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Temperature effect on the rubbing-induced optical phase retardation of a side group liquid crystalline polymer film

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Recently we observed an unusual temperature dependence of the pretilt angle of a nematic liquid crystal generated at the rubbed surface of a side group liquid crystalline polymer film. To understand the mechanism, a detailed investigation of the temperature effect on the rubbing-induced optical phase retardation of a side group liquid crystalline polymer film has been carried out. On heating the film above the glass transition temperature of the polymer, a clear change is seen in the temperature dependence of the optical phase retardation. We infer from this investigation that the thermal variation of the rubbing-induced optical phase retardation results in a change in the temperature variation of the pretilt angle.

1. Introduction

Liquid crystalline polymers attract much attention, mainly because they possess the properties of both liquid crystals (LCs) and polymers. In fact, LC polymers are being widely considered as potential media for optical data storage and fabrication of optical components. In addition, LC polymers are currently emerging as good orientation layers [1–4] for aligning molecules in a display cell. Orientation layers are essential to achieve defect-free homogeneous alignment of the LC molecules.

It is a matter of common understanding that defect-free alignment of LC molecules over a large area is a prerequisite for the efficient functioning of various types of liquid crystal display (LCD) [5]. Among the various parameters affecting the LC alignment, the most important is the pretilt angle which is defined as the angle subtended between the nematic director and its projection on the surface of the substrate. A non-zero pretilt angle is indispensable to avoid the creation of reverse tilt disclination defects in the twisted nematic (TN) device mode. High pretilt angles are needed to prevent the occurrence of two-dimensional stripe instabilities in supertwisted nematic (STN) displays and the formation of zigzag defects in surface stabilized ferroelectric liquid crystal (SSFLC) displays. As a result there is a growing demand for materials exhibiting high pretilt angles.

Recently, we have shown [2] that a high pretilt angle can be realized at the rubbed surfaces of side group liquid crystalline polymers (SGLCPs). Interestingly, pretilt angles generated at these rubbed surfaces exhibit an unusual temperature dependence [6]. This warranted thorough experimental investigation to understand the actual phenomena behind this temperature dependence of the pretilt angle. It is known that orientation of the polymer chains is achieved by a rubbing process, and Geary *et al.* [7] experimentally verified this by measuring the rubbing-induced optical phase retardation. Also, Van Aerle *et al.* [8] have shown the correlation between the induced optical phase retardation (ϕ) and the pretilt angle (θ) generated at the rubbed surfaces of polymer orientation layers. It seemed of considerable importance to know the effect of temperature on ϕ, but to the best of our knowledge, no such studies have hitherto been performed. In this paper we present the result of a study on the effect of temperature on ϕ for a rubbed SGLCP film.

2. Experimental

The side group polymer 2-[4-(4-cyanophenoxycarbonyl)phenoxy]ethyl acrylate (LCP 100) was obtained from Merck. The molecular structures of LCP 100 is given in figure 1. The polymer was dissolved in tetrachloroethane (2 wt %). Solid material in the solution was made to dissolve by subjecting it to magnetic stirring

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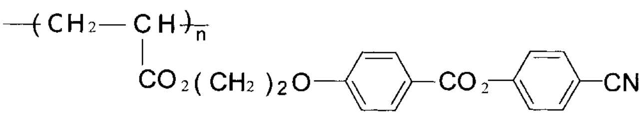

Figure 1. The molecular structure of side group liquid crystalline polymer LCP 100.

at room temperature for a long time. Millipore filter (0.5 μm pore size) was finally used to filter the solution. The filtered solution was then spin coated onto the glass substrates. The film was baked at 150°C for 30 min to evaporate the solvent and then annealed for 4 h at a temperature very close to the clearing temperature of the LC polymer. The thickness of the films was measured using a surface profilometer and found to be typically 100–200 nm. The surface of the film was then rubbed unidirectionally using a rayon cloth. Empty cells were then fabricated; typically the cell thickness was about 65 μm. The crystal rotation method [1] was used to measure θ. The monomeric LC material TL 205 from Merck was used for θ measurements.

We measured ϕ using a set-up similar to that described by Lim and Ho [9]. A glass plate coated with LCP 100 was used as the sample for the ϕ measurements; the coated surface was unidirectionally rubbed using a rayon cloth. To vary the temperature of the sample, it was placed inside a specially designed heater. During measurements, the sample temperature was controlled very precisely, its stability being better than 10 mK.

3. Results and discussion

We have previously reported [6] the temperature dependence of θ for LC molecules in the nematic phase, and figure 2 shows a plot of the temperature variation of θ for the LC material TL 205. The most interesting feature is that θ shows an unusual temperature behaviour. To begin with θ showed a high tilt value over a range of temperature and was seen to be nearly temperature independent. On increasing the temperature further, θ started to decrease, but from 70°C onwards it was again temperature independent with a low tilt value. However, in the vicinity of the nematic to isotropic (N–I) transition of the LC material TL205, θ decreased drastically to zero. On cooling the LC material from the isotropic phase, θ increased from zero and then became stabilized at the low tilt value. Microscopic observation of the optical textures showed a clear change in the alignment after heating the sample. One plausible explanation for this behaviour is that the polymer surface morphology is affected by the higher temperatures.

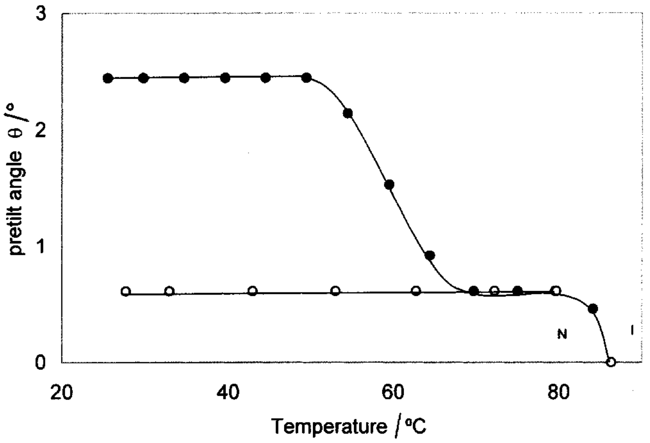

Figure 2. The thermal variation of θ for LC material TL 205 aligned on a rubbed surface of LCP 100. The material is filled into a cell of thickness about 65 μm. The N–I transition temperature for LC material TL 205 is at 87°C. Here, ● and ○ represent the data obtained on heating and cooling, respectively. Solid lines are only a guide to the eye.

In order to find the effect of heating the rubbed surface of LCP 100 on the value of θ generated, we carried out the following experiments. Empty cells were heated to 50, 60, 70, 80, 90 and 100°C, for about 15 min. After cooling the cells to room temperature, the LC material (TL 205) was injected into each cell; then θ was measured using each of these cells. A plot of θ as a function of the temperature to which the LCP 100 had been heated before injection of the LC material into the cell is shown in figure 3. It can be seen from this figure that θ showed a temperature dependence of more or less similar shape to that seen in figure 2. However, the rate of decrease of θ and the overall decrease in θ are seen to be less in figure 3 than in figure 2. The drastic decrease of θ in figure 2 may be due to the interaction of the LC molecules with the visco-elastic phase of LCP 100 at higher temperatures. It can be seen from both the figures

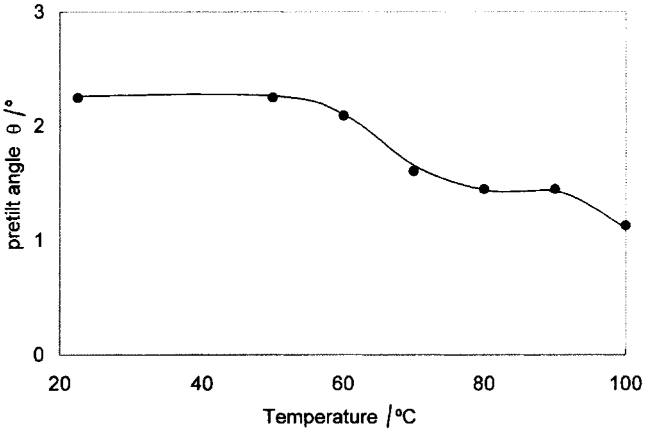

Figure 3. A plot of θ as a function of the temperature to which the empty cells were heated prior to filling with LC material TL 205. Empty cells were fabricated using two glass substrates, the inner surfaces of which were coated with LCP 100. The thickness of the empty cell was about 65 μm. The solid line is a guide to the eye.

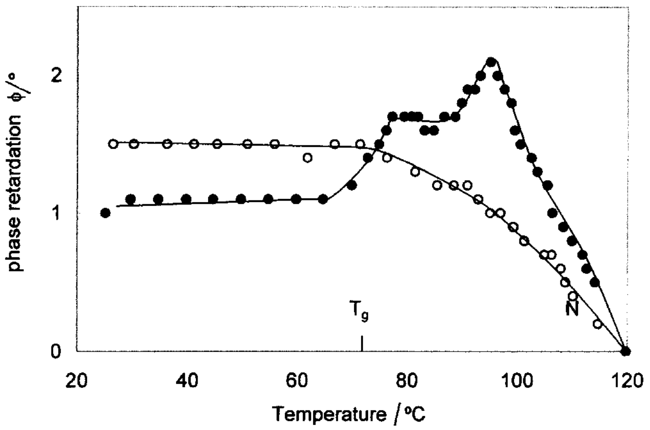

Figure 4. Temperature variation of ϕ for the rubbed thin film of LCP 100. The sample consisted of a glass plate coated with LCP 100, the coated surface being unidirectionally rubbed using a rayon cloth. Here, ● and ○ represent the data obtained on heating and cooling, respectively. Solid lines are a guide to the eye.

that at a particular temperature, which happens to be the glass transition temperature (T_g) of LCP 100, θ shows a change in its temperature dependence. It appears then that reorientation of the polymer chain could be one reason for the temperature variation of θ.

To ascertain this we undertook the measurement of effect of temperature on the rubbing-induced ϕ of thin LCP 100 films. As mentioned above, LCP 100 was spin coated onto the glass substrate and the surface was rubbed unidirectionally using a rayon cloth. Figure 4 is a plot of ϕ as a function of temperature. This figure has the following interesting features:

(1) ϕ is nearly temperature independent in the glassy state;
(2) temperature dependence for ϕ is seen above T_g (marked on the baseline);
(3) on nearing the clearing temperature, ϕ decreases drastically, finally reaching zero at the transition temperature (120°C);
(4) on cooling the film from the isotropic phase, ϕ increases slowly and gradually tends to saturate in the glassy state.

It can be seen that on heating the film above T_g, ϕ increases in the nematic phase. This increase in ϕ could be associated with the reorientation of the polymer chains and this would result in an increase in the structural anisotropy of the surface layer. For the same reason, the value of ϕ in the glassy state for the film cooled from the isotropic phase is more than that for the film before heating. This supports our earlier inference that polymer chain reorientation takes place in the nematic phase and results in a change in the thermal behaviour of ϕ. Similar observations have been made by Ivanov *et al.* [10]. They observed an increase in the induced birefringence on heating from the glassy state in the nematic phase of photochromic comb-shaped LC copolymer films.

The increase in the value of ϕ on heating the film above T_g could be associated with the increase in the chain orientational order. Consequently, θ shows a temperature variation. Van Aerle *et al.* [8] have shown that there exists a correlation between ϕ and θ. In the light of the above discussion we believe that the thermal variation of ϕ is primarily responsible for the change in the temperature dependence of θ at higher temperatures.

In conclusion, on heating the film above T_g, ϕ shows a clear temperature variation. In the nematic phase, ϕ is increased considerably, and this can be associated with chain reorientation. It is known that there is good correlation between ϕ and θ; hence the temperature variation of ϕ results in a change in the temperature dependence of θ at higher temperatures.

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