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Study on the molecular orientation of an anti-ferroelectric liquid crystal by two-dimensional correlation polarized infrared spectroscopy

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Polarization-dependent infrared spectra of an antiferroelectric liquid crystal in the SmA_1^* phase were measured at 60°C , for investigation of the relative orientation of the terminal alkyl chain and mesogen. The polarization angle-dependent infrared spectra obtained were analysed by two-dimensional (2D) correlation spectroscopy. The orientation of the mesogen segment and the alkyl chains in the SmA_1^* phase is similar to that in the SmC^* phase. Four new CH_3 and CH_2 stretching modes were observed from the 2D correlation spectra. From these we can clearly separate the vibrational mode for two hydrocarbon chains and conclude that the orientations of the two chains are different. The $\text{C}=\text{O}$ group adjacent to the chiral segment is also separated by 2D correlation spectra into two bands, which may arise from either the $\text{C}=\text{O}$ group hydrogen-bonded with the phenyl ring, or from another rotational conformation of the molecule.

1. Introduction

Surface-stabilized ferroelectric liquid crystals (SSFLCs) are one of the more interesting liquid crystal forms because of their potential applications in high resolution flat panel displays and fast electro-optic devices [1–6]. The physical and electro-optical properties of FLCs are dependent on their molecular shape and local environment, which determine the statistical distribution and equilibrium population of each conformational state of the molecules. The electric field interacts with the polarization and dielectric anisotropy of the molecules during the process of electro-optical switching, which depends strongly on the molecular conformation and orientational freedom of different segments about the average molecular long axis. Specifically, the terminal alkyl chain orientation with respect to the rigid core, and hindered rotation of molecular segments such as carbonyl groups having a large dipole moment located near the chiral carbon, are expected play an important role in the emergence of spontaneous polarization, and thus may influence the dynamical behaviour of the system.

As the vibrational frequencies are very sensitive to small changes in the bonding and geometrical arrangement of atoms in the molecules, infrared absorption

and Raman scattering techniques can provide very useful information about the conformation and orientation of individual segments of the LC molecules [7–9]. However, a detailed understanding of the conformational and orientational behaviour in chiral liquid crystal molecules, especially in chiral macromolecules, is far from exact. The infrared bands from different segments of chiral molecules overlap each other, and it is difficult to assign them in the spectra. Usually, only the average conformational and orientational behaviour can be determined from infrared spectra.

In our previous paper [10], polarization-dependent and time-resolved infrared spectroscopy was used to study the electric field-induced ferroelectric phase (SmC^*) of a molecule at different temperatures. Polarization-dependent infrared spectra under a d.c. electric field reveal that the average alkyl chain axis does not coincide with the mesogen axis and is less tilted with respect to the layer normal than is the mesogen. The analysis of absorption changes of infrared bands at different time delays provides clear evidence for biased orientation and hindered rotation of almost all the molecular segments around the average molecular long axis; the rotation of the whole molecule around its axis is also hindered. In this paper, we report the results of two-dimensional (2D) correlated and polarized infrared spectroscopy of

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the chiral antiferroelectric liquid crystal (AFLC) material, 4-(1-methyheptyloxycarbonyl)phenyl 4-(4-octyloxy)benzoate at 60°C. The orientation of the mesogen segment and the alkyl chains in the SmA_1^* phase has been studied.

Generalized 2D correlation spectroscopy [11] is a technique whereby the spectral intensity is plotted as a function of two independent spectral variables. By spreading peaks along the second dimension, 2D correlation spectroscopy sorts out complex or overlapped spectral features and enhances spectral resolution. The technique enables one to extract additional useful information that cannot be obtained directly from the conventional one-dimensional spectrum.

In the present case, generalized 2D correlation spectroscopy is utilized to analyse the polarization angle-dependence of infrared band intensities. The change of polarization angle is used as a perturbation. Our primary aim in the present study is to provide deeper insight into the structure and orientation of the various molecular segments in a chiral antiferroelectric liquid crystal.

2. Experimental

The sample AFLC, 4-(1-methyheptyloxycarbonyl)-phenyl 4-(4-octyloxy)benzoate (abbreviated MHOCPOOB) was described in ref. [10]. The chemical structure and phase transition sequence are shown in figure 1. The homogeneously aligned sample cell was prepared between two CaF_2 substrates transparent to both visible and IR. The substrates were coated with a thin conducting layer of indium tin oxide (ITO) and polyvinyl alcohol rubbed in one direction. The distance between the two plates, as determined from the interference fringe pattern, was adjusted to 5.1 μm with a polyethylene spacer. The cell was filled with sample by capillary action, heated to the LC isotropic phase, and then slowly cooled to room temperature.

Polarized infrared spectra were obtained using an IFS-66V Fourier-transform IR spectrometer equipped with a MCT detector. A KRS-5 wire grid polarizer was rotated about the axis parallel to the direction of the IR radiation. The polarization angle was taken as zero when the polarization direction of the incident infrared radiation coincided with the rubbing direction. The

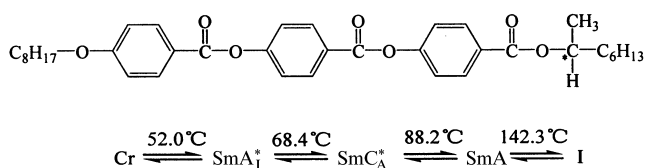


Figure 1. Structure of MHOCPOOB antiferroelectric liquid crystal and its phase transition temperatures.

temperature was controlled to an accuracy of $\pm 0.05^\circ\text{C}$ with the aid of a DWT702 thermo controller. 2D analysis was run on the 2D-POCHA program presented by Kwansai Gakuin University.

3. Results and discussion

3.1. Band assignments and orientation analysis

Figure 2 shows the polarized IR spectra as a function of the polarization angle for a monodomain of the sample in the SmA_1^* phase at 0° and 90° . The polarization angle is the angle between the direction of rubbing and the polarization direction of the incident IR radiation, and is taken to be zero when these two directions coincide. From these spectra the dichroic ratio D , defined as the ratio of absorbances for the parallel and perpendicular polarizations of the light, is calculated for different bands. The table lists the assignment of the individual and relevant bands, based on expected group frequency considerations and previous work [12–14], together with their dichroic ratios. It should be noted that due to the presence of CH_2 and CH_3 groups in both the achiral and chiral chains, only averaged information can be obtained from the C–H stretching modes. For bands related to the mesogen segments, the dichroic ratios vary from 1.03 to 1.82 and are markedly less than that of MHOCPOOB in the SmC_A^* phase ($D=2.3$ to 7.6) [10]. A noticeable feature is that the dichroic ratios for the alkyl chain and C=O modes are close to 1, which can be ascribed to the isotropic nature of the hydrocarbon chains. For the alkyl chain, two possible reasons can lead to $D=1$. One is that all the CH_2 group are in disorder. Another is that two hydrocarbon chains are in different even perpendicular orientations, resulting in an average D of about 1. The dichroic ratios of the core

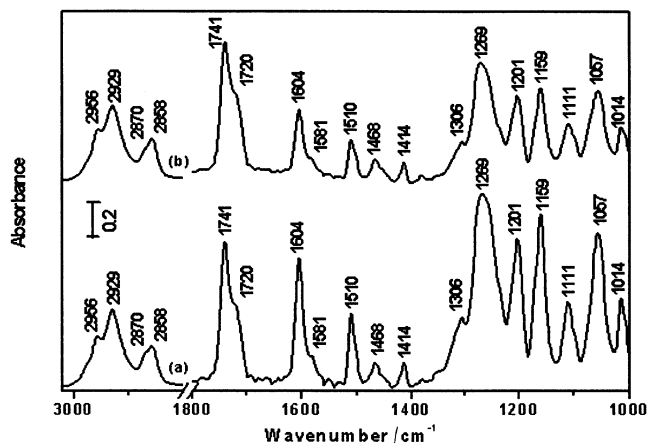


Figure 2. Polarized FTIR spectra of MHOCPOOB at 60°C in the (a) parallel and (b) perpendicular polarization geometries.

Table. Vibrational band assignment and dichroic ratio of the relevant peaks in the infrared spectra of MHOCPOOB in the SmA_I^* phase.

Wavenumber / cm^{-1}	$D(A_{\parallel}/A_{\perp})$	Assignment
2956	1.01	CH_3 asym. st.
2929	0.96	CH_2 asym. st.
2870	0.99	CH_3 sym. st.
2858	0.95	CH_2 sym. st.
1741	0.84	$\text{C}=\text{O}$ st. (core)
1720	0.90	$\text{C}=\text{O}$ st. (chiral)
1604	1.77	Phenyl $\text{C}=\text{C}$ st.
1581	1.30	Phenyl $\text{C}=\text{C}$ st.
1510	1.70	Phenyl $\text{C}=\text{C}$ st.
1468	1.03	CH_2 scissoring mode and CH_3 asym. def.
1414	1.21	CH_2 scissoring mode
1306	1.68	Phenyl $\text{C}=\text{C}$ in plane
1269	1.62	$\text{C}-\text{O}$ asym. st.
1201	1.71	$\text{C}-\text{O}$ st.
1159	1.82	Phenyl $\text{C}-\text{H}$ in plane def.
1111	1.45	$\text{C}-\text{C}-\text{C}$ in plane stretch and CH_3 rock
1057	1.67	Phenyl $\text{C}-\text{H}$ in plane def.
1014	1.58	Phenyl $\text{C}-\text{H}$ in plane def.

part in the SmA_I^* phase show the same trend as in the SmC_A^* phase. This suggests that antiferroelectric LC molecules take a similar conformation and orientation in both the SmA_I^* and SmC_A^* phases, but the orientational distributions are quite different.

An interesting feature in the IR spectrum is the observation of two components in the $\text{C}=\text{O}$ stretching mode region at 1741 and 1720 cm^{-1} . The former is attributed to the $\text{C}=\text{O}$ groups between the phenyl rings, the latter to the $\text{C}=\text{O}$ groups adjacent to the chiral segment. Figure 3 depicts the second derivative



Figure 3. The second derivative spectra of MHOCPOOB in the 1760–1700 cm^{-1} region.

spectrum of MHOCPOOB in the 1760–1700 cm^{-1} region. It can be seen that one more band at 1712 cm^{-1} is observed, which is also attributed to the $\text{C}=\text{O}$ groups adjacent to the chiral segment, and may arise from either the $\text{C}=\text{O}$ group hydrogen-bonded with the phenyl ring, or from another rotational conformation of the molecule [15].

Figure 4 shows the peak absorbance $A(\omega)$ as a function of polarizer rotation angle ω for different transition dipole moments of the molecular segments. It is clear from this figure that absorbance peaks of the mesogen exhibit maximum intensity at $\theta=0^\circ$ and 180° while the alkyl chain stretching modes show no maximum or minima. This means that the transition dipole moments of the mesogen are nearly parallel to the average molecular long axis.

There are many overlapping peaks in figure 2. It is difficult to detect slight differences by ordinary spectra, so in this study we applied 2D correlation spectroscopy to analyse a series of polarization angle-dependent infrared spectra.

3.2. Two-dimensional infrared correlation spectroscopy

2D correlation analysis can provide much information, that is barely recognized by ordinary infrared spectroscopy. Figures 5(a) and 5(b) show, respectively, synchronous and asynchronous correlation spectra constructed from the polarization angle-dependent infrared spectra of MHOCPOOB in the 3050–2800 cm^{-1} region. Eight auto-peaks at 2974, 2964, 2952, 2936, 2920, 2877, 2860 and 2848 cm^{-1} are found in figure 5(a). The curve fit was made using these eight wave numbers (not shown here); from the intensities of each peak, the bands at 2974, 2964 and 2952 cm^{-1} can be assigned to

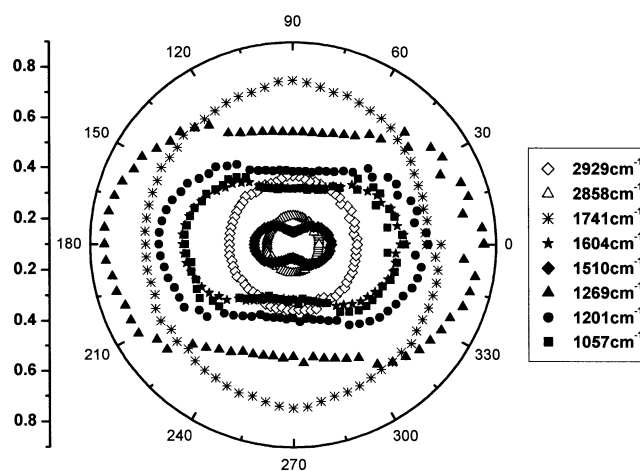


Figure 4. Polar plots of the peak absorbance $A(\omega)$ vs the polarization angle ω for representative bands of MHOCPOOB in the SmA_I^* phase at 60°C.

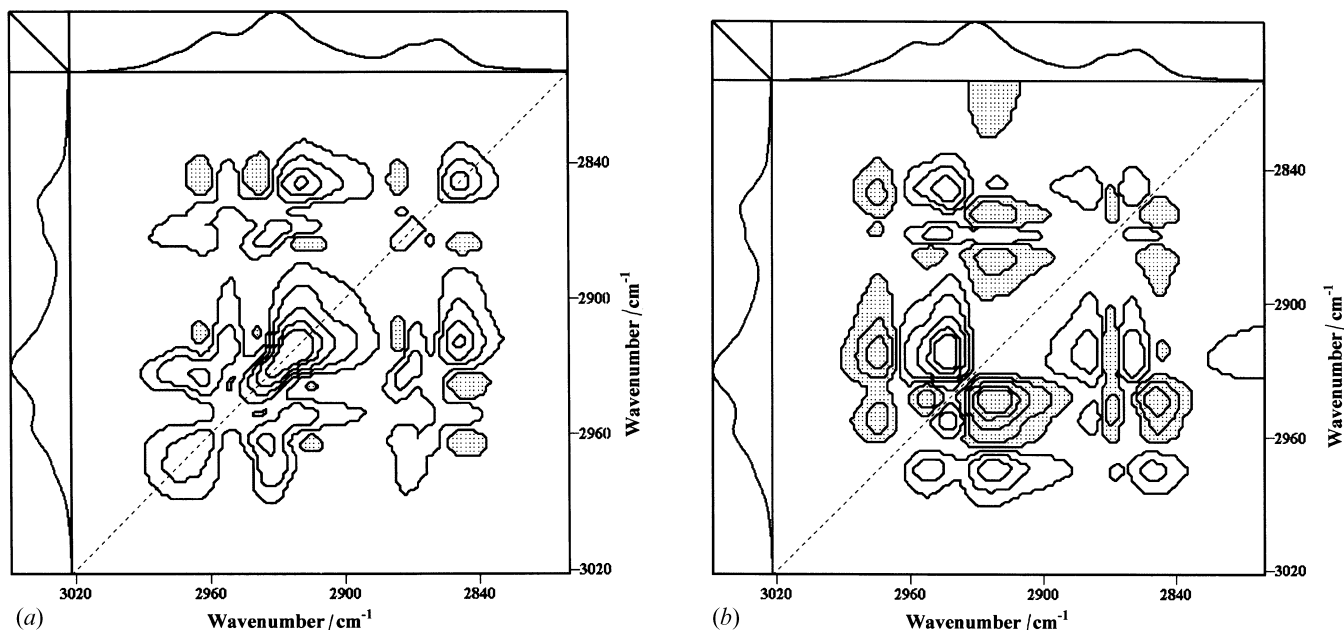


Figure 5. Synchronous (a) and asynchronous (b) 2D infrared correlation spectra in the 3050–2800 cm^{-1} region generated from the polarization angle-dependent polarized spectral variations of MHOCPPOB in the SmA_1^* phase at 60°C.

CH_3 asymmetric stretching mode. The bands at 2936 and 2920 cm^{-1} are due to the CH_2 asymmetric stretching mode of $\text{C}_8\text{H}_{17}\text{O}-$ and $\text{C}_6\text{H}_{13}\text{O}-$, a respectively. The bands at 2877 and 2860 cm^{-1} are from the CH_3 symmetric stretching mode and the band at 2848 cm^{-1} can be assigned to a CH_2 symmetric

stretching mode. The sign of the cross-peaks at (2974 vs 2936, 2877), (2964 vs 2936, 2877), (2952 vs 2920, 2848), (2920 vs 2848) and (2877 vs 2936, 2860) cm^{-1} show a positive sign; six negative cross-peaks are developed at (2964 vs 2920, 2848), (2936 vs 2920, 2848) and (2877 vs 2920, 2848) on the upper left side of the

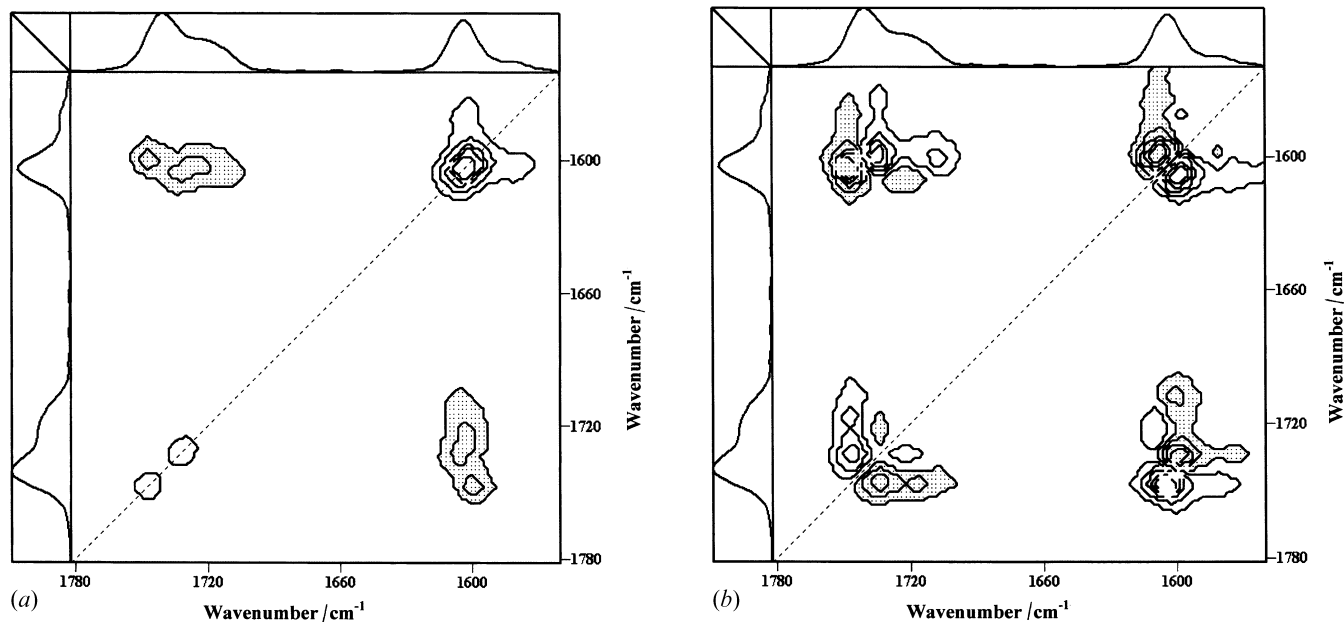


Figure 6. Synchronous (a) and asynchronous (b) 2D infrared correlation spectra in the 1780–1580 cm^{-1} region generated from the polarization angle-dependent polarized spectral variations of MHOCPPOB in the SmA_1^* phase at 60°C.

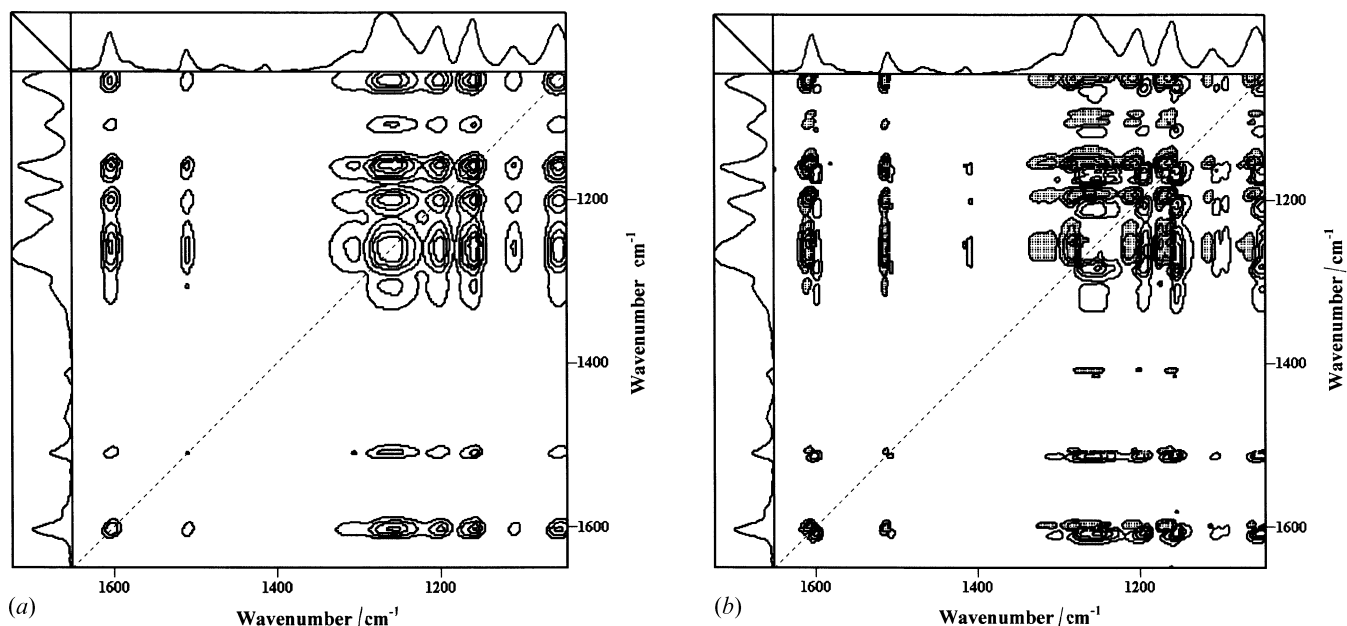


Figure 7. Synchronous (a) and asynchronous (b) 2D infrared correlation spectra in the $1650\text{--}1050\text{ cm}^{-1}$ region generated from the polarization angle-dependent polarized spectral variations of MHOCPOOB in the SmA_1^* phase at 60°C .

spectrum of figure 5(a). These bands at 2974 , 2964 , 2952 , 2936 , 2877 and 2860 cm^{-1} have different polarization angle-dependent intensity changes from those at 2922 and 2848 cm^{-1} . We can conclude from this that the two hydrocarbon chains show different orientation behaviour on the polarimeter.

The results from hybrid two-dimensional correlation spectra ($3020\text{--}2800\text{ cm}^{-1}$ region correlated with $1800\text{--}1000\text{ cm}^{-1}$ region) show that the 2933 cm^{-1} band maintains the same trend with the mesogen segment when the polarization angle changes; however the 2922 and 2948 cm^{-1} bands give opposite behaviour. Thus the conformation of the shorter hydrocarbon chain is all-*trans* zig-zag, and its orientation is parallel to the molecular long axis. This conclusion is in agreement with calculated results [16, 17].

Figures 6(a) and 6(b) show, respectively, synchronous and asynchronous correlation spectra in the $1780\text{--}1580\text{ cm}^{-1}$ region. Note that four auto-peaks can be seen at 1747 , 1733 , 1716 and 1608 cm^{-1} . The former three bands are assigned to C=O stretching modes and the latter band is ascribed to the phenyl ring stretching mode. We observe two negative cross-peaks at (1747 vs 1608) and (1731 vs 1608) in figure 6(a). The negative sign of the cross-peaks indicates that one of the spectral intensities is increasing while the other is decreasing. Thus, we suggest the polarization angle-dependent intensities of the C=O stretching bands and the phenyl ring stretching band change in reverse directions. In figure 6(b), three cross-peaks are developed at (1747 vs 1608), (1733 vs 1608) and (1716 vs

1608) cm^{-1} . This suggests that the C=O stretching bands exist in three modes. This conclusion is in agreement with the results obtained in figure 3.

Figures 7(a) and 7(b) show, respectively, synchronous and asynchronous correlation spectra in the $1650\text{--}1050\text{ cm}^{-1}$ regions. It can be seen from the synchronous correlation spectrum that the signs of all cross-peaks in this region are positive. This means that all the bands in this region show almost the same trend with change in polarization angle.

4. Conclusions

In the present study, we have applied the generalized 2D correlation technique to a set of polarized infrared spectra of MHOCPOOB at 60°C . The following conclusions can be reached from the present study: (1) Four new CH_3 and CH_2 stretching modes and one more C=O stretching mode are observed in the 2D correlation spectra. From this we can clearly separate the vibrational modes from the two hydrocarbon chains, and conclude that the orientations of the two chains are different. (2) The C=O groups have three stretching vibration modes; the band at 1747 cm^{-1} is attributed to the C=O groups between the phenyl rings, bands at 1731 and 1716 cm^{-1} are assigned to the C=O group adjacent to the chiral segment.

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References

- [1] LAGERWALL, S. T., CLARK, N. A., DIJON, J., and CLERC, J. F., 1989, *Ferroelectrics*, **94**, 3.
- [2] CLARK, N. A., and LAGERWALL, S. T., 1980, *Appl. Phys. Letts.*, **36**, 899.
- [3] CLARK, N. A., and LAGERWALL, S. T., 1984, *Ferroelectrics*, **59**, 25.
- [4] MATSUMOTO, S., MARUYAMA, A., HATHO, H., KINOSHITA, Y., HARAI, H., ISHIKAWA, M., and KAMAGANI, S., 1988, *Ferroelectrics*, **85**, 235.
- [5] BAHADUR, B., 1990, *Liquid Crystals: Application and Uses* (World Scientific).
- [6] GOODBY, J. W., BLINC, R., CLARK, N. A., LAGERWALL, S. T., OSIPOV, M. A., PIKIN, S. A., SAKURAI, T., YOSHINO, K., and ZEKS, B., 1991, *Ferroelectric Liquid Crystals: Principles, Properties and Applications* (Gordon and Breach).
- [7] KIM, K. H., ISHIKAWA, K., TAKEZOE, H., and FUKUDA, A., 1995, *Phys. Rev. E*, **51**, 2166.
- [8] JIN, B., LING, Z., TAKANISHI, Y., ISHIKAWA, K., TAKEZOE, H., FUKUDA, A., KAKIMOTO, M., and KITAZUME, T., 1996, *Phys. Rev. E*, **53**, R4295.
- [9] KIM, K. H., MIYACHI, K., ISHIKAWA, K., TAKEZOE, H., and FUKUDA, A., 1994, *Jpn. J. appl. Phys.*, **33**, 5850.
- [10] VERMA, A. L., ZHAO, B., BHATACHARJEE, A., and OZAKI, Y., 2001, *Phys. Rev. E*, **63**, 051704.
- [11] NODA, I., 1993, *Appl. Spectrosc.*, **47**, 1329.
- [12] KOCOT, A., WRZALIK, R., ORGASINSKA, B., PEROVA, T., VIJ, J. K., and NGUYEN, H. T., 1999, *Phys. Rev. E*, **59**, 552.
- [13] URANO, T. I., and HAMAGUCHI, H., 1992, *Chem. Phys. Lett.*, **195**, 289.
- [14] KOHRI, S., KOBAYASHI, J. J., TAHATA, S., KITA, S. C., KARINO, T., and YOKOYAMA, T., 1993, *Appl. Spectrosc.*, **47**, 1368.
- [15] VERMA, A. L., ZHAO, B., JIANG, S. M., SHEN, J. C., and OZAKI, Y., 1997, *Phys. Rev. E*, **56**, 3053.
- [16] WRZALIK, R., MERKEL, K., KOCOT, A., and CIEPLAK, B., 2002, *J. chem. Phys.*, **117**, 4889.
- [17] CHENG, J. B., CHENG, Y. C., XU, W. Q., and ZHAO, B. *J. Chem. Phys.* (submitted).