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Liquid Crystals

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Liquid crystalline hexa-amides and side chain polysiloxanes of azacrown [18]-N_6

Mingyang Zhao[a]; Warren T. Ford[a]; Stefan H. J. Idziak[bc]; Nicholas C. Maliszewskyj[b]; Paul A. Heiney[b]
[a] Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma, U.S.A. [b] Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania, U.S.A. [c] Materials Department and the Materials Research Laboratory, University of California, Santa Barbara, California, U.S.A.

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Liquid crystalline hexa-amides and side chain polysiloxanes of azacrown [18]-N_6

by MINGYANG ZHAO and WARREN T. FORD*
Department of Chemistry, Oklahoma State University, Stillwater,
Oklahoma 74078, U.S.A.

STEFAN H. J. IDZIAK†, NICHOLAS C. MALISZEWSKYJ
and PAUL A. HEINEY
Department of Physics, University of Pennsylvania, Philadelphia,
Pennsylvania 19104, U.S.A.

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The hexa-4-dodecyloxybenzoyl derivative **1** of azacrown **[18]**-N_6 was originally reported to have a 'tubular' mesophase on the basis of its large central ring and 6-fold symmetry. Starting in the mesophase, annealing of **1** under a cover slip results in formation of a new crystalline phase that melts directly to an isotropic liquid at the temperature previously observed for the mesophase to isotropic transition. Thus the phase behaviour of **1** is kinetically controlled. The analogous hexa-3,4-bisdodecyloxybenzoyl derivative **2** of azacrown **[18]**-N_6 has no kinetic limitations to its phase changes and has an enantiotropic columnar liquid crystalline phase. We have synthesized side chain copolysiloxanes with a $(CH_2)_{11}$ spacer and 75–84 per cent by weight of the same 4-dodecyloxybenzoyl-**[18]**-N_6 mesogen. The polysiloxanes also display a liquid crystalline phase.

1. Introduction

The first azamacrocyclic liquid crystals were reported by Lehn, Malthête, and Levelut [1] to have 'tubular' hexagonal mesophases. The supramolecular structures were cleverly illustrated by perfectly stacked columns with all-*trans* side chains. Their intriguing paper has led to further investigation of the original hexa-4-dodecyloxybenzoyl-**[18]**-N_6 **(1)** [2–8] and numerous similar mesogenic and non-mesogenic azacrown compounds [2–12]. Molecular modeling and computer simulations [4] indicate that the cores of the molecules tend to collapse so that the internal 'tube' is vanishingly small. Furthermore, the hexagonal structure of the mesophase of **1** is a matter of controversy [4, 6, 7]. The original compound **1** shown in figure 1 has different glass and melting transition temperatures when prepared in four different laboratories [1–4], but the same texture and approximate isotropization temperature of the mesophase called tubular have been identified by all four research groups. Rigid substituents such as benzoyl or cinnamoyl on the macrocycle nitrogen atoms and at least six long chains on the perimeter are required for mesophase formation [2–4].

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*Author for correspondence.

†Present address: Materials Department and the Materials Research Laboratory, University of California, Santa Barbara, California 93106, U.S.A.

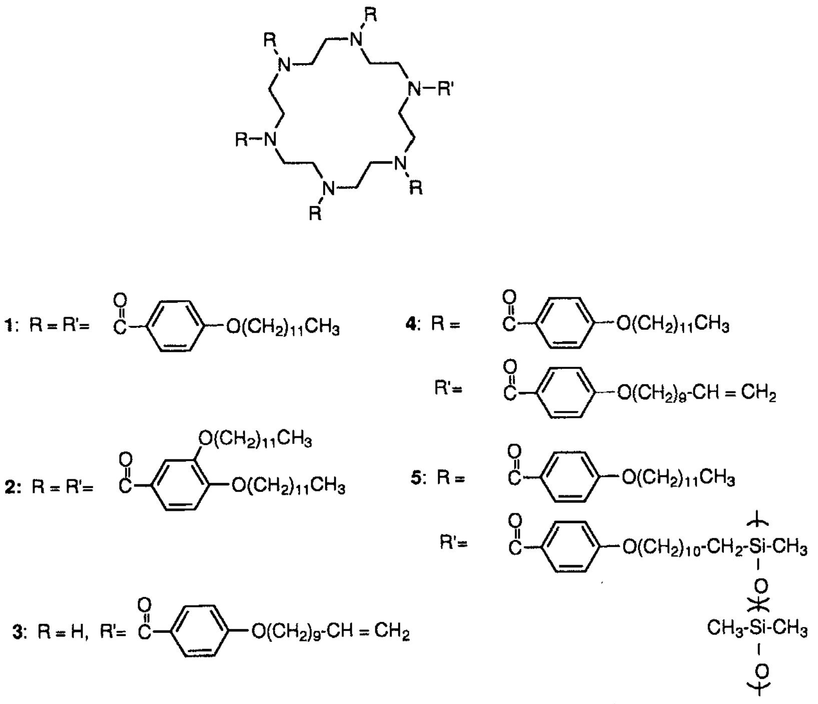

Figure 1. Structures of **[18]**-N_6 materials.

The clearest evidence for hexagonal order in azacrown compounds comes from X-ray diffraction measurements of two cinnamoyl analogues of **1**, one having one bromine atom in each of six *meta*-positions and the other having twelve chlorine atoms in the *meta*-positions [6]. Derivatives of the azacrown [14]-N_4 with *meta*-substituents have mesophases, while those without *meta*-substituents do not. Amines produced by reduction of the liquid crystalline macrocyclic amides have no reported mesophases [4, 12]. In this paper we report a new crystalline phase of compound **1** and side chain polysiloxanes having the same 4-dodecyloxybenzoyl-substituted [18]-N_3 mesogen. The structures of the materials are shown in figure 1.

2. Experimental

2.1. *Materials and analytical methods for syntheses*

All organic reagents were obtained from Aldrich and were used without further purification unless otherwise stated. Triethylamine and dichloromethane were distilled from calcium hydride. 1,4,7,10,13,16-Hexa-azacyclo-octadecane (**[18]**-N_6) was prepared by the method of Atkins, Richman, and Oettle [13]. 4-(10-Undecylenyloxy)benzoyl chloride, 4-dodecyloxybenzoyl chloride and 3,4-bis(dodecyloxy)benzoyl chloride were prepared by analogy to the literature [3]. NMR spectra were recorded at 300 MHz for ^1H and at 75·43 MHz for ^{13}C in $CDCl_3$ solutions with TMS as internal standard at room temperature, unless otherwise specified. IR spectra were taken on a grating instrument with KBr disks. Thin layer chromatography was performed with silica gel plates (HPTLC-HL, Analtech Inc.). Silica gel (40 μm, Baker) was used for flash chromatography. High pressure liquid chromatographic (HPLC) analyses were performed with a normal phase 5 μm silica column 250 mm long × 4·6 mm i.d. (Whatman PARTISIL 5) and 254 nm UV detection. Size exclusion chromatographic analyses of polymer molecular weights were performed using three polystyrene gel columns of 10^2, 10^3 and 10^4 Å pore size (Polymer Laboratories, PL gel columns) with THF eluant at 1·0 ml min^{-1}, 254 nm detection, an Interactive Microwave data station, and monodisperse polystyrenes as standards. Elemental analyses were performed at Atlantic Microlab Inc.

2.2. *1,4,7,10,13,16-Hexa-(4-dodecyloxybenzoyl)-1,4,7,10,13,16-hexa-azacyclo-octadedane (1)*

[18]-N_6 (0·52 g, 2·0 mmol), 4-dodecyloxybenzoyl chloride (3·90 g, 12 mmol) in 30 ml of DMF (*N*,*N*-dimethylformamide), and DMAP [4-(*N*,*N*-dimethylamino)-pyridine] were stirred for 14 h at 80°C [3]. The crude product was crystallized from ethanol and finally dried by lyophilization of a benzene solution [10] to yield 73 per cent of analytically pure **1** having ^{1}H and ^{13}C NMR spectra consistent with the structure. Analysis calculated for $C_{126}H_{198}N_6O_{12}$: C, 76·10; H, 10·03; N, 4·22. Found: C, 76·16; H, 10·03; N, 4·41 per cent.

2.3. *1,4,7,10,13,16-Hexa-(3,4-bisdodecyloxybenzoyl)-1,4,7,10,13,16-hexa-azacyclo-octadecane (2)*

A solution of [18]-N_6 (0·26 g, 1·0 mmol), the acid chloride from 3,4-bis(dodecyloxy)benzoic acid (3·50 g, 7·0 mmol), DMAP (1·71 g, 14·0 mmol), and 30 ml of DMF was stirred under nitrogen for 48 h at 80°C. The DMF was removed under water aspirator vacuum, and 50 ml of chloroform added. The organic layer was washed twice with 100 ml of water, and the concentrated mixture was separated by silica gel chromatography using 98/2 (v/v) chloroform/methanol as eluant. The chromatographed product was recrystallized from ethanol to yield 1·87 g (60 per cent) of **2**. ^{1}H NMR (50°C): δ 0·89 (t, 36 H, CH_3), 1·28 (m, 192 H, CH_2), 1·45 (m, 24 H, CH_2), 1·78 (m, 24 H, CH_2), 3·74 (m, 24 H, NCH_2), 3·90, 3·98 (m, 24 H, CH_2O), 6·78 (m, 18 H, Ar). ^{13}C NMR (50°C): δ 14·0 (CH_3), 22·6, 26·1, 29·3, 29·4, 29·5, 29·6, 31·9 (CH_2), 47–49 (br., NCH_2), 69·3, 69·6 (CH_2O), 113·1, 113·4, 120·0, 127·6, 149·4, 151·1 (Ar), 172·3 (C=O). IR (KBr): 2935 (s), 2860 (s), 1635 (m), 1470 (m), 1274 (s) cm^{-1}. Analysis calculated for $C_{198}H_{342}N_6O_{18}$: C, 76·84; H, 11·14; N, 2·72. Found: C, 76·80; H, 11·18; N, 2·69 per cent. Mass spectrum (FAB, 2-nitrophenyl octyl ether/*p*-toluenesulphonic acid 2/1 v/v) *m*/*z* 3096 [$(M+H)^+$, calculated for $^{12}C_{197}{}^{13}CH_{343}N_6O_{18}$ 3095·91].

2.4. *1-[4-(10-Undecylenyloxy)benzoyl]-1,4,7,10,13,16-hexa-azacyclo-octadecane (3)*

A solution of 4-(10-undecylenyloxy)benzoyl chloride (3·08 g, 10·0 mmol) in 0·5 l of dichloromethane was added dropwise over 3 h at 40°C to a stirred solution of [18]-N_6 (7·83 g, 30·0 mmol), triethylamine (4·04 g, 40·0 mmol) and 2 l of dichloromethane. After 14 h the solid residue was removed by filtration, and the mixture was concentrated and washed with water. Dichloromethane was removed and residual oil (about 6 g) was separated by flash chromatography using 20/5/1 (volume) chloroform/methanol/28 per cent ammonium hydroxide as eluant. Pure product 1·14 g (22 per cent) was obtained as a viscous oil. ^{1}H NMR: δ 1·33 (m, 12 H, CH_2), 1·75 (m, 2 H, CH_2), 2·05 (m, 7 H, CH_2, NH), 2·70, 2·85, 3·58 (m, 24 H, NCH_2), 3·95 (t, 2 H, CH_2O), 4·95 (m, 2 H, =CH_2), 5·80 (m, 1 H, CH=), 6·88, 7·38 (dd, 4 H, Ar).

^{13}C NMR: δ 25·9, 28·8, 29·0, 29·1, 29·2, 29·3, 29·4, 33·6 (CH_2), 48·3, 48·8, 49·0 (NCH_2), 68·1 (CH_2O), 114·0 (=CH_2), 139·0 (CH=), 114·3, 128·5, 129·0, 160·0 (Ar), 172·4 (C=O).

2.5. *4,7,10,13,16-Penta-(4-dodecyloxybenzoyl)-1-[4-(10-undecylenyloxybenzoyl)]-1,4,7,10,13,16-hexa-azacyclo-octadecane (4)*

A solution of **3** (0·66 g, 1·2 mmol), triethylamine (2·40 g, 24·0 mmol), 4-dodecyloxybenzoyl chloride (3·00 g, 9·2 mmol), and 60 ml of dichloromethane was stirred at 40°C for 72 h. The solvent and excess of triethylamine were removed under aspirator vacuum, and 30 ml of chloroform was addded. The organic layer was washed twice with 100 ml of water, and the concentrated mixture was separated by chromatography using 98/2 (v/v) chloroform/methanol as eluant. The product was recrystallized from ethanol to give 1·27 g (53 per cent) of white solid. ^{13}C NMR (50°C): δ 14·0 (CH_3), 22·5, 25·9, 29·0, 29·1, 29·2, 29·3, 29·4, 29·5, 31·8, 33·2 (CH_2), 47·5 (br CH_2N), 68·2 (CH_2O), 114·4 (=CH_2), 139·0 (CH=), 114·5, 126·9, 128·7, 160·5 (Ar), 171·9 (C=O). The ^1H NMR spectrum was the same as that of compound **1**, except for small peaks at 4·95 and 5·82 ppm (CH=CH_2). Analysis calculated for $C_{125}H_{194}N_6O_{12}$: C, 76·10; H, 9·91; N, 4·26. Found: C, 76·00; H, 9·74; N, 4·17 per cent.

2.6. *Polymer 5a*

Compound **4** (0·81 g, 0·41 mmol), poly(methylhydrosiloxane-co-dimethylsiloxane) (0·19 g, 0·40 mmol Si—H) and 5 ml of dry toluene were added to a 10 ml glass tube containing a micro stirring bar. The polymer from Petrarch, $M_n = 2000–2500$, was reported to contain 15–18 per cent of hydromethylsiloxane repeating units. A stream of argon was bubbled through the solution for 15 min, and 4 μl of platinum divinyltetramethyldisiloxane catalyst (3·0–3·5 wt per cent platinum solution in xylene from Petrarch) was added. The tube was sealed and kept at 100°C for 48 h. The Si—H IR absorption at 2140 cm^{-1} had disappeared. The polymer was precipitated into 60 ml of methanol with stirring and separated by centrifugation. It was reprecipitated 12 times from chloroform by slow addition of methanol with continuous stirring to remove residual compound **4** (which comprised about 40 per cent of the initial product by SEC analysis) to yield 80 mg (8 per cent) of purified polymer **5a**.

2.7. *Polymer 5b*

The procedure above was followed using 0·45 g of **4** (0·23 mmol), copolysiloxane (0·03 g, 0·2 mmol Si—H), and 5 μl of an ethanol solution containing chloroplatinic acid (H_2PtCl_6, 0·1 mg). The starting polymer from Petrarch, $M_n = 900–1000$ ($DP_n = 14$), contained 50–55 per cent of hydromethylsiloxane repeat units reported by the supplier and 53 per cent hydromethylsiloxane and $M_n = 1300$ ($DP = 17$) determined by ^{29}Si NMR analysis [14]. The polymer **5b** was isolated by 3 precipitations from chloroform into methanol and purified by fourteen 0·1 ml injections of a THF solution containing a total of 200 mg of the polymer into the SEC at a flow rate of 1 ml min^{-1} to yield 53 mg (11 per cent) of purified **5b**.

2.8. *Characterization of the phases*

Thermal transitions of macrocycles **1**, **2**, and **4** and polymers **5a** and **5b** were studied with 5–10 mg samples on a Perkin-Elmer DSC 2C differential scanning calorimeter at heating and cooling rates of 20 K min^{-1}, unless noted otherwise. Two separate scans were done for polymer samples: from about −100°C to 50°C under nitrogen, and from 20°C to about 180°C under air. The first order transitions reported are the extrema of the endothermic and exothermic peaks. Glass transition temperatures (T_g) are reported as the midpoint of the change of heat capacity. Temperature and ΔH measurements were calibrated with indium. The thermal transitions and anisotropic textures were observed on a Nikon 104 optical polarizing microscope fitted with a Nikon 35 mm automatic camera and an Instec hot stage (Boulder, Colorado). X-ray measurements were performed using a Rigaku Ru-200 rotating anode X-ray generator with CuK_α radiation selected and focused by a bent LiF monochromator. For some measurements the signal was detected by LiF analyser and NaI scintillation detector; for other measurements detection was accomplished with an Inel 120° curved position-sensitive detector.

3. Results and discussion

3.1. *Syntheses*

The **[18]-N_6** derivatives **1**–**5** were synthesized as shown in figure 2 and presented in the experimental section. A major problem in the synthesis of mono-substituted azamacrocyclic compounds is the minimization and separation of the multi-substituted by-products. In the synthesis of mono-*N*-acylated azamacrocyclic compound **3**, a large excess of **[18]-N_6** was used to reduce multi-*N*-acylation. Even at a molar ratio of **[18]-N_6** to acyl chloride of 3, about 30 per cent of the three isomeric di-substituted macrocycles and also tri-substituted compounds were detected by TLC and ^{1}H NMR.

The side chain polymers **5** were prepared by hydrosilylations. To reduce the steric hindrance, copolysiloxanes with 15–18 per cent and 50–55 per cent of Si—H bonds were used as starting materials. Both ^{1}H NMR and SEC analyses (see table 1) show that about 32 per cent and 79 per cent, respectively, of the Si—H bonds of the two copolysiloxanes were substituted with azamacrocyclic groups. The products contain 75 per cent and 84 per cent of mesogen by weight. Due to use of substantial excesses of compound **4** over the Si—H groups of the copolymers, extensive reprecipitations were needed to remove **4** from the products. We assume that steric hindrance at the backbone prevents further hydrosilylation over a long time with excess of alkene **4** and extra Pt catalyst. Since no Si—H bonds were detected in the products, we presume that the Si—H bonds that did not hydrosilylate did react by hydrolysis or oxidation with traces of water or oxygen [15, 16]. Less than quantitative yields of hydrosilylation of siloxanes have been reported even with a discotic mesogen of molecular weight 827 [17], much less than the molecular weight of 1973 of compound **4**. To our knowledge this is the largest mesogenic group ever used for a side chain polysiloxane.

3.2. *Liquid crystalline phases*

3.2.1. *Hexa-amide* **1**

The liquid crystalline behaviour of the macrocyclic hexa-amide **1** has been investigated at length [1–4, 6, 7]. It depends on the method of purification and the thermal history. The first sample of this material studied at Oklahoma State University [3] apparently contained a non-stoichiometric amount of water that was not removed by drying under vacuum, and it had a lower melting transition temperature and a lower transition temperature from the mesophase to the isotropic phase than samples reported by other groups [1,2,4]. Now we find that lyophilization of a benzene solution, as suggested by Lattermann [10], gives us a new sample of **1** that is analytically pure.

DSC analysis shows that not only were the first heating curves of azamacrocycle **1** different from the second ones, but the transitions also were affected by

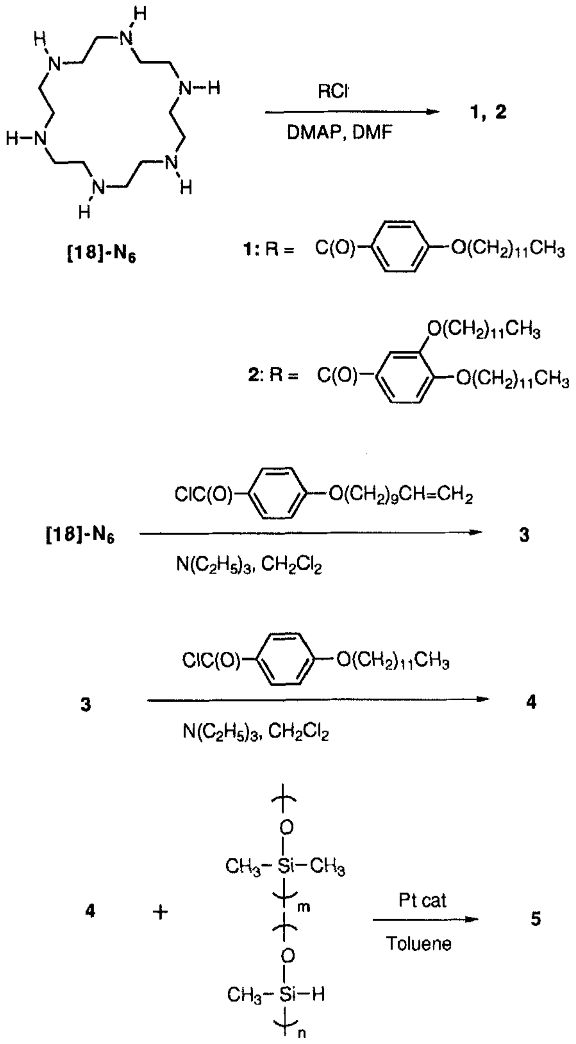

Figure 2. Synthetic scheme.

Table 1. Polymer properties.

Sample	M_w	M_n	Hydrosilylation per cent yield	Wt% mesogen
5a	12 230	7830	79	75
5b	10 130	7430	32	84

recrystallization conditions and thermal history. Different DSC results have been reported for this compound prepared in different laboratories [1–4]. Table 2 summarizes our new results and all of the results in the literature on the phase transitions of **1**. New thermograms are in figure 3. Polarizing microscopic textures of **1** obtained by cooling from the isotropic phase at 0·5 K min^{-1} and shearing at 100°C resemble that reported first [1]. However, if cooling was stopped and the sample squeezed between glass plates at about 100–110°C for one or more days, crystals formed as shown in figure 4. By contrast, the same compound held at a 0·5 mm capillary tube at 120°C for 26 days did not show any evidence, via X-ray diffraction, of a crystalline phase. A sample between glass plates at 120°C crystallized more slowly than at 100–110°C. These results most likely indicate that the glass slides act to nucleate a crystal phase that is more stable than the mesophase, but it is also conceivable that the amide-glass interface energetics stabilize a crystal phase that would otherwise be unfavourable. Spherulites with a maltese cross pattern grew from primary nuclei until they met in approximately straight boundaries. During spherulite growth at 105°C no new nuclei were observed once crystallization reached the stage shown in figure 4 (*a*). When the temperature was reduced after incomplete crystal growth, new nuclei formed. The rate of growth at 105°C was 18 μm h^{-1}. The induction time for nucleation from the supercooled melt at 105°C was about 10 hours. Compound **1** was stable during the annealing process. Its ^{1}H NMR spectrum, TLC, and HPLC behaviour did not change. The thermogram of the melt-crystallized **1** was much different from any previously reported (see figure 5). Despite the sharp X-ray diffraction pattern, the melt-crystallized **1** had a smaller enthalpy of melting (ΔH_m = 18·8 kcal mol^{-1}) than the solution-crystallized **1** (24–36 kcal mol^{-1} for various samples to transform the room temperature phase to the mesophase). Although

Table 2. DSC phase transitions of macrocycle **1**.

	Transitions/°C (ΔH/kcal mol^{-1})	Reference
First heating	C 121·5 (35·7) D 141·5 (0·7) I	[1]
	C 108·0 (25·4) D 140·0 (0·6) I	[2]
	C 102·0 (30·4) D 131·0 (0·7) I	[3]
	C 110·0 (7·0) D_1 118·0 (17·4) D_2 140·0 I	[4]
	C 110·0 (28·8) D 138·4 (0·7) I	†
	C 107·7 (13·7) D_1 119·4 (20·4) D_2 138·7 (0·6) I	‡
	C 77·2 (3·0) D 138·2 (0·7) I	§
Second heating	G 80·0 D 137·0 (0·5) I	[3]
	G 75·0 D 140·0 I	[4]
	G 75·0 D 138·6 (0·6) I	†
	G 70·0 D 138·5 (0·6) I	‡
	G 77·0 D 138·3 (0·6) I	§
	C 138·6 (18·6) I	‖
	C 141·0 (18·8) I	¶

C = crystal, D = discotic mesophase, I = isotropic liquid, G = glass.
†This work, recrystallized from ethanol.
‡This work, recrystallized from chloroform/ethanol (1:1).
§This work, isolated by lyophilization of a benzene solution.
‖Annealed at 100°C for 3 days.
¶Sample with spherulitic texture removed from cover glass slips.

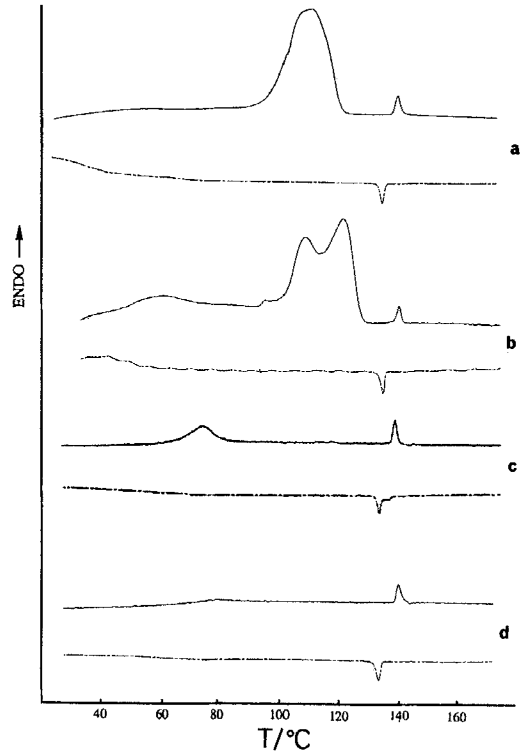

Figure 3. DSC thermographs of **1**. (*a*) First heating and cooling of a sample recrystallized from ethanol. (*b*) First heating and cooling of a sample recrystallized from chloroform/ethanol (1/1 v/v). (*c*) second heating and cooling of all samples. (*d*) First heating and cooling of a sampled obtained by lyophilization of a benzene solution.

melt-crystallization between glass slides gave bigger, better formed crystals, the ΔH_m of the melt-crystallized sample is less than ΔH_m of the solution-crystallized samples. After heating into the isotropic phase and cooling there was no difference between samples obtained from solution and samples obtained by melt-crystallization.

Scanning electron microscopy showed significant morphological differences between solution- and melt-crystallized **1** (see figure 6). Well-developed lamellae are visible in the annealed sample, whereas the sample isolated from solution shows less regular, smaller crystals. The lamellae of **1** resemble previous micrographs of frozen smectic multilayers [18].

X-ray diffraction measurements of melt-crystallized **1** were carried out on a sample obtained by annealing between glass microscope slides, and on a powder sample scraped from a slide and loaded into a capillary. The sample still on the glass slide shows considerable preferential alignment. A diffraction pattern collected in a reflection geometry from this sample (see figure 7) shows a single set of lamellar reflections with a periodicity in $q=0{\cdot}1416\pm0{\cdot}0014\,\text{Å}^{-1}$, corresponding to a layer spacing of 45·2 Å. Diffraction measurements in a glancing-angle configuration reveal a two-dimensional powder pattern. The entire in-plane plus out-of-plane X-ray diffraction pattern can be indexed with a monoclinic unit cell, with sides of 45·2,

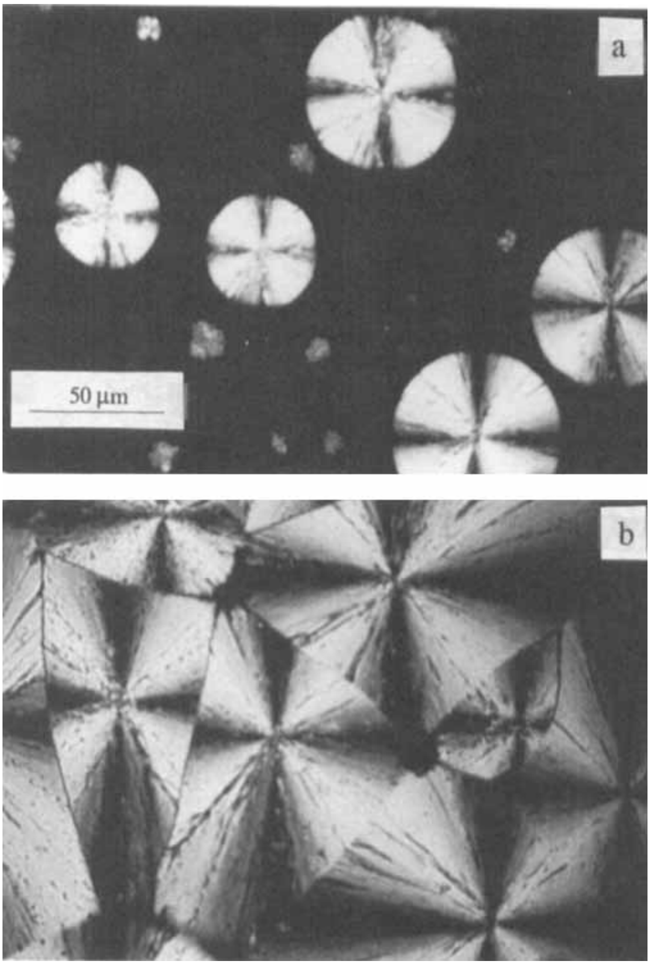

Figure 4. Polarizing micrograph of **1** taken (*a*) after 35 h at 105°C; (*b*) after 59 h.

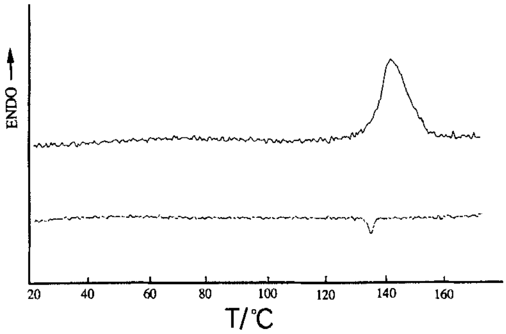

Figure 5. DSC thermographs of annealed **1** with spherulitic morphology removed from cover glass slips.

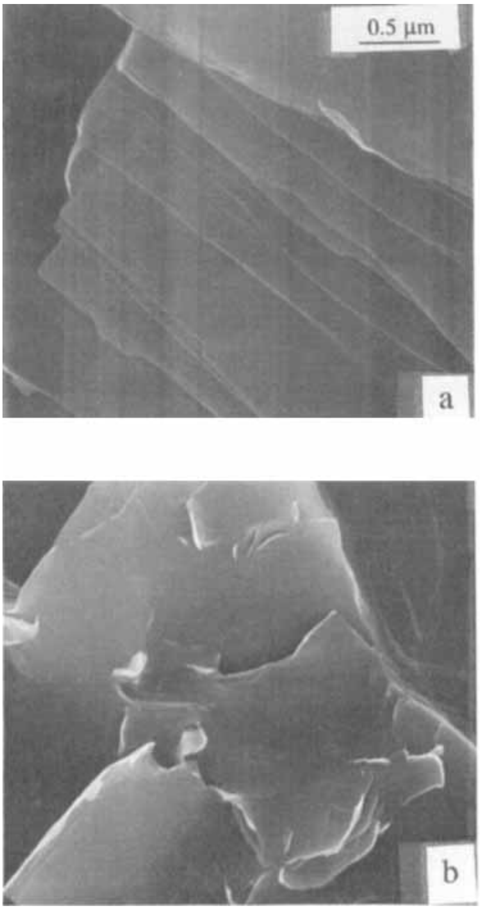

Figure 6. Scanning electron micrographs of **1**. (*a*) Annealed sample with spherulitic morphology. (*b*) Sample obtained by recrystallization from chloroform/ethanol.

28·1, and 9·6 Å, and a 118° angle between the shorter sides. This gives a unit cell volume of 10 800 Å^3. Assuming four molecules per unit cell there are $3{\cdot}7\times10^{20}$ molecules per cm^3, and the density of the crystal is 1·222 g cm^{-3}.

The 45·2 Å spacing of the crystal exceeds the 32·6 Å spacing previously measured for the monomer **1**, but is less than the end-to-end distances of about 50 Å calculated by molecular modeling for a linear conformation of **1** [4]. In conjunction with an in-plane structure that is close to, but not exactly, hexagonal, this suggests that in the melt-grown phase the structure is the following: The molecules assume a linear conformation, more similar to that proposed for a smectic structure than that of a hexagonal structure [4]. Within the layers, the molecules are close packed in a lattice that is close to hexagonal. The molecules are tilted by ~26° in a low symmetry direction, breaking the hexagonal symmetry and reducing the layer spacing from 50 to 45 Å. While this model is physically appealing and is consistent with the measured lattice parameters, we emphasize that a detailed intensity analysis of our XRD data is not possible at this time, and that the proposed structure is only hypothetical.

The above X-ray data are much different from those reported earlier [4] for crystals obtained from CH_2Cl_2/CH_3OH, in that the melt-crystallized sample has more, different, and sharper peaks, even though TLC and HPLC show that the two compounds are the same. Evidently more than one crystal phase is possible in this compound, and the phase actually achieved depends on the history of the sample.

3.2.2. *Hexa-amide 2*

Macrocyclic hexa-amide **2** with two dodecyloxy substituents per benzene ring has clear enantiotropic phase behaviour by DSC (see figure 8) analogous to that of the C_{10} homologue reported by Lattermann [10]. Its longer chains give the C_{12} compound **2** lower melting and isotropization temperatures. None of the complications of the phase behaviour of compound **1** was observed. The first and second DSC heating and cooling scans were identical. The phase transitions in °C were (ΔH in kcal mol^{-1}):

$$\begin{array}{l} C_1 \quad 8{\cdot}4 \quad (11{\cdot}5) \quad C_2 \quad 106{\cdot}7 \quad (6{\cdot}1) \quad D \quad 126{\cdot}5 \quad (2{\cdot}2) \quad I \\ \xrightarrow{\hspace{9cm}} \\ \xleftarrow{\hspace{9cm}} \\ C_1 \quad -4{\cdot}9 \quad (10{\cdot}9) \quad C_2 \quad 89{\cdot}8 \quad (3{\cdot}7) \quad D \quad 116{\cdot}7 \quad (2{\cdot}5) \quad I \end{array}$$

On cooling the isotropic melt of hexa-amide **2**, the mesophase grew from digitated stars, and developed a focal-conic texture with spherulitic domains (shown

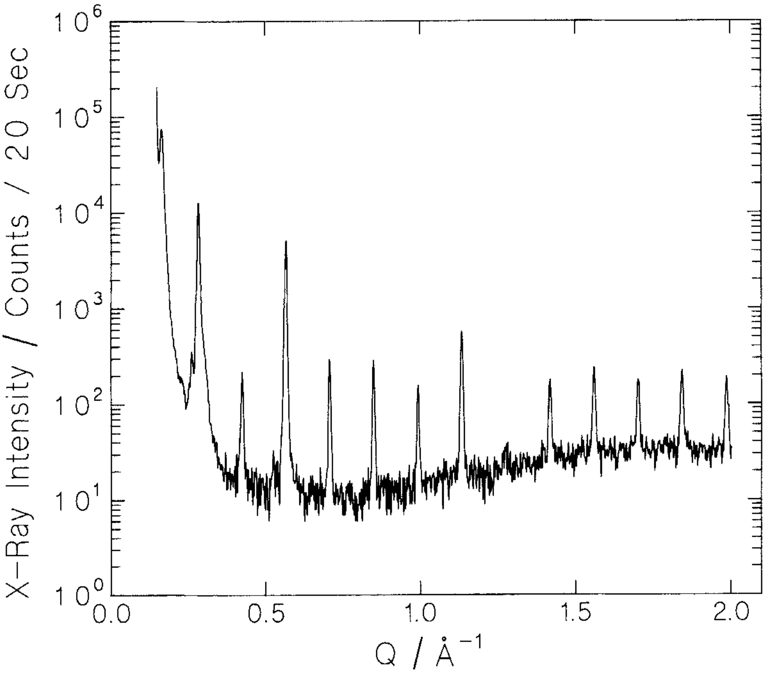

Figure 7. Reflection-geometry X-ray diffractogram at 27°C of a sample of **1** annealed on a glass slide. Since the momentum transfer was perpendicular to the surface, this scan probes planes parallel to the glass substrate. Note semi-logarithmic scale.

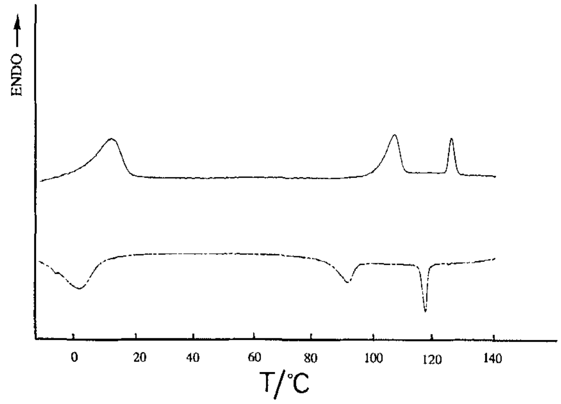

Figure 8. DSC thermographs of **2**; second heating and cooling.

in figure 9) similar to those of discotic liquid crystals with hexagonal columnar (D_{hd}) phases [2, 11]. There was no obvious change of the texture on cooling from 80° to the C_2 phase at 5°C, but there was a continuous change in the colour. During the second heating, the texture and the colour changed between 100 and 130°C as streaks appeared in the focal-conic domains (see figure 10). The change of colour and a streak texture have been reported by Lattermann for the D_{hd} mesophase of some sugar-based discotic liquid crystals [11]. X-ray diffraction shows many peaks and a diffuse halo at 80°C. In the absence of a two-dimensional indexing scheme for the sharp peaks we have assigned the phase between 8 and 107°C to an unidentified crystal. At 110°C there is one sharp peak corresponding to $d = 33$ Å and a diffuse halo. This is the signature of either a smectic or a columnar phase. Given the structure of the molecule, the most likely structure is columnar.

3.2.3. *Polysiloxanes* **5a** *and* **5b**

The unsymmetrical macrocyclic hexa-amide **4** used to prepare the polymers was also liquid crystalline. Crystallized from solution, **4** had phase behaviour and texture similar to that of symmetrical macrocycle **1**, but with lower transition temperatures (in °C): G 67 D 120 I. Spherulitic crystals also developed from the annealed mesophase.

The polymers **5a** and **5b** have the highest molecular weight mesogen of all discotic side chain polymers reported. They are birefringent waxy solids at room temperature. The DSC curve of the first heating of **5a** consisted of a glass transition at about 68°C and an isotropic transition at 101°C, as shown in figure 11. There was no exotherm in cooling scans. In the second scan, only a weak glass transition was detected. Without annealing the polymers exhibited only a featureless grainy birefringent texture. Both polymer samples annealed at 80–100°C for long time failed to crystallize like **1**, had a schlieren texture (shown in figure 12 for the anisotropic glass at room temperature) that was stable at room temperature for at least six months, and had an isotropic transition temperature at about 100–110°C.

An X-ray diffractogram of polymer **5a** is shown in figure 13. The sample was cooled from the isotropic phase at 125°C to the mesophase at 100°C, held 15 min at 100°C, cooled rapidly to room temperature, and reheated to 98°C to give a peak at

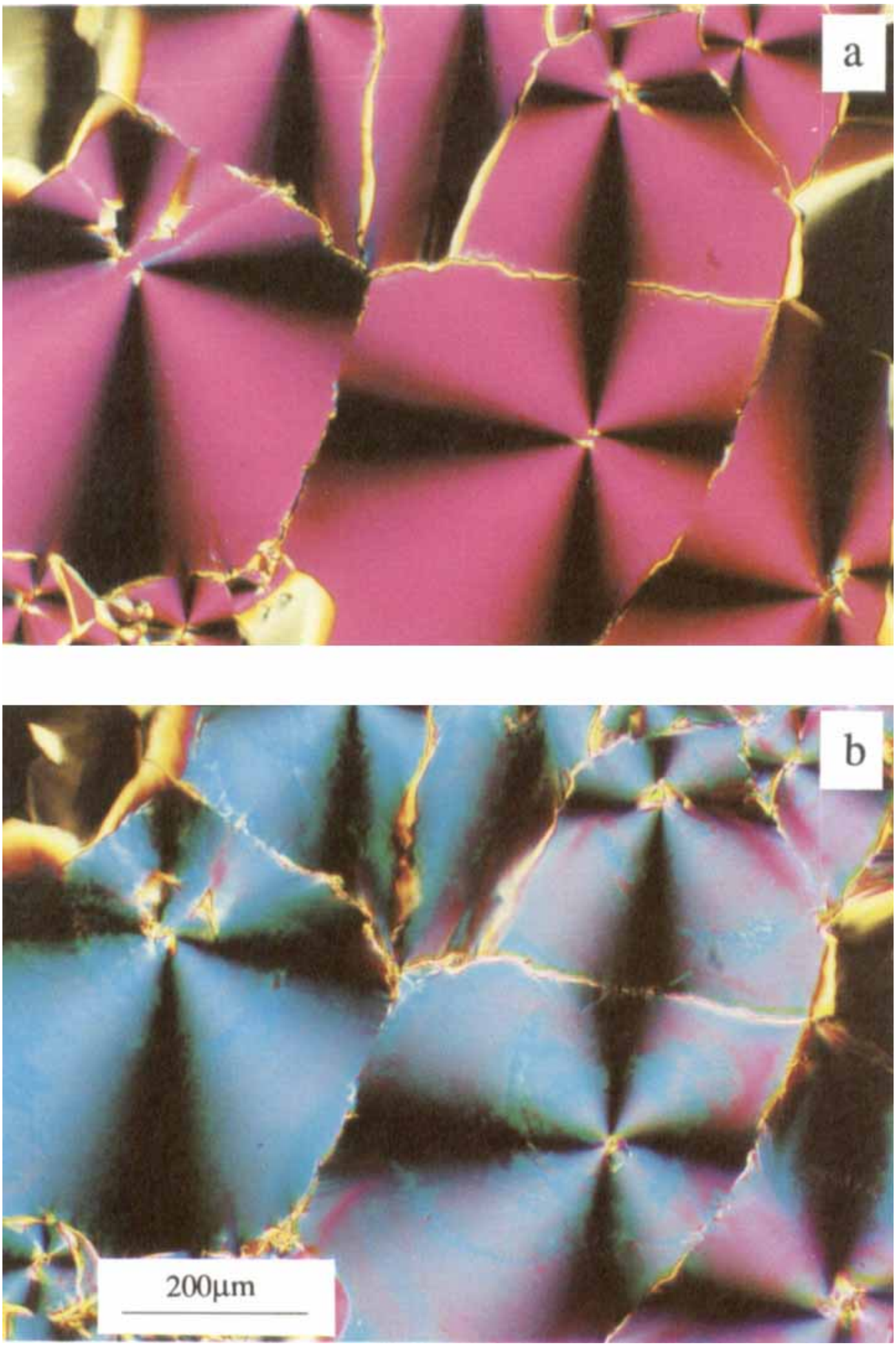

Figure 9. Polarizing microscopic textures of **2** obtained by cooling from the isotropic phase to (*a*) the mesophase at 120°C and (*b*) the C_2 phase at 5°C.

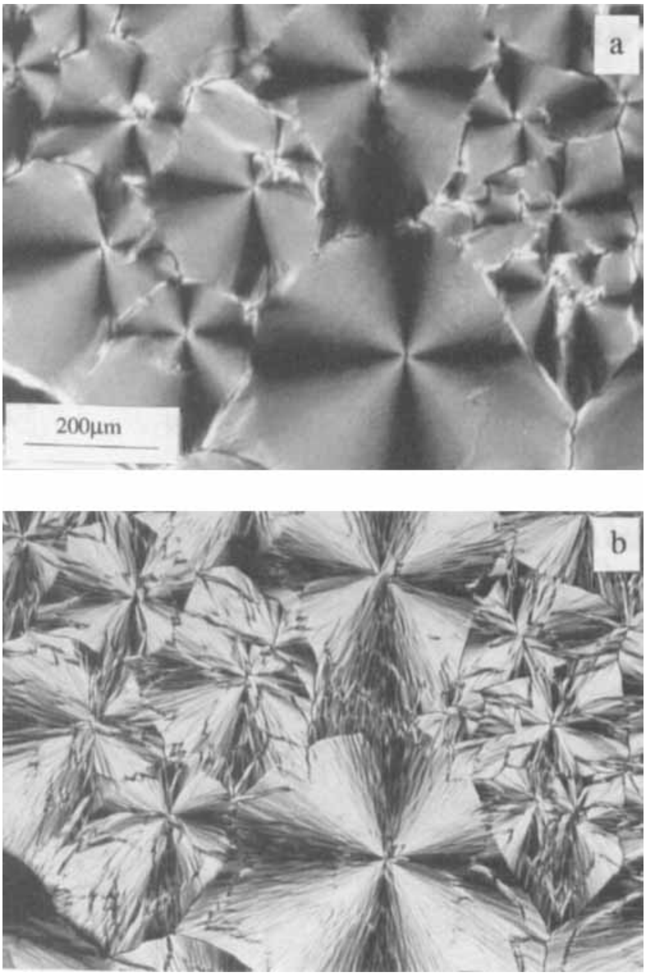

Figure 10. Polarizing microscopic textures of **2** obtained by second heating to (*a*) the C_2 phase at 80°C and (*b*) the mesophase at 120°C.

$q(=4\pi\sin\theta/\lambda=2\pi/d)=0{\cdot}1620\,\text{Å}^{-1}$, together with a diffuse maximum at larger wavevector. High resolution synchrotron X-ray diffraction on a sample prepared in the same way showed that the width of the peak at $0{\cdot}1620\,\text{Å}^{-1}$ was $0{\cdot}003\,\text{Å}^{-1}$. These data correspond to a nematic phase having a correlation length of 600–700 Å and a *d*-spacing of 38·8 Å. The broad feature at $1{\cdot}4\,\text{Å}^{-1}$ most likely arises from short-range correlations between paraffinic tails. The lesser order of the polymer mesophase compared to the parent macrocycle **1** is likely due to its being a mixture of oligomers with a range of substitution of the side chain mesogen on the copolysiloxane.

4. Conclusions

The phase behaviour of macrocyclic amide **1**, previously said to have a tubular mesophase, is more complicated than known before. When confined between microscope slides, the mesophase crystallizes by annealing to a phase that is different from the crystal phase obtained by precipitation from solution. The crystals obtained from the melt have a well-defined preferential orientation on the glass slides. However, when contained in a capillary, the mesophase is stable for at least tens of days, indicating that the amide–glass interface is crucial to nucleation of the melt-grown crystal phase. The analogue **2**, having twelve rather than six C_{12} chains, has an enantiotropic columnar mesophase, and the polysiloxanes **5a** and **5b** with the same mesogenic moiety as **1** have a nematic mesophase.

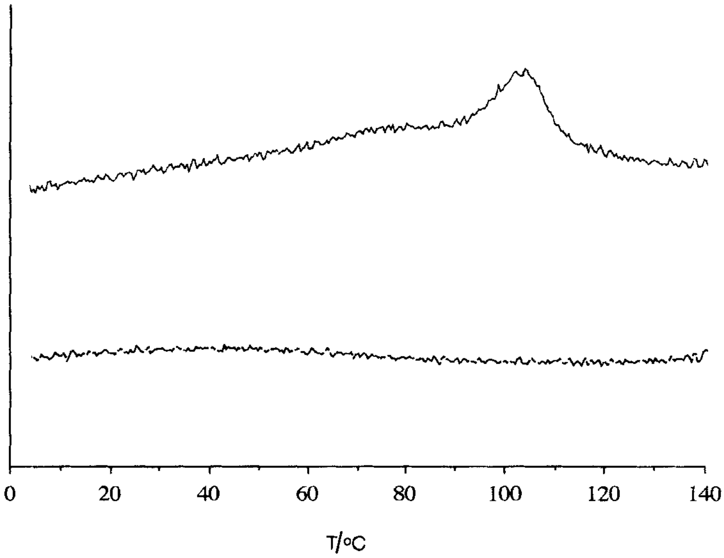

Figure 11. DSC thermographs of polymer **5a**, first heating and cooling.

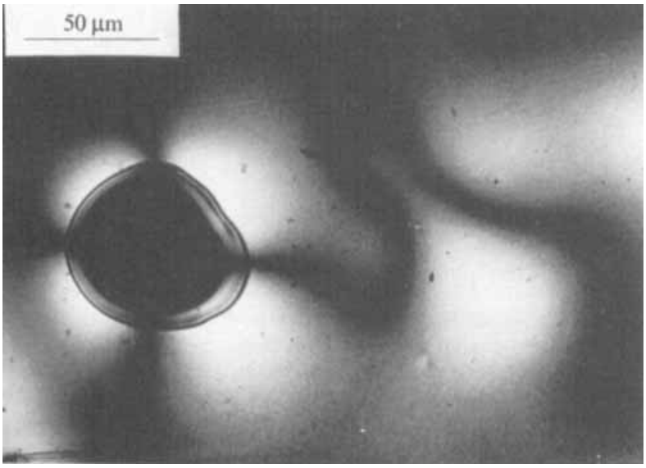

Figure 12. Polarizing microscopic texture of polymer **5b** annealed at 100°C for 5 days.

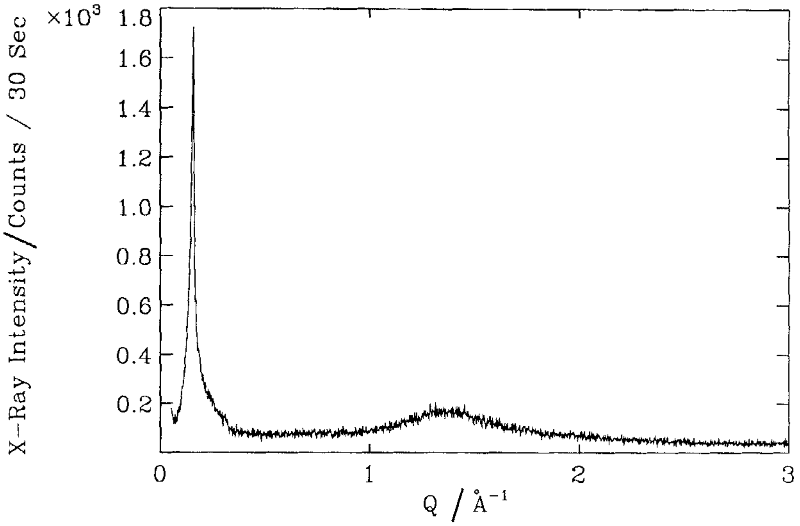

Figure 13. X-ray powder diffractogram of polymer **5a** measured in the bulk mesophase at 98°C. The strong maximum at $0{\cdot}1620\,\text{Å}^{-1}$, in conjunction with polarizing microscopy observations, supports the assignment of this phase as a nematic. The broad feature at $1{\cdot}4\,\text{Å}^{-1}$ most likely arises from short range correlations between paraffinic tails.

In chloroform solution, macrocycle **1** has more than one low symmetry conformation of the macrocycle interconverting on the NMR time scale at room temperature [3]. Both the macrocycle and the side chains must be disordered in the mesophases of low molar mass compounds **1**, **2**, and **4**, and polymers **5** as well. Low order is indicated by the very small entropies of isotropization of the materials. We pointed out previously that with disordered conformations, columns of **1** cannot have a large tube in the centre [3].

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