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PRELIMINARY COMMUNICATION

Polymeric nematic schlieren textures with singularities of high strength

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The observation of polymeric nematic schlieren textures with singularities of high strength ($|S|>1$) is reported. The polymers studied are of the type with two dimensional mesogenic units. Inversion walls were also observed in the liquid crystal state of these polymers.

When the preparations are relatively thin (10 to a few tens of micrometres thick) nematic liquid crystals often form schlieren textures which are characterized by dark brushes meeting at a dark point. An example of a nematic schlieren texture observed in a thin layer of a polymeric liquid crystal (polymer C, $n=8$, below) between crossed polarizers is given in figure 1.

If the polarizer and the analyser are rotated simultaneously, the black brushes move continuously over the field, indicating a continuous change in the direction of the

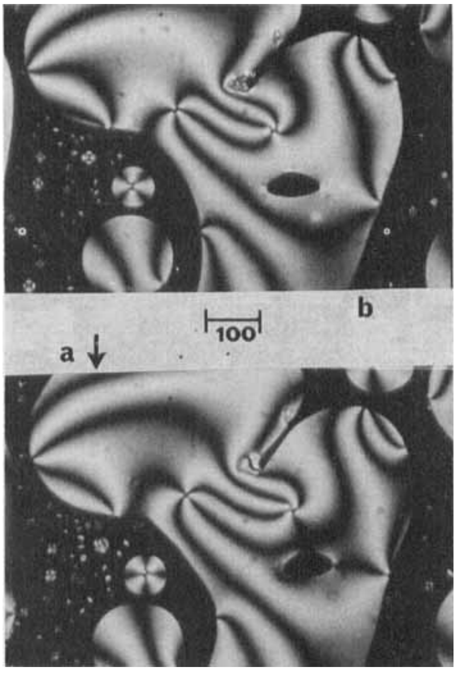

Figure 1. Schlieren texture of polymer C with point singularities of $S=\pm 1$. (*b*) The two polarizers in the cross position were rotated simultaneously anticlockwise by 45° relative to the position of (*a*). The photos were taken at 170°C. The scale is in microns.

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optical axis in the layer. On the other hand, the point from which the brushes start does not change its position during the rotation of the polarizers. According to Nehring and Saupe [1], this type of point is caused by line singularities perpendicular to the layer, and the term 'point singularities' was suggested for this type of line singularities because of their appearance. Nehring and Saupe were also able to show that the point singularities are characterized by

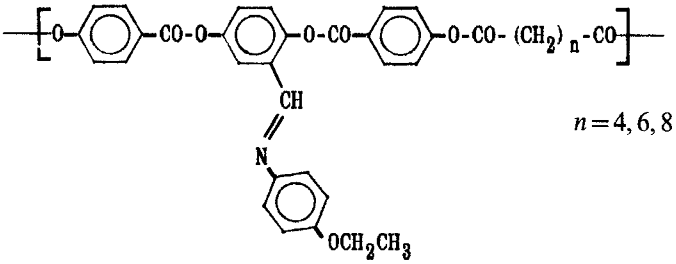
$$|S| = \frac{\text{number of brushes}}{4}$$

and have a positive sign when the brushes rotate in the same direction as that in which the polarizer and analyser are simultaneously rotated in the crossed position, and a negative sign when they turn in the opposite sense. Figure 1 (*b*) was obtained after the polarizers were rotated anticlockwise by 45° relative to the position in the case of figure 1 (*a*). The actual vibration directions for the polarizer and analyser are shown by the dark cross in the image of a nematic spherulite. In figure 1 (*a*), the vibration direction of the analyser is vertical, in 1 (*b*) it is at the position turned anticlockwise by 45°. The two point singularities in the middle of the figures were thus assigned the S values of $+1$ and -1, respectively. The neighbouring singularities which are connected by brushes are always of opposite sign.

The theory of Nehring and Saupe predicted that S may have absolute values of 1/2, 1 and higher. However, singularities with absolute S values of 1/2 and 1 are the most often observed. Those of higher S values, as also suggested by the theory, are energetically unfavourable and there have been only very few experimental observations of high strength singularities [2–5]. For example, in mixtures of a nematogen and a plate-like non-mesogenic compound, Madhusudana and Pratibha [4] were able to observe not only singularities of $S = \pm 1/2$, ± 1, but also that of $S = \pm 3/2$ and ± 2. These observations were made either on mixtures or on lyotropic systems. The observation of high strength singularities with 12 brushes in a single component low molar mass liquid crystal (5CB) was reported only very recently by Lavrentovich [6].

In this communication we would like to report our observations of high strength singularities formed in a few single component thermotropic polymer liquid crystals.

As shown by figures 2 and 3, we have been fortunate to observe singularities with $S = -3/2$ and $S = +2$ in addition to that of $S = \pm 1/2$ and ± 1 in polymer liquid crystals with two dimensional mesogenic units [7, 8]. The polymer was synthesized by the polycondensation of the hydroquinone monomer 2,5-dihydroxybenzylidene-4′-phenetidine with the diacid chloride monomer 1,8-bis(4-chloroformylphenyloxy)carbonyloctane as reported in [8] and has the following molecular structure (polymer C, $n = 8$ with M_n of 2900 and M_w of 5200):



The structure of polymers A, B, and C
(Polymer A: $n = 4$; polymer B: $n = 6$; polymer C: $n = 8$).

Polymers A and B were similarly prepared. As reported in [8], the three polymers are thermotropically liquid crystalline. Their respective peak temperatures (in °C) of the melting and clearing transitions as determined with a Du Pont 1090 DSC instrument and a heating rate of 20°C min^{-1} are 92°C and 220°C for polymer A ($M_n = 4800$, $M_w = 8400$); 92°C and 217°C for polymer B ($M_n = 4600$, $M_w = 8100$); and 85°C and 172°C for polymer C ($M_n = 2900$, $M_w = 5200$). A Leitz Laborlux 12 Pol polarizing microscope with a Leitz 350 heating stage was used for the texture observations. Glass slides were cleaned with nitric acid, deionized water, and acetone, and dried. No intentional surface treatment was made before use. The photographs were all taken in the course of cooling from above the clearing points and in the temperature range of the liquid crystal phase of each sample. The temperatures at which the photos were taken are noted in the captions of the figures.

In figure 2, one point singularity with six dark brushes is shown at about the centre of each of the two figures 2(*a*) and (*b*). Again figure 2(*b*) was obtained after the polarizers had been rotated anticlockwise by 45° relative to the position for figure 2(*a*). The brushes rotated in the opposite direction (clockwise) while the meeting point of the

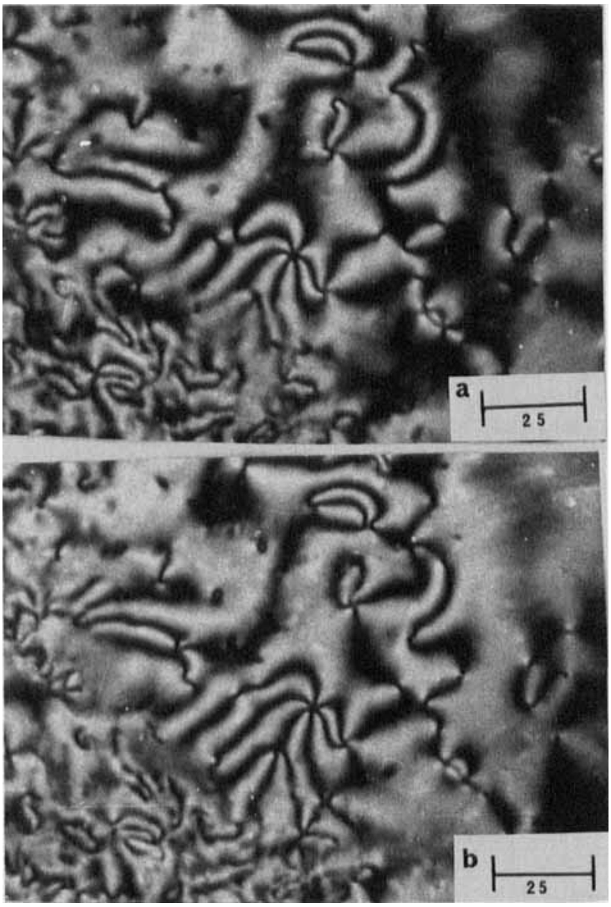


Figure 2. Schlieren textures of polymer C with point singularities with six brushes ($S = -3/2$). From (*a*) to (*b*) the two polarizers were rotated anticlockwise by 45°. The photos were taken at 150°C. The scale is in microns.

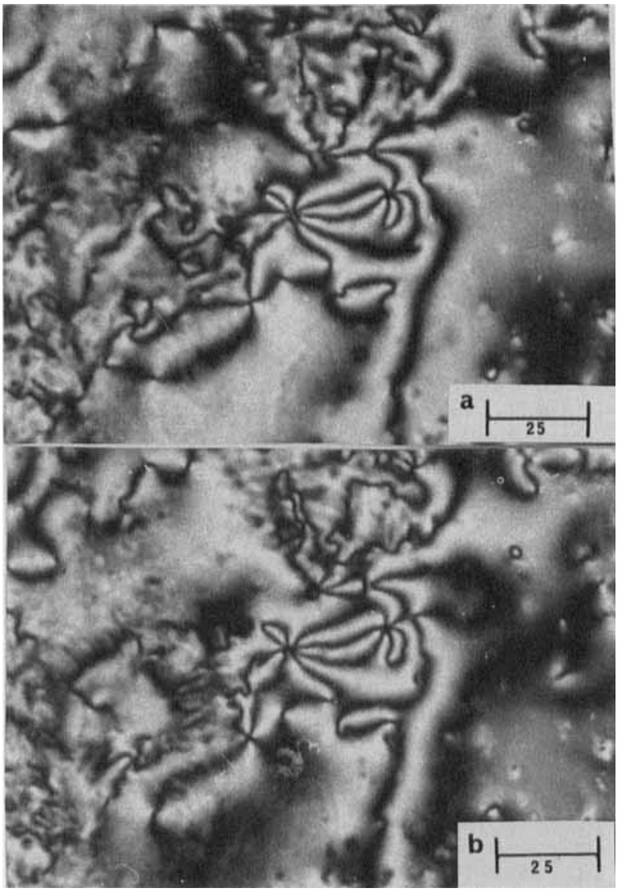


Figure 3. Polymer C with paired defects with six and eight brushes, $S=-3/2$ and $+2$, respectively. From (*a*) to (*b*) the two polarizers were rotated anticlockwise by 45°. The photos were taken at 150°C. The scale is in microns.

six brushes (the point singularity) did not change its position and kept its darkness. This point singularity has thus an S of $-3/2$ according to Nehring and Saupe. At about 1 cm to the southeast of this point singularity we see another singularity with four brushes which rotated simultaneously with the polarizers and also in the anticlockwise sense, for which an S of $+1$ was assigned. It was also noted that the rotation rate was lower for the six brushes than that for the 4 brushes. The four brushes returned to their original position after a 360° rotation of the polarizers, whereas in contrast it took a rotation of 540° to bring the six brushes (after a rotation of $-360°$) back to their original position. The rotation of the brushes of a singularity of $-3/2$ is slower than that of the polarizers. This observation is also in agreement with the theory of Nehring and Saupe which claims that when the crossed polarizers are rotated by an angle β around the z axis, the brushes rotate by an angle β/S.

It is interesting to note that in figure 3 we can see a singularity of $S=+2$ in the middle of the two figures. Again to obtain figure 3(*b*) the polarizers were rotated anticlockwise by 45° relative to their positions for figure 3(*a*). The eight brushes rotate with the polarizers in the same direction, but with a much slower rate: the polarizers

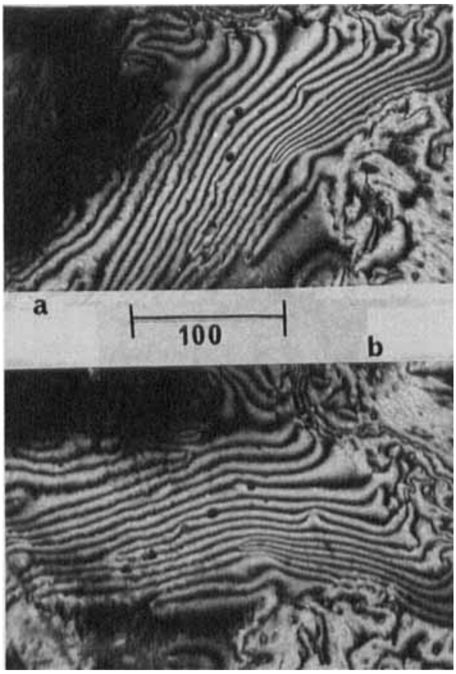
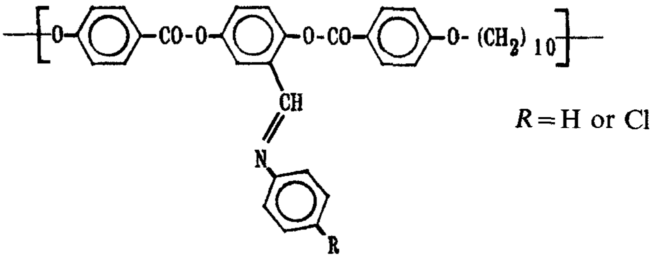


Figure 4. Inversion walls in the liquid crystal phase of polymer A. From (*a*) to (*b*) the stage was rotated clockwise by 45°. The photos were taken at 170°C. The scale is in micron.

were rotated by 720° whenever the brushes returned to their original positions after a 360° rotation. This is again in agreement with the theoretical value β/S. To the east of the $S=+2$ singularity, there is another singularity of $S=-3/2$ with six brushes, offering one example of the paired high strength defects, one with a strength of $+2$, the other of $-3/2$. Other singularities with absolute S values of 1 and 1/2 are also seen in the figure.

Of the three polymers A, B, and C in this study, only polymer C was found to form textures with singularities of high strength, but all three polymers form inversion walls. According to Nehring and Saupe [1], inversion walls are of the schlieren texture type but arise when the surfaces try to impose a uniform orientation on the sample. In this case, point singularities are then located in inversion walls normal to the layer. The brushes generally appear in nearly parallel pairs connecting point singularities of the type $S=+1$ or $S=-1$, and also of $S=\pm 1/2$. A model of the molecular alignment in inversion walls was also provided by Nehring and Saupe. Therefore we would like to mention only that in our polymers with two dimensional mesogenic units, the schlieren textures can be relatively rich in inversion walls. This is shown by figure 4 (polymer A, $M_n=4800$, $M_w=8400$) in which figure 4 (*b*) was obtained after a 45° clockwise rotation of the stage which corresponds to a 45° anticlockwise rotation of the polarizers relative to the position when figure 4 (*a*) was taken. It so happened that in the centre of the image field there was a dark point which did not change its position nor its darkness with rotation of the stage. This dark point is shown in the figure and serves as a reference point, and so it was very easy for us to follow the dark–bright conversion of the bands (the walls) after every 45° rotation of the stage or of the polarizers.

Other polymer liquid crystals found in this study to form defects of high strength have the following molecular structure (named here as polymer-Cl when $R=Cl$ and polymer-H when $R=H$) [9]:



Structure of the polymer-H and polymer-Cl.

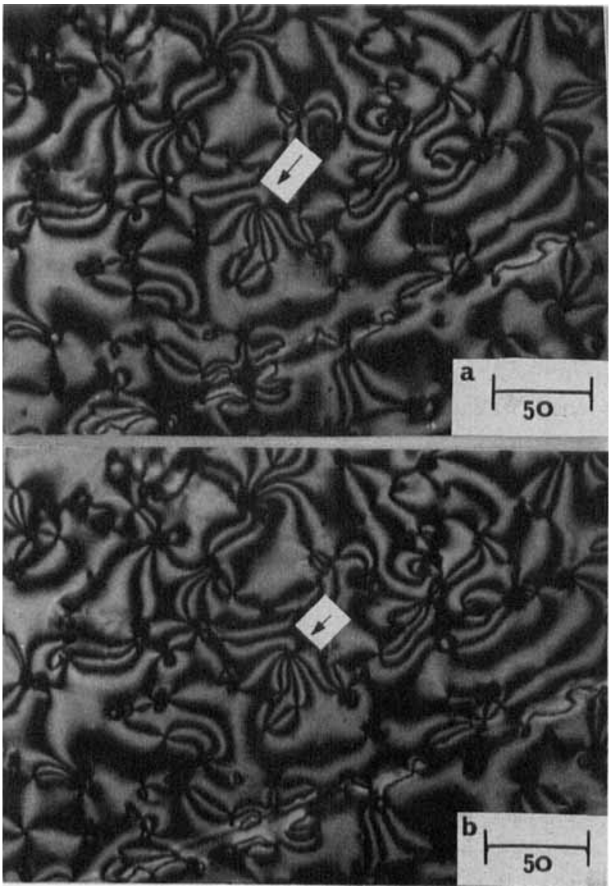


Figure 5. Nematic schlieren texture of polymer-Cl showing a defect with eight brushes (with $S=+2$). From (*a*) to (*b*) the two polarizers were rotated anticlockwise by 22·5°. The photos were taken at 130°C. The scale is in microns.

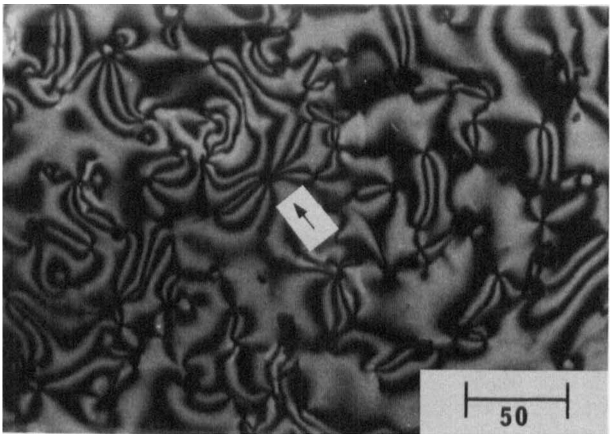


Figure 6. Nematic schlieren texture of polymer-Cl showing a defect with ten brushes. The photos were taken at 130°C. The scale is in microns.

Polymer-Cl was synthesized by polycondensation of the diacid chloride monomer 1,10-bis(4-chloroformyl)phenoxydecane and the 2-substituted hydroquinone monomer 2,5-dihydroxybenzylidene-4′-chloroaniline. The sample used in this study has a molecular weight of $M_n = 8500$ and $M_w = 12000$, which melts at 123°C, the clearing temperature of its nematic phase is 148°C.

Figure 5 was taken at 130°C, and shows one defect of $S = +2$ in the nematic phase of polymer-Cl. For figure 5 (*b*) a 22·5° anticlockwise rotation of the polarizers, relative to their position when figure 5 (*a*) was taken had been made.

On one occasion, a defect with ten brushes was also observed for polymer-Cl and this is shown by figure 6. However, this defect was of low stability and was observed to break down into two defects of which one had two brushes and the other had four brushes. Unfortunately we failed to photograph the breaking down process and are not able to show it here.

Polymer-H was also observed to form defects with eight brushes. Other homologues of this series of polymers with $R = $ CN, NO_2, OC_2H_5, CH_3 or CF_3 were also studied, but no high strength defects have been observed in their nematic phases.

Finally, an examination of the schlieren textures shown in figures 2, 3, 5 and 6 would suggest that the isotropic core is wider for the high strength disclinations (especially for the one with brushes in figure (6) than that for the ordinary ones of lower strength with two or four brushes. It seems to us that a wider core might have the function of releasing partially the stress generated by the greater number of turns of the molecular director about a defect with higher strength (for a defect of $S = \pm 1/2$, the director rotation is 1π, for $S = \pm 1$ it is 2π, for $S = \pm 3/2$ it is 3π, for $S = \pm 2$ it is 4π, and so on), and is thus helpful to the stabilization of the high strength disclinations. However, in contrast with this observation, the texture given by Lavrentovich [6] shows no relation between the core size and the strength of the singularities, in which the 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 requested for a better understanding of the core size and topology.

In conclusion, in a few single-component nematic phases of some liquid crystal polymers with two dimensional mesogenic units we have observed high strength defects with six, eight or ten dark brushes. This relatively easy formation of high strength defects, by comparison with other thermotropic liquid crystal polymers, may be attributed to the unique shape of the molecular mesogenic units.

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