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Steep Electro-optical Properties Enhanced by Smectic-like Local Order in Nematic Liquid Crystal

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Effects of the chemical structure of a side chain type liquid crystalline polymer (LCP) on the steepness of an orientational change of the nematic director-applied voltage curve have been investigated for the (LCP/low molecular weight liquid crystal) composite systems in a nematic state. The (LCP/LC) composite using LCP with longer spacer showed the steeper electric response than the composite using LCP with shorter spacer. This indicates that the side chain type LCP with longer alkylspacer can easily form the mechanically stable smectic layer. The (LCP/LC) composite using LCP with higher degree of polymerization showed the steeper electric response than the composite using LCP with lower degree of polymerization. Also, this indicates that the LCP with higher degree of polymerization can form higher smectic-type continuity along the polymeric main chain.

1. INTRODUCTION

Development of new liquid crystalline materials with a sharper electro-optical response characteristic are desired to achieve higher contrast display. The electro-optical steepness of nematic liquid crystalline molecules strongly depends on the magnitude of elastic constants of the liquid crystalline director. It has been reported that the electro-optical steepness increases with a decrease in the ratio of elastic constants of the bend mode to the splay one, K_3/K_1 when the homogeneous or twisted alignment of nematic liquid crystalline molecules is transformed to the homeotropic one.[1)] The elastic constants might be related to the molecular dimension such as the ratio of length to width.[2)] Also, it is theoretically predicted that the magnitude of K_3/K_1 could decrease with an increase in the smectic-like short range ordering in a nematic phase.[3,4)] From the point of view of the structure factor, it might be effective to create a fairly well smectic-like short range ordering in a nematic liquid crystal in order to realize a sharp electro-optical steepness.

It has reported that the steep electro-optical response can be realized for the nematic (LCP/LC) composite system in which the smectic-like short range ordering is formed due to the comb-like molecular structure of LCP dispersed moleculally in LC.[5-7)] This paper deals with chemical structure of LCP dependence of smectic-like short range ordering induced by LCP in a nematic phase of the (LCP/LC) composite system, considers the mechanism that LCP induces a smectic-like short range ordering.

2. EXPERIMENTAL

A commercially available nematic mixture of cyanobiphenyl and cyanoterphenyl derivatives, E7 and a side chain type liquid crystalline polymer, PS6EC(n=3, 40), PS3EC(n=40) shown in Figure 1

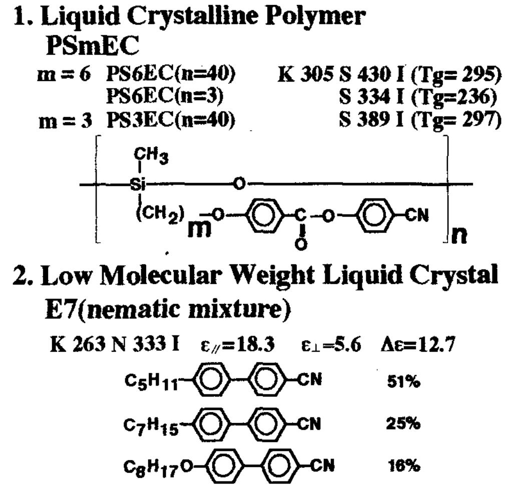

Figure 1 Chemical structure of liquid crystalline polymer and low molecular weight liquid crystal

were used as the components of the (LCP/LC) composite system. The [PSmEC(m=3,6)/E7] composite film was prepared by a solvent cast method from an acetone solution. The phase transition behavior and the aggregation state of the composite system were investigated on the basis of the differential scanning calorimetric (DSC), polarizing optical microscope and X-ray diffraction studies. The magnitude of the K_3/K_1 ratio was evaluated by a curve-fitting of the plots of applied electric voltage against electric capacitance for the homogeneous alignment cell.[8]

3. RESULTS AND DISCUSSION

3.1 Spacer length dependence

From DSC measurement and polarizing optical microscope observation, it was revealed that the [PS6EC(n=3,40)/E7] composite systems above 59 mol% of E7 are in a nematic phase and that below 49 mol% of E7 are in a smectic one at 298 K, respectively. Also, it was revealed that the [PS3EC (n=40)/E7] composite system above 59 mol% of E7 is in a nematic phase and that below 39 mol% is in a smectic one at 298 K. Figure 2 shows the E7 fraction dependence of the K_3/K_1 ratio and the integrated X-ray intensity for the [PS6EC(n=40)/E7] and [PS3EC(n=40)/E7] composite systems. As shown in Figure 2(a), the integrated X-ray intensity for (PS6EC/E7) composite system increased with an increase in the fraction of PS6EC(n=40). Also, the value of K_3/K_1 decreased with an increase in the fraction of PS6EC(n=40). Based on the theoretical calculation performed by Meer et al., eq (1) was derived[9]

$$\frac{K_3}{K_1} \propto \frac{L^2}{D^2}\left(\ln\left(C|F|^2\right) - \ln I\right) \qquad (1)$$

where L and D are the molecular length and width of LC molecules, respectively. F, I and C are the structure factor of an ideal smectic layer structure, the experimental integrated intensity of X-ray diffraction from smectic-like short range ordering, and the constant, respectively. The terms in a parenthesis corresponds to the smectic-like short range ordering. Therefore, eq (1) indicates a strong correlation between K_3/K_1 and strength of smectic-like short range ordering. The (PS6EC/E7) composite using LCP with longer spacer showed the smaller K_3/K_1 values than the (PS3EC/E7) composite using LCP with shorter spacer as shown in Figures 2(a) and (b). Figure 3 show the electric voltage dependences of the electric capacitance for the homogeneous cells of E7 and the [PSmEC(m= 3,6)/E7] composite systems in the vicinity of the Freedericksz transition. The change of electric capacitance may arise from the reorientation of LC

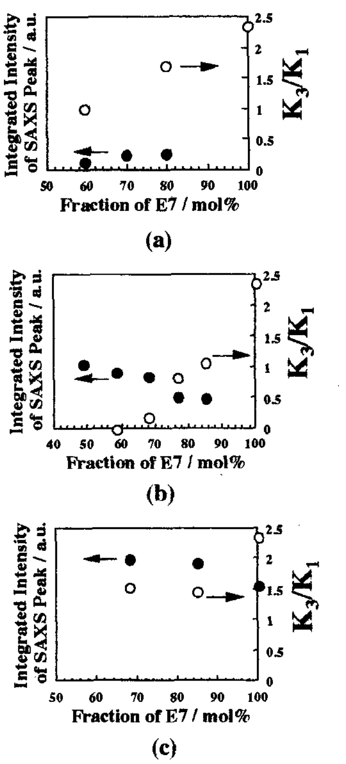

Figure 2 E7 fraction dependence of integrated SAXS intensity and K_3/K_1 for [PS6EC(n=40)/E7] (a), [PS3EC(n=40)/E7](b), [PS6EC(n=3)/E7](c)

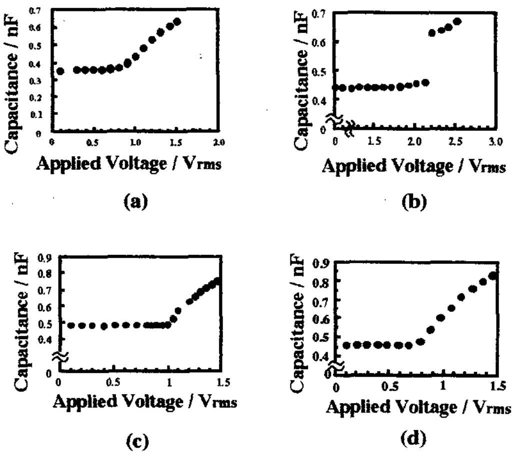

Figure 3 Applied electric voltage dependence of electric capacitance around the Freedricksz transition for the homogeneous cell of E7(a), [PS6EC(n=40)/E7](b), [PS3EC(n=40)/E7](c), [PS6EC(n=3)/E7](d)

molecules. The capacitance for the [PS6EC(n=40)/E7] composite system (Figure 3(b)) increased discontinuously at the threshold voltage, and on the other hand, the [PS3EC(n=40)/E7] composite system (Figure 3(c)) didn't show such phenomenon. The discontinuous jump of the capacitance shown in Figure 3(b) reveals that the steepness of the molecular reorientation upon application of an electric field is remarkably enhanced by adding PS6EC(n=40) to E7.

This results indicated that the side chain type LCP with longer alkylspacer can easily form the mechanically stable smectic layer. Therefore, it seems reasonable to consider that higher smectic-like short range ordering might exist in the nematic phase for (LCP with longer spacer/LC) composite system.

3.2 Polymerization degree dependence

Figure 2(c) shows the E7 fraction dependence of the K_3/K_1 ratio and the integrated X-ray intensity for the [PS6EC(n=3)/E7] composite systems. Though the integrated X-ray intensity increased with an increase in the fraction of PS6EC(n=3), the value of K_3/K_1 didn't almost decrease as shown in Figure 2 (c). Also, The (LCP/LC) composite using LCP with higher degree polymerization showed the smaller K_3/K_1 values than the case of LCP with lower degree polymerization shown in Figures 2(a) and (c). Figure 3(d) shows the electric voltage dependence of the electric capacitance for the homogeneous cell of the [PS6EC(n=3)/E7] composite system in the vicinity of the Freedericksz transition. The capacitance for [PS6EC(n=3)/E7] composite system (Figure 3(d)) didn't discontinuously change at the threshold voltage.

The smectic-like short range ordering for the [PS6EC(n=3)/E7] composite system is higher than that for the [PS6EC(n=40)/E7] composite syste The magnitude of K_3/K_1 for the [PS6EC(n=3)/E composite system is nevertheless much larger th that for the [PS6EC(n=40)/E7] composite syste Furthermore, in the case of the [PS6EC(n=3)/E composite system, the steepness of the L molecular reorientation upon application of electric field couldn't be enhanced. This reason such results is supposed as follows.

Figure 4 shows the small angle X-r scattering (SAXS) patterns of the oriented [PS6EC =3,40)/E7] composite systems upon the applicati of an electric field. The X-ray beam was incide perpendicular to the direction of an applied electr field. The scattering spot from the quasi-lay structure of the smectic-like short range ordering a nematic state was observed on the meridian at t small angle (2θ=2~4 degree). The shape scattering spot might be related to the shape, lengt orientation and irregularity of smectic-like lay structure.(9) Figure 5 shows the schemat illustration of relation between aggregation states layer structure and shape of scattering spot. Whe the layer is more well-ordered, the scattering sp becomes sharper (Figure 5(a)). Also, when the lay has a distribution of orientation around t azimuthal direction of the layer normal, the sp becomes broader with a crescent-shaped arc (Figu 5(b)). A decrease in the lateral width of the lay structure corresponds to a change from the crescen shaped arc to the flattened arc (Figure 5 (c)). T SAXS results shown in Figure 4 indicate that th smectic-like layer structure in the [PS6EC(n=3)/E composite system was laterally short due to laterall short continuity of the smectic-like layer compose of the side chain mesogenic groups of LCP and L molecules. And also, the smectic-like layer in th [PS6EC(n=40)/E7] composite system has

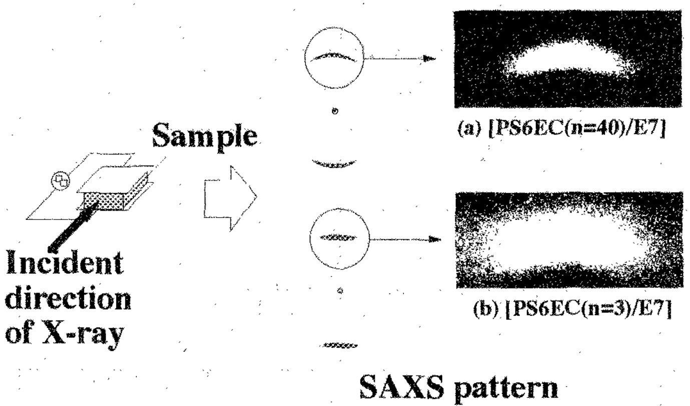

Figure 4 SAXS pattern of [PS6EC(n=3, 40)/E7] composite systems

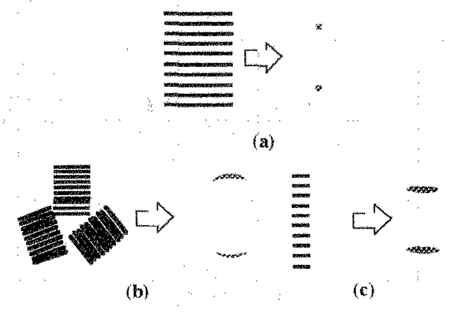

Figure 5 schematic illustration of relation between aggregation states of layer structure and shape of scattering spot distribution of their orientations around the azimuthal direction of the layer normal.

Next, the relationship among the presence of smectic-like short range ordering, the value of K_3/K_1 and the ratio of molecular length, L to width, D, L/D. It was reported that K_3/K_1 decreases with a decrease in L/D. It seems reasonable to consider that one molecular assembly with the smectic-like short range ordering in a nematic phase may behave as an apparent single molecular unit with respect to the electro-optical response characteristic, as shown in Figure 6. Since D' may be apparently larger than D, it is apparent that the addition of LCP into E7 results in a decrease in K_3/K_1 due to an apparent decrease in L/D' as the molecular unit. Furthermore, it is expected that the LCP with higher degree of polymerization can form higher smectic-like lateral continuity along the polymeric main chain than that with lower degree of polymerization. In other words, apparent width D' may be larger than D", that well corresponds to the results in Figure 6. Therefore, it seems reasonable to conclude that the (LCP/LC) composite system using the LCP with higher degree of polymerization shows smaller K_3/K_1 and steeper electric response shown in Figure 3(a).

4. CONCLUSION

It was revealed that the smectic-like short range ordering induced by LCP in nematic phase for (LCP/LC) composite system depended on the chemical structure of LCP. The (LCP/LC) composite system using with longer spacer showed the steeper molecular reorientation upon application of an electric field than that using LCP with shorter spacer. This indicates that the side chain type with longer alkylspacer can easily form the mechanically stable smectic layer. Also, the (LCP/LC) composite system using LCP with higher degree of polymerization showed the steeper electric response than that using LCP with lower degree of polymerization. This indicates that the LCP with higher degree of polymerization can form smectic-like short range ordering with higher continuity along the polymeric main chain.

ACKNOWLEDGMENT

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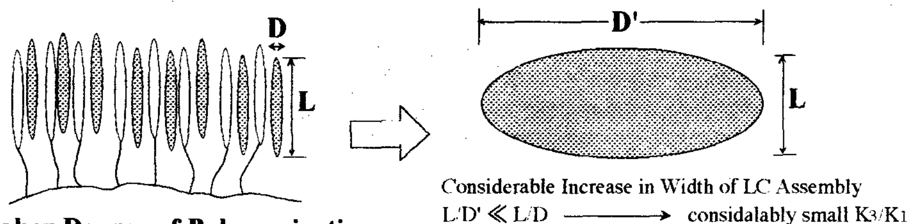
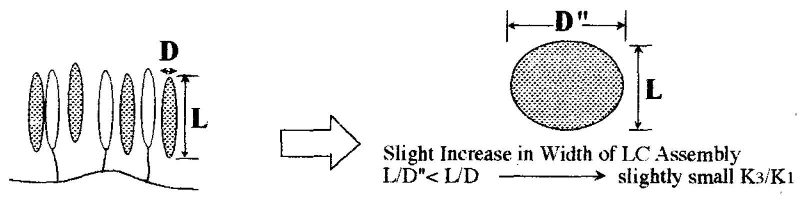
REFERENCE

1) G. Baur, *Mol. Cryst. Liq. Cryst.*, **63**, 45(1981).
2) F. Leenhouts, H. J. Roebers, A. J. Dekker and J. J. Jonker, *J. Phys.*, **40**, C3-291(1979).
3) B. W. van der Meer, F. Posma, A. J. Dekker and W. H. de Jeu, *Mol. Phys.*, **45**, 1227(1982).
4) M. J. Bradshaw, E. P. Raynes, I. Fedak and A. J. Leadbetter, *J. Phys.*, **45**, 157(1984).
5) T. Kajiyama, H. Kikuchi, A. Miyamoto, S. Moritomi and J. C. Hwang, *Chem. Lett.*, **1989**, 817 (1989).
6) H. Finkelmann, H. Ringsdorf and J. H. Wendorf, *Makromol. Chem.*, **179**, 273(1978).
7) H. Kikuchi, S. Kibe, T. Kajiyama, *Proc. SPIE*, **2408**, 141(1995).
8) T. Uchida and Y. Takahashi, *Mol. Cryst. Liq. Cryst.*, **72(Lett.)**, 1339(1981).
9) R. Bonart, R. Hosemann, *Makromol. Chem.*, **39**, 105(1960).



Higher Degree of Polymerization



Lower Degree of Polymerization

Figure 6 Schematic representation of molecular assemblies of the composite systems with higher and lower degree of polymerizations of LCPs