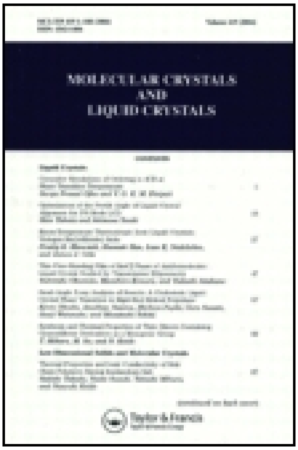

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Polycondensation in Mesomorphic Phases: Spinal Columnar Liquid Crystals Based on Octasubstituted Phthalocyanine Siloxane Derivatives

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POLYCONDENSATION IN MESOMORPHIC PHASES : SPINAL COLUMNAR LIQUID CRYSTALS BASED ON OCTASUBSTITUTED PHTHALOCYANINE SILOXANE DERIVATIVES [1]

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Abstract Within the liquid crystalline domain, dihydroxysilicon(IV) octakis(dodecyloxymethyl) phthalocyanine is polycondensed to give a distribution of polysiloxanes. These latter form a mesophase with lamellar order. For the first time polycondensation has been carried out in a columnar mesophase and a new type of oligomeric mesogen has been obtained. The term spinal columnar liquid crystal is proposed to designate such a mesophase.

INTRODUCTION

Phthalocyanines substituted with long alkane chains have been shown to form columnar liquid crystals over extended ranges of temperature : columnar mesophases are formed by segregation in space between rigid aromatic cores and flexible alkane chains[2,3]. Unsubstituted dihydroxysilicon (IV) phthalocyanines are well known, on the other hand, to lead to polysiloxanes by heating under vacuum[4,5]. This paper is concerned with (i) the synthesis and the study of the mesomorphic properties of an octaalkylsubstituted dihydroxysilicon (IV) phthalocyanine, (ii) its polycondensation in the liquid crystalline state into the corresponding polysiloxane derivative, (iii) its characterization by absorption spectrophotometry and gel permeation chromatography (G.P.C.) (iv) the characterization of the mesomorphic state of the oligomers by optical microscopy and X-ray diffraction at small angles. While disk-like molecules have been used to prepare polymers[6,7], it is the first time that a polymeric backbone surrounded with alkylsubstituted macrocycles is shown to form mesophases : the term spinal columnar liquid crystals has been proposed to designate such mesophases[8].

SYNTHESIS AND CHARACTERIZATION OF THE MONOMER

Dihydroxysilicon (IV) octakis(dodecyloxymethyl) phthalocyanine $(C_{12}H_{25}OCH_2)_8PcSi(OH)_2$ (1) is obtained by condensation of 5,6-bis(dodecyl-oxymethyl) 1,3-diiminoisoindoline[3] in presence of silicium tetrachloride in quinoline at 150°C. The dichlorosilicon (IV) phthalocyanine initially formed is directly hydrolyzed with water at R.T.. (1) is purified by chromatography over SiO_2.

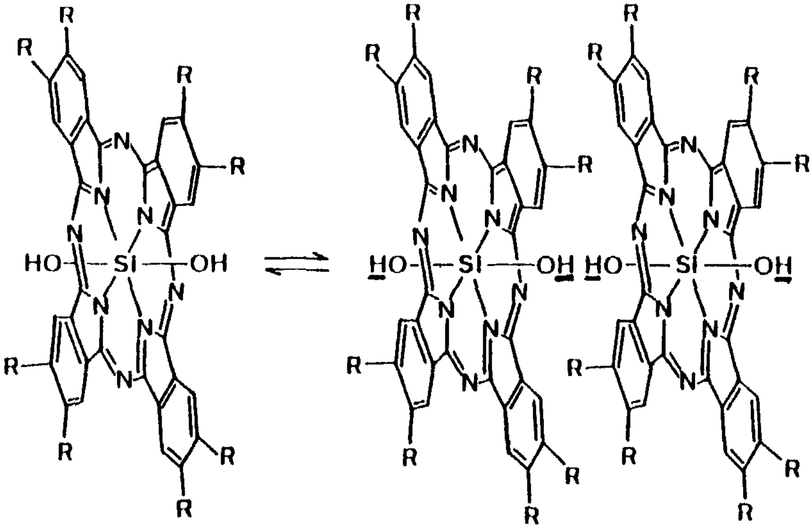

FIGURE 1 Schematic representation of the dimerization of $(C_{12}H_{25}OCH_2)_8PcSi(OH)_2$. The two different types of SiOH (inner and outer) are indicated.

The ^1H NMR spectra of (1) in $CDCl_3$ solution have been carried out as a function of concentration (from 14 mM to 65 mM). Two SiO-H singlets are observed in the upfield region showing a dimerization process (Figure 1) : inner SiO-H gives a peak at -2.35 ppm whereas outer SiO-H yields a peak at 0.1 ppm. By postulating that only monomers and dimers are present, dimerization constant is calculated to be of the order of $4x10^2$M.

Optical microscopy shows a birefringent viscous mass from R.T. to 300°C with no visible transition. D.S.C. reveals a transition at -7°C (ΔH = 15 Kcal M^{-1}). X-ray diffractions at small angles have been carried out at R.T. and 150°C. A series of five sharp Bragg reflections with reciprocal spacings in the ratio $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{25}$ are observed. This is indicative of a classical two-dimensional hexagonal packing of columns (intercolumnar distance : 30Å). A halo in the range q=1.3-1.4 $Å^{-1}$ ($q=4\pi\sin\theta/\lambda$) is related to 4.5-4.7 Å interparaffinic distance for quasi-molten chains. A narrow line at 19.8 Å must correspond to the previously described "pincement de Skoulios-de Gennes"[9].

POLYCONDENSATION IN THE LIQUID CRYSTALLINE PHASE

Polycondensation is achieved by heating monomer (1) in the liquid crystalline phase (Figure 2). U.V.-visible absorption spectroscopy and G.P.C. have been used to characterize the polycondensation process. Samples (2) and (3) have been obtained by heating (1) in air at 180°C for one hour and 7 hours, respectively.

The electronic spectra of oligomers obtained with unsubstituted $PcSi(OR)_2$ are quite sensitive to the number of macrocycles within the polycondensate : blue shifts are observed for Q and B bands when the polysiloxane chain length is increased. In the monomer, Q and B are centered at 665 nm and 351 nm, in the dimer the bands are shifted to 630 and 329 nm and in the trimer to 618 nm and 327 nm, respectively[10]. The same behaviour is observed in the case of oligomerisation of (1)

(Figure 3). In sample (2), bands at 647 nm and 347 nm are observed which can be attributed to the dimer. In sample (3), polycondensation is more complete : the Q band at 646 nm is much larger, its intensity relative to B band has decreased and the remaining monomer concentration is undetectable.

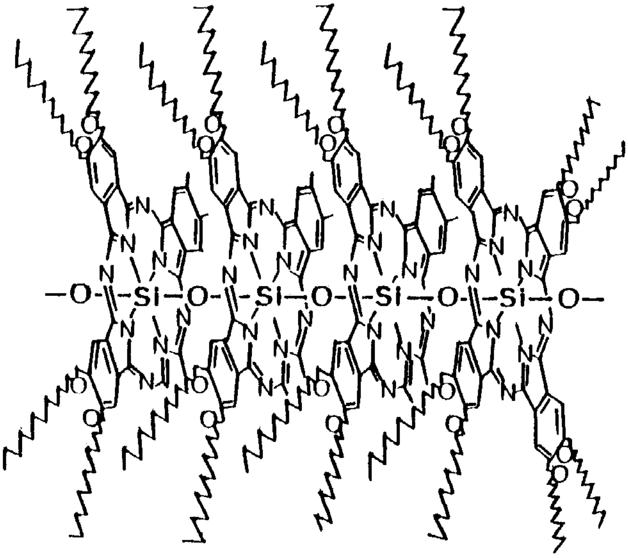

FIGURE 2 Structure of the polysiloxane obtained from (1).

G.P.C. on microstyragel in toluene was carried out using double detection:refractive index and optical density at 345 nm where the extinction coefficients of the oligomers are approximately equal[10] (Figure 4). The monomer is eluted at V_e(1)= 44.5ml. Tonometry in toluene yields M_n = 2.2×10^3g in good agreement with the molecular weight of the monomer M_w=2161.4g :aggregation is therefore not important in toluene. Chromatogram analysis was carried out by combining universal calibration $\log V_H(Å^3) = -0.35 V_e(ml) + 20.4$, viscosity law for rigid macromolecules $\log V_H \; \alpha \; \log M$ and the V_e(1) value previously determined. Sample (2) contains 40%

monomer,40% dimer and 15% trimer.This distribution is in good agreement with the corresponding absorption spectrum.G.P.C. analysis on sample (3) gives by the same procedure:30% monomer,30% dimer,20% trimer and 20% higher oligomers.

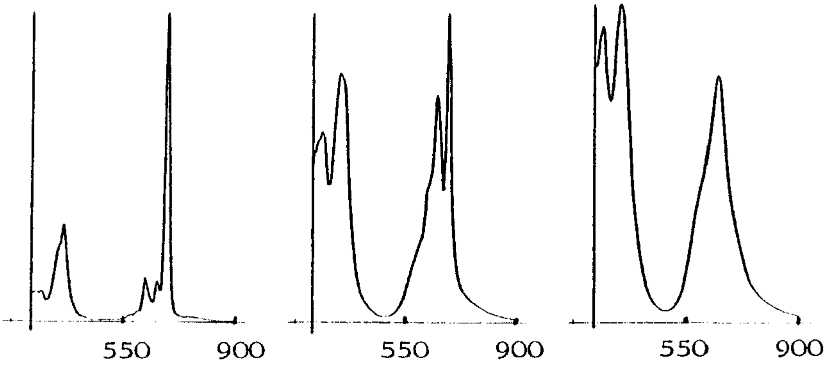

FIGURE 3 U.V.-visible spectra in CCl_4 of (1), sample (2) ((1) at 180°C for 1 hour) and sample (3) ((1) at 180°C for 7 hours) from left to right.

X-ray patterns of sample (3) is dramatically modified as compared to the monomer one : a series of three Bragg reflections with reciprocal spacings in the ratio 1:2:4 is indicative of a lamellar order (interlamellar distance : 31 Å). This is not modified from R.T. to 60°C. Two broad and diffuse outer rings corresponding to 4.5Å and 3.4Å are observed. The first one is characteristic of quasi-molten paraffinic chains. The second one is related to interplanar spacing along the polymeric chains. For temperatures higher than 60°C, optical microscopy and X-ray diffraction both show the formation of an isotropic liquid.

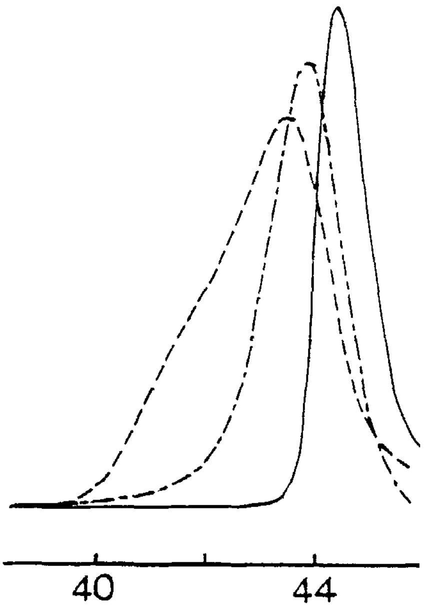

FIGURE 4 Gel permeation chromatograms of (1), samples (2) and (3), from right to left (Microstyragel; eluent: toluene).

CONCLUSION

A new type of oligomeric liquid crystal has been synthesized and characterized. Further studies are in progress to increase the molecular weight of the siloxane polymer obtained.

Acknowledgments Mr.P.Hemery is thanked for tonometric determination. Mr.C.Chassagnard is acknowledged for NMR experiments. Helpful discussions with Mr. L. Leibler permitted us to analyze the gel permeation chromatograms.

EXPERIMENTAL PART

Instruments used : Tonometer Knauer, G.P.C.Waters equipped with Refractive Index R410 and U.V.-vis. Lambda-Max 481 detectors.

Synthesis of $(C_{12}H_{25}OCH_2)_8PcSi(OH)_2$

In dried vessel , 1.8g (3.3 mmoles) of 5,6-bis (dodecyloxymethyl) 1,3-diiminoisoindoline and 4 ml (33 mmoles) of freshly distilled quinoline are added under a stream of nitrogen. After addition of 750 µl (6.6 mmoles) of $SiCl_4$, the reaction mixture is rapidly brought at 150°C for 30 mn. After cooling, 4 ml H_2O are added. Organic derivatives are extracted with CH_2Cl_2. After evaporation to dryness, the residue is triturated with EtOH and chromatographied over SiO_2 (eluent : Et_2O $0 \rightarrow 10\%$ in CH_2Cl_2).

Further purification is achieved by preparative T.L.C. (eluent : Et_2O 4% in $CHCl_3$). Yield : 10%. Rf (Et_2O 2.5% in $CHCl_3$)=0.25. ^1H NMR ($CDCl_3$):-2.35 and 0.1(SiOH,2s,2H), 0.85 (CH_3,t,J=7,24H), 1.25 (CH_2,b,160H), 1.78(H_2C^3,b,16H), 3.65(H_2C^2,b,16H), 5.15(H_2C^1O,bt,16H), 8.95(CH,b,8H). ^{13}C NMR ($CDCl_3$): 14.07(H_3C^{12}),22.72(C^{11}),26.57(C^2),29.44(C^9), 29.85 (C^{4-8}),30.16(C^3),32.00(C^{10}),71.14 and 71.44(CH_2O), 123.32 (CH) , 134.47, 140.47 and 149.02 (ar.); $C_{136}H_{226}O_{10}N_8Si$(2164.41);calc.(%):C 75.58,H 10.54, N 5.18,Si 1.30 ; found(%):C 75.26,H 10.88, N 4.70, Si 1.21.

REFERENCES

1. Annelides Part XXIV. For the Part XXIII see B.Blanzat, C.Barthou, N.Tercier, J.-J.André and J.Simon, *J.Amer.Chem.Soc.*, submitted. Work performed within the Groupe de Recherches Interdisciplinaires sur les Matériaux Moléculaires (GRIMM).
2. C.Piechocki,J.Simon,A.Skoulios,D.Guillon and P. Weber, *J.Amer.Chem.Soc.*, 104, 5245 (1982); *Mol. Cryst. Liq.Cryst.*,100,275(1983).
3. C.Piechocki and J.Simon, *Nouv.J.Chim.*, 9, 159 (1985).

4. R.D.Joyner and M.E.Kenney, Inorg.Chem., 1, 236, 717 (1962), 2, 1064 (1963).
5. B.W.Diel, T.Inabe, J.W.Lyding, K.F.Schoch Jr., C.R. Kannewurf and T.J.Marks, J.Amer.Chem.Soc., 105, 1539, 1551 (1983); Mol.Cryst.Liq.Cryst., 93, 355 (1983).
6. W.Kreuder and H.Ringsdorf, Makromol.Chem.Rapid. Commun., 4, 107 (1983); O. Herrmann-Schönherr, J.H. Wendorff, W.Kreuder and H.Ringsdorf, ibid., 7, 97 (1986).
7. G.Wenz, Makromol.Chem.Rapid.Commun., 6, 577 (1985).
8. C.Sirlin, L.Bosio and J.Simon, J.Chem.Soc.Chem. Commun., 379, (1987).
9. P.G. de Gennes, J.Phys.Lett., 44, L567 (1983); D. Guillon, P. Weber, A. Skoulios, C. Piechocki and J. Simon, Mol.Cryst.Liq.Cryst., 130, 223, (1985).
10. A.R. Kane, J.F. Sullivan, D.H. Kenney and M.E. Kenney, Inorg.Chem., 9, 1445 (1970).