

Synthesis of polymers containing crown ether and ferrocene units

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Polyketone containing crown ether and ferrocene moieties was obtained by means of the reaction of 1,1'-ferrocenedicarboxylic acid with dibenzo-18-crown-6 in Eaton's reagent at room temperature. The structure of the polymer was confirmed by various methods. Copyright © 1996 Elsevier Science Ltd.

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Introduction

Since Pedersen's¹ pioneering invention, macrocyclic polyethers, crown ethers and cryptands in particular have attracted considerable interest because of their potential for a large number of applications. The reason for their current development is based on their powerful and selective complexation properties. The syntheses and properties of crown ethers and their large number of derivatives have been studied extensively².

Crown ethers containing ferrocene units have recently received considerable attention in the chemical literature^{3–5}. In general these compounds have been synthesized so that guest metal cations are held close to the ferrocene metal atom. The electrochemical recognition of charged guest species by redox-active ionophores is an area of intense current interest of relevance to the advancement of chemical sensor technology. Thus these ligand systems can be designed to be redox-responsive to the binding of metal and ammonium cations as well as anionic guest species such as halides, nitrate and phosphate. The addition of sodium or potassium cations to electrochemical solutions of redox-active ionophores perturbs the redox potential of the ferrocene/ferricinium couple by a mechanism involving transmission of the electrostatic effect through the π -electron system.

A procedure for acylating benzo crown ether with carboxylic acid functional groups by the action of phosphorus pentoxide in methanesulfonic acid (Eaton's reagent)⁶ as condensing agent and solvent was reported by Bradshaw and co-workers⁷. This method was applied to the synthesis of polyketones containing dibenzo-18-crown-6 units in the main chain by Ueda *et al.*⁸.

To the best of our knowledge, the synthesis of polyketones with both crown ether and ferrocene units in the main chain has not been reported previously. Therefore, we now report the synthesis of a polyketone containing crown ether and ferrocene moieties in the main chain and its model compound, 2,3:11,12-bis(4',4''- or 4',5''-ferrocenoyl benzo)-18-crown-6 (1), using Eaton's reagent.

Experimental

Materials. Ferrocene derivatives and methanesulfonic acid were purchased from Fluka and used as received. Dibenzo-18-crown-6 was synthesized according to the

literature. Eaton's reagent was prepared in a weight ratio of 1/10 (phosphorus pentoxide/methanesulfonic acid).

Synthesis of 2,3:11,12-bis(4',4''- or 4',5''-ferrocenoylbenzo)-18-crown-6 (1). A solution of 0.180 g (5×10^{-4} mol) of dibenzo-18-crown-6 and 0.230 g (10^{-3} mol) of 1-ferrocenecarboxylic acid in 2.4 ml of Eaton's reagent was stirred at room temperature for 24 h, after which the reaction mixture was poured into ice-water and neutralized. The crude product was filtered and washed with water, and dried *in vacuo*. Yield was 0.378 g (96%). It was recrystallized from acetone/heptane (1/1; v/v), yielding red crystals, m.p. 160–180°C. Elemental analysis ($C_{42}H_{40}O_8Fe_2$): calc. C 64.28%, H 5.10%; found C 63.93%, H 5.13%.

Direct polycondensation. To 2.9 ml of Eaton's reagent was added 0.250 g (9.1×10^{-4} mol) of 1,1'-ferrocenedicarboxylic acid and 0.329 g (9.1×10^{-4} mol) of dibenzo-18-crown-6. The reaction mixture was stirred at room temperature for 24 h, diluted with methanesulfonic acid, poured into ice-water, and stirred for 2 h. The red polymer was filtered and washed with hot water and ethanol, and dried *in vacuo*. Yield: 0.51 g (93%). Elemental analysis ($C_{32}H_{30}O_8Fe \cdot \frac{1}{2}H_2O$): calc. C 63.26%, H 5.27%; found C 63.22%, H 5.05%. Inherent viscosity (η_{inh}): 0.13 dl g⁻¹ (in methanesulfonic acid at 30°C with concentration = 0.45 g dl⁻¹).

Measurements. Nuclear magnetic resonance (n.m.r.) spectra were measured on Bruker instruments (at 200 and 250 MHz for ¹H spectra and 52.288 MHz for ¹³C spectra). Infra-red (i.r.) spectra were recorded on a Jasco 5300 FT-IR spectrophotometer. Differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.) were conducted on a Mettler TA 4000 and Netzsch STA 409, respectively. Inherent viscosities were measured with a Cannon-Fenske viscometer.

Results and discussion

The synthesis of 2,3:11,12-bis(4',4''- or 4',5''-ferrocenoylbenzo)-18-crown-6 (1) by direct condensation of 1-ferrocenecarboxylic acid with dibenzo-18-crown-6 was carried out in Eaton's reagent at room temperature in order to demonstrate the preparative utility of the