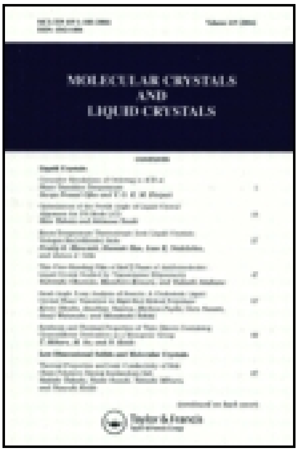

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Configuration Control of Liquid Crystal in the Droplet Dispersed in the Polymer with Mesogenic Side Group

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CONFIGURATION CONTROL OF LIQUID CRYSTAL IN THE DROPLET DISPERSED IN THE POLYMER WITH MESOGENIC SIDE GROUP

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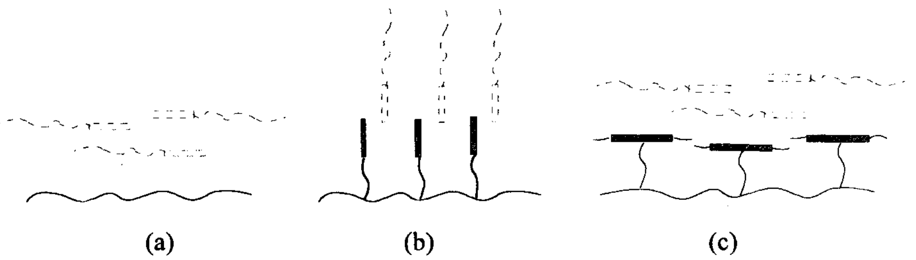
Abstract A side chain liquid crystalline polymer was applied to control the alignment of liquid crystal molecules at the interface to the direction of mesogenic side group. The aspects of the alignment were monitored by observing the droplet in the PDLC film. When the composition of the mesogenic side group increases, the configuration of LC droplets changes from bipolar to radial one as designed.

INTRODUCTION

Alignment of liquid crystal molecules at the polymer interface plays an important role in determining the performances of polymer dispersed liquid crystal (PDLC) film as well as liquid crystal displays(LCD). In this study, it has been focused to control the configuration of the LC molecules in the PDLC droplet by using the polymers with the mesogenic side group. In fact, the polymers were originated from the well known side chain liquid crystalline polymer(SCLCP). Figure 1 shows the schematic model of controlling the LC configuration by imposing an interfacial condition.



(a) (b) (c)

FIGURE 1 A model of controlling the configuration of LC molecules by using the side chain liquid crystalline polymers.

A radial configuration has been rarely observed in a submicron LC droplet, in which the liquid crystal molecules are anchored perpendicularly to the wall with a point defect at the center[1]. By applying the SCLCP similar to the Figure 1(b), which are discussed in this study, it can be easily expected to have a homeotropic alignment at the interface. On the other hand, for the shake of good electro-optic properties of PDLC films, the structure like Figure 1(c) is preferred by the following reasons; parallel alignment at the interface can form bipolar droplets; enough free volume by long spacer makes the LC molecules respond easily to the electric field[2]. But the latter subject is not considered here.

EXPERIMENTAL

The polymers were prepared by copolymerization of methylmethacrylate(MMA) and cyanobiphenylacrylate(CBA0) in benzene solution using AIBN as initiator. The latter monomer was obtained by the esterification of acryloylchloride and 4-hydroxybiphenyl carbonitrile as suggested by Alimoglu[3]. For purification, homopolymer and copolymers are dissolved into DMF and chloroform respectively, and then poured into ten-fold excess of methanol. The composition of the copolymers was identified by ^{1}H NMR and IR spectra and calorimetric measurement were made by DSC (20 °C/min). The layer spacing of the homopolymer PCBA0 was investigated by powder X-ray diffraction data after annealing.

TABLE 1 Composition of the polymers and glass transition temperatures.

Polymer	Composition of MMA and CBA (molar base)	Tg (°C)
PMMA	10 : 0	105
P(MMA-CBA0)(9:1)	9.4 : 0.6	125
P(MMA-CBA0)(6:4)	6.2 : 3.8	139
P(MMA-CBA0)(4:6)	4.2 : 5.8	148
PCBA0	0 :10	152

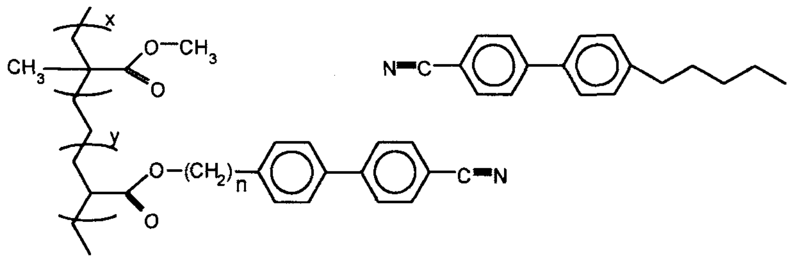


FIGURE 2 Structure of the polymer(n=0) and cyanobiphenyl liquid crystal molecule.

The polymers and E7 were blended with 4:6 weight percent, then typical phase separation technique was used to form the LC droplets[4]. The same cyanobiphenyl mesogens with the side group would increase the interaction at the interface. For the clear observation under the crossed polarizing microscope, thin submicron films were fabricated in hot press then cooled slowly to make the droplets grow up. The configurations of the LC molecules were monitored under the rotating crossed polarizers by 10 degrees.

RESULTS AND DISCUSSION

A) Thermal properties of the polymers

Thermal properties of the polymers are shown in Figure 3. In this experiment the amount of initiator was reduced than the previous work to increase the molecular weight, which was indicated by increased intrinsic viscosity(1.83 dl/g). Development of the mesophase was dependent on the molecular weight, so that there were missing mesophases in a series of phase transition when the molecular weight was not high enough[5]. The homopolymer PCBA0 shows two clear endotherms and there appeared an unpredicted nematic phase between 255 and 285 °C. Neverthless, by the polarizing microscope, we could observe it only if the film was pressed or sheared (Figure 4(a)).

Even though smectic phase was hard to be obtained by cooling the isotropic melt, its texture in Figure 4(b) is believed to be the S_A, similar to the undeveloped fan-like texture. Smectic ordering is originated from the packing of the side mesogenic groups which are attached to the flexible main chain as suggested by Magagnini[6]. Compared with biphenylacrylate, melting temperature appeared in the similar range but the glass transition temperature increased by 40 °C. It may be due to the effect of the increased interaction of -CN group with ester bond or biphenyl ring resulting in stiffness in the amorphous state, but

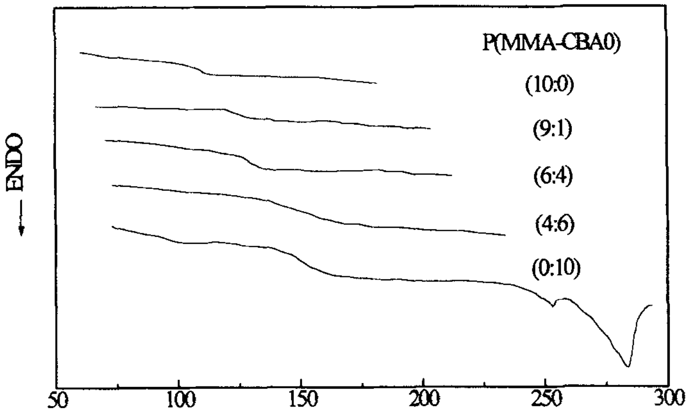


FIGURE 3 DSC thermograms of copolymers according to the monomer composition. (10:0) and (0:10) means homopolymer PMMA and PCBA0, respectively.

not so strong to reduce packing distance in the crystalline state. The powder X-ray diffraction pattern indicated the interplanar spacing to be 22.6 Å, the same periodicity with the biphenylacrylate.

Calorimetric data of the copolymers show an increasing pattern of Tg by the composition of the monomer CBA0. All the copolymers were amorphous and Tg were increased abruptly by the small portion of the CBA0.

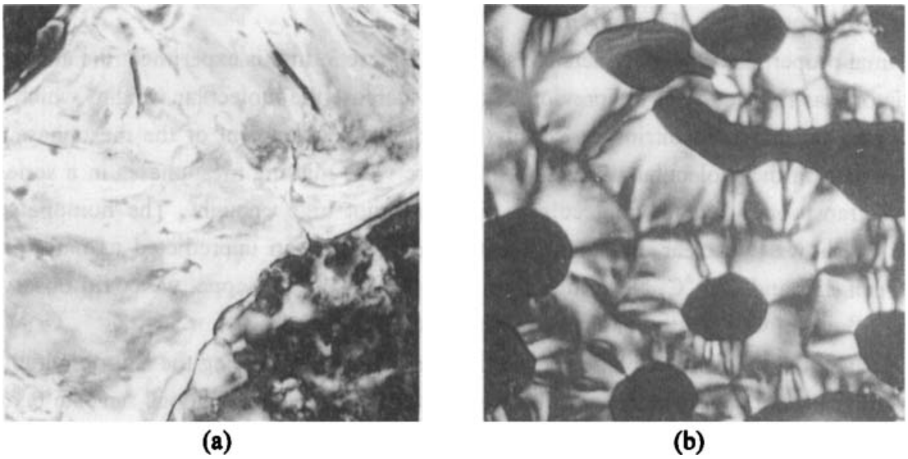
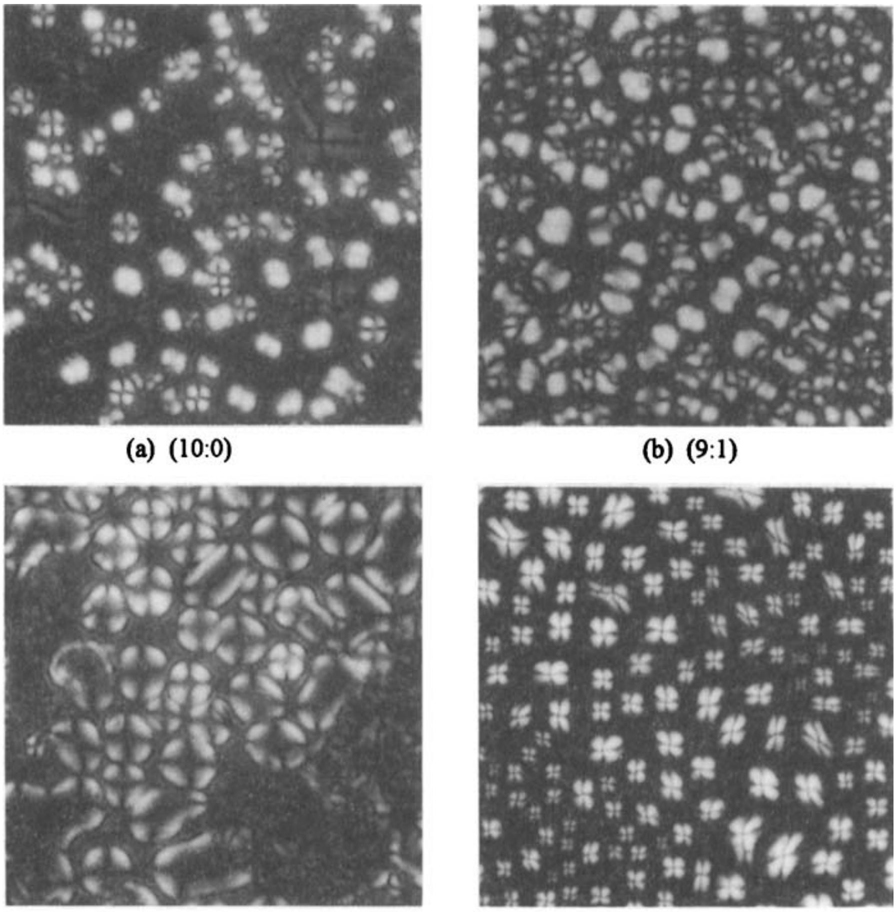


FIGURE 4 Polarizing micrographs of PCBA0.(a) 260 °C, x50 (b) 220 °C, x50. See Color Plate I.

B) Configuration transition in the LC droplets

Configuration of the LC molecules in the droplets could be monitored under the rotating crossed polarizers[7]. When the CBA0 content was lowered or none, the bipolar configuration is obtained, where the molecules are anchored parallely to the polymer matrix with two defect at the poles. Its textures appear very complicated with the orientation of the droplet directors connecting the two poles. So the various textures of the bipolar droplet are shown in Figure 4 (a) and (b), which are consistent with the simulated patterns of other researchers[7,8]. When the CBA0 content is increased the radial configuration can be attained as expected, in which the microscopic texture does not change with rotating polarizers. Figure 4 (c) and (d) show the cross-shaped texture in all droplets, which means all directors are orienting to the center of the droplets.

Parallel anchoring of the LC molecules to PMMA interface can be explained simply by FCK rule where the polymer has higher surface tension than E7, even though the matrix surface tension would be changed during the phase separation[9]. On the other hand, the more the CBA0 portion, the more interaction and steric effect exert the ordering of the E7 molecules to the direction of the side group. So, approximately over 40 % of the CBA0 composition, the mesogenic side group could change the LC anchoring at the interface from parallel to perpendicular alignment, therefore the configuration in the droplet would be also changed from the bipolar to the radial one.



(a) (10:0) (b) (9:1)

(c) (6:4) (d) (4:6)

FIGURE 5 Polarizing micrographs of the E7 droplets dispersed in the polymers P(MMA-CBA0)(x:y). (a) and (b) shows bipolar configuration, whereas (c)and (d) shows radial configuration. (a)~(c) : x1300, (d) : x420. See Color Plate II.

CONCLUSION

The homopolymer PCBA0 exhibits smectic A and nematic phase and the ordering can be promoted by the larger molecular weight. The configuration of LC in the droplet can be changed by the polymer with the different composition of the mesogenic side group, and the effect is originated from the interface where the LC molecules follow the direction of the mesogenic side group of the polymer matrix.

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