

SHORT COMMUNICATION

Electroinitiated Polyesters from Phthalic Anhydride and Propylene Oxide

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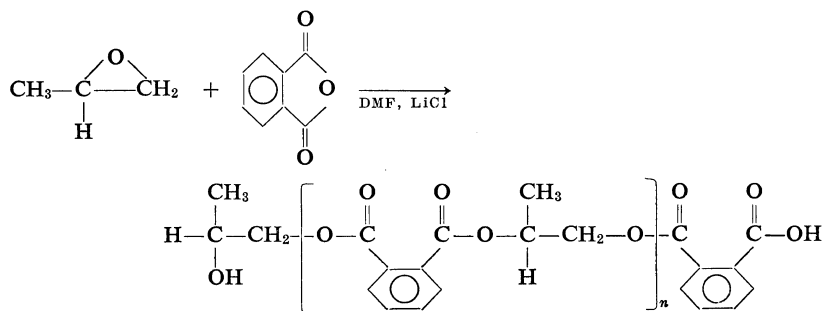
Electroinitiated polymerizations have been applied mostly to vinyl monomers.¹⁻³ For instance, Funt and coworkers⁴⁻⁷ have studied electroinitiated vinyl polymerization of methyl methacrylate, acrylonitrile and styrene. Nonvinyl monomers such as benzene,⁸ pyridine⁹ and substituted xylenes¹⁰ have been electropolymerized by means of anionic mechanism. The initiation occurred by electrons released at the cathode. Recently, electrochemical condensation of 4,4'-diacetyldiphenylethane to polypinacols has been reported by Laube and Higgins.¹¹ No investigations have been carried out related to the synthesis of polyesters from anhydride and epoxides using electroinitiation. In this communication, we wish to present the previously unreported electroinitiated polyester synthesis from the reaction of propylene oxide with phthalic anhydride.

The reaction was carried out in DMF at 25°C using carbon electrodes and LiCl as the electrolyte. At a current density of 20 mA/cm² and at a constant voltage of 10 V applied for 23 hr, a polyester having an average molecular weight of 3500 based on the acid number was obtained.

The polyester yield was about 54%. When the reaction time was extended to 30 hr, the polyester yield increased to about 60%. However, when the current density was varied from 10 to 40 mA/cm², neither the yield nor the molecular weight of the polyester changed.

The IR absorption spectrum of the polyester displayed a strong peak at 1725 cm⁻¹ indicative of the ester carbonyl.¹² This peak was absent in the spectrum of the reactants. Homopolymerization of the epoxide had not occurred as demonstrated from the NMR spectrum of the polyester. The ratio of the methyl to aromatic protons was 3:4. This ratio also suggests that the anhydride had opened the epoxide ring to form the polyester with OH and COOH groups at the two ends of the polyester. A portion of the polyester when hydrolysed with aqueous KOH, gave phthalic acid and 1,2-propanediol.

We believe that the mechanism of initiation of polyesterification occurs as a result of electron addition to phthalic anhydride and thus the anhydride ring opens to form a radical anion. This in turn reacts with the epoxide to form the



polyester. This electroinitiation step is similar to other systems previously reported.^{13,14}

EXPERIMENTAL

In a 500-ml cylindrical pyrex cell 7.5 cm in diameter were placed 100 ml of DMF, 49.0 g (0.3 mol) of phthalic anhydride, 29.0 g (0.5 mol) of propylene oxide, and 1.0 g of LiCl. Two carbon electrodes 0.6 cm in diameter were kept 3.75 cm apart in solution. The leads to the electrodes were placed through a tight-fitting teflon cap which carried a reflux condenser and a gas inlet tube. The solution was flushed for a few minutes with dry nitrogen and placed in a silicone-oil bath maintained at $25^{\circ}\text{C} \pm 0.1$. The solution was agitated by a magnetic stirrer and when it became homogeneous a constant voltage of 10 V was applied for 23 hr by Trigon Electronics model HR 40-750. The current was measured with a Keithley electrometer model 610-Q. During the course of the reaction, the acid values were determined and when this value reached a constant the electrolysis was terminated. Excess propylene oxide was removed under reduced pressure and the residue was poured into 500-ml water. A light-yellow viscous mass separated. This was washed several times with water, dissolved in 500-ml xylene and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the yellow residue obtained was dried *in vacuo* at 50°C for 24 hr; yield, 36 g (54% based on anhydride).

The IR absorption spectrum (film) showed principal bands at 3500 (mw), 2980 (ms), 1725 (s), 1630 (m), 1600 (m), 1580 (m), 1485 (m), 1450 (m), 1380 (m), 1270 (s, broad), 1130 (s), 1065 (s), 850 (mw), 780 (ms), 750 (s), 710 (ms). The acid number of the polyester was 16.

Acetone and tetrahydrofuran each containing 1-% LiCl were also investigated under the conditions described above. In acetone solvent a polymer with an average molecular weight of 2900 (acid number 19.0) was isolated in 42-% yield. In tetrahydrofuran no polymer was obtained.

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