

20.4: FTIR study of E7 liquid crystals confined to perfluorinated carboxylic acid treated cylindrical cavities of Anodisc membranes

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Abstract

Orientation of E7 liquid crystals (LCs) confined to 200 nm – diameter cylindrical cavities of Anodisc membranes are investigated by FTIR dichroism techniques. The cavity walls of the confining pores are chemically modified with different perfluorinated carboxylic acids (PCA, $C_nF_{2n+1}COOH$, $n=3, 4, 5, 6$). From the FTIR spectra of PCA treated alumina Anodisc membranes, we found the salt formation between –COOH group of PCA and Anodisc membrane. From the FTIR spectra of LC filled Anodisc membranes, we found abrupt alignment direction change of LC molecules between $n=4$ and 5 for 1 mM PCA treated Anodisc membranes, from parallel to perpendicular direction to the cavity walls. But 5mM PCA treated Anodisc membranes, alignment direction of LC molecules changed between $n=3$ and $n=4$, from parallel to perpendicular direction.

1. Introduction

A lot of studies have been performed to measure the orientational order of LCs confined in porous Anodisc membranes using deuterium nuclear magnetic resonance (2H -NMR) spectroscopy [1-3]. To measure 2H -NMR spectra of confined liquid crystals to Anodisc cavities, we need LCs which are selectively deuterated on the β position of the hydrocarbon chain. To obtain a sufficient signal-to-noise ratio for a 2H -NMR experiment, approximately 40 strips must be stacked on one another [3]. To overcome these problems, we would like to use FTIR spectroscopic techniques to measure the orientation of liquid crystals in the cavities of Anodisc membranes. Transmission FTIR sampling technique, where the electric field vector is parallel to the substrate surface, has been used to study the anchoring mechanism of PCA after reaction with alumina 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 different 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 know the polarization tendency of LC molecules. Table I shows the polarization tendencies of each peaks of 5CB, which is the major component of E7.

The intensity of IR absorption mode is

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

C = proportionality constant

\mathbf{E} = electric field vector of incident IR beam

\mathbf{M} = transition moment vector of vibrational mode

θ = the angle between the two vectors

Using the relationship in equation (1), we can identify the orientation of LC molecules.

Table I. FTIR Peak Assignments for 5CB LC [4].

Peak (cm^{-1})	Polarization Tendency	Assignment
2957		asymmetric stretching mode of CH_3
2929	\perp	asymmetric stretching mode of CH_2
2871		symmetric stretching mode of CH_3
2857	\perp	symmetric stretching mode of CH_2
2227		stretching mode of $C\equiv N$

|| -parallel transition moment tendency;

\perp -perpendicular transition moment tendency

2. Experimental

A. Materials

The cylindrical channels of Anodisc membranes (pore size 200 nm, 600 nm thick and 25 mm circular membrane) were purchased from Whatman. All PCAs (perfluorobutyric acid, perfluoropentanoic acid, perfluorohexanoic acid and perfluoroheptanoic acid) and solvents were purchased from Aldrich. Nematic LC E7 (Cr-N= -10 °C and N-I= 60 °C, MERCK) was used to fill the cavities of Anodiscs. E7 is a eutectic liquid crystal mixture of 51% 5CB, 25% 7CB, 16% 8OCB, and 8% 5CT [4]. 1-5 mM solutions of PCAs in methanol were used to modify cavity walls of Anodic membranes. After 1 minute soaking of Anodisc membrane in the solution, the membrane was removed from the solution and put on the 70 °C hot plate for 10 minutes and placed in the vacuum oven for 1 hr at 140 °C to remove solvent. After drying, the membranes were put in the 5.0 vol % of E7 in hexane solution at room temperature for 1 minute. After filling E7 LC, they were removed and put on the hot plate at 80 °C for 30 minutes to remove hexane solvent, cooled slowly to room temperature for 30 minutes.

B. Instrumentation.

To study molecular orientation change of the LC by PCA treatment of Anodisc membranes, a FTIR 620 (Jasco) was used to take transmission FTIR spectra. 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 PCA molecules to alumina Anodisc wall surface, we measured FTIR spectra of Anodisc, bulk perfluorobutyric acid (using KBr disk), perfluorobutyric acid treated Anodisc. To identify the reaction between PCA and Anodisc more clearly, we obtained difference spectrum by subtracting the FTIR spectrum of Anodisc from the spectrum of PCA treated Anodisc. The result for perfluorobutyric acid treated one is shown in Fig. 1(d). According to difference spectrum of Fig. 1(d), C=O peak of $-\text{COOH}$ at 1774 cm^{-1} , which appears in Fig. 1(c) for pure perfluorobutyric acid, disappeared completely and new peaks at 1604 , 1568 and 1454 cm^{-1} with a weak peak at 1696 cm^{-1} appeared, showing the formation of salt between $-\text{COOH}$ group of perfluorobutyric acid and alumina Anodisc membrane. Therefore, $-\text{COOH}$ groups of perfluorobutyric acid which reacted with Anodisc cavity walls to form salt, anchor perfluorobutyric acid molecules to the walls of Anodisc cavities. The remaining $\text{CF}_3\text{CF}_2\text{CF}_2^-$ of perfluorobutyric acid will point to the center of cavities. The same trend was observed for other PCA treated Anodiscs.

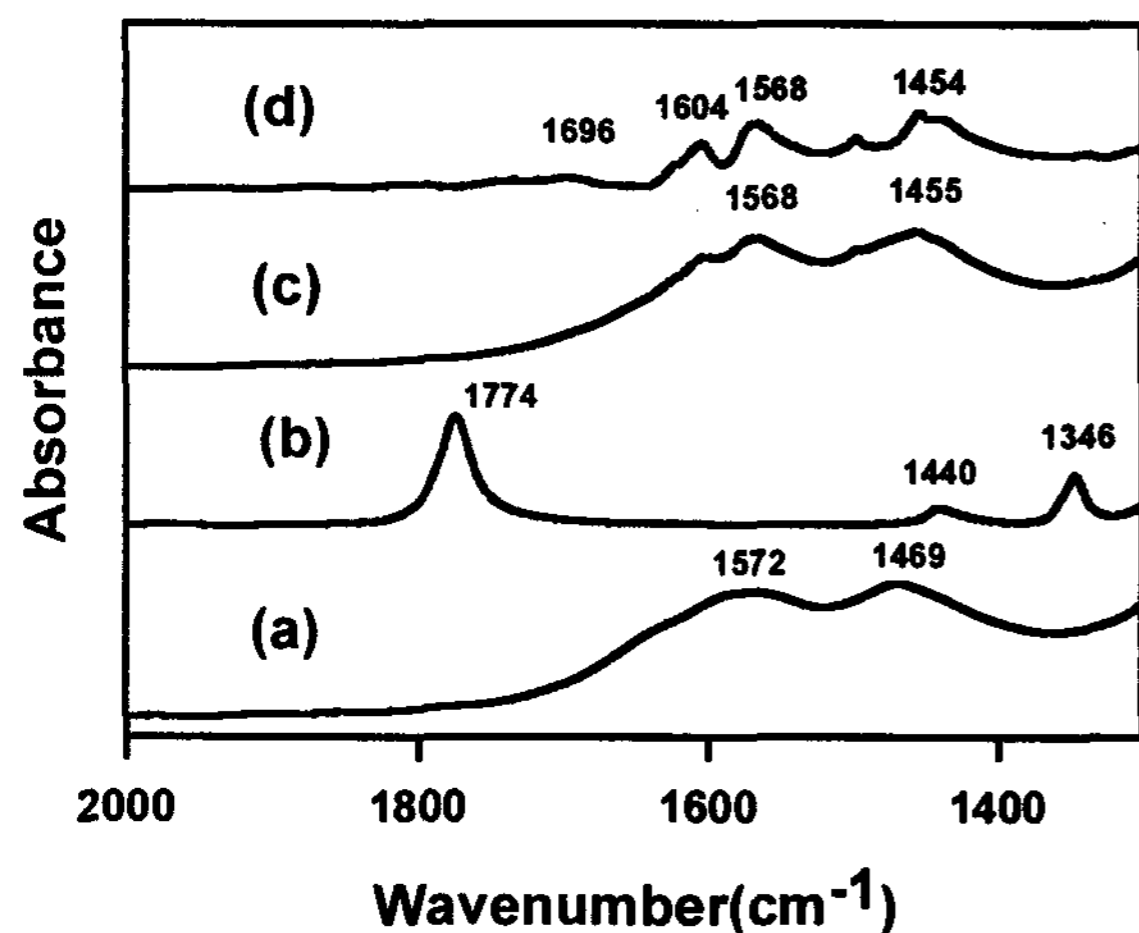


Fig. 1. FTIR spectra of : (a) Anodisc; (b) pure perfluorobutyric acid; (c) perfluorobutyric acid treated Anodisc; (d) difference obtained by subtracting (a) from (c).

2.2 E7 liquid crystal alignment in the

cavities of PCA treated Anodisc membrane.

To investigate the effect of PCA treatment on the orientation of confined liquid crystals in membrane cavities, we measured FTIR spectra of E7 filled Anodisc membranes treated with 1 mM PCAs with different chain length ($n=3, 4, 5, 6$). To measure the orientation of E7 only, we subtracted PCA treated Anodisc spectrum from the spectrum of E7 filled PCA treated Anodisc. The results are shown in Fig. 2. According to Fig. 2, the LC peak height of $-\text{C}\equiv\text{N}$ at 2227 cm^{-1} changed between perfluoropentanoic acid ($n=4$) and perfluorohexanoic acid ($n=5$) treated Anodisc, from parallel to perpendicular direction to the long axis of cavity of Anodisc membrane. Treating with 1 mM PCAs with longer chain length ($n=7, 8, 9, 10, 11, 17$) showed the same trend as $n=4$ and 5. perpendicular direction to the long axis of cavity of Anodisc membrane.

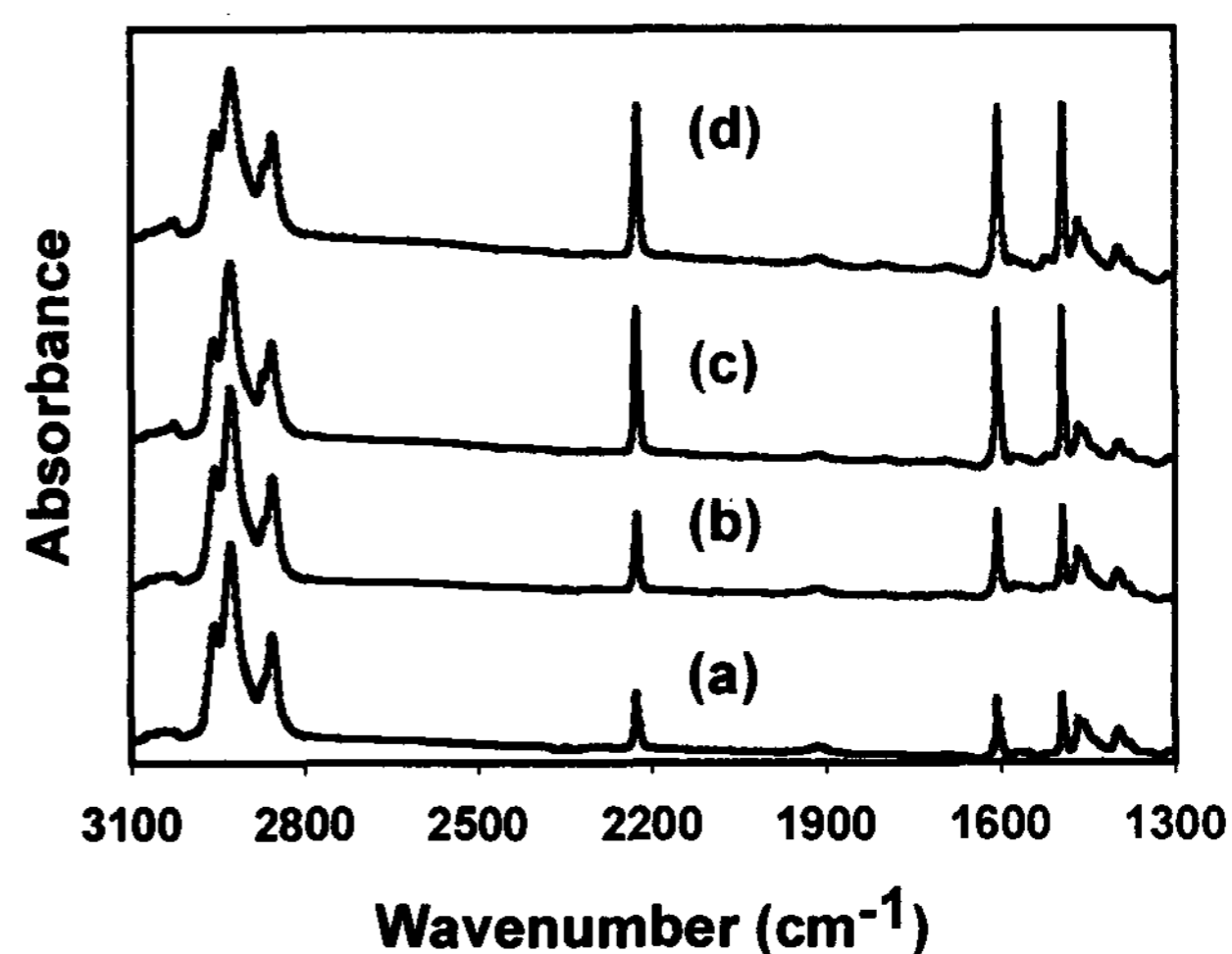


Fig. 2. FTIR spectra of E7 confined to 1 mM PCA treated Anodiscs. (a) perfluorobutyric acid; (b) perfluoropentanoic acid; (c) perfluorohexanoic acid; (d) perfluoroheptanoic acid

For 3 mM PCA treated ones showed the same trend as in Fig. 2. therefore, we increased the concentration of PCA to 5 mM to treat Anodisc membranes. For 5 mM PCA treated ones in Fig. 3, the LC peak height of $-\text{C}\equiv\text{N}$ at 2227 cm^{-1} changed between perfluorobutyric acid ($n=3$) and perfluoropentanoic acid ($n=4$) treated Anodisc, from parallel to perpendicular direction to the long axis of cavity of Anodisc membrane.

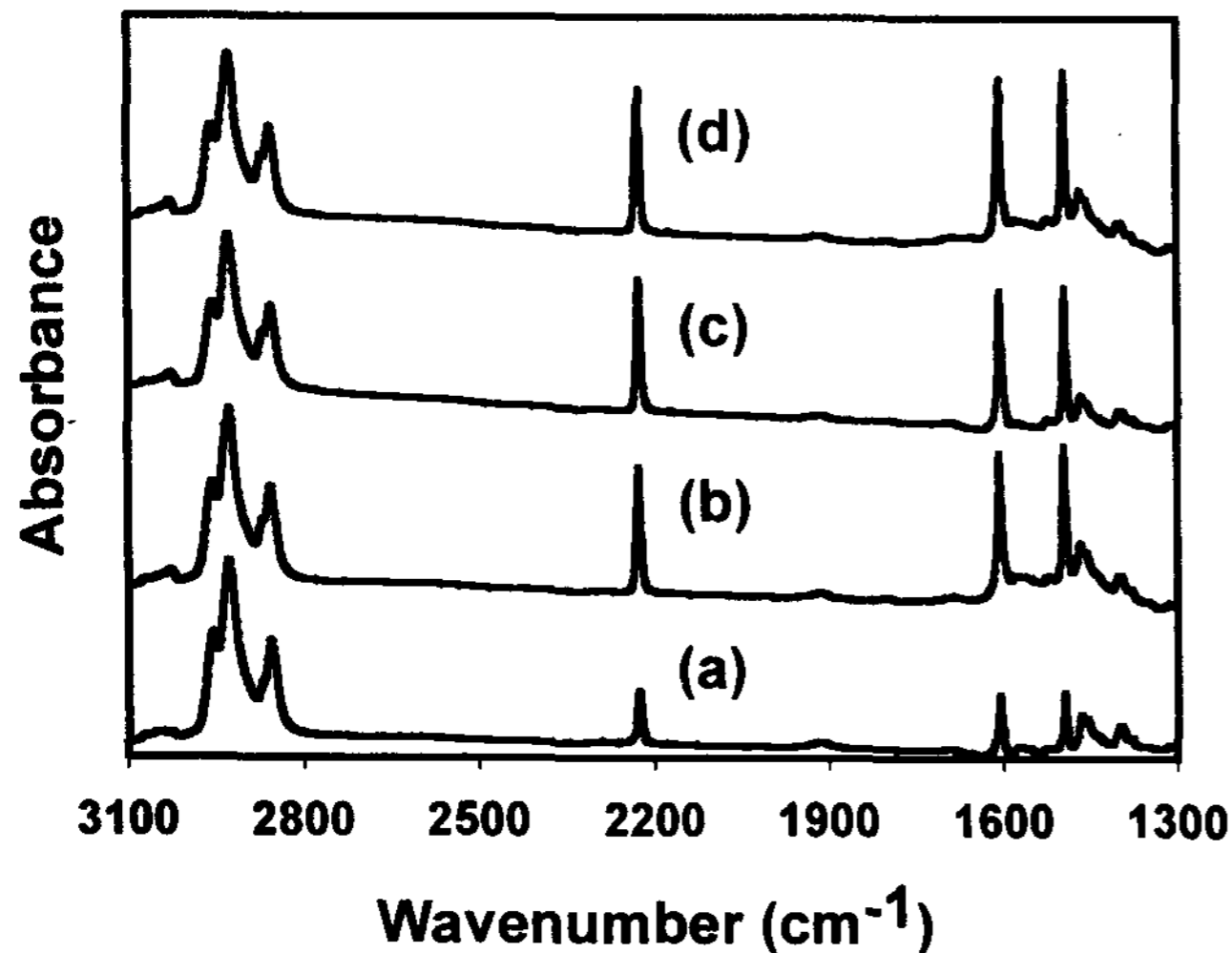


Fig.3. FTIR spectra of E7 confined to 5 mM PCA treated Anodiscs. (a) perfluorobutyric acid; (b) perfluoropentanoic acid; (c) perfluorohexanoic acid; (d) perfluoroheptanoic acid

To compare the difference between aliphatic acid and PCA treatment effects, we treated 2% and 4% aliphatic acids with different length to Anodisc membranes to investigate LC orientation change depending on the length of the aliphatic acids. For 2% aliphatic acid treated Anodisc membranes shown in Fig. 4, the LC peak height of $-C\equiv N$ at 2226cm^{-1} changed between heptanoic acid ($n=6$) and octanoic acid ($n=7$) treated Anodisc, from parallel to perpendicular direction to the long axis of cavity of Anodisc membrane.

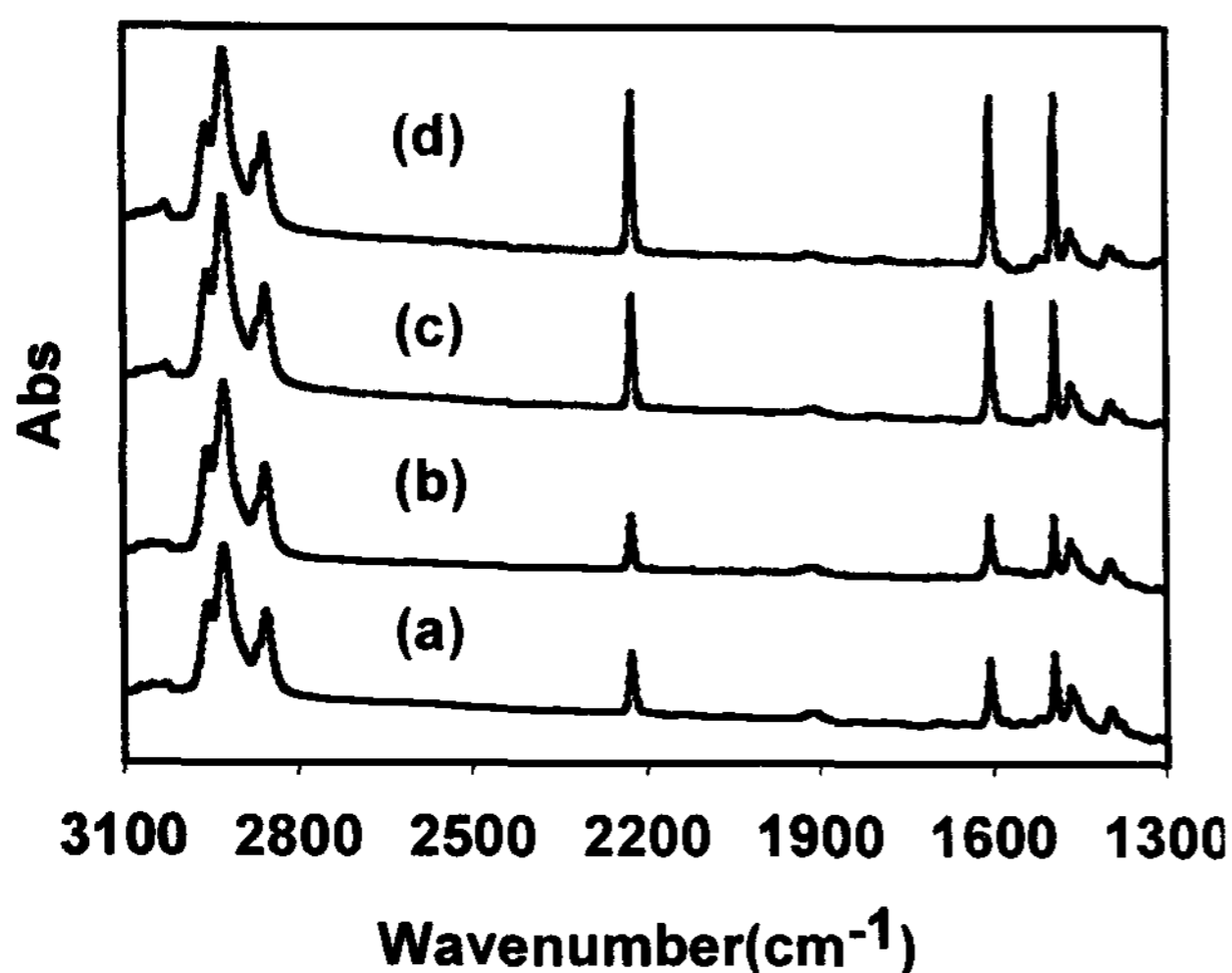


Fig. 4. FTIR spectra of E7 confined to 2% aliphatic acid treated Anodiscs. (a) hexanoic acid; (b) heptanoic acid; (c) octanoic acid; (d) decanoic acid

For 4% aliphatic acid treated ones shown in Fig. 5, the LC peak height of $-C\equiv N$ at 2226cm^{-1} changed between hexanoic acid ($n=5$) and heptanoic acid ($n=6$) treated Anodisc, from parallel to perpendicular direction to the long axis of cavity of Anodisc membrane [5]. The concentrations of aliphatic acids used to treat Anodisc membranes are much higher than those of PCAs; mM concentrations for 2% aliphatic acids are as follows; 137.6 mM for $n=5$, 122.7 mM for $n=6$, 110.8 mM for $n=7$, 92.8 mM for $n=9$. mM concentrations for 4% aliphatic acids are as follows; 275.2 mM for $n=5$, 245.5 mM for $n=6$, 221.6 mM for $n=7$, 185.5 mM for $n=9$. These different effects between aliphatic acid treatment and PCA treatment may be caused by the lower surface energy of PCAs due to $-(\text{CF}_2)\text{CF}_3$ than those of $-(\text{CH}_2)\text{CH}_3$ of aliphatic acids, and stronger acidity of PCA's than that of aliphatic acids.

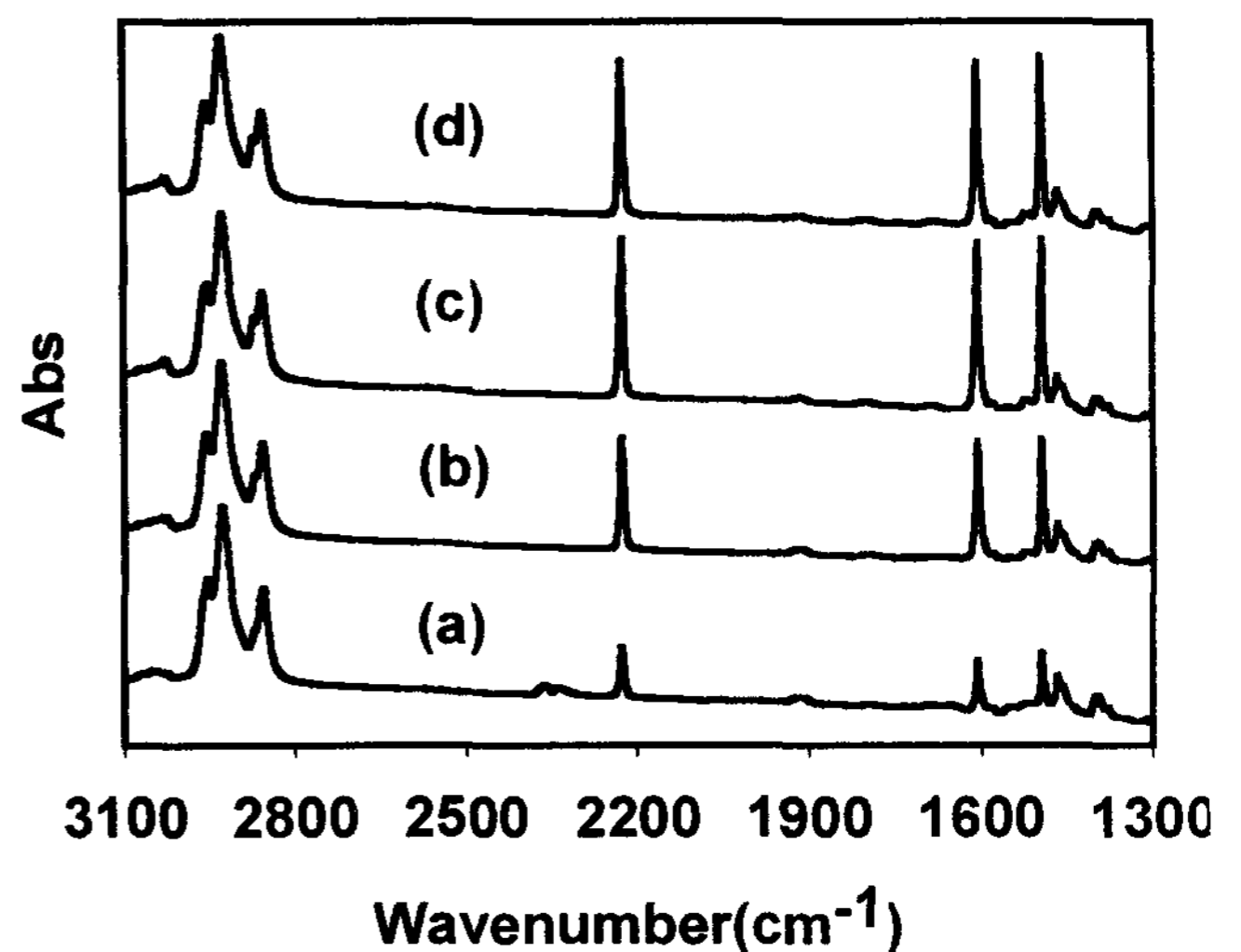


Fig. 5. FTIR spectra of E7 confined to 4% aliphatic acid treated Anodiscs. (a) hexanoic acid; (b) heptanoic acid; (c) octanoic acid; (d) decanoic acid

4. Conclusions

FTIR spectroscopic technique allowed us to measure alignment direction of LCs with only one LC filled membrane, compared to $^2\text{H-NMR}$ technique which requires deuterated LCs and approximately 40 stacks of LC filled membranes to obtain good signal-to-noise ratio. Also we found the anchoring mechanism of PCA to alumina Anodisc was formation of salt between PCA and alumina membrane. We found abrupt E7 LC orientation change in the 1 mM and 3 mM PCA treated Anodisc membrane, between perfluoropentanoic acid ($n=4$) and perfluorohexanoic acid ($n=5$) treated Anodisc, from parallel to perpendicular direction to the long axis of cavity of Anodisc membranes. We found abrupt E7 LC orientation change for 5mM PCA treated Anodisc membrane, between perfluorobutyric acid ($n=3$) and perfluoropentanoic acid ($n=4$) treated Anodisc, from parallel to perpendicular direction to the long axis of cavity of Anodisc membranes. The LC orientation occurred much shorter length and weaker concentrations of PCA treated Anodisc membranes than those of aliphatic acids treated Anodisc membranes. These differences may be caused by the stronger acidity and lower surface energy of PCA's than those of

aliphatic acids. Therefore, FTIR spectroscopic technique can be used to measure the orientation of confined LCs and the anchoring mechanism of PCA to Anodisc membrane more easily than using ^2H -NMR technique.

5. Acknowledgement

This work was supported by grant No. ~~(R12-2002-055-03002-0)~~ from the Basic Research Program of the Korea Science & Engineering Foundation.

6. References

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