

FTIR study of E7 liquid crystals confined to 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 aliphatic acids ($C_nH_{2n+1}COOH$, $n=5, 6, 7, 9$). From the FTIR spectra of aliphatic acid treated alumina Anodisc membranes, we found the salt formation between –COOH group of aliphatic acid and Anodisc membrane. From the FTIR spectra of LC filled Anodisc membranes, we found abrupt alignment direction change of LC molecules between $n=6$ and 7 for 2% aliphatic acid treated Anodisc membranes, from parallel to perpendicular direction to the cavity walls. But 4% aliphatic acid treated Anodisc membranes, alignment direction of LC molecules changed between $n=5$ and $n=6$, from parallel to perpendicular direction. The same trend was observed for 2H -NMR measurements.

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, has been used to study the orientation of aliphatic acid after reaction with 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 different 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 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

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

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 molecules.

Table I. FTIR Peak Assignment 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 aliphatic acids (hexanoic acid, heptanoic acid, octanoic acid and decanoic acid) and solvents were purchased from Aldrich. Nematic LC E7 (K-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]. A 2-4 % by weight solution of the aliphatic acid in methanol was 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 ~40°C 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 aliphatic acid 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 aliphatic acid with alumina Anodisc membrane

To investigate the mechanism of the anchoring of aliphatic acid to alumina Anodisc wall surface, we measured FTIR spectra of Anodisc, bulk aliphatic acid (using KBr disk), aliphatic acid treated Anodisc.

To identify the reaction between aliphatic acid and Anodisc more clearly, we obtained difference spectrum by subtracting the FTIR spectrum of Anodisc from the spectrum of aliphatic acid treated Anodisc. The results for hexanoic acid treated ones are shown in Fig. 1. According to difference spectrum of Fig. 1(d), C=O peak of -COOH at 1711 cm⁻¹, which

appears in Fig. 1(c) for pure hexanoic acid, disappeared and new peaks at 1569 and 1468 cm⁻¹ with a shoulder at 1604 cm⁻¹ appeared, showing the formation of salt between aliphatic acid and alumina Anodisc membrane. By comparing Fig. 1(b) and Fig. 1(c) in the region of -CH₂ and -CH₃ stretching region, we found higher intensity decrease of -CH₃ peaks compared to -CH₂ peaks for aliphatic acid treated Anodisc than for those of pure hexanoic acid, meaning -CH₃ group of hexanoic acid may be pointing outside of the cavities, in parallel to the cavity walls after reaction with Anodisc. Therefore, hexanoic acid of -COOH group reacted with Anodisc membrane cavity walls to form salt, but -CH₃ groups of acid molecules were pointing outside of the cavities. The same trend was observed for the other aliphatic acid treated Anodiscs.

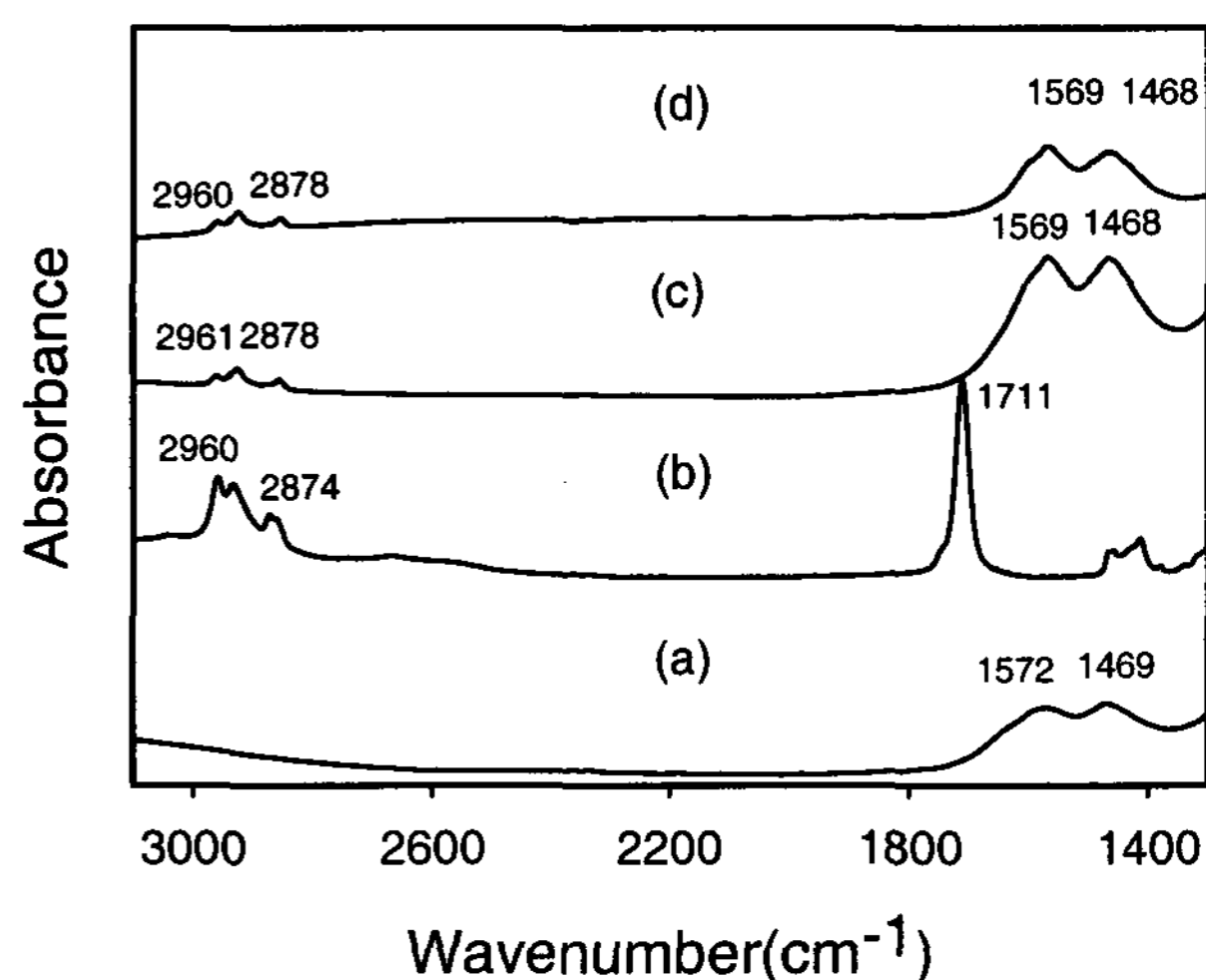


Fig. 1. FTIR spectra of : (a) Anodisc; (b) pure hexanoic acid; (c) hexanoic treated Anodisc; (d) difference obtained by subtracting (a) from (c).

2.2 E7 liquid crystal alignment in the cavities of aliphatic acid treated Anodisc membrane.

To investigate the effect of aliphatic acid treatment on the orientation of confined liquid crystals in membrane cavities, we measured FTIR spectra of E7 filled Anodisc membranes treated with 2% aliphatic acids with different chain length (n=5, 6, 7, 9). To measure the orientation of E7 only, we subtracted aliphatic acid treated Anodisc spectrum from the spectrum of E7 filled aliphatic acid treated Anodisc. The results are shown in Fig. 2. According to Fig. 2,

the LC peak height of $-C\equiv N$ at 2227 cm^{-1} changed between heptanoic acid ($n=6$) and octanoic acid ($n=7$) treated Anodisc, from parallel to perpendicular direction to cavity walls of Anodisc.

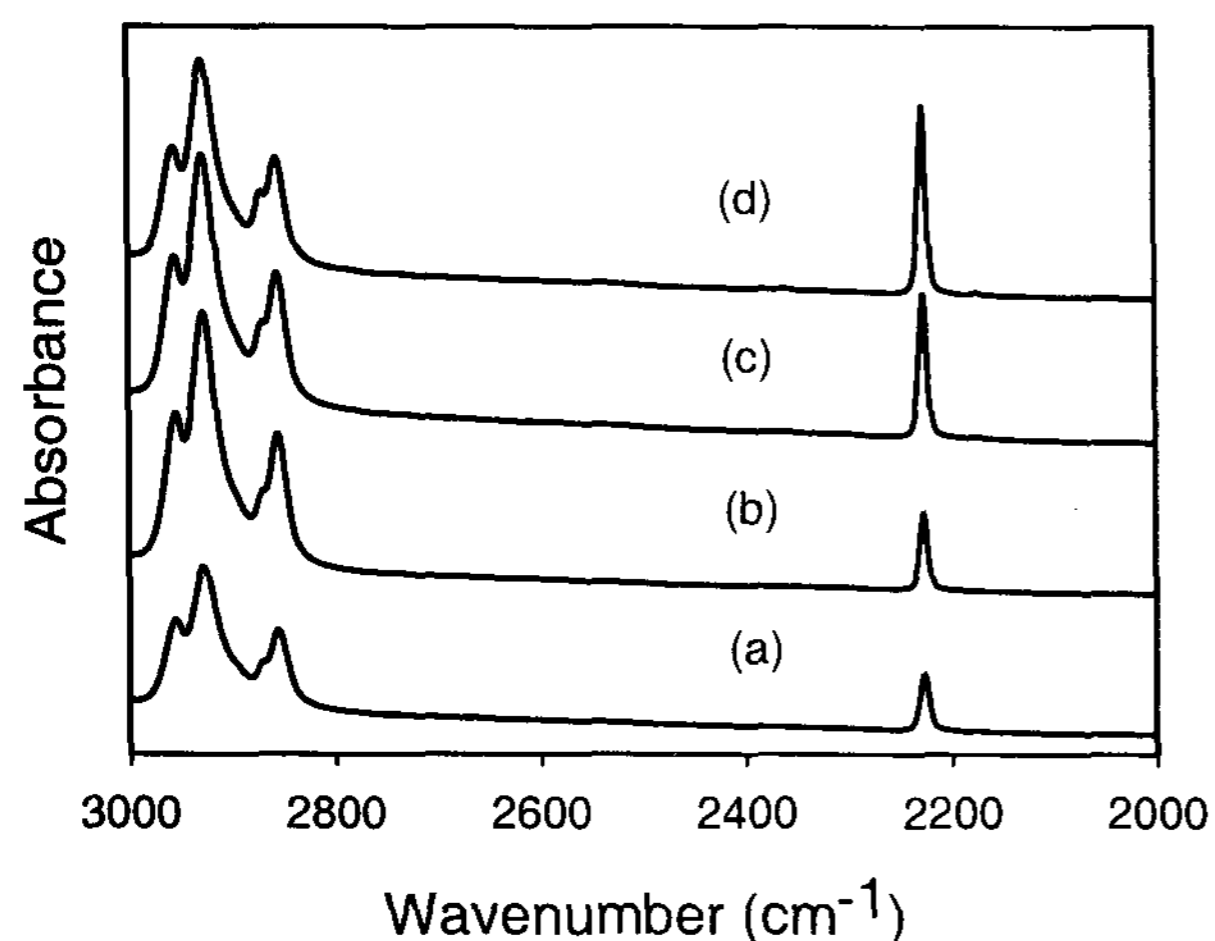


Fig. 2. FTIR spectra of E7 confined to 2% aliphatic acid treated Anodiscs. (a) hexanoic acid;

(b) heptanoic acid; (c) octanoic acid; (d) decanoic acid

For 4% aliphatic acid treated ones in Fig. 3, the LC peak height of $-C\equiv N$ at 2227 cm^{-1} changed between hexanoic acid ($n=5$) and heptanoic acid ($n=6$) treated Anodisc, from parallel to perpendicular direction to cavity walls of Anodisc. The same trend was observed by $^2\text{H-NMR}$ [3].

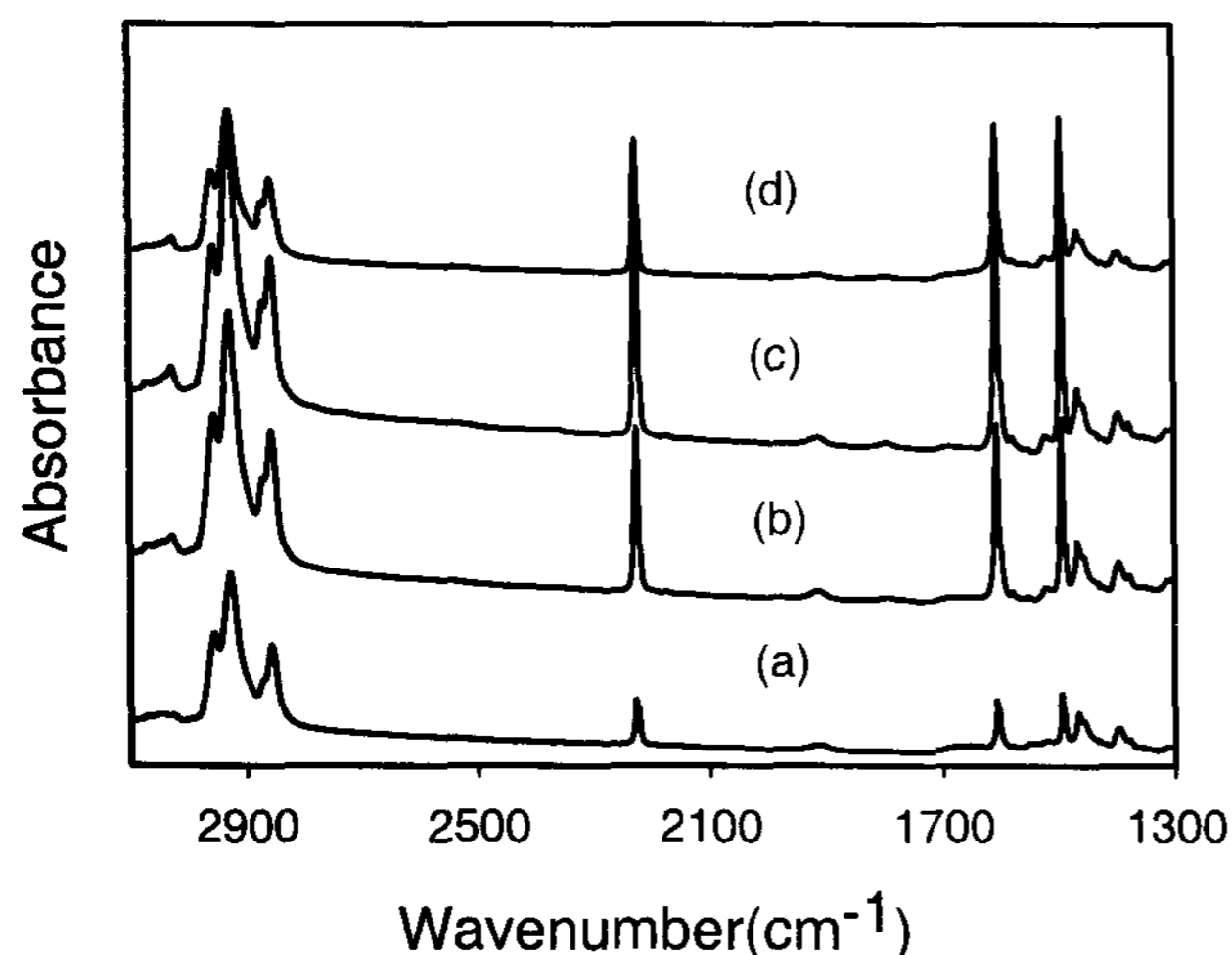


Fig.3. FTIR spectra of E7 confined to 4% aliphatic

acid treated Anodiscs. (a) hexanoic acid; (b) heptanoic acid; (c) octanoic acid; (d) decanoic acid

4. Conclusion

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 aliphatic acid to alumina Anodisc was formation of salt between aliphatic acid and alumina membrane. We also found that the $-\text{CH}_3$ group of aliphatic acid after reaction with Anodisc was pointing out of the Anodisc cavities. Therefore, FTIR spectroscopic technique can be used to measure the orientation of confined LCs and the anchoring mechanism of aliphatic acids to Anodisc membrane more easily than using $^2\text{H-NMR}$ technique.

5. Acknowledgement

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6. References

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