/min. Measurements were carried out under the nitrogen gas atmosphere.

2.7. Film preparation

Films of curdlan esters with a thickness of ca. 50 μm were prepared by solution casting (0.3 g of curdlan esters dissolved in 15 mL of solvent on a Naflon® petri dish) at room temperature under atmospheric pressure. CH_2Cl_2 and $CHCl_3$ were used as solvents for CDAc and other esters, respectively.

2.8. Dynamic mechanical analysis (DMA)

Dynamic mechanical behaviors were investigated by a DVA-200S (IT Measurement Control Co., Ltd.). Temperature scans at a frequency of 10 Hz were performed from −70 to the temperature at which the storage modulus became smaller than 10^4 Pa at a heating rate of 5 °C/min under the nitrogen gas atmosphere. Specimens (20 mm × 4 mm × 0.5 mm) were prepared by heat-sealing of ten cast films.

2.9. Tensile test

Stress–strain curves of curdlan ester films were obtained using an EZ Test (Shimadzu Corp.) with a tensile speed of 20 mm/min at 25 °C. Films with a thickness of ca. 50 μm were trimmed to obtain rectangular-shaped specimens with dimensions of 25 mm × 4 mm. The initial distance between chucks was set to 10 mm.

2.10. Wide-angle X-ray diffraction (WAXD)

WAXD measurements were conducted using a RINT-2200 (Rigaku Corp.) operating at 40 kV and 40 mA with Cu Kα (λ = 0.15418 nm) radiation in the symmetrical reflection mode, equipped with a graphite monochromator ($2\theta_M = 26.58°$ for Cu Kα) at the scattered X-ray position. Scanned 2θ range was set to 3–50° with a step size of 0.05°, where θ is the Bragg angle. All measurements were carried out at room temperature under atmospheric pressure. Silicon powder was used as a standard sample. The degree of crystallinity (X_c) for each curdlan ester film was estimated from the following equation:

$$X_c = \frac{\int_{2\theta_1}^{2\theta_2} I_c(2\theta)d(2\theta)}{\int_{2\theta_1}^{2\theta_2} I(2\theta)d(2\theta)} \times 100 \quad (1)$$

where the values of $2\theta_1$ and $2\theta_2$ used in this study are 6.5 and 40°, respectively, $I_c(2\theta)$ is the diffraction intensity from the crystalline phase, and $I(2\theta)$ is the diffraction intensity from both the crystalline and amorphous phases. $I_c(2\theta)$ was evaluated by using the melt-quenched [i.e., amorphous; $I_c(2\theta) = 0$] and cast [i.e., semicrystalline; $I_c(2\theta) \geq 0$] samples according to the previously reported method (Marubayashi, Asai, & Sumita, 2012; Marubayashi, Asai, & Sumita, 2013).

3. Results and discussion

3.1. Esterification of curdlan

Table 1 shows the results of esterification of curdlan by various saturated carboxylic acids.

M_w of curdlan esters ranged from 6.0×10^5 to 1.6×10^6 and M_w/M_n was about 2. Fig. 1 shows ^{1}H NMR spectra of CDAc, CDPr, CDBu, and CDLa. The peaks derived from the methyl and methylene protons in the ester substituents as well as those of the ring-protons were clearly observed and reasonably assigned in terms of peak positions and areas, as mentioned above (Section 2.2). DS was defined as the average number of substituted hydroxyl groups per glucose unit of curdlan. ^{1}H NMR confirmed that DS values of all curdlan esters are 3, i.e., the complete acylation of curdlan. Polymer yields were 70–90%. Thus, high-molecular-weight and fully-acylated curdlan was obtained with relatively high yield in a simple way.

Table 1
Results of esterification of curdlan and physical properties of curdlan esters.

name	$M_w \times 10^{-5}$	M_w/M_n	DS	Yield (%)	$T_{d\_50\%}$ (°C)	T_g (°C)	T_m (°C)	σ_t (MPa)[e]	ε_b (%)[f]	E (MPa)[g]
CDAc	–[a]	–[a]	3	86	361	171[b]	287	21.2 ± 4.0	12 ± 3	448 ± 33
CDPr	6.0	1.8	3	80	391	110[b]	213	23.7 ± 4.2	46 ± 20	260 ± 99
CDBu	8.9	1.9	3	71	386	74[b]	190	15.4 ± 1.9	26 ± 5	204 ± 12
CDVa	13.0	2.0	3	82	376	51[c]	168	12.4 ± 2.3	79 ± 9	149 ± 35
CDHe	14.0	2.0	3	83	361	69[c]	167	14.7 ± 1.0	150 ± 28	92 ± 10
CDOc	14.0	2.1	3	85	373	50[c]	n.d[d]	6.0 ± 2.0	112 ± 43	46 ± 3
CDDe	16.0	2.1	3	77	378	55[c]	n.d[d]	4.6 ± 0.4	144 ± 11	19 ± 1
CDLa	16.0	2.3	3	77	381	47[c]	n.d[d]	1.7 ± 0.3	172 ± 35	12 ± 1

[a] Not measured due to its insolubility in the GPC eluent ($CHCl_3$).
[b] Determined by DSC (second heating run).
[c] Determined by DMA (tan δ).
[d] Not detected.
[e] Tensile strength (maximal stress value).
[f] Elongation at break.
[g] Young's modulus.

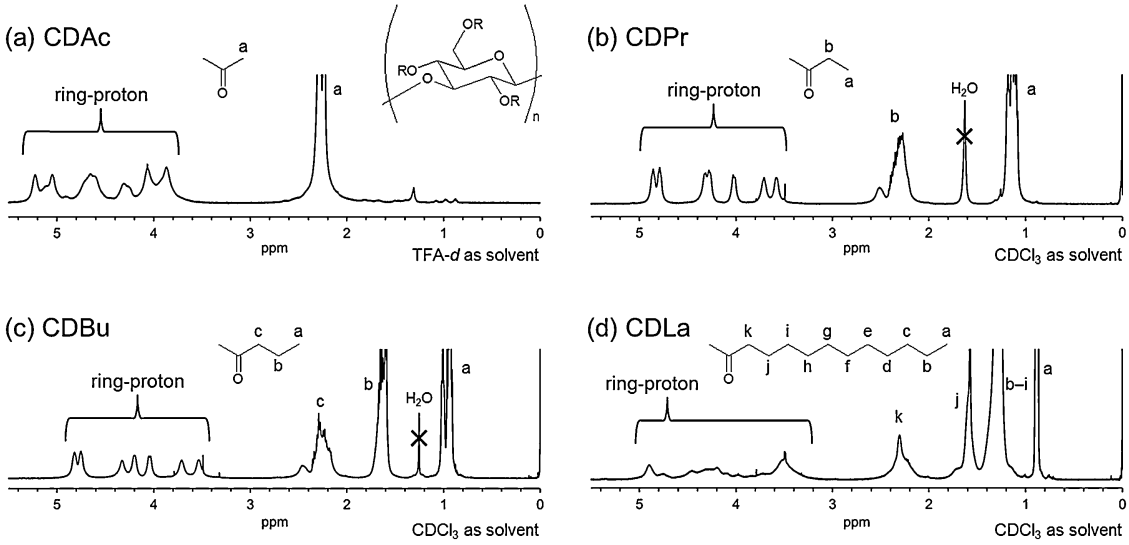

Fig. 1. ^{1}H NMR spectra of representative curdlan esters.

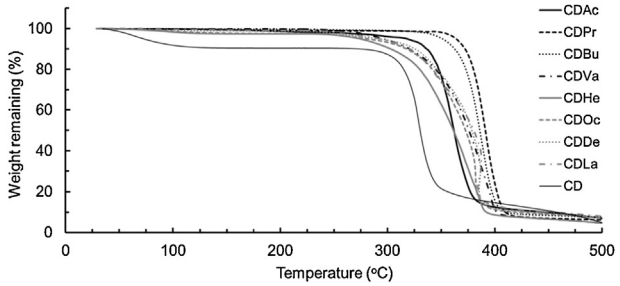

Fig. 2. Thermogravimetric curves of curdlan esters.

3.2. Thermal decomposition behaviors of curdlan esters

Fig. 2 shows thermogravimetric curves of a series of curdlan esters.

The temperature at which weight remaining became 50% ($T_{d\_50\%}$) is shown in Table 1. Here, weight loss of curdlan from room temperature to ca. 100 °C (ca. 10%) would be evaporation of water in curdlan. $T_{d\_50\%}$ of curdlan was 331 °C. Esterification of curdlan resulted in an increase in $T_{d\_50\%}$ (+30 to 60 °C). There was no definite dependence of $T_{d\_50\%}$ on the side-chain length. It can be said that esterification improves thermal stability of curdlan in terms of $T_{d\_50\%}$. In general, it is well-known that pyrolysis of polysaccharides yields levoglucosan (volatile), which is independent of the polysaccharide linkage position (1,3-, 1,4-, or 1,6-linkage) and anomericity (α or β) (Ponder & Richards, 1994; Ponder, Richards, & Stevenson, 1992). It has been confirmed that the major volatile product of vacuum pyrolysis of curdlan is levoglucosan (pyranose and furanose) (Richards & Shafizadeh, 1982). The complete substitution of hydroxyl groups in curdlan would hinder the formation of levoglucosan, resulting in the improvement of thermal stability, as seen in other polysaccharide ester derivatives (Aburto et al., 1999; Enomoto-Rogers et al., 2013, 2014; Fang et al., 2002; Fundador et al., 2012a,b; Malm et al., 1951b).

3.3. Glass transition, crystallization, and melting behaviors of curdlan esters

A DSC measurement of curdlan was not conducted because of adsorbed water in curdlan, as mentioned above. Alternatively, differential thermal analysis (DTA) was performed at the same time as TGA. Before the drastic weight loss of curdlan occurred in TGA, neither endothermic nor exothermic peak was observed in the DTA curve. Namely, thermal decomposition of curdlan occurred without melting during the DTA heating scan, which would be due to its strong hydrogen bonding. Fig. 3a shows the DSC heating runs of various curdlan ester derivatives. The curdlan esters with C2–C6 side chains showed melting endotherms. Especially, CDAc (C2) and CDPr (C3) possessed the melting temperature (T_m) higher than 200 °C (287 and 213 °C, respectively), which is comparable to those of high-T_m semicrystalline polymers such as poly(ethylene terephthalate) [T_m = 232–266 °C (Groeninckx, Reynaers, Berghmans, & Smets, 1980)] and cellulose triacetate [T_m = 293 °C (Kamide & Saito, 1985)]. With increasing the side-chain carbon number, T_m decreased and when the side-chain carbon number reached 8 (CDOc), melting endotherms were no longer observed. For the curdlan esters having C3–C6 side chains, exothermic peaks corresponding to cold crystallization were also seen during the second heating scans.

The glass transition temperature (T_g) was observable only for CDAc, CDPr, and CDBu. T_g of CDAc (171 °C) was comparable to that of cellulose triacetate [T_g = 186–194 °C (Kamide & Saito, 1985)]. Compared to poly(ethylene terephthalate) [T_g = 74 °C (Okazaki & Wunderlich, 1996)], CDPr had higher T_g (110 °C) and CDBu possessed equivalent T_g (74 °C). T_g's of other curdlan esters were estimated by DMA measurements (i.e., peak positions of tan δ). Fig. 3b shows the dependence of T_g and T_m on the carbon number per side chain. Both T_g and T_m decreased with increasing the carbon number per side chain and when the side-chain carbon number became equal to or higher than 5, almost constant T_g (ca. 50 °C) and T_m (ca. 170 °C) values were obtained. A similar tendency of T_m has been reported for cellulose triesters (Malm et al., 1951b; Sealey et al., 1996). Thus, it was found that thermal properties of curdlan esters can be controlled by changing the side-chain length. Although CDAc has the highest T_m value among C2–C12 curdlan esters, a difference between the melting and thermal decomposition temperatures is relatively small. Therefore, it can be said that CDPr is superior to CDAc in terms of dry processing. Crystallinity of curdlan esters will be discussed later in more detail based on WAXD data.

3.4. Films of curdlan esters

Fig. 4 displays solution-cast films of CDAc, CDPr, CDBu, CDOc, and CDLa. As can be seen, all cast films of curdlan esters were colorless and highly transparent. With increasing the side-chain carbon number, the cast film became soft and rubbery.

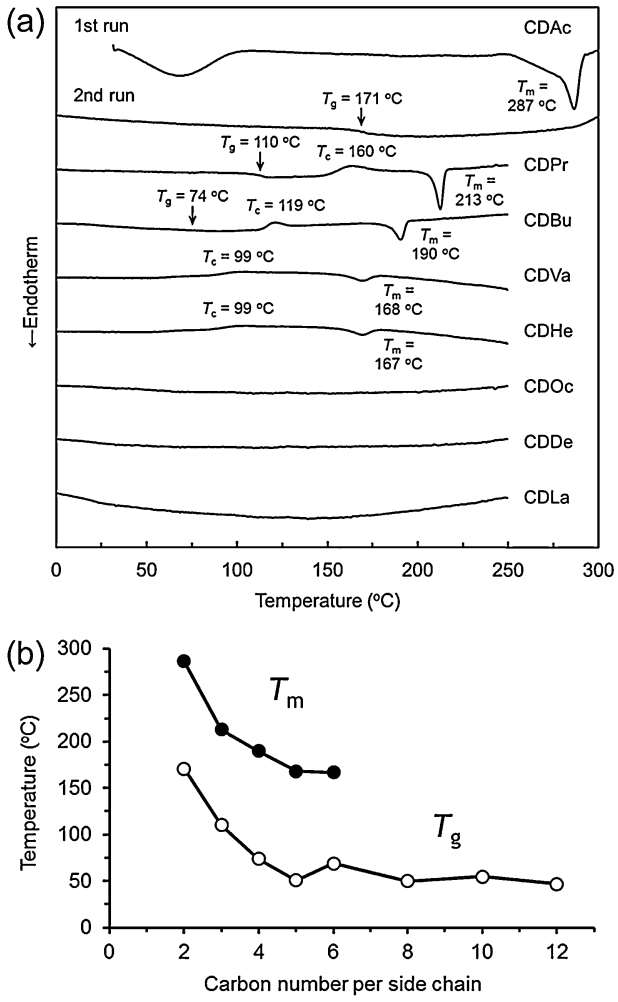

Fig. 3. (a) DSC curves of curdlan esters (1st and 2nd heating runs for CDAc; only 2nd heating runs for others). (b) Changes in T_g and T_m as a function of the carbon number per side chain.

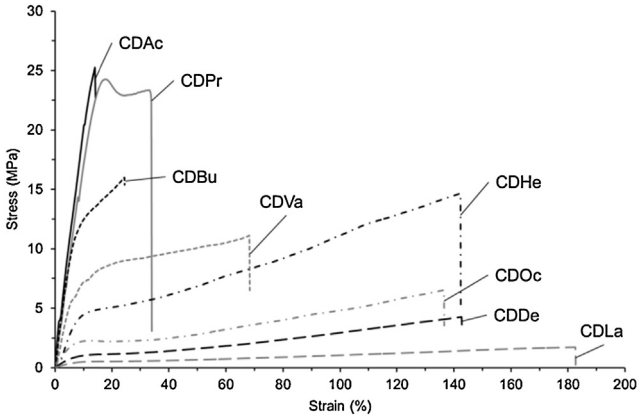

Fig. 5. Stress–strain curves of films of curdlan esters (melt-quenched film for CDPr; cast films for others).

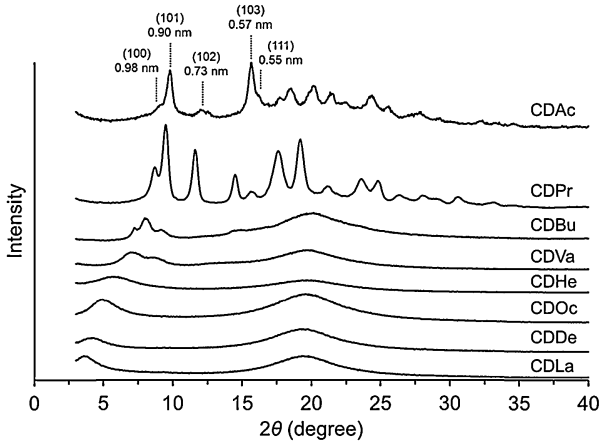

Fig. 6. WAXD curves of cast films of curdlan esters (Cu Kα).

3.5. Mechanical properties of curdlan esters

Fig. 5 exhibits stress–strain curves of films of curdlan esters and Table 1 shows their tensile properties. Since the CDPr cast film was too brittle to be fixed on a tensile testing machine, its melt-quenched film was used as an alternative (melting at 240 °C and quenching by ice–water). By an increase in the side-chain carbon number, the tensile strength and Young's modulus decreased and the elongation at break increased. Namely, curdlan ester films became soft with increasing the side-chain carbon number, which would be due to the enhancement of the internal plasticizing effect of ester groups (Aburto et al., 1999). Such an enhanced plasticizing effect with increasing the side-chain length was also seen in T_g, as mentioned above (Fig. 3). A similar tendency of the tensile properties has been observed in other polysaccharide esters with alkyl side chains (Aburto et al., 1999; Enomoto-Rogers et al., 2014; Fundador et al., 2012b; Malm et al., 1951b; Sagar & Merrill, 1995).

3.6. Crystallinity of curdlan esters

Fig. 6 shows WAXD curves of cast films of curdlan esters. In the cases of CDAc and CDPr, many diffraction peaks were observed. The diffraction peaks at $2\theta_{Cu\ K\alpha} = 9.8°$ ($d = 0.90$ nm) and 15.7° ($d = 0.57$ nm) of CDAc can be assigned to (1 0 1) and (1 0 3) reflections of curdlan triacetate, respectively (Okuyama et al., 1996). Curdlan triacetate forms the hexagonal unit cell with $a = b = 1.100$ nm, c (fiber axis) = 2.291 nm, and $\gamma = 120°$, in which the 6/1 single helix is contained (space group of $P6_1$). For CDBu and CDVa, diffraction peaks were still observed, although their number and intensity were much smaller compared to CDAc and CDPr. X_c of CDAc, CDPr, CDBu, and CDVa were 41.1, 55.6, 12.9, and 6.0%, respectively. Additional annealing treatments are expected to improve the degrees of crystallinity of crystallizable curdlan esters.

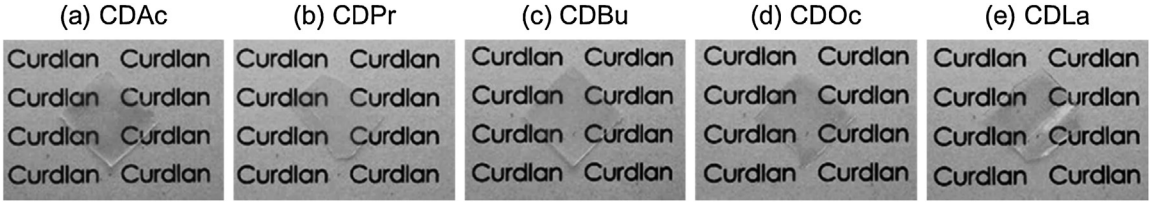

Fig. 4. Photographs of cast films of representative curdlan esters.

Here, diffraction peak intensities and positions of CDAc, CDPr, CDBu, and CDVa were distinctly different from each other, indicating differences of their crystal structures. It is well-known that the side-chain groups in polysaccharide esters have a great effect on the molecular and crystal structures, as seen in cellulose and amylose triesters (Steinmeier & Zugenmaier, 1987; Zugenmaier & Steinmeier, 1986). With increasing further the side-chain carbon number, only broad scattering was seen at $2\theta_{\mathrm{Cu\,K\alpha}} \approx 5^\circ$ (halo-1) and $2\theta_{\mathrm{Cu\,K\alpha}} \approx 20^\circ$ (halo-2). Taking together with the DSC results, this broad scattering would be amorphous halo. With increasing the side-chain length, halo-1 shifted to the lower angle. This result clearly indicates that the most probable distance between the backbone chains increases with the alkyl side-chain length. Namely, halo-1 would correspond to the most probable distance between the backbone chains and halo-2 would be derived from other distances such as the most probable distance between the side chains. A similar trend has been reported for cellulose esters (Crepy et al., 2011) and xylan esters (Fundador et al., 2012b).

The molecular and crystal structures of CDPr, CDBu, and CDVa are of interest and currently being investigated using the fiber diffraction methods for the uniaxially-oriented samples.

4. Conclusions

In this study, a series of ester derivatives of curdlan with varying alkyl chain lengths (C2–C12) were synthesized and their structure and properties were systematically investigated for the purpose of revealing the substituent effect on their structure and properties and developing bio-based crystalline thermoplastics with excellent properties. By the heterogeneous reaction using trifluoroacetic anhydride, various fully-acylated curdlans with high molecular weight ($M_w \geq 6 \times 10^5$) were successfully synthesized. By esterification of curdlan, 30–60 °C higher $T_{d\_50\%}$ was obtained. All curdlan esters showed the glass transition and melting at the temperatures sufficiently lower than the thermal decomposition temperatures. Namely, thermoplasticity was successfully introduced into curdlan by esterification. It was found that the curdlan esters having C2–C6 side chains are crystallizable and those with C8, C10, and C12 ester groups are amorphous polymers. In particular, T_m of CDAc (C2) and CDPr (C3) was higher than 200 °C, and T_g of CDAc and CDPr was higher than 100 °C. The longer ester groups gave the lower T_g (170 → 50 °C) and T_m (290 → 170 °C). With increasing the side-chain length, tensile deformation behavior of curdlan films changed from hard to soft behaviors. Thus, curdlan esters with a wide range of properties were able to be obtained by changing the length of alkyl ester groups. WAXD results clearly indicate that the longer ester side chain reduces crystallinity and furthermore changes the crystal structure. Precise control of the crystal and higher-order structures is expected to improve further properties of the semicrystalline curdlan esters. In terms of crystallinity and a difference between the melting and thermal decomposition temperatures, it can be said that CDPr is the most appropriate candidate for high-T_m crystalline thermoplastic materials.

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