NOTES

# Radical Alternating Copolymerization of Tri-O-acetyl-D-glucal with Maleic Anhydride

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Polysaccharides are important for their unique structures and properties which are generally different from those of synthetic polymers.[1] Polymerization using sugar compounds as a monomer is of interest as the product polymers consist of natural and synthetic building blocks. They are anticipated to be tractable and exhibit useful properties of polysaccharides and synthetic polymers. For the synthesis of these polymers, polycondensation and polyaddition using several combinations of saccharide monomers and difunctional compounds such as dicarboxylic acid chlorides and diisocyanates have been reported.[2-11] The polymerization produced polyamides, polyesters, polyureas, and polyurethanes consisting of saccharide units in the main chain. Radical polymerization of mono- and oligosugar monomers with a vinyl group has been reported to give polymers with pendant sugar residues.[12] Vinyl ethers are used as monomers for various polymerization reactions. The radical copolymerization of vinyl ethers with maleic anhydride (MAn) was achieved to give 1:1 alternating copolymers.[13,14] The polymerization involved intermediates of charge transfer complexes. Glycals, 1,2-dideoxy sugars, have a structure of cyclic olefinic ether, and thus should be useful as monomers similar to vinyl ethers. The polymerization of glycals, however, has not been reported so far.

This paper describes the radical alternating copolymerization of the sugar material, tri-O-acetyl-D-glucal (1) with MAn (Scheme 1). This copolymerization reaction provides a quite new approach of polymerization using a sugar monomer.

## EXPERIMENTAL

### Materials

Monomers 1 and MAn were commercially available as extra grade and used without further purification.



Scheme 1.

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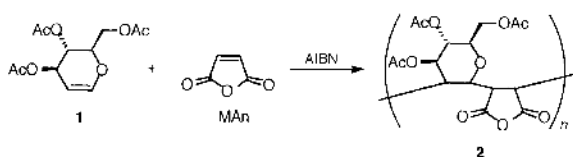
Initiator, $\alpha,\alpha'$-azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol. Solvents were purified by distillation.

### Copolymerization

A typical run was as follows (entry 9). Under nitrogen, 1 (0.273 g, 1.0 mmol), MAn (0.0981 g, 1.0 mmol), and AIBN (0.0164 g, 0.10 mmol) were placed in a polymerization tube which was then sealed. After heating at 80°C for 23 h, the tube was opened and the reaction mixture was dissolved in chloroform. The solution was poured into a large amount of diethyl ether to precipitate the polymeric product. The precipitate was isolated by filtration and dried *in vacuo* to give alternating copolymer 2 (0.0857 g) in 23.2% yield.

### Alkaline Hydrolysis of 2

Alternating copolymer 2 (0.370 g, 1.0 mmol) was suspended in 20% KOH aqueous solution and the solution was heated at 60—80°C for 2 h. Hydrochloric acid (6 M) was added to the solution to make it acidic. The solvent was coevaporated azeotropically with toluene several times and the concentrated material was dried *in vacuo*. Ethanol was added to the residue and insoluble potassium chloride was removed by filtration. The filtrate was concentrated by evaporation and the concentrated solution was poured into a large amount of diethyl ether to precipitate a product. The product polymer was isolated by filtration and dried *in vacuo* to give hydrolyzed polymer 3 (0.198 g, 0.76 mmol) in 75.7% yield.

### Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 spectrometer. IR spectra were recorded on a HORIBA FT-200 spectrometer. GPC analysis was performed using a Hitachi 655A-11 with RI detector under the following conditions: TSKgel G3000H$_{XL}$ column, with chloroform as eluent, at a flow rate of $1.0 \, \text{mL} \cdot \text{min}^{-1}$. A calibration curve was obtained using polystyrene standards.

## RESULTS AND DISCUSSION
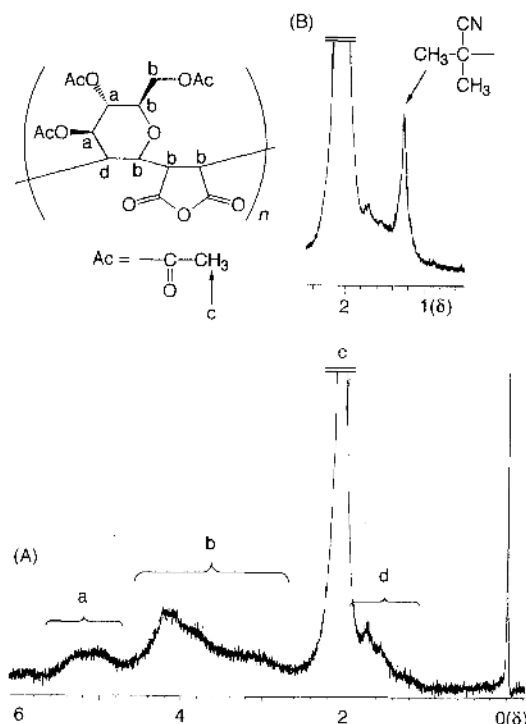
### Alternating Copolymerization of 1 with MAn

The copolymerization of 1 with MAn was carried out with AIBN initiator at the desired temperature. The

**Table I.** Alternating copolymerization of
1 with MAn initiated by AIBN

| Entry | AIBN/ mol% | Solvent | Temp/°C | Time/h | Yield/%[a] | $M_n$[b] |
|-------|------------|---------|---------|--------|------------|----------|
| 1  | 5  | Toluene | 80 | 23 | 16.1 | 1900 |
| 2  | 5  | Toluene | 80 | 38 | 16.1 | 2300 |
| 3  | 10 | Toluene | 80 | 16 | 19.8 | 2300 |
| 4  | 5  | DMF     | 80 | 23 | 0    |      |
| 5  | 10 |         | 60 | 23 | 12.7 | 3200 |
| 6  | 20 |         | 60 | 23 | 19.0 | 3600 |
| 7  | 20 |         | 60 | 70 | 22.1 | 3500 |
| 8  | 5  |         | 80 | 23 | 17.2 | 1900 |
| 9  | 10 |         | 80 | 23 | 23.2 | 2100 |
| 10 | 20 |         | 80 | 23 | 31.0 | 3000 |

[a] Diethyl ether insoluble portion. [b] Determined by GPC with chloroform eluent at 40°C using polystyrene standards.



**Figure 1.** ¹H NMR spectra of alternating copolymers 2 with high molecular weight (entry 6) (A) and low molecular weight (entry 8) (B) in CDCl₃.



**Figure 2.** ¹³C NMR spectrum of alternating copolymer 2 in CDCl₃.

product copolymer was isolated as a diethyl ether insoluble fraction. Table I summarizes the copolymerization results under various conditions. The copolymerization occurred in toluene or without solvent, but yield and molecular weight of the copolymers were not high. The reaction did not take place in $N,N$-dimethylformamide (DMF) solvent. A large amount of initiator (20 mol% for monomer) gave the copolymer in higher yield. Higher reaction temperature (80°C) gave polymers with lower molecular weights. The structure was determined by the ¹H NMR, ¹³C NMR, and IR spectra as well as elemental analysis. Figure 1(A) shows the ¹H NMR spectrum of the product copolymer in CDCl₃ (entry 6). Small broad peaks centered at $\delta$ 1.73 were due to a sugar proton at position 2 (1H) partly overlapping with a large peak at $\delta$ 2.08 ascribable to methyl protons of the acetate groups (9H). Broad peaks at $\delta$ 2.80—4.70 were ascribable to sugar protons at position 1, 5, and 6

and methine protons of the succinic anhydride (6H). Small peaks at $\delta$ 4.70—5.60 were due to sugar protons at position 3 and 4 (2H). Broad multiplet peaks were observed centered at $\delta$ 1.21 in the ¹H NMR spectrum of the product (entry 8) with a low molecular weight (Figure 1(B)). The peaks were assignable to the methyl protons of 1-cyano-1-methylethyl group, derived from the initiator, located at the chain end of the polymer molecule, whose chemical shift was similar to that of the other polymers initiated with AIBN according to the previous literature[15,16] No peak attributable to olefinic protons was observed in the spectrum, indicating that the olefinic copolymerization of 1 with MAn proceeded giving rise to copolymer 2. From the integrated ratio of these peaks, the content of monomers 1 and MAn in the copolymer was calculated as 50%.

The ¹³C NMR spectrum of the same sample is shown in Figure 2. Peak assignments were as follows; a large peak at $\delta$ 20.7 due to methyl carbons of the acetate groups, a small peak at $\delta$ 25.3 due to a sugar carbon at position 2, broad peaks centered at $\delta$ 44.7 due to methine carbons of the succinic anhydride, broad peaks at $\delta$ 58.0—80.0 due to sugar carbons at positions 1, 3, 4, 5, and 6, and a peak at $\delta$ 170.7 due to carbonyl carbons of the acetate and anhydride groups.

The IR spectrum of the product (Figure 3 (a)) exhibits characteristic absorptions at 1743 cm⁻¹ ascribable to C=O of the ester groups and 1784 and 1863 cm⁻¹ assignable to C=O of the succinic anhydride. Anal. Calcd for $(C_{16}H_{18}O_{10})_n$: C, 51.90; H, 4.90. Found: C, 51.20; H, 5.08. All above spectroscopic and elemental analysis data support the structure of alternating copolymer 2. The spectroscopic data of the other copolymers obtained under the conditions of Table I were identical with those above.

The 1 : 1 alternating composition of the copolymers was always attained regardless of the feed molar ratio (Figure 4). Thus, the monomer reactivity ratio is $r_1 = r_{MAn} = 0.0$.

The present alternating copolymerization probably proceeded through a charge transfer complex intermediate. This is because 1 has an olefinic ether structure, an electron donating group similar to vinyl ether, whereas MAn is a well known electron accepting monomer for the copolymerization with vinyl ethers through the
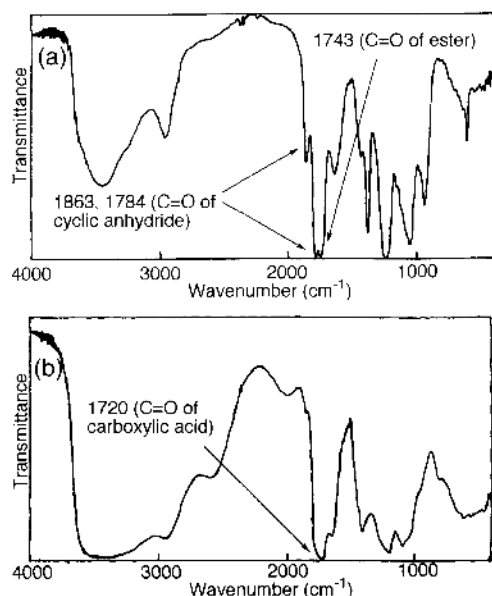
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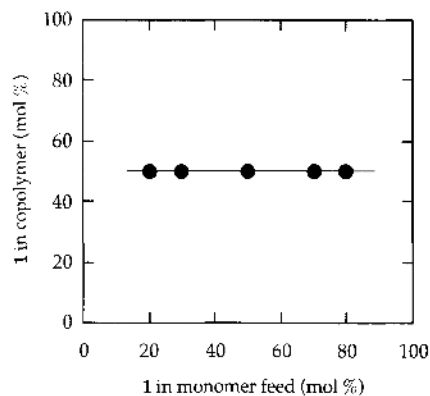Figure 3. IR spectra of alternating copolymer 2 (a) and hydrolyzed copolymer 3 (b).



Figure 4. Copolymer composition curve of the 1-MAn copolymerization.

intermediates of the charge transfer complexes.[13,14,17]

*Alkaline Hydrolysis of Alternating Copolymer 2*

Alternating copolymer 2 was converted to 3 with free sugar units and carboxylic acid groups by an alkaline hydrolysis (Scheme 2). The reaction was carried out in 20% KOH aqueous solution at 60—80°C. Initially, the solution was heterogeneous and gradually became homogeneous, indicating the production of water soluble product by the hydrolysis of 2. The product material isolated as a diethyl ether insoluble fraction was soluble in water and higher polar organic solvents such as dimethyl sulfoxide (DMSO), methanol, and ethanol.

Figure 5 shows the $^1$H NMR spectrum of the product polymer ($D_2O$). Peak assignments are shown in Figure 5 for 3. No peak due to the methyl protons of the acetate groups at around $\delta$ 2.0 appeared, supporting that complete deacetylation took place.

The IR spectrum of the hydrolyzed product in Figure 3(b) exhibits disappearance of absorption at 1784 and 1863 cm$^{-1}$ due to succinic anhydride of 2 in Figure 3(a) and appearance of a strong absorption at 1720 cm$^{-1}$ due to C=O of the carboxylic acid groups. All the above spectroscopic data indicate that complete hydrolysis of
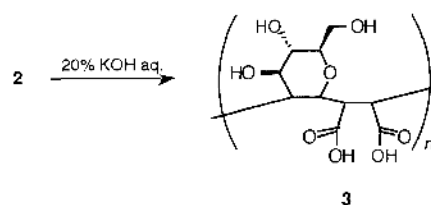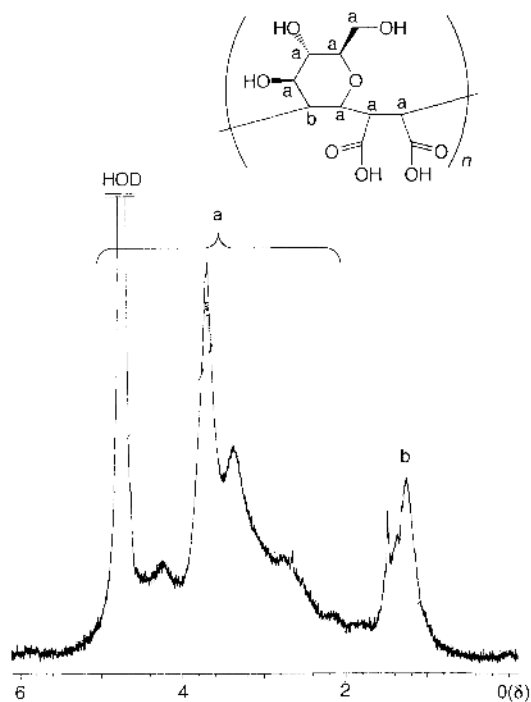


Scheme 2.



Figure 5. $^1$H NMR spectrum of hydrolyzed copolymer 3 in $D_2O$.

acetyl ester and succinic anhydride groups took place to give polymer 3 having free sugar units and carboxylic acid groups.

## CONCLUSIONS

The alternating copolymerization of 1 with MAn proceeded with AIBN initiator to give 1 : 1 alternating copolymer 2. The reaction possibly occurred through charge transfer complex. The alkaline hydrolysis of 2 produced polymer 3. The present alternating copolymerization provides a novel approach to polymerization using a sugar monomer.

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