Poly(ester-acetals) from Azelaaldehydic Acid-Glycerol Compounds

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Synopsis
Poly(ester-acetals) have been prepared from isopropylideneglyceryl azelaaldehydate dimethyl acetal and from methyl azelaaldehydate glycerol acetal. Acid hydrolysis of isopropylideneglyceryl azelaaldehydate led to oligomeric poly(ester-acetals) with six to seven repeating units and carboxylic acid endgroups from which the sodium salt and the methyl ester could be prepared. The polymer sodium salt showed some surfactant properties. Methyl azelaaldehydate glycerol acetal, a mixture of geometric and structural isomers, was polymerized under typical polyesterification conditions. Lime was the best catalyst found. Molecular weights of 5000 to 12000 were obtained. Some of these polymers contained significant quantities of calcium as the carboxylate salt. A tough elastomer was prepared by heating a poly(ester-acetal) with p-toluenesulfonic acid and zinc oxide.

INTRODUCTION
Methyl azelaaldehydate is one product when methyl esters of fatty acids having unsaturation at the C_9 position are ozonized. Selective modification of either the ester or the aldehyde function through suitable choice of reaction conditions was described earlier, as well as use of this selectivity to prepare polymers.

Four compounds are possible from 1 mole each of methyl azelaaldehydate and glycerol, two glycerol monoesters (I) and two glycerol acetals (II). Each compound is a bifunctional molecule theoretically capable of homopolymerization to give a poly(ester-acetal).

\[
\begin{align*}
\text{CH}_2\text{OCo(CH}_3\text{)}\text{CCHO} & & \text{CH}_2\text{OH} \\
& | \text{CHOH} & | \text{CH}_2\text{OH} \\
& | \text{CH}_2\text{OH} & \text{Ia} \\
\text{CH}_3\text{O} & \text{CHO—CH(CH}_3\text{)}\text{COOCH}_3 & \text{CH}_3\text{O} \\
& | \text{HOCH} & | \text{CH}_2\text{O} \\
& | \text{CH}_2\text{OH} & \text{IIa} \\

\text{CH}_2\text{OH} & \text{CH}_2\text{OCo(CH}_3\text{)}\text{CCHO} & \text{CH}_2\text{OH} \\
& | \text{CHOH} & | \text{CH}_2\text{OH} \\
& | \text{CH}_2\text{OH} & \text{Ib} \\
\text{CH}_3\text{O} & \text{HOCH} & \text{CH(CH}_3\text{)}\text{COOCH}_3 \\
& | \text{CH}_2\text{O} & | \text{CH}_2\text{O} \\
& | \text{CH}_2\text{OH} & \text{IIb}
\end{align*}
\]

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In a preliminary communication we reported the preparation of isopropylideneglyceryl azelaaldehydate dimethyl acetal, a derivative of Ia, and its polymerization by a new technique to oligomeric poly(ester-acetals). We also discussed preparation of compound II (a mixture of isomers) and its polymerization to similar but higher molecular weight polymers. This paper covers further investigations on these monomers and the polymers therefrom. The effects of isomeric structure on polymer properties are described in another paper.

**EXPERIMENTAL**

**Monomer Preparation**

**Isopropylideneglyceryl Azelaaldehydate Dimethyl Acetal.** This compound (III) was prepared by two methods.

\[ \text{III: } \text{CH}_2\text{OCO(CH}_2\text{)}_7\text{CH(OCH}_3\text{)}_2 \]

\[ \text{CHO} \quad \text{CH}_3 \]

\[ \text{C} \quad \text{CH}_3 \]

\[ \text{CH}_2\text{O} \quad \text{CH}_3 \quad \text{III} \]

**Ozonolysis of Monoolein.** Monoolein (IV) was prepared from methyl oleate and glycerol essentially by the method of Mattil and Sims. This monoolein, which contained 80% \( \alpha \)-monoglyceride, was ozonized in methanol, and glycerol monoa azelaaldehydate (Ia) was recovered in 93% crude yield after reduction with zinc and acetic acid. The crude product (30 g) was heated with 100 ml methanol and 100 ml dimethoxypropane at reflux, with 0.1 g potassium bisulfate as catalyst. Methanol and dimethoxypropane were removed on a steam bath under vacuum, the residue was dissolved in methylene chloride, and this solution was washed first with water and then with a saturated salt solution. After the washed solution was dried with sodium sulfate, solvent was removed and the volatile pelargonaldehyde acetal was distilled at ca. 0.1 mm. Distillation of the residue gave a 58% yield of III, bp 156–162°C/0.07 mm, \( \delta_\text{D}^{30} \) 1.4436. Analytical data are given in the following paragraph.

**Alcoholysis of Methyl Azelaaldehydate Dimethyl Acetal with Isopropylideneglycerol.** The procedure of Norris was adapted for this synthesis. Isopropylideneglycerol (13 g, 0.1 mole), methyl azelaaldehydate dimethyl acetal (23 g, 0.1 mole), and litharge (0.2 g) were mixed and heated at 190–222°C for 1 hr until distillation of methanol (2.5 ml, 62% of theory) stopped. The reaction mixture was filtered and distilled. Unreacted iso-
propyldenglycerol (4.0 g) and methyl azelaaldehydate dimethyl acetal (8.6 g) were recovered. The desired product was obtained in 52.8% conversion and 83.8% yield based on unrecovered methyl azelaaldehydate dimethyl acetal. A sample, redistilled for analysis, boiled at 148–150°C/0.05 mm, \( n_D^{30} = 1.4431 \). The infrared spectrum of this product was the same as that of the product obtained by ozonolysis of monoolein with absorption at 1053, 1076, 1126, 1150, and 1190 cm\(^{-1}\), due to the acetal structure, and at 1370 and 1385 cm\(^{-1}\), due to the gem-dimethyl group. The nuclear magnetic resonance spectrum with peaks at \( \delta \) 1.28 (\( \text{CCH}_3 \) ), 1.35 (\( \text{CH}_2 \) ), 2.27 (\( \text{CH}_2\text{C}=\text{O} \) ), and 3.20 ppm (\( \text{OCH}_3 \) ), and with the acetal and glyceryl protons unresolved at 5.5–6.5 ppm agreed with the assigned structure.

Use of sodium methoxide instead of litharge as catalyst gave essentially identical results.

**Anal.** Caled for C\(_{17}\)H\(_{32}\)O\(_6\): C, 61.42%; H, 9.70%. Found: C, 61.74%; H, 9.64%.

**Methyl Azelaaldehydate Glycerol Acetal (IIa,b).** The glycerol acetal of methyl azelaaldehydate (MAzGA) was prepared by the transacetalation procedure reported previously.\(^2\) This procedure leads to a mixture of four isomers as determined by gas–liquid chromatography.\(^6\)

**Polymerization**

**Isopropyldenglyceryl Azelaaldehydate Dimethyl Acetal (III), Hydrolysis Polymerization.** Table I gives details on reaction conditions for a number of hydrolysis polymerizations or hydrolytic transacetalations.\(^1\) In a typical procedure, compound III (34 g) was dissolved in 340 ml of benzene. This solution was stirred magnetically with 340 ml concentrated hydrochloric acid in a water bath at 7–9°C for 1 hr. The benzene layer was separated and washed with ten 250-ml portions of water. The final wash was neutral to universal pH paper. The benzene solution was dried over sodium sulfate. Solvent was removed to leave 17.7 g (77%) of colorless viscous liquid, \( n_D^{30} = 1.4822 \), which set to a semisolid on standing (V, R=H).

The molecular weight, determined in chloroform solution with a vapor-pressure osmometer, was 1530, equivalent to 6.7 repeating units.

To obtain the sodium salt of the polymer, the benzene solution from a smaller (5 g) run was washed with four 25-ml portions of water and with 25 ml of 5% sodium carbonate solution. This last wash caused formation of a thick emulsion, which could be broken only partially by addition of salt and ethanol. After drying over sodium sulfate, the benzene solution was still milky. The solvent was removed under vacuum on a steam bath. To remove residual water more benzene was added and this mixture was
TABLE I
Hydrolysis of Isopropylideneglyceryl Azelaaldehyde Dimethyl Acetal

<table>
<thead>
<tr>
<th>Monomer concentration, %</th>
<th>Temperature, °C</th>
<th>Time, hr</th>
<th>Washed with</th>
<th>Product</th>
<th>% Yield</th>
<th>Molecular wt</th>
<th>nD</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>7-9</td>
<td>1</td>
<td>Water</td>
<td>1.4822</td>
<td>1530</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>24-30</td>
<td>1</td>
<td>Water</td>
<td>1.4736</td>
<td>—</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>23-31</td>
<td>1</td>
<td>Water</td>
<td>1.4717</td>
<td>550</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5-6</td>
<td>1</td>
<td>Water</td>
<td>1.4805</td>
<td>720</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5-7</td>
<td>2</td>
<td>Water</td>
<td>1.4785</td>
<td>820</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>6</td>
<td>Water</td>
<td>1.4760</td>
<td>750</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>5e</td>
<td>1-3</td>
<td>6</td>
<td>Water</td>
<td>1.4784</td>
<td>820</td>
<td>86</td>
<td></td>
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<tr>
<td>10</td>
<td>27-34</td>
<td>1</td>
<td>Na₂CO₃</td>
<td>d</td>
<td>—</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Room</td>
<td>2</td>
<td>Na₂CO₃</td>
<td>1.4550</td>
<td>—</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>26-27</td>
<td>0.25</td>
<td>Na₂CO₃</td>
<td>d</td>
<td>—</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>25-32</td>
<td>1</td>
<td>Na₂CO₃</td>
<td>d</td>
<td>—</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Room</td>
<td>1</td>
<td>NaOH</td>
<td>d</td>
<td>(35)e</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Room</td>
<td>1</td>
<td>NaHCO₃</td>
<td>1.4756</td>
<td>—</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Room</td>
<td>1</td>
<td>Piperidine</td>
<td>1.4875</td>
<td>—</td>
<td>44</td>
<td></td>
</tr>
</tbody>
</table>

* All hydrolyses were run in benzene, except as indicated, with concentrated hydrochloric acid. Wash solutions were 5% concentration.
* Molecular weights of the solid polymer salts have been omitted because of solubility problems in the determinations.
* Methylene chloride was the solvent.
* Solid polymer V, R==Na, was isolated.
* Gel formation probably lowered yield.

stripped. The final residue was 2.7 g (72%) of a white, coarse, foamlike, slightly tacky polymer (V, R==Na), which softened at 105-115°C. On resolidifying, the polymer gave diffraction patterns in polarized light. The molecular weight, determined as above, was 1560, equivalent to seven repeating units. Surface tension measurements of aqueous solutions of V (R==Na) were made with a Du Noüy tensiometer.

Further polymerization of V (R==H) was achieved by heating. After 18 hr at 270-280°C/0.1 mm, a light-yellow, insoluble, infusible gel had formed. Another sample heated at 220-230°C gave after 18 hr an extremely viscous liquid, after 24 hr a soft, tacky solid, and after 36 hr a gel.

For esterification of V (R==H), an ethereal solution of diazomethane was added to a solution of 10.2 g of hydrolysis polymer (mol. wt. 1530, nD 1.4822) in 50 ml of ether until the yellow persisted. A little chloroform was added to give a clear solution. Excess diazomethane was destroyed with acetic acid. The solvents were removed under vacuum. About 200 ml of benzene was added to the residue and then distilled to remove any water or acetic acid. The product was 9.9 g of hydrolysis polymer methyl ester (V, R==CH₃), nD 1.4804. This esterified polymer (2.0 g) was placed
in a side-arm test tube together with about 20 mg of lime. The mixture was heated to 242–253°C/0.1–0.2 mm with nitrogen ebullition for 5 hr to give a light brown, fairly tough, resilient polymer, soluble in chloroform, melting at about 97–104°C.

**Methyl Azelaaldehydate Glycerol Acetal (IIa,b), Polytransesterification.** The isomeric mixture of MAzGA was polymerized in bulk with different catalysts in different proportions (Table II). A continuous stream of nitrogen was passed through the melt during polymerization to keep insoluble catalysts in suspension. Polymerizations were carried out under vacuum, which was slowly increased from 40 mm to 0.1–0.05 mm as the temperature was increased from 240 to 285°C over 4–6 hr. Evolved methanol was collected by a Dry Ice trap in better than 98% yield.

The crude poly(ester-acetal) was dissolved in benzene (1:25), and the solution was filtered through a medium porosity sintered glass filter, then evaporated in a rotary evaporator, up to 140–160°C (0.05 mm). Precipitated polymers listed in Table II were precipitated in methanol from concentrated benzene solution and dried at 150°C/1 mm. Solubilities (Table III) were determined by the procedure of Sorenson and Campbell. Melting points (Table II) were determined with a hot-stage polarizing microscope. Other thermal data also given in Table II were recorded with a Du Pont 900 differential thermal analyzer and 950 thermogravimetric analyzer. Intrinsic viscosities were determined in chloroform at 30°C within a few hours after dissolution, and number-average molecular weights, by vapor-pressure osmometry in benzene at 37°C.

Endgroup analyses were carried out by conversion of hydroxyl endgroups to titratable carboxylic acid endgroups with succinic anhydride. Because titrating dark (high-ash) polymers was difficult, a nonaqueous, potentiometric titration was developed. The polymer sample (ca. 0.2 meq) was dissolved in 75 ml of anhydrous ethyl acetate to which several millimoles of an aliphatic ammonium tosylate, such as tetraethylammonium tosylate, had been added. Solutions of the polymer before (control) and after conversion were titrated under dry nitrogen at room temperature with 0.1N potassium hydroxide in methanol–ethylene glycol (1:10). The glass and calomel electrodes used were equilibrated for several days in solvent containing electrolyte. A range of −70 to −330 mv was observed.

Infrared spectra were obtained from liquid films on KBr disks. Ash was determined by heating the sample at 600°C for several hours and repeatedly treating it with 35% nitric acid.

**RESULTS AND DISCUSSION**

**Monomer Preparation**

Two methods of preparation of glycerol monoazelaaldehydate (Ia) were studied: ozonolysis of monoolein and glycerolysis of a methyl azelaaldehydate acetal. By either method, simple derivatives of the monomeric
| Polymer* | Catalyst | Type | Amt, wt-% | Melting range, °C | Ash, % | $\bar{M}_n$ | TGA analysis maxima, °C | Remarks | TGA temperature, °C | $T_0$ | $T_{10}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Lime | 1 | 78–82 | 2.91 | 7,000 | | | | | 260 | 381 |
| 2 | Pyrolyzed | 1 | 50–62 | 5,580 | | | | | | 231 | 381 |
| 3 | CaCO$_3$ | | | | | | | | | 285 | 385 |
| 4 | Na$_2$CO$_3$ | 1 | 41–47 | 0.16 | 0.29 | 5,110 | | | | 291 | 383 |
| 5 | Lime | 1 | 49–135 | 3.64 | 0.29 | 14,460 | $-22.5$ (6.5) | $-3$ (24) | 80.5 (29) | | |
| 6 | Polymer | 1 | | | | | | | | 261 | 378 |
| 7 | Lime | 1 | 41–105 | 3.19 | 0.27 | 10,500 | $-21$ (18) | 50 (21) | | | |
| 8 | Lime | 0.10 | 43–50 | 0.43 | 5,310 | | | | | 272 | 387 |
| 9 | Lime | 0.01 | 40–50 | 0.70 | 0.30 | 11,600 | $-25$ (9.5) | 50 (35.8) | | | |

TABLE II
Poly(ester-acetals) from Methyl Azelaaldehydate Glycerol Acetal (MazGA)
| 10 | Lim | 0.01  | 45-48  | 0.04 | 3,850 | 272 | 387 |
| 11 | Lim | 0.01  | 42-45  | 0.0  | 4,690 | 306 | 372 |
| 12 | Lim | 0.01  | 45-52  | 0.01  | 0.33 | 8,640 | -28 (12) | 48 (33) |
| 13 | Li  | 0.05  | 42-114 | 0.37  | 0.34 | 6,650 | -21 (11) | 44 (33) |
| 14 | LiOCH₅ | 0.05 | 47-106 | 8.0 | 0.37 | 4,850 | -24 (10) | 44 (22) |
| 14P | 0.08 | 0.37 | 8,810 | 6,180 | -20 (10) | 51 (53) | 256 | 357 |
| 14PA | 0.05 | 10,000 | 6,280 | 15 | Lim | 1 | 49-75 | 5.8 | 0.35 | 7,080 | -22 (19.5) | 51 (34) |
| 15P | 1.43 | 0.35 | 11,390 | 3,610 | -23.5 (13) | 52 (26) | 222 | 376 |
| 15PA | 0.35 | 7,143 | 3,710 | 16 | Lim | 0.02 | 46-54 | 0.07 | 0.37 | 4,320 | -23.1 (10.3) | 52.2 (42.5) | 244 | 370 |
| 16P | 0.05 | 0.38 | 7,575 | 7,870 | -23.5 (19.5) | 49.4 (85) | 229 | 357 |
| 16PA | 0.03 | 0.33 | 7,673 | 7,970 | 46 | 15PA | 0.35 | 7,143 | 3,710 | 16P | 0.05 | 0.38 | 7,575 | 7,870 | -23.5 (19.5) | 49.4 (85) | 229 | 357 |

* P = precipitated polymer; A = polymer had —OH endgroups converted to —OCO(CH₂)₂COOH.

* Vapor-pressure osmosmetry in C₆H₆ at 37°C.

* Endgroup analysis in ethyl acetate at room temperature.

* Heating rate, 10°C/min; range, ca. -100 to 300°C. (On two cycles, range extended slightly beyond Tₘ and Tₙ.) Tₘ = melting point; Tₙ = crystallization temperature; Tₙ = glass transition temperature; ΔT = recovery temperature minus onset temperature.

* Thermogravimetric analysis, heating rate 10°C/min; Tₙ = temperature at start of weight loss; T₁₀ = temperature at 10% weight loss.

* 43% of polymer 5 and 1.35% of polymer 7 did not dissolve.

* Determined in ethyl acetate.

* Determined by gel-permeation chromatography in tetrahydrofuran.
TABLE III

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Time, min&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene chloride</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Chloroform</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Benzene</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Pyridine</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>3</td>
<td>6</td>
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<tr>
<td>Carbon tetrachloride</td>
<td>3</td>
<td>14</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>3</td>
<td>29</td>
</tr>
<tr>
<td>Acetone</td>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1</td>
<td>—</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>1</td>
<td>—</td>
</tr>
</tbody>
</table>

<sup>a</sup>Polymer 15P (Table II), 0.1 g in 2 ml solvent.
<sup>b</sup>1 = Melted or sticky in hot solvent; 2 = soluble in hot solvent, precipitated cold; 3 = soluble in cold solvent.
<sup>c</sup>Time required for dissolution with intermittent stirring.

ester were made in which the aldehyde group was protected as the acetal. By neither method was the monomeric free aldehyde isolated.

Ozonolysis of α-monoolein (IV) proceeded smoothly with no apparent attack on the vic-glycol. Distillation of the crude product gave a viscous, cloudy, yellowish semisolid. Attempted preparation of a 2,4-dinitrophenylhydrazone gave a red oil and a minute quantity of solid with a wide melting range. No solid hydroxyl derivative could be formed.

Because of the apparent heterogeneity of the free aldehyde, isolation as the dimethyl acetal was attempted to minimize possible condensation reactions of the aldehyde function. In the preparation of the dimethyl acetal (VI), dimethoxypropane was used as a water scavenger.\textsuperscript{16,17} Hydrolysis

\[
\begin{align*}
CH_2OCO(CH_3)\text{CH(OCH}_2\text{)}_2 \\
CHOH \\
\text{CH}_4\text{OH}
\end{align*}
\]

VI

of dimethoxypropane furnished acetone, and this liberated ketone reacted with the free hydroxyl groups of the glycerol monoester to form a ketal. The final reaction product was isopropylideneglyceroyl azelaaldehydate dimethyl acetal (III). Infrared and nuclear magnetic resonance spectra were consistent with such a structure.

The alternate route to glycerol monoazelaaldehydate is ester glycerolysis, but to ensure a uniform product of known composition it is necessary to block two of the glycerol hydroxyls,\textsuperscript{18} as well as to protect the aldehyde group. Consequently, isopropylideneglycerol was used in an alcoholysis
reaction with methyl azelaaldehydate dimethyl acetal. This reaction went smoothly to give compound III in good yield.

Hydrolysis of compound III did not give the expected monomer Ia, but III could be used directly in a particular polymerization. Other attempts to prepare compounds I or VI did not succeed, either by glycerolysis of methyl azelaaldehydate dimethyl acetal under conditions for monoglyceride synthesis or by reaction of III with B(OCH₃)₃.

MAzGA (II) was prepared by transacetalation of methyl azelaaldehydate dimethyl acetal with glycerol. This procedure gave a mixture of structural and geometric isomers, the identification, characterization, and polymerization of which are described in another paper.

Polymerization

Isopropylideneglyceryl Azelaaldehydate Dimethyl Acetal. Isopropylideneglyceryl esters of simple fatty acids readily hydrolyze under mild conditions to the corresponding α-monoglycerides. Attempted hydrolysis of compound III with 5% sulfuric acid, however, resulted in recovery of starting material. Treatment with warm 1:1 hydrochloric acid appeared to effect hydrolysis, but the product, a viscous oil, contained only about 20% α-monoglyceride. Further attempts at hydrolysis under a variety of conditions gave similar results. The products were cloudy, viscous oils, many of which turned to gelatinous solids on standing. Refractive indices of the products varied with hydrolysis conditions. Chemical and infrared analyses showed that none of the products contained more than small amounts of α-monoglyceride. Even in reactions carried out at −40°C the free glycerol azelaaldehydate was not isolated.

In acidic media acetals exist in labile equilibrium with their component aldehydes and alcohols. Thus, the conditions for acetal hydrolysis are essentially those for acetal formation. When the ester-acetal was hydrolyzed, the free glycerol ester-aldehyde apparently reacted rapidly with other liberated molecules of glycerol ester-aldehyde, and the product isolated was a poly(ester-acetal) (V, \( R = H \)). The different properties obtained under different conditions can be ascribed to varying degrees of polymerization and to the presence of some monomer (I) or internal acetal (VII), or both, which might also be formed under some conditions.

In a typical hydrolysis-polymerization, a solution of compound III in benzene or in methylene chloride was stirred vigorously with an equal volume of concentrated hydrochloric acid. Without vigorous stirring there was little apparent reaction. When the organic phase was washed
free of mineral acid with water, the recovered polymer was the viscous, water-insoluble oil described. This procedure represents a new polymerization technique for the preparation of poly(ester-acetals) in which the ketal of the glycerol monoesteracetal is converted to a polymer at an aqueous–organic interface. The new technique might be considered similar to interfacial polymerization, because the initial hydrolysis and possibly the subsequent polymerization take place at an interface; however, this hydrolysis polymerization is a homopolymerization with the monomer precursor entirely in the organic phase. The aqueous phase contains only the catalyst for hydrolysis and polymerization. The polymer remains in the organic phase and is recovered from it.

The products were low molecular weight oligomers; the maximum molecular weight was 1530, representing 6.7 repeating units. That the polymerizing chain was terminated by hydrolysis of the ester group was indicated by the following observations.

When the polymer solution was washed with 5% sodium carbonate solution to remove the last traces of mineral acid, an exceedingly stable emulsion formed. The product isolated from this emulsion was a white, foamlke solid that did not melt sharply but only softened at about 110°C. It swelled in benzene, apparently dissolved in chloroform difficultly, but dissolved in water readily. These properties lead to the conclusion that the original polymer (V, R=H) had an acidic group that could be neutralized to form a salt (V, R=Na). The properties of the salt varied somewhat from experiment to experiment, perhaps corresponding to the variations in the acid polymer. Additional confirmation of the presence of the carboxyl end group was found in the esterification of V, R=H, with diazomethane to give a methyl ester V, R=CH₃.

Some effects of varied reaction conditions on properties and yields of polymer are shown in Table I. All the experiments shown were run with concentrated hydrochloric acid. Use of 1:1 concentrated hydrochloric acid:water gave reasonably satisfactory results; more dilute acid gave little hydrolysis, if any.

Optimum conditions consisted of a 10% solution of monomer in benzene stirred with an equal volume of concentrated hydrochloric acid for 1 hr at 7–9°C. Raising the temperature lowered both yield and molecular weight. Lower concentrations of monomer at the higher temperature increased yield. Conducting the reaction near the freezing point of benzene did not improve yields significantly even with longer reaction times. That the low molecular weight was not the result of the freezing solvent was demonstrated by substituting methylene chloride for benzene. Although the yield was higher, molecular weight was affected only slightly.

Experiments in which the salt of the polymer was isolated by washing with aqueous alkali, as outlined above, supplemented those in which acid polymer was isolated. Yields of polymer salt were generally higher than those of acid obtained under comparable conditions. The apparent high
yield was probably caused by inclusion of some inorganic salt with the polymer. Increased hydrolysis time at room temperature may have caused some degradation since the final product was not a solid and yield was low. Reducing the hydrolysis time lowered yield only slightly. Reducing monomer concentration increased yield as in the series with isolation of acid. When the polymer solution was washed with 5% sodium hydroxide, a stable gel formed that made isolation difficult and, accordingly, lowered the yield. Washing with sodium bicarbonate or piperidine, bases weaker than sodium carbonate, also did not give a solid product.

The stability of emulsions formed during isolation indicated that the polymer salt had surfactant properties. Surface tension measurements on aqueous solutions of the polymer sodium salt are summarized in Table IV.

Although the hydrolysis-polymerization technique did not produce high polymers directly, the oligomers could be used as prepolymer. When polymer acid V (R=H), was heated under vacuum (conditions for polymerization of hydroxyacids), the viscosity increased until gelation occurred.

<table>
<thead>
<tr>
<th>Concentration of solution, %</th>
<th>Surface tension at 23°C, dyne/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>72.1</td>
</tr>
<tr>
<td>0.02</td>
<td>50.4</td>
</tr>
<tr>
<td>0.1</td>
<td>47.4</td>
</tr>
<tr>
<td>1.0</td>
<td>45.0</td>
</tr>
</tbody>
</table>

The gelation was the result of crosslinking brought about by the acidic nature of the polymer itself. The polymer ester V, R=CH₃, polymerized to an ungelled, essentially linear poly(ester-acetal) when it was heated under vacuum with lime as catalyst.

**Methyl Azelaaldehydate Glycerol Acetal.** In contrast to the low molecular weight poly(ester-acetals) obtained by the hydrolysis-polymerization method, molecular weights in the range of 5000-10000 were obtained by polycondensation of II. Of the catalysts tested (CaO, PbO, Sb₂O₅, Zn(OAc)₂, Li, Na, Na₂CO₃, LiOCH₃, and CaCO₃) (Table II), lime was best for the polycondensations at 240-285°C and was used in most of the polymerizations described below. The latent crosslinking activity of these poly(ester-acetals) was demonstrated when crosslinked polymers were obtained with use of zinc acetate or excessive heating during polymerization.

When present in amounts of about 1%, lime was bound to the polymer as carboxylate salt, as shown by the ash content of precipitated polymers, the occurrence of carboxylate absorption at 1550 cm⁻¹ in their infrared spectra, and by anomalous molecular weight measurements. A dilute sulfuric acid wash of the polymer was partially successful in removing bound calcium and lowered the ash content by two-thirds.
Agreement was excellent for molecular weight measurements of polymers without bound calcium by vapor-pressure osmometry, gel-permeation chromatography (GPC), and endgroup analysis, but the intrinsic viscosities of these amorphous polymers did not have a simple relationship to molecular weight as in the Mark-Houwink equation. For polymers with bound calcium, the molecular weight by GPC and vapor-pressure osmometry in ethyl acetate was half that by vapor-pressure osmometry in benzene and double that by endgroup analysis. Dissociation of the calcium polymer dicarboxylate in polar solvents as opposed to lack of dissociation in non-polar solvents would explain these anomalous results.

GPC was carried out and interpreted by a commercial laboratory for two precipitated polymers (15P and 16P, Table II) and for one unprecipitated polymer (16, Table II). Since an accurate value for the Q factor (molecular weight per unit Ångström) has not as yet been determined for these polymers, a nominal value of 25, characteristic of polyesters, was selected as most reasonable. The molecular weight ratios \( \overline{M}_w/\overline{M}_n \) for polymers 15P and 16P were 2.15 and 2.16, with \( \overline{M}_n \) 6125 and 7400, respectively. Polymer 16, which contained material of lower molecular weight, had an \( \overline{M}_n \) value of 5000 and a molecular weight ratio of 2.69. The molecular weight distributions for 16P and 16 were essentially identical for the upper 70% of the range. Agreement was excellent among \( \overline{M}_n \) values for polymer 16P determined by GPC, vapor-pressure osmometry, and endgroup analysis.

In differential thermal analyses the polymers melted over a broad range, with endothermic maxima at 45-50°C and glass transitions at -20 to -25°C (Table II). High-ash polymers also had a series of broad and shallow endotherms at 50-145°C. High-ash polymers had a broader, higher melting range and seemed slightly more stable thermally (Table II).

A tough, tan elastomer was prepared from precipitated polymer 14P by heating it to 250-260°C at 0.3 mm for 0.5 hr with 0.05% p-toluenesulfonic acid and 3% zinc oxide filler. This elastomer was only partially soluble in ethyl acetate, benzene, chloroform, or dichloromethane. The swelling ratio was 2295, with 14.9% solubility in chloroform. Corresponding values were 697 and 30.2% in ethyl acetate after 6 days at room temperature. The elastomer had a glass transition at -21°C and endothermic maximum at 47°C.

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References


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