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Characterization of Some Fluorinated Mesogens for Application in Liquid Crystal Displays

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The long-range orientational order of some fluoro-substituted liquid crystals with different molecular structure was determined on the basis of the optical birefringence measurements. The high values of the second-rank order parameter in the whole mesophase range for the liquid crystals studied were found. The liquid crystals with the negative dielectric anisotropy were mixed with an arachidic acid at various molar fractions. The behavior of the mixtures in monolayers formed by using Langmuir-Blodgett technique was investigated.

Keywords Fluorinated liquid crystal; homeotropic orientation; Langmuir-Blodgett technique; optical birefringence; order parameter

1. Introduction

In last years, fluourinated liquid crystals have been a focus of intensive research. The fluorine atom combines the properties of having the large electronegativity and small size, which does not cause the excessive broadening of the molecule. The introduction of fluorine atoms into molecular system has a dramatic effect on its properties. Usually the decrease of the melting point and reduction of viscosity is observed. The fluoro-substituted liquid crystals are characterized by good optical and chemical stability, extended mesophase range, low viscosity, high specific resistance, low threshold voltage [1–3]. Due to their unique physical and material properties they are of great interest as components of mixtures for twisted nematic (TN) or super-twisted nematic (STN) liquid crystal displays, especially with the use of thin film transistor (TFT) technology [4,5]. The laterally fluoro-substituted liquid crystals are particularly interesting because they may exhibit both the positive and negative dielectric anisotropy as a result of the moderately polar C-F bond. The nematogens with the negative dielectric anisotropy can be used in displays operating in the multi-domain vertical alignment (MVA) mode [5]. Such displays are very attractive

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for large-area liquid crystal monitor and TV applications. Modern MVA panels can offer wide symmetrical viewing angle, high contrast, fast response time, good color reproduction and black depth. MVA displays require the initial homeotropic alignment of nematogenic molecules. One of the possibilities to achieve such alignment is covering the display surfaces with amphiphilic molecules using Langmuir-Blodgett technique [6].

The most physical properties of liquid crystals are strongly dependent on the molecular orientation, thus investigations of the degree of order of novel synthesized substances are very important. Here, we present the results of the study of the long-range orientational order of nine fluourinated liquid crystals. Two of them have positive dielectric anisotropy arising from the presence, beside of the fluorine atom in the lateral position, the strongly polar terminal cyano group. Six other liquid crystals, having two fluorine atoms in lateral positions, are characterized by negative dielectric anisotropy. The negative anisotropy has also the liquid crystal with two lateral and one terminal fluorine atoms. Optical birefringence measurements were used to determine the order parameter of liquid crystalline compounds. Next, the liquid crystals with the negative dielectric anisotropy were mixed with an arachidic acid at various molar fractions. The behavior of the mixtures in monolayers formed at air-water (Langmuir films) and air-solid substrate (Langmuir-Blodgett films) interfaces was studied. The attempt to achieve homeotropic alignment of liquid crystal molecules was made.

2. Experimental Methods

The molecular structure of compounds investigated is given in Figure 1. All liquid crystals were synthesized and chromatographically purified in Prof. R. Dąbrowski's Laboratory, Military Academy of Technology, Warsaw (Poland). All substances were used without further purification; their phase transition temperatures in the bulk, determined on the basis of textures observed by means of polarizing microscope equipped with a hot stage are given in Table 1. The data for liquid crystal 8OCFPB, 8OCPFB and 5DBF3 are in agreement with the data given in the literature [7,8]. Most of the liquid crystals under investigation have only a nematic (N) phase between the solid and isotropic phases. Only 5DBF3 has both nematic and smectic A (SmA) phases. Arachidic acid (AA) with a quoted purity of >99% was purchased from Sigma-Aldrich and used as received.

The most important parameter which describes the long-range orientational order in the liquid crystals with a sufficient accuracy is the second-rank order parameter [9]:

$$S = \langle P_2 \rangle = \frac{1}{2}\langle 3\cos^2 \beta - 1 \rangle, \tag{1}$$

where β is the angle between the long molecular axis and the direction of orientation of liquid crystal molecules, described by the director. The second-rank order parameter of the liquid crystals investigated was obtained on the basis of the optical birefringence measurements by using the following relation:

$$S_{\Delta n} = \frac{\Delta n}{\Delta n_{\max}}, \tag{2}$$

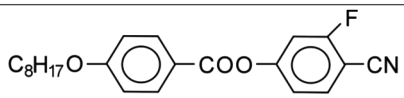
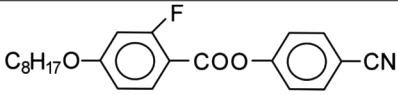
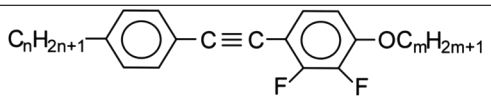
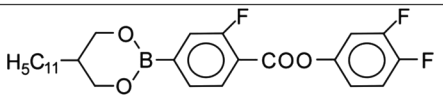
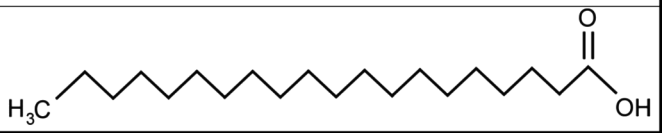
Compound	Molecular Structure
liquid crystals with positive dielectric anisotropy	
8OCFPB	
8OCPFB	
liquid crystals with negative dielectric anisotropy	
Nnm n = 3,5 m = 2,3,4	
5DBF3	
arachidic acid	
AA	

Figure 1. Molecular structure of compounds used.

where Δn and Δn_{max} denote the optical birefringence at a given temperature and at the absolute zero, respectively. Δn_{max} was obtained by using the procedure of extrapolation of Δn to 0 K, where the liquid crystal exists in a perfectly aligned phase [10].

The liquid crystal birefringence, Δn, was determined on the basis of Newton rings observed at $\lambda = 590$ nm by means of the polarizing microscope (ZPO, Warsaw,

Table 1. Phase transition temperatures for liquid crystals investigated

	Phase transition temperature/°C					
Compound	Cr		SmA	N		I
	liquid crystals with positive dielectric anisotropy					
8OCFPB	•	53.5	•	•	56.4	•
8OCPFB	•	58.4	•	•	65.4	•
	liquid crystals with negative dielectric anisotropy					
N32	•	68.8	•	•	(64.1)	•
N33	•	46.0	•	•	(39.5)	•
N34	•	34.7	•	•	50.2	•
N52	•	57.4	•	•	60.9	•
N53	•	35.6	•	•	44.5	•
N54	•	34.4	•	•	54.0	•
5DBF3	•	50.1	• (42.9)	•	69.6	•

( ) – monotropic phase.

Poland) equipped with the heating stage. The planar alignment of the liquid crystalline molecules between glass surface and glass lens was obtained by using rubbing procedure. The temperature was stabilized with an accuracy of $\pm 0.1^{\circ}C$. The further details of the method are described elsewhere [11].

The Langmuir and Langmuir-Blodgett (LB) films were created in a Minitrough 2 (KSV Instruments Ltd., Finland) equipped with two barriers for monolayer compression, a Wilhelmy plate balance for the surface pressure determination and a temperature control system. The subphase was deionized water obtained from Milli-Q system (Millipore Corporation, Austria). The AA-liquid crystal mixture solutions were made at a constant concentration (0.1 mM) with an appropriate amount of the AA, in order to achieve required molar fraction X_M of the liquid crystal. After the solution was spread onto subphase and left for 10 minutes to allow the solvent to evaporate, the experiment was started. During the symmetrical compression of the monolayer at a barriers motion speed of 5 mm/min., the surface pressure π was measured. Further experimental details about Langmuir film creation are given elsewhere [7,12]. LB films were deposited on polished quartz plates ($35 \times 10 \times 1\,mm^3$) with a rate of 5 mm/min by using vertical dipping method. The deposition process was performed at two values of the surface pressure which correspond to different stages of the Langmuir film creation. For the LB films obtained the absorption spectra were recorded in the ultraviolet-visible (UV-Vis) spectral region by means of a spectrophotometer Varian CARY 400.

3. Results and Discussion

3.1. *Order Parameter of Liquid Crystals*

Figure 2 shows the dependence of the order parameter, S, determined from Eq. (2) for liquid crystals 8OCFPB, N54 and 5DBF3, as examples, *versus* reduced temperature $T_{red} = T/T_{NI}$, where T_{NI} is the temperature of the nematic-isotropic phase transition. The character of the temperature dependence of S in the nematic phase is similar for all the liquid crystals investigated. It is characteristic for nematogens and is in agreement with the mean-field theories of the nematic phase [13,14]. However, with the rise of temperature, S varies somewhat differently for various liquid crystals. The liquid crystal 5DBF3 has additional smectic A phase, in which the temperature dependence of S is significantly weaker than that in the nematic phase, as it was observed also for other liquid crystals [15–17].

In Table 2 the values of S for all the liquid crystals investigated at three reduced temperatures in the nematic phase are presented. Comparing the results for liquid crystals 8OCFPB and 8OCPFB it is seen how influence on the order parameter has the position of the lateral fluorine atom. When the fluorine atom is located near the polar cyano group the order parameter of the compound is lower than when this atom is located in the vicinity of the alkoxy chain. It can result from possibility of the free rotation of the benzene ring with connected fluorine atom in 8OCPFB around the long molecular axis, *i.e.*, around the cyano-group axis. In the case of compound 8OCFPB the fluorine atom is substituted in the *ortho*-position, rigid with respect to the cyano-group. The presented data show that in such a case the orientational ability of the mesogenic molecules is less than that for 8OCPFB. Recently [18], the strong difference between the dielectric anisotropy of these two liquid crystals was found as a result of their different tendency to the antiparallel molecular aggregation.

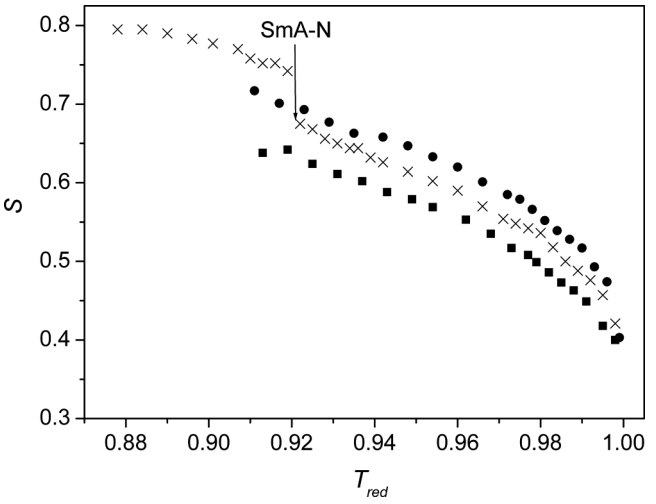


Figure 2. Temperature dependence of the order parameter for liquid crystals: 8OCFPB (squares), N54 (circles) and 5DBF3 (crosses). The arrow indicates the SmA-N transition temperature for 5DBF3. The uncertainty of S is ≈1%.

The temperature dependences of the order parameter for liquid crystals Nnm are not markedly different and from Table 2 follows that S assumes high values. At the lowest possible temperature it is above 0.7, and closely to T_{NI} decreases only to ≈0.4. However, the odd-even effect [19] can be noticed. The order parameter for the liquid crystals with the odd number of carbon atoms in alkoxy chain is higher than that for the liquid crystals with the even number of carbons. The number of carbon atoms in the alkyl chain seems to have also some influence on the value of S. It decreases with the rise of the chain length.

The liquid crystal 5DBF3 in the nematic phase is characterized by a little lower order parameter than other liquid crystals with the negative anisotropy, but in SmA phase the increase of S up to 0.8 is observed (Fig. 2).

Table 2. Order parameter of liquid crystals investigated at three reduced temperatures in the nematic phase

	S		
Compound	$T_{red} = 0.940$	$T_{red} = 0.975$	$T_{red} = 0.990$
8OCFPB	0.59	0.51	0.45
8OCPFB	0.62	0.53	0.47
N32	–	0.65	0.58
N33	–	0.73	0.57
N34	0.67	0.60	0.54
N52	0.66	0.58	0.51
N53	0.70	0.61	0.54
N54	0.66	0.58	0.52
5DBF3	0.63	0.55	0.49

3.2. *Characterization of Langmuir and Langmuir-Blodgett Films*

The liquid crystals 8OCFPB and 8OCPFB are able to form themselves compressible Langmuir films, which can be transferred onto the solid substrates making LB films. The characterization of both kinds of films of these two liquid crystals is described in [7].

None of the investigated liquid crystals with the negative dielectric anisotropy (even 5DBF3 which possess terminal polar fluorine atom) can produce compressible and stable monolayer on the water surface. Therefore, in order to study the properties of these liquid crystals in Langmuir and LB films it was necessary to use the supporting matrix. The liquid crystals were mixed with an arachidic acid at various concentrations. It was ascertained that up to the liquid crystal molar fraction $X_M = 0.6$, the compression of the monolayers formed of liquid crystal/AA mixtures was possible and stable Langmuir films were obtained.

The most basic and widely used technique for the characterization of Langmuir films [6,20] is the measurement of the surface pressure *versus* the average area available for one molecule at the constant temperature (π-A isotherm). For monolayers, π is defined as the surface tension of pure subphase minus the surface tension of the subphase-monolayer system. Figure 3 shows representative π-A isotherms obtained for AA (curve 1) and its mixtures with liquid crystal N52 at $X_M = 0.1$–0.6 (curves 2–7). It is seen that the addition of the liquid crystal to AA changes the shape of π-A isotherm. For mixed Langmuir films the plateau region, characteristic for many thermotropic liquid crystals of rod-like shaped molecules [7,21,22], appears. The appearance of the plateau is thus indicative of incorporation of the liquid crystal molecules in a monolayer. For N52/AA mixtures the plateau occurs at $\pi = 7.5$ mN/m, for other liquid crystals the plateau at π from 1.4 (for N34) to 3.7 (for N53) is observed. In all the cases the value of the surface pressure at which the plateau region appears is independent of the mixture composition.

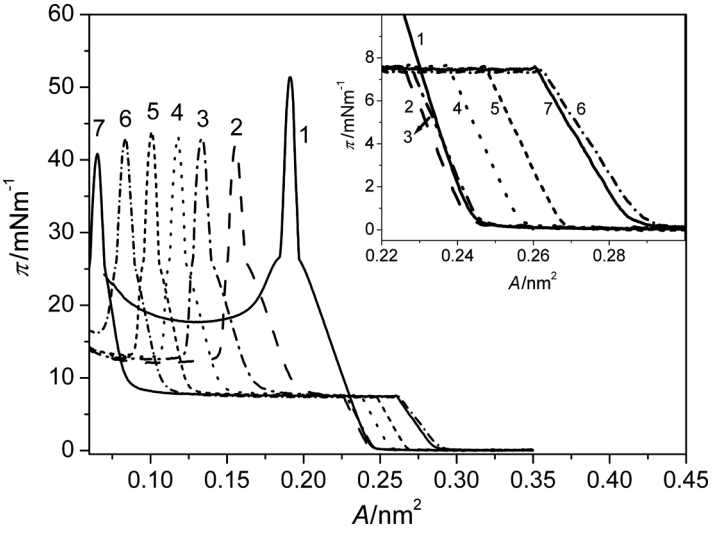


Figure 3. Surface pressure-area isotherms for arachidic acid (1) and arachidic acid mixed with liquid crystal N52 at molar fraction $X_M = 0.1$ (2), 0.2 (3), 0.3 (4), 0.4 (5), 0.5 (6) and 0.6 (7). Insert contains enlarged isotherms for area 0.22–0.30 nm^2.

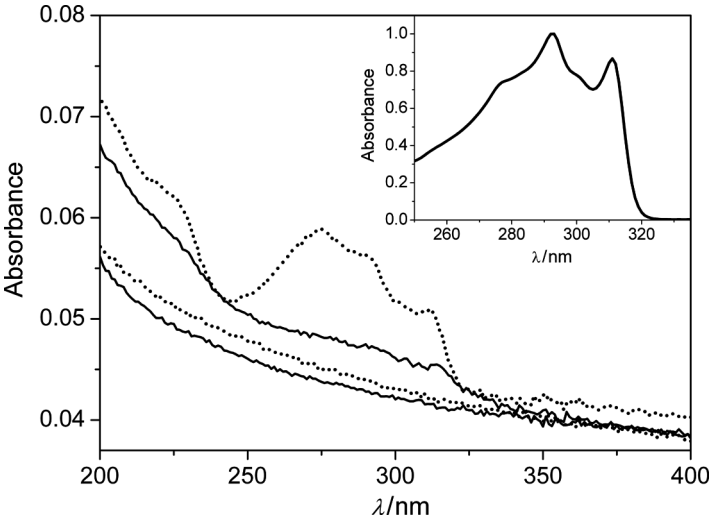


Figure 4. UV absorption spectra for LB films of AA (lower lines) and AA/N54 mixture at $X_M = 0.5$ (upper lines) transferred at $\pi = 2\,mN/m$ (dotted lines) and $20\,mN/m$ (solid lines). In insert the normalized absorption spectrum of N54 dissolved in chloroform at $X_M = 1.5 \cdot 10^{-7}$ is shown.

The monolayer floating on the water was transferred on the quartz substrate at two different surface pressures: before the plateau region and at the second rise of π. For the LB films obtained the absorption spectra were recorded. Typical results are presented in Figure 4. The decrease of the absorbance at higher π is observed, which can be indicative that in LB films transferred at such surface pressure the liquid crystal molecules are aligned perpendicularly to the substrate surface. The proposed model of AA and liquid crystal molecules alignment is shown in Figure 5. When

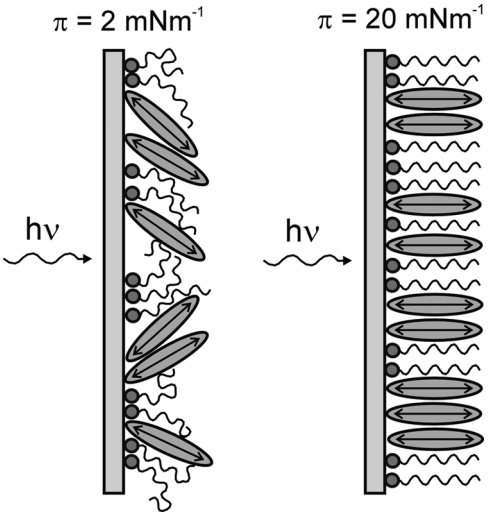


Figure 5. Model of organization of arachidic acid/liquid crystal mixture molecules transferred at the substrate in two different stages of the Langmuir film creation.

the transfer takes place at low surface pressure ($\pi = 2\,\mathrm{mN/m}$ for N54) the molecules are not densely packed and as a result the long axes of liquid crystal molecules are tilted with respect to the quartz surface. For rod-shaped liquid crystal molecules it can be assumed that the absorption transition moment is directed along the long molecular axis [23]. As the absorption intensity is related to the projection of the absorption transition moment on the surface, tilted alignment of molecules results in higher absorbance of the LB film. At higher π (20 mN/m for N54), when the molecules are strongly compressed, they align more vertically and the projection of the absorption transition moment on the surface decreases. This leads to the absorbance diminishing. Thus, in this way the homeotropic orientation of the liquid crystal molecules in the first monolayer at the solid surface can be reflected.

4. Conclusions and Perspectives

The ordering ability of nine newly synthesized fluoro-substituted liquid crystals, two with a positive dielectric anisotropy and seven with a negative dielectric anisotropy, was studied. The order parameter values obtained by means of optical birefringence measurements indicated that the place of the lateral substitution of the fluorine atom to the main part of the liquid crystal molecule influences the orientational order. The length of the terminal alkyl and/or alkoxy chains plays also some role. The liquid crystals under investigation are characterized by high order parameter in the whole mesophase region. As most of them have also the convenient range of the nematic phase existence, they can be consider as promising candidates to utilize them in technologically important mixtures. Especially interesting are liquid crystals with the negative dielectric anisotropy, for which it succeeded to obtain homeotropic alignment by using Langmuir-Blodgett technique. The results presented here are preliminary ones. In following, the utilization of the LB film of one of fatty acids or a fatty acid/liquid crystal mixture as "command layer" to align liquid crystal molecules in display devices is expected.

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