Liquid Crystalline Polymeric Phthalocyanines

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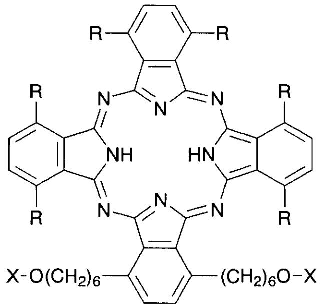
The first examples of phthalocyanine linear mainchain polymers showing liquid crystal properties are described.

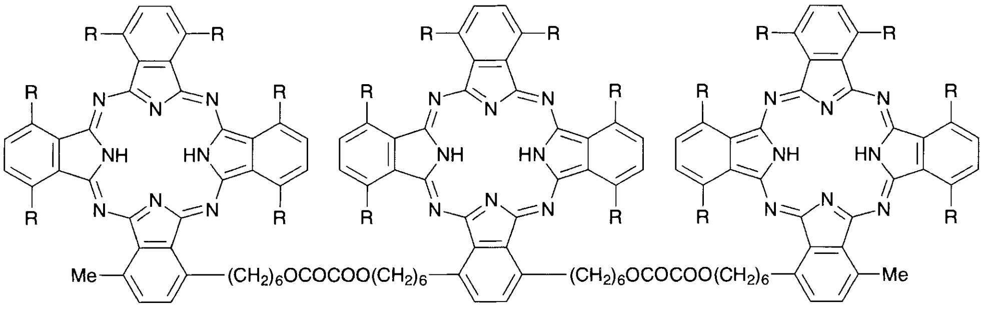
The incorporation of thermotropic liquid crystalline moieties within a polymer can, in principle, provide robust materials possessing interesting optical and electrical properties which are tunable by heating. Most liquid crystalline polymers[1] contain calamitic (rod-like) mesogens but there is a growing interest in introducing discotic mesogens. Liquid crystalline polymers containing the latter fall into three categories. The two more general types are mainchain polymers, where the discs are an integral part of the backbone, and side group polymers where they hang from the backbone like pendants. The third category comprises special cases where the discs can be linked *via* atoms or ligands to a metal atom at the centre of a metallomesogen to give a linear 'shish kebab' polymer. Pioneering work on the first two systems by Ringsdorf's group resulted in the formation of discotic liquid crystalline polymers of triphenylene units.[2,3] The extensive research into liquid crystalline phthalocyanines has centred primarily on mononuclear derivatives;[4] at the present time the most studied mesogenic phthalocyanine polymers are those of the 'shish kebab' type.[5–9] Van der Pol *et al.* constructed cross-linked and side group polymers from peripherally substituted liquid crystalline phthalocyanine monomers. The former retained the mesomorphic packing of the monomer while the latter did not display liquid crystalline behaviour.[10] Recently, we reported that trinuclear phthalocyanines of type **1** exhibit one or more liquid crystal phases.[11] These compounds are mixed oxalate esters of two types of monomeric mesogenic phthalocyanine which bear either one or two hydroxylated sidechains, an example of the latter being **2a**. We now report that polymers formed by esterifying **2a** alone through oxalyl linkages provide the first examples of mesogenic phthalocyanine linear mainchain polymers.

Polymers were generated under two sets of conditions, Scheme 1. In the first, **2a** was reacted with excess oxalyl chloride to form **2b** and the latter reacted with a further equivalent of **2a** in dichlorobenzene at 90 °C for 48 h. The solution was filtered, reduced in volume and the polymer, denoted as poly-Pc1, precipitated by addition of acetone. The second set of conditions, yielding poly-Pc2, were as above but with the addition of pyridine in the first step and a catalytic amount of 4-dimethylaminopyridine in the second step. Both products, poly-Pc1 and poly-Pc2, are soluble in solvents such as THF, pyridine, benzene, toluene, $CHCl_3$ and CH_2Cl_2, but only sparingly so in hydrocarbon solvents such as hexane. They differ in the degree of polymerisation. Fig. 1 shows the differential polymer molecular mass distribution obtained by gel permeation chromatography, GPC. For poly-Pc1, M_w = 7180; M_n = 4140 (polystyrene equivalent molecular mass) and for poly-Pc2, M_w = 157000; M_n = 8740. Both polymers show one or two low molecular mass peaks, presumably arising from oligomers. These have not been characterised further but their presence in apparently significant amounts suggests they are either cyclic or are due to the presence of monoesterified impurity terminating polymerisation. The GPC trace for poly-Pc2 also shows a high molecular mass tail. This, together with the significant amount of low molecular mass material at the other end of the distribution, accounts for the large polydispersity (M_w/M_n) of the sample. The difference in the extent of polymerisation within the two polymers is also apparent from their ^1H NMR spectra. The 400 MHz spectrum ([$^2H_2$]-1,1,2,2 tetrachloroethane) for the lower molecular mass poly-Pc1 shows a signal at δ 3.4 assigned to terminal -CH_2-OH protons whereas there is no comparable signal apparent in the spectrum of poly-Pc2. Integration of the signal in the former against that for the aromatic protons gives a ratio of *ca.* 20:1. This corresponds to an average of *ca.* 10 phthalocyanine units were the polymer a simple linear one but rather fewer if cyclic oligomers are present.

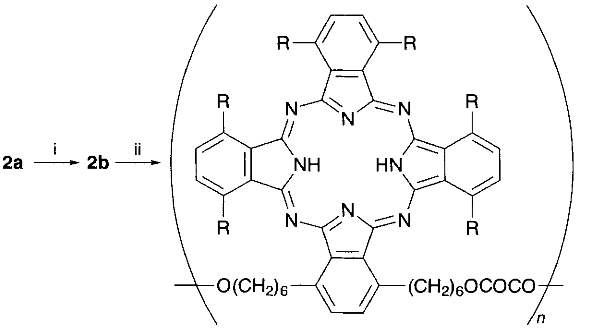
Both polymers exhibit discotic liquid crystal behaviour. Differential scanning calorimeter traces showed a single endothermic peak, at 158 °C for poly-Pc1 and at 161 °C for poly-Pc2, corresponding to transition into the isotropic liquid. On cooling, the two samples displayed a fan type birefringence texture when viewed through a polarising microscope. The textures appeared at 150 °C for poly-Pc1 and 154 °C for poly-Pc2 and grew slowly into small domains. These are maintained



2 R = C_8H_{17}
a X = H
b X = COCOCl



on cooling down to room temperature. Fan textures are characteristic of the hexagonal discotic columnar mesophase which is common among monomeric mesogenic phthalocyanines[4] and was observed for the trinuclear compound **1**.[11] Further evidence that the polymers are developing columnar stacks which mimic those of the simpler mesogens is forthcoming from visible region spectroscopy. Formulations of the polymers as spin coated films were cooled from elevated temperature into the mesophase temperature range where they show broad band absorption with maxima at *ca.* 664–668, 702–706 and a shoulder at *ca.* 731 nm. Band shape and absorption maxima are closely similar to those observed for the disordered hexagonal columnar mesophase of **1** when formulated similarly. Columnar packing in the polymers would limit mobility and could account for their high viscosity and the slow development of birefringence textures.



Scheme 1 Route to poly-Pcs. *Reagents*: i, ClCOCOCl; ii, **2a**

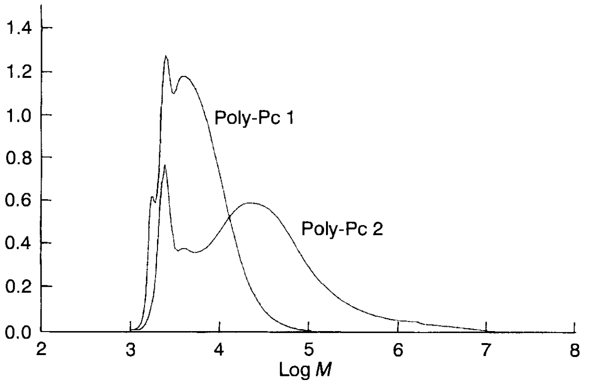


Fig. 1 Gel permeation chromatograms for poly-Pc1 and poly-Pc2

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