

SHORT COMMUNICATION

Ruthenium Catalyzed Oxidation of Polysaccharide

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Cellulose is one of the renewable natural polysaccharides, and chitin is a natural mucopolysaccharide having a similar chemical structure to cellulose. Although these are widely distributed in nature and show hydrophilic properties because of hydroxyl groups in their molecules, they are known to be insoluble in most common solvents. The insolubility of these polysaccharides has been suggested to be due to rigid crystalline structure through intra- and intermolecular hydrogen bonds.¹ Many attempts at disrupting these bonds in order to prepare water soluble derivatives of these polysaccharides have consisted in chemical modifications such as acylation or alkylation.^{2,3} Although two step oxidation of cellulose is one of the well known procedures for preparing water soluble derivatives of cellulose,⁴⁻⁸ oxidation products prepared by one step oxidation using periodic acid⁴⁻⁸ or metallic species such as ruthenium^{9,10} were reported to be insoluble in water. In the present study, water soluble derivatives of celluloses and chitins were successfully prepared by one step oxidation with ruthenium catalyst.

Celluloses used in this paper were Avicel SF, Whatman CF-11, and Toyo filter paper No. 6 which were purchased from Asahi Chem. Ind.

Co., Ltd., Whatman Chem. Ind. Co., Ltd., and Advantec Toyo Co., Ltd., respectively. Chitin (shrimp shell) was supplied from Wako Pure Chemical Industries, Ltd.

A typical procedure for the oxidation of cellulose by ruthenium is as follows: ruthenium trichloride (0.02 g, 0.1 mmol) was dissolved in 0.1 M* aq carbonate buffer solution (40 ml, pH=9.8). Sodium bromate (1.50 g, 10 mmol) and cellulose (0.54 g) were added to the solution and the mixture was stirred for the prescribed time at 34°C. Undissolved material was removed by centrifugation at 18,000 rpm. Dissolved material was recovered by precipitation with 50% aq ethanol. After treatment of the oxycellulose with cation-exchange resin (DAIAION SK-1B; H-type), the content of the carboxyl group was estimated by titration with 0.05 M aq NaOH. Molecular weight was determined by GPC with pullulan as the standard on a Shimadzu LC-3A apparatus (column, Asahipak GS-220H, GS-310H, GS-510H; eluent, 0.05 M aq NaNO₃; flow rate, 1 ml min⁻¹; column temp, 50°C).

RESULTS AND DISCUSSION

Ruthenium catalyzed oxidation of cellulose was carried out under heterogeneous condi-

* 1 M = 1 mol dm⁻³

Table I. Oxidation of various celluloses^a

Run No.	Cellulose	Time/h	Yield/wt%		d.s. ^b	MW ^c ($\times 10^4$)
			Soluble	Insoluble		
1	Avicel SF	12	89	18	1.9	1.2
2		18	107	2	2.0	1.0
3	Whatman CF-11	18	71	30	1.7	1.0
4		72	85	3	2.5	0.9
5	Filter paper ^d	18	53	56	1.9	1.3
6 ^e		18	60	55	2.4	1.3

^a Cellulose, 0.54 g (3.3 mmol as glucose residue); RuCl₃, 0.1 mmol; NaBrO₃, 10 mmol; solvent, 40 ml of 0.1 M carbonate buffer (pH 9.8); Temp, 34°C.

^b d.s. of the soluble polymer was estimated by titration with 0.05 M aq NaOH solution.

^c Molecular weight of the soluble polymer was determined by GPC using 0.05 M aq NaNO₃ as eluent based on pullulan as standard.

^d Toyo filter paper No. 6.

^e RuCl₃, 0.2 mmol; NaBrO₃, 20 mmol.

tions and gave water soluble products. As shown in Table I, Avicel SF which was microcrystalline cellulose was dissolved easily in buffer solution within 18 h of oxidation (Run 2). In the case of Whatman CF-11 or Toyo filter paper No. 6, about 70% or 50% of cellulose added became water soluble by 18 h of oxidation (Run 3 and 5). Even if twice the amounts of catalyst (RuCl₃) and oxidant (NaBrO₃) were used, the amount of water soluble polymer did not increase (Run 6). The yield of water soluble polymer from Whatman CF-11 increased with oxidation time (Run 4). The content of the carboxyl group per glucose residue (d.s.) increased with reaction time or amounts of catalyst and oxidant (Run 4 and 6). The IR absorption spectra of the soluble fractions prepared in this study showed a significant peak at 1740 cm⁻¹ (C=O stretching).¹¹ The structure of the oxycelluloses was further confirmed by ¹³C NMR spectroscopy in D₂O. Since the C-6 carbon of glucose residue ($\delta = ca.$ 62 ppm) was not observed and signals of the carbonyl carbon appeared at the lower field ($\delta = 175$ – 178 ppm), most of hydroxyl groups at C-6 position of cellulose would be oxidized. Moreover, the high d.s. values of oxycelluloses suggested that hydroxyl groups

Table II. Oxidation of chitin^a

Run No.	Time/h	Yield/wt%		d.s. ^b	MW ^c ($\times 10^4$)
		Soluble	Insoluble		
1	6	40	45	1.3	1.3
2	12	60	19	1.6	1.0
3	18	70	10	1.4	0.9
4	24	46	0	2.0	0.8

^a Chitin (shrimp shell), 0.51 g (2.5 mmol as *N*-acetylglucosamine residue); RuCl₃, 0.1 mmol; NaBrO₃, 10 mmol; solvent, 40 ml of 0.1 M carbonate buffer (pH 9.8); temp, 34°C.

^b d.s. of soluble polymer was estimated by titration with 0.05 M aq NaOH solution.

^c Molecular weight of soluble polymer was determined by GPC using 0.05 M aq NaNO₃ as eluent based on pullulan as standard.

of celluloses were oxidized to carboxyl groups not only at the C-6 position but also at the C-2 or C-3 position.

Although attempts to oxidize chitins have also been made using periodate,¹² oxidation products reported were insoluble in water. In this paper, water soluble derivatives of chitin were found to be easily prepared by ruthenium catalyzed oxidation. As shown in Table II, chitin was oxidized to give water soluble

polymer in 60–70% yields by 12–18 h of oxidation. The content of the carboxyl group per *N*-acetylglucosamine residue (d.s.) increased with reaction time. The IR absorption spectra of the soluble fraction also showed a significant peak at 1740 cm^{-1} (C=O stretching). In analogy with oxycellulose, ^{13}C NMR analysis revealed that most of hydroxyl groups at C-6 position of chitin would also be oxidized. As the d.s. values of oxidation products were 1.3 to 2.0, it was suggested that hydroxyl groups of chitin were also oxidized to carboxyl groups not only at the C-6 position but also at the C-3 position, as mentioned above in cellulose oxidation.

A detailed study on the structure and properties of various celluloses and chitins oxidized will be published in near future.

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