Synthesis of a New Crystalline Polymer: Polymetacyclophane

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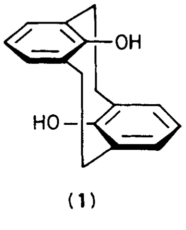
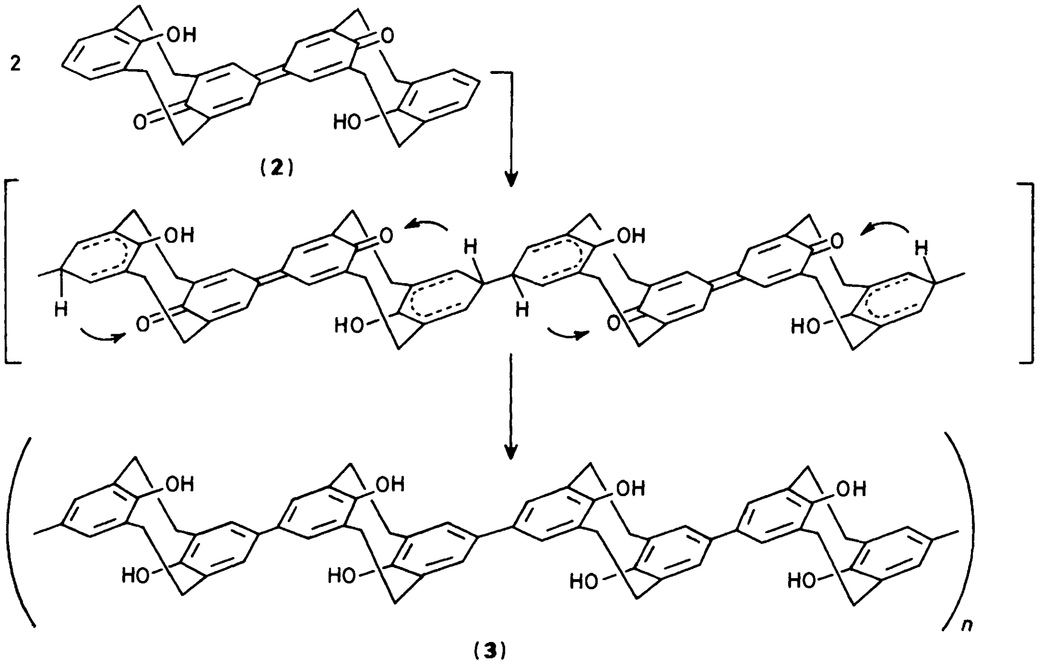
A new cyclophane polymer composed of metacyclophane and phenol moieties was obtained by a new polycondensation reaction of an oxidative dimer of 8,16-dihydroxy[2.2]metacyclophane.

In a recent communication,[1] we reported the first synthesis of a cyclophane polymer which can be electrically conductive through longitudinal π-electron overlap.[2] The starting cyclophane monomer, 8,16-dihydroxy[2.2]metacyclophane (**1**),[3] has also been polymerized *via* a diphenoquinone linkage by oxidative polycondensation with an $FeCl_3$ catalyst. The goal of this study is to create a polycyclophane having an intramolecular quinhydrone interaction along a molecular stacking axis, which, as has been suggested by Vogler *et al.*,[4] can exhibit intrinsic metallic conductivity. However, such a polymer could not be obtained through reduction of the diphenoquinone-metacyclophane polymer.[1] In this communication we report on the second known polycyclophane (**3**) which consists of 4,4′-dihydroxybiphenyl linked metacyclophane units. Although (**3**) is the completely reduced form of the first polymetacyclophane,[1] it was synthesized using a totally different route from the latter and was obtained as well-formed whiskers having oriented molecular chains.

When (**1**) was left in a chloroform solution in the absence of catalyst, very fine whiskers were deposited after about ten days at room temperature. Typically, whiskers had dimen-



(**1**)



Scheme 1. Polymerization mechanism for polymetacyclophane.

sions of about 2 μm × 2 μm × 1 mm and assumed a bright reddish-orange colour characteristic of the diphenoquinone moiety. It was shown from elemental analysis, n.m.r., Fourier transform i.r., and mass spectra that the whiskers had a dimeric structure (**2**). The oxidative conversion of (**1**) into (**2**) proceeded in the presence of dissolved oxygen in chloroform and sunlight but the detailed reaction mechanism is not clear at present. Thermogravimetric analysis of (**2**) in a nitrogen atmosphere showed that (**2**) had abnormally high heat-resistance for a low molecular weight compound. Compound (**2**) did not have a melting point but slowly decomposed at about 400 °C and had a char yield of about 25% at 1000 °C, which suggests a secondary reaction during the heating process. Differential scanning calorimetry showed an exothermic peak at about 300 °C, indicating thermal polycondensation of the dimer (**2**).

Figure 1 shows i.r. absorption spectra of the dimer (**2**) heat-treated at various temperatures. The pristine dimer [Figure 1(a)] has an exceptionally low C=O stretching band at about 1600 $\mathrm{cm^{-1}}$, which is a well known phenomenon for the diphenoquinone skeleton. On heating at 300 [Figure 1(c)]—400 °C [Figure 1(d)], this carbonyl band disappeared and some new features were observed; namely, the absorption bands of a phenolic O–H group at about 3400 and 1200 $\mathrm{cm^{-1}}$ became considerably stronger than those of the pristine dimer. The cyclophane skeleton was not thought to be broken in this temperature region because the absorption band of aliphatic C–H was still retained. At higher temperatures, however, the cyclophane skeleton also started to decompose [Figure 1(e)]. From these results we propose the polycondensation mechanism depicted in Scheme 1. When the dimer (**2**) is thermally polymerized, the hydrogen atoms eliminated from end-benzene rings may reduce the quinone carbonyl groups which are located quite near to the hydrogen atoms. The obtained polymer (**3**) is an all aromatic-type cyclophane polymer. Elemental analysis data agreed well with calculated values. The reaction which includes intramolecular transfer of hydrogen atoms is unique and may be characteristic of the cyclophane compounds.

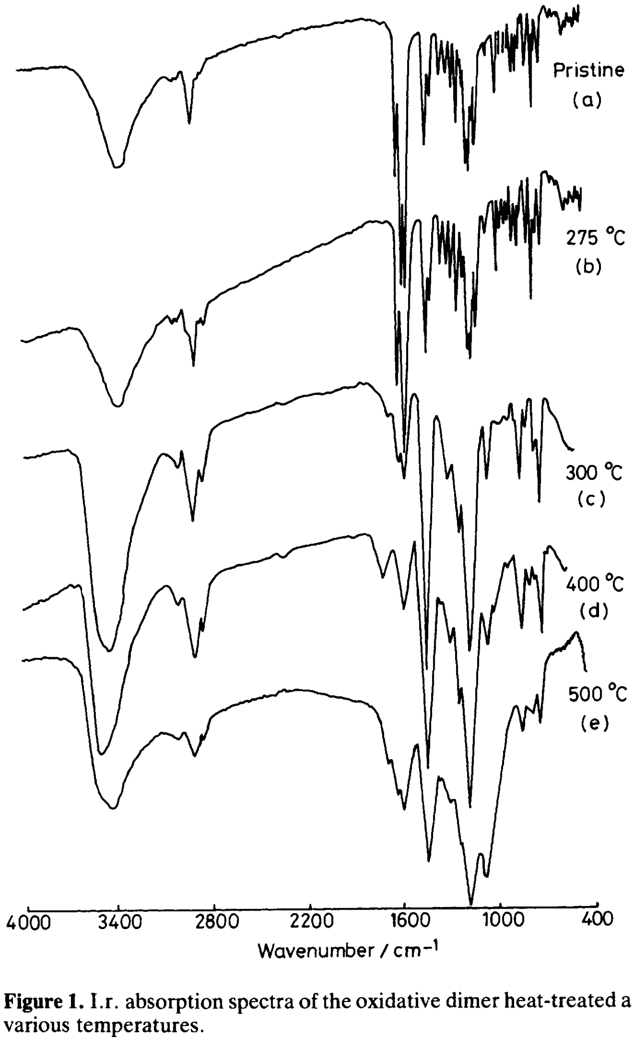


Figure 1. I.r. absorption spectra of the oxidative dimer heat-treated at various temperatures.

This polymer did not dissolve in solvents and did not melt without decomposition, in contrast with the pristine dimer which dissolved in polar solvents such as dimethyl sulphoxide. The polymer had a benzenoid absorption band at about 300 nm which was not observed in quinoid-type compounds and had a long wavelength tailing till 700 nm being attributable to the longitudinal π-electron overlap. The polymer assumed a bright golden colour, suggestive of a highly oriented polymer, which was confirmed by polarizing microscopy. Between crossed polarizers, the golden whisker (**3**) showed a strong birefringence along the whisker axis. The colour with a 530 nm test-plate was blue when the whisker was set along the Z'-axis and yellow along the X'-axis. This indicates that the molecular orientation in the whiskers is parallel to the whisker axis.

Electron diffraction measurement showed that strong diffraction spots exist along the whisker axis and at right angles to the whisker axis. Particularly, the diffraction spots at right angles to the whisker are denser than that along the whisker axis. This agrees very well with the results of polarizing microscopy. However there are strong halos in the electron diffraction pattern, indicating the presence of a non-crystalline phase. Hence, the golden polymer obtained at 300—400 °C is composed of highly oriented macromolecules embedded in an amorphous phase. The electrical conductivity of the polymer whisker was about 10^{-9} S cm^{-1} at room temperature. When doped with H_2SO_4 vapour, a conductivity of 0.25 S cm^{-1} was reached within 10 min. This value is more than 3 orders of magnitude higher than that of the all-quinoid-type polymetacyclophane, which may be the result of both the high electron-donating ability and high crystallinity of the phenol-type polycyclophane.

In conclusion a new polycondensation reaction unique to cyclophane compounds yielded a new polyconjugated system which has repeated metacyclophane and 4,4′-dihydroxybiphenyl moieties as its skeleton.

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