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## Liquid Crystals

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## High strength disclinations in the nematic and smectic states of 2,5-bis(4-alkoxybenzoyloxy)-*p*-benzoquinones

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High strength disclinations were observed in both nematic and smectic phases exhibited by members of the 2,5-bis(4-alkoxybenzoyloxy)-*p*-benzoquinone series, beyond 4-*n*-pentoxy. The shorter members of the series show only a nematic mesophase, the highest members only a smectic mesophase, while intermediate members exhibit both types of mesophase. These high strength disclinations seen in a single component system are very stable due to energy dispersion and the high viscosity of the smectic state. All the high strength disclinations are negative in sign.

### 1. Introduction

It is well known that nematic liquid crystals, when heated above their melting point, show schlieren textures that can be observed by polarized optical microscopy (POM). Sometimes, smectic liquid crystals also show schlieren textures. When a comparatively thick layer (greater than 100 μm) of a nematic liquid crystal is examined using POM, thread-like textures can be observed. In the case of a thin layer, say 10–100 μm, schlieren textures can be observed, containing singular points with emanating dark brushes of extinction. Rotating the crossed polarizers with respect to the sample causes the dark brushes to rotate either in the same sense or in the reverse sense as the rotation of the polarizers, while the singular points remain stationary, indicating the continuous change in molecular orientation. These singular points are defined as disclinations [1, 2]. The strength of the disclination can be simply defined as  $|S| = N/4$ , where  $N$  is the number of the associated dark brushes. Disclinations of strength  $S = \pm 1/2$  and  $\pm 1$  can always be observed. In contrast, high strength disclinations ( $|S| > 1$ ) are difficult to observe because the elastic distortion energy of the disclinations is proportional to  $S^2$ , and the disclination is increasingly unstable with the increase of  $|S|$  [2].

A few papers have been published on the observation of high strength disclinations in low molar mass liquid crystals. Singularities up to +4 in mixtures of lyotropic and thermotropic liquid crystals were reported by Lee and Labes [3]. Madhusudana and Pratibha [4] found disclinations of strength up to +7/2 in mixtures of several nematic compounds with plate-like non-mesomorphic molecules. Recently, Cui *et al.* [5] reported high strength disclinations induced by hydrogen bond dissociation in the nematic phases of *p*-alkoxycinnamic acids. The first observation of high strength disclinations ( $|S| = 3/2$ ) in a single component low molar mass liquid crystal consisting of rigid-rod-like molecules was reported by Viney *et al.* [6]. The authors considered that these nematic samples exhibited disclinations of strength  $\pm 1/2$  and  $\pm 1$ . However, when these nematic samples were stirred by vigorously agitating the top cover slide for a few seconds, occasional transient singularities of strength  $\pm 3/2$  were found. The lifetime of these disclinations was so short that it was difficult to distinguish between disclinations of strength +3/2 and -3/2 by rotating the crossed polarizers. Lavrentovich and Nastishin reported high strength and zero strength defects which possess complex asymmetrical structures in degenerate hybrid aligned nematic LC films on an isotropic liquid surface. These complex defects contain not only a planar radial-like distribution of the directors, but also a director resolution out of the layer plane [7, 8].

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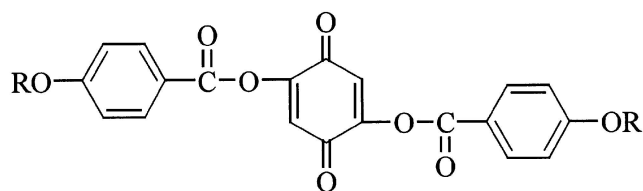


Figure 1. Molecular structure of 2,5-bis(4-alkoxybenzoyloxy)-*p*-benzoquinones ( $OR = O(CH_2)_nCH_3$ ,  $n = 0, 1, 2, 3, 4, 5, 7, 9, 11, 13, 15$ ).

A series of liquid crystal polymers (LCPs) with two-dimensional mesogenic units has been synthesized [9]. It is interesting to find that 2,5-bis(4-alkoxybenzoyloxy)-*p*-benzoquinones, the intermediates of these LCPs, can form stable high strength disclinations in both nematic and

smectic mesophases without the induction of hydrogen bonds or the aid of other components. In this paper, we present the observation of high strength disclinations,  $S = -2$ ,  $-3$  and  $-4$  in nematic and smectic mesophases of single component materials.

## 2. Experimental

The synthesis of 2,5-bis(4-alkoxybenzoyloxy)-*p*-benzoquinone has been described in detail elsewhere [9]; the chemical structure is shown in figure 1.

Transition temperatures were measured using a TA 2704 differential scanning calorimeter (DSC) with a heating rate of  $10 \text{ K min}^{-1}$ . Glass slides were soaked in concentrated nitric acid for at least one day, then washed with acetone, and used without further treatment. Samples

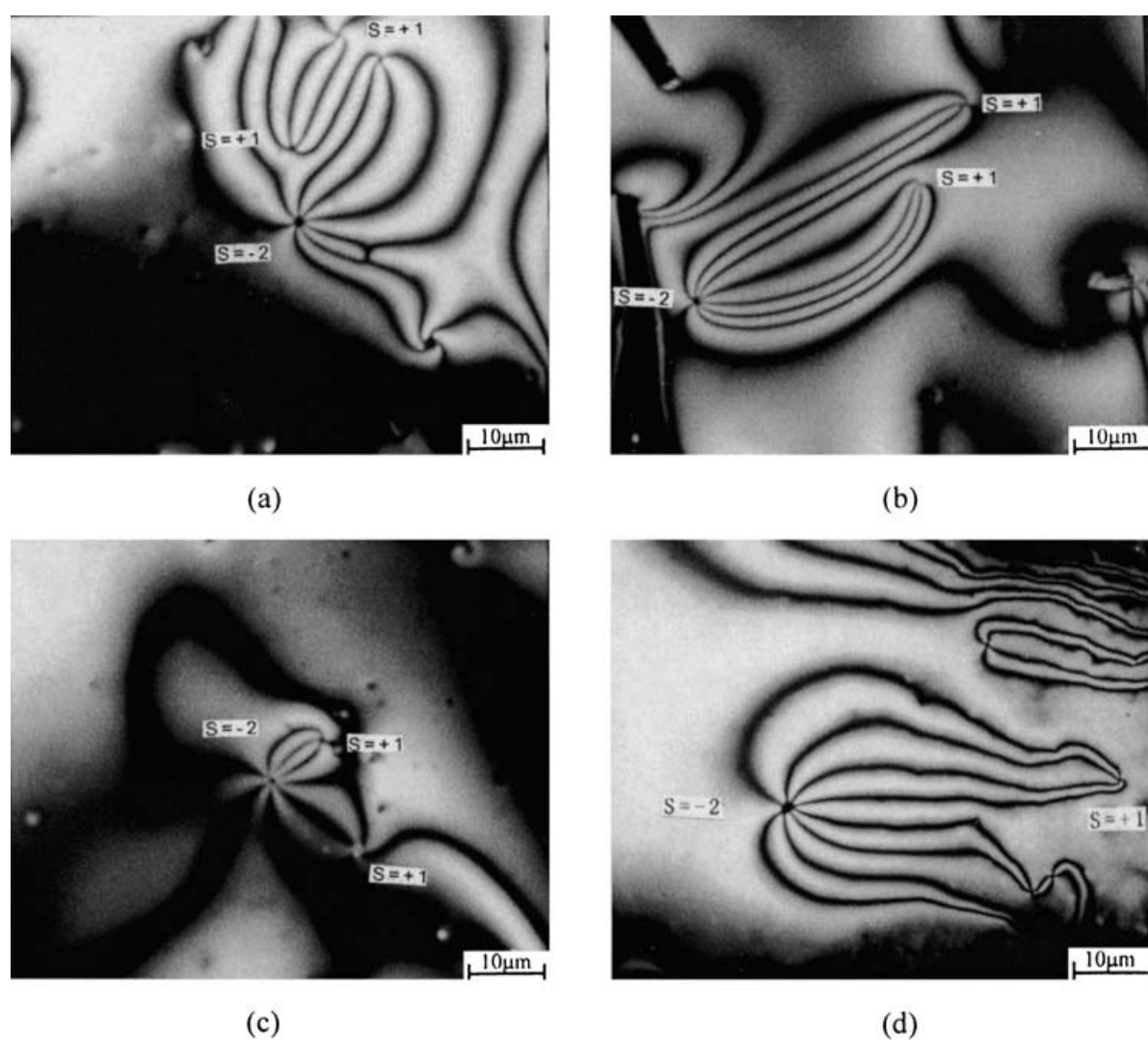


Figure 2. Schlieren textures observed in nematic mesophases of 2,5-bis(4-alkoxybenzoyloxy)-*p*-benzoquinones: (a) 4-*n*-pentoxy,  $139^\circ\text{C}$ ; (b) 4-*n*-pentoxy,  $140^\circ\text{C}$ ; (c) 4-*n*-hexoxy,  $138^\circ\text{C}$ ; (d) 4-*n*-decyloxy,  $149^\circ\text{C}$ ; (e) 4-*n*-pentoxy,  $139^\circ\text{C}$ ; (f) 4-*n*-decyloxy,  $145^\circ\text{C}$ ; (g) 4-*n*-dodecyloxy,  $150^\circ\text{C}$ ; (h) 4-*n*-decyloxy,  $145^\circ\text{C}$ .

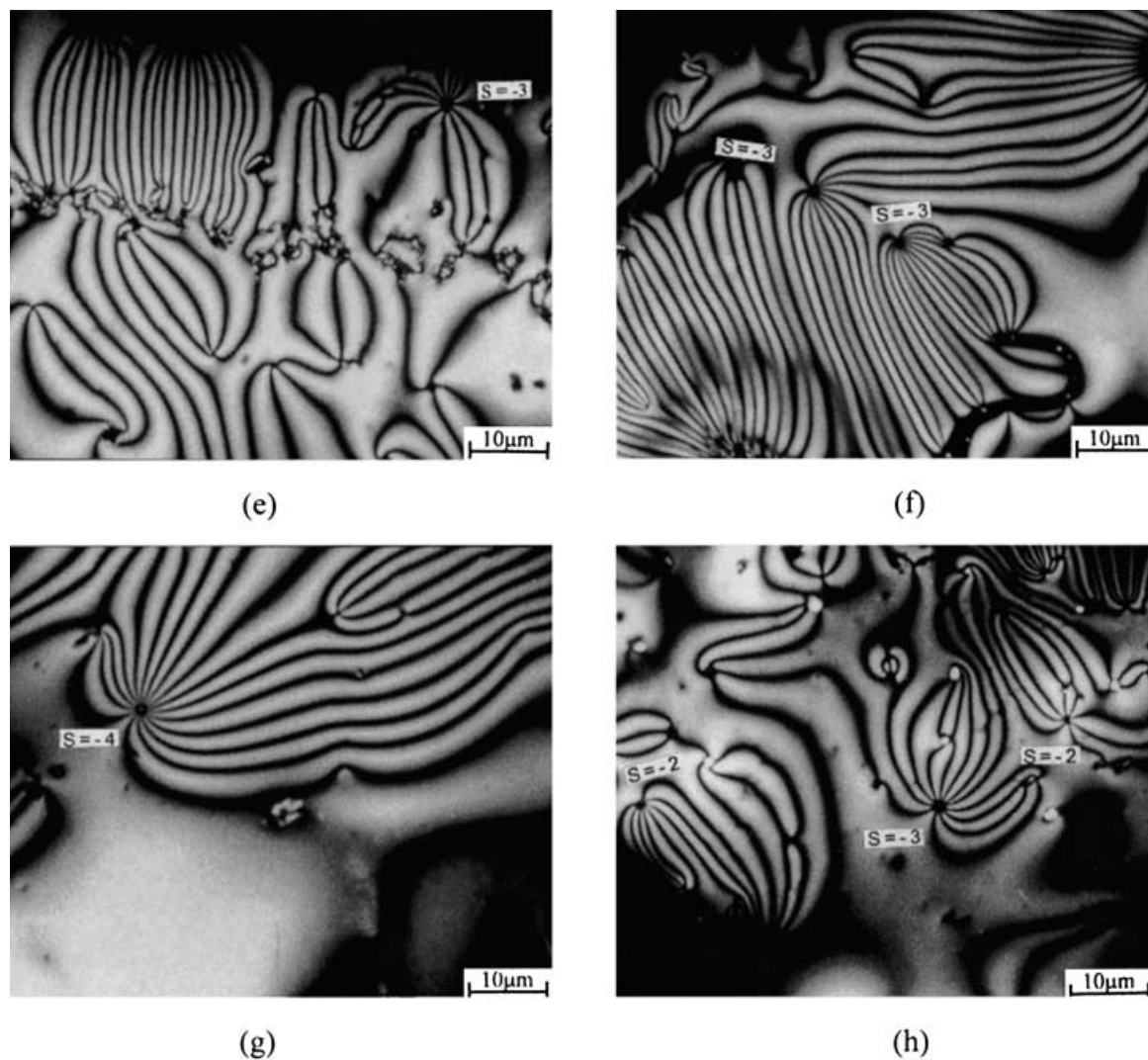


Figure 2. (Continued.)

were sandwiched between two glass slides and observed using an Olympus polarizing microscope (BH-2) equipped with a Mettler FP-52 hot stage. The thickness of the samples was about 10–20  $\mu\text{m}$ .

### 3. Results and discussion

The phase transition temperatures of the 2,5-bis-(4-alkoxybenzyloxy)-*p*-benzoquinones are listed in the table. The first three members of the homologous series are monotropic and unstable, decomposition occurring around the clearing temperature. On increasing the length of the alkoxy chains, the nematic mesophase becomes stable, then both nematic and smectic mesophases were observed; further increases result in exclusively smectic properties being observed. These results are similar to Harbert's work on the liquid crystalline behaviours

Table. Transition temperatures of the 2,5-bis(4-*n*-alkylenedioxy)hydroquinones.

<i>n</i>	Transition temperature $^{\circ}\text{C}$
0	Cr 185 N 211 I <sup>a</sup>
1	Cr 184 N 205 I <sup>a</sup>
2	Cr 156 N 225 I <sup>a</sup>
3	Cr 134 N 217 I
4	Cr 120 N 182 I
5	Cr 121 N 175 I
7	Cr 122 N 176 I
9	Cr 114 SmC 134 N 165 I
11	Cr 109 SmC 147 N 157 I
13	Cr 112 SmC 149 N 151 I
15	Cr 113 SmC 149 I

<sup>a</sup>Clearing with decomposition.

of 4-*n*-alkoxybenzoic acids [10]. It was shown that when the length of the molecule is similar to its width, no mesomorphic properties were observed; the addition of alkoxy chains, up to the point at which the physical length of the chain is comparable to the length of the -oxybenzoic segment, produces largely nematic behaviour. When the alkoxy chains become longer, purely smectic properties are observed. For the 4-*n*-alkoxybenzoic acids, when smectic properties first appear, the alkoxy chain is almost half the length of the whole molecule. In our case, two 4-*n*-alkoxybenzoic acids were linked through 2,5-dihydroxy-*p*-benzoquinone by ester bonds, which is different from the dimerization of 4-*n*-alkoxybenzoic acids by hydrogen bonds as occurs in liquid crystal phases. Thus, all the compounds listed in the table show liquid crystalline properties and these have broader liquid crystalline phases than do the corresponding 4-*n*-alkoxybenzoic acids. Exclusively nematic behaviour is seen from the methoxy to 4-*n*-octyloxy homologues. Both nematic and smectic mesophases are found for the 4-*n*-decyloxy to 4-*n*-tetradecyloxy members of the series while only smectic behaviour appears for 2,5-bis(4-*n*-hexadecyloxybenzoyloxy)-*p*-benzoquinone. Thus, long alkoxy substituents favour smectic mesophases, whereas short substituents favour nematic mesophases [11].

Two types of schlieren defects, namely, simple disclinations and complex disclinations, have been reported in nematics. Generally, there is a simple relationship between the strength  $S$  of the defects and the number  $N$  of dark brushes and specifically,  $|S| = N/4$ . By comparison, the relationship between  $S$  and  $N$  for complex defects is complex [7, 8].

Although high strength disclinations are difficult to observe, they can be found easily in the 2,5-bis(4-alkoxybenzoyloxy)-*p*-benzoquinones, beyond the 4-*n*-pentoxy member. High strength disclinations observed in the nematic mesophase are shown in figure 2. By using a quartz wedge in the polarizing microscope, it was seen that the observed defects in the samples were simple disclination. None of the multiple dark brushes of the schlieren texture disintegrated; they remained constant in number and turned in the opposite direction when rotating the crossed polarizers. It is safe to say that the high strength disclinations are genuine and not the aggregate of neighbouring singularities. These nematic high-strength disclinations showed broad cores, and the radii of the cores increased with increasing disclination strength, agreeing well with Nehring and Saupe's theory [2].

The high strength disclinations are not independent of each other, but instead most connect with neighbouring disclinations of lower strength, with the opposite sign of  $S$ . A close examination shows that disclinations with strength of  $-2$  in figures 2(a)–2(d) are connected by two singularities with strength of  $+1$ . In figure 2(e)–2(h), the disclinations with strength of  $-3$  and  $-4$  are connected to opposite sign defects. No pairs of high strength disclinations connected to each other were found because of the high distortion energy required. All the observed high strength disclinations are very stable although they are energetically unfavourable. They persisted even after annealing for several tens of minutes.

High strength disclinations in mixtures of low molar mass liquid crystals are attributed to the surface tension

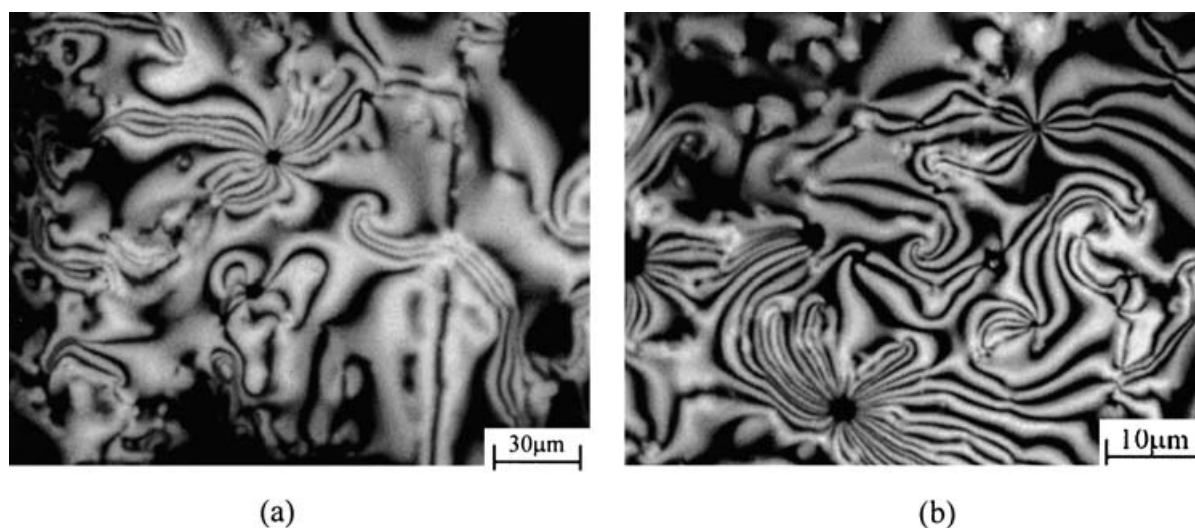


Figure 3. Smectic C schlieren textures observed for 2,5-bis(4-alkoxybenzoyloxy)-*p*-benzoquinones: (a) 4-*n*-tetradecyloxy, 125°C; (b) 4-*n*-hexadecyloxy, 128°C.

gradient at the interface with the submicroscopic droplets [3] or to concentration gradients [4]. High strength disclinations induced by hydrogen bonding stem from the phase separation and formation of isotropic areas [5]. In this study, every high disclination is stabilized by connection with lower strength disclinations or defects with opposite sign. The sum over the  $S$  numbers of all the singularities in a local area tends to zero, therefore, the energy of the system is a minimum [2].

It is interesting that high strength defects can also be observed in the smectic C phase of the samples (figure 3). These smectic schlieren textures display similarities to nematic schlieren textures. The former occurs particularly in thin specimens, at the edges of wedge-shaped samples, or at free surfaces. In smectic C schlieren textures, the layers are parallel to the glass slides and the projections of the tilted molecules on to the  $xy$ -plane can continuously change their directions [12]. These disclinations can last longer than those in a nematic mesophase at constant temperature. It is suggested that, in this case, the distortion energy may be easily dispersed in the glass slides in order to stabilize them in the thin film [12, 13]. On the other hand, the longer lifetime of smectic defects is also attributed to the high viscosity in a smectic mesophase as found in polymeric nematic mesophases [13, 14]. It is noteworthy that all the observed high strength disclinations are negative.

#### 4. Conclusions

Stable high strength disclinations were observed in both nematic and smectic mesophases exhibited by

2,5-bis(4-alkoxybenzoyloxy)-*p*-benzoquinones without the induction of hydrogen bonds or the aid of other components. The stability of these high disclinations may be attributed to energy dispersion and the high viscosity in smectic mesophases.

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