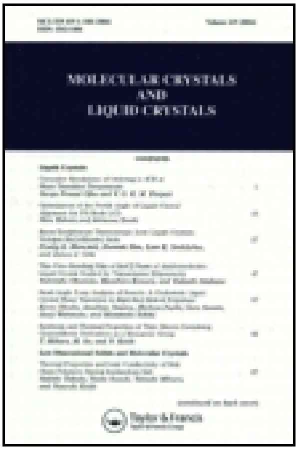

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Temperature Dependence of the Pretilt Angle Generated on the Rubbed Surface of a Side Chain Liquid Crystalline Polymer

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Temperature Dependence of the Pretilt Angle Generated on the Rubbed Surface of a Side Chain Liquid Crystalline Polymer

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While a wealth of data is available on the pretilt angle measurements at room temperature, there exist only a few reports on the temperature dependence of the pretilt angle. The present investigation is on the thermal variation of the pretilt angle of nematic liquid crystal molecules aligned on treated substrates. Glass substrates are coated with side chain-liquid crystalline polymer poly(4-cyanophenyl-4′-ethoxybenzoyloxy) acrylate (LCP100). An unusual temperature behavior is seen in way of two stable values for the pretilt angle (θ). As the temperature is increased θ changed from one stable value to another. On cooling the sample from the isotropic phase θ increased from zero to a second stable value and thereafter remained as a temperature invariant.

Keywords: Nematic, pretilt angle, temperature, side chain liquid crystalline polymer.

INTRODUCTION

It is well known that uniform alignment of liquid crystals over a large area is a prerequisite for the optimal performance of various types of liquid crystal display devices[1]. There are several surface alignment techniques[2–6] that are in practice to get such a homogeneous alignment. Among these, at present, the most viable method in LCD mass production facilities is the rubbing of the polymer layer. The resulting initial molecular tilt at the surface, the so called pretilt angle (θ), depends on many factors, like the conditions of rubbing. This angle is one of the important parameters of LCD's influencing their contrast, viewing angle characteristics, electro-optic properties and good display uniformity. Also, a non-zero pretilt angle is essential to avoid the creation of reverse tilt disclination defects in twisted nematic modes[7], occurrence of two dimensional stripe instabilities in super twisted nematic modes[8] and formation of zigzag defects in surface stabilized ferroelectric liquid crystal (SSFLC) displays[9]. Therefore, a considerable amount of interest is centered on the measurement of θ and the materials in which these angles are generated. As a

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result, there exists a large amount of data on the θ measurements at room temperature[10-17]. On the contray, very few reports[18-22] exist on the measurement of θ as a function of temperature.

Recently, liquid crystalline polymers are being extensively studied[23-26] as an orientation layer for LCDs. In fact, the efficacy of one such material as an alignment layer has already been shown by our group[23] for the SSFLC cell. In our previous paper[24] we showed that the high pretilt surface can be realized by rubbing side chain liquid crystalline polymer films. From this investigation we found that the surface pretilt angle depends on both the structures of the polymer used as an alignment layer and the liquid crystalline material. In this paper a more detailed experimental study on the temperature dependence of θ for nenatic liquid crystal molecules aligned on rubbed SCLCP films is described.

EXPERIMENTAL

We used side chain liquid crystalline polymer poly (4 cyanophenyl-4′-ethoxybenzoyloxy) acrylate (LCP 100) for the experiment. This polymer was obtained from Merck. The chemical structures along with the transition temperature are given in Figure 1. Tetrachloroethane solvent was used to dissolve LCP 100. Complete dissolution of the solid contents (about 2 wt%) was achieved by subjecting it to magnetic stirring at room temperature for a long duration. The solution was then filtered using a Millipore filter (.5 μm pore size) and spin coated onto the glass substrate. Then the film was annealed at 5 °C below the clearing temperature after baking it at 150 °C for 30 minutes. The surface of the polymer film was then rubbed using a rayon cloth after ensuring that the rubbing pressure is quite adequate to yield stable and good alignment. The thickness of the spacer used in the test cell is about 65 μm. Pretilt angle measurements were performed using crystal rotation method as described in our previous paper[24].

During the measurments the temperature of the sample was controlled very precisely by using a specially designed heater and the temperature stability is better than 10 mK.

We used four commercially available liquid crystalline mixtures (obtained from Merck) for the experiment. These mixtures are so chosen that the experiment could

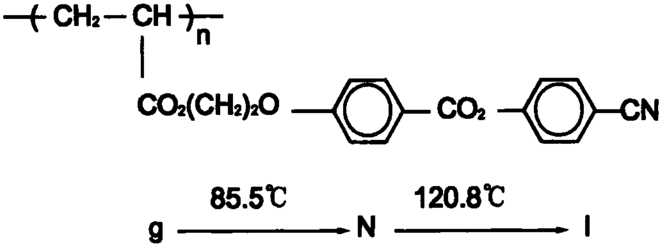

FIGURE 1 The chemical structure of side chain liquid crystalline polymer LCP100.

be performed using the crystal rotation method since the pretilt angles for these materials are less than 10 degrees. The N-I transition temperatures along with the values of average epsilon ($\bar{\varepsilon}$) for these mixtures are given in Table I.

RESULTS AND DISCUSSION

Figure 2 is a plot of the temperature variation of the pretilt angle (θ) for the LC material BL001 aligned on LCP100. Also shown for the sake of comparison is the data obtained for the LC material BL001 aligned on polyimide AL5417. Evidently on approaching the N-I transition temperature θ decreases. This observed decreas-

TABLE I

N-I transition temperatures and $\bar{\varepsilon}$ of various LC materials used for the investigation.

LC material	N-Itransition(°C)	$\bar{\varepsilon}$	$n_e + n_o$
BL001	60	9.80	3.268
ZLI2293	85	7.40	3.1302
ZLI1565	85	6.03	3.114
TL205	87	5.77	3.271

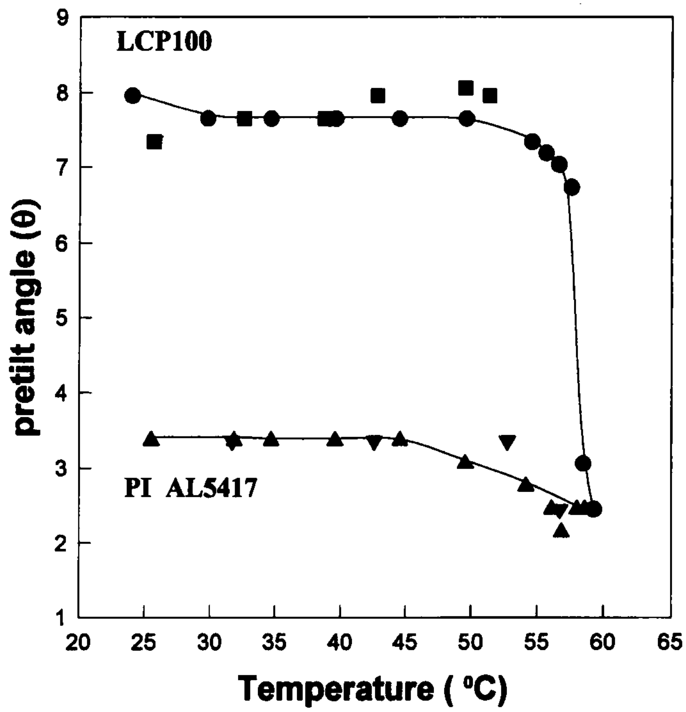

FIGURE 2 Temperature variation of θ for the LC material BL001. Here ●, ▲ represents the data in the heating mode and ■,▼ represents the data in the cooling mode. Solid lines are a guide to the eye.

ing tendency in θ is in very good agreement with the earlier reports$^{18-21}$. However, Han and Uchida^{22} have seen a reversed tendency. The overall variation in θ looks to be identical for both LCP100 and PI AL5417. It is also significant to notice that on cooling the sample from the isotropic phase no change in the temperature behavior of θ was seen, implying thereby that the surface morphology of the polymer was not affected by heating it up to 60 °C.

To see whether the LCP100 surface morphology is affected on heating it to higher temperatures we carried out the following studies. We measured θ as a function of temperature for three more LC materials for which the N-I transition temperature is above 85 °C, as can be seen from Table 1. In Figure 3 we show the temperature variation of θ for the LC material TL 205. The most striking feature in this diagram is that θ shows an unusual temperature behavior and is the first of its kind to be reported. Up to a certain temperature θ appears to be nearly temperature independent and showed a stable value $\theta_1(\theta_1 = 2.4$ degrees). Then θ starts decreasing although a bit slowly and at around 70 °C settles down to another stable value $\theta_2(\theta_2 = 0.6$ degrees). On further heating θ decreased drastically to zero at the vicinity of the N-I transition. On cooling the sample from the isotropic phase, θ increased and then got stabilized at the θ_2 value. It remained as a temperature invariant even up to room temperature. In other words, θ did not increase to θ_1 value even when cooling it down to room temperature. It is quite significant then to notice that the temperature behavior of θ is different for heating and cooling modes. This probably indicates that the polymer surface morphology must have been affected because of the interaction of the LC molecules with the LCP at higher temperatures. In order

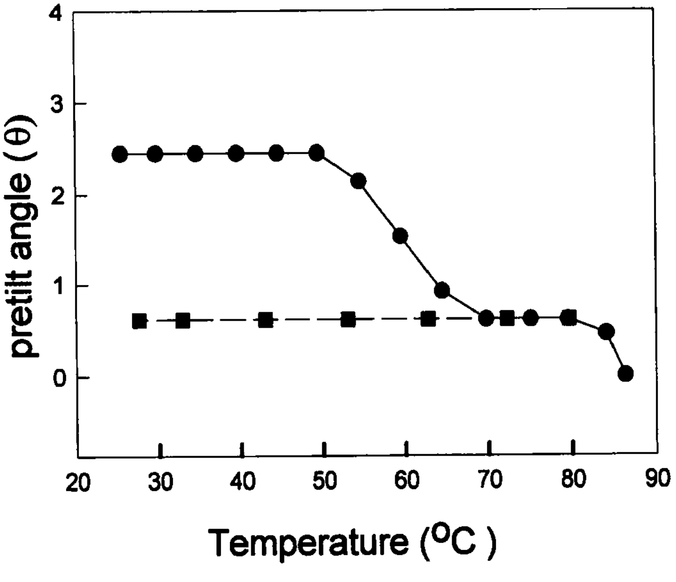

FIGURE 3 Thermal variation of θ for the LC material TL 205 aligned on rubbed surface of LCP100. Here ●, ■ represents the data in the heating and cooling modes respectively. Solid lines are a guide to the eye.

to find out whether the bulk alignment of the sample has been affected we looked at the optical texture of the sample that had been heated to a higher temperature using a polarizing microscope in the orthoscopic condition. We compared it with the quality of the sample alignment that it showed before heating. A clear change in the sample alignment was seen. The sample alignment certainly had gone bad by heating it to higher temperatures as is evident from Figure 4.

Similar temperature behavior was seen for the LC material ZLI 2293 and ZLI 1565. In order to know whether the temporal behavior of θ depends on the LC material a plot carrying the θ variation for all the studied LC materials is shown together in Figure 5. Evidently the total variation and the rate of variation of θ with temperature increases with the increase in the initial value of θ which in turn depends on the $\bar{\varepsilon}$ of the LC materials, a result that is in conformity with our earlier observations[24]. More precisely, in the temperature range below 60 °C, the pretilt angles depend strongly on the LC materials used. However, no such systematic material dependence for θ is seen at higher temperatures (> 60 °C). It coluld be seen that at higher temperatures θ decreases appreciably to a very low value. As mentioned earlier, microscopic observation showed a clear change in the sample alignment indicating that the surface morphology of the polymer has changed at higher temperatures. This could then be one plausible reason for the observed behavior of θ at higher temperatures (> 60 °C).

It should be remarked that very recently Han and Uchida[22] have studied the temperature variation of θ for the LC molecules aligned on both main chain and side chain ployimides. They observed θ to vary with the increase in temperature and decrease irreversibly on decreasing the temperature to room temperature. This irreversible change is larger for those LC materials possessing a larger dielectric constant. They attributed this change to the change in the polymer morphology at the surface caused by the solvent effect of LC. Furthermore LCs with a large dielectric constant show a strong solvent effect because of the strong interaction between the

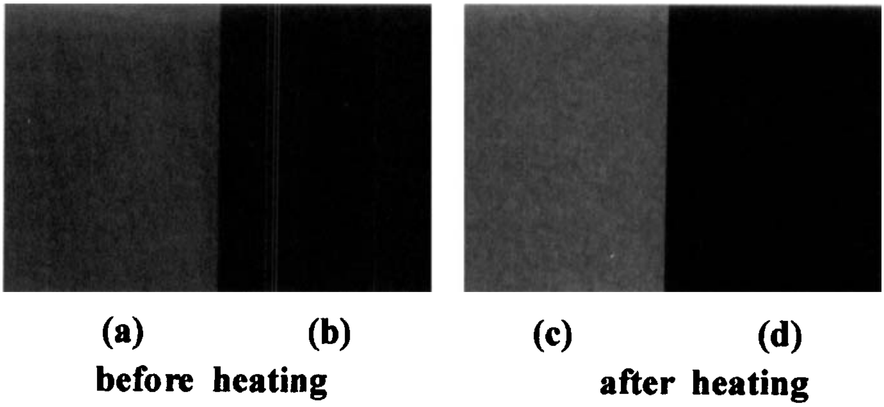

FIGURE 4 Microscopic photograph of the optical texture seen under a polarizing microscope. Here (a) & (c) correspond to the pictures taken when the rubbing direction is at 15 degrees to the polariser and (b) & (d) represent the pictures taken when the rubbing direction is parallel to the polariser. See Color Plate XI.

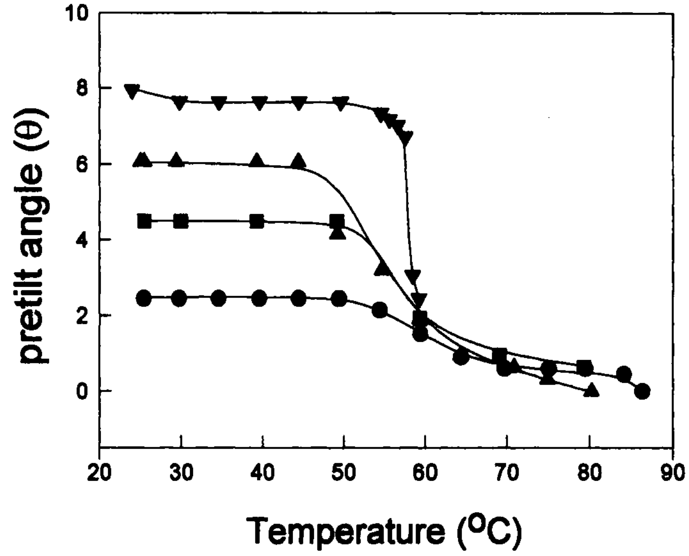

FIGURE 5 Temperature variation of θ for the LC materials in the heating mode. Here the symbols represent the data for ▼-BL001,▲-ZLI2293,■-ZLI1565 and ●-TL205 respectively. Solid lines are a guide to the eye.

polymer and the LC molecules. Their observed change in θ for heating and cooling modes is in close agreement with our experimental findings.

CONCLUSIONS

We have carried out a precise measurement of temperature dependence of the pretilt angles for the nematic liquid crystal molecules aligned on the rubbed surface of side chain polymer LCP100. An unusual temperature behavior is seen for the pretilt angle in the sense that it varied from one stable value to another on heating the LC material. On cooling it got stabilized at the second stable value and thereafter it remained as a temperature invariant. Microscopic observations reveal that the sample alignment goes bad after heating the LC material to high temperature. This probably indicates that the LCP surface morphology has changed because of the strong interaction between LC molecules and the polymer at high temperatures. For a clear understanding of these phenomena many other experimental data are needed, towards which some work is in progress.

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