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Synthesis and co-polymerization of an unsaturated 1,5-anhydro-D-fructose derivative

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Abstract—An unsaturated derivative, 3,6-di-*O*-acetyl-1,5-anhydro-4-deoxy-D-*glycero*-hex-3-enopyranos-2-ulose (3), was obtained via regioselective elimination and acetylation of monohydrated 1,5-anhydro-D-fructose (1) in a single step reaction. High yield (80%) was achieved without any dimeric by-products. Its co-polymerization to saccharide polymers was investigated with different commercial vinyl co-monomers. Co-polymers were obtained and characterized. © 2004 Elsevier Ltd. All rights reserved.

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1. Introduction

With respect to a sustainable chemistry, unsaturated sugar monomers are useful building blocks for copolymers with special properties like biocompatibility, biodegradability, hydrophilicity/hydrophobicity balance and skin compatibility.

These properties are of major importance in many fields such as pharmaceuticals, drugs and cosmetics. Up to now several saccharide monomers have been investigated in free radical polymerization with a wide range of commercially available co-monomers. Vinylsaccharides give rise to polymers bearing sugar appendages in the side chains. Saccharide derivatives with an exocyclic or endocyclic double bond, like **3**, build saccharide polymers incorporating one or two ring carbon atoms in the backbone of the polymer chain, respectively.^{1–12}

The difficulty in synthesizing enolones, such as 3, from hexuloses (e.g., 1) is that dimerization occurs in concentrated hexulose solutions leading to the formation of

unsymmetrically linked, dimeric hemiacetals (e.g., **5** and **6**),¹³ which undergo acetylation to give stable acetylated dimers instead of the required enolone.

The saccharide monomer 3,6-di-*O*-acetyl-1,5-anhydro-4-deoxy-D-*glycero*-hex-3-enopyranos-2-ulose **3** was first synthesized in 1997 from 1,5-anhydro-D-fructose **1**,^{14,15} which nowadays can be enzymatically produced by degradation of α -(1 \rightarrow 4)-glucans like starch.¹⁶ The preparation involved an acetylation–elimination reaction to give **3** directly from freeze dried **1** but with low (50%) yields.^{14,15}

The reason for this is the dimerization of dried 1 by ketal formation between 1 and 2. The equilibrium mixture contains only 30% of monomer 1 in pyridine¹⁴ and 40% in Me₂SO.¹⁵ The dimers 5 and 6 react with acetic anhydride and form stable acetylated derivatives without olefinic double bond. Lichtenthaler and co-workers synthesized acetylated 3,2-enolone from monohydrated acetylated uloses and benzoylated 3,2-enolone.^{17,18}

We have now investigated the hydration of 1 in order to shift the equilibrium in favour of 1 and the α -diol 2, which were acetylated in pyridine with acetic anhydride followed by spontaneous elimination to give 3 in high yields (Scheme 1). The pyranoid enolone 3 was

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Scheme 1. Dimerization equilibrium of 1,5-anhydro-D-fructose and synthesis of 3.

investigated in radical co-polymerization reaction in order to produce new types of polymers, based in part on carbohydrates as renewable resources.^{9,10}

2. Results and discussion

It has already been shown^{14,15} that **1** in an aqueous solution exists as the monohydrate **2**. This would make the elimination impossible, because this reaction pathway requires an electron-attracting function like a carbonyl group. It is to be assumed that **1** and its acetylated forms are present in equilibrium in a rather low concentration, although it cannot be detected in ¹H and ¹³C NMR spectra.¹⁶ However the carbonyl form is essential for the elimination step, which is the dominant reaction under appropriate conditions. This is comparable to fructose equilibrium in an aqueous solution wherein the ketose is the reactive species with an amount of less than 1%.¹⁹

Since no acetylated dimer was formed, the yield of 3 could be increased up to 83%. The by-products and solvents were removed by washing and evaporation. The product obtained is used in co-polymerization.

The optimized reaction conditions are room temperature (the reaction rate is too low at lower temperatures), the molar ratio of 1 to water is 1–20, the reaction time 33 h (24 h for the hydration step and 9 h for the elimination step). Degradation occurs at high temperatures (60 °C) and after longer reaction times (24 h) for the elimination step. Further experiments with other bases such as NaOAc in catalytic amounts and Ac₂O as solvent gave low yields only.

2.1. Co-polymerization of 3

The reactivity of both monomers for a co-polymerization should be nearly the same to obtain co-polymers with a homogenous composition. The reactivity is defined as Q-values by Alfrey and Price,²⁰ which indicate the stabilization by resonance of the radical monomer unit at the end of the growing polymer chain. But their electronic effects should differ, so the *e*-values should have opposite signs.

Electron-donating monomers have got negative *e*-values and electron-attracting monomers have got positive ones. Former investigations of enonolactones in co-polymerization showed low reactivity and an electron-attracting effect.^{7–12} The enolone should attract electrons more than the enonolactones, because the +M-effect of the endocyclic oxygen in allylic position is weaker than that of the carboxylic group in an enonolactone (Scheme 2).

For this reason the electron-donating vinyl compounds 1-vinyl-2-pyrrolidone 7, vinyl butyl ether 9 and vinyl acetate 11 were used as co-monomers (Scheme 3).

The polymerizations were carried out in bulk with different monomer feed composition. Two radical initiators, 2,2'-azoisobutyronitrile (AIBN) and benzoyl peroxide (BOP), with different decomposition rates were used in every reaction to make sure that radicals are available during the whole reaction time. The molar ratio of radical initiators with respect to the monomers was constant. The homopolymerization of **3** is sterically hindered. The homopolymer was detected only by TLC, but could not be isolated until now.¹¹ The monomer decomposed when the reaction time was extended. This corresponds to former investigations of homopolymerizations of saccharide monomers with an endocyclic double bond.⁷⁻¹² The glass transition temperature (T_g) of the homopolysaccharide should be in a range of 200-300 °C. It has been demonstrated previously in a few experiments, that co-polymers of 3 can be obtained,



Scheme 2. Structural elements of 3: (a) acrolein-, (b) allylic ether-, (c) vinyl ester-type.



Scheme 3. Scheme of the co-polymers of 3.

but no detailed information on reaction conditions and their influence on products formed was presented.^{9,10}

2.2. Co-polymerization of 3 with *n*-vinyl-pyrrolidone 7

We obtained yields of up to 58 wt % of co-polymer 8 (Scheme 3) with reference to the monomer feed. In general the yield of the co-polymer decreases with an increasing amount of the sugar derivative 3 in the feed. The molar weights extend from 22,950 to 73,310 g/mol with no linear relationship to co-polymer composition or yield (Table 1). Up to 50 mol% of 3 in the feed, the proportion of 3 in the co-polymer is higher than that in the feed. Beyond 50 mol%, there is a limit of around $60 \mod \%$ of 3 in the co-polymer composition. The change in polymer composition is indicated by IRspectroscopy. The increasing content of 3 in the copolymer is demonstrated by the decreasing peak at $1678 \,\mathrm{cm}^{-1}$ for the amide group and the increasing peak at 1230 cm^{-1} for the acetyl-group (Fig. 1). The most important value is the azeotropic composition. It is of technical interest because at this point the compositions of the feed and co-polymer are always equal during a

 Table 1. Yield and properties of co-polymer 8 with different composition of monomer in the feed

| Соро | Compound 3 | | Yield | $M_{ m W}$ | |
|------|----------------|-----------------|--------|------------------|--|
| | Feed (mol%) | Entry (mol%) | (wt %) | (g/mol) | |
| 8.1 | 10.03 | 16.8 | 59 | $4.1 	imes 10^4$ | |
| 8.2 | 20.02 | 36.4 | 43 | $2.7 	imes 10^4$ | |
| 8.3 | 30.00 | 43.3 | 39 | $2.6 	imes 10^4$ | |
| 8.4 | 40.00 | 47.6 | 29 | $2.3 	imes 10^4$ | |
| 8.5 | 47.11 | 48.6 | 33 | $4.2 	imes 10^4$ | |
| 8.6 | 60.23 | 50.8 | 25 | $6.0 	imes 10^4$ | |
| 8.7 | 75.01 | 55.7 | 19 | $6.5 	imes 10^4$ | |
| 8.8 | 84.92 | 57.6 | 10 | $7.3 	imes 10^4$ | |



Figure 1. IR-spectra of 8 with different co-polymer compositions.

reaction even at high conversions. For 7 as co-monomer, it is a molar ratio of 46.3% of 3 in the feed. A T_g was not detected. It would be in the range of 200– 300 °C, but the polymers decompose before showing any DSC trace.

2.3. Co-polymerization of 3 with butyl vinyl ether 9

Compound 9 is a more hydrophilic co-monomer and has a lower tendency than 7 for homopolymerization. A statistical co-polymer should be formed. The amount of 3 integrated into the co-polymer composition is rather high even at low content of 3 in the feed (Table 2). The highest yield is up to 41.0 wt% and the azeotropic monomer ratio is 48.3 mol% of 3. At this ratio the amount of both co-monomers in the feed and in the copolymer are equal. The average molecular weight (M_W) increases linearly with an increasing amount of 3 in the co-polymer.

The T_g of a co-polymer is limited by the T_g 's of the homopolymers. The T_g of poly(vinyl butyl ether) is of about $-55 \,^{\circ}\text{C}^{22}$ and that of the homopolysaccharide should be in a range of 200–300 °C. However the T_g of **9** does not fit a Gordon–Taylor trend. It decreases with an increasing amount of **3** in the co-polymer composition and also with an increasing M_W . It is assumed that the

 Table 2. Yield and Properties of co-polymer 10 with different compositions of monomer in the feed

| Соро | Compound 3 | | Yield | $M_{ m W}$ | $T_{\rm g}$ |
|------|----------------|-----------------|--------|-------------------|-------------|
| | Feed (mol%) | Entry (mol%) | (wt %) | (g/mol) | (°C) |
| 10.1 | 10.32 | 35.5 | 14 | $2.0 	imes 10^4$ | 78 |
| 10.2 | 25.49 | 38.8 | 41 | $2.6 	imes 10^4$ | 99 |
| 10.3 | 42.85 | 40.8 | 38 | $3.6 	imes 10^4$ | 92 |
| 10.4 | 66.30 | 52.3 | 14 | $8.3	imes10^4$ | 73 |
| 10.5 | 75.56 | 52.6 | 8 | $9.2 	imes 10^4$ | 67 |
| 10.6 | 88.66 | 76.9 | 6 | $18.4 	imes 10^4$ | 25 |



Figure 2. ¹H NMR-spectra of 10 with a sugar content of 35.5 mol% in the co-polymer composition (10.1).



Figure 3. IR-spectra of 10 with different co-polymer compositions.

branching fraction increase with an increasing amount of **3** due to an increasing number of acetyl groups in the co-polymer composition, which lowers the T_g . Figures 2 and 3 present the ¹H NNR and IR-spectra, respectively.

2.4. Co-polymerization of 3 with vinyl acetate 11

Compound 11 is the least electron-donating co-monomer, but also the least reactive one. The yields are rather low. The reaction time influences the co-polymer composition. For a reaction time of 5 h, feed and co-polymer composition are approximately equal. An increasing reaction time causes an increase of 3 in the co-polymer composition. Figure 4 presents the IR-spectra. The azeotropic feed composition is about 50 mol% 3 to obtain a statistical co-polymer with 11 as co-monomer. Compound 11 has a higher tendency to homopolymerize than 7 and 9. The average molecular weight (M_W) depends on reaction time and feed composition (Table 3).



Figure 4. IR-spectra of 12 with different co-polymer compositions.

 Table 3. Yields and properties of co-polymer 12 with different compositions of monomer in the feed

| Соро | Compound 3 | | Yield | $M_{ m W}$ | $T_{\rm g}$ | Т |
|-------|----------------|-----------------|--------|-------------------|-------------|-----|
| | Feed (mol%) | Entry (mol%) | (wt %) | (g/mol) | (°C) | (h) |
| 12.1 | 14.41 | 14.7 | 30 | $3.8 	imes 10^4$ | 89 | 5 |
| 12.2 | 24.58 | 24.7 | 25 | $4.1 	imes 10^4$ | 80 | 5 |
| 12.3 | 23.18 | 33.6 | 23 | $2.8 	imes 10^4$ | 108 | 5 |
| 12.4 | 35.63 | 35.2 | 17 | $7.4 	imes 10^4$ | 106 | 5 |
| 12.5 | 15.43 | 18.9 | 40 | $2.9 	imes 10^4$ | 80 | 12 |
| 12.6 | 24.62 | 34.3 | 25 | $2.3 	imes 10^4$ | 102 | 12 |
| 12.7 | 35.73 | 38.9 | 18 | $6.0 	imes 10^4$ | 105 | 12 |
| 12.8 | 49.24 | 50.0 | 9 | $9.2 	imes 10^4$ | | 12 |
| 12.9 | 63.65 | 50.0 | 5 | $11.9 	imes 10^4$ | 101 | 18 |
| 12.10 | 75.77 | 57.5 | 2 | $39.9 	imes 10^4$ | 110 | 18 |
| 12.11 | 85.67 | 60.4 | 1 | $19.7 	imes 10^4$ | 86 | 18 |

The M_W in general increases with an increasing amount of **3** in the co-polymer composition for 5 h reaction time. For 18 h the highest M_W 's are obtained, but they decrease with an increasing amount of **3**, with more than 50 mol% of **3** in the feed and the co-polymer composition. The T_g tends to increase from 80 to 110 °C with contents of **3** above 30 up to 60 mol% in the co-polymer, independent of the reaction time. This effect has also been observed with other sugar derivatives as comonomers where T_g values in general tend to increase with the content of sugar derivative in the co-polymer. The T_g does not fit strongly a Gordon–Taylor trend. The reason is that **11** undergoes cross-linking easily. The T_g of poly(VAc) is of about 32 °C.²²

3. Conclusions

The yield of 3,6-di-O-acetyl-1,5-anhydro-4-deoxy-Dglycero-hex-3-enopyranos-2-ulose 3 obtained by acetylation of 1,5-anhydro-D-fructose has been improved significantly (80%). The synthesis and purification is efficient, but may be further optimized especially with respect to a more sustainable chemistry. The potential of 3 as a building block in polymerization has been demonstrated. We synthesized three new types of co-polymers based on 3 and commercial vinyl compounds according to appropriate steric and electronic properties of 3 and the respective co-monomers. The co-polymer composition of each co-monomer was varied to obtain different properties such as molecular weight and glass transition temperature. Other properties such as biocompatibility of the co-polymers will be investigated for utilization in medicine and pharmacy. Besides the synthesis of polymers with other co-monomers to obtain special properties, the acetyl groups could also be removed in order to enhance hydrophilicity. The present work represents first steps in the utilization of the now easily accessible carbohydrate synthon 3.

4. Experimental

4.1. General methods

All experimental investigations were carried out with pyridine (Grüssing), acetic anhydride (Fluka) and vinyl compounds (Fluka) as received. The initiators were dried and stored under argon atmosphere at -8 °C. The co-polymer compositions were determined by elemental analysis, IR- and NMR-spectroscopy. IR-spectra were recorded with KBr pellets at Bio-Rad FTS-25 FT-IRspectrophotometer. NMR spectra were recorded at Bruker AM 400 spectrometer at 400.1 MHz for ¹H and 100.6 MHz for ¹³C-spectra. Chemical shifts are referenced to Si(CH₃)₄ and internal CDCl₃ to $\delta = 7.270$ and 77.00 ppm. Elemental analysis were determined using a Carlo Erba Instrumentazione Elemental Analyzer 1106 with a heat conductivity detector. The average molecular weights and the polydispersities were obtained by gel permeation chromatography with an apparatus of Shimadzu with a refractive index detector RID-6A coupled with a Wyatt Dawn DSP multiangle light scattering detector. Three chromatographic columns operating in series were used for fractionating; one from Polymer Standard Services Gram 3000 10 μ m and the other two from Polymer Laboratories Plgel 5 μ m MIXED-C. The eluent was HPLC-grade THF with a flow rate of 1 mL min⁻¹ at a pressure of 109 bar and a temperature of 35 °C. The glass transition temperatures of the polymers were determined by differential scanning calorimetry with Mettler Toledo calorimeter 12E. The optical rotation were determined with a Dr. Kernchen Elektronik Automation Sucromat Digital Automatic Saccharimeter.

4.2. Synthesis of 3,6-di-*O*-acetyl-1,5-anhydro-4-deoxy-Dglycero-hex-3-enopyranos-2-ulose 3

Freeze-dried 1 (0.600 g (0.0037 mol)) was dissolved in 1.62 g (0.09 mol) distilled water and stirred at room temperature for 24 h. Pyridine (32.4 g, 0.41 mol) and then Ac₂O 10.8 g (0.11 mol) was added at 0 °C. The reaction mixture was stirred at 25 °C for 9h. The solvents and by-products like acetic acid were evaporated. The residue was dissolved in CH₂Cl₂, washed with 4 M HCl, saturated aqueous Na₂CO₃ and water, decoloured with charcoal, dried with Na2SO4 and evacuated under diminished pressure. The yield is 83%. The resulting brown syrup is stored at -8 °C under argon atmosphere. The spectroscopic data are identical to those already published.^{14,15} The optical rotation differs from former published values. $[\alpha]_{\rm D}$ -39.2 (*c* 1.76, CHCl₃). $[\alpha]_{\rm D}$ -43.7 (*c* 1.71, CHCl₃),¹⁴ $[\alpha]_{\rm D}$ -17.7 (*c* 0.34, CH₂Cl₂).¹⁵ FT-IR (KBr) $\nu_{\rm max}$ 2958, 1743, 1711, 1652, 1431, 1370, 1201, 1147, 1047, 1012, 908, 603 cm⁻¹. Anal. Calcd for $C_{10}H_{12}O_6$ (228.2 g/mol) C, 52.63; H, 5.30; O, 42.07. Found C, 52.58; H, 5.33; O, 42.09.

4.3. Co-polymerization of 3 with vinyl compounds

The reaction mixtures were degassed under diminished pressure in liquid nitrogen by two freeze-pump-thaw cycles.²¹ The polymerizations were carried out in bulk under argon atmosphere at 80 °C for 5 h with different monomer feed composition. Benzoyl peroxide (BOP) (1 mol %) and 1 mol % of 2,2'-azobisisobutyro-nitrile (AIBN) with respect to the sum of monomers were used as initiators. The reactions were stopped by cooling and supplying oxygen. The reaction mixtures were dissolved in CH₃Cl and the polymers were precipitated in less polar solvents.

4.3.1. Poly(acAPM-co-VPy) **8.** Besides the monomer and the initiators $30 \mod \%$ of water was added to the reaction mixture. The polymers were precipitated in Et₂O. The feed compositions, yields and properties are

show in Table 1. FT-IR (KBr) v_{max} 2972, 2956, 1742, 1678, 1462, 1422, 1370, 1282, 1230, 1042, 751, 727, 663 cm⁻¹. ¹H NMR (400.1 MHz, CDCl₃) δ 1.0–2.6 (12H, CH₃–, AcO–, H-2', H-3', H-6'), 2.8–3.7 (1H, H-4'), 3.8–6.2 (6H, H-1, H-5, H-6, H-5'); ¹³C NMR (100.6 MHz, CDCl₃) δ 18.0 (C-3'), 21.0 (C-acetyl), 30.0 (C-4'), 35.0 (C-2'), 41.0 (C-5'), 45.0 (C-6'), 50–52 (C-4), 65–70 (C-1, C-5, C-6), 80 (C-3), 168 (–COO–), 171 (–COO–), 175 (C-1'), 200 (C-2).

4.3.2. Poly(acAPM-co-VBE) 10. The polymer was precipitated in 1:1 Et₂O-petroleum ether. The feed compositions, yields and properties are shown in Table 3. FT-IR (KBr) v_{max} 2964, 2936, 1742, 1466, 1430, 1366, 1234, 1150, 1094, 1038, 755, 667, 603 cm⁻¹. ¹H NMR (400.1 MHz, CDCl₃) δ 0.8–1.0 (3H, H-4'), 1.2–1.6 (4H, H-2', H-3'), 1.7–2.3 (8H, CH₃–, AcO–, H-6'), 2.6–3.7 (4H, H-1', H-5', H-4), 3.8–5.1 (5H, H-1, H-5, H-6); ¹³C NMR (100.6 MHz, CDCl₃) δ 14.0 (C-4'), 19.0 (C-3'), 21.0 (C-acetyl), 32.0 (C-2', C-6'), 41.0 (C-4'), 45 (C-1'), 50–52 (C-4, C-5'), 65–80 (C-1, C-3, C-5, C-6), 168 (–COO–), 171 (–COO–), 200 (C-2).

4.3.3. Poly(acAPM-co-VAc) 12. The polymers were precipitated in 1:1 Et₂O-petroleum ether. The feed compositions, yields and properties are shown in Table 3. FT-IR (KBr) ν_{max} 2960, 2904, 2257,1742, 1434, 1366, 1230, 1110, 1030, 910, 759, 647, 603 cm⁻¹. ¹H NMR (400.1 MHz, CDCl₃) δ 1.6–2.3 (11H, acetyl, H-2', H-4'), 3.0–3.2 (1H, H-4), 3.7–5.2 (6H, H-1, H-5, H-6, H-3'); ¹³C NMR (100.6 MHz, CDCl₃) δ 20–22 (C-acetyl, C-2'), 37.0–38.0 (C-4'), 52–54 (C-4), 63–75 (C-1, C-3, C-5, C-2).

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