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Loop-like light extinction in the precipitation film of a presheared lyotropic polymeric liquid crystal

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This paper reports a novel light extinction pattern of polymers in a polarizing microscope, termed as loop-like extinction by the authors. Such a phenomenon is found together with the Maltese cross, in the precipitation film of presheared poly(1,4-phenylene terephthalamide) (PPTA) solution, a popular lyotrophic polymeric liquid crystal. A plausible supermolecular structure is assumed, which comprises one +1 defect and a pair of −1/2 defects. The key structure is that besides the core of the nematic droplet, the matrix is also anisotropic due to preshearing. Calculated birefringence patterns find good agreement with the experimental micrographs. Copyright © 1996 Elsevier Science Ltd.

(Keywords: liquid crystalline (LC) polymer; polarized optical microscopy (POM); extinction pattern)

INTRODUCTION

Over the past several decades, polarized optical microscopy (POM) has been a conventional means to study the internal supermolecular structures of anisotropic entities[1–31]. The most famous extinction pattern may be the Maltese cross, which can be found in many cases such as the polymer spherulites[3–8,31] and some liquid crystalline (LC) droplets[1,2,22–30]. In this paper, we report an interesting pattern, which is tentatively termed as loop-like extinction by the authors. This kind of extinction was found in our studies on an LC polymer. Observed in a polarized optical microscope under crossed polars, the specimen takes on either Maltese cross or loop-like extinction, depending upon the relative angle between the preshearing direction and the polarizer. In the following sections, we will report our findings and give our explanations. Corresponding internal structure will be put forward, and the calculated birefringence patterns agree with the experimental photographs satisfactorily. Hence, this paper introduces a new member into the family of extinction patterns of polymers and might be meaningful for the investigation of pre-oriented polymers.

EXPERIMENTAL

Poly(1,4-phenylene terephthalamide) (PPTA) is a kind of rigid macromolecule and shows a nematic mesophase in concentrated solutions of sulfuric acid. (The systematic IUPAC name of PPTA is poly(imino-1,4-phenylene-iminoterephthaloyl).) This study is concentrated on PPTA film. The specimen is afforded by Chinese Textile University (M_W 40000). First, PPTA was dissolved in 100 wt% H_2SO_4 at a concentration of 12 wt%. Then, the solution was sheared between two slides by hand. The sheared anisotropic solution of PPTA was very quickly precipitated by dipping into water. The dried film was observed with a Leitz polarizing microscope under crossed polars at room temperature. The source is the white light with orthoscopic incidence.

RESULTS AND DISCUSSION

PPTA is insoluble in water and the sample is then rapidly precipitated or coagulated after immersing into water (*Figure 1*). The interesting phenomenon is that not only Maltese cross, but also the so-called loop-like extinction is, depending on the relative orientation of shear direction to the polarizer, found in a polarizing microscope. In *Figures 1b* to *1d*, the polarizer and analyser are rotated clockwise simultaneously. Further rotation with the angles between 45° and 90° make the loop-like extinction convert gradually to the Maltese cross again. The same phenomenon can be seen by anti-clockwise rotation of both polars with the only difference in the extinction quadrants. Our observations show that the loop-like extinction has something to do with the anisotropy of the matrices around the nematic droplet. Such an opinion is further confirmed by adding a Leitz tilting compensator, as indicated by *Figure 2*.

We will attempt to explain the phenomenon about the loop-like extinction as follows. The key is that the matrix is also anisotropic. A corresponding molecular orientation, or in strict sense, a director configuration, is put forward and presented in *Figure 3*, which can, albeit roughly, be divided into three regions. The core is a nematic droplet, assigned as region I, where the

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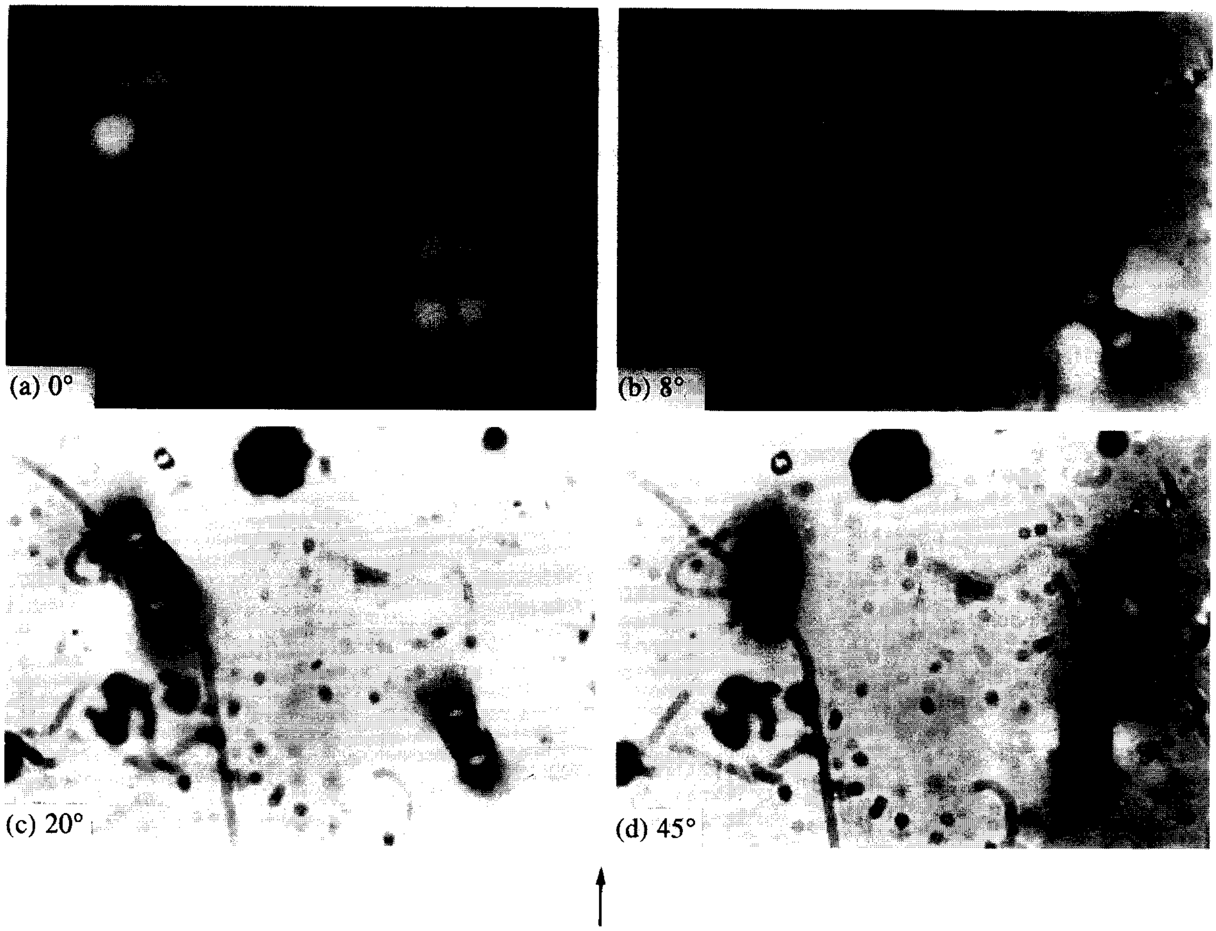

Figure 1 Polarizing micrographs of the precipitation PPTA film with loop-like extinction under crossed polars: (a) specimen in orthogonal position; (b)–(d) clockwise rotation of both polarizer and analyser away from this position by the noted angles. The shearing direction is indicated by the arrow. The diameters of the nematic droplets are about 15 μm

molecules are oriented tangentially as indicated in *Figure 3*. From another point of view, the core includes a +1 defect. Region III refers to the matrix far away from the nematic droplet. In this region, the rod-like macromolecules are parallel with each other due to the memory of shear aligning. It can hence be reasonably imagined that the director field near the core must have been splayed and comprises region II, which includes a pair of −1/2 defects. The loop-like extinction occurs mainly in region I and region II. The total defect strength is zero (1−0.5 × 2), which is stable in light of the defect energy, according to the previous studies on LC by deGennes[1].

Our observations confirm the presumed internal structure considerably. With the polars rotated, the background becomes brighter and brighter (*Figures 1a–d*), which strongly supports that the matrix (region III) is anisotropic and corresponding molecules are oriented parallel to the previous shear direction. After inserting a Leitz rotating compensator, no colour change occurs at first when the compensating phase angle is zero. Then, by rotating the drum of compensator clockwise, the first and third quadrants become blue whereas the second and fourth quadrants become yellow. The colours are altered by rotating the drum anticlockwise. Such a compensation phenomenon is, according to our contrast experiment, the same as that in the poly(ethylene oxide) (PEO) bulk crystal, a well-known negative polymer spherulite, i.e. $n_r < n_t$, where n_r and n_t denote the refractive indices along the radial direction and tangential direction of the spherulite, respectively[31]. Hence, the change of compensating colours proves the axial or tangential orientation of rod-like molecules in region I. It is well known that in LC polymers, the Frank's elastic constant for the splay deformation (k_{11}) is usually much larger than that for bend deformation (k_{33})[32]. Therefore, the axial chain orientation in region I is favourable for reducing the elastic free energy for the LC system.

With the gridding method introduced by the authors[25–28], we have calculated the birefringence patterns corresponding to the presumed structures (*Figure 4*). The loop-like extinction is theoretically reproduced as well as Maltese cross. The main characteristics of the calculated loop-like extinction are similar to the micrographs with the same orientation angles relative to the previous shearing directions and polars. The theoretical results on the quadrants of loop-like extinction are the same as corresponding experimental observations, after considering the difference of shearing direction and rotation direction in *Figures 1* and *4*. The calculated compensating effect in *Figure 5* also agrees with the experimental counterpart in *Figure 2*.

Our theoretical and experimental studies testify the previous knowledge of the extinction behaviours of defects. The +1 defect has four brushes under crossed polars, where the −1/2 defect has two brushes. In the rotation of both polars, with an angle of θ, the brushes

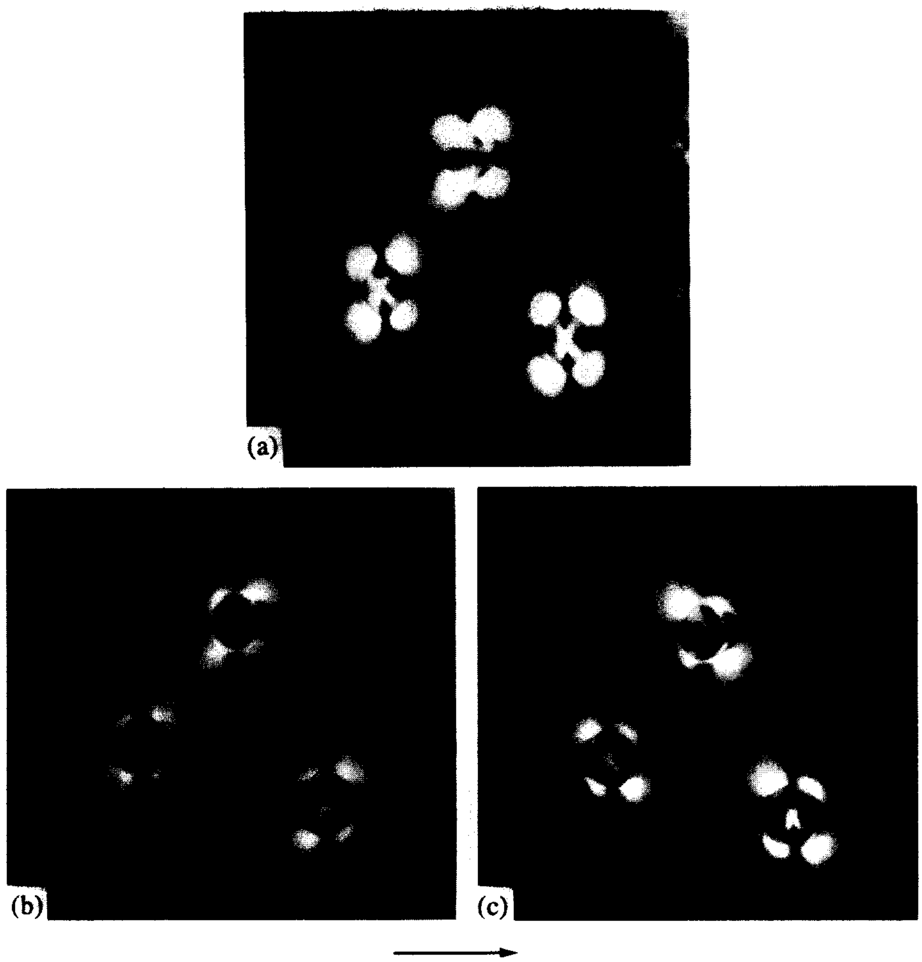

Figure 2 Polarizing micrographs of the precipitation PPTA film with loop-like extinction under crossed polars and in orthogonal position: (a) without compensation; (b)–(c) with a tilting compensation plate inserted between polarizer and specimen, the vibration direction of which is from upper-left to lower-right in (b), while from upper-right to lower-left in (c). The shearing direction is indicated by the arrow. The diameters of the nematic droplets are about 15 μm. The compensator has the retardation $(n_e - n_o)d = 0.02\,\mu$m, where d denotes the depth of the compensator, n_o and n_e indicate the indices corresponding to the ordinary light and extraordinary light, respectively

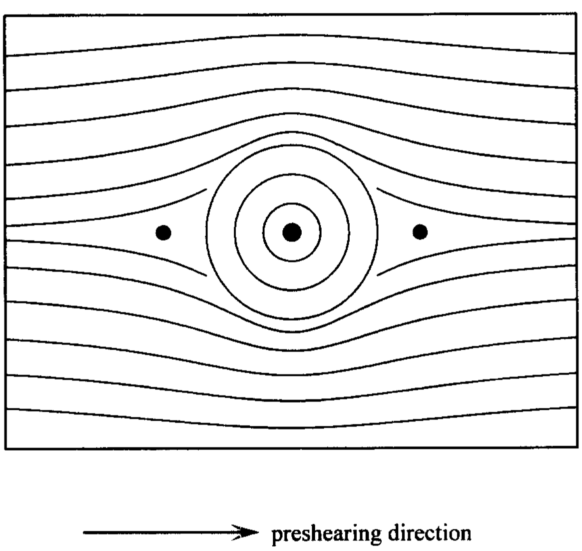

Figure 3 The presumed optical director or molecular orientation associated with loop-like extinction. The structure includes one +1 point defect in the core (region I) and one pair of −1/2 point defects beside the core and along the previous shear direction (region II). Far away from the core (region III), the molecules are oriented parallel to the previous shearing direction as noted by the arrow

in +1 defect rotate also with the angle of θ whereas those in −1/2 defect with the angle of -2θ. This is the case in *Figures 1* and *4*.

It should be pointed out that a similar phenomenon has been found by Pratibha and Madhusudana[29]. In that paper, they reported a +1 point defect with radial alignment and a ring disclination of strength +1/2. Besides the types of defects, their sample was also different from ours. Their system was a mixture of two kinds of low molecular LCs, and was observed in the fluid state. In contrast to this, our system is composed of one type of rod-like macromolecules, PPTA, and is observed in the solid state with the frozen LC phase formed after precipitation. The extinction pattern in their observation was also different. Hence, the present paper reports a novel extinction pattern in polymers.

We shall describe qualitatively the mechanism of the formation of the supermolecular structure as indicated in *Figure 3* Our assumption is based on the fact that subjected to shearing, the rod-like macromolecules, PPTA, are oriented uniformly along shearing direction and a monodomain is macroscopically formed whereas some small defects and impurities still remain. Due to the high viscosity and the fastness of the precipitation (less than 1 s), most of the aligned molecules cannot be relaxed to the structure in

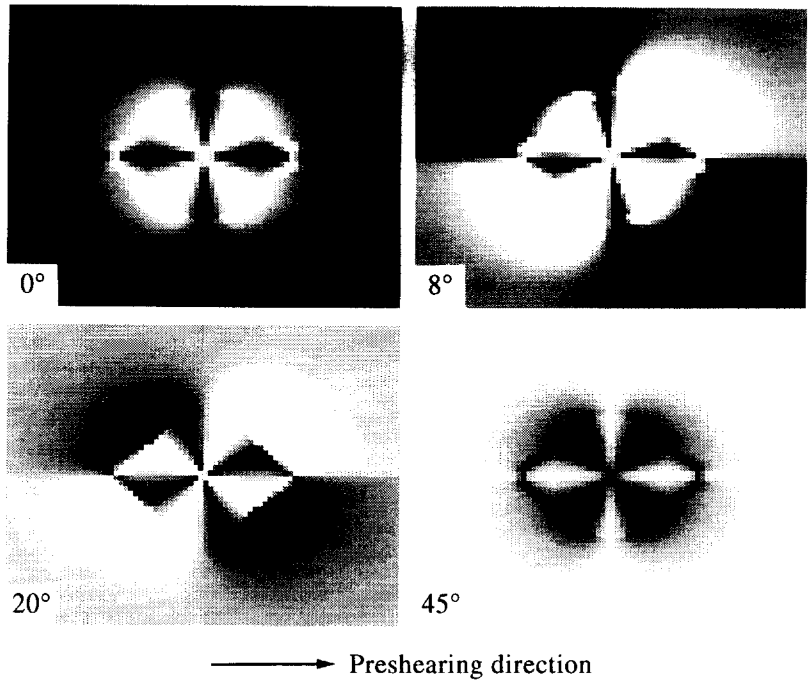

Figure 4 Calculated birefringence patterns of the entity with the supermolecular structure presented in *Figure 3*: (a) in orthogonal position under crossed polars; (b)–(d) anticlockwise rotation of both polarizer and analyser from this position by the noted angles. The shearing direction is along horizontal and indicated by the arrow

equilibrium, which makes the matrix anisotropic and forms the region III. Meanwhile, in some places with defects or impurities, the nucleation can take place easily, and region I is therefore, formed with a +1 defect. Region II with one pair of −1/2 defects is the reasonable result in order to achieve the smooth transition between region I and region III, although this region is not as ideal as that indicated in *Figure 3* and in fact, only a pair of loose −1/2 defects are included. Due to the high viscosity and the fast precipitation, the paired singularities are frozen and the defects annihilation is prevented. Such a mechanism is, of course, rather rough, and some questions are still open. For instance, it is also possible that region I is a spherulite growing around a defect or an impurity, although it might not alter the optical director configuration of the system since, according to many experiments[33,34], the crystals formed from a nematic phase keep the global chain orientations in the systems. The extensive investigation is desired, together with many other questions such as the degree of

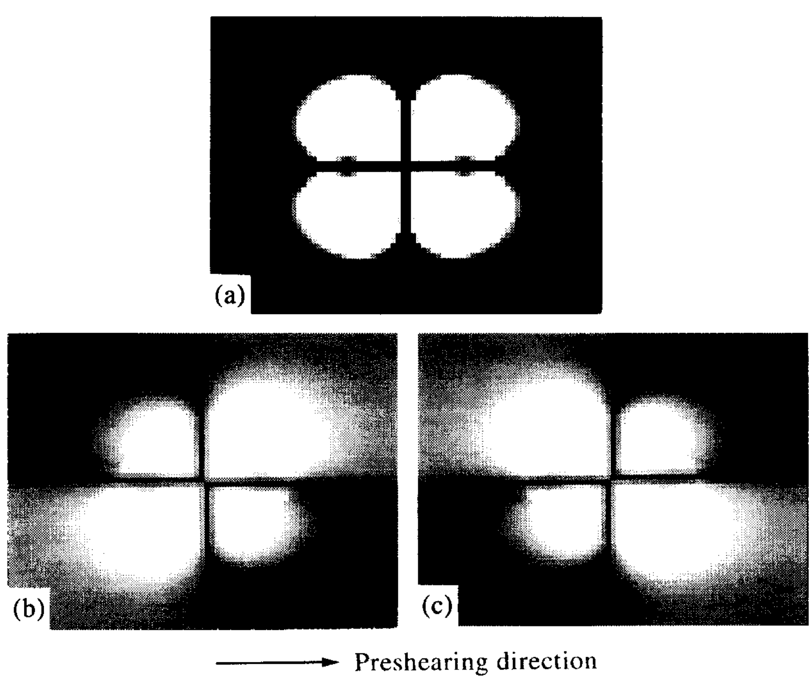

Figure 5 Calculated compensating effect: (a)–(c) corresponding to *Figures 2a–2c*, respectively. The entity is the rotation body of the supermolecular structure presented in *Figure 3* around the connection line through the defects. The retardation for the entity is assumed to be 0.4 μm while that for the compensator is assumed to be 0.02 μm

liquid crystallization in three regions, the effect of the remaining water and sulfuric acid on the anisotropic entity, etc.

CONCLUSIONS

We have studied a popular kind of rigid macromolecule, PPTA, which forms a lyotropic polymeric LC in concentrated sulfuric acid. The present topic is about the precipitation film, in which the loop-like extinction is observed in a polarizing microscope under crossed polars. The corresponding supermolecular structure is assumed and comprises three regions: region I is a core of nematic droplet with a $+1$ point defect; region II and region III are solidified LCs, where region II is composed of a pair of loose $-1/2$ defects and region III refers to the anisotropic matrix resulting from the memory of shearing history. The analyses of the structure coincide with those of experimental observations very well. The theoretical birefringence patterns have also been calculated and find good agreement with polarizing micrographs. The formulation mechanism of this structure is further put forward qualitatively.

The key to the occurrence of the loop-like extinction is, in our opinion, an anisotropic core immersed in an anisotropic and parallel-orientated matrix, no matter whether the core is a spherulite or an LC droplet, and whether the anisotropic matrix is induced by shearing, elongation or even residue stress. On the other hand, the loop- like extinction may be employed to study the factors mentioned above. The authors believe that such a phenomenon could be found in many cases besides the PPTA film, only if the researchers had a prepared head.

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