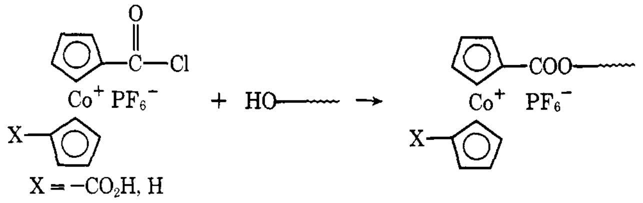
Preparation and Characterization of Polymer III. Monomer I (1.87 g, 4.06×10^{-3} mol) was dissolved in 200 ml of dry, freshly distilled acetonitrile. To this, a solution of 1,4-bis(hydroxymethyl)benzene (0.60 g, 4.35×10^{-3} mol, recrystallized from hexane) in 30 ml of acetonitrile was added over a 20-min period at 0° under a partial vacuum of 150 mm. After the addition was completed, the partial vacuum was maintained for 30 min and then the solution was refluxed in extra acetonitrile for 2 hr. A green solid was obtained upon removing most of the acetonitrile which was only partially soluble in heated acetonitrile. Extraction with acetone gave two fractions. The acetone-soluble fraction was purified by repeated precipitations from acetone into petroleum ether to give a 50% yield of a yellow powder after drying overnight at 20 mm. The acetone-insoluble fraction was soluble in DMF, and it was purified by repeated precipitations from DMF into 30–70 acetone–ether to give a 30% yield of a yellow powder. The acetone-soluble portion darkened in air at 130–160°, while the acetone insoluble fraction darkened only above 200°.

The infrared spectra of the acetone-soluble fraction showed an intense ester carbonyl stretch at 1720 cm^{-1}, no trace of residual acid chloride, and strong C–O stretching bands at 1160 and 1280 cm^{-1}. Other bands appeared at 3130, 1440, 1363, 1035, 971, 872, 833, 792, and 533 cm^{-1}.

Elemental analysis indicated some anion exchange. *Anal.* Calcd: Co, 12.1; P, 6.41; H, 3.29; C, 49.5. Found: Co, 11.4; P, 3.54; H, 3.58; C, 46.8. Exchange of PF_6^- for chloride is indicated by analysis which found 2.71% Cl.

Viscosity measurements[8] in dimethylformamide confirmed that polymeric product had been formed. Intrinsic viscosities between 0.120 and 0.095 dl/g were obtained on a series of polymers prepared as described above. Further confirmation of polymer formation was provided by gel permeation chromatography (using a Waters Associates Model 301 instrument). Applying a universal calibration approach to the calculation of molecular weight from the chromatogram indicated an $\bar{M}_n$ of about 2500. However, the intrinsic viscosity used in these calculations was measured in DMF while the chromatograms were run in THF where the polymer molecules are less solvated and more coiled. A standard calibration with an approximated Q factor indicated an $\bar{M}_n$ of about 3000–4000. High-molecular-weight tailing out to 8000 is observed. It must be concluded that the polymer is a low-molecular-weight species of from 4 to 20 repeating units. Some dimer and trimer are also resolved by gel permeation chromatography.

The synthesis of polyesters from I appears promising, and high-molecular-weight polymers should be obtained when samples of I free of carboxyl groups or traces of monosubstituted derivatives are obtained. Small percentages of carboxyl group in monomer I will cause termination of the polymerization under these mild conditions.[9] To obtain high-molecular-weight derivatives, we are attempting to obtain I of high purity. Alternatively, we are evaluating the use of the dimethyl ester of acid chloride I in transesterification polycondensations.



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(9) The monocarboxylic acid, which is present as a trace contaminant, could be formed from traces of cyclopentadiene in methylcyclopentadiene or by decarboxylation of the dianion of the 1,1′-diacid.

(10) (a) University of Alabama; (b) Huntsville Campus, University of Alabama; (c) Rider College; (d) NSF Undergraduate Research Participant, Bowdoin College, Brunswick, Me., 1967–1969.

C. U. Pittman, Jr.,*[10a] O. E. Ayers,[10a] S. P. McManus[10b]
J. E. Sheats,[10c] C. E. Whitten[10d]
Department of Chemistry, University of Alabama,
Tuscaloosa, Alabama 35486
Department of Chemistry, Rider College
Trenton, New Jersey 08602

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Page 399, column 1, third paragraph. In the section "Synthesis of the Monomer," *nitrate* should read *nitrite*.