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Polymer 45 (2004) 2309–2312

polymer

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High strength disclinations in liquid crystalline polymers with X-shaped two-dimensional mesogenic units

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Received 2 December 2003; received in revised form 21 January 2004; accepted 22 January 2004

Abstract

Textures of liquid crystalline polymers with two-dimensional mesogens have been investigated by using polarizing optical microscopy. Disclinations, strength $|S|$ up to 3/2 and 5/2, were found easily in each sample. Occasionally, even high strength disclination pair can be found. These high strength disclinations are very sable in high temperature although they are energy unfavorable according to the theory of Nehring and Saupe. The rare textures may be ascribed to the unique shape of the molecular mesogenic units. The stability of the high strength disclination is attributed to the energy dispersion and high viscosity in polymer melt.

Keywords: High-strength disclination; Textures

1. Introduction

It is well known that nematic liquid crystals (LC) show schlieren textures when they are heated above the melting point, which can be observed by polarized optical microscopy (POM). Usually thread textures can be observed when a comparatively thick layer (more than 100 μm in thickness) of nematic liquid crystals is examined under POM. In the case of a thin layer, say 10–100 μm in thickness, of nematic liquid crystals, schlieren texture can be observed, in which singular points with dark brushes of extinction emanate from these points. Rotating the cross polarizers with respect to the samples will cause 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 disclination [1,2]. The strength of the disclination can be simply defined as $|S| = N/4$, where N is the number of the dark brushes of the corresponding disclination. The strength of disclination $S = \pm 1/2$ and ± 1 can always be observed. By contrast, high strength disclinations ($|S| > 1$) are difficult to be observed because the elastic distortion energy of the disclinations is proportional to S^2, and the disclinations become unstable with the increase of $|S|$ [2].

However, to date, there are a few references related to the observation of high strength disclinations in mixtures of low mole mass thermotropic and lyotropic liquid crystals because of their instabilities [2–5]. The disclinations are not independent, they may interact and extinguish one another so that the phase can achieve a state of minimum tension. Recently, stable high strength disclinations of small-molecular liquid crystals in single component system were found by Cui [6] and Li [7], respectively.

To our knowledge, high-strength disclinations were seldom to be found in thermotropic liquid crystalline polymers (LCPs) [8]. Zhou [9] and Song [10] have reported high-strength disclinations ($|S| = 3/2$, 2 and 5/2) in LCPs with T-shape two-dimensional mesogenic units, respectively. Disclinations of strength up to 3/2 and 2 were observed in liquid crystalline polyacetylene when the rotational force was applied to the sample [11]. High-strength disclinations in smectic mesophase have been found in a series of new LCPs having chiral center and dipolar groups isoregically arranged along the polymers backbones [12].

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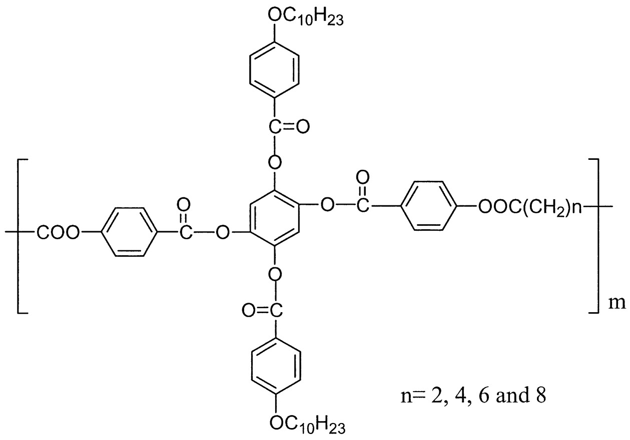
doi:10.1016/j.polymer.2004.01.041

In a previous work [7], we investigated the liquid crystalline behaviors of the homologous series of 2, 5-bis(*p*-*n*-alkylenedioyloxy)hydroquinone (ADHQ) and found that ADHQ can form stable high-strength disclinations in both nematic and smectic mesophases without induction of hydrogen bonds or the aid of other components, beyond *p*-*n*-pentoxy. So it was decided to study the liquid crystal textures of X-shaped LCPs containing ADHQ mesogenic units in the main chain. Up to now, only a few LCPs with bilaterally linked mesogens have been reported. This type LCPs are expected to exhibit interesting bilateral phase properties [13–15].

In this context, we would like to present the observation of high strength disclinations ($|S| = 3/2$ and $5/2$) of the novel kind of polymers in nematic mesophase.

2. Experimental

The LCP samples used in this work are four thermotropic aromatic polyesters with X-shape two-dimensional mesogenic units and have the following molecular structure (sample A, $n = 2$; sample B, $n = 4$; sample C, $n = 6$; sample D, $n = 8$).



The synthesis and properties of the samples have been described in detail elsewhere [16]. Their respective peak temperature (in °C) of the melting and clearing transition as determined with a Shimadzu DSC-50 instrument and a heating rate of 10 °C/min are 96 and 181 °C (enthalpies of the phase transition $\Delta Hi = 5.8$ J/g) for sample A; 93 and 177 °C ($\Delta \mathrm{Hi} = 4.0$ J/g) for sample B; 105 °C and 175 °C ($\Delta \mathrm{Hi} = 4.5$ J/g) for sample C; 116 °C and 168 °C ($\Delta \mathrm{Hi} = 4.2$ J/g) for sample D.

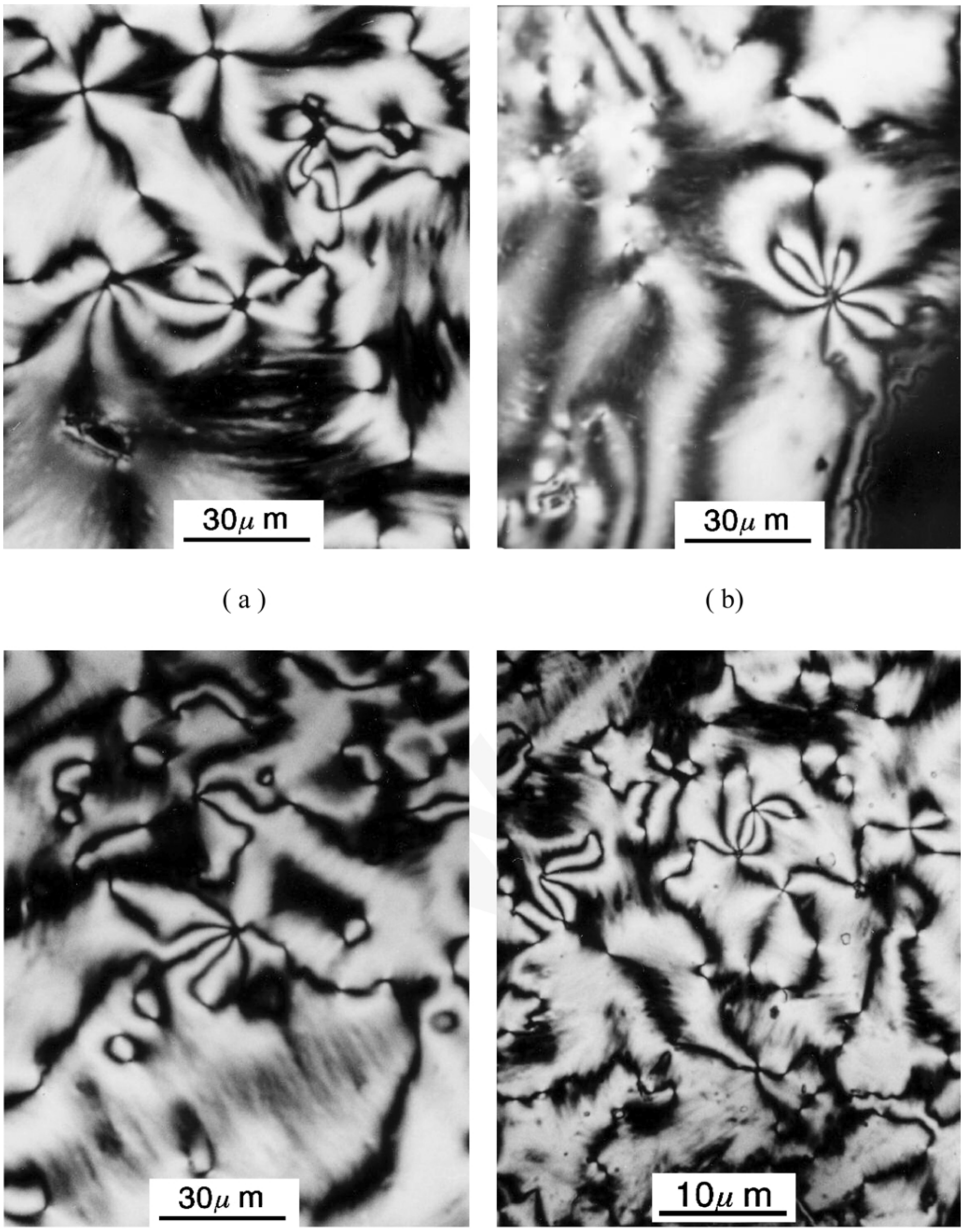
The glass slides were soaked in concentrated nitric acid for at least one day, then washed by acetone, and used without any other surface treatment. The samples were sandwiched between two glass slides and observed by Olympus polarizing microscope (BH-2) equipped with a Mettler FP-52 hot stage. The temperatures at which the photos were taken are noted in the captions of the figures.

3. Results and discussions

All the samples show strong birefringence and typical nematic schlieren textures under POM above melting temperature The textures are observed when the sample is cooled from the isotropic state to the nematic mesophase. Two types of schlieren defects, simple disclination and complex disclination, in nematic have been reported. Generally, there is a simple relation between the strength S of the defects and the number *N* of dark brushes as $|S| = N/4$. While the relation between the strength *S* and the number of the dark brushes *N* of complex defects is complex [17,18]. By using a quartz wedge in the polarizing microscope, it is indicated that the observed defects in our samples are simple disclinations.

Although high strengths disclinations are energy unfavorable [2], they can be easily found in our samples. Disclinations of strength up to 3/2 and 5/2 in nematic mesophase are observed as shown in Fig. 1(a)–(c). Occasionally, even high strength disclination pair can be found. A pair of disclination of $S = \pm 3/2$ is shown in Fig. 1(d). By comparison with the liquid-crystalline state of low-molecular-weight compounds [5], the high strength disclinations of all the samples are quite stable. They can persist for a long time at the temperature range of nematic mesophase and even be kept as the nematic glass state by quenching the samples at room temperature. So it is easy for us to determine the sign of disclinations by rotating the cross polarizers. If the dark brushes rotate in the same sense as the rotation of the polarizers, the sign of the singularity is positive, whereas negative. All these multiple dark brushes of a schlieren texture do not break up and keep constant number when rotating the crossed polarizer. It is safe to say that the high-strength disclinations are genuine ones but not the aggregate neighboring singularities [10].

The stability of high strength disclinations in the mixtures of low mole mass liquid crystals is attributed to the surface tension gradient at the interface with the submicroscopic droplets [2] or concentration gradients [3]. High strength disclinations induced by hydrogen bond benefited from the phase separation and isotropic areas formation [6]. In our case, a close examination shows that the high strength disclinations are not independent of each other and most of them connect with their neighboring disclinations of lower strength, with the opposite sign of S. The sum over the *S* numbers of all singularities in the local area tends to be zero; therefore, the energy of the system is the lowest [2]. So the high disclination is stabilized by connecting lower strength disclinations or defects with opposite sign in this study. In our previous work, it was found that high strength disclinations up to 3 and 4 in low molecular mass single component system could be stabilized by this means because of energy dispersion [7].



(a) (b)

(c) (d)

Fig. 1. Polarizing optical microscope micrograph of schlieren textures of (a) sample A at 135 °C, a disclination of strength +3/2; (b) sample B at 136 °C, a disclination of strength −5/2; (c) sample D at 138 °C, a disclination of strength +3/2; (d) sample C at 140 °C, a +3/2 and −3/2 pair of disclination.

It is demonstrated that how a high strength disclination is stabilized by the connecting lower strength disclinations in Fig. 2(a) and (b). In the two figures, a point singularity with six dark brushes and two point singularities with four dark brushes were observed. Again Fig. 2 (b) was obtained after the stage had been rotated anticlockwise by 45° relative to the position of Fig. 2(a). The six-brush singularity can serve as a reference point; we can determine the sign of the singularity conveniently. So the multiple brushes singularity has an S of +3/2, while the two point singularities with four brushes have an S of −1 according to Nehring and Saupe [2]. Further observation shows that the rotation rate is slower for the six brushes than that of the 4 brushes. This result is also in agreement with the theory of Nehring and Saupe [2].

These high-strength disclinations show broad cores and the radii of the cores increase with increasing disclination strength, which agrees well with Nehring and Saupe's theory and facilitate the energy dispersion [2].

We have found that high strength disclinations in smectic

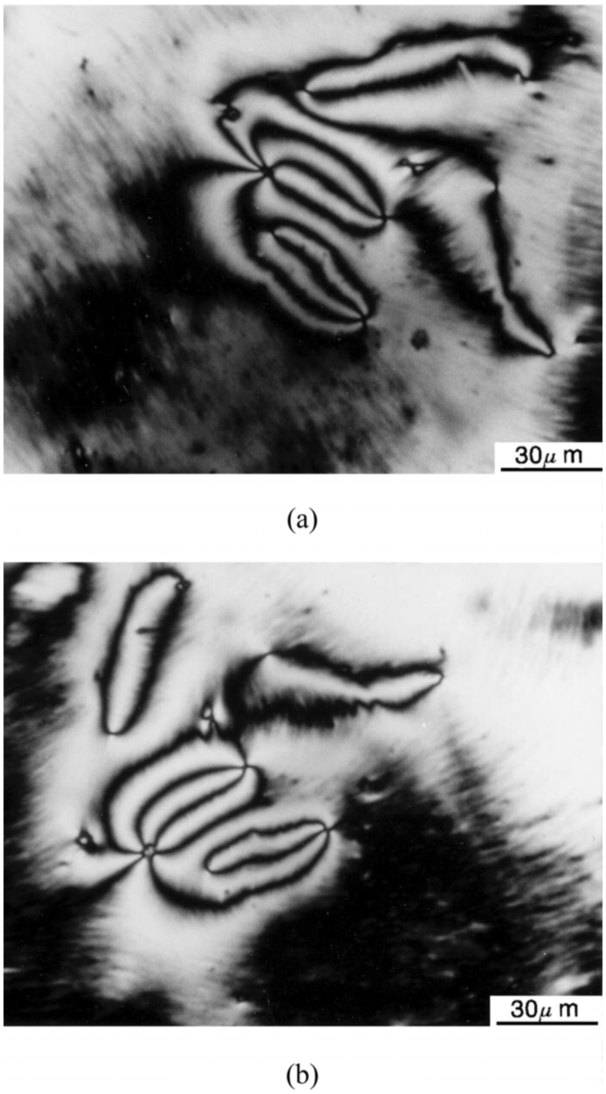


Fig. 2. Schlieren textures of sample D with point singularities with six brushes ($S = +3/2$) and four brushes ($S = -1$). From (a) to (b), the stage was rotated clockwise by 45°. The photos were taken at 145 °C.

mesophase could last longer time than that of in nematic mesophase because of high viscosity in the former [7]. Usually, polymer LC melt has much higher viscosity than low molecular mass liquid crystal. The high viscosity can hinder the motion of singularities to keep from annihilation. It is speculated that this is another reason that high strength disclinations can be stabilized [19,20].

In conclusion, high strength disclinations with six or ten dark brushes have been found in single-component nematic mesophase of LCPs with X-shaped two-dimensional mesogenic units. This relatively easy formation of the rare textures is ascribed to the unique shape of the molecular mesogenic units. These high strength disclinations are very stable even in high temperature which is attributed to the energy dispersion and high viscosity in polymer melt.

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