Novel Polyamides from Disaccharide-Derived Dicarboxylic Acids

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Introduction

As carbohydrates represent 75% of the annually renewable biomass, they are - aside from their traditional uses for food, lumber, paper, and heat - the major bio-feedstocks from which to develop industrially and economically viable organic chemicals and materials that can replace those derived from petrochemical resources [2,3].

Polyamides being million-ton scale industrial products, the generation of their components - diacids and diamines - from renewables, i.e. from carbohydrates has been addressed repeatedly by substituting glucaric acid, galactaric acid [4], and fructose-derived furan-2,5-dicarboxylic acid [5] for petroleum-based adipic and terephthalic acid as one of the monomer components:

Disaccharides such as sucrose, lactose and isomaltulose belong to the least expensive yet multi-ton-scale accessible low molecular weight carbohydrates [3]. Thus, dicarboxylic acids derived therefrom are surmised to have even higher industrial potential as monomer building blocks since the resulting polyamides are apt to combine biocompatibility with biodegradability due to the presence of a readily cleavable disaccharide linkage. These polymers are also deemed to be highly hydrophilic, hence water-soluble - a feature of relevance for medical applications.
Disaccharide Dicarboxylic Acids

Thus, large-scale adaptable preparative protocols were developed for the generation of the diacids 1 - 4 from the respective disaccharides (in brackets):

Sucrose-6,6’-dicarboxylic acid (1)
Because of the persistence of an intersaccharidic water-bridge of the 2°-HO...H₂O...HO-1’ type in aqueous solution [6], oxidation of sucrose with air in the presence of 0.5% Pt/C at 35°C gives an approximate 1:1 mixture of the 6°- and 6’-saccharonic acids which particularly when using large amounts of the Pt catalyst and higher temperature (0-100°C), are further oxidized to the sucrose-6°,6’-dicarboxylic acid 1, isolable in up to 70% yield by continuous electrodialytic removal.
4-O-(β-D-Galactosyl)-D-glucaric acid 6,3-lactone (2)
Of the two primary OH groups in lactobionic acid, the first Pt/air oxidation product of lactose, the CH2OH of the gluconic acid part is oxidized further with high preference (access of the catalyst to the galactosyl-6-OH is obviously sterically hindered by the axial 4-OH). Hence:

Lactose \( \xrightarrow{\text{Pt/air}} \) Lactobionic acid

\( \xrightarrow{\text{water, pH7 75°C}} \) Lactobionic acid

5-O-(α-D-Glucuronyl)-D-arabinonic acid (3) and 5-(α-D-glucuronoloxymethyl)-furoic acid (4)
The industrial production of isomaltulose from sucrose has made it a lucrative target for generating disaccharide intermediates of industrial potential. For example, air oxidation in strongly alkaline solution smoothly provides the glucosyl-α(1-5)-D-arabinonic acid in the form of its lactone (87%, [7]), subsequent Pt/air oxidation the diacid 3 (85%).
Esters and Amides of Disaccharide Acids

**Diesters:** Conversion of the Na salts of 1 - 4 into their respective methyl esters is smoothly and efficiently effected by stirring a suspension in dry MeOH in the presence of MeOH-washed Amberlite IR-120 (H\(^+\) form) and molecular sieve at ambient temperature for 2h; Yields: 85-90%.

In similar fashion, higher alcohols (octanol, dodecanol) gave the respective diesters albeit requiring longer reaction times.

**Diamides:** Simple aminolysis of the dimethyl esters of 1 and 4, or of the mono-methyl ester of lactone 2 (DMF, 60°C), with octyl- and dodecylamine gave the respective diamides in quant. yield, e. g.

Surface-tensidometric evaluations showed all esters and amides to have \( \sigma \) values at cmc point in the 25-40 nM/m range as compared to \( \sigma = 30.4 \) of commercial APG (Alkyl Polyglycoside).

The top value was observed for the isomaltulose-derived di-\( n \)-octylamide.
Polyhydroxypolyamides

Three diamines were used for condensation polymerization with dimethyl ester 1 and 4 as well as monomethyl esters of lactones 2 and 3, namely petroleum-derived 1,6-diaminohexane, phenylenediamine, and the 'green', HMF-derived 2,5-bis(aminomethyl)furan.

Condensation Polymerizations were effected apting conditions used by Kiely [3] previously (aminolysis in MeOH, or DMSO/glycol, or both consecutively), as exemplified by sucrose-

**POLYAMIDES: 3 STEPS AWAY FROM SUCROSE**

The novel disaccharide/diamine hybrid copolymers were characterized by their elemental composition (C, H, N), melting points, glass transition temperature (Tg), average molecular weights (Mn) derived from 'H NMR end-group analysis, and their solubility in water. Results are listed in the table.
Polyhydroxypolyamides prepared from methyl esters of disaccharide dicarboxylic acids and diamines

<table>
<thead>
<tr>
<th>Disaccharide Educt</th>
<th>Polyamide</th>
<th>$M_n^a$</th>
<th>Repeating Units</th>
<th>mp</th>
<th>Water Solubility</th>
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<td>Sucrose</td>
<td><img src="image1" alt="Sucrose" /></td>
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<td>21</td>
<td>172</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Derived from $^1H$ NMR end-group analysis.
Literatur


