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Liquid Crystals

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Online publication date: 06 August 2010

To cite this Article Rais, K. , Gharbia, M. , Gharbi, A. , Nguyen, H. T. , Destrade, C. and Daoud, M.(1999) 'Elliptical diffusion of dye in hexagonal columnar polycatenar mesophases', *Liquid Crystals*, 26: 7, 1079 – 1084

To link to this Article: DOI: 10.1080/026782999204435

URL: <http://dx.doi.org/10.1080/026782999204435>

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Elliptical diffusion of dye in hexagonal columnar polycatenar mesophases†

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(Received 19 October 1998; accepted 13 January 1999)

We have studied polycatenar compounds which exhibit hexagonal columnar mesophases. In the planar orientation of these mesophases, the elliptical diffusion of the dissolved dyes is visualized by taking several pictures of the sample. The diffusion ratio $D_{//}/D_{\perp}$ is deduced for these columnar mesophases. Furthermore, using a classical optical absorption technique, we present measurements of dye diffusion in the same mesophases. The diffusion constants are measured in two geometries, along and perpendicular to the columns. The diffusion anisotropy ratios are in agreement with those deduced from the ellipse axes. The structure of these new columnar mesophases exhibited by rod-like mesogens is compared with that of disk-like mesogens.

1. Introduction

It is well known that the new family of rod-like mesogens named 'phasmids', or generally polycatenar compounds, exhibit a rich thermotropic mesomorphism. The relationships between molecular architecture and mesomorphic properties are determined largely by the global shape of the rod-like molecules of the mesogen. Several previous studies have shown that the resulting polymorphism may include nematic, lamellar, cubic and columnar liquid crystal phases [1–4].

Recently, we have used an optical technique based on the detection of transmitted light through columnar discotic liquid crystals in the presence of appropriate diffusing dyes. This study allows us to measure the diffusion coefficients $D_{//}$ and D_{\perp} in the hexagonal columnar mesophases for the two configurations, along and perpendicular to the columns. The results show clearly the presence of anisotropic diffusion in these mesophases, leading to a better understanding of their columnar discotic structure [5–8].

In this paper, the dye diffusion is represented by an experimental ellipse, whose axes allow us to deduce the diffusion anisotropy ratio $D_{//}/D_{\perp}$. Experiments have been performed on a number of hexagonal columnar polycatenar mesophases. A comparison of the results with the values measured by a classical optical technique allows us to conclude that this experimental approach can be used to show the anisotropy of the diffusion of matter in columnar mesophases. Thus, this technique may be used to undertake a comparative study of the diffusion of matter in the columnar polycatenar and discotic mesophases, providing a better understanding of the molecular organization. We discuss, in particular, the nature of this diffusion in connection with the structure of these new types of hexagonal columnar mesophases. We distinguish between the ways the molecules stack in disk-like and rod-like mesogens.

2. Experimental

2.1. Materials

The polycatenar compounds present a clear rod-like core which is composed of an elongated polyaromatic part containing, in general, five rings connected in the *para* position, and a number of normal aliphatic chains

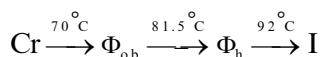
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† This work has been written in memory of the late C. Destrade.

linked only onto the two terminal benzene rings in the *para* and/or *meta* positions [1, 2, 9, 10]. They exhibit columnar mesophases which might be called Col_D phases like those of disc-like compounds [11–13]. However, the term ‘phasmidic’ mesophases (denoted by Φ , the initial letter of the Greek root) is used to distinguish these new types of columnar mesophases from the disc-like ones, due to the difference in their molecular organization. In fact, the columnar structure of discotic liquid crystals is shaped by the better arrangement of disc-like molecules as they pile up in the column [11, 14], whereas the molecular packing of polycatenar mesophases is based on the packing of molecules with rod-like cores as given in a model previously designed for hexacatenar compounds [9]. This model considers that a slice of a column consists of a cluster of rigid cores arranged side by side and surrounded by aliphatic chains. In each slice, the number of molecules is three for the hexacatenar and four to five for the tetracatenar mesogens [1, 9].

Experiments were performed with the following polycatenar compounds:

- (i) *A hexacatenar mesogen* [3(mpm)+3(mpm)] (named ‘phasmid’ from the name of six legged stick-like insects) [1]. This is a polycatenar mesogen with three alkyloxy chains $R = n\text{-C}_n\text{H}_{2n+1}\text{O-}$ ($n = 12$) connected in the *meta*, *para* and *meta* positions at each end of the molecule, figure 1(a). It undergoes the following phase transitions [3]:



where Φ_{ob} and Φ_{h} denote phasmidic mesophases with, respectively, an oblique and a hexagonal two dimensional lattice.

- (ii) *Two tetracatenar mesogens* [2(mm)+2(mm)] (named ‘biforked’ mesogens) [10, 15, 16]. This type of molecule has two alkyloxy chains $R = n\text{-C}_n\text{H}_{2n+1}\text{O-}$ ($n = 10$ or 14) connected in the *meta*, *meta*

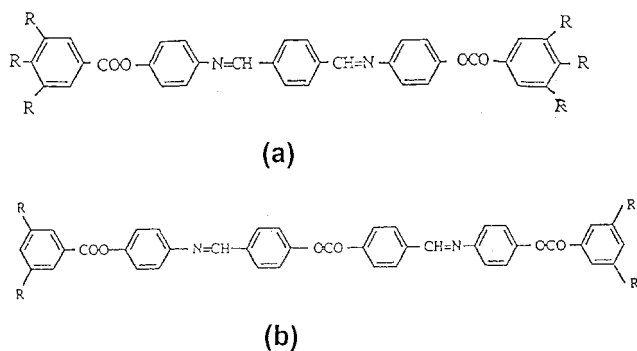
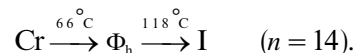
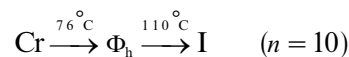


Figure 1. Chemical formulae of two types of polycatenar mesogens: (a) a hexacatenar [3(mpm)+3(mpm)], (b) a tetracatenar [2(mm)+2(mm)].

positions, at each end of the molecule, figure 1(b). They, respectively, exhibit the following hexagonal mesophases:



The choice of these hexacatenar and tetracatenar compounds was made because they all have a thermotropic hexagonal mesophase Φ_{h} . The different number, position and length of the aliphatic chains allow us to examine the influence of these parameters on the anisotropic diffusion ratio D_{\parallel}/D_{\perp} .

2.2. Experimental method

The sample was placed between two glass plates L_1 , L_2 with a thickness $e = 20\ \mu\text{m}$ (figure 2). The upper glass plate, supplied by the Physical Research Department of Pierre et Marie Curie University (Paris VI), had a circular hole in the centre of about 1 mm diameter, allowing us to place the diffusing dye in contact with the liquid crystal. The experimental set-up and the techniques used for observing the phase transitions, the annealing of the sample between two transitions as well as for orientating the mesophases, are described in references [5, 17].

Before orientating the columns in the two configurations, parallel to the plates (planar orientation) or perpendicular to them (homeotropic orientation), a PVA treated glass was used to orient the hexacatenar C_{12} , and a clean glass to orient the tetracatenar C_{10} and C_{14} specimens. The preliminary glass treatment facilitates the homeotropic orientation of the columns.

The dye diffusing into these mesophases was an appropriate biological stain, the Red Oil O (dye content $\approx 85\%$), the chemical structure of which, 1-[4-(xylylazo)xylylazo]-2-naphthol, is presented in figure 3. A thin film of this dye, which has a melting point $T_f = 120^\circ\text{C}$, well beyond the temperature domain of the mesophases studied, was carefully placed in the hole of the upper glass, in contact

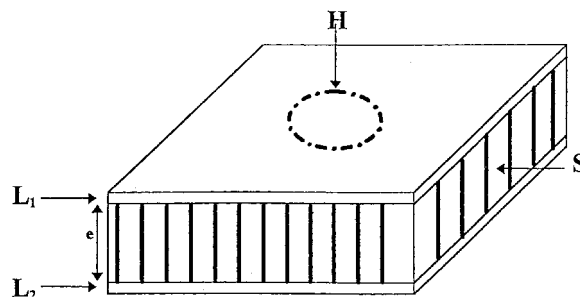


Figure 2. Experimental set-up: L_1 , L_2 = glass plates, H = hole, S = sample, e = thickness.

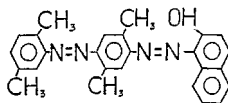


Figure 3. Chemical formula of a dye, the 1-[4-(xylylazo)-xylylazo]-2-naphthol.

with the liquid crystal. The dye molecules which diffused into the liquid crystal could be directly observed with an optical polarizing microscope.

Quantitatively, to determine the concentration of dye diffusing along the columns or perpendicular to them, and consequently to deduce the diffusion coefficients, we used a technique consisting in measuring the diffusion profile, versus the position x and versus the column orientations. In practice several pictures of the dye diffusion profiles into the mesophases were taken at different times. The study of these pictures shows that the diffusion symmetry is circular for the homeotropic orientation (figure 4) and elliptical for the planar orientation (figure 5). The mean axes of the ellipse correspond to dye diffusion into the mesophase along the columns and perpendicular to them. Measurement of the lengths of the axes of the ellipse allows us to deduce the ratio D_{\parallel}/D_{\perp} of the diffusion coefficients.

3. Theory

For a 1D treatment of molecular diffusion, the dye concentration $C(x, t)$ is related to the diffusion coefficient according to the second Fick's law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C(x, t)}{\partial x^2} - \langle \Gamma_0 \rangle C(x, t) \quad (1)$$

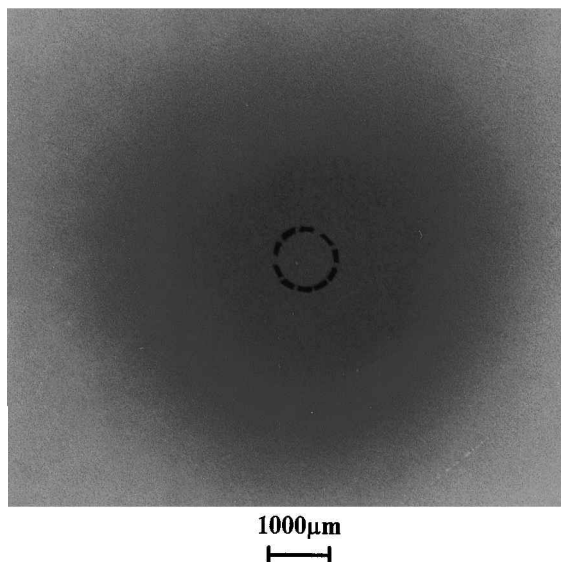


Figure 4. Circular geometry of the dye concentration of profile in homeotropic orientation of the hexacatenar columnar mesophase ($t = 180$ h).

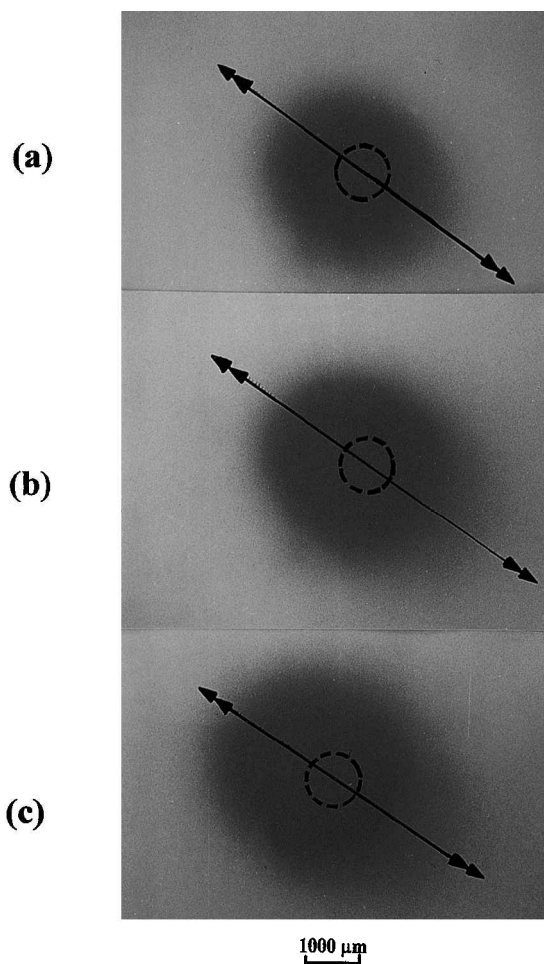


Figure 5. Elliptical geometry of the dye concentration profile in planar orientation of the hexacatenar columnar mesophase for three time intervals: (a) $t_1 = 15$ h, (b) $t_2 = 29$ h, (c) $t_3 = 42$ h.

where D is the diffusion coefficient and $\langle \Gamma_0 \rangle$ is the jump frequency.

As in the discotic columnar mesophases [5, 7], we assume that the polycatenar columns behave like a solid line made by a cluster of rigid cores surrounded by an aliphatic crown. Using the atomic theory [18], the diffusion coefficient in these columns is given by:

$$D = \frac{1}{n} \Gamma_0 L^2 \quad (2)$$

where n , and L represent, respectively, the number of sites and the mean free path. Taking $L = 10$ nm and $n = 6$, we have estimated a jump frequency Γ_0 of about 10^8 s $^{-1}$.

Equation (1) leads to a solution of the form:

$$C(x, t) = C(0, t) \exp\left(-\frac{x^2}{4Dt}\right) \quad (3)$$

where $C(0, t)$ is the concentration at the origin, and is given by:

$$C(0, t) = \frac{Q}{(\pi Dt)^{1/2}} \exp(-\langle \Gamma_0 \rangle t) \quad (4)$$

with

$$Q = \int_0^\infty C(x, t) dx \quad (5)$$

where Q represents the relative quantity of dye molecules diffused by unit area. Equation (3) predicts that $C(x, t)$ is given by half a gaussian centred on $C(0, t)$. Equation (4) shows that $C(0, t)$ decreases as $(t)^{-1/2}$ with an attenuation factor of $\exp(-\langle \Gamma_0 \rangle t)$.

The equation of the ellipsoid without the influence of a hole is given by

$$\frac{X^2}{A^2} + \frac{Y^2}{B^2} = 1$$

with

$$A \cong (D_{||}t)^{1/2} \text{ and } B \cong (D_{\perp}t)^{1/2}. \quad (6)$$

Hence from equation (6) we can derive the ellipticity at all times as:

$$\frac{A}{B} = \left(\frac{D_{||}}{D_{\perp}} \right)^{1/2}$$

4. Results and discussion

We first consider the planar orientation of the mesophases. From the elliptical geometry (figure 5) of dye diffusion in the mesophases, the lengths of the ellipse

Table 1. Measurements of the anisotropic ratios $D_{||}/D_{\perp}$ for polycatenar mesogens by the ellipsoid axes.

Mesogen	Ratio $D_{ }/D_{\perp}$
Hexacatenar C ₁₂	2.0 ± 0.1
Tetracatenar C ₁₀	2.3 ± 0.1
Tetracatenar C ₁₄	1.8 ± 0.1

Table 2. Measurements of the dye diffusion constants $D_{||}$, D_{\perp} and ratios $D_{||}/D_{\perp}$ by the optical absorption technique, in polycatenar and discotic mesogens [5].

Mesogen	$D_{\perp} \times 10^7/\text{cm}^2 \text{ s}^{-1}$	$D_{ } \times 10^7/\text{cm}^2 \text{ s}^{-1}$	$D_{ }/D_{\perp}$
<i>Polycatenar</i>			
Hexacatenar C ₁₂	1.52 ± 0.03	3.08 ± 0.06	2.02 ± 0.08
Tetracatenar C ₁₀	1.00 ± 0.02	2.28 ± 0.05	2.28 ± 0.09
Tetracatenar C ₁₄	2.04 ± 0.04	3.80 ± 0.08	1.86 ± 0.08
<i>Discotic</i>			
C ₅ HET	0.94	1.49	1.58
C ₆ HET	1.5	1.9	1.27
C ₈ HET	1.75	1.93	1.1

axes are measured and the values of $D_{||}/D_{\perp}$ deduced. We present in table 1 the results of the three polycatenar compounds (**C**₁₀, **C**₁₂, **C**₁₄). To compare these results with the discotic mesogens ones, we present in table 2 the values of $D_{||}/D_{\perp}$ obtained by an optical absorption technique described in reference [5]. We determined the $D_{||}/D_{\perp}$ ratios of polycatenar mesogens by measuring the concentration $C(x, t)$ of dye molecules which diffuse into the mesophase versus the position x , at many time intervals (figure 6). We calculate the logarithm of the ratio $C(0, t)/C(x, t)$; the plot of $\ln[C(0, t)/C(x, t)]$ versus x^2 shows a linear behaviour (figure 7). From the slope, one can deduce the diffusion coefficients D_{\perp} and $D_{||}$ and the ratio $D_{||}/D_{\perp}$ which are reported in table 2. We observe perfect agreement of the measured values with those deduced from the ellipse axes.

Let us consider now the mesophases in homeotropic orientation. As expected, a circular geometry is obtained (figure 4) and we conclude that the orientation of the sample is almost perfect. In fact, the symmetry of the elliptical diffusion (planar orientation) and the circular diffusion (homeotropic orientation) provides strong

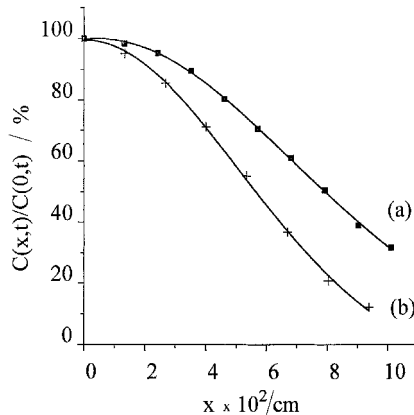


Figure 6. Plot of relative evolution of the dye concentration $C(x, t)$ in the hexacatenar columnar mesophase versus the position x ($t = 2$ h): (a) in homeotropic orientation, (b) in planar orientation.

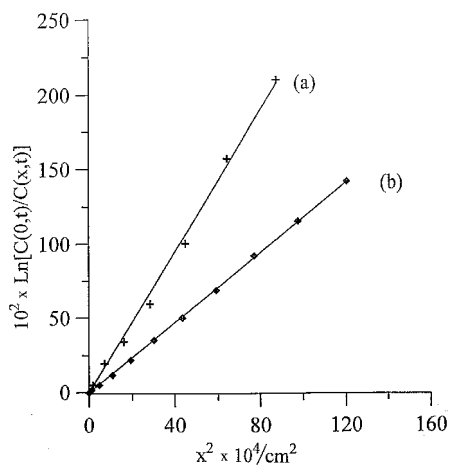


Figure 7. Plot of $\ln[C(0, t)/C(x, t)]$ versus x^2 : (a) in homeotropic orientation, (b) in planar orientation.

evidence of the very good orientation quality in both directions.

These results lead to the following observations. First, in the three compounds (C_{10} , C_{12} , C_{14}), the diffusion coefficients D_{\perp} and D_{\parallel} increase with the lengths of the aliphatic chains. This result is in good agreement with previous studies concerning discotic mesogens [5, 6]. It was interpreted as being due to the increase in the volume occupied by the aliphatic chains which form an average paraffinic crown around the columns and facilitate dye diffusion. As in discotic mesogens, the columnar polycatenar mesophases present anisotropic ratios which decrease with the chain lengths as: $(D_{\parallel}/D_{\perp})_{C_{14}} < (D_{\parallel}/D_{\perp})_{C_{12}} < (D_{\parallel}/D_{\perp})_{C_{10}}$ (tables 1 and 2). This means that the anisotropy becomes less pronounced when the chain lengths increase. In particular, the number of molecules in a column slice (three for the hexacatenars and four to five for the tetracatenars) seems to be insignificant.

Second, for a better explanation of dye diffusion in the Φ_h mesophases, it is useful to compare the columnar polycatenar results with the discotic results [5]. Table 2 gives the anisotropic ratios, showing that in the columnar polycatenar mesophases, we obtain $1.86 \leq D_{\parallel}/D_{\perp} \leq 2.28$, with an experimental error ≈ 0.08 ; whereas this ratio varies as $1.10 \leq D_{\parallel}/D_{\perp} \leq 1.58$ in the columnar discotic mesophases. We notice that the polycatenar anisotropic ratios are larger than the corresponding ratios in discotic mesophases. However, in both cases, to be more specific about the comparison between the diffusion along the columns and perpendicular to them, we calculate the average ratio $\Sigma D_{\text{POLYCATENARS}}/\Sigma D_{\text{DISCOTICS}}$ and find:

$$\frac{\Sigma D_{\perp \text{POLYCATENARS}}}{\Sigma D_{\perp \text{DISCOTICS}}} \approx 1$$

$$\frac{\Sigma D_{\parallel \text{POLYCATENARS}}}{\Sigma D_{\parallel \text{DISCOTICS}}} \approx 2.$$

The first ratio (≈ 1) shows that diffusion perpendicular to the columns is comparable in both columnar mesophases. If we assume that the molecules are aligned along the radius of a circular crown, a very dense paraffinic zone is obtained [2]. As in the discotic case, the matter diffusion in polycatenar mesogens bypasses the central part of columns and takes place in the paraffinic crown. The second ratio (≈ 2) shows that diffusion along the columns is quicker in the polycatenar mesophases. This effect can be explained mainly by the increase of the lateral chain lengths. Furthermore, using a chemical affinity we can also justify this effect by the impurity polarity (presence of phenol function in Red Oil O) leading to greater solubility in polycatenar compounds containing a polar group ($-\text{CH}=\text{N}-$). This effect may also be explained as a relatively more disordered disposition of the molecules along a column in comparison to the long range order observed in the discotic columns [14].

Thirdly, a comparison of dye diffusion in columnar polycatenar mesophases with some nematic phases shows a similar ratio D_{\parallel}/D_{\perp} . For instance, the diffusion of an impurity, Methyl-Red (MR), at 22°C , into a nematic mesophase exhibited by *p*-methoxybenzilidene-*p*'-*n*-butylaniline (MBBA) gives an anisotropic ratio $D_{\parallel}/D_{\perp} = 1.7$ [19]. Furthermore, this result seems to be in agreement with a recent study of diffusivity by Light Beating Spectroscopy in thermotropic nematic discotic mesophases exhibited by disk-like mesogens [20]. It was shown that the nematic order can be manifest in the packing of a few molecules (≈ 15 to 25) to form relatively short columns of the diameter of an individual disk.

Finally, for the tetracatenar compounds, we notice that interference colours are seen in the light transmitted by the sample, placed between crossed nichol prisms and illuminated by parallel white light. This can be explained by the existence of a short optical path difference (some wavelengths) which is probably due to a column inclination θ . This inclination can be estimated as follows:

- (1) Using a compensator, we measure the corresponding optical path difference and find $\delta = 0.4 \mu\text{m}$ for a thickness $e = 50 \mu\text{m}$. We deduce an effective birefringence such that $\Delta n_{\text{eff}} = n_{\text{eff}} - n_o \approx 0.008$, where n_{eff} is given, versus the ordinary index n_o and the extraordinary index n_e , by the ellipsoid of indexes:

$$\frac{1}{n_{\text{eff}}^2} = \frac{\sin^2 \theta}{n_e^2} + \frac{\cos^2 \theta}{n_o^2}$$

- (2) To measure the ordinary refractive indice n_o , we have used a Michelson interferometer; this gave $n_o = 1.52 \pm 0.02$.
- (3) Using the conoscopy technique with $n_o = 1.52 \pm 0.02$, the birefringence is found to be $\Delta n = |n_e - n_o| = 0.047 \pm 0.003$.

Therefore, we estimate a column inclination of about 5° to 6° with an arbitrary direction varying from one grain to another. However, the symmetry of the diffusion pictures (circular for the homeotropic orientation and elliptic for the planar orientation) proves the quality of the average macroscopic orientation.

5. Conclusion

It has been shown that elliptical diffusion in the planar orientation of some polycatenar mesogens can be used to determine the anisotropic diffusion ratios of dyes in the hexagonal phasmodic mesophases; we find $D_{||}/D_{\perp} = 1.8, 2.0$ and 2.3 . By a comparison of these values with results obtained from discotic columnar mesogens, we show that in both cases the anisotropic behaviour becomes less pronounced when the chain lengths increase. The average ratios

$$\frac{\sum D_{\perp \text{POLYCATENARS}}}{\sum D_{\perp \text{DISCOTICS}}} \approx 1 \text{ and } \frac{\sum D_{|| \text{POLYCATENARS}}}{\sum D_{|| \text{DISCOTICS}}} \approx 2$$

let us conclude that the molecular structure of a polycatenar holds an intermediate position between mesogenic discs and mesogenic rods.

Experimentally, we have observed an inclination of the column with an arbitrary direction varying from one grain to another. The measurement of the birefringence allows us to estimate the inclination θ of the columns to be about 5° to 6° . However, this inclination seems to have little effect on the diffusion profile, which is circular in the homeotropic or elliptic in the planar geometry.

The authors are indebted to J. P. Marcerou and J. Malthête for their contributions.

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