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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Yasuda, Akio , Nito, Keiichi and Matsui, Eriko(1993) 'Time-resolved FT-IR study of ferroelectric liquid crystals with SiO obliquely evaporated alignment layers', *Liquid Crystals*, 14: 6, 1725 – 1734

To link to this Article: DOI: 10.1080/02678299308027711

URL: <http://dx.doi.org/10.1080/02678299308027711>

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Time-resolved FT-IR study of ferroelectric liquid crystals with SiO obliquely evaporated alignment layers

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Time-resolved FT-IR spectroscopy was performed to monitor the behaviour of ferroelectric liquid crystals on a microsecond time scale. A bookshelf geometry was obtained by alignment with SiO obliquely evaporated layers in a CaF₂ cell with 2 μm gap. Six kinds of FLC mixtures were examined, all of which were three-component systems consisting of chiral molecules of 5 wt% and two kinds of phenyl pyrimidine molecules of 47.5 wt% each. All IR spectra were dominated by vibrational modes from the phenyl pyrimidines. Typical vibrational modes from core and alkyl chain parts are selected in order to compare the movement of the alkyl chain as a function of the chiral components. A novel parameter $\alpha = (\text{intensity of largest peak at } 2925 \text{ cm}^{-1} / \text{intensity of smallest peak at } 2925 \text{ cm}^{-1}) / (\text{intensity of largest peak at } 1432 \text{ cm}^{-1} / \text{intensity of smallest peak at } 1432 \text{ cm}^{-1})$ for evaluating the alkyl chain movement is introduced. It was found that the length of the rigid or flexible parts of the chiral molecules and the parameter α are correlated. Moreover, relations between the cone angle and α and between the rise time and α were found.

1. Introduction

During the past decade ferroelectric liquid crystals (FLCs) have been studied intensively with the aim of realizing flat panel displays. FLCs are said to be suitable for flat panel displays because of their fast response time (1000 times faster than twisted nematic liquid crystal devices), wide viewing angle, and memory effect, which make it possible to address more than 1000 lines by passive matrix driving. One of the basic problems of FLCs is the dynamics of FLC molecules when they respond to an applied electric field which is not well-understood.

Recently, time-resolved FT-IR spectroscopy has been considered to be a potentially powerful tool for investigating the movement of FLC molecules on a time scale of the order of μs under an applied electric field [1]. However, because of the chevron geometry of the FLC cells, it was very difficult to determine how the molecules switched when the electric field was applied. In order to obtain exact information on the molecular dynamics, a time-resolved FT-IR study on well-defined molecules in a bookshelf layer structure was desired.

For that purpose, SiO obliquely evaporated alignment layers were used to realize a bookshelf geometry, and simple three-component systems consisting of chiral molecules of 5 wt% and phenylpyrimidine bases of 47.5 wt% were introduced. The six kinds of chiral molecules used may be classified into two types, namely biphenyl and ester-containing chiral compounds. Cells with a gap of 2 μm were constructed from CaF₂ substrates.

Upon investigation of the molecular dynamics under the conditions described previously, a newly introduced molecular parameter α was found to exhibit good

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correlation with the cone angles and response times. In addition, it was found that the lengths of the flexible and rigid parts of the chiral molecules are also correlated with α .

2. Experimental

2.1. Reagents

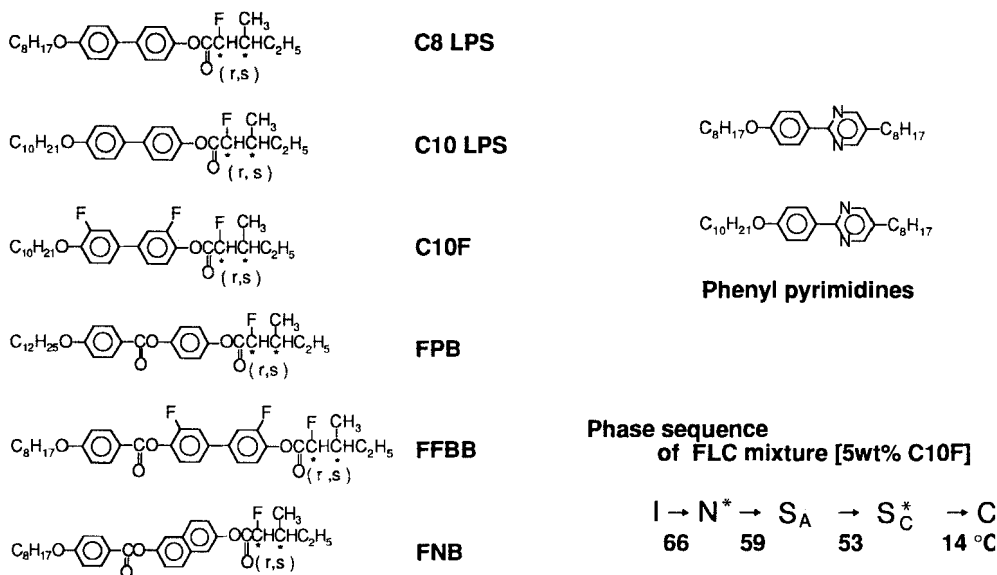
SiO powder was purchased from Furuuchi Kagaku Ltd. and used as received. All the chiral and host molecules used are shown in figure 1. Six kinds of fluorinated chiral molecules and phenylpyrimidines were synthesized as reported previously [2].

2.2. Instrumentation

Time-resolved FT-IR spectroscopy was monitored by using a JEOL JIR-6500 system with a time-resolved attachment and microscope unit [3], with which transition phenomena occurring within the order of μs can be observed. FLCs were switched by $1\text{kHz} \pm 15\text{V}$ square wave pulses at 40°C . The temperature was controlled by a Mettler FP82 hot stage unit with a controller. The bookshelf geometry was determined by X-ray diffraction. The X-ray source was a copper anode in a Rigaku RU-300 X-ray diffraction system. The $K\alpha$ line was selected by a monochromator and the source was operated at 50 kV and 200 mA. The cell for the X-ray measurements was $100\ \mu\text{m}$ thick with glass dimensions of $10 \times 10\ \text{mm}$ with a $500\ \text{\AA}$ sputtered ITO film.

2.3. FLC cell

The CaF_2 substrates measured $20 \times 20 \times 1\ \text{mm}$ with a $500\ \text{\AA}$ thick sputtered ITO film. The SiO obliquely evaporated film was made with a ULVAC EBX-14D



Chiral liquid crystal molecules

Figure 1. Molecular structure of the chiral and phenylpyrimidine molecules and the phase sequence of the C10F 5 wt%, phenyl pyrimidine (47.5 wt%) system.

vacuum evaporator. The angle between the SiO flux direction and surface normal of the substrate was set at 85° . The SiO film was thermally annealed at 300°C in order to increase the surface stability [4]. The cell was fabricated with the SiO films antiparallel to each other, in order to obtain a tilted bookshelf geometry.

3. Results and discussion

3.1. X-ray diffraction of the C10F system

X-ray diffraction measurements were made of the phenylpyrimidine system containing 5 wt% C10F in order to clarify the layer structure of the system. X-ray diffraction measurements were performed as follows. In the first scan, the director was varied from 40 to 140° with respect to the surface parallel. In the second scan, the cell was set upside down and then X-ray diffraction was monitored in the same way as the first scan. The tilt angle was determined using the mean of the two peak angles as the surface normal in order to avoid instrumental alignment error. A tilted bookshelf geometry was determined as shown in figure 2. The layer tilt angle was 25.8° .

3.2. Time-resolved FT-IR spectra

Time-resolved FT-IR spectra of the C8 LPS system are shown in figure 3. The gate width was $10\ \mu\text{s}$ and the interval was $30\ \mu\text{s}$. The polarizer was set at 45° to the aligning direction (SiO flux direction). The concentration of the chiral molecules was only 5 wt%, so that the spectra observed were mainly attributable to the spectra of the phenylpyrimidines. The background of the spectra increased in the lower wave number region because of the absorption of the longer wavelength light by CaF_2 substrates. The vibrational modes parallel to the molecular long axis ($1432\ \text{cm}^{-1}$) decreased with time, while the vibrational modes perpendicular to the molecular long axis ($2925\ \text{cm}^{-1}$) increased with time. Within $90\ \mu\text{s}$ switching was completely finished.

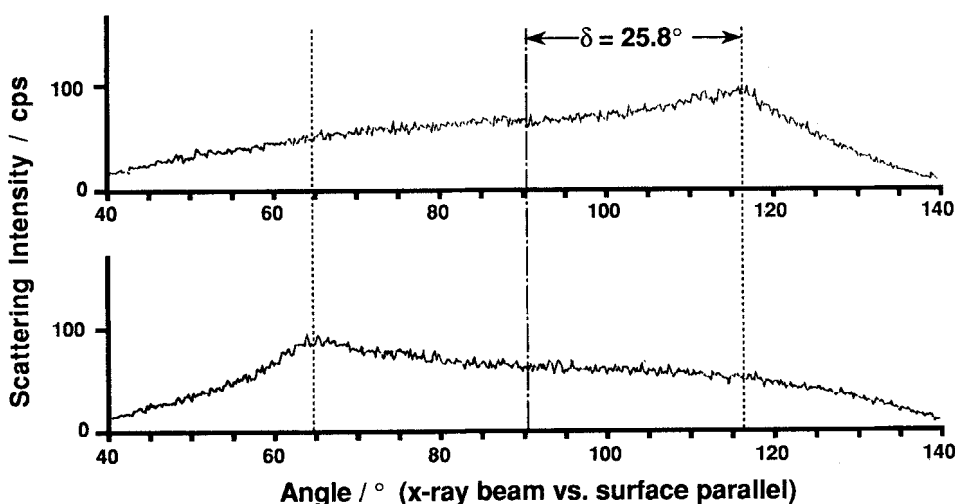


Figure 2. X-ray diffraction pattern of the C10F chiral system. The upper spectrum was measured in the first scan and the bottom in the second scan. In the second scan, the cell was set upside down.

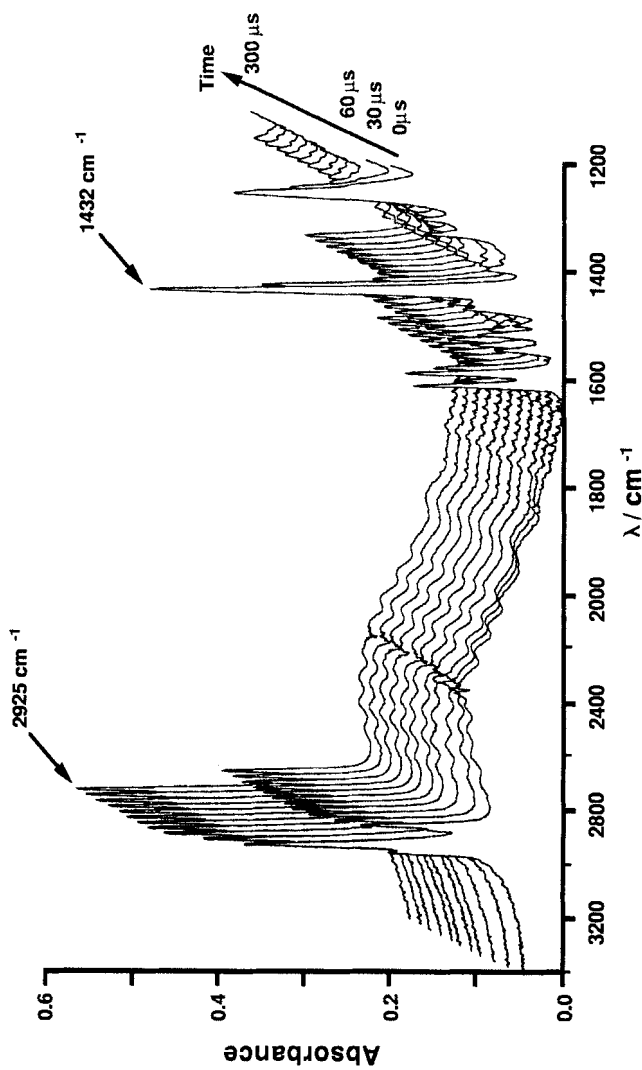


Figure 3. Time-resolved FT-IR spectra of the C8 LPS system. 5 wt% C8 LPS and the phenylpyrimidines are 47.5 wt% each. 10 μs gate width and 30 μs step.

In figure 4, a relation between the time and the peak intensity of the bands at 1432 cm^{-1} and 2925 cm^{-1} is shown. The band at 1432 cm^{-1} is attributable to the vibrational mode of the pyrimidine skeleton, parallel to the molecular long axis, while the band at 2925 cm^{-1} is that of the alkyl chain, parallel to the molecular short axis. The bands represent the modes of the core and alkyl chain parts, respectively. The band at 2925 cm^{-1} should be assigned to antisymmetric stretching vibration of the methylene group. Since the mode of an antisymmetric vibration of a methylene group was observed beyond 2920 cm^{-1} , the structure of the alkyl chain is considered to be not all-*trans* but a *gauche* containing conformation. The infrared dichroic ratio was 8 to 11 in the $1200\text{--}1700\text{ cm}^{-1}$ region, but was 1.5 in the region of stretching vibration mode of the alkyl chain.

It is thought, that the alkyl chain plays an important role in switching. It is possible to evaluate the movement of the alkyl chain in switching by using time-resolved FT-IR spectroscopy of the order of μs . Thus, a novel parameter α was introduced as follows. $\alpha = (\text{intensity of largest peak at } 2925\text{ cm}^{-1} / \text{intensity of smallest peak at } 2925\text{ cm}^{-1}) / (\text{intensity of largest peak at } 1432\text{ cm}^{-1} / \text{intensity of smallest peak at } 1432\text{ cm}^{-1})$.

For example, for the C8 LPS system, α is calculated as follows:

$$\alpha = 0.3476(t = 300\ \mu\text{s}) / 0.2946(t = 0) / 0.4334(t = 0) / 0.1188(t = 300\ \mu\text{s}) = 0.32.$$

In this case, peak intensities at $300\ \mu\text{s}$ are used because the peak intensity becomes constant after $90\ \mu\text{s}$. It is also permissible to use an average value in the constant peak intensity region ($t = 90\text{--}300\ \mu\text{s}$). The parameter α has proved to be very convenient for evaluating the movement of alkyl chains with respect to a rigid core part of the molecules.

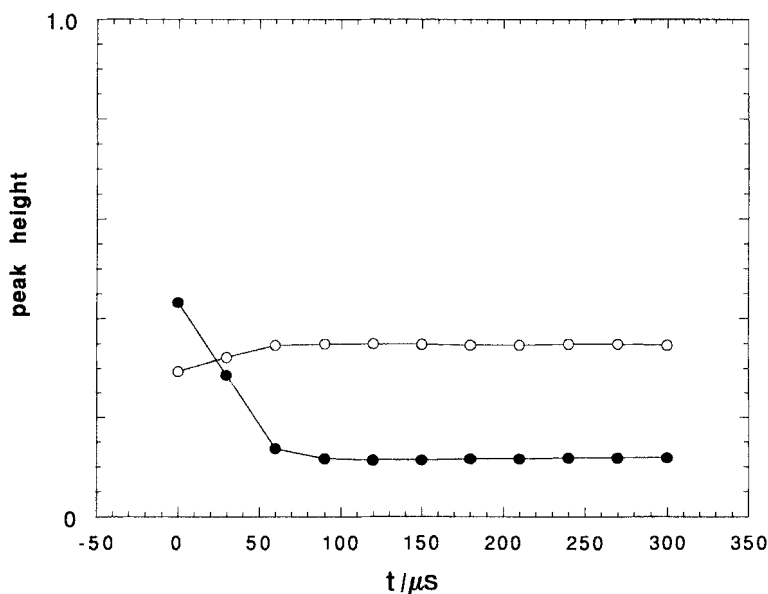


Figure 4. Peak intensity changes versus time for the C8 LPS system. The band at 1432 cm^{-1} (●) is attributable to the core part and the band at 2925 cm^{-1} (○) to the alkyl chain.

Response times and cone angles are important characteristics of FLCs for application to flat panel displays. The rise time is defined as the time required for transmittance to increase from 0 to 90 per cent. The cone angle was monitored from the direction parallel to the surface normal, so that actual cone angles were smaller than the cone angles observed because the pretilt angle does not equal zero. A relation between α and rise time is shown in figure 5. Two trends may be recognized, one governing the C8 LPS, C10 LPS, and C10F series and the other the FFBB, FNB, and FPB series. The former have a biphenyl group and the latter series an ester-containing core part. Those with a biphenyl group, the response time increases with an increase of α , while for the ester-containing series the response time decreases with an increase of α . Thus the relation between α and rise time depends on the structure of the chiral molecules. Chiral molecules, comprising only 5 wt% of the mixture, determine the movement of the host phenyl pyrimidine molecules.

The relation between α and the observed cone angles is shown in figure 6. It is clarified that a relation between α and cone angles, which depends on the kind of chiral molecular structures, clearly exists.

Thus we may expect that the novel molecular parameter α probably reveals important information on the molecular dynamics.

In addition, the relation between the cone angles and rise times is shown in figure 7. The correlation in this case also depends on the kind of chiral compounds. For the biphenyl systems, the rise time decreases slightly for an increase in cone angle, while for the ester-containing chiral molecules, the rise time increases for an increase in cone angle.

3.3. Relation between molecular structure and the parameter α

The parameter α represents the movement of the alkyl chain with respect to that of the core. It is considered that since the movement of the phenyl pyrimidines is determined by that of the chiral molecules, the structure of the chiral molecule is crucial. The structure of the chiral molecule is characterized by the presence of rigid and flexible parts.

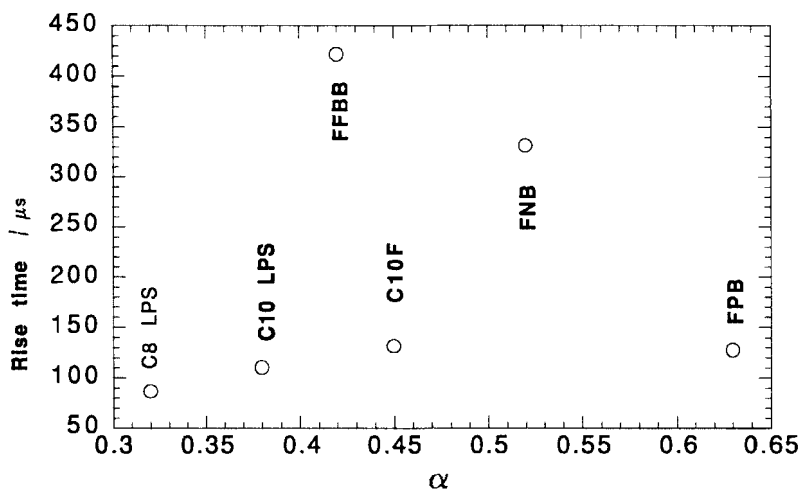


Figure 5. Relation between α and rise time (○).

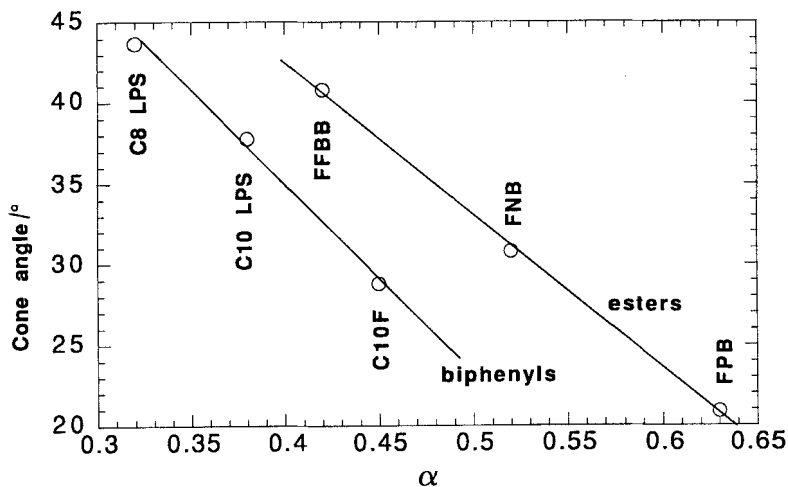


Figure 6. Relation between α and observed cone angle (\circ).

Therefore, the lengths of the rigid and flexible parts of the chiral molecules in the optimized molecular structure were calculated by using MOPAC (MNDO method) on a ALLIANT FX/2800/SLM/1 computer. The results are shown in figure 8. A rigid length is defined as the length between the fluorinated chiral carbon and the methylene carbon attached to an oxygen in the case of the biphenyl chiral molecules, and is defined as the length between the fluorinated chiral carbon and an ester carbon in the ester-containing chirals. A flexible length is defined as the length of the alkyl chain in the case of biphenyl compounds, and is defined as the length from the ester carbon to the end of the alkyl chain in the case of the ester-containing chiral molecules.

Figure 9 shows the relations between the lengths of the rigid or flexible parts and α . For the flexible parts, α increases with an increase of flexible length, while for the

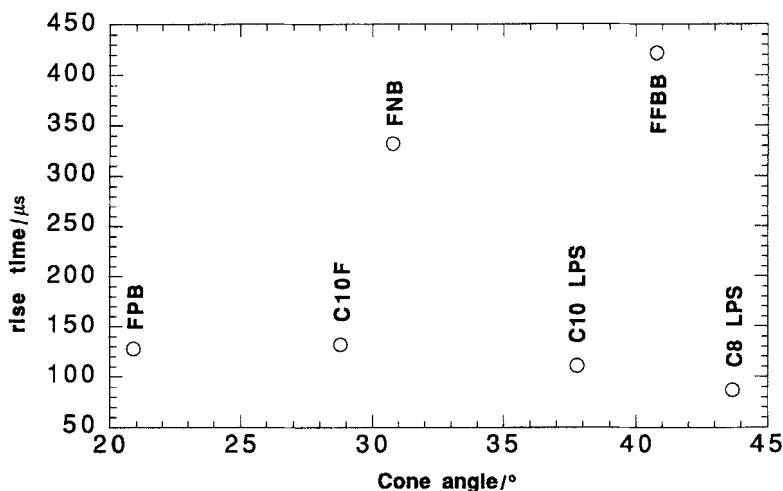


Figure 7. Relation between cone angle and rise time (\circ).

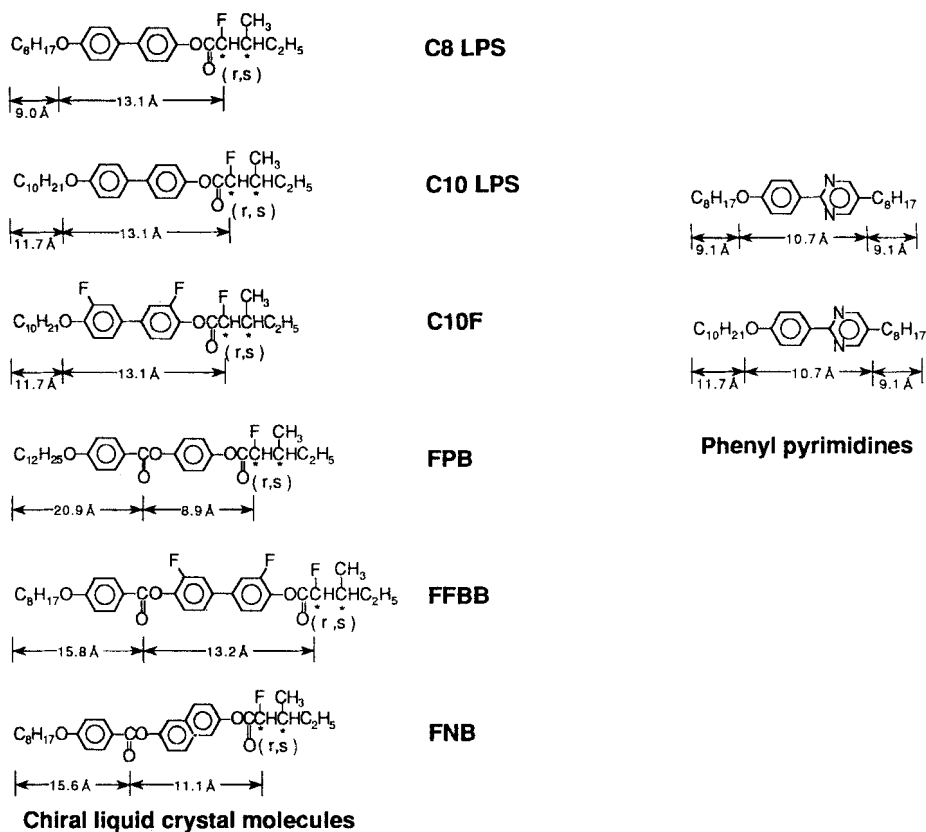


Figure 8. Molecular structures of the chiral molecules and their rigid and flexible lengths.

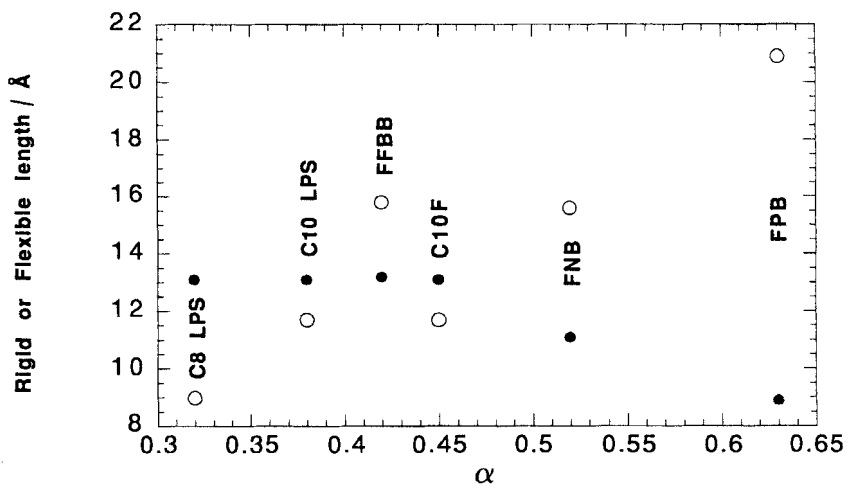


Figure 9. Relation between α and the rigid (●) and flexible (○) lengths.

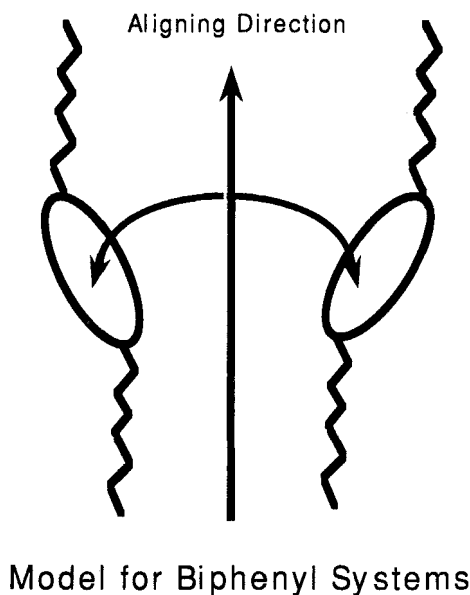


Figure 10. A switching model for the biphenyl systems.

rigid parts, the rigid length decreases in the range of $\alpha \geq 0.45$. Therefore, α can be controlled by changing the length of the rigid and/or flexible parts. In particular, flexible parts play an important role in affecting the α value.

Consequently, a low α value signifies that the orientation of the alkyl chain is more parallel to the aligning direction, as shown schematically in figure 10. For the biphenyl systems, as the flexible length becomes shorter, the α value becomes smaller. That is, as the flexible length becomes shorter, the response speed becomes faster (cf. figure 5). Thus, for biphenyl systems, the model shown in figure 10 is suitable for faster response. The rigid part seems not to affect the α value. Therefore, the flexible part should determine the switching behaviour in biphenyl systems. This may indicate that the flexible part is related to the rotational viscosity because a spontaneous polarization is not the determinant factor in this case. The spontaneous polarization values are 3 nC cm^{-2} for C8 and C10 LPS and 6 nC cm^{-2} for C10F. Therefore, the rotational viscosity of the alkyl chain is probably a key factor in determining the switching process in biphenyl systems.

On the other hand, for the ester-containing system it is difficult to distinguish the effect of a flexible part from that of a rigid part. Either part may affect the switching process. In ester-containing systems, as the α value becomes larger, the response speed becomes faster and the cone angle becomes smaller. Therefore, the longer flexible part may decrease the cone angle, and the faster response speed may be attributable to the shorter rigid part.

4. Summary

Time-resolved FT-IR spectroscopy of the order of μs was performed for systems with well-defined molecular structures containing six kinds of fluorine-containing chiral molecules. A tilted bookshelf geometry was realized by SiO obliquely

evaporated aligning layers. Time-resolved spectra are found to depend remarkably on the kinds of chiral molecules. The newly introduced molecular dynamic parameter α is found to have good correlations with rise time and with cone angles. Furthermore, the α value is closely related to the lengths of the rigid and/or flexible parts of the chiral molecules. By using the parameter α , a new classification of molecular switching process depending on the kind of chiral molecular structure is proposed.

The authors are very grateful to Messrs K. Masutani and H. Terashima for their cooperation in FT-IR spectroscopy measurements and also thank Dr S. Arakawa of the Sony Corporation Research Center for synthesis of the chiral molecules.

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