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Preliminary communication

High strength disclinations induced by hydrogen bond dissociation in the nematic phases of *p*-alkoxycinnamic acids

LI CUI, JINNAN LIU†, PING XIE and RONGBEN ZHANG*
PCLCC‡, Institute of Chemistry, The Chinese Academy of Sciences,
Beijing 100080, PR China
†Department of Applied Chemistry, Beijing University of Chemical Technology,
Beijing 100029, PR China

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Disclinations of high strength ($|S| > 1$) in the hydrogen bond-induced nematic phases of *p*-alkoxycinnamic acids are reported. The existence of the disclinations of high strength is ascribed to the partial dissociation and regeneration of the hydrogen bonds in a mesastable equilibrium state around the clearing point and the core of the high strength disclination is an isotropic area.

The different types of liquid crystals are usually identified by observation of thin liquid crystal films by polarizing microscopy. When the films are relatively thin (~10 μm), schlieren textures, in which a core bears several dark brushes, are often found in nematic liquid crystals. The core does not change while the sample is rotated between the crossed polarizer and analyser, but the dark brushes rotate around the centre, indicating a continuous change in the direction of the optical axis. The dark brushes occur in areas in which the nematic director **n** lies either parallel or perpendicular to the polarization plane of the incident beam. Normally, only two and four extinguished brushes emanating from a core are observed, corresponding to the disclination strength $S = \pm 1/2$ and ± 1, respectively. Because the elastic distortional energy of the core is proportional to S^2, the core of a high strength disclination is unstable [1]. There are only a few reports on the observation of high strength disclination cores [2–10]. Lee and Labes [2] reported disclination cores of strength $S = 3/2$, $+2$, $\pm 5/2$, $+3$ and $+4$ in an emulsion of a lyotropic and a thermotropic liquid crystal. Madhusudana and Pratibha [3] observed disclination cores of strength $\pm 3/2$, ± 2, $+3$ and $+7/2$ in mixtures of some nematic compounds with plate-like molecules. High strength disclination cores were also reported [4] in the nematic phase of a single component system; these could only exist for 0.5 min, and, because of their poor stability, it was difficult to distinguish between cores of $+3/2$ and $-3/2$ by rotating the crossed polarizers. Lavrentovich and Nastishin [5] also reported high strength and zero strength defects possessing complex asymmetrical structures in degenerate hybrid aligned nematic LC films on an isotropic liquid surface. These latter conditions were then shown by Twieg *et al.* [6] to allow formation of stable high strength disclination cores in the single component materials of ref. [4].

For nematic liquid crystalline polymers, Galli *et al.* [7] have found disclinations of strength $|S| = 3/2$ and 2, Witteler *et al.* [8] have reported several defects of $\pm 3/2$, ± 2 and -3 in mixtures of polymers, and Zhou *et al.* [9] observed defects of $\pm 3/2$, ± 2 and $\pm 5/2$. However, there has not been a report of high strength disclinations in hydrogen bonded LCs and the nature of the high strength disclination has not been clarified.

The existence of thermotropic mesophases stemming from the formation of hydrogen bonds is well known in the case of 4-alkyl- [11] and 4-alkoxy- [12] benzoic acids and also in the corresponding *trans*-cyclohexanecarboxylic acids [13]. Probably the existence of liquid crystalline properties can also be observed in the case of *p*-alkoxycinnamic acids due to the formation of hydrogen bonds. More recently, a biaxial thermotropic nematic phase has been reported for a trisubstituted cinnamic acid [14]. Because non-covalent bonds are weaker than covalent bonds, the mesogenic cores formed through hydrogen bonds are easy to dissociate. Here, we report the observation of high strength disclinations

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*Author for correspondence.

‡Polymer Chemistry Laboratory, Chinese Academy of Sciences and China Petro-Chemical Corporation.

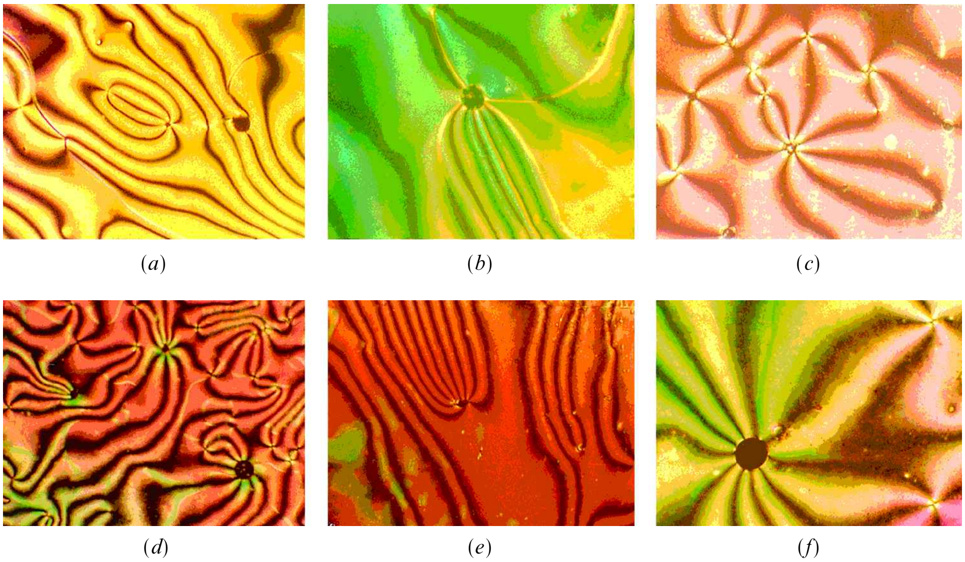
(*a*) (*b*) (*c*)
(*d*) (*e*) (*f*)

Figure 1. Schlieren textures observed in *p*-alkoxycinnamic acids: (*a*) *p*-hexyloxycinnamic acid, 166°C, 100×; (*b*) *p*-hexyloxycinnamic acid, 174°C, 100×; (*c*) *p*-methoxycinnamic acid, 168°C, 100×; (*d*) *p*-hexyloxycinnamic acid, 175°C, 40×; (*e*) *p*-methoxycinnamic acid, 180°C, 100×; (*f*) *p*-hexyloxycinnamic acid, 171°C, 100×.

due to the partial dissociation of hydrogen bonds in *p*-alkoxycinnamic acids around the clearing point.

The synthesis of *p*-methoxycinnamic acid and *p*-hexyloxycinnamic acid was reported in ref. [15]. *p*-Methoxycinnamic acid exhibits a nematic phase between 174 and 188°C, and *p*-hexyloxycinnamic acid has a nematic phase between 148 and 183°C.

The infrared spectra used to assess the hydrogen bonding were recorded at different temperatures by a Perkin Elmer 2000 FTIR system with a hot stage.

The cover glasses for sample preparation were immersed in concentrated nitric acid for one day, then washed with water followed by alcohol, and used without any other modification. The sample was sandwiched between two cover glasses and observed using a Xintian XP1A model (China) polarizing optical microscope equipped with a Mettler FP82 hot stage. A RICOH F-2 camera was used to take photomicrographs.

The schlieren textures of *p*-methoxycinnamic acid and *p*-hexyloxycinnamic acid, in which there were two or four extinct dark brushes around the centres, could be observed. In addition, however, high strength defects too could often be observed. As examples, figure 1 shows defects bearing 6, 8 and 10 brushes.

Experiments were done to check that the large cores were not air bubbles trapped in the samples or generated by decomposition. The initial samples were known to be pure by elemental analysis and NMR, and the NMR spectrum of a sample was unaffected by heating the material for 30 min at 190°C. Moreover, no degradation peaks were observed by DSC even when samples were

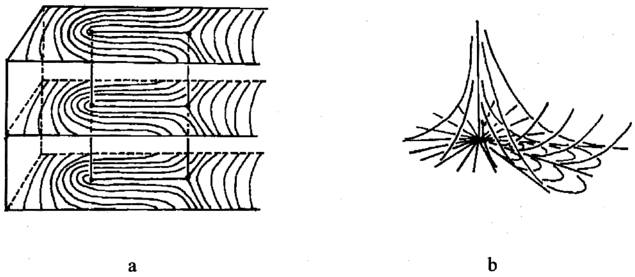

Figure 2. Schematic representation of the simple (*a*) disclination and the complex (*b*) disclination. The revolution of the molecular director is limited in the layer plane in a simple disclination. The complex disclination involves not only director revolution in the plane, but also director revolution out of the plane.

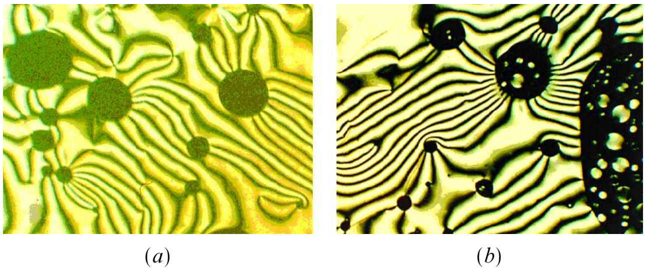
(*a*) (*b*)

Figure 3. The wider disclination cores involved in the process of formation of the high strength disclinations: (*a*) the liquid crystal droplets have merged into each other and a wider core has formed, 173°C, 100×; (*b*) nematic droplets have formed in the isotropic wide core area when the temperature is decreased, 171°C, 100×.

heated above 250°C. Also the dark core areas were checked microscopically by removing the analyser, whereby isotropic areas and air bubbles are readily distinguished.

As follows from numerous observations [2–10] and theoretical studies [16–21], two types of schlieren defects in nematics have been reported; they are denoted as the simple disclination and the complex disclination. Their structures are shown in figure 2.

In general, the simple disclination is observed as shown in figure 2 (*a*) with the revolution of the LC directors limited in the sample layer plane. And from the simple theoretical model and observations, simple disclinations possess the following properties:

(1) The distribution of director around the defect is symmetrical.

(2) There is a simple relation between the strength S of the defect and the number N of dark brushes in the corresponding texture:

$$|S| = N/4.$$

(3) High strength defects ($|S| > 1$) are destabilized in nematics, because a greater S implies a greater curvature of the director $\mathbf{n}$ and, as a result, a greater elastic energy F.

According to Lavrentovich [5, 21], the complex disclination possesses an asymmetrical distribution of the LC director $\mathbf{n}$, which includes sectors with different $\mathbf{n}$ curvatures. In other words, the complex defect contains not only a planar radial-like distribution of the directors, but also a director $\mathbf{n}$ revolution out of the layer plane, as shown in figure 2 (*b*).

A detailed observation of the present defects by using a sensitive colour plate and a quartz wedge in the polarizing microscope indicated that the observed defects in the *p*-alkoxycinnamic acids were simple disclination. Figure 1 (*a*) shows a disclination core of $S = -3/2$ connected with another core of $S = +1$. Figure 1 (*b*) shows a defect core containing not only dark brushes, but also bright silk-like lines. An $S = +2$ and an $S = +5/2$ disclination core are shown in figures 1 (*c*) and 1 (*f*), respectively. They are also connected with other defect cores of $|S| = 1/2$ or 1. No pairs of high strength disclination cores connected to each other were observed because of their poor stability. Several different high strength disclination cores can be found in figure 1 (*d*), including two cores bearing eight brushes and one core bearing six brushes. The brushes in figure 1 (*e*) were disposed to be on one side of the core due to flow of the sample.

The formation process of the high strength defects was observed during cooling of the sample from above clearing point. When the sample was kept around the transition from the isotropic state to the nematic state, the anisotropic nematic droplets merged together and dark isotropic areas surrounded by many dark brushes could be observed (figure 3). The dark area underwent shrinking and some of the dark brushes merged into each other on decreasing the temperature. The high strength disclination could still be recorded despite the decreasing number of dark brushes around a core during the cooling process.

Generally, high strength disclinations are energetically unfavourable and rarely observed. In our study, the core size increases with the number of brushes around it. Zhou [9] suggested that a wide disclination core might fulfil the function of releasing partially the stress generated by the greater number of turns of the molecular director around a core of higher strength, and that this is helpful

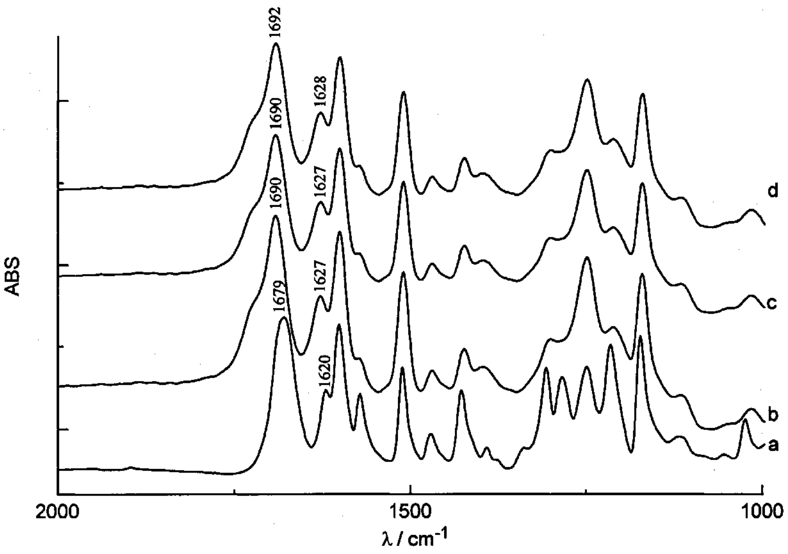

Figure 4. FTIR spectra of *p*-hexyloxycinnamic acid at different temperatures: (*a*) 20°C, (*b*) 160°C, (*c*) 170°C, (*d*) 190°C.

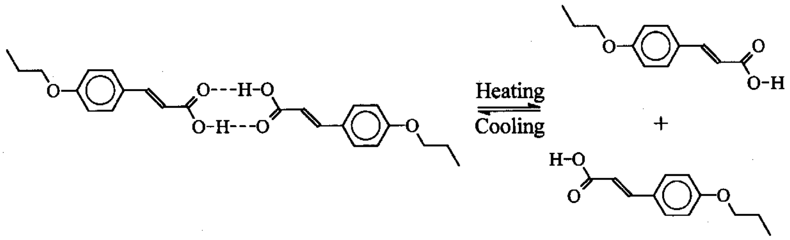

Figure 5. Equilibrium between the dissociation and regeneration of hydrogen bonds.

to the stabilization of the high strength disclination. However, in contrast with our observation, the textures given by Lavrentovich [22] show no relation between the core size and the strength of singularities and that cores of $S = \pm 1$ are in many cases much wider, but in other cases narrower than that of $S = \pm 3$. Further studies are needed for a better understanding of the relation between core size and topology.

Figure 4 shows the FTIR of p-hexyloxycinnamic acid in the range of 1000–2000 cm^{-1} from 20°C to 190°C. The carbonyl band of p-hexyloxycinnamic acid shows significant changes at the melting and isotropization transitions. The carbonyl peak in curve (*a*) that was recorded at 20°C was at 1679 cm^{-1}. When the temperature was raised from 20°C to above the melting point, the carbonyl peak shifted from 1679 to 1690 cm^{-1}; this could be attributed to thermal motion reducing the intermolecular hydrogen bonding interaction. In addition, the peak corresponding to the C=C adjacent to the aromatic ring also shifted to higher frequency. When the temperature was raised above the clearing point, there was a blue shift from 1690 to 1692 cm^{-1} in the carbonyl peak, showing that the hydrogen bonding interaction decreased further with the increase of temperature. The equilibrium is schematically shown in figure 5.

It can be suggested that around the clearing point, the hydrogen bonds are partially dissociated and some of the mesogenic cores are degenerated. Phase separation may then occur and isotropic areas are formed. At the same time, some of the hydrogen bonds reform and new mesogenic cores are regenerated with random directions due to the fluctuation of the temperature. Therefore, the revolution of the nematic director might often happen at the boundary of an isotropic area. Because the isotropic area as a defect core was often wider at the beginning, there might be many dark brushes around the core due to dissipation of the stress of the director revolution. In this way therefore, high strength defects were often formed in the samples under study.

In summary, dissociation of the hydrogen bonds induces phase separation and forms the isotropic disclination core bearing many brushes in the nematic phase. Then with decreasing temperature, the high strength defect develops and is stabilized.

References

[1] Nehring, J., and Saupe, A.,1972, *J. chem. Soc. Faraday Trans. II*, **68**, 1.
[2] Lee, H., and Labes, M. M., 1982, *Mol. Cryst. liq. Cryst.*, **82**, 199.
[3] Madhusudana, N. V., and Pratibha, R., 1983, *Mol. Cryst. liq. Cryst.*, **103**, 31.
[4] Viney, C., Brown, D. J., Dannels, C. M., and Twieg, R. J., 1993, *Liq. Cryst.*, **13**, 95.
[5] Lavrentovich, O. D., and Nastishin, Yu. A., 1990, *Europhys. Lett.*, **12**, 135.
[6] Twieg, R. J., Chu, V., Nguyen, C., Dannels, C. M., and Viney, C., 1996, *Liq. Cryst.*, **20**, 287.
[7] Galli, G., Laus, M., Angeloni, A. S., Ferruti, P., and Chiellini, E., 1985, *Eur. Polym. J.*, **21**, 727.
[8] Witteler, H., Lieser, G., Wegner, G., and Schulze, M., 1993, *Makromol. Chem., rapid Commun.*, **14**, 471.
[9] Zhou, Q. F., Wan, X. H., Zhang, F., Zhang, D., Wu, Z., and Feng, X. D., 1993, *Liq. Cryst.*, **13**, 851.
[10] Song, W., Chen, S., and Qian, R., 1993, *Makromol. Chem., rapid Commun.*, **14**, 605.
[11] Weygand, C., and Gabler, R., 1940, *Z. phys. Chem.*, **B46**, 270.
[12] Gray, G. W., and Jones, B., 1953, *J. chem. Soc.*, 4179; Gray, G. W., 1962, *Molecular Structure and the Properties of Liquid Crystals* (London: Academic Press).
[13] Schubert, H., Dehne, R., and Vilig, V., 1972, *Z. Chem.*, **12**, 219.
[14] Praefcke, K., Kohne, B., Ǧundogan, B., Singer, D., Demus, D., Diele, S., Pelzl, G., and Bakowsky, U., 1991, *Mol. Cryst. liq. Cryst.*, **198**, 393.
[15] Cui, L., Jin, W., Liu, J. N., Tang, Y. X., Xie, P., and Zhang, R. B., 1998, *Liq. Cryst.*, **25**, 757.
[16] Guidone Peroli, G., and Virga, E. G., 1996, *Phys. Rev. E*, **54**, 5235; Guidone Peroli, G., and Virga, E. G., 1997, *Phys. Rev. E*, **56**, 1819.
[17] Lubensky, T. C., Petty, D., Currier, N., and Stark, H., 1998, *Phys. Rev. E*, **57**, 610.
[18] Chuang, I., Yurke, B., Pargellis, A. N., and Turok, N., 1993, *Phys. Rev. E*, **47**, 3343.
[19] Immacolata, S., Frencesco, G., and Giuseppe, M., 1998, *Liq. Cryst.*, **24**, 419.
[20] Hans-Rainer, T., 1998, *Liq. Cryst.*, **24**, 127.
[21] Lavrentovich, O. D., and Pergamenshchik, V. M., 1995, *Int. J. mod. Phys. B*, **9**, 2389.
[22] Lavrentovich, O. D., 1992, *Liq. Cryst. Today*, **2**, 4.