



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and
subscription information:

<http://www.tandfonline.com/loi/gmcl18>

Peripherally Octasubstituted Phthalocyanines with Branched Alkoxy Chains

P. G. Schouten^a, J. F. Van Der Pol^a, J. W. Zwikker^a, W. Drenth^a
& S. J. Picken^{a b}

^a Department of Organic Chemistry, University at Utrecht,
Padualaan 8, 3584, CH Utrecht, The Netherlands

^b Akzo Corporate Research Laboratories, Velperweg 76, 6800, SB
Arnhem, The Netherlands

Version of record first published: 24 Sep 2006.

To cite this article: P. G. Schouten, J. F. Van Der Pol, J. W. Zwikker, W. Drenth & S. J. Picken
(1991): Peripherally Octasubstituted Phthalocyanines with Branched Alkoxy Chains, *Molecular
Crystals and Liquid Crystals*, 195:1, 291-305

To link to this article: <http://dx.doi.org/10.1080/00268949108030908>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any
substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing,
systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any
representation that the contents will be complete or accurate or up to date. The
accuracy of any instructions, formulae, and drug doses should be independently
verified with primary sources. The publisher shall not be liable for any loss, actions,
claims, proceedings, demand, or costs or damages whatsoever or howsoever caused
arising directly or indirectly in connection with or arising out of the use of this material.

Peripherally Octasubstituted Phthalocyanines with Branched Alkoxy Chains

P. G. SCHOUTEN, J. F. VAN DER POL, J. W. ZWIKKER, W. DRENTH† and S. J. PICKEN‡

Department of Organic Chemistry, University at Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

(Received May 8, 1990)

Phthalocyanines (H₂Pc) octasubstituted with branched alkoxy chains were synthesized: 2,3,9,10,16,17,23,24-octakis(3,7-dimethyloctoxy)phthalocyanine (**1a**) and 2,3,9,10,16,17,23,24-octakis(3,7,11-trimethyldodecoxy)phthalocyanine (**1b**). Their mesomorphic properties were studied by DSC, polarization microscopy and X-ray diffraction. Compound **1a**, which was initially crystalline at room temperature, maintains its mesomorphic structure on cooling back to room temperature. Compound **1b** is mesomorphic at room temperature. It shows a $D_{ho} \rightarrow D_{hd}$ transition at 34°C and a transition of unknown nature at 173°C. Both compounds display a $D \rightarrow I$ transition.

Keywords: *discotic liquid crystals, columnar mesophase, phthalocyanine*

INTRODUCTION

In recent years many reports have appeared on the synthesis of new phthalocyanine (Pc) derivatives with specific properties.^{1–6} One of the main reasons for investigating the Pc derivatives is the search for new electronic materials based on stacked Pc molecules.^{1,7,8,9} It was found that the attachment of long aliphatic chains to the peripheral positions of the Pc molecule causes the compound to become liquid crystalline.^{2,3,4} In the columnar mesophases of these liquid crystalline compounds, the Pc cores are stacked in hexagonally arranged columns.

Recently, we reported on the liquid crystalline behaviour of peripherally octa-*n*-alkoxy substituted Pc's (Figure 1, compounds **2a** and **2b**).^{10,11} In the mesophase these disc-like molecules are stacked in hexagonally arranged columns. Results obtained using the time-resolved microwave conductivity technique on this class

†To whom correspondence should be sent.

‡Akzo Corporate Research Laboratories, Velperweg 76, 6800 SB Arnhem, The Netherlands.

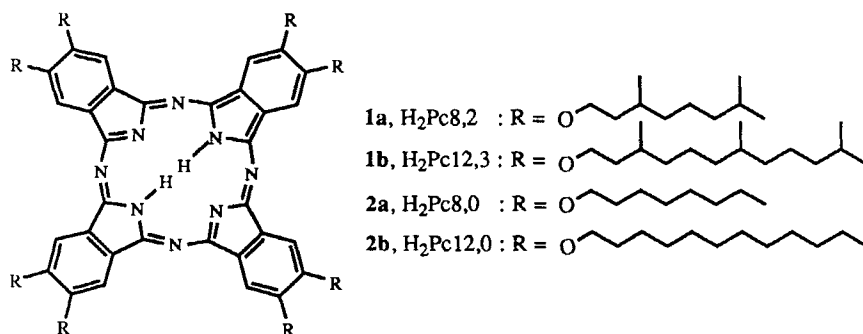


FIGURE 1 Chemical structures of the phthalocyanine derivatives.

of Pc's, demonstrated that after charge separation, caused by a short pulse of high energy radiation, recombination of charge carriers occurs with a rate which is found to depend exponentially on the length of the hydrocarbon chains.¹² This indicated that charge recombination occurs via electron tunneling through the intervening hydrocarbon mantle.^{12,13}

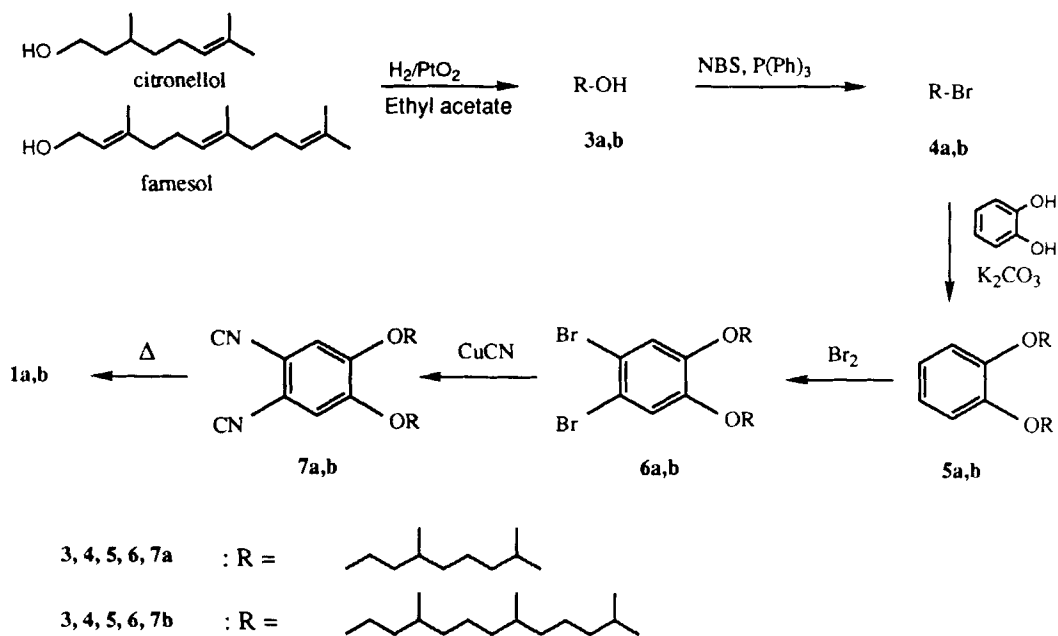
In order to obtain more information about the influence of hydrocarbon structure on the tunneling mechanism, we decided to synthesize Pc's peripherally substituted with branched alkoxy chains. Recently, Collard and Lillya showed that when branching points are introduced into the aliphatic side chains of hexa(*n*-alkanoyloxy)benzenes and 1,2,3,4,5,6-*all-trans*-hexakis(*n*-alkanoyloxy)cyclohexanes, the temperature range over which the columnar mesophase is stable, is widened.¹⁴ However, the type of mesophase formed was not affected by the introduction of the branching points.

Here we report the synthesis of two phthalocyanines, each peripherally substituted with a racemic mixture of eight branched alkoxy chains. These chains are derived from the terpenes citronellol and farnesol, leading to a Pc containing alkoxy chains with eight carbon atoms and two branching methyl groups (H₂Pc8,2, **1a**) and a Pc containing alkoxy chains with twelve carbon atoms and three branching methyl groups (H₂Pc12,3, **1b**), as displayed in Figure 1. The mesomorphic properties of these Pc's as studied by DSC, optical microscopy and X-ray diffraction will be discussed here.

SYNTHESIS

The general aspects of the synthetic route are shown in Scheme 1. Commercially obtained citronellol and farnesol were hydrogenated according to a procedure reported earlier.¹⁵ Replacing the hydroxyl group by a bromine atom was carried out using *N*-bromosuccinimide and triphenylphosphine in methylene chloride.¹⁶

The following steps, leading to the Pc's, were carried out according to procedures used before in our group: alkylation of catechol in the presence of a base, bromination using molecular bromine, a Rosenmund-Von Braun reaction yielding the dicyanides and finally the conversion of the dicyanides into the Pc's by refluxing

SCHEME 1 Synthetic pathway to $\text{H}_2\text{Pc}_{8,2}$ (1a) and $\text{H}_2\text{Pc}_{12,3}$ (1b).

in ethanol in the presence of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN). It turned out that the precursors of these Pc's with branched aliphatic chains are viscous liquids instead of the usual solids. Only the dicyanides crystallized and they were extensively purified before converting them into the Pc's.

RESULTS AND DISCUSSION

DSC. In order to detect phase transitions and to determine the corresponding transition temperatures and enthalpies, differential scanning calorimetry (DSC) was performed on the compounds $\text{H}_2\text{Pc}_{8,2}$ and $\text{H}_2\text{Pc}_{12,3}$. The heating and cooling rates were $10^\circ\text{C}/\text{min}$.

Table I shows the DSC data, together with data obtained earlier by Van der Pol *et al.* for phthalocyanines substituted with unbranched alkoxy chains (2a and 2b).¹¹ The peak onset in the DSC was defined as the transition temperature. During the first heating run both samples give rise to two exothermic peaks; subsequent cooling and heating shows only the peak at higher temperature to be reversible. As will be discussed below, in the first heating run the peak at 70°C for $\text{H}_2\text{Pc}_{8,2}$ is related to the crystalline to mesophase transition ($K \rightarrow D$). When heating $\text{H}_2\text{Pc}_{12,3}$ the peak at 34°C is related to a $D \rightarrow D'$ transition. For both compounds the peaks at higher temperature correspond to the mesophase to isotropic phase transition ($D \rightarrow I$). $\text{H}_2\text{Pc}_{8,2}$ reaches this point at 295°C and $\text{H}_2\text{Pc}_{12,3}$ at 185°C . The isotropic phase

TABLE I

Phase transition temperatures and enthalpies* of peripherally octasubstituted phthalocyanines with branched and unbranched alkoxy chains**

$H_2Pc_{n,k}$		K		D_{ho}		D_{hd}		I
$H_2Pc_{8,2}$	T	•	70	-		•	295[293]	•
	ΔH	•	54.6	-		•	8.3	•
$H_2Pc_{12,3}$	T	-		•	34	•	185[183]	•
	ΔH	-		•	12.6	•	4.9	•
$H_2Pc_{8,0}^{***}$	T	•	94[77]	•		-		-
	ΔH	•	98	•		-		-
$H_2Pc_{12,0}^{***}$	T	•	83[65]	•		-		-
	ΔH	•	109	•		-		-

* Determined by DSC; heating and cooling rate: 10 °C/min.

** The meaning of the signs used in this table is: n : number of main chain carbons in alkoxy chain, k : number of branching methyl groups, T: temperature in °C, ΔH : transition enthalpy in kJ mol⁻¹, K: crystalline phase, D_{ho} : hexagonal, ordered columnar phase, D_{hd} : hexagonal, disordered columnar phase, I: isotropic phase, •: the phase is observed, -: the phase is not observed, []: transition temperature observed upon cooling.

*** Results obtained from ref. 11.

lasts until 356 and 346°C, respectively; above these temperatures the Pc's start to decompose (determined by thermogravimetric analysis). This is the first time that thermodynamically stable isotropic phases have been obtained for mesomorphic phthalocyanines which are peripherally substituted with nonfunctionalized alkoxy chains.

From Table I it is apparent that branching the alkoxy chains reduces the $K \rightarrow D$ transition temperature far more than lengthening the chains. When the alkoxy chains of $H_2Pc_{8,0}$ are branched, yielding $H_2Pc_{8,2}$, the transition temperature is reduced by 24°C while extension by 4 carbon atoms, yielding $H_2Pc_{12,0}$, reduces the transition temperature by only 11°C. The reduction of the melting point by branching is thought to be related to additional steric crowding by neighbouring chains as a consequence of the branching, and to more conformational disorder in the vicinity of the branch.¹⁴ This causes the aliphatic chains to melt at lower temperatures and, thus, to reduce the transition temperature to the liquid crystalline state. It should also be noted, that our samples actually will be mixtures of both diastereoisomers and enantiomers.

It can be seen that the enthalpy change for the $D \rightarrow I$ transition decreases with an increase in the alkoxy chain length; this decrease is a consequence of the lower order in the mesomorphic arrangement as is known for discotic hexasubstituted triphenylenes from the work of Destradé *et al.*¹⁷

Finally, it is worthwhile mentioning that the change in enthalpy corresponding

to the $K \rightarrow D$ transition, normally increases with increasing chain length.¹¹ When, however, the transition enthalpies of $H_2Pc_{8,2}$ with $H_2Pc_{12,3}$ for the low temperature peak during the first heating run are compared a decrease is observed. This decrease indicates that the transition at 34°C for $H_2Pc_{12,3}$ is not related to a $K \rightarrow D$ phase transition.

Optical microscopy. At room temperature a sample of $H_2Pc_{8,2}$ appears as very sharp light-green coloured crystalline needles. Upon heating, these crystals start to melt at 72°C into a dark-green highly viscous and birefringent mass. On further heating, the sample becomes fluid and optically isotropic above 295°C. This $D \rightarrow I$ transition is reversible. Upon slow cooling (2°C/min) a mesophase texture reappears. At different spots nucleation starts and the nuclei grow to form a texture shown in Figure 2a which is characterized by digitated lines. There is a strong resemblance to the digitate stars observed for Pc's substituted with unbranched alkoxy chains that have a D_{ho} phase.¹¹ On further cooling these digitate domains merge together into a texture which becomes somewhat striated (Figure 2b). Supercooling is observed for the $D \rightarrow K$ transition. A gradual return to the crystalline state over a period of days at room temperature was indicated by periodic measurements of the microwave conductivity of the sample.¹⁸

When a sample of $H_2Pc_{12,3}$ is placed between two glass slides at room temperature the dark green, spreadable substance is found to be birefringent. No definite texture can be observed, possibly due to the mechanical distortion. However, it seems certain that this phthalocyanine exhibits permanent liquid crystalline behaviour even at room temperature. Upon heating, a highly fluid isotropic liquid appears above 185°C. Upon slow cooling a fan-shaped texture with straight boundaries appears at 183°C, characteristic of a hexagonal, disordered columnar mesophase.¹⁹ On further cooling, at 170°C suddenly concentric striates appear which are directed perpendicular to the direction of the fans. These striations disappear at 173°C when the phthalocyanine is heated again. Figures 3a and 3b display a region of the sample before and after this optical transition temperature.

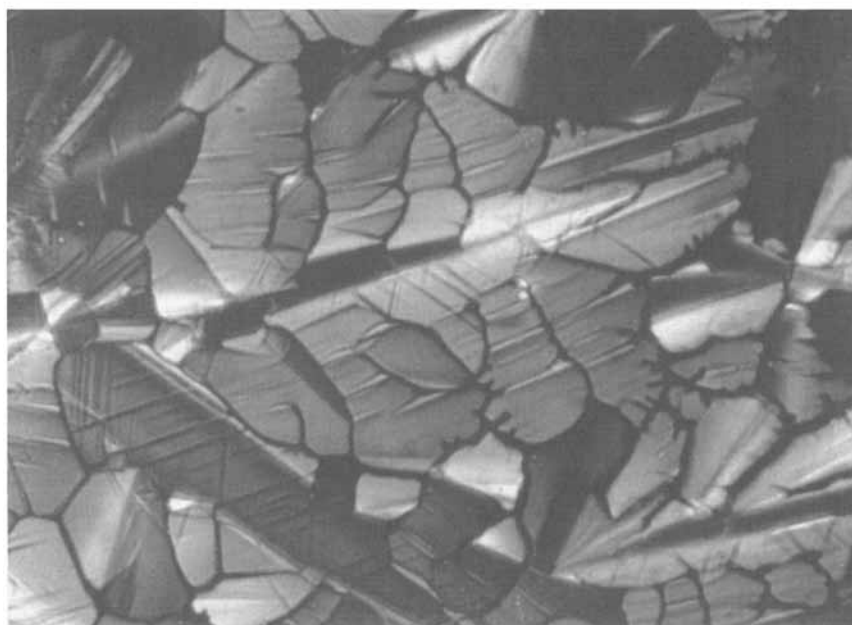
This reversible optical change does not give rise to an energy peak in the DSC thermograms. Earlier Guillon *et al.* observed such an optical transition for an octa(dodecyloxymethyl)phthalocyanine.⁵ However, no definite link with any change in internal structure was found. In the work of Mamlok *et al.* striates appear in mesomorphic 2,3,7,8,12,13-hexaalkanoxybenzo[1,2-*b*:2',4-*b'*:5,6-*b''*]trisbenzofurans as a consequence of transitions from a hexagonal ordered to a rectangular disordered or from a rectangular disordered to an oblique disordered mesophase structure.²⁰ However, as will be described below, X-ray measurements on our Pc's are not in line with these observations. Finally, further cooling to room temperature did not give rise to any optical change indicating that the mesomorphic structure is maintained.

X-ray. X-ray diffraction measurements have been performed on the newly synthesized phthalocyanines as a function of temperature. The diffraction spacings and related parameters are displayed in Table II.

For $H_2Pc_{8,2}$ at room temperature a series of reflections is present characteristic of a crystalline lattice. When an X-ray photograph is taken in the mesophase at 150°C a pattern of reflections at low angles is observed together with a broad



(a)

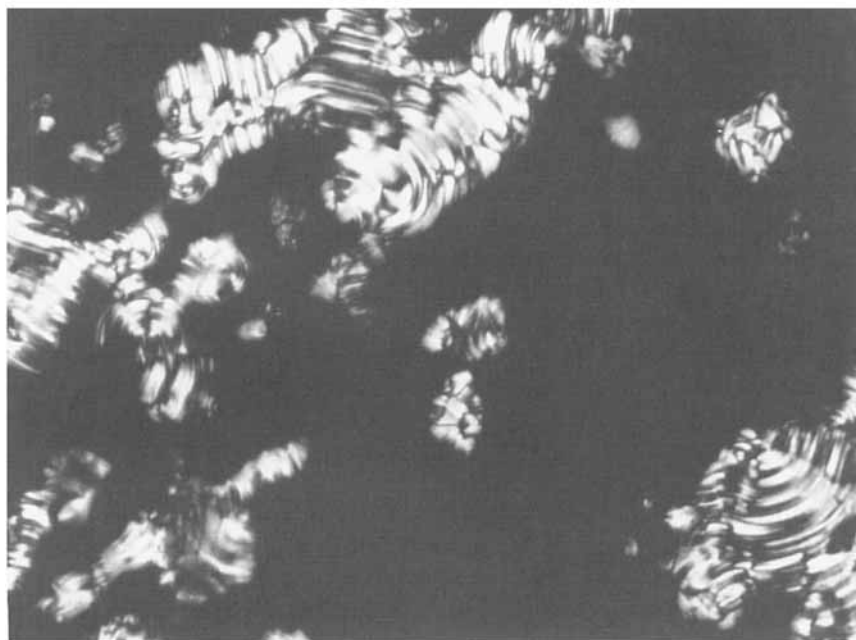


(b)

FIGURE 2 Optical textures observed for $H_2Pc8,2$: 3a, digitate domains at 290°C; 3b, striated texture at 200°C ($\times 360$). See Color Plate X.



(a)



(b)

FIGURE 3 Optical textures observed for $H_2Pc_{12,3}$ textures at the same spot before (3a) and after (3b) the optical transition at $173[170]^{\circ}C (\times 360)$. See Color Plate XI.

TABLE II

X-ray diffraction data (Å) of peripherally octasubstituted phthalocyanines with branched alkoxy chains, H₂Pc8,2 and H₂Pc12,3, at various temperatures*

hkl	H ₂ Pc8,2		H ₂ Pc12,3			
	150 °C(<i>H</i>)	20 °C(<i>C</i>)	20 °C	40 °C(<i>H</i>)	180 °C(<i>C</i>)	20 °C(<i>C</i>)
100	24.89	24.64	31.09	31.09	27.95	31.09
110	-	15.59	18.46	17.19	16.4	17.19
200	13.90	13.87	16.09	14.68	-	14.86
210	10.03	10.44	12.02	11.37	-	11.27
300	8.83	9.47	-	-	-	-
D	30.60	31.95	34.00	33.90	29.60	34.20
L	4.87	4.92	4.83	4.87	-	4.83
h	b3.53	s3.39	s3.38	b3.47	-	b3.45

* Meaning of the signs used in this table are: hkl: Miller indices, *H*: temperature obtained on heating, *C*: temperature obtained on cooling, D: intercolumnar distance, L: correlation length of side chains, h: stacking period along the columns, b: broad reflection, s: sharp reflection.

reflection at 5.0 Å corresponding to the liquid like order of the aliphatic chains¹⁰ and a diffuse reflection at 3.5 Å indicating a disordered packing of the discs in the columns.¹⁰ For phthalocyanines substituted with unbranched alkoxy chains, in the mesophase normally the 100, 110, 200 and 210 reflections are observed corresponding to a hexagonally arranged column packing.¹⁰ The reflections of H₂Pc8,2 are less clearly assigned. The best way of assignment is to regard them as 100, 200, 210 and 300 reflections of a hexagonal columnar packing, as was indicated by optical microscopy. One weak reflection remains at 11.74 Å of which the origin is not fully understood. Upon cooling, the substance does not recrystallize and at 20°C an X-ray photograph is obtained where the low angle Bragg reflections are somewhat shifted and the correspondence to a hexagonal packing of the columns is improved. The reflection which is related to the packing of the discs, however, has sharpened up completely and is shifted to 3.39 Å, *i.e.* the packing appears to have become ordered.

If the reflections of the X-ray photograph of H₂Pc12,3 obtained at 20°C, are indexed, it is clear that even at room temperature the structure consists of hexagonally packed columns in which the phthalocyanine discs are closely packed according to the sharp reflection at 3.36 Å. The relatively sharp reflection at 4.83 Å relating to the aliphatic chains, indicates that there is not much freedom of movement at this temperature. Together with the optical observation that the substance is spreadable and birefringent, we conclude that the phthalocyanine is

liquid crystalline at room temperature. After heating the substance up to 50°C the reflection at 3.36 Å has become broad indicating that the exothermic phase transition measured with DSC at 34°C is related to a transition in which the discs become disorderly packed in the columns. So far a $D_{ho} \rightarrow D_{hd}$ transition has only been spotted in hexa(hexylthio)triphenylene.^{21,22,23} Bringing the Pc into the isotropic phase at 200°C followed by slow cooling, the X-ray diffraction pattern as shown in Figure 4a was obtained at 180°C. Without the use of any external force the columns in the mesophase are apparently aligned homeotropic and only six spots at angles of 60°C are observed. Although the intensities are low, it is possible to see the second order reflections as well. On cooling this sample to 20°C the X-ray photograph displayed in Figure 4b is obtained, indicating that the columns are aligned homogeneously. It can be seen that the reflections at low angles are present perpendicular to the broad reflection originating from the spacing between the phthalocyanine discs. This latter reflection at an average spacing of 3.45 Å is rather broad indicating that the discs maintain their disordered packing and do not become ordered, as was observed for the H₂Pc_{8,2}.

With the help of X-ray photographs we also tried to obtain more information about the change which was displayed for H₂Pc_{12,3} at 173[170]°C in optical microscopy. Therefore, we heated the sample again to the isotropic phase and took photographs after cooling down to 180 and 160°C. The results are displayed in Figures 5a and 5b respectively. No large differences are observed except that the reflections become a bit broader at 160°C indicating that the alignment has changed somewhat. Possibly, the substance between the glass slides also changes its alignment at 170°C, causing an optical transition. Unfortunately, the photograph at 180°C does not again demonstrate a perfectly aligned sample.

CONCLUSIONS

Two phthalocyanines peripherally substituted with branched alkoxy chains were synthesized (**1a** and **1b**). They display more phase transitions than were observed before for the corresponding homologous series of Pc's with unbranched alkoxy chains. The observed transitions are summarized in Figure 6.

Earlier we succeeded in obtaining Pc materials in which the structure of the mesophase was stabilized at ambient temperature by means of polymerization.^{24,25} However, by means of the introduction of branching points in the aliphatic chains it is possible to reduce the $K \rightarrow D$ transition temperature to such an extent that for H₂Pc_{12,3} a columnar mesophase is observed even at room temperature. Furthermore, it is possible to reach the thermodynamically stable isotropic phase.

Finally, an optical transition is observed in H₂Pc_{12,3} around 170°C. However, no structural changes were observed using X-ray diffraction around this transition.

Solid state NMR-studies and work concerning the energy and electron transport properties of this class of phthalocyanines are in progress and will be reported in forthcoming papers.

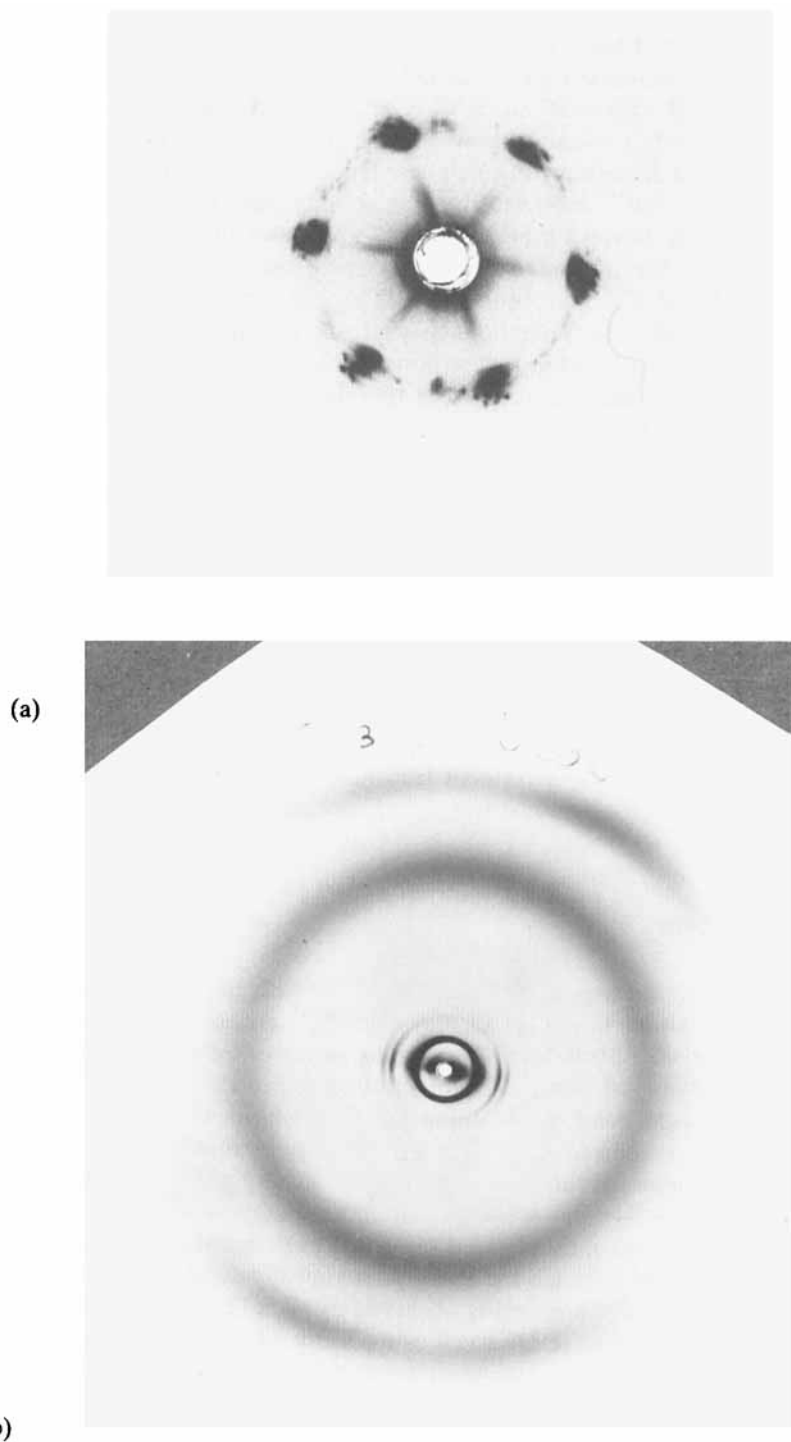


FIGURE 4 X-ray diffraction photographs of homeotropically (4a, at 180°C) and homogeneously (4b, at room temperature) aligned $H_2Pc_{12,3}$.

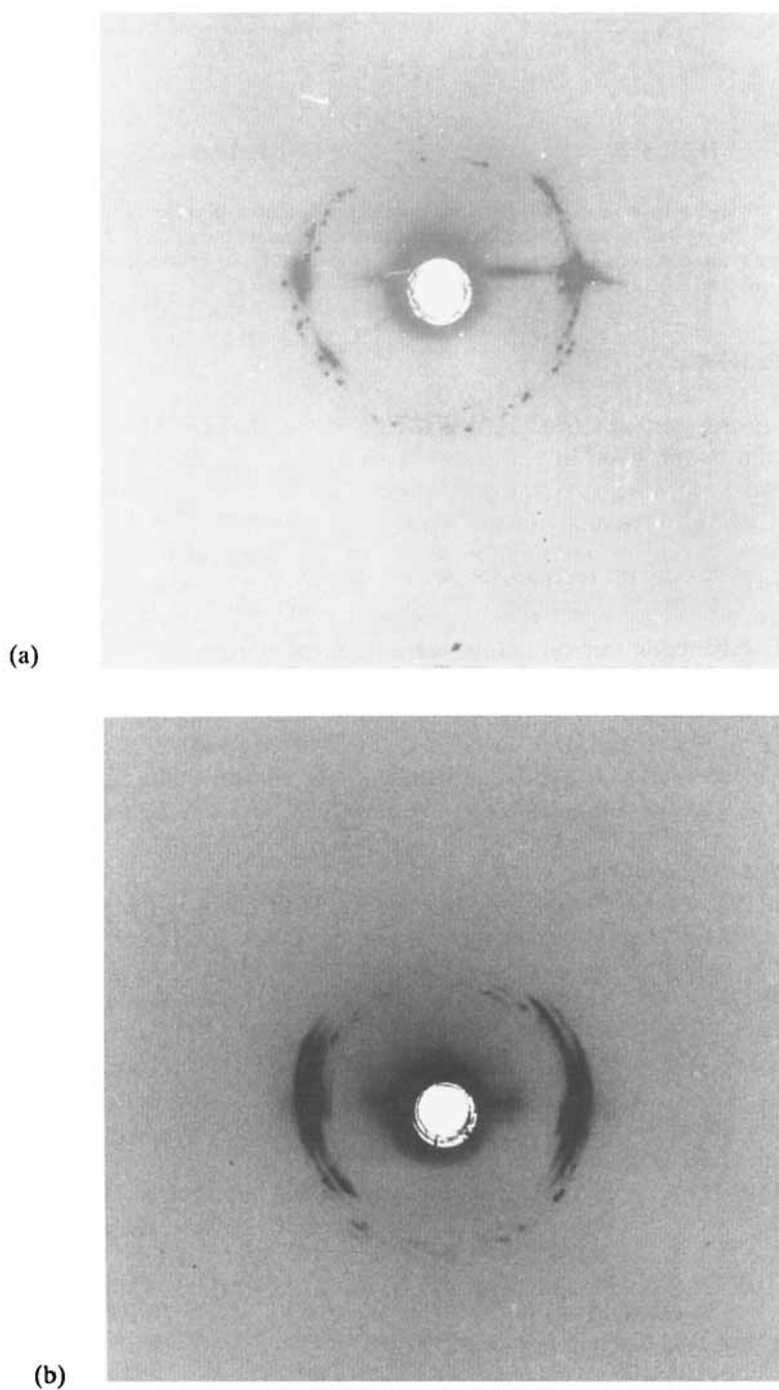


FIGURE 5 X-ray diffraction photographs of $H_2PC_{12,3}$ above (5a, $180^\circ C$) and below (5b, $160^\circ C$) the optical transition at $173[170]^\circ C$.

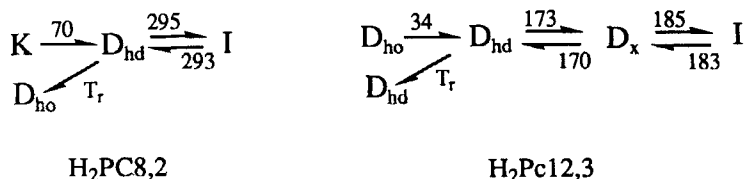


FIGURE 6 Phase transitions ($^{\circ}\text{C}$) for peripherally octasubstituted phthalocyanines with branched alkoxy chains, K: crystalline phase, D_{ho} : hexagonal ordered discotic mesophase, D_{hd} : hexagonal disordered discotic mesophase, D_{x} : unassigned discotic mesophase, T_r : room temperature.

EXPERIMENTAL

^1H NMR spectra were recorded on Varian EM-360 and Bruker AC-200 instruments. Chemical shifts are given in ppm relative to TMS. Infrared and UV/Vis spectra were recorded on a Perkin-Elmer 283 and Perkin-Elmer 555 spectrometer, respectively. Abbreviations used are: *s*, singlet; *d*, doublet; *t*, triplet; *m*, multiplet; *br*, broad; *str*, strong; *m*, medium; *w*, weak; *sh*, shoulder. DSC thermograms were determined on a Perkin-Elmer DSC-4 differential scanning calorimeter. MS spectra were recorded on a Kratos MS80, FAB mass spectra on a VG ZAB 2F spectrometer. X-ray diffraction measurements were performed using a Kiessig camera (Ni-filtered $\text{Cu-K}\alpha$ radiation). Catechol was recrystallized three times from toluene and stored at 4°C under nitrogen. Citronellol, farnesol, bromine and CuCN were commercial products and used as received. DMSO and DMF were stored over molecular sieve (4 \AA). Ethyl acetate, methylene chloride and chloroform were distilled from CaCl_2 prior to use.

3,7-Dimethyl-1-octanol (**3a**)

Citronellol, 39.00 g (0.25 mol) in ethyl acetate (500 ml) was hydrogenated over Adams catalyst (200 mg) under magnetical stirring. Pt was filtered off over infusorial earth and the solvent evaporated in vacuum; yield 39.14 g (99%) of **3a** as a yellow liquid. MS m/z : 157 ($\text{M}^+ - \text{H}$), 140 ($\text{M}^+ - \text{H}_2\text{O}$). IR (NaCl): 3600–3100 (OH —stretch), 2960–2840 (CH_3/CH_2) cm^{-1} . ^1H NMR (CDCl_3) δ : 0.90 (9H, *d*, CH_3), 1.23 (*br*, 8H, *s*, CH_2), 1.50 (2H, *m*, CH), 1.85 (1H, *s*, OH), 3.65 (2H, *t*, OCH_2).

3,7,11-Trimethyl-1-dodecanol (**3b**)

This compound was synthesized from farnesol as described for **3a**. Yield 99%. MS m/z : 227 ($\text{M}^+ - \text{H}$), 210 ($\text{M}^+ - \text{H}_2\text{O}$). IR (NaCl): 3600–3100 (OH —stretch), 2965–2840 (CH_3/CH_2) cm^{-1} . ^1H NMR (CDCl_3) δ : 0.90 (12H, *d*, CH_3), 1.23 (*br*, 14H, *s*, CH_2), 1.50 (3H, *m*, CH), 2.62 (*br*, 1H, *s*, OH), 3.65 (2H, *t*, OCH_2).

1-Bromo-3,7-dimethyloctane (**4a**)

To a solution of 60.03 (0.38 mol) **3a** and 109.50 g (0.42 mol) of triphenylphosphine in 200 ml CH_2Cl_2 was added 71.00 g (0.40 mol) of *N*-bromosuccinimide in portions,

with occasional ice-bath cooling, keeping the temperature below 30°C. After stirring for 16 h at room temperature, the solvent was removed in vacuum. The residue was extracted with 500 ml hexane and filtered off. After evaporation of the solvent, distillation (37°C, 0.005 mm Hg) gave 71.86 g (86%) of a colourless liquid. MS m/z : 221 (M^+). IR (NaCl): 643 (C—Br) cm^{-1} . ^1H NMR (CDCl_3) δ : 0.90 (9H, *d*, CH_3), 1.23 (*br*, 8H, *s*, CH_2), 1.50 (2H, *m*, CH), 3.42 (2H, *t*, BrCH_2).

1-Bromo-3,7,11-trimethyldodecane (4b)

This compound was synthesized from **3b** as described for **4a**. Distillation (92°C, 0.005 mm Hg) yielded 89% of **4b**. IR (NaCl): 645 (C—Br) cm^{-1} . ^1H NMR (CDCl_3) δ : 0.90 (12H, *d*, CH_3), 1.25 (*br*, 14H, *s*, CH_2), 1.65 (3H, *m*, CH), 3.45 (2H, *t*, BrCH_2).

1,2-Bis(3,7-dimethyloctoxy)benzene (5a)

From the two-phase system of 48.61 g (0.21 mol) of **4a** and 11.02 g (0.10 mol) of catechol in 250 ml of DMSO dissolved oxygen was removed by repeated evacuation followed by admission of nitrogen. K_2CO_3 (96.68 g; 0.70 mol) was added followed again by removal of oxygen. The reaction mixture was heated for 7.5 h at 85°C in a dry nitrogen atmosphere with magnetic stirring. The mixture was poured into 1250 ml of water and 300 ml of CHCl_3 was added. The organic layer was separated and the aqueous layer extracted three times with 50 ml of CHCl_3 . The combined organic extracts were washed three times with 100 ml of water, and dried over MgSO_4 . Filtration, evaporation of the chloroform and removal of the excess of **4a** by distillation yielded 38.74 g (88%) of a yellow viscous liquid of **5a**. MS m/z : 390 (M^+). IR (NaCl): 735 (*o*-substituted benzene), 1050 (ArOC) cm^{-1} . ^1H NMR (CDCl_3) δ : 0.90 (18H, *d*, CH_3), 1.28 (*br*, 16H, *s*, CH_2), 1.72 (4H, *m*, CH), 4.20 (4H, *t*, OCH_2), 6.86 (4H, *s*, ArH).

1,2-Bis(3,7,11-trimethyldodecoxy)benzene (5b)

The same procedure as for **5a** yielded 99% of a yellow viscous liquid of **5b**. IR (NaCl): 735 (*o*-substituted benzene) cm^{-1} . ^1H NMR (CDCl_3) δ : 0.90 (24H, *d*, CH_3), 1.25 (*br*, 28H, *s*, CH_2), 1.60 (6H, *m*, CH), 4.07 (4H, *t*, OCH_2), 6.90 (4H, *s*, ArH).

1,2-Dibromo-4,5-bis(3,7-dimethyloctoxy)benzene (6a)

Compound **5a** (20 g, 0.049 mol) was dissolved in 100 ml of CH_2Cl_2 . To this solution 5.3 ml (0.0103 mol) Br_2 in 10 ml of CH_2Cl_2 was added in approximately 2.5 h. The first equivalent at 0°C, the second at room temperature. After stirring for 2 h at room temperature the mixture was washed twice with 50 ml 10% aqueous NaHSO_3 , once with 75 ml of 10% aqueous NaHCO_3 and finally twice with 50 ml of water. The organic layer was dried over MgSO_4 and after filtration and evaporation of the solvent, 25.64 g (92%) of a viscous yellow liquid was obtained. MS m/z : 548 (M^+). IR (NaCl): 649 (ArBr), 1020 (ArOC) cm^{-1} . ^1H NMR (CDCl_3) δ : 0.85 (18H, *d*, CH_3), 1.26 (*br*, 16H, *s*, CH_2), 1.70 (4H, *m*, CH), 3.98 (4H, *t*, OCH_2), 7.06 (2H, *s*, ArH).

1,2-Dibromo-4,5-bis(3,7,11-trimethyldodecoxy)benzene (6b)

In the same manner as described for **6a**, **6b** was synthesized in 96% yield. MS m/z : 688 (M^+). IR (NaCl): 650 (ArBr), 1020 (ArOC) cm^{-1} . ^1H NMR (CDCl_3) δ : 0.90 (24H, *d*, CH_3), 1.25 (*br*, 28H, *s*, CH_2), 1.75 (6H, *m*, CH), 4.00 (4H, *t*, OCH_2), 7.06 (2H, *s*, ArH).

1,2-Dicyano-4,5-bis(3,7,-dimethyloctoxy)benzene (7a)

A mixture of 15 g (0.026 mol) of **6a** and 6.18 g (0.069 mol) of CuCN was refluxed in 125 ml of DMF in a dry nitrogen atmosphere for 6 h. Subsequently, the mixture was poured into 1 liter of concentrated ammonium hydroxide and air was bubbled through the solution for 63 h. The precipitated solid was collected by filtration and was washed with 10% aqueous ammonia until the filtrate was colourless. Subsequently, the solid was washed with water until the washings were neutral. The product (green because of the presence of copper phthalocyanine) was dried at 70°C under low pressure (3 mm Hg). The solid was dissolved in 100 ml of acetone and eluted over a short column (SiO_2) and further purified by recrystallization from hexane. Yield 5.48 g (47%) of a white solid; m.p. 105°C. MS m/z : 440 (M^+). IR (KBr): 2222 (CN), 1090 (ArOC) cm^{-1} . ^1H NMR (CDCl_3) δ : 0.90 (18H, *d*, CH_3), 1.25 (*br*, 16H, *s*, CH_2), 1.70 (4H, *m*, CH), 4.08 (4H, *t*, OCH_2), 7.10 (2H, *s*, ArH).

1,2-Dicyano-4,5-bis(3,7,11-trimethyldodecoxy)benzene (7b)

The procedure followed was the same as for **7a**. However, the crude product was eluted over a short silica column using CHCl_3 /acetone = 100:3 (v/v) as eluents. Further purification was carried out by recrystallization from ethanol. Yield 30%; m.p. 63°C. FAB MS m/z : 580 (M^+). IR (KBr): 2230 (CN), 1092 (ArOC) cm^{-1} . ^1H NMR (CDCl_3) δ : 0.90 (24H, *d*, CH_3), 1.25 (*br*, 28H, *s*, CH_2), 1.80 (6H, *m*, CH), 4.08 (4H, *t*, OCH_2), 7.10 (2H, *s*, ArH).

2,3,9,10,16,17,23,24-Octakis(3,7-dimethyloctoxy)phthalocyanine (1a)

A solution of 4.5 g (0.01 mol) of **7a** and 1.24 g (0.01 mol) of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in 30 ml ethanol was refluxed for 63 h under a nitrogen atmosphere. The mixture was poured into 450 ml of acetone. After filtration the solid was purified by column chromatography over SiO_2 (eluent: hexane/chloroform = 20:80 (v/v)). Precipitation from cold acetone for several times yielded analytically pure product. Yield 0.9 g (20%) of green crystalline phthalocyanine. $K \rightarrow M$: 70°C, $K \rightarrow I$: 295°C. FAB MS m/z : 1762 (M^+). IR (KBr): 3298 (*w*, NH), 2960/2935/2875 (*str*, CH), 1280 (*str*, ArO), 1100 (*m*, ArOC), 740 (*m*, CH out of plane) cm^{-1} . ^1H NMR 200 MHz (CDCl_3) δ : 0.91 (72H, *d*, CH_3), 1.07–1.65 (64H, CH_2 , CH), 1.87 (*br*, 16H, *s*, OCH_2CH_2), 4.56 (*br*, 16H, *s*, OCH_2), 7.26 (*br*, 18H, *s*, ArH). UV/Vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}(\log \epsilon/(\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}))$: 702 (5.27), 667 (5.17), 640 (*sh*), 600 (4.42), 423 (4.61), 345 (4.99), 293 (4.83).

2,3,9,10,16,17,23,24-Octakis(3,7,11-trimethyldodecoxy)phthalocyanine (1b)

Both the synthesis and working up procedure were the same as for **1a**. Yield 11% of dark green greasy product. $M \rightarrow I$: 185°C. FAB MS m/z : 2320 (M^+). IR (KBr):

3298 (w, NH), 2957/2928/2870 (str, CH), 1279 (str, ArO), 1100 (m, ArOC), 740 (m, CH out of plane) cm^{-1} . ^1H NMR 200 MHz (CDCl_3) δ : 0.85 (96H, d, CH_3), 1.11–1.50 (120H, CH_2 , CH), 1.93 (br, 16H, s, OCH_2CH_2), 4.63 (br, 16H, s, OCH_2), 8.80 (br, 18H, s, ArH). UV/Vis (CHCl_3) $\lambda_{\text{max}}/\text{nm}$ (log $\epsilon/(\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})$): 702 (5.36), 665 (5.26), 640 (sh), 599 (4.59), 421 (4.731), 347 (5.09), 295 (4.91).

Acknowledgment

Mr. R. Visser and Dr. J. Aerts of Akzo Corporate Research, Arnhem, are gratefully acknowledged for performing the X-ray diffraction experiments. These investigations are supported by the Netherlands' Foundation for Chemical Research (SON) with financial aid from the Netherlands' Technology Foundation (STW).

References

1. C. Piechocki, J. Simon, A. Skoulios, D. Guillon and P. Weber, *J. Am. Chem. Soc.*, **104**, 5245 (1982).
2. M. Hanack, A. Beck and H. Lehmann, *Synthesis*, 703 (1987).
3. D. Guillon, P. Weber, A. Skoulios, C. Piechocki and J. Simon, *Mol. Cryst. Liq. Cryst.*, **130**, 223 (1985).
4. M. J. Cook, M. F. Daniel, K. J. Harrison, N. B. McKeown and A. J. Thomson, *J. Chem. Soc. Chem. Commun.*, 1086 (1987).
5. D. Guillon, A. Skoulios, C. Piechocki, J. Simon and P. Weber, *Mol. Cryst. Liq. Cryst.*, **100**, 275 (1983).
6. I. Cho and Y. Lim, *Mol. Cryst. Liq. Cryst.*, **154**, 9 (1988).
7. M. Maitrot, G. Guillard, B. Boudjema, J.-J. André, H. Strzelecka, J. Simon and R. Even, *Chem. Phys. Lett.*, **133**, 59 (1987).
8. Z. Belarbi, M. Maitrot, K. Ohta, J. Simon, J.-J. André and P. Petit, *Chem. Phys. Lett.*, **143**, 400 (1988).
9. J. F. van der Pol, M. P. de Haas, J. M. Warman and W. Drenth, *Mol. Cryst. Liq. Cryst.*, **183**, 411 (1990).
10. J. F. van der Pol, E. Neeleman, J. W. Zwikker, R. J. M. Nolte and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **107**, 615 (1988).
11. J. F. van der Pol, E. Neeleman, J. W. Zwikker, R. J. M. Nolte, W. Drenth, J. Aerts, R. Visser and S. J. Picken, *Liq. Cryst.*, **6**, 577 (1989).
12. J. M. Warman, M. P. de Haas, J. F. van der Pol and W. Drenth, *Chem. Phys. Lett.*, **164**, 581 (1989).
13. J. M. Warman, M. P. de Haas, K. J. Smit, M. N. Paddon-Row and J. F. van der Pol, *Mol. Cryst. Liq. Cryst.*, **183**, 375 (1990).
14. D. M. Collard and C. P. Lillya, *J. Am. Chem. Soc.*, **111**, 1829 (1989).
15. P. Grammatica, P. Manitto, D. Mianti and G. Speranza, *Tetrahedron*, **43**, 4481 (1987).
16. E. E. Schweizer, W. S. Creasy, K. K. Light and E. T. Shaffer, *J. Org. Chem.*, **34**, 212 (1969).
17. C. Destrade, M. C. Mondon and J. Malthête, *J. Phys. (Paris)*, **40**, 3 (1979).
18. P. G. Schouten, J. F. van der Pol, W. Drenth, J. M. Warman, M. P. de Haas and W. Chen, unpublished results.
19. C. Destrade, P. Foucher, H. Gasparoux, N. H. Tinh, A. M. Levelut and J. Malthête, *Mol. Cryst. Liq. Cryst.*, **106**, 121 (1984).
20. L. Mamlök, J. Malthête, N. H. Tinh, C. Destrade and A. M. Levelut, *J. Phys. Lett.*, **43**, 641 (1982).
21. E. F. Gramsbergen, H. J. Hoving, W. H. de Jeu, K. Praefcke and B. Kohné, *Liq. Cryst.*, **1**, 397 (1986).
22. E. F. Fontes, P. A. Heiney and W. H. de Jeu, *Phys. Rev. Lett.*, **61**, 1202 (1988).
23. P. A. Heiney, E. F. Fontes, W. H. de Jeu, A. Riera, P. Carroll and A. B. Smith, *J. Phys. France*, **50**, 461 (1989).
24. J. F. van der Pol, E. Neeleman, R. J. M. Nolte, J. W. Zwikker and W. Drenth, *Makromol. Chem.*, **190**, 2727 (1989).
25. J. F. van der Pol, E. Neeleman, J. C. van Miltenburg, J. W. Zwikker, R. J. M. Nolte and W. Drenth, *Macromolecules*, **22**, 155 (1990).