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## Liquid Crystals

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# FTIR study of E7 liquid crystal orientations confined to cylindrical cavities of Anodisc membranes

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The orientation of E7 liquid crystal (LC) confined within 200 nm diameter cylindrical cavities of Anodisc membranes was investigated by FTIR dichroism techniques. The cavity walls of the confining pores were chemically modified with different length aliphatic acids ( $C_nH_{2n+1}COOH$ ,  $n=5, 6, 7, 9$ ) at 2 and 4% concentrations. From the FTIR spectra of the aliphatic acid-treated alumina Anodisc membranes, we found salt formation between the  $-COOH$  group of the aliphatic acids and the Anodisc membranes. From the FTIR spectra of LC-filled Anodisc membranes, we found an abrupt alignment direction change, from parallel to perpendicular, of the LC molecules along the long axis of the cavities between  $n=6$  and  $n=7$  for the 2% concentration of aliphatic acid. However for the 4% concentration of aliphatic acid the parallel to perpendicular alignment direction of LC molecules changed between  $n=5$  and  $n=6$ . The same trend was previously observed for  $^2H$  NMR measurements by other researchers.

## 1. Introduction

Many studies have been made of the orientational order of LCs confined in porous Anodisc membranes using deuterium nuclear magnetic resonance ( $^2H$  NMR) spectroscopy [1–3]. NMR spectroscopy can determine the molecular configuration, the orientational order parameter and, in most cases, surface-induced orientational order of LCs in the isotropic phase.

But, to measure the  $^2H$  NMR spectra of liquid crystals confined to Anodisc cavities, we need LCs which are selectively deuterated at the  $\alpha$ - or  $\beta$ -position of the hydrocarbon chain. To obtain a sufficient signal-to-noise ratio for a  $^2H$  NMR experiment, approximately 40 strips must be stacked one on another [3]. To overcome these problems, we propose to use FTIR spectroscopic techniques to measure the orientational order of liquid crystals in the cavities of Anodisc membranes. We have used the transmission FTIR sampling technique, where the electric field vector is parallel to the substrate surface, to study the anchoring mechanism of aliphatic acids to alumina Anodisc membranes, and the orientation of LC molecules confined in the cavities of aliphatic acid treated Anodisc membranes. The cavity walls of the Anodisc membranes were chemically modified with 2 and 4%

concentrations of different length aliphatic acids ( $C_nH_{2n+1}COOH$ ) such as hexanoic acid ( $n=5$ ), heptanoic acid ( $n=6$ ), octanoic acid ( $n=7$ ) and decanoic acid ( $n=9$ ).

To investigate the alignment direction of the LC, we must first know the polarization tendency of the LC molecules. Table 1 shows the polarization tendencies of each peak of 5CB, which is the major component of E7.

The intensity of the IR absorption mode is

$$I = C(\mathbf{EM})^2 = C(EM\cos\theta)^2 \quad (1)$$

where  $C$  = proportionality constant,  $\mathbf{E}$  = electric field vector of incident IR beam,  $\mathbf{M}$  = transition moment

Table 1. FTIR peak assignments for E7 LC [4, 5].

Peak / $cm^{-1}$	Polarization tendency	Assignment
2955	$\parallel^a$	asymmetric stretching mode of $CH_3$
2928	$\perp^b$	asymmetric stretching mode of $CH_2$
2869	$\parallel$	symmetric stretching mode of $CH_3$
2855	$\perp$	symmetric stretching mode of $CH_2$
2226	$\parallel$	stretching mode of $C\equiv N$
1912	$\perp$	overtone of the CH-out-of-plane deformation of the benzene C–H groups
1605	$\parallel$	stretching mode of $C=C$ phenyl ring
1494	$\parallel$	stretching mode of $C=C$ phenyl ring

<sup>a</sup> $\parallel$  denotes parallel transition moment tendency.

<sup>b</sup> $\perp$  denotes perpendicular transition moment tendency.

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vector of vibrational mode,  $\theta$  = the angle between the two vectors.

Using this relationship, we can measure the orientation of E7 LC molecules in the Anodisc membrane cavities. Figure 1 is a schematic diagram of the measurement of the transmission FTIR spectrum of LC-filled Anodisc membranes. If LCs align parallel with the cavity long axis, peaks with a polarization tendency parallel to the molecular long axis, such as  $-\text{C}\equiv\text{N}$  stretching at  $2226\text{ cm}^{-1}$  (see table 1), will show weak absorbance, but the overtone peak at  $1912\text{ cm}^{-1}$  with a polarization tendency perpendicular to the long molecular axis will show strong absorbance. If LCs align perpendicular to the cavity long axis, the reverse trend will occur, strong for  $-\text{C}\equiv\text{N}$  stretching at  $2226\text{ cm}^{-1}$  and weak for the overtone peak at  $1912\text{ cm}^{-1}$ .

## 2. Experimental

### 2.1. Materials

The Anodisc membranes—25 mm diameter,  $60\text{ }\mu\text{m}$  thick and with  $200\text{ nm}$  diameter cylindrical channels—were purchased from Whatman. As seen from the surface scanning electron microscope (SEM) photographs in figure 2 (a), Anodisc membranes have almost circular pores. Also, as seen from the cross-sectional photographs in figure 2 (b), the cavities appear to be

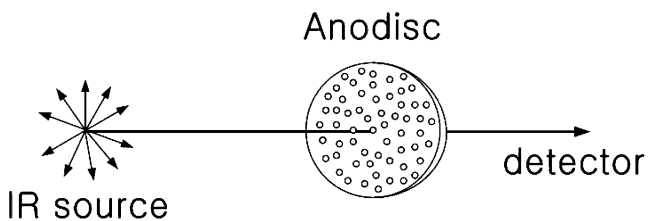


Figure 1. Schematic diagram of the measurement of the transmission FTIR spectrum of an LC-filled Anodisc membrane.

nearly cylindrical extending through the bulk of its thickness. All the aliphatic acids (hexanoic, heptanoic, octanoic and decanoic acids), aluminum stearate and solvents used in our experiment were purchased from Aldrich. Nematic LC E7 (Cr-N =  $-10^\circ\text{C}$  and N-I =  $60^\circ\text{C}$ , Merck) was used to fill the cavities of the Anodisc membranes. E7 is a eutectic liquid crystal mixture of 51% 5CB, 25% 7CB, 16% 8OCB, and 8% 5CT [4]. Two and 4% by weight solutions of the aliphatic acid in methanol were used to modify the cavity walls of the Anodisc membranes. After 1 min. soaking in the solution, the membrane was removed from the solution and placed on a  $70^\circ\text{C}$  hot plate for 10 min, then placed in a vacuum oven for 1 h at  $140^\circ\text{C}$  to remove remaining solvent. After drying, the membranes were placed in a 5.0 vol% of E7 in hexane solution at room temperature for 1 min. After filling the E7 LC, the membranes were removed and placed on the hot plate at  $80^\circ\text{C}$  for 30 min to remove hexane solvent, then cooled slowly to room temperature over 30 min.

### 2.2. Instrumentation

To study the interaction between aliphatic acids and Anodisc membranes, and the molecular orientation change of the LC after the aliphatic acid treatment of the Anodisc membranes, a FTIR 620 (Jasco) instrument was used to obtain the transmission FTIR spectra at room temperature. To reduce the noise level, 200 scans were obtained at  $2\text{ cm}^{-1}$  resolution.

## 3. Results and discussion

### 3.1. LC orientation in Anodisc membranes

To study the feasibility of using FTIR for the measurement of the orientation of LCs in the Anodisc membranes, we measured the FTIR spectra of 200 nm

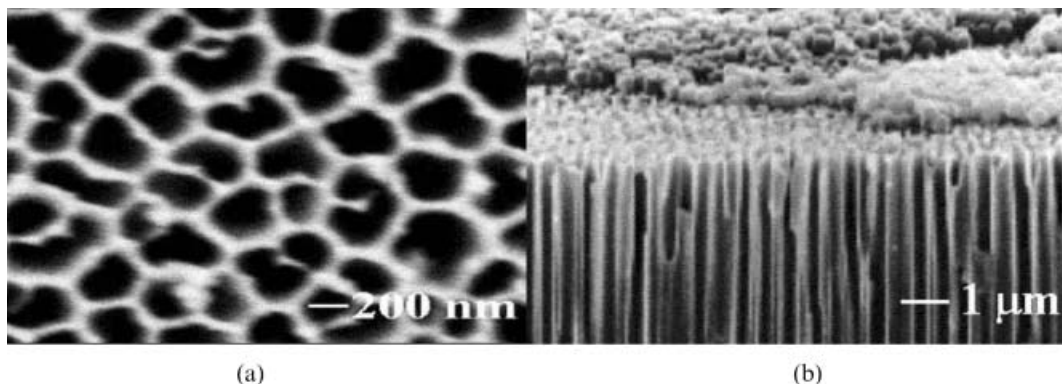


Figure 2. SEM photographs of an Anodisc membrane with 200 nm nominal pore size: (a) top surface, (b) cross-section (from www.whatman.com).

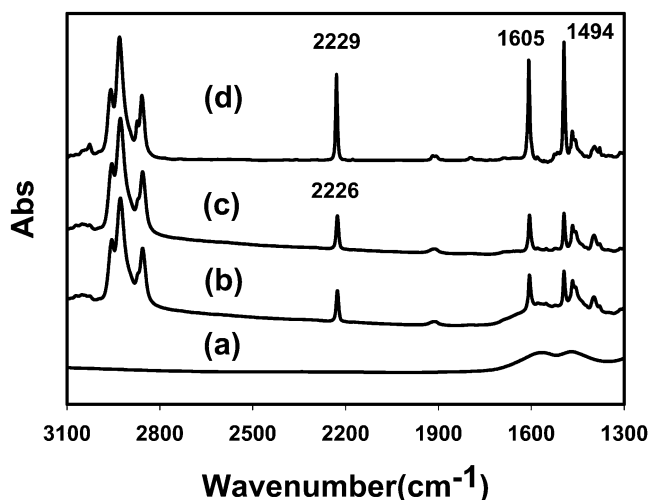


Figure 3. FTIR spectra of E7 LC confined in cavities of 200 nm Anodisc membranes: (a) Anodisc, (b) E7 LC confined to 200 nm Anodisc membrane, (c) difference obtained by subtracting (a) from (b), (d) E7 LC spectrum obtained from a 0.4 wt%  $\text{CCl}_4$  solution.

cylindrical Anodisc membrane channels, E7 LC solution in  $\text{CCl}_4$ , and E7 LC confined to the Anodisc membrane, as shown in figure 3. As indicated in figure 3(a), the FTIR spectrum of an Anodisc membrane showed little absorbance except for three major broad peaks at 3404 (out of range), 1572 and 1469  $\text{cm}^{-1}$  [6]. Figure 3(b) is a FTIR spectrum of an E7 LC-filled Anodisc membrane. To obtain an E7 LC-only FTIR spectrum, we subtracted the Anodisc spectrum (obtained from a different Anodisc) from that of an E7 LC-filled Anodisc by changing the subtraction factor according to equation (2), to eliminate the 1572 and 1469  $\text{cm}^{-1}$  peaks of the Anodisc; the resulting spectrum is shown figure 3(c).

$$\text{Difference spectrum} = \text{Sample spectrum} - (\text{Reference spectrum} \times \text{Subtraction factor}). \quad (2)$$

In our case, the sample spectrum is the E7 LC-filled Anodisc spectrum, and the reference spectrum is the Anodisc spectrum.

Alkyl cyanobiphenyl liquid crystals have a tendency for spontaneous perpendicular orientation on a metallic substrate [7], therefore to eliminate the spontaneous orientation of E7 LC on a solid substrate such as a KBr disk, we used a 0.4 wt% E7 solution in  $\text{CCl}_4$  to obtain the random orientation of E7 LC. Figure 3(d), which was measured on a 0.4 wt% solution of E7 in  $\text{CCl}_4$ , using pure  $\text{CCl}_4$  as background, was used as a reference to compare the orientation of E7 LC in the Anodisc cavities. If we normalize the asymmetric  $\text{CH}_2$  stretching peak at 2928  $\text{cm}^{-1}$  for figures 3(c) and 3(d), we find weaker peaks at 2226, 1605 and 1494  $\text{cm}^{-1}$  in

figure 3(c) for E7 LC in the Anodisc membrane, which exhibit parallel polarization tendencies as shown in table 1. These results support the parallel orientation of E7 LCs in Anodisc membrane cavities. The change of the  $-\text{C}\equiv\text{N}$  peak position at 2226  $\text{cm}^{-1}$  for LCs in Anodisc membranes to 2229  $\text{cm}^{-1}$  for the  $\text{CCl}_4$  solution, signifies the weakening of interactions of the polar  $-\text{C}\equiv\text{N}$  groups of the LC on dilution with  $\text{CCl}_4$ .

For closer examination of the  $-\text{CH}_3$  and  $-\text{CH}_2$  stretching region, we enlarged the spectrum of figures 3(c) and 3(d) for the 3050–2800  $\text{cm}^{-1}$  region, see figure 4. Comparing figures 4(a) and 4(b), we find relatively weaker  $-\text{CH}_3$  peaks at 2955 and 2869  $\text{cm}^{-1}$  in figure 4(a) than in figure 4(b), which have parallel polarization tendencies as shown in table 1. These results also strongly suggest that the orientation of E7 LC confined in the Anodisc membrane is parallel to the long axis of the Anodisc cavity.

### 3.2. Salt formation of an aliphatic acid with alumina Anodisc membrane

To investigate the mechanism of the anchoring of an aliphatic acid to an alumina Anodisc wall surface, we measured FTIR spectra of Anodisc, bulk aliphatic acid (using KBr pellet), and an aliphatic acid treated Anodisc, see figure 5. To identify the reaction between aliphatic acid and Anodisc more clearly, we obtained the difference spectrum by subtracting the spectrum of a different Anodisc from the spectrum of an aliphatic acid treated Anodisc, changing the subtraction factor according to equation (2). The results for hexanoic acid-treated discs are shown in figure 5(d). From the

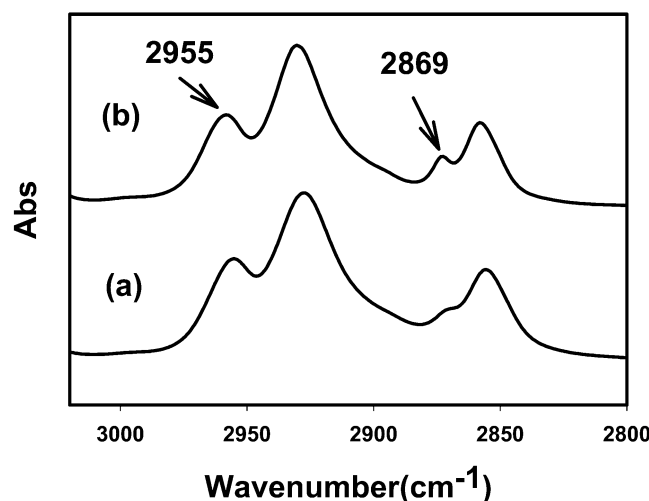


Figure 4. FTIR spectra of E7 LC: (a) LC confined in cavities of 200 nm Anodisc membrane, (b) E7 LC spectrum obtained from 0.4 wt% solution in  $\text{CCl}_4$ .

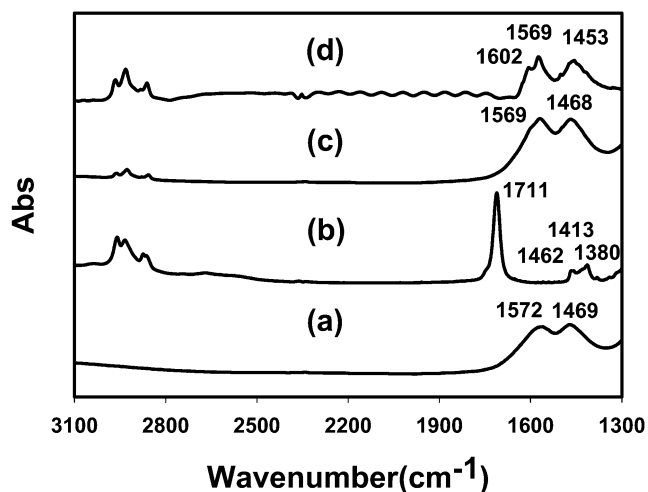


Figure 5. FTIR spectra of (a) anodisc, (b) pure hexanoic acid, (c) hexanoic acid-treated Anodisc, (d) difference obtained by subtracting (a) from (c).

difference spectrum of figure 5(d), the C=O peak of  $-\text{COOH}$  at  $1711\text{ cm}^{-1}$ , which appears in figure 5(c) for pure hexanoic acid, disappeared completely and new peaks at  $1569$  and  $1453\text{ cm}^{-1}$  with a shoulder at  $1602\text{ cm}^{-1}$  appeared, showing the formation of a salt between aliphatic acid and alumina Anodisc membrane. Allara and Nuzzo found  $\text{COO}^-$  asymmetric stretching at  $1608\text{ cm}^{-1}$  and  $\text{COO}^-$  symmetric stretching at  $1475$  and  $1417\text{ cm}^{-1}$  for palmitic acid ( $\text{C}_{15}\text{H}_{31}\text{COOH}$ ) adsorbed on oxidized aluminum, by infrared reflection spectroscopy [8]. Ferri *et al.* found asymmetric and symmetric stretching of  $\text{COO}^-$  at  $1569$  and  $1414\text{ cm}^{-1}$ , respectively, for  $\text{CH}_3\text{COOH}$  adsorbed on an alumina film, by FTIR ATR spectroscopy [9]. To confirm salt formation between hexanoic acid and the Anodisc membrane, we obtained the FTIR spectrum of aluminum stearate using the KBr pellet method. We found asymmetric and symmetric stretching of  $-\text{COO}^-$  at  $1589$  and  $1468\text{ cm}^{-1}$ , respectively. Therefore, the disappearance of the C=O peak of  $-\text{COOH}$  at  $1711\text{ cm}^{-1}$  and the formation of new peaks at  $1569$  and  $1453\text{ cm}^{-1}$  for the hexanoic acid-treated Anodisc membrane are evidence that the  $-\text{COOH}$  group of hexanoic acid reacted with the Anodisc membrane cavity walls to form a salt. The same trend was observed for Anodiscs treated with the other aliphatic acids.

### 3.3. E7 liquid crystal alignment in the cavities of aliphatic acid treated Anodisc membranes

To investigate the effect of aliphatic acid treatment on LC orientation in Anodisc membrane cavities, we must calculate dichroic ratios ( $R$ ) according to

equation (3)

$$R = A_{\perp} / A_{\parallel} \quad (3)$$

where  $A_{\perp}$  = area of the absorbance peak which has perpendicular polarization tendency, and  $A_{\parallel}$  = area of the absorbance peak which has parallel polarization tendency. A larger  $R$  value indicates a more parallel alignment of LC molecules with the long axis of the Anodisc cavities.

To calculate  $R$  values, several peaks with suitable polarization tendency can be used. But C-H region peaks from  $3000$  to  $2800\text{ cm}^{-1}$  are difficult to use due to the overlap of a possible new peak at  $2897\text{ cm}^{-1}$  which is not assigned in table 1 [10]. We therefore used two peaks to measure  $R$  values: one is the first overtone of the CH-out-of-plane deformation of the benzene CH groups at  $1912\text{ cm}^{-1}$  and the other is the  $-\text{C}\equiv\text{N}$  stretching peak at  $2226\text{ cm}^{-1}$ ; they have perpendicular and parallel polarization tendencies, respectively, and have been used to study the orientation change of 5CB [5]. We measured the area of the overtone peak at  $1912\text{ cm}^{-1}$  ( $1945.9\text{--}1890.9\text{ cm}^{-1}$  region) and the area of the  $-\text{C}\equiv\text{N}$  stretching peak at  $2226\text{ cm}^{-1}$  ( $2250.0\text{--}2205.2\text{ cm}^{-1}$  region) of E7 LC from the FTIR spectra of filled Anodiscs, to calculate  $R$  values and determine their variation with the different length of aliphatic acid used in the Anodisc treatment.

The 0.4 wt% E7 in  $\text{CCl}_4$  solution showed the overtone of the CH-out-of-plane deformation of the benzene CH groups at  $1918$  and  $1907\text{ cm}^{-1}$  as a doublet, and the  $-\text{C}\equiv\text{N}$  stretching at  $2229\text{ cm}^{-1}$ . The  $R$  value calculated using equation (3) was 0.13. But E7 LC in the anodisc showed  $-\text{C}\equiv\text{N}$  stretching at  $2226\text{ cm}^{-1}$  and an overtone peak of the CH-out-of-plane deformation of the benzene CH groups at  $1912\text{ cm}^{-1}$  as a single peak, due to mutual strong interactions of E7 LC molecules with the polar  $-\text{C}\equiv\text{N}$  groups.

To investigate the effect of aliphatic acid treatment on the orientation of confined liquid crystals in membrane cavities, we obtained the FTIR spectra of E7-filled Anodisc membranes treated with 2 and 4% solutions of aliphatic acids with different chain length ( $n=5, 6, 7, 9$ ). In this case, we used the same aliphatic acid-treated Anodisc spectrum as reference spectrum; therefore, the subtraction factor according to equation (2) is 1. The results for 2% solution treatment are shown in figure 6, which are normalized to the  $2928\text{ cm}^{-1}$  peak. According to figure 6, the  $-\text{C}\equiv\text{N}$  peak height at  $2226\text{ cm}^{-1}$  changed between heptanoic acid ( $n=6$ ) and octanoic acid ( $n=7$ ), indicating a change from parallel to perpendicular orientation to the cavity long axis in the Anodisc membrane. To compare the LC orientations, we calculated  $R$  values according to equation (3). The results are shown in table 2. The  $R$

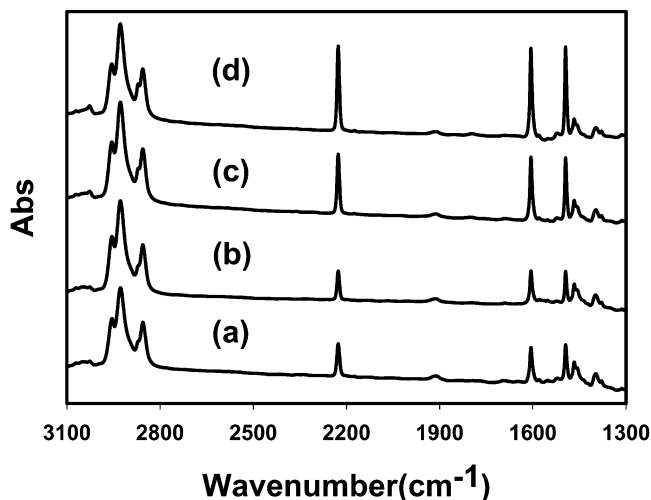


Figure 6. FTIR spectra of E7 confined to 2% aliphatic acid-treated Anodiscs: (a) hexanoic acid, (b) heptanoic acid, (c) octanoic acid, (d) decanoic acid.

Table 2. Peak area ratio change of E7 LC for 2% aliphatic acid-treated anodisc membranes.

$n$	Area of overtone, $\gamma_1(\text{CH})$	Area of $\text{C}\equiv\text{N}$ stretching peak	$A(1912\text{ cm}^{-1})/ A(2226\text{ cm}^{-1})$
5	0.292	1.221	0.24
6	0.416	1.589	0.26
7	0.351	3.356	0.10
9	0.393	5.142	0.08

value changed from 0.24→0.26→0.10→0.08 with increase of  $n$  of the aliphatic acids. On comparing with the  $R$  value of 0.13 for E7 in  $\text{CCl}_4$  solution, we found an orientation change of E7 LC from parallel to perpendicular for  $n=7$  and upward.

The results for 4% aliphatic acid solution treatment are shown in figure 7; the  $\text{C}\equiv\text{N}$  peak height at  $2226\text{ cm}^{-1}$  changed between hexanoic acid ( $n=5$ ) and heptanoic acid ( $n=6$ ) treatment indicating a change, from parallel to perpendicular orientation to the cavity long axis in the Anodisc membrane. To compare the LC orientations, as above, we again calculated  $R$  values according to equation (3). The results are shown in table 3. The  $R$  value changed from 0.32→0.12→0.07→0.05 with increase of  $n$  of the aliphatic acids. On comparing with the  $R$  value of 0.13 for E7 in  $\text{CCl}_4$  solution, we found an orientation change of E7 LC from parallel to perpendicular from  $n=6$  and upward. The same trends were observed by  $^2\text{H}$  NMR by other researchers [3].

#### 4. Conclusions

FTIR spectroscopy allowed us to measure LC alignment direction with only one LC-filled membrane,

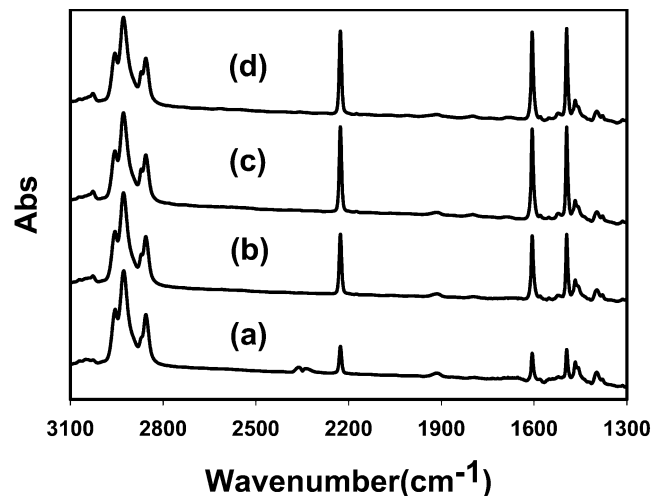


Figure 7. FTIR spectra of E7 confined to 4% aliphatic acid-treated Anodiscs: (a) hexanoic acid, (b) heptanoic acid, (c) octanoic acid, (d) decanoic acid.

Table 3. Peak area ratio change of E7 LC for 4% aliphatic acid treated anodisc membranes.

$n$	Area of overtone, $\gamma_1(\text{CH})$	Area of $\text{C}\equiv\text{N}$ stretching peak	$A(1912\text{ cm}^{-1})/ A(2226\text{ cm}^{-1})$
5	0.344	1.088	0.32
6	0.454	3.706	0.12
7	0.320	4.395	0.07
9	0.159	3.267	0.05

this compares with the  $^2\text{H}$  NMR technique, which requires deuterated LCs and approximately 40 stacks of LC filled membranes to obtain a good signal-to-noise ratio. We found that the mechanism of anchoring of an aliphatic acid to an alumina Anodisc was salt formation between the aliphatic acid and the membrane. We found an abrupt E7 LC orientation change between heptanoic acid ( $n=6$ ) and octanoic acid ( $n=7$ ), in the 2% solution-treated Anodisc membrane, from parallel to perpendicular to the cavity long axis. For 4% acid solution-treated Anodisc membranes, the change was between hexanoic acid ( $n=5$ ) and heptanoic acid ( $n=6$ ), again from parallel to perpendicular. The FTIR spectroscopic technique can thus be used more easily than the  $^2\text{H}$  NMR technique to measure the orientation of confined LCs and the anchoring mechanism of aliphatic acids to Anodisc membranes.

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