# Synthesis of novel saccharide-pendant vinyl polymer and application to oxygen barrier film

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Poly(vinylidene chloride) (PVDC) film, which has a high oxygen barrier property, has been widely used as packaging material, however, PVDC creates significant environmental problems. When burned, it forms chloric acid which is liberated into the atmosphere, becoming a component of the acid rain that damages forests. Therefore, many other materials have been substituted for PVDC in packaging applications. Of these alternative packaging materials, cellulose i.e., cellophane is the most environment-friendly material, and also has a high oxygen barrier property in dry conditions. Cellulose, which has been used in various matrix-forming materials, has long been developed. Although cellulose is a sustainable material, it has characteristics of rigidity derived from inter- and intramolecular hydrogen bonding. Therefore, cellulose shows poor workability due to thermal stability, poor controllability of chemical reactions and low solubility in water and common organic solvents [1, 2]. Cellulose derivatives such as e.g., acylate [3] and xanthate [4], or the cellulose complex with copper such as cupra [5], are required to mold cellulose.

In order to overcome the poor characteristics of cellulose, we focused on a functional polymer with a constitutional unit of cellulose, namely cellobiose in the side chain, and developed the novel synthetic monovinylcellobiose. In addition, the synthetic monomer was converted into a polymer by free-radical polymerization in aqueous solution. It is important to determine whether typical cellulose properties (such as functionality, biodegradability [6] and biocompatibility [7] can be advantageously retained in this new synthetic, so in this paper we report the characterization of the synthetic monovinylcellobiose and the obtained polymer, comparing with the characteristics of the corresponding monosaccharide derivative.

As a packaging material, the novel saccharide-pendant vinyl polymer has potential as a coating layer for oxygen barrier film. In this study, we investigated its oxygen barrier property by measuring the change of humidity.

The synthesis of monovinylcellobiose monomer was carried out without the use of protecting groups for the cellobiose component, as shown in Scheme 1.

As reported by Likhosherstov *et al.* [8], a high yield of cellobiosylamine could be obtained by reductive amination of cellobiose. Due to the reactivity difference between the amino group and the remaining hydroxyl groups of the cellobiose, the introduction of a variety of functional group to the anomeric position became possible [9]. Due to a lack of by-products, especially acid, salts and fission products, we adopted coupling with 2-(methacryloyloxy)ethy isocyanate (MOI) [10], which reacts mildly. The typical procedure for the synthesis of 2-(methacryloyloxy)ethylureido cellobiose (MOU-Cell) is described below. Cellobiose (15 g, 43.8 mmol) was dissolved in water (100 ml) and solid ammonium hydrogen carbonate (30 g, 379.7 mmol) was added at intervals of 24 h, and was stirred at $37\,^{\circ}$C for 2 days. Next, the residue was diluted to 200 ml with water and concentrated to 50 ml. This procedure was repeated until the disappearance of the odor of ammonia. The purity of the freeze-dried product was 81% [11]. Cellobiosylamine (8.1 g, 23.7 mmol) was dissolved in $1.0 \times 10^{-3}$ M KOH aqueous solution (100 ml). MOI (9.20 g, 59.3 mmol) was added and stirred at $3\,^{\circ}$C for 12 h, producing white precipitation as a by-product. The precipitation was removed by filtration. The filtrate was washed with diethyl ether to remove traces of unreacted MOI and freeze-dried. The raw product was dissolved in water/methanol and recrystallized from acetone/diethyl ether. The yield was 8.78 g (74.5%). m.p.149.4–153.2. The structure of MOU-Cell is confirmed by its ^{1}H-NMR and IR spectra. ^{1}H-NMR (D$_2$O, ppm): 1.95 (s, 3H, CH$_2$=C(C$\underline{\text{H}}_3$), 3.41–4.02 (m, 12H, from sugar), 3.66 (t, 2H, C$\underline{\text{H}}_2$), 4.26 (t, 2H, C$\underline{\text{H}}_2$), 4.51 (d, 1H, H′-1), 4.85 (d,
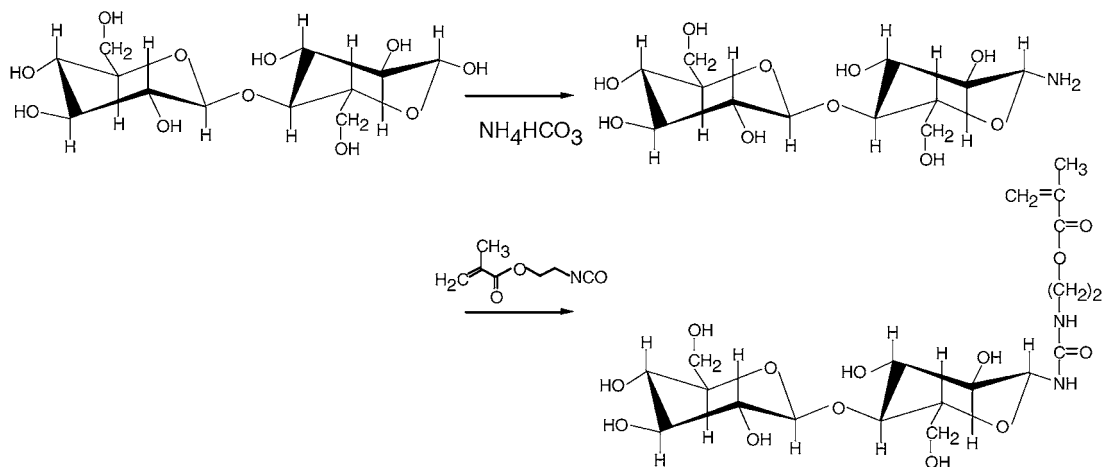
*Scheme 1* Synthesis of 2-(methacryloyloxy)ethylureido cellobiose.

1H, H-1), 5.72 (s, 1H, $\underline{CH_2}$=C(CH$_3$) (cis)), 6.14 (s, 1H, $\underline{CH_2}$=C(CH$_3$) (trans)). IR (cm$^{-1}$): 3350, $\nu_{O-H}$; 2930, $\nu_{C-H}$; 1720, $\nu_{C=O}$(ester); 1640, $\nu_{C=O}$(amide); 1590, $\delta_{N-H}$. Elemental analysis (%): Calculated for C$_{19}$H$_{32}$N$_2$O$_{13}$: C, 45.96; H, 6.49; N, 5.64; Found: C, 44.56; H, 6.56; N, 5.29. MOU-Cell is soluble in water, DMF, DMSO and DMAc, and partially soluble in methanol and ethanol but insoluble in ether, acetone and THF. The obtained monomer was polymerized in aqueous solution by redox-initiators using ammonium persulfate/$N, N, N', N'$-tetraethylethylenediamine. The obtained crude polymer was purified by dialyzing in a dialysis tube [12] for 3 days in order to remove remaining monomer. The product was finally freeze-dried. The poly(2-(methacryloyloxy)ethylureido cellobiose) (MOU-Cell polymer) was soluble in water, DMF, DMSO and DMAc but insoluble in other common organic solvents.

In addition, we discussed the molecular weight of the MOU-Cell polymer as determined by size exclusion chromatography (SEC) using the packed column [13] with an exclusion molecular weight value of $2.0 \times 10^7$, comparing with vinylmonomer having a glucose as a monosaccharide in the side chain. The SEC elution behavior of MOU-Cell polymer was measured in ultrapure water as eluent. The elution of MOU-Cell polymer took 0.67 times as long as that of the maximum molecular weight standard pullulan, i.e., $M_w$ $7.88 \times 10^5$, and therefore the determination of molecular weight became impossible. In addition, the molecular weight was estimated using SEC with lithium bromide aqueous solution as eluent. Fig. 1 shows the SEC chromatograms of pullulan standards and MOU-Cell polymer, using ultrapure water and lithium bromide aqueous solution, respectively, as eluent. The pullulan do not conform the aggregate by inter- and intramolecular hydrogen bonding [14, 15]. As expected, no significant changes in SEC behaviors occurred for pullulan standard using the modified eluent, i.e., molecular weight distribution and elution time, because of their lack of aggregation in solvent. In contrast, the elution of MOU-Cell polymer in the modified eluent occurred much later than that of MOU-Cell polymer using ultrapure water as an eluent. The SEC behaviors for MOU-Cell polymer indicated
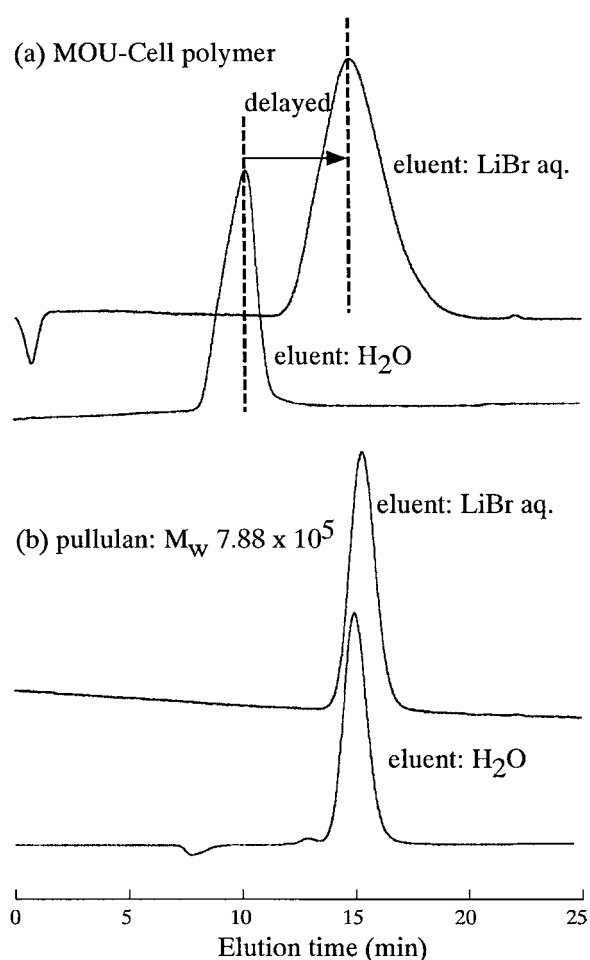


*Figure 1* SEC chromatograms of pullulan standard and MOU-Cell polymer, using water and lithium bromide aqueous solution as eluents, respectively. Flow rate: 0.5 ml/min. Temperature: 20 °C. Column: Shodex Ohpak SB-806M HQ (300 × 8.0 mm I.D.).

that the domain size of MOU-Cell polymer in pure water is huge. We suspected that the MOU-Cell polymer conformed a huge aggregate caused by inter- and intramolecular hydrogen bonding among cellobiose in the side chain in water. As a result, the weight-average molecular weight of MOU-Cell polymer was estimated at ca. $3.14 \times 10^6$, as determined by SEC using modified eluent. The corresponding glucose derivative polymer

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**TABLE I** Oxygen transmission rate (OTR) of the film

| Film | %RH | OTR (cc/m$^2$·day·atm) |
|---|---|---|
| Coated film[a] | 13 | 0.15 |
| | 72 | 0.45 |
| Non-coated film[b] | 13 | 35 |
| | 72 | 210 |

[a]Nylon-6 film coated by MOU-Cell polymer.
[b]Nylon-6 film.

was obtained in the same conditions as polymerization for the MOU-Cell monomer. The polymer had a weight-average molecular weight of $5.84 \times 10^5$, as determined by SEC using modified eluent. A much higher molecular weight was obtained with cellobiose derivative than with the corresponding glucose derivative. The difference in their molecular weights was probably caused by the specific conformation from inter- and intramolecular hydrogen bonding among the side chains in water.

As an application in packaging material, MOU-Cell polymer was used as the coating layer for oxygen barrier film. MOU-Cell polymer was dissolved in dimethyl sulfoxide with water content of 22%. The corona-treated nylon-6 film was covered by 10 wt% MOU-Cell polymer solution. After drying, film of 1.2 $\mu$m thickness was obtained. The oxygen barrier property of the film was evaluated using an OX-Tran permeability tester (Modern Controls, Inc.).

As shown in Table I, the oxygen transmission rate (OTR) of the non-coated film i.e., the corona-treated nylon-6 film, was 35 cc/m$^2$·day·atm at %RH 13%, and was 210 cc/m$^2$·day·atm at %RH 72%. The OTR for both films increased with increasing relative humidity (RH). On the other hand, the OTR of the nylon-6 film coated by MOU-Cell polymer was 0.15 cc/m$^2$·day·atm at %RH 13%, although the coating thickness was very thin, 1.2 $\mu$m. Even though %RH was 72%, the OTR was 0.45 cc/m$^2$·day·atm. In spite of the high humidity condition, the OTR of the film coated with MOU-Cell polymer showed a very small value.

These values are much smaller than those of other conventional oxygen barrier films, i.e., cellophane, poly(ethylene-vinyl alcohol) copolymer (EVOH) [16] and PVDC [17]. Hydrophilic polymers, such as nylon-6, EVOH and cellophane, show increasing OTR with increasing %RH, e.g. Long *et al*. [18, 19]. The superior oxygen barrier effect showed that the oxygen molecule

was unable to permeate due to inter- and intramolecular hydrogen bonding derived from the rigidity of the cellobiose unit.

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