

## Spinal Columnar Liquid Crystals based on Octasubstituted Phthalocyanine Siloxane Derivatives<sup>1</sup>

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Dihydroxysilicon(IV) octakis(dodecyloxymethyl)phthalocyanine forms columnar liquid crystal at temperatures ranging from  $-7^{\circ}\text{C}$  to more than  $300^{\circ}\text{C}$ ; polycondensation occurs in the mesophase to yield a series of polysiloxanes which lead to a lamellar liquid crystalline phase.

Dihydroxysilicon(IV) derivatives of unsubstituted phthalocyanines are well known to yield polysiloxanes when heated *in vacuo*.<sup>2</sup> On the other hand, the liquid crystalline properties of phthalocyanines substituted with long alkyl side chains are now well established:<sup>3,4</sup> columnar mesophases are formed by segregation of the rigid aromatic cores and the flexible alkane chains. Herein we report (i) the synthesis and characterization of the mesomorphic properties of a dihydroxysilicon(IV) derivative of octakis(dodecyloxymethyl)phthalocyanine, (ii) the polycondensation of this compound in the liquid crystalline phase into the corresponding polysiloxane oligomers (Figure 1), (iii) the characterization of the oligomers by absorption spectra and gel permeation chromatography (g.p.c.), and (iv) studies of the mesomorphic state of the oligomers by optical microscopy and X-ray diffraction at small angles. The structure of the mesogen led us to propose the term 'spinal columnar liquid crystal' to designate the corresponding mesophases.<sup>1</sup> The only other related work concerns a tetramethoxytetraoctyloxy-phthalocyaninato-siloxane polymer which was shown to form Langmuir-Blodgett films.<sup>5</sup>

The dihydroxysilicon(IV) derivative,  $(\text{C}_{12}\text{H}_{25}\text{OCH}_2)_8\text{PcSi}(\text{OH})_2$  (Pc = phthalocyanine) (**1**), was synthesized by condensing 5,6-bis(dodecyloxymethyl)-1,3-di-iminoisoindoline (4 mol) in the presence of  $\text{SiCl}_4$  in quinoline at  $150^{\circ}\text{C}$ . The dichloro-derivative formed was directly converted into the corresponding dihydroxy-derivative by adding water to the reaction medium. Compound (**1**) was then purified by chromatography over  $\text{SiO}_2$  (eluent  $\text{CHCl}_3\text{-Et}_2\text{O}$  96:4).<sup>†</sup> Optical microscopy showed a birefringent viscous mass between room temperature and  $300^{\circ}\text{C}$  with no visible transition. Differential scanning calorimetry revealed a transition at  $-7^{\circ}\text{C}$  [ $\Delta H$  15 kcal mol<sup>-1</sup> (cal = 4.184 J)]. X-Ray diffraction experiments at small angles were carried out between room temperature and  $150^{\circ}\text{C}$ ; they demonstrated unambiguously that a hexagonal-type columnar liquid crystal is present over this temperature range (intercolumnar distance 30.8 Å). A halo in the range  $q = 1.3\text{--}1.4 \text{ \AA}^{-1}$  ( $q = 4\pi \sin\theta/\lambda$ ) may be related to the 4.5–4.7 Å interalkyl distance characteristic of molten alkane chains.<sup>3</sup> A narrow line observed at 19.8 Å probably corresponds to the previously described 'pincement de Skoulios-de Gennes'.<sup>6</sup>

Polycondensation was achieved by heating (**1**) in the liquid crystalline phase. At  $180^{\circ}\text{C}$ , the formation of dimers was shown by the u.v.-visible absorption spectrum [ $\lambda_{\text{max}}$  ( $\text{CCl}_4$ ) 646 nm]<sup>7</sup> and g.p.c. When heated in air for 7 h at  $180^{\circ}\text{C}$ , g.p.c. yielded the following approximate distribution of products: 30% monomer, 30% dimer, 20% trimer, and 20% higher oligomers<sup>‡</sup> (Figure 2). The X-ray pattern demonstrated a

corresponding major change in the organization state. A lamellar order with a periodicity of 31 Å (three narrow Bragg reflections with 1:2:4 reciprocal spacing) was observed between room temperature and  $60^{\circ}\text{C}$ . Two broad and diffuse outer rings were observed at 4.5 (corresponding to interalkyl chain spacing) and 3.4 Å. The latter is related to the

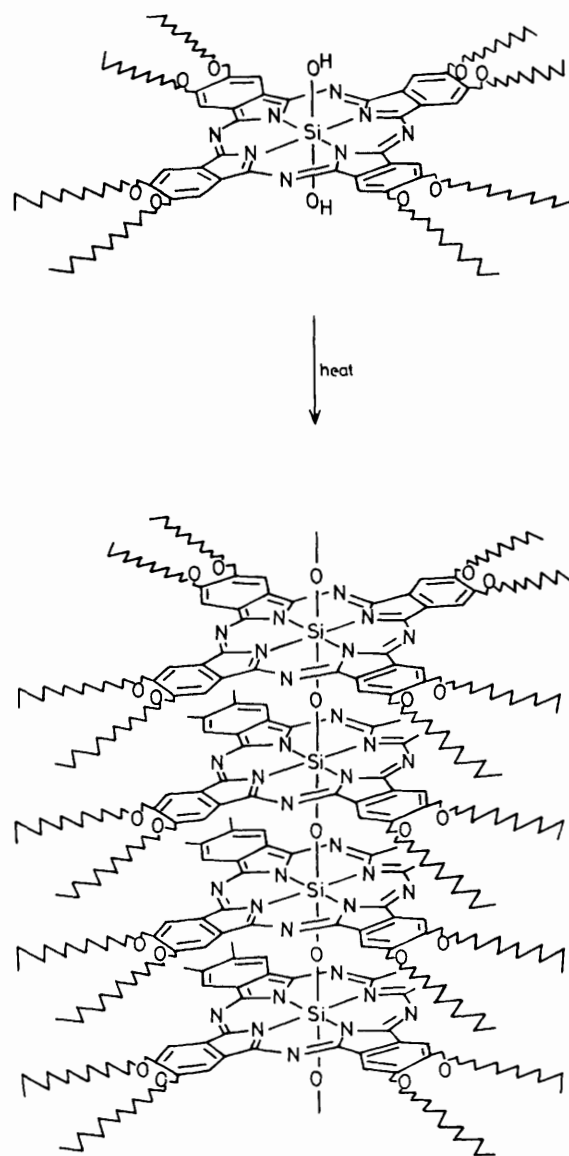
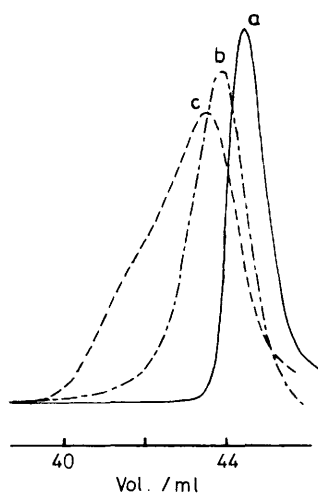


Figure 1. Molecular structures of  $(\text{C}_{12}\text{H}_{25}\text{OCH}_2)_8\text{PcSi}(\text{OH})_2$  (**1**) and the corresponding polysiloxane obtained by polycondensation and dehydration.

<sup>†</sup> The compound (**1**) was characterized by absorption [ $\lambda_{\text{max}}$  ( $\text{CCl}_4$ ) 682 nm], and  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra, and microanalysis (C, H, N, and Si).

<sup>‡</sup> The column (Microstyrigel, eluent: toluene) was calibrated using the monomer (**1**) as reference compound ( $V_e$  44.5 ml). Chromatogram analysis was carried out by combining universal calibration and viscosity law for rigid macromolecules.



**Figure 2.** Gel permeation chromatograms of the products synthesized, showing the absorption at 345 nm vs. the volume of elution: (a) (1); (b) (2), obtained by heating (1) in air for 1 h; and (c) (3), obtained by heating (1) in air for 7 h ( $T = 180^\circ\text{C}$ ).

intermacrocycle distance along the columns. At temperatures higher than  $60^\circ\text{C}$ , optical microscopy and X-ray patterns both indicate the formation of an isotropic liquid.

In conclusion, a new type of oligomeric liquid crystal was synthesized and characterized. Such molecular materials<sup>8</sup> should demonstrate interesting semiconductor properties.<sup>9</sup> Conductivity data for unsubstituted  $\{[\text{PcSiO}]_x\}_n$  in Kevlar fibres have already been reported.<sup>10</sup>

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