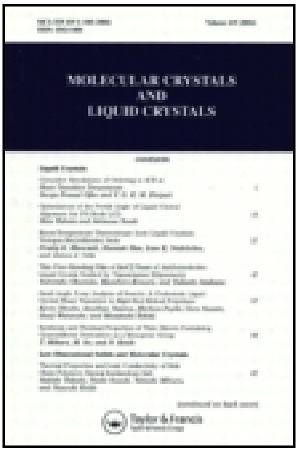


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Infrared Linear-Dichroism (IR-LD) Study of the Nematic Liquid Crystals Doped with Polymer

S. Shoarinejad [a] & M. S. Zakerhamidi [b]

[a] Physics Department, Science Faculty, Alzahra University, Tehran, Iran

[b] Research Institute for Applied Physics and Astronomy, University of Tabriz, Tabriz, Iran

To cite this article: S. Shoarinejad & M. S. Zakerhamidi (2011): Infrared Linear-Dichroism (IR-LD) Study of the Nematic Liquid Crystals Doped with Polymer, Molecular Crystals and Liquid Crystals, 547:1, 135/[1825]-141/[1831]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.572807

Mol. Cryst. Liq. Cryst., Vol. 547: pp. 135/[1825]–141/[1831], 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.572807

Infrared Linear-Dichroism (IR-LD) Study of the Nematic Liquid Crystals Doped with Polymer

S. SHOARINEJAD[1] AND M. S. ZAKERHAMIDI[2]

[1]Physics Department, Science Faculty, Alzahra University, Tehran, Iran
[2]Research Institute for Applied Physics and Astronomy, University of Tabriz, Tabriz, Iran

Recently liquid crystal doped with polymer is used to enhance physical and photo physical properties of these materials. The primary subject in the doped liquid crystal is the qualitative determination of the order parameter. Infrared spectroscopy has become the most informative tool in the study of conformation and orientational order of liquid crystalline materials. In the present paper, we used polarized Fourier transform infrared (FT-IR) spectroscopy to analyze the orientational ordering of the liquid crystal doped with polymer. We obtained information about the head orientational order of liquid crystal in these systems by observing the band corresponding to the vibrations of the relevant functional groups.

Keywords Doped liquid crystal; FTIR spectroscopy; photo polymerization; polarized spectroscopy

1. Introduction

The molecules of nematic liquid crystals tend to align parallel to each other and therefore have long-range orientational order. The molecular structure induces a locally preferred common direction, known as the director. Due to the orientational ordering of the rod-like molecules, most of the nematic liquid crystals have uniaxial symmetry with the principal axis parallel to the long molecular axes. Therefore, the nematic liquid crystals exhibit an electrical and optical anisotropy. The anisotropy of the physical properties is very important not only from the viewpoint of molecular theory but also practical applications, because it strongly affects the electro-optical properties of liquid crystal displays, especially the contrast ratio, the viewing angle, and the threshold voltage. Recently liquid crystal doped with polymer is used to enhance physical and photo physical properties of these materials. The primary subject in the doped liquid crystal is the qualitative determination of the order parameter for practical applications.

The orientational order of nematic liquid crystals have been obtained from the polarization characteristics of nuclear magnetic resonance (NMR) [1], fluorescence [2,3], Raman scattering [4], and infrared spectroscopy [5–8]. However, these methods

---

Address correspondence to S. Shoarinejad, Physics Department, Science Faculty, Alzahra University, Tehran, Iran. Tel.: +98-21-88044051-8(Ext.2607); E-mail: sshoari@alzahra.ac.ir have been applied to a very limited number of nematic liquid crystals. Infrared spectroscopy has become the most informative tool in the study of conformation and orientation of liquid crystalline materials. As rich literature [9–17] show, the polarized IR spectra of liquid crystals yield interesting information from the point of view of both the degree of ordering in mesophases and characteristics of particular vibrational modes.

In the present paper, we used polarized Fourier transform infrared (FT-IR) spectroscopy to analyze the orientational ordering of the liquid crystal-polymer mixtures. We used the different compositional percentage of polymer to obtain information about the orientational order of the head part of the liquid crystals (−CN and −NCS substituents), by observing the bands corresponding to the vibrations of the relevant functional groups.

2. Experimental Methods

2.1. *Materials*

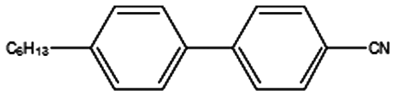
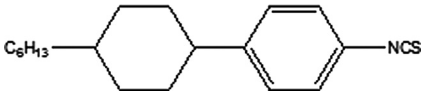
The pure nematic liquid crystals (6CB, 6CHBT) used in our experiments as anisotropic hosts were synthesized in the Institute of Chemistry of Military Technical Academy, Warsaw, Poland. The chemical structures of the used liquid crystals are shown in Table 1, [18].

NOA65 (Norland Products, Inc.), a photocurable thiol-ene type prepolymer, was used with different compositional percentage (1%, 5%, 10%, 20%, 30% and 40% W/W). The liquid crystal mixed with NOA65 monomer was sandwiched between two KBr plates. Homogeneous treatment on the substrates was obtained by rubbing the plates with a leather cloth process and two mylar spacers (~6 μm) were used. To polymerize the liquid crystal cell, a sandwich of mixed liquid crystal and monomers was placed under ultraviolet light [19] with a maximum absorption within the 380 nanometers and $I = 50\,mW/cm^2$ for 15 min at $T = 25°C$.

2.2. *Vibrational Spectroscopy*

Vertex 70 Scan FT-IR spectrophotometer was used for recording vibration spectra over a wave number range 400–4000 cm^{-1} which combined with a KRS-5 polarizer (IR polarizer in this range) and cell temperature controller with accuracy of ±0.1°C.

Table 1. Molecular structure of the nematic liquid crystals

Liquid crystal	T_c/°C	Molecular structure
6CB	28.8	
6CHBT	42.8	

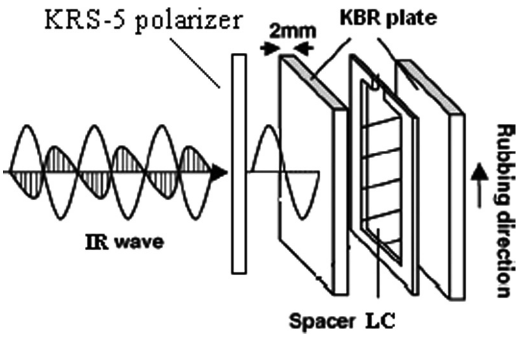


Figure 1. Set up of KRS-5 in a sample of FT-IR study.

2.3. *Method*

The order parameter, S, is defined as

$$S = \frac{1}{2} < 3\cos^2\theta - 1 >, \tag{1}$$

where Θ is the angle between the molecular long axis and a preferred orientation of molecules. The basis for the quantitative analysis of the order degree and the transition dipole moments are presented in Figure 2.

The experimentally estimated value is the dichroic ratio $R = A_{\|}/A_{\perp}$, where $A_{\|}$ and $A_{\perp}$ are absorbances measured for parallel and perpendicular polarization of the IR beam. The order parameter can be expressed by the following equation [9, 19, 20]

$$S = \frac{R-1}{R+2}\frac{2}{3\cos^2\alpha - 1}. \tag{2}$$

If the α angle is equal to 0° (i.e., the transition dipole moment is parallel to the long axis of a molecule) the order parameter S is given by the ratio

$$S = \frac{(R-1)}{(R+2)}. \tag{3}$$

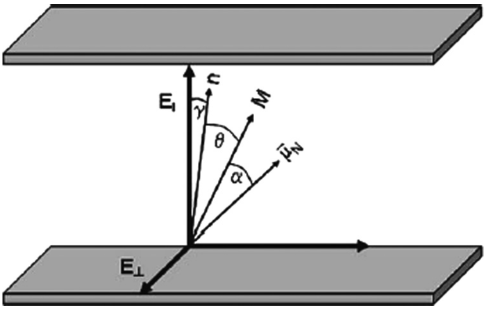


Figure 2. Scheme of vectors of polarized light electric fields ($E_{\|}$ and $E_{\perp}$), the director (n), molecular long axis for individual molecule (M) and the transition dipole moment of a vibrational mode (μ_N), with respect to the cell windows.

The choice of a most convenient mode for the estimation of the S value is not a simple task because in the vibration mode of these liquid crystals a broad (continuous) absorption takes place and some of vibration modes of NOA65 mask the liquid crystal active vibration mode. It should be emphasized that the amount of the obtained order parameters will be accrued when the vibrations of functional groups in the head part of the molecule are oriented parallel to the transition dipole moment of a molecule.

In this study, we used CN and NCS substituent's stretching modes as indicator of orientation in infrared spectroscopy. These vibration modes exist in the head part of these liquid crystal molecules. Then, the transition dipole moment in this part of liquid crystal molecule is orienting parallel to the long axis of the molecule. Also in these regions, NOA65 does not have active vibration mode.

3. Results and Discussion

3.1. *Order Parameters of Pure Liquid Crystals*

In 6CB and 6CHBT major vibration absorption bands (CN and NCS) occur in the $2227\,\mathrm{cm}^{-1}$ and $2125\,\mathrm{cm}^{-1}$ region [21], respectively. The Figures 3 and 4 show the FTIR spectra of these liquid crystals in homogeneous orientation and the polarized IR exposure. The order parameters of these liquid crystals, in stretching mode of $-C{\equiv}N$ and $-N{=}C{=}S$ are calculated by using equation (3) and reported in Table 2.

The obtained order parameters show that the orientational order of 6CB liquid crystal is higher than 6CHBT liquid crystal. The order parameter of this liquid crystal is increased due to two aromatic rings and proper aligned CN group in the long molecular axis.

3.2. *Order Parameter of Liquid Crystals Doped with Polymer*

We considered the vibrational stretching modes of CN and NCS to estimate the order parameter values of doped liquid crystals with NOA65 polymer in different compositions (1%, 5%, 10%, 20%, 30% and 40% W/W). NOA65 does not have active vibration modes in these regions [22]. The order parameters of doped liquid

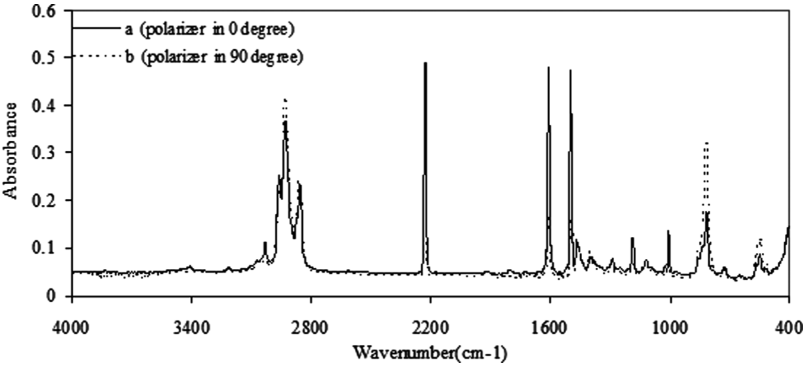


Figure 3. FTIR spectra of 6CB with polarized IR wave.

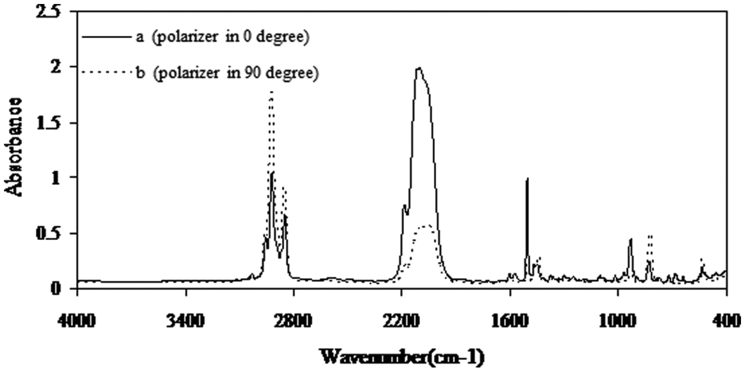


Figure 4. FTIR spectra of 6CHBT with polarized IR wave.

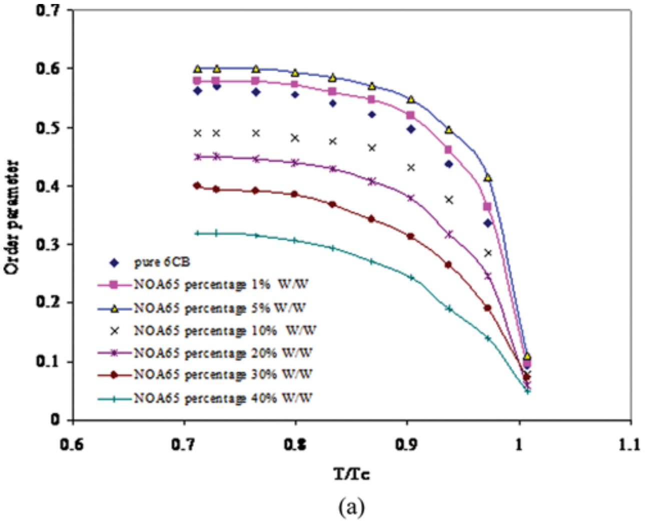
crystals with the different compositional percentage of polymer, in stretching modes of $-C\equiv N$ and $-N=C=S$, are reported in Table 2.

The temperature dependence of the order parameters of the doped liquid crystals with different compositional percentage of polymer is shown in Figure 5.

It is evident that by increasing the polymer concentration, the obtained order parameters increase in low compositional percentage of NOA polymer (1% and 5% W/W) and decrease in middle and high compositional percentage of NOA polymer (10%, 20%, 30% and 40% W/W). In low percentage of the polymer, the orientational order of the liquid crystal arrangement, as impacted by the polymer main chain, increases. However, the side chains in polymer matrix increase by increasing the concentration of the polymer, higher than 10% W/W. Then the orientational order of the liquid crystal is influenced by both polymer side and main chain matrix

Table.2 The order parameters of the pure and doped liquid crystals in stretching mode of $-C\equiv N$ and $-N=C=S$ in 25°C

Liquid crystal	NOA65 percentage w/w	R	S
Stretching mode of C=N			
6CB	0%	5.03	0.57
6CB	1%	5.14	0.58
6CB	5%	5.5	0.6
6CB	10%	3.88	0.49
6CB	20%	3.45	0.45
6CB	30%	3	0.4
6CB	40%	2.4	0.32
Stretching mode of NCS			
6CHBT	0%	4.7	0.55
6CHBT	1%	4.66	0.55
6CHBT	5%	5.31	0.59
6CHBT	10%	3.36	0.44
6CHBT	20%	2.84	0.38
6CHBT	30%	2.28	0.3
6CHBT	40%	1.85	0.22



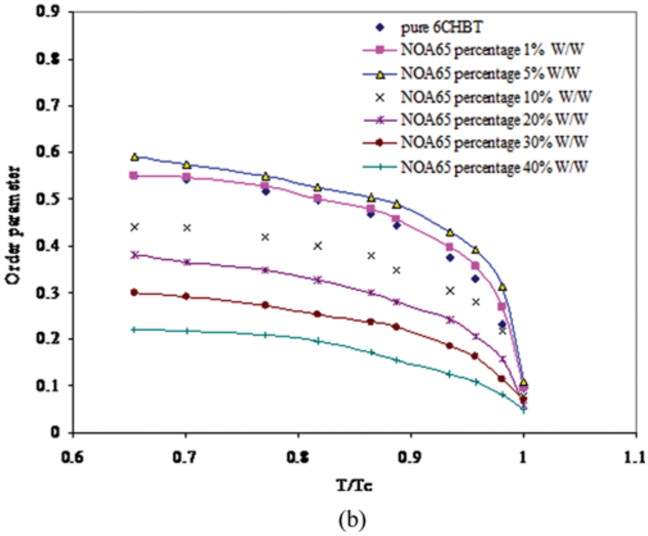


Figure 5. Temperature dependence of the order parameters of pure and doped liquid crystals with different compositional percentage of polymer (a) 6CB, (b) 6CHBT. (Figure appears in color online.)

direction that leads to decrease their initial order parameters. On the other hand, by increasing polymer concentrations, strict hindrance effects of side chain of polymer decrease the initial order parameter.

4. Conclusions

We have found the strong dependence of the IR absorption of nematic liquid crystals on the alignment and ordering, in both pure state and mixed with polymer. The obtained order parameters show that in the pure state, the orientational order of 6CB liquid crystal is higher than 6CHBT liquid crystal. The order parameters of the doped liquid crystals with NOA65 polymer, in different concentrations, change by increasing the polymer concentration. The orientational orders of the liquid crystal arrangement, as impacted by the polymer side chain direction, decrease the initial order parameter when the concentration of the polymer increases higher than 10% W/W.

References

[1] Khetrapal, C. L., & Kunwar, A. C. (1983). *Adv. Liq. Cryst.*, *8*, 173.
[2] Chapoy, L. L., & Dupre, D. B. (1979). *J. Chem. Phys.*, *70*, 2250.
[3] Yoshida, H., Kobinata, S., & Maeda, S. (1985). *Mol. Cryst. Liq. Cryst.*, *131*, 209.
[4] Yoshida, H., Nakajima, Y., Kobinata, S., & Maeda, S. (1981). *J. Phys. Soc. Jpn.*, *50*, 3525.
[5] Prasad, J. S., Abdoh, M. M. M., Shastry, C. I. V., & Shivaprakash, N. C. (1984). *Mol. Cryst. Liq. Cryst.*, *104*, 141.
[6] Chingduang, P., Bualek, S., & Phaovibul, O. (1986). *Mol. Cryst. Liq. Cryst.*, *132*, 131.
[7] Jede, F., Stratmann, A. W., & Schrader, B. (1986). *Mol. Cryst. Liq. Cryst.*, *140*, 287.
[8] Park, W. S., & Uchida, T. (1989). *Liq. Cryst.*, *5*, 1405.
[9] Park, Woo-Sang. (2000). *J. Korean Phys. Soc.*, *37*, 331.
[10] Ha, Kiryong. (2004). *Liq. Cryst.*, *31*, 753.
[11] Yakubov, A. A. (1999). *J. Mol. Struct.*, *484*, 11.
[12] Binder, Hans. (1999). *Vib. Spectr.*, *21*, 151.
[13] Kolev, Tsonko, Ivanova, Bojidarka, & Bakalska, Rumyana (2006). *J. Mol. Struct.*, *794*, 138.
[14] Ido, Hiroaki, Furue, Hirokazu, Niori, Teruki, Watanabe, Junji, & Hatano, Jun (2005). *Mat. Sc. Eng. B*, *120*, 37.
[15] Arnaudov, Michael, Ivanova, Bojidarka. & Prangova, Lilia (2002). *Bull. Chem. Techn. Macedonia*, *21*, 151.
[16] Ivanova, Bojidarka B. (2005). *J. Mol. Struct.*, *738*, 233.
[17] Wua, Shin-Tson & Wang, Qiong-Hua (2002). *J. Appl. Phys.*, *92*, 7146.
[18] Bielejewska, N., Chrzumnicka, E., Mykowska, E., Przybylski, R., Szybowicz, M., Wãladysiak, K., & Bauman, D. (2006). *Acta Phys. Pol. A*, *110*, 777.
[19] Saupe, A. (1964). *Z. Naturforsch.*, *19A*, 161.
[20] Korte, E. H. (1983). *Mol. Cryst. Liq. Cryst.*, *100*, 127.
[21] Pavia, D., Lampman, G., & Kriz, G. (1979). *Introduction to Spectroscopy*, Second Edition, Sweders College Publishing.
[22] Rafferty, Wade, Koenig, Jack L., Magyar, Gregory, & West, John L. (2002). *Appl. Spectr.*, *56*, 1549.