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Condensation Polymerization of α,α'-Dimethoxycarbonyl-p-Xylylenedicyanide (1) and Oxidation to a Quinodimethane Polymer

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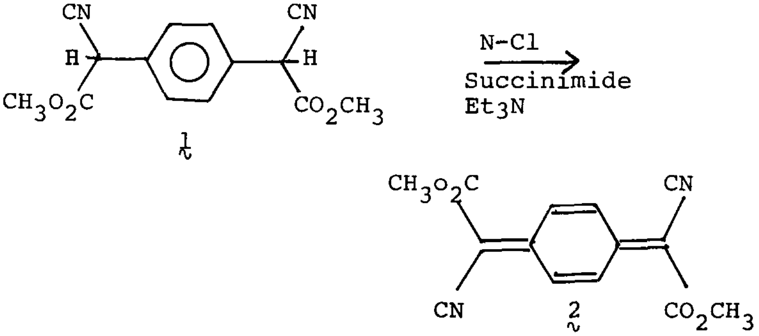
Summary

α,α'-di(methoxycarbonyl)-p-xylylenedicyanide and oxydiethanol were treated with Ti(OBu)$_4$ to produce a linear soluble polyester. Long reaction times led to the formation of an insoluble cross-linked polymer by reaction of the cyano groups.

Treatment of the soluble polyester with N-cholro-succinimide and Et$_3$N resulted in oxidation to a quinodimethane polymer.

Results and Discussion

The high electrical conductivity of the tetrathiofulvalene (TTF)-Tetracyanoquinodimethane (TCNQ) charge transfer complex has prompted work in the area of polymers containing donor and acceptor groups (WEGNER, 1981). To our knowledge there has been only one reported polymer containing TCNQ in the chain backbone (HERTLER, 1976). In the preceding paper we reported the synthesis of 7,8-di(methoxycarbonyl)-7,8-dicyanoquinodimethane (TMCQ) (2) from the facile oxidation of α,α'-di(methoxycarbonyl)-p-xylylenedicyanide (1) (HALL, CRAMER, MULVANEY, 1982).



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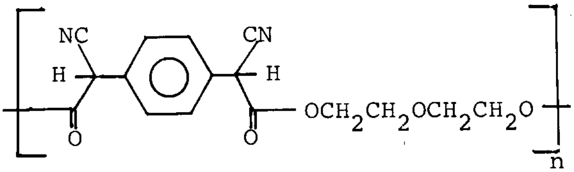
We report here the synthesis of a tractable, well-characterized condensation polymer of 1 which can be oxidized to a polymer containing an electron-accepting quinodimethane unit in the polymer backbone.

Transesterification of 1 with ethylene glycol or 1,4-butanediol under a number of conditions led to cross-linked darkened polymers. However, treatment of 1 with oxydiethanol at 185-190 with Ti(OBu) for a relatively short period of time (~1.5 hr.) yielded a soluble (CH_3CN,DMSO) glassy polyester (3) which formed a somewhat brittle melt-pressed film (Scheme 1).

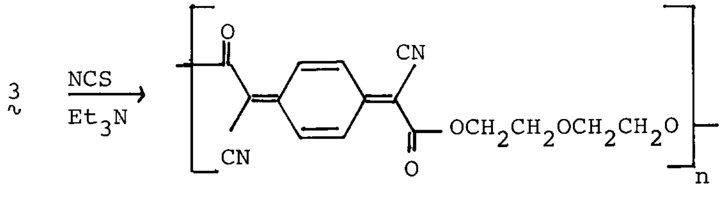
$$1 + HOCH_2CH_2OCH_2CH_2OH \xrightarrow[Ti(OBu)_4]{190^\circ}$$



3

Microanalysis, infrared and 'H-NMR spectra were consistent with structure 3 (see Experimental). Similar results were obtained with tributyl tin acetate or potassium phenoxide as catalysts. Longer reaction times afforded cross-linked polymers which formed gels in CH_3CN or DMSO, most likely due to imino ester formation by reaction of the glycol with the cyano groups.

When an acetonitrile solution of polymer 3 containing N-chlorosuccinimide was treated with Et_3N, in a manner analogous to the oxidation of monomer 1 to monomer 2, a yellow precipitate of polymer 4 was formed in quantitative yield. Although microanalytical data



are consistent with structure 4, the C,H and N contents of 3 and 4 are sufficiently close so that we cannot tell to what extent oxidation to 4 has occurred. Although 4 is considerably less soluble than 3, 4 is partially soluble in DMSO.

When a suspension of 4 in warm CH_3CN was treated with a CH_3CN solution of TTF, the formation of charge transfer complex was indicated by the appearance of the characteristic purple color of the DMCQ (2)-TTF reaction (HALL, CRAMER, MULVANEY (1982).

Methods

Experimental

Polymer 3

To 0.8 g (2.9 mmole) α,α'-di(methoxycarbonyl)-p-xylylene dicyanide melt at 150° under argon was added 1.2 mL (12.6 mmole) 2,2'-oxydiethanol and 5 µL $Ti(OBu)_4$ catalyst. The temperature was raised to 190° and a vacuum of 2 torr was applied for 1.5 hr. The reaction mixture was colled and an amber glassy material was collected, 0.9 g, 90% yield, softening point 185°.

η_{inh} = 0.13; 0.5% con, in CH_3CN

IR (KBr): 2250, 1750 cm^{-1}.

^1H-NMR (DMSO-d_6): δ = 7.5 (s, 4 H), 5.6 (s, 2 H) 4.1 (m, 4 H), 3.4 (m, 4 H) ppm.

Anal calc'd for $C_{16}H_{14}N_2O_5$: C, 61.1; H, 4.4; N, 8.9. Found: C, 61.2; H, 4.7; N, 8.6.

Polymer 4

To 314 mg (1 mmole) of polymer 3 was added 266 mg (2 mmole) N-chlorosuccinimide in 3 mL acetonitrile. After stirring for 5 minutes in an ice bath, 0.01 mL Et_3N was added followed by stirring for an additional 5 minutes. The precipitate was filtered and dried, yielding 310 mg product, dec. 260°, softened 85°, partially soluble in DMSO

IR (KBr): 3500(s), 1720 cm^{-1}.

NMR (DMSO-d_6): 7.90 (s, 4 H), 4.3 (s, 4 H), 3.7 (s, 4 H) ppm.

Anal calc'd for $C_{16}H_{12}N_2O_5$: C, 61.5; N, 3.8; N, 8.9. Found: C, 60.2; N, 3.8; N, 8.6.

Instrumentation

NMR spectra were obtained using a Varian T-60 instrument. Infrared spectra were determined on a Perkin-Elmer 337 grating infrared spectrophotometer. Elemental analyses were performed by Micro Tech, Skokie, Illinois or by the University Analytical Center, Department of Chemistry, University of Arizona, Tucson. Melting points were determined in °C in a Thomas-Hoover melting point appartus and are uncorrected.

Acknowledgement

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