Rubbing induced orientation of a side chain liquid crystalline polymer with high pretilt angle

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Rubbing induced orientation of a side chain liquid crystalline polymer with high pretilt angle

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We have investigated the pretilt angle generated in the nematic phase of different liquid crystal materials aligned on side chain liquid crystalline polymer films. High pretilt angles (> 10 degrees) can be achieved by unidirectionally rubbing the liquid crystalline polymer layers. We have also measured the anchoring strengths of these aligning films. The results of our studies indicate that the pretilt angle and the anchoring energy are found to depend in a systematic way on the liquid crystal material and also on the chemical structure of the liquid crystalline polymer films.

1. Introduction

Recently there has been a surge of activities in the field of liquid crystal displays in understanding the surface mediated liquid crystal alignment. Electro-optic performances of the majority of the LCDs such as twisted nematic (TN), supertwisted nematic (STN) and ferroelectric liquid crystal (FLC) displays depend strongly on the surface alignment of the liquid crystal (LC) molecules. As a matter of fact, one of the criterion for the optimal performance of many such displays is to have the homogeneous, defect free alignment of the LC molecules. In order to get such a homogeneous alignment of the LC layer various surface alignment techniques are in practice, like rubbed polyimide (PI films) [1], oblique evaporation of SiO films [1], PI Langmuir–Blodget films [2], polypyrrole films [3], polarized light irradiated polymer films [4] and also films whose surface is structured with microprocessed grooves [5]. However, at present the method that has been found to be the most practicable for many of the display mass productions is the rubbing of the polyimide layers. One of the most disadvantageous feature regarding these conventional polyimide materials is that they possess very high curing temperatures and hence limit their application in the LCD fabrication technology. Therefore, it is neces-

sary to look for alternate alignment layers for aligning LC molecules.

In this regard, we started investigating liquid crystal polymer (LCP) film as an alignment layer as LCPs have the properties of both the liquid crystals and the polymers. In fact, the efficacy of such an alignment layer has been shown by our group [6] for the surface stabilized ferroelectric liquid crystal (SSFLC) cell. Recently, side chain LCPs (SCLCP) are being widely used as an potential media for the storage of the optical data as well as for optical components [7]. Also, SCLCPs have been used by Ohmura et al. [8], as an alignment layer in a FLC display and Murakami et al. [9], for aligning the nematic liquid crystal.

In the alignment of the LC molecules, it is necessary to give a pretilt angle to avoid the creation of the reverse tilt disclination defects in twisted nematic LCD modes. Controlling the pretilt angle of a liquid crystal alignment is very important in order to achieve display uniformity in LCDs. For the optimal performance of a STN display a high pretilt angle is required to prevent the occurrence of two-dimensional stripe instabilities in the LC. Also, in the case of a SSFLC cell, to realize a good bookshelf geometry the pretilt angle has to be high. However, it is very difficult to obtain a high pretilt surface. Various attempts [10–13] have been made in this direction but still there is a growing demand for materials with high pretilt angles owing to their technological importance. SCLCPs may be the best candidates for providing high pretilt angles as has been already reported [14, 15] in

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that high pretilt angles can be induced by rubbing the surface of side chain PI materials. In this paper we investigate the surface properties of rubbed SCLCP films by measuring the pretilt angles and the anchoring strengths for various liquid crystal materials in order to understand better their material dependence.

2. Experimental

Two types of side chain LCPs were used in the experiment. The chemical structure along with the transition temperatures are given in figure 1. The liquid crystal polymer poly(4-methoxy-4'-hexyloxy biphenyl) methacrylate (P1) was synthesized in our laboratory and the polymer LCP100–poly(4-cyanophenyl-4'-ethoxybenzoyloxy)acrylate (P2) was obtained from Merck. Both the LCPs were dissolved in tetrachloroethane (2 wt %). Solid contents in the solution were made to dissolve completely by subjecting it to magnetic stirring at room temperature for a long duration. The
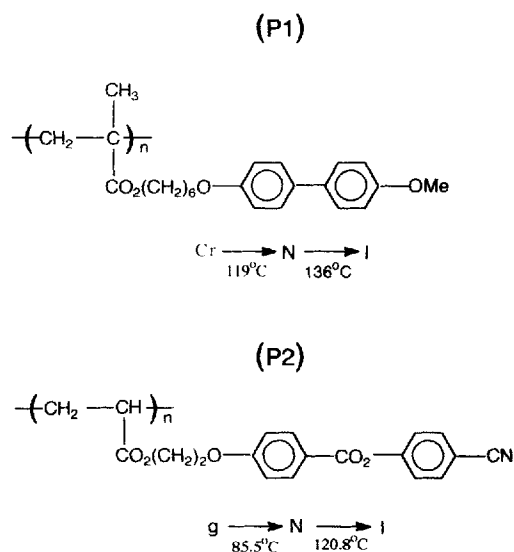

Figure 1. Chemical structures of poly(4-methoxy-4'-hexyloxy biphenyl)methacrylate (P1) and poly(4-cyanophenyl-4'-ethoxybenzoyloxy)acrylate (P2).

solutions so prepared were then filtered through a Millipore filter (0·5 μm pore size). The filtered solution was spin coated onto the glass substrate. The films were baked at 150°C for 30 min for the solvent to evaporate. The sample was then annealed for 4 h. The annealing temperature in each case was 5°C below the clearing temperature. The thickness of the films was measured using a surface profilometer and typically was found to be 100–200 nm. Films were then rubbed unidirectionally with rayon cloth after ensuring that the rubbing pressure was sufficient to yield good alignment. The cell gap in the test cell was about 65 μm. The crystal rotation method [16] was used for materials showing pretilt angles less than 10 degrees and the magnetic null method [17] for those showing pretilt angles greater than 10 degrees.

In order to estimate the polar anchoring energy, we used the 'high electric field technique' [18, 19] and measured the extrapolation length. A sinusoidal voltage was applied step by step from 0 V and up to 100 V. The capacitance (C) and the optical retardation (R) are measured simultaneously as a function of the applied voltage (V). We used the same cell that has been used to measure the pretilt angles as the cell thickness has to be quite high so as to work in the high voltage range in which the linear relation between R/R_0 and $1/CV$ holds where R_0 is the optical retardation for $V = 0$.

3. Results and discussion

The alignment of the LC material was first evaluated by looking at the optical texture of the sample using a polarizing microscope. We used only those cells which showed good homogeneous alignment throughout the sample. In all, we used seven commercially available liquid crystal mixtures (all obtained from Merck) for the determination of the pretilt angles. The mixtures were so chosen that there was a systematic variation in their physical properties. The measured pretilt angles along with the various physical properties for these materials are shown in the table. For each LC material, the pretilt angle was measured in three or four different places in

Pretilt angles and the various physical properties of the LC samples used.

| Sample | Pretilt angle | | Δn | $\bar{n}$ | $\Delta\varepsilon$ | $\bar{\varepsilon}$ | $\varepsilon_\parallel$ | $\varepsilon_\perp$ |
	P1	P2						
BL012	13·0	11·0	0·2616	1·624	15·70	13·30	23·80	8·1
BL036	11·2	9·0	0·2670	1·616	17·00	11·76	23·10	6·1
BL005	10·6	—	0·1900	1·580	15·80	11·37	21·90	6·1
BL001	10·3	8·5	0·2246	1·596	13·80	9·80	19·00	5·2
ZLI2293	8·8	5·4	0·1322	1·543	10·00	7·40	14·10	4·1
TL205	8·1	4·7	0·2170	1·599	5·01	5·77	9·11	4·1
ZLI1565	7·6	4·4	0·1297	1·535	7·00	6·03	10·70	3·7

the cell and the value given in the table is the average of these values. The fact that we observed good reproducibility in the pretilt angle measurements leads us to remark that the sample alignment is almost uniform throughout the cell. It can be seen from the table that the pretilt angle varies systematically with the average dielectric constant ($\bar{\varepsilon}$). Figure 2 shows the plot of pretilt angle against $\bar{\varepsilon}$ for the two polymers. The most striking features in the figure are as follows: (i) Both polymers show high pretilt angles. (ii) The pretilt angle for **P1** is found to be greater than for **P2** clearly indicating that the pretilt angle depends on the chemical composition of the polymer used as the alignment layer. (iii) The pretilt angles show a good correlation with the average dielectric constant ($\bar{\varepsilon}$). This is quite significant for it hints at the dipolar contribution towards the generation of the pretilt angles. (iv) In both cases the solid line in the figure is obtained by fitting the data. It is quite interesting to see that the above mentioned feature (iii) is reflected in both the polymers.

It is noted that quite recently Noh *et al.* [20], observed rubbing induced side chain alignment at the surface of an *N*-substituted aromatic polyamide film. They suggested that the induction of good alignment and high pretilt angle is closely related to the molecular structure of the side chain. This clearly supports our experimental results. Myrvold *et al.* [21], reported the studies on the relationship between the bulk properties of nematic liquid crystals and their pretilt angles. For all of the LC materials investigated by us, no exact structural data are available as they are commercial mixtures, hence a precise study of material dependence on the pretilt angle is difficult. However, the general trend of the pretilt angle depending on the presence of optical polarizing groups in the LC materials appears to be true in our experiment. Nishikawa *et al.* [13] have suggested from their studies that the pretilt angles in the polyimides are probably caused by the electrical interaction between
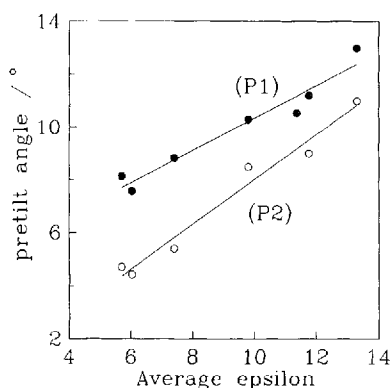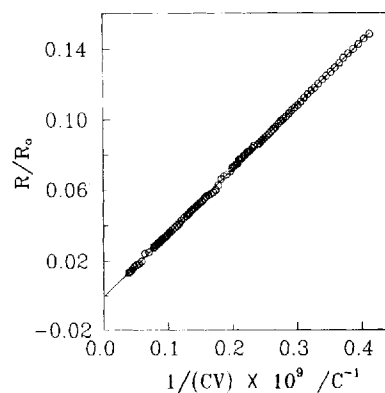

Figure 3. The plot of R/R_0 versus $1/CV$ for TL205 aligned on a rubbed **P2** film.

dielectric constant perpendicular to the director ($\varepsilon_\perp$) of LC and alignment layer and $\varepsilon_\perp$, hence is an important parameter in the determination of the pretilt angle. This is in very good agreement with our experimental findings.

Figure 3 shows the plot of R/R_0 versus $1/CV$ observed for the nematic LC material TL205 aligned on a rubbed **P2** film. The solid line in the figure is obtained by a linear-least-squares fitting of the data. The extrapolation length has been deduced from the intercepts with the ordinate axis. Using the extrapolation length thus obtained and knowing the splay elastic constant of the LC material the polar anchoring energy is calculated. The polar anchoring strengths of these SCLCP rubbed films are seen to be quite strong. We have observed the extrapolation length in the case of rubbed **P1** films to be nearly zero indicating strong anchoring. The polar anchoring energy measured for the **P1** film is of the order of $3 \times 10^{-3}\,\mathrm{J\,m^{-2}}$ and is at least one order of magnitude greater than that of the **P2** film. Hence, it is clear that the polar anchoring energies of these rubbed films depend strongly on the chemical structure of the alignment layer.

Figure 4 shows the plot of extrapolation length versus $\bar{\varepsilon}$ of some of the nematic LC mixtures aligned on rubbed **P2** film. It is interesting to see that the extrapolation length varies quite systematically with the $\bar{\varepsilon}$ of the LC. Consequently, this indicates that there is a good correlation between the polar anchoring energy and $\bar{\varepsilon}$ of the LC.

It has been proposed [22] that the generation of the pretilt angle is due to the steric interactions of the bulk LC molecules with those at the surface that are firmly anchored to the well-oriented polymer chains. An alternative suggestion initially given by Okano [23] and later by Sugiyama *et al.* [24], is that the pretilt angle generation can be related to the interaction of the bulk LC molecules with the highly oriented alkyl branches present at the polymer surface. In a recent investigation Seo

Figure 2. Plot of pretilt angle versus average epsilon ($\bar{\varepsilon}$). The solid line is a best fit to the straight line.

et al. [15], proposed a microscopic model according to which the pretilt angle is generated by a micro-asymmetric triangular surface excluded volume effect on a rubbed PI film having side chains. In the light of the above microscopic models it is likely that the steric interactions between the LC molecules and the oriented side chains of the SCLCP along with the dipole–dipole interactions may be responsible for the generation of the pretilt angle.

Some detailed studies on the temperature variation of the pretilt angle and the anchoring strengths, alignments of the SCLCP films by the non-contact method, for example, by light irradiation or by external electric field, are in progress.

4. Conclusions

We have investigated the aligning characteristics of two types of SCLCP films by measuring the pretilt angle and the extrapolation length. The result of our preliminary studies suggests that high pretilt angles of more than 10 degrees can be realized using these highly oriented films. The pretilt angle and anchoring energy are found to show a good correlation with the average dielectric constant $\bar{\varepsilon}$ of the LC materials. They also show a good dependence on the chemical composition of the aligning layer.

Figure 4. A plot of the extrapolation length versus $\bar{\varepsilon}$ of the LC aligned on a rubbed **P2** film. The solid line is a best fit to the straight line.

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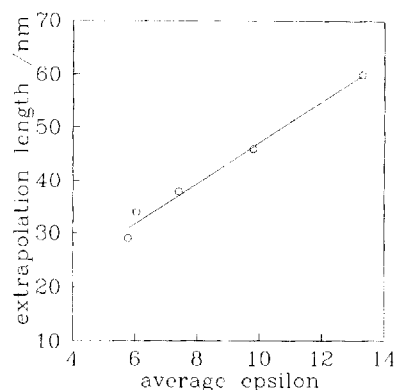
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