849. *Polymerisation of Unsaturated Derivatives of 1,2:5,6-Di-*O*-isopropylidene-*D*-glucofuranose.*

By W. A. P. Black, E. T. Dewar, and D. Rutherford.

The 3-methacryloyl ester and the 3-vinyl ether of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose have been synthesised and polymerised with free-radical and cationic catalysts, respectively; certain physical properties of the polymers are briefly described. The methacrylic polymer has been converted by hydrochloric acid into the water-soluble poly-(3-*O*-methacryloyl-D-glucose), which has been subjected to acetylation, methylation, phenylcarbamoylation, oxidation, and other reactions. The 3-allyl ether failed to give a polymer of high molecular weight.

One method of preparing linear polymers containing carbohydrate residues (X) involves synthesising and polymerising vinyl derivatives ($CH_2{:}CHX$) to form hydrocarbon polymer chains $[CH_2{\cdot}CHX]_n$ with the residues attached to every second carbon atom. Haworth and his co-workers[1] found that substituted carbohydrates containing two acrylate or methacrylate groups polymerised to infusible, insoluble, and consequently intractable resins. The presence of only one vinyl group prevents such cross-linking on polymerisation and, recently, several examples of these monomers have been polymerised, including 3-*O*-acryloyl- and 3-*O*-methacryloyl-D-mannitol 1,2,4,5,6-pentanitrate,[2] 1-acrylamido-1-deoxy- and 1-deoxy-1-methacrylamido-D-glucitol,[3] and 1,2:3,4-di-*O*-isopropylidene-6-*O*-vinyl-D-galactose.[4] We now report the preparation and polymerisation of monovinyl derivatives of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (I).

The 3-methacrylate (II) was prepared in 50—70% yield by esterification with

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[1] Haworth, Gregory, and Wiggins, *J.*, 1946, 488.

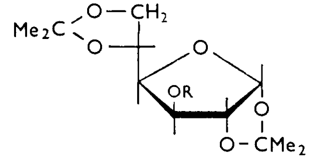
[2] Wolfrom, Swan, Ennor, and Chaney, *J. Amer. Chem. Soc.*, 1959, **81**, 5701.

[3] Whistler, Panzer, and Roberts, *J. Org. Chem.*, 1961, **26**, 1583.

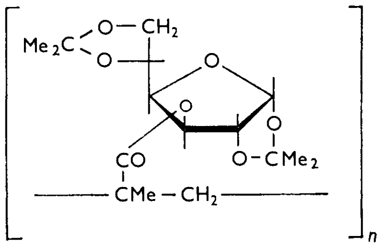
[4] Whistler, Panzer, and Goatley, *J. Org. Chem.*, 1962, **27**, 2961.

methacrylic anhydride and pyridine, but alternative syntheses with methacryloyl chloride and pyridine, and with methacryloyl chloride and the 3-potassio-salt of di-isopropylideneglucose, led to lower yields (30—50%). Purification of the ester by high-vacuum distillation required the presence of an inhibitor to prevent gelling, owing to polymerisation at the elevated temperature; tetrachloroquinol was satisfactory since it had a high enough boiling point to prevent codistillation with the monomer. The syrup obtained slowly crystallised (m. p. 34—35°). Since the publication of our preliminary note,[5] the synthesis and polymerisation of this ester have been reported from Japan.[6]

The monomer polymerised readily, in the absence of a solvent, with free-radical catalysts such as benzoyl peroxide and azobisisobutyronitrile, but the product of bulk polymerisation was a hard, insoluble, intractable glass. Polymerisation in benzene solution, however, yielded poly-(1,2:5,6-di-*O*-isopropylidene-3-*O*-methacryoyl-α-D-glucofuranose) (V) of appreciable molecular weight (inherent viscosity 0·5), soluble in organic solvents but insoluble in water. The polymer had a specific rotation (—49° in tetrachloroethane) significantly lower than that of the monomer (—32° in tetrachloroethane), and this value was independent of viscosity, catalyst, and general polymerisation conditions. Unsuccessful attempts were made to initiate anionic polymerisation of the monomer with metal amides [$LiNH_2$, KNH_2, and $Ba(NH_2)_2$] in liquid ammonia,[7] but the overall reaction resulted in ammonolysis of the sugar ester to methacrylamide and di-isopropylideneglucose.



(I : R = H)
(II : R = CO·CMe:CH_2)
(III : R = CH_2·CH:CH_2)
(IV : R = CH:CH_2)



(V)

Heating polymer (V) with N-hydrochloric acid at 100° gave the water-soluble poly-(3-*O*-methacryloyl-D-glucose) (VI) with a molecular weight of 100,000 (determined by a viscosity–sedimentation method) and a positive rotation ($[\alpha]_D$ +50° in water) in agreement with the pyranose structure suggested. The derivative strongly reduced Fehling's solution and quantitative determination of reducing power with sodium hypoiodite[8] gave a value of 94·5%, compared with 97·3% for 3-*O*-methyl-D-glucose. On the other hand, the reducing power exhibited towards Somogyi's (1952) reagent[9] was negligible (1·9% of that of D-glucose) and very much less than that (46·7%) shown by 3-*O*-methyl-D-glucose. The fact that the reducing group is attached to a polymer chain appears to have an influence on this non-stoicheiometric reaction.

Derivatives were formed from this polymer (VI) by subjecting it to standard carbohydrate reactions. Acetylation, methylation, and phenylcarbamoylation yielded approximately trisubstituted derivatives, all of which were soluble in organic solvents and gave solutions of appreciable viscosity. Complete substitution of all four free hydroxyl groups could not be effected owing, possibly, to shielding of one hydroxyl group by the polymer chain. Oxidation with chlorous acid at pH 3 yielded a polymeric acid which was

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[5] Bird, Black, Dewar, and Rutherford, *Chem. and Ind.*, 1960, 1331.

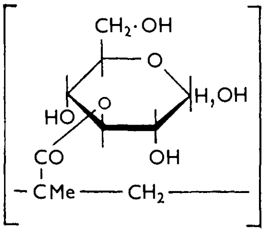
[6] Kimura and Imoto, *Makromol. Chem.*, 1961, **50**, 155; Imoto and Kimura, *ibid.*, 1962, **53**, 210; Kimura, Hirai, and Imoto, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1962, **65**, 688; Kimura and Hirai, *Makromol. Chem.*, 1962, **58**, 232.

[7] Goode, Snyder, and Fettes, *J. Polymer Sci.*, 1960, **42**, 367.

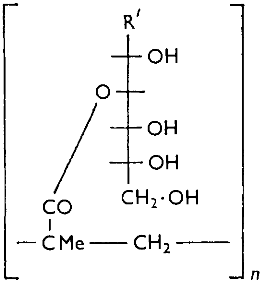
[8] Hirst, Hough, and Jones, *J.*, 1949, 928.

[9] Somogyi, *J. Biol. Chem.*, 1952, **195**, 19.

basically poly-(3-*O*-methacryloyl-D-gluconic acid) (VII), with certain similarities to the naturally occurring polyuronic acids such as alginic acid. Whereas aqueous solutions of the polyacid tended to retrograde quickly, those of the sodium salt (VIII) were more stable. Replacement of the sodium by multivalent cations, notably the bivalent calcium. barium, copper, and lead, caused precipitation.



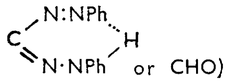
(VI)



(VII : R′ = CO_2H)

(VIII : R′ = CO_2Na)

(IX : R′ = CH:N·NHPh or CHO)



(X : R′ = $\mathrm{C}\genfrac{}{}{0pt}{}{\diagup \mathrm{N{:}NPh}\cdots}{\diagdown\!\!\diagdown \mathrm{N{\cdot}NPh}\diagup}\mathrm{H}$ or CHO)

(XI: R′ = $CH(SEt)_2$ or CHO)

Reactions of the reducing group in the polymer (VI) led to partly substituted derivatives, complete substitution being prevented, it is believed, by precipitation of the polymer before the reaction had gone to completion. Thus the polymer phenylhydrazone (IX) had a nitrogen content consistent with approximately two units substituted out of three, and the diphenylformazan (X) prepared from it probably had an even lower degree of substitution. The polymer dithioacetal (XI) had only a half of the calculated sulphur content.

The 3-allyl ether (III) was prepared almost quantitatively by heating di-isopropylideneglucose (I) with allyl bromide in dioxan solution in the presence of sodium hydroxide.[10] The pure ether, however, failed to yield polymer of sufficiently high molecular weight to be precipitated in methanol, when subjected to free-radical initiation in benzene solution or in the absence of solvent, even at high catalyst concentration. A similar effect, caused by degradative chain transfer during polymerisation, has been noted with other allyl ethers.[11,12]

Vinylation of di-isopropylideneglucose (I) with acetylene under high pressure in the presence of potassium hydroxide has been reported[13,14] to give the 3-vinyl ether (IV), which formed a resinous polymer, of very short chain length, after treatment with boron trifluoride dihydrate at 0°.[15] In an attempt to find milder conditions for vinylation, Watanabe and Conlon's[16] transetherification method was successfully applied to the preparation of the vinyl ether (IV), vinyl exchange being used with an excess of isobutyl vinyl ether, catalysed by mercuric acetate. Treatment of the product with sodium was necessary to decompose contaminating organomercury compounds before distillation at a high vacuum. Low-temperature, cationic, heterogeneous polymerisation of the highly purified monomer in hexane–methylene chloride (3 : 1 v/v) with boron trifluoride–ether complex then gave poly-(1,2:5,6-di-*O*-isopropylidene-3-*O*-vinyl-α-D-glucofuranose) (XII) of high molecular weight ([η] 0·65). The product had a low positive rotation ($[\alpha]_D$ +2—5°) which was independent of inherent viscosity, although the use of stannic chloride as catalyst led to polymers with slightly higher rotations ($[\alpha]_D$ +8—13°). Only polymers of low viscosity resulted from homogeneous polymerisation in methylene chloride solution.

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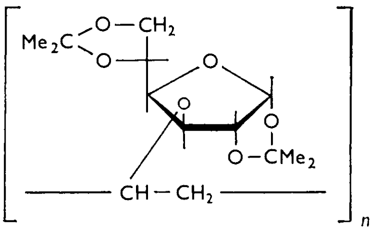
[10] Corbett and McKay, *J.*, 1961, 2930.
[11] Sakurada and Takahashi, *Chem. High Polymers* (Japan), 1954, **11**, 266.
[12] Gaylord, *J. Polymer Sci.*, 1956, 22, 71.
[13] Reppe *et al.*, *Annalen*, 1956, **601**, 81.
[14] Mikhant'ev and Lapenko, *Zhur. obshchei Khim.*, 1957, **27**, 2840.
[15] Reppe and Hecht, U.S.P. 2,157,347/1939.
[16] Watanabe and Conlon, *J. Amer. Chem. Soc.*, 1957, **79**, 2828.

Attempted removal of the isopropylidene groups from the poly(vinyl ether) (XII) in the manner described for the methacrylate polymer caused breakdown, with the liberation of free glucose. No poly-(3-*O*-vinyl-D-glucose) was isolated even under milder conditions, in 50% v/v acetic acid. The reason for this possibly lies in the stereochemistry of the structures involved: study of Catalin models shows that the poly(vinyl ether) has a more closely packed, less flexible structure than that of the polymethacrylate.



(XII)

EXPERIMENTAL

Concentrations were carried out under reduced pressure. M. p.s and polymer melt temperatures were determined on a Kofler microscope stage. Isolated compounds were dried at 20°/0·5 mm. over phosphoric oxide. Unless otherwise stated, specific rotations were measured for tetrachloroethane solutions at 20° in a 2-dm. tube; inherent viscosities $\{[\eta] = c^{-1}\ln(\eta_{\text{soln.}}/\eta_{\text{solv.}})dl./g.\}$ were measured in tetrachloroethane (*c* 0·5 g./100 ml.; 25°). Percentage concentrations are given on a weight/volume basis, unless expressed otherwise. Acetyl content was determined both by Kunz and Hudson's [17] and by Whistler and Jeanes's method.[18] Partition chromatography was carried out on Whatman No. 1 paper (descending development) with butan-1-ol–ethanol–water (40 : 11 : 19 v/v), and benzidine–trichloroacetic acid spray [19] was used for detection.

Liquid reagents were purified by drying, where necessary, and redistillation; solid materials were recrystallised. Special care was taken with (i) tetrachloroethane, which was purified by Vogel's method [20] except that distillation was carried out under reduced pressure (b. p. 60°) to avoid decomposition, (ii) methylene chloride, which was dried over calcium chloride for several months before distillation, and (iii) mercuric acetate, which after recrystallisation was washed with ice-cold water until free from acetic acid.

1,2:5,6-*Di*-O-*isopropylidene*-3-O-*methacryloyl*-α-D-*glucofuranose*.—A stirred solution of di-*O*-isopropylidene-D-glucofuranose (20 g.) and methacrylic anhydride (20 ml.) in pyridine (100 ml.) was heated at 65° for 3·5 hr. and for a further 1 hr. with water (50 ml.) added. After 17 hr. at 30°, the mixture was extracted with light petroleum (b. p. 30—40°; 3 × 100 ml.), and the combined extracts were washed with 5% sodium hydroxide solution and water (3 × 100 ml.) and dried (Na_2SO_4). Tetrachloroquinol (0·020 g.) was added before the extract was concentrated to a syrup, which was twice distilled to give the *methacrylate* in 50—70% yield. The ester was also obtained by treatment of di-*O*-isopropylidene-D-glucofuranose with methacryloyl chloride and pyridine, and by treatment of the 3-potassio-salt of di-*O*-isopropylidene-D-glucofuranose with methacryloyl chloride in light petroleum (b. p. 60—80°), in 33% and 47% yield, respectively. The colourless syrup had b. p. 106—108°/0·2 mm., n_D^{18} 1·4614, $[\alpha]_D$ −37·0° (*c* 1 in EtOH), −40·0° (*c* 1 in $CHCl_3$), −32·2° (*c* 1 in tetrachloroethane), $\nu_{\max.}$ 1650 (C=C),[21] 1735 (ester C=O) cm.$^{-1}$ (Found: C, 57·9; H, 7·1. $C_{16}H_{24}O_7$ requires C, 58·5; H, 7·4%). It slowly crystallised at 0° to form plates, m. p. 34—35°.

Polymerisation of 1,2:5,6-*Di*-O-*isopropylidene*-3-O-*methacryloyl*-D-*glucofuranose*.—Before polymerisation, crystalline monomer (53·7 g.) was dissolved in light petroleum (b. p. 30—40°; 200 ml.), and the solution was washed with 5% sodium hydroxide solution (5 × 100 ml.), dried

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[17] Kunz and Hudson, *J. Amer. Chem. Soc.*, 1926, **48**, 1978.

[18] Whistler and Jeanes, *Ind. Eng. Chem., Analyt.*, 1943, **15**, 317.

[19] Whelan, Bailey, and Roberts, *J.*, 1953, 1293.

[20] Vogel, " A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1956, p. 176.

[21] Davison and Bates, *J.*, 1953, 2607.

(Na_2SO_4), and concentrated to a syrup which was twice distilled in the presence of tetrachloroquinol (0·050 g.). The highly purified monomer (40·84 g.) was dissolved in benzene (41 ml.) and polymerised at 70° ± 0·1° for 24 hr. with azobisisobutyronitrile (0·408 g.) under nitrogen. Polymer was precipitated by pouring the viscous solution, after dilution with benzene (41 ml.), into stirred methanol (2 l.). The white solid (32·57 g.) was centrifuged, washed thoroughly with methanol, and dried. Reprecipitation in methanol (2 l.) from a solution in benzene (80 ml.) yielded *poly-*(1,2:5,6-*di-*O-*isopropylidene-*3-O-*methacryloyl-α-D-glucofuranose*) as a white powder (31·21 g., 76%), soluble in benzene, acetone, chloroform, and tetrachloroethane, $[\alpha]_D$ $-47·6°$, [η] 0·50, polymer melt temperature 198—202°. There was no evidence of unsaturation at 1650 cm.$^{-1}$ in the infrared spectrum [Found: C, 58·3; H, 7·35. $(C_{16}H_{24}O_7)_n$ requires C, 58·5; H, 7·4%].

Poly-(3-O-*methacryloyl-*D-*glucose*).—The above polymer (20 g.) was heated with N-hydrochloric acid (400 ml.) at 100° for 2 hr. with rapid stirring while acetone was allowed to escape. The insoluble gel was centrifuged and washed with water (3 × 200 ml.), and the combined solution and washings were neutralised with 4N-sodium hydroxide. After dialysis to remove sodium chloride, the solution was filtered through kieselguhr before concentration to 100 ml., and was poured into ethanol (670 ml.). *Poly-*(3-O-*methacryloyl-*D-*glucose*), was centrifuged off, washed with ethanol and ether, and isolated as a white powder (9·74 g., 64%); a further quantity (1·47 g., 10%) was obtained from rehydrolysis of the insoluble gel. The product strongly reduced Fehling's reagent; it darkened at >185° but did not melt, and had $[\alpha]_D$ +50° (*c* 0·53 in H_2O), [η] 0·42 (*c* 0·53 in H_2O) [Found: C, 48·1; H, 6·4. $(C_{10}H_{16}O_7)_n$ requires C, 48·4; H, 6·5%]. It was soluble in dimethylformamide but insoluble in most organic solvents.

Poly-(*tri-*O-*acetyl-*3-O-*methacryloyl-*D-*glucose*).—Poly-(3-*O*-methacryloyl-D-glucose) (1 g.), dissolved in dimethylformamide (50 ml.), was treated [22] with pyridine (6 ml.) and acetic anhydride (12 ml.) at 20° for 24 hr., then poured into water (400 ml.). The precipitate was centrifuged off, washed with water, dried, and reprecipitated from solution in chloroform (15 ml.) with light petroleum (b. p. 40—60°; 150 ml.). The *triacetate* was a white powder (1·324 g., 88%), $[\alpha]_D$ +43°, [η] 0·38 [Found: C, 51·3; H, 6·2; Ac, 32·5. $(C_{16}H_{22}O_{10})_n$ requires C, 51·3; H, 5·9; Ac, 34·5%].

Poly-(3-O-*methacryloyl-tri-*O-*methyl-*D-*glucose*).—The polymer (VI) (0·2 g.) was dissolved [23] in dimethylformamide (8 ml.), methyl iodide (3 ml.), and silver oxide (3·0 g.) were added in portions, and the mixture was shaken at 20° for 17 hr. The residue was extracted with dimethylformamide (10 ml.) and chloroform (10 ml.), and the combined solution and extracts were treated with 1% potassium cyanide solution (100 ml.) and extracted with chloroform (5 × 20 ml.). The combined chloroform extracts were washed with water, dried (Na_2SO_4), and concentrated to 10 ml. before being poured into light petroleum (b. p. 40—60°; 100 ml.). The partially methylated polymer (0·151 g.; OMe, 30·0%) was further methylated by five treatments with methyl iodide (10 ml.) and silver oxide (1 g.) at 45° for 6 hr., to give the tri-*O*-methyl derivative as a white powder (0·111 g., 47%), $[\alpha]_D$ +18°, [η] 0·20 [Found: C, 53·8; H, 7·2; OMe, 32·55. $(C_{13}H_{22}O_7)_n$ requires C, 53·8; H, 7·6; 3OMe, 32·1%].

Poly-(3-O-*methacryloyl-tri-*O-*phenylcarbamoyl-*D-*glucose*).—A solution of the polymer (VI) (0·200 g.) in dimethylformamide (10 ml.) was heated with phenyl isocyanate [24] (1 ml.) at 100° for 3 hr. and poured into ethanol (100 ml.). The precipitate was treated again in the same way to yield a pale brown powder (0·393 g.), which was reprecipitated by light petroleum (b. p. 40—60°; 100 ml.) from acetone (10 ml.). The white *triphenylcarbamate* (0·375 g., 77%) had $[\alpha]_D$ +26°, [η] 0·32 [Found: C, 60·9; H, 5·1; N, 6·9. $(C_{31}H_{31}N_3O_{10})_n$ requires C, 61·5; H, 5·2; N, 6·9%].

Oxidation of Poly-(3-O-*methacryloyl-*D-*glucose*). An aqueous solution (50 ml.) of the polymer (VI) (0·500 g.), 2M in acetic acid and 0·4M in sodium chlorite,[25] was kept in the dark at 20° until the rotation was constant ($[\alpha]_D$ +2°; 26 hr.) and then dialysed to remove chlorite, chlorine dioxide, and acetic acid before concentration and deionisation with Amberlite IR-120(H^+) resin (10 ml.). Freeze-drying of the eluate afforded the polyacid as a non-reducing white solid (0·483 g., 91%), which gave 83% of the calculated carboxyl content on titration.

The polyacid (0·1 g.) was treated with 0·01N-sodium hydroxide (50 ml.) for 2 hr. at 20° and

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[22] Schlubach and Repenning, *Angew. Chem.*, 1959, **71**, 193.

[23] Kuhn, Trischmann, and Löw, *Angew. Chem.*, 1955, **67**, 32.

[24] Bouveng, *Acta Chem. Scand.*, 1961, **15**, 87.

[25] Davidson and Nevell, *J. Textile Inst.*, 1955, **46**, T407.

dialysed against distilled water after neutralisation with 0·01N-sulphuric acid. The dialysate was concentrated and freeze-dried, to yield the sodium salt as a white solid (0·079 g., 73%), $[\alpha]_D$ +3° (*c* 0·45 in H_2O), $[\eta]$ 0·45 in H_2O [Found: Na, 8·0. $(C_{10}H_{15}O_8Na)_n$ requires Na, 8·0%].

A 0·5% aqueous solution (3 ml.) of the sodium salt of the polymer acid mixed with 1% aqueous solutions (3 ml.) of various salts gave insoluble salts with most multivalent cations, notably calcium, barium, copper, and lead, and gave a slight precipitate with silver.

Phenylhydrazone Formation.[26]—The polymer (VI) (0·1 g.), dissolved in 10% (v/v) acetic acid (10 ml.), was treated with freshly distilled phenylhydrazine (1 ml.). The orange precipitate which separated immediately was washed with 10% acetic acid and ethanol, and dried to a yellow powder, the polymeric phenylhydrazone (0·102 g.) [Found: N, 6·0. Calc. for $(C_{16}H_{22}N_2O_6)_n$: N, 8·3%. Substitution of two of three units in the polymer requires N, 6·1%].

Diphenylformazan Formation.—A solution of freshly distilled aniline (2·5 g.) in 18% w/w hydrochloric acid (12·5 ml.) at 0—5° was treated [27] with sodium nitrite (2·0 g.) in water (4 ml.), dropwise with stirring, and then diluted to 25 ml. A portion (1 ml.) of this solution was added dropwise with stirring to the phenylhydrazone (0·1 g.) in 1 : 1 pyridine–ethanol (10 ml.) at −5°. After 10 min., the bright red precipitate, which separated immediately, was poured into ice–water, set aside overnight, centrifuged off, washed with water, and dried to a red powder (0·128 g.) [Found: N, 8·4. Calc. for $(C_{22}H_{26}N_4O_6)_n$: N, 12·7%. Substitution at every second unit requires N, 8·1%].

Diethyl Dithioacetal Formation.—Ethanethiol (0·5 ml.) was added to a solution of the polymer (VI) (0·1 g.) in 11N-hydrochloric acid (5 ml.) at 0° and shaken for 1 hr. at 0° before neutralisation in the cold with concentrated ammonia solution (*d* 0·880; 3 ml.).[28] The resulting white precipitate was washed with water and dried to a white powder (0·051 g.) [Found: S, 9·3. Calc. for $(C_{14}H_{24}O_6S_2)_n$: S, 18·1%].

3-O-*Allyl*-1,2:5,6-*di*-O-*isopropylidene*-α-D-*glucofuranose.*—The allyl ether, prepared as described by Corbett and McKay,[10] had b. p. 88°/0·08 mm., n_D^{20} 1·4578, $[\alpha]_D$ −27·1° (*c* 2·5 in EtOH), −28·8° (*c* 2·5 in $CHCl_3$).

1,2:5,6-*Di*-O-*isopropylidene*-3-O-*vinyl*-α-D-*glucofuranose.*—Di-*O*-isopropylidene-D-glucofuranose (25 g.), mercuric acetate (6·25 g.), and isobutyl vinyl ether (250 ml.) were refluxed for 6 hr.,[16] and the solution rapidly cooled, washed with 5% sodium hydroxide solution (3 × 100 ml.), dried ($CaSO_4$), and treated with sodium wire (7·5 g.) at 20° for 17 hr. The supernatant liquid was decanted from the solid and, together with light petroleum washings (b. p. 60—80°; 100 ml.), was washed with 5% sodium hydroxide solution (3 × 100 ml.) and dried ($CaSO_4$). The crude product (7·676 g., 28%), obtained by evaporation of the solvents and distillation, was purified by triple distillation over sodium wire to give the pure *ether* (5·938 g., 22%), b. p. 68°/0·008 mm., n_D^{20} 1·4593, $[\alpha]_D$ −23·8° (*c* 1 in EtOH), −30·5° (*c* 1 in $CHCl_3$), −22·8° (*c* 1 in tetrachloroethane), $\nu_{max.}$ 1620, 1645 cm.$^{-1}$ (C=C vinyl ether doublet [19]) (Found: C, 58·6; H, 7·5. Calc. for $C_{14}H_{22}O_6$: C, 58·7; H, 7·75%). Unchanged di-*O*-isopropylidene-D-glucofuranose was recovered in 50—70% yield by extraction of the first sodium hydroxide solution washings with chloroform (3 × 100 ml.).

Polymerisation of 1,2:5,6-*Di*-O-*isopropylidene*-3-O-*vinyl*-α-D-*glucofuranose.*—The vinyl ether (5 g.) was dissolved in methylene chloride (5 ml.)–hexane (15 ml.), the solution cooled to −78°, and boron trifluoride–ether complex (0·120 g.) was added dropwise to the stirred system in 1·5 hr. Polymerisation started. After a further 30 min., concentrated ammonia solution (*d* 0·880; 5 ml.) and methanol (50 ml.) were added and the rubbery polymer was triturated vigorously in this medium, breaking down into a white solid as it approached room temperature. Crude polymer (5·031 g.), after being washed with methanol, was purified by reprecipitation in stirred methanol (500 ml.) from solution in chloroform (50 ml.) containing pyridine (1 ml.). The *poly*-(1,2:5,6-*di*-O-*isopropylidene*-3-O-*vinyl*-α-D-*glucofuranose*) was washed with methanol and dried to a white powder (3·872 g., 77%), soluble in chloroform and tetrachloroethane, with $[\alpha]_D$ +2°, $[\eta]$ 0·65, polymer melt temperature 210—212°, and no evidence of the characteristic vinyl ether doublet at 1620, 1645 cm.$^{-1}$ [Found: C, 58·7; H, 7·9. $(C_{14}H_{22}O_6)_n$ requires C, 58·7; H, 7·75%].

In later polymerisations, to prevent possible degradation by the catalyst on attaining room temperature, the reaction was stopped by the addition of chloroform (45 ml.) and pyridine

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[26] Barry and Mitchell, *J.*, 1954, 4020.

[27] Mester and Major, *J. Amer. Chem. Soc.*, 1955, **77**, 4297.

[28] Wolfrom and Karabinos, *J. Amer. Chem. Soc.*, 1945, **67**, 500.

(5 ml.) at −60°, instead of by the methanol–ammonia treatment. The polymers readily dissolved on warming to room temperature and were reprecipitated in methanol as before.

Attempted Preparation of Poly-(3-O-*vinyl*-D-*glucose*).—The above poly(vinyl ether) (0·5 g.) was heated at 100° for 2 hr. with N-hydrochloric acid (10 ml.), and insoluble material (0·195 g.) was separated from the hydrolysate. Glucose (R_F 0·225) was shown chromatographically to be the major component in the deionised hydrolysate and no polymer was precipitated when the solution was poured into ethanol.

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