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Studies on the E7 liquid crystal orientations confined to perfluorinated carboxylic acid-treated cylindrical cavities of Anodisc membranes by FTIR spectroscopy

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The orientation of E7 liquid crystal (LC) confined within 200 nm diameter cylindrical cavities of Anodisc membranes are investigated by FTIR dichroism techniques. The cavity walls of the confining pores were chemically modified with different length perfluorinated carboxylic acids (PCAs, $C_nF_{2n+1}COOH$, n=3, 4, 5, 6) at 1, 3 and 5 mM concentrations. From the FTIR spectra of PCA-treated alumina Anodsic membranes, we found salt formation between the –COOH group of the PCAs 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=4 and n=5 for the 1 mM concentration of PCA. However, for the 5 mM concentration of PCA, the parallel-to-perpendicular alignment direction of LC molecules changed between n=3 and n=4. These LC orientation changes for PCA-treated Anodisc membranes occurred at shorter length than for hydrocarbon carboxylic acid (HCA, $C_nH_{2n+1}COOH$)-treated Anodisc membranes. This change may be caused by the lower surface energy of the $–(CF_2)_nCF_3$ chain of PCA than that of the $–(CH_2)_nCH_3$ chain of HCA.

1. Introduction

Many studies have been made of the orientational order of LCs confined in HCA-treated porous alumina Anodisc membranes using deuterium nuclear magnetic resonance (^2H NMR) spectroscopy [1–3] and FTIR spectroscopy [4]. But PCAs, which are materials totally fluorinated by the replacement of hydrogen atoms in the alkyl chain of HCA, have not previously been used to treat Anodisc membranes to study the effect on the orientational order of LCs confined to their cavities. A fluorocarbon chain $–(CF_2)_nCF_3$ of PCAs is more hydrophobic, more rigid, and has a higher cross-sectional area than a hydrocarbon chain $–(CH_2)_nCH_3$ of HCAs. Moreover, a carboxylic acid head-group attached to a fluorinated carbon atom is known to be much more acidic than a normal carboxylic acid [5]. Therefore, we used different length PCAs to treat Anodisc membranes, to study the effect of PCA treatment on the orientation of LCs confined in Anodisc membrane cavities.

We used the transmission FTIR sampling technique, where the electric field vector is parallel to the substrate surface, to study the anchoring mechanism of PCAs to Anodisc membranes and the orientation of LC molecules confined in the cavities of PCA treated Anodisc membranes. The cavity walls of the Anodisc membranes were chemically modified with 1, 3 and 5 mM concentrations of different length PCAs ($C_nF_{2n+1}COOH$) such as perfluorobutyric acid (n=3), perfluoropentanoic acid (n=4), perfluorohexanoic acid (n=5) and perfluoroheptanoic acid (n=6). To investigate the alignment direction of the LC, we must first know the polarization tendency of the LC molecules. Table I shows the polarization tendencies of each peak of 5CB, which is the major component of E7.

The intensity of IR absorption mode is

$$I = C(EM)^2 = C(EM\cos\theta)^2 \qquad (1)$$

where C is a proportionality constant, **E** is the electric field vector of the incident IR beam, **M** is the transition moment vector of the vibrational mode, and θ is the angle between the two vectors.

Using this relationship, we can measure the orientation of E7 LC molecules in 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

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Table 1. FTIR peak assignments for E7 LC [6, 7].

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≡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

[a] Parallel transition moment tendency. [b] Perpendicular transition moment tendency.

molecular long axis, such as –C≡N stretching at 2226 cm^{-1} (see table 1), will show weak absorbance, but the overtone peak at 1912 cm^{-1} with 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 –C≡N stretching at 2226 cm^{-1} and weak for the overtone peak at 1912 cm^{-1}.

2. Experimental

2.1. *Materials*

The Anodisc membranes (25 mm diameter, 60 µm thick and with 200 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 nearly cylindrical extending through the bulk of the membrane thickness. All the PCAs used in our experiments were purchased from vendors: perfluorobutyric acid (99%, Aldrich), perfluoropentanoic acid (98%, Lancaster), perfluorohexanoic acid (Oakwood Products, Inc.), perfluoroheptanoc acid (98%, Oakwood Products, Inc.). Other reagents included aluminum trifluoroacetate monohydrate (Gelest, Inc.), silver heptafluorobutyrate (97%, Aldrich), and methanol and hexane solvents (Aldrich). All chemicals were used as received.

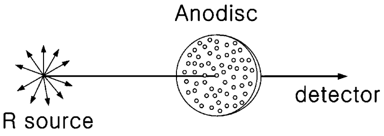

Figure 1. Schematic diagram of measurement of the transmission FTIR spectrum of LC-filled Anodisc membrane.

Nematic LC E7 (Cr–N = −10°C, N–I = 60°C, Merck) was used to fill the cavities of Anodisc membranes. E7 is a eutectic liquid crystal mixture of 51% 5CB, 25% 7CB, 16% 8OCB, and 8% 5CT [6]. 1, 3 and 5 mM solutions of the PCA in methanol were used to modify the cavity walls of the Anodisc membranes. After 1 min soaking in the 5 ml of the PCA solution, the membrane was removed from the solution and rinsed with methanol, placed on a 70°C hot plate for 10 min, then placed in a vacuum oven for 1 h at 140°C to remove remaining solvent. After drying, the membrane was placed in a 5.0 vol% of E7 in hexane solution at room temperature for 1 min. After filling the E7 LC, the membrane was removed and placed on the hot plate at 80°C for 30 min

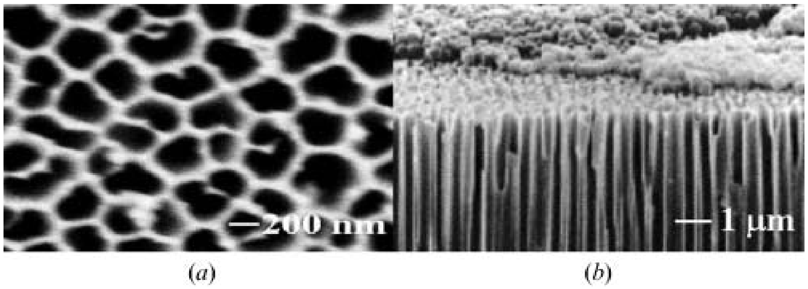

Figure 2. SEM photographs of an Anodisc membrane of 200 nm nominal pore size: (*a*) top surface, (*b*) cross-section (from www.whatman.com).

to remove hexane solvent; it was then cooled slowly to room temperature over 30 min.

2.2. *Instrumentation*

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

3. Results and discussion

3.1. *Salt formation of PCA with alumina Anodisc membrane*

To investigate the mechanism of the anchoring of a PCA to an alumina Anodisc wall surface, we measured the FTIR spectra of Anodisc, bulk perfluorobutyric acid (using a KBr pellet), and perfluorobutyric acid-treated Anodisc, see figure 3. The spectrum of the Anodisc showed broad peaks at 1572 and 1469 cm^{-1} as shown in figure 3 (*a*), but the the pure perfluorobutyric acid spectrum in figure 3 (*b*) showed a strong –C=O stretching of –COOH at 1774 cm^{-1}. The peak position of the –C=O stretching of PCAs was shifted towards higher wavenumbers than that of HCAs due to the substitution of H atoms of HCAs by strong electron-withdrawing F atoms in PCAs [8].

To identify the reaction between perfluorobutyric acid and Anodisc more clearly, we obtained the difference spectrum by subtracting the Anodisc spectrum in figure 3 (*a*) (obtained from a different Anodisc) from the perfluorobutyric acid-treated Anodisc spectrum in figure 3 (*c*) by changing the subtraction factor according to equation (2), to eliminate the 1572 and 1469 cm^{-1} peaks of the Anodisc; the resulting spectrum is shown in figure 3 (*d*).

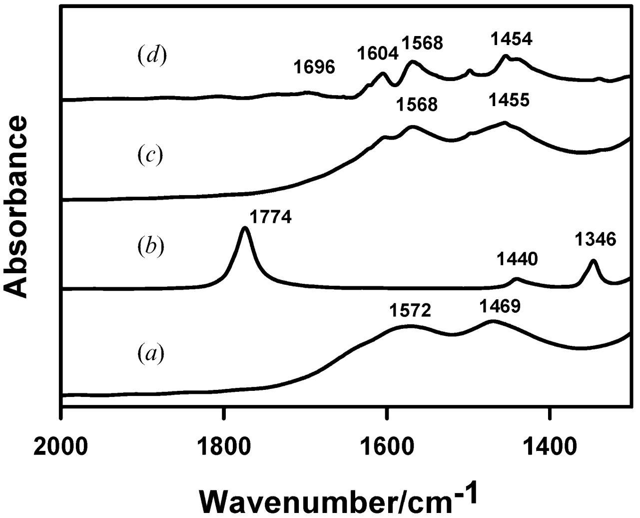

Figure 3. FTIR spectra of (*a*) Anodisc, (*b*) pure perfluorobutyric acid, (*c*) perfluorobutyric acid-treated Anodisc, (*d*) difference obtained by subtracting (*a*) from (*c*).

$$\text{Difference spectrum} = \text{sample spectrum} - (\text{reference spectrum} \times \text{subtraction factor}). \quad (2)$$

In our case, the sample spectrum is the perfluorobutyric acid-treated Anodisc spectrum, and the reference spectrum is the Anodisc spectrum.

According to difference spectrum of figure 3 (*d*), the C=O peak of –COOH at 1774 cm^{-1}, which appears in figure 3 (*b*) for pure perfluorobutyric acid, disappeared completely and new peaks at 1604, 1568, 1498 and 1454 cm^{-1} with a shoulder at 1622 cm^{-1} appeared, showing the formation of a salt between perfluorobutyric acid and the alumina Anodisc membrane. To confirm salt formation between perfluorobutyric acid and alumina Anodisc membrane wall, we obtained FTIR spectra of aluminum trifluoroacetate monohydrate and silver heptafluorobutyrate using the KBr pellet method. We found strong asymmetric stretching of –COO^- at 1678 cm^{-1} for aluminum trifluoroacetate monohydrate and 1682 cm^{-1} for silver heptafluorobutyrate, and symmetric stretching of –COO^- at 1435 and 1403 cm^{-1} respectively. Therefore, the disappearance of the C=O peak of –COOH at 1774 cm^{-1} and formation of new peaks at 1604, 1568, 1498 and 1454 cm^{-1} with a shoulder at 1622 cm^{-1} for perfluorobutyric acid-treated Anodisc membrane are evidence that the –COOH group of perfluorobutyric acid reacted with the Anodisc membrane cavity walls to form a salt. The same trend was observed in Anodiscs treated with the other PCAs. Therefore, –COOH groups of the PCA anchor on to the surface of the Anodisc membrane cavity walls by forming a salt, and the remaining $\text{–C}_n\text{F}_{2n+1}$ chain of the PCA make contact with E7 LC molecules to control their orientation. We express this concept schematically in figure 4.

3.2. *E7 liquid crystal alignment in the cavities of PCA-treated Anodisc membrane*

3.2.1. Effect of PCA concentration and chain length. To investigate the effect of PCA 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=area of the absorbance peak which has parallel polarization

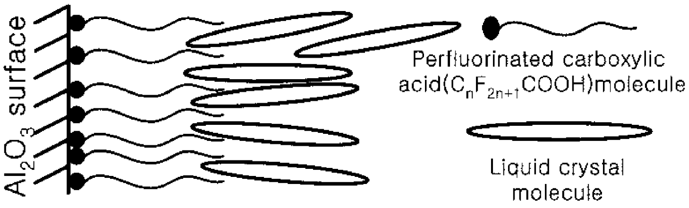

Figure 4. Schematic diagram of the interaction of alumina Anodisc cavity wall with –COOH groups of $C_nF_{2n+1}COOH$ and orientation control of LCs by $-C_nF_{2n+1}$ chains of $C_nF_{2n+1}COOH$.

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. However, C-H region peaks from 3000 to 2800 cm^{-1} are difficult to use due to the overlap of a possible new peak at 2897 cm^{-1} which is not assigned in table 1 [9]. 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 cm^{-1}, and the other is the –C≡N stretching peak at 2226 cm^{-1}; they have perpendicular and parallel polarization tendencies, respectively, and have been used to study the orientation change of 5CB [7]. We measured the area of the overtone peak at 1912 cm^{-1} (in the 1945.9–1890.9 cm^{-1} region) and the area of the –C≡N stretching peak at 2226 cm^{-1} (2250.0–2205.2 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 PCAs used in the Anodisc treatment.

To investigate the effect of PCA treatment on the orientation of LCs confined in membrane cavities, we obtained the FTIR spectra of E7-filled Anodisc membranes treated with 1, 3 and 5 mM solutions of PCAs with different chain length (n=3, 4, 5, 6). To measure the orientation of E7 only, we subtracted the PCA-treated Anodisc spectrum from the spectrum of E7-filled PCA-treated Anodisc spectrum according to equation (2). The results for 1 mM solution treatment are shown in figure 5, which are normalized to the 2928 cm^{-1} peak. According to figure 5, –C≡N peak height at 2226 cm^{-1} changed between perfluoropentanoic acid (n=4) and perfluorohexanoic acid (n=5), indicating a change from parallel to perpendicular orientation to the cavity long axis in the Anodisc membrane. Treating with 1 mM PCAs with longer chain length (n=7, 8, 9, 10, 11, 17) for 1 min showed the same trend as n=5, perpendicular direction to the long axis of cavity of Anodisc membrane.

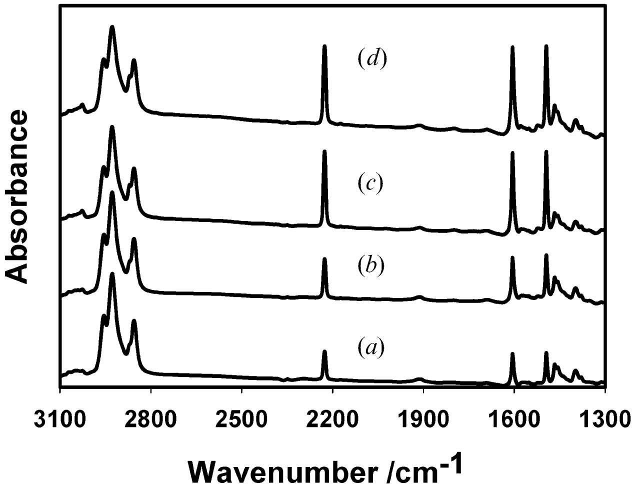

Figure 5. FTIR spectra of E7 confined in 1 mM PCA-treated Anodiscs: (*a*) perfluorobutyric acid, (*b*) perfluoropentanoic acid, (*c*) perfluorohexanoic acid, (*d*) perfluoroheptanoic acid.

To compare the LC orientations, we calculated R values according to equation (3). The results are shown in table 2. The R value changed from 0.21→0.16→0.07→0.08 with increase of n of the PCAs. On comparing with the R value of 0.13 for 0.4 wt% E7 in CCl_4 solution, which is supposed to align without preferential orientation [4], we found an

Table 2. Peak area ratio change of E7 LC for 1 mM PCA-treated Anodisc membranes.

$C_nF_{2n+1}COOH$	Area of overtone, γ_1(CH)	Area of C≡N stretching peak	$A(1912\,cm^{-1})/A(2226\,cm^{-1})$
n=3	0.362	1.765	0.21
n=4	0.315	1.933	0.16
n=5	0.239	3.523	0.07
n=6	0.277	3.549	0.08

orientation change of E7 LC from parallel to perpendicular for n=5 and upward.

We found the same trend for 3 mM PCA solution-treated membranes, showing an abrupt E7 LC orientation change between perfluoropentanoic acid (n=4) and perfluorohexanoic acid (n=5); therefore, we increased the concentration of PCA solution to 5 mM to treat Anodisc membranes. The results for 5 mM PCA solution treatment are shown figure 6: the –C≡N peak height at 2226 cm^{-1} changed between perfluorobutyric acid (n=3) and perfluoropentanoic acid (n=4) 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 values changed from 0.20→0.07→0.06→0.06 with increase of n of the PCAs. On comparing again with the R value of 0.13 for 0.04 wt% E7 in CCl_4 solution, we found an orientation change of E7 LC from parallel to perpendicular from n=4 and upward.

On comparing PCA solution-treated LC orientation change results with our previous LC orientation change of HCA solution-treated results [4], we find that E7 LC orientation change occurs at shorter chain length for PCA solution-treated Anodisc membranes [for 1 mM and 3 mM PCA solution-treated Anodisc membranes, the change was between perfluoropentanoic acid (n=4) and perfluorohexanoic acid (n=5); for 5 mM PCA solution-treated Anodisc membranes, the change was between perfluorobutyric acid (n=3) and perfluoropentanoic acid (n=4)] than those for HCA-solution treated Anodisc membranes [for 2% HCA solution-treated Anodisc membranes, the change was between heptanoic acid (n=6) and octanoic acid (n=7); for 4% HCA solution-treated Anodisc membranes, the change was between hexanoic acid (n=5) and heptanoic acid (n=6)]. These differences may be caused by the lower surface energy of the $–C_nF_{2n+1}$ chain of PCAs than the $–C_nH_{2n+1}$ chain of HCAs. Typical values of surface tension for the $–CF_3$ group, which will be located preferentially at the cavity wall surface of PCA-treated Anodisc membrane, is 15 dyn cm^{-1}, and for the $–CH_3$ group similarly located preferentially at the cavity wall surface of HCA-treated Anodisc membrane, is 30 dyn cm^{-1} [10].

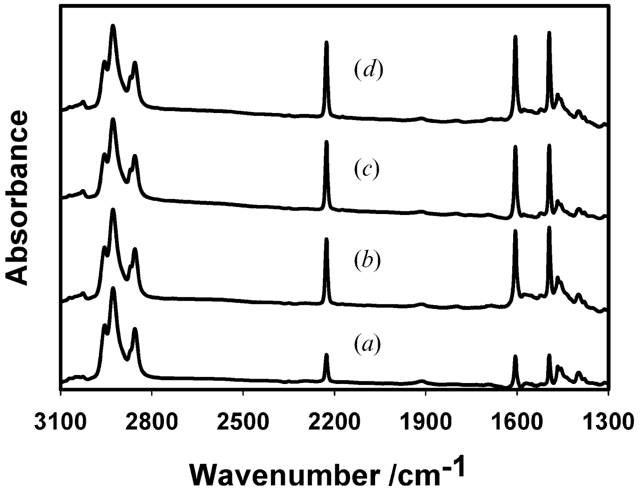

Figure 6. FTIR spectra of E7 confined in 5 mM PCA-treated Anodiscs: (*a*) perfluorobutyric acid, (*b*) perfluoropentanoic acid, (*c*) perfluorohexanoic acid, (*d*) perfluoroheptanoic acid.

3.2.2. Treatment time effect. To investigate the effect of PCA treatment time on the orientation of confined LCs in Anodisc membrane cavities, we obtained the FTIR spectra of E7-filled Anodisc membranes treated with 5 mM perfluoropentanoic acid solution with different treatment time (40, 50, 60, 80 s). In this case, we used the same treatment time treated Anodisc spectrum as the reference spectrum to obtain the difference spectrum according to equation (2) using subtraction factor as 1. The results for 5 mM perfluoropentanoic acid solution with different treatment times are shown in figure 7. The –C≡N peak height at 2226 cm^{-1} changed between 40 s and 50 s treatment times, indicating a change from parallel to perpendicular orientation to the cavity long axis in the Anodisc membrane. To compare the LC orientataions, we calculated R values according to equation (3); the results are shown in table 4. The R value changed from 0.28→0.07→0.07→0.08 with increase of treatment time. On comparing again with the R value of 0.13 for 0.4 wt% E7 in CCl_4 solution, we found an orientation change of E7 LC from parallel to perpendicular for 50 s treatment time and upward. From these results, we found about 50 s are necessary for 5 mM perfluoropentanoic acid solution to react with Anodisc membrane to cover the Anodisc cavity wall surface with $–CF_2–CF_2–CF_2–CF_3$. Covering the Anodisc membrane cavity wall surface with $–C_4F_9$

Table 3. Peak area ratio change of E7 LC for 5 mM PCA-treated Anodisc membranes.

C_nF_{2n+1} COOH	Area of overtone, γ_1(CH)	Area of C≡N stretching peak	$A(1912\,cm^{-1})/A(2226\,cm^{-1})$
n=3	0.268	1.316	0.20
n=4	0.236	3.481	0.07
n=5	0.273	4.415	0.06
n=6	0.218	3.514	0.06

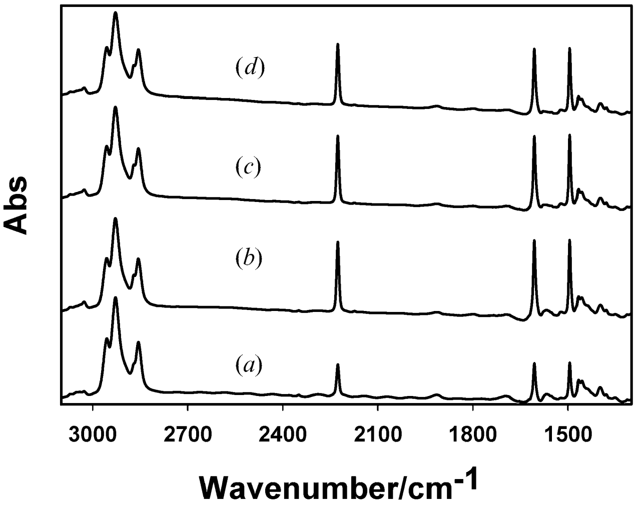

Figure 7. FTIR spectra of E7 confined in 5 mM perfluoropentanoic acid-treated Anodiscs with different treatment time: (*a*) 40 s, (*b*) 50 s, (*c*) 60 s, (*d*) 80 s.

chains by reacting with perfluoropentanoic acid gives the surface a very low surface energy, which facilitates the perpendicular orientation of LCs in the cavities of Anodisc membranes.

4. Conclusions

FTIR spectroscopy allowed us to measure LC alignment direction with only one LC filled membrane; this compares with the ^{2}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 a PCA to an alumina Anodisc was salt formation between the PCA and the membrane. We found an abrupt E7 LC orientation change between perfluoropentanoic acid (n=4) and perfluorohexanoic acid (n=5), in the 1 mM and 3 mM solution treated Anodisc membranes, from parallel to perpendicular to the cavity long axis. For 5 mM PCA solution-treated Anodisc membranes, the change was between perfluorobutyric acid (n=3) and perfluoropentanoic acid (n=4), again from parallel to perpendicular. If we compare PCA solution-treated results with our previous HCA solution-treated results [4], we found the E7 LC orientation change to occur at shorter chain length for PCA solution-treated Anodisc membranes than that for the HCA case, due to the lower surface energy of –C_nF_{2n+1} chains than –C_nH_{2n+1} chains. From results of the treatment time effect on LCs orientation, we found that about 50 s is necessary for 5 mM perfluoropentanoic acid solution to react with Anodisc membrane to give sufficient coverage of the cavity wall surface with low surface energy of –CF_2–CF_2–CF_2–CF_3 chains.

Table 4. Peak area ratio change of E7 LC for 5 mM perfluoropentanoic acid-treated Anodiscs with different treatment time.

Treatment time/s	Area of overtone, γ_1(CH)	Area of C≡N stretching peak	A(1912 cm^{-1})/ A(2226 cm^{-1})
40	0.307	1.083	0.28
50	0.185	2.569	0.07
60	0.236	3.481	0.07
80	0.325	3.881	0.08

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