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Steep electro-optical response of nematic liquid crystalline molecules induced by addition of polymeric chains

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The steepness increases with a decrease in the ratio of elastic constants of the bend to the splay mode, K_3/K_1. The elastic constants of nematic directors are affected by the geometrical shape of a liquid crystalline molecule and a short range ordering for the alignment of liquid crystalline molecules. The magnitude of K_3/K_1 and the reorientational steepness of the nematic director were evaluated by an electric capacitance measurement of the (side chain-type liquid crystalline polymer (PS6EC)/low molecular weight liquid crystal (E7)) composite system cell. It became apparent from X-ray diffraction studies that the smectic-like short range ordering increases with increasing the fraction of PS6EC even in the nematic state of the composite system. Furthermore, a remarkably steep electro-optical response was successfully achieved.

1. Introduction

In order to achieve a higher contrast display, the synthesis of liquid crystalline materials with an excellent light transmission-applied voltage characteristic has been attempted. 'Steep response' means 'steep change of light transmittance for an electro-optical transmission curve' or 'steep change of the tilt angle of the optic axis in the middle of the layer in the homogeneous cell as a function of the applied voltage. The reorientational steepness of nematic liquid crystalline molecules is strongly dependent on the magnitude of elastic constants of the liquid crystalline director. It has been reported that the reorientational steepness increases with a decrease in the ratio of elastic constants of the bend to the splay mode, K_3/K_1, when the homogeneous or twisted alignment of nematic liquid crystalline molecules is transformed to the homeotropic alignment [1–3].

Chemical and structural factors affecting the elastic constants have been extensively studied for nematic liquid crystals. Leenhouts *et al.* [4], experimentally indicated that the elastic constants might be related to the molecular dimension such as the ratio of length, L, to width, D, L/D. Meer *et al.* [5], theoretically predicted that the magnitude of K_3/K_1 could decrease with an increase in the smectic-like short range ordering. Furthermore, Bradshaw experimentally supported this prediction based on X-ray diffraction measurement [6]. From the point of view of the structural factor, it might be effective to create a somewhat smectic-like local ordering in a nematic liquid crystal in order to realize a sharp electro-optical response characteristic in the homogeneous or twisted nematic cell.

An aggregation state and novel electro-optical properties for the (side chain-type liquid crystalline polymer (LCP)/low molecular weight liquid crystal (LC)) composite systems have been extensively investigated [7–10]. It has been revealed that the composite system consisting of a smectic LCP and nematic LC shows a continuous phase change from the smectic to nematic phase with an increase in the LC fraction. It seems reasonable to consider from the phase diagram of the (LCP/LC) composite that a smectic-like short-range ordering, to induce a steeper reorientation characteristic of LC molecules, might be formed even in the nematic state [11].

This paper deals with the smectic-like short-range ordering in the nematic (LCP/LC) composite system in order to realize the sharp steepness for the electro-optical response.

2. Experimental

2.1. *Materials*

A commercially available nematic mixture of cyanobiphenyl and cyanoterphenyl derivatives, E7, and a side chain-type liquid crystalline polymer, PS6EC, shown in figure 1, were used as the components of the (LCP/LC) composite system. PS6EC was synthesized following the method reported by Finkelmann *et al.* [12]. The (PS6EC/E7) composite film was prepared by the solvent cast method from an acetone solution.

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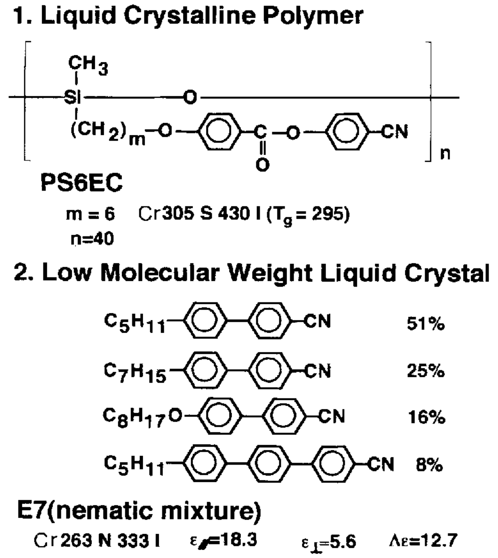

Figure 1. Chemical structures of the liquid crystalline polymer and low molecular weight liquid crystal

2.2. *Phase transition behaviour and aggregation states of the composite system*

The phase transition behaviour and the aggregation state of the composite system were investigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD). DSC thermograms were recorded at a heating rate of $5\,\mathrm{K\,min^{-1}}$ using a Rigaku 8230B DSC under a dry nitrogen purge. Polarizing optical micrographs were taken under crossed nicols using a Nikon polarized optical microscope. X-ray diffraction studies were carried out using CuK_α radiation from a MACSCIENCE M18XHF X-ray generator.

2.3. *Measurement of the K_3/K_1 ratio*

The magnitude of the K_3/K_1 ratio was evaluated by a curve-fitting of the plots of the applied electric voltage versus electric capacitance for the homogeneous alignment cell [13]. The magnitude of electric capacitance was evaluated from the magnitude of the electric current between the sample surfaces upon application of an electric voltage by using the equipment shown in figure 2.

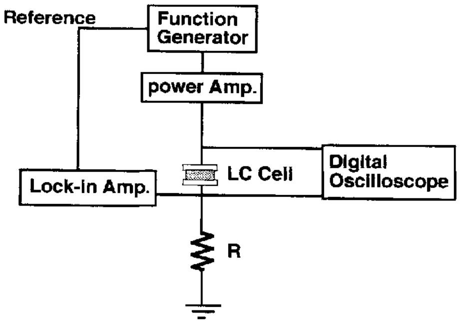

Figure 2. Measuring system of the electric capacitance of the liquid crystal cell.

The electric capacitance, C, of the homogeneous liquid crystal cell changes with the magnitude of applied voltage, V, as shown in figure 3 (*a*). The following equations (1) are valid in a large V region [13]:

$$\left.\begin{aligned}
\frac{C}{C_0} &= \gamma + 1 + \beta\frac{V_{\mathrm{th}}}{V},\\
\beta &= -\frac{2\gamma}{\pi}(1+\gamma)^{1/2}\int_0^1\left(\frac{1+\kappa\psi^2}{1+\gamma\psi^2}\right)^{1/2}\mathrm{d}\psi,\\
\gamma &= \frac{\Delta\varepsilon}{\varepsilon_\perp},\\
\kappa &= \frac{K_3}{K_1} - 1,
\end{aligned}\right\} \qquad (1)$$

where C_0, V_{th}, ψ, $\Delta\varepsilon$, and $\varepsilon_\perp$ are the capacitance at $V = 0$, the threshold voltage, sin of molecular tilt angle with respect to the substrate, the dielectric anisotropy of the liquid crystal, and the dielectric constant of the liquid crystal along the direction perpendicular to **n**, respectively. In the region of sufficiently large V, the plot of C/C_0 versus V_{th}/V provides a linear relationship as shown in figure 3 (*b*). The K_3/K_1 ratio can be obtained from the slope of the C/C_0 versus V_{th}/V plot.

2.4. *Evaluation of the steepness for electro-optical switching*

The conventional TN cell of the (PS6EC/E7) composite system in the nematic state was constructed in order to investigate the steepness of the electro-optical response. The composite system was sandwiched between two glass substrates with transparent electrodes of indium–tin oxide (ITO) which were separated by a gap of 14 μm. The surfaces of the substrate plates were coated with a thin polyimide film, and then rubbed unidirectionally to control the alignment of the liquid crystalline molecules in the cell. The rubbing directions of the upper and lower glass plates were mutually perpendicular so that the molecules twisted by 90 degrees about the direction perpendicular to the substrate surface over the thickness of the liquid crystal cell. The optical axes of the polarizer and analyser were set to be perpendicular to each other and also, parallel to the rubbing directions of both sides of the TN cell. The steepness of the electro-optical response was evaluated by the experimental set-up as shown in figure 4. A He–Ne laser was used as the incident light source. The electric voltage dependence of the transmitted light intensity through the TN cell under crossed nicols was obtained with a photodiode.

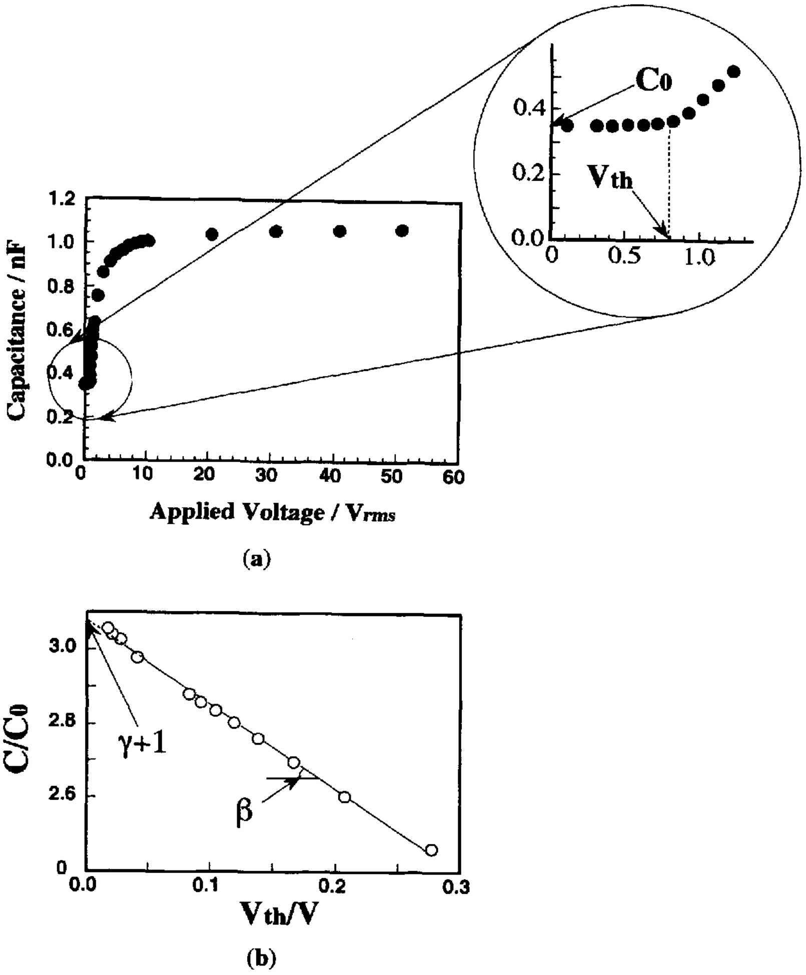

Figure 3. Schematic explanation of the evaluation of the K_3/K_1 ratio from the capacitance–voltage relationship.

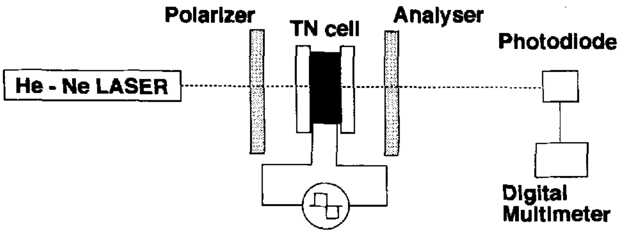

Figure 4. Experimental set-up for the measurement of the electro-optical steepness of the TN cell.

3. Results and discussion

3.1. *Relationship between reorientational steepness and the* K_3/K_1 *ratio*

The steepness of the liquid crystal molecular reorientation in the cell depends critically upon the elastic constants of nematic director, **n**, and the mode of the molecular reorientation. Nematic liquid crystals with a parallel alignment of **n** are in a minimum free energy state. When **n** is perturbed by a combination of an applied electric field and an anchoring effect at the interface with an external medium (substrate), three contributions from the distortion of **n**, anchoring effect and electric field, should be taken into consideration to minimize the free energy of the system. Let us focus our attention on a simple case, such that the nematic liquid crystalline molecules with a positive dielectric anisotropy are enclosed between the parallel plane substrates of distance *d* [14]. The surfaces of the substrates were treated to make the liquid crystalline molecules orient along a specific direction parallel to the substrate surface, resulting in homogeneous alignment. The anchoring strength at the interfaces was assumed to be so strong that the extrapolation length defined by de Gennes [15] is comparable to the molecular dimension. Therefore, the alignment of the liquid crystalline molecules anchored at the interface is not influenced by the bulk alignment of other molecules. Thus, this indicates that the contribution from an anchoring effect is negligible to describe the equilibrium state of disturbed **n**. Therefore, the magnitudes of free energy per unit volume attributed to the distortion of **n**, f_d and a dielectric effect,

f_e are expressed by equations (2) and (3), respectively:

$$f_d = \frac{1}{2}[K_1(\operatorname{div}\mathbf{n})^2 + K_2(\mathbf{n}\cdot\operatorname{rot}\mathbf{n})^2 + K_3(\mathbf{n}\times\operatorname{rot}\mathbf{n})^2], \quad (2)$$

$$f_e = -\frac{1}{2}\varepsilon_0\Delta\varepsilon(\mathbf{E}\cdot\mathbf{n})^2, \quad (3)$$

where K_1, K_2 and K_3 are the Frank elastic constants associated with splay, twist and bend deformations, respectively. Also, $\Delta\varepsilon$ and $\mathbf{E}$ are the dielectric anisotropy of the nematic liquid crystal and the applied electric field, respectively. If the electric field is applied in a direction normal to the substrate surface of the cell, the resulting alignment pattern is found to minimize the total free energy, per unit area of the sample, F_t. F_t is derived by integrating the summation of f_d and f_e as given by equation (4):

$$F_t = \int_0^d f_t\,\mathrm{d}z = \int_0^d (f_d + f_e)\,\mathrm{d}z. \quad (4)$$

When the tilt angle of $\mathbf{n}$ and the axis normal with respect to the substrate surface are denoted by θ $(-\pi/2 \leqslant \theta \leqslant \pi/2)$ and z, respectively, equation (5) can be obtained from equations (2), (3) and (4):

$$F_t = \frac{1}{2}\int_0^d \left[(K_1\cos^2\theta + K_3\sin^2\theta)\left(\frac{\partial\theta}{\partial z}\right)^2 - \varepsilon_0\Delta\varepsilon E^2\sin^2\theta\right]\mathrm{d}z \quad (5)$$

In the case of an equilibrium state, F_t is a minimum and furthermore, the magnitude of θ must satisfy equation (6), the Euler–Lagrange equation:

$$\frac{\partial f_t}{\partial\theta} - \frac{\mathrm{d}}{\mathrm{d}z}\frac{\partial f_t}{\partial\left(\frac{\mathrm{d}\theta}{\mathrm{d}z}\right)} = 0. \quad (6)$$

Then, from equations (5) and (6), the equilibrium condition for a nematic crystal alignment can be obtained as equation (7):

$$\frac{\mathrm{d}}{\mathrm{d}z}\left[(K_1\cos^2\theta + K_3\sin^2\theta)\left(\frac{\partial\theta}{\partial z}\right)^2 + \varepsilon_0\Delta\varepsilon E^2\sin^2\theta\right] = 0. \quad (7)$$

That is,

$$(K_1\cos^2\theta + K_3\sin^2\theta)\left(\frac{\partial\theta}{\partial z}\right)^2 + \varepsilon_0\Delta\varepsilon E^2\sin^2\theta = C. \quad (8)$$

The constant C can be determined from the fact that $\theta(z)$ should be the maximum value, $\theta_{\max}$ at $z = d/2$. In other words, $\partial\theta/\partial z = 0$ at $z = d/2$. Consequently, $C = \varepsilon\Delta\varepsilon E^2\sin^2\theta\max$. Then equation (9) is obtained directly from equation (8):

$$(\varepsilon_0\Delta\varepsilon)^{1/2}E\,\mathrm{d}z = \left(\frac{K_1\cos^2\theta + K_3\sin^2\theta}{\sin^2\theta_{\max} - \sin^2\theta}\right)^{1/2}\mathrm{d}\theta \quad (9)$$

From the boundary condition that $\theta = 0$ at the interface of the liquid crystal and substrate surface in the cell, that is, at $z = 0$ and $z = d$, equation (10) can be derived:

$$(\varepsilon_0\Delta\varepsilon)^{1/2}E\int_0^{d/2}\mathrm{d}z = \int_0^{\theta_{\max}}\left[\frac{K_1\cos^2\theta + K_3\sin^2\theta}{\sin^2\theta_{\max} - \sin^2\theta}\right]^{1/2}\mathrm{d}\theta \quad (10)$$

Taking the limit $\theta_{\max} \to 0$ to calculate the threshold voltage, V_{th}, equation (11) is found:

$$V_{th} = \frac{E_c}{d} = \pi\left(\frac{K_1}{\varepsilon_0\Delta\varepsilon}\right)^{1/2} \quad (11)$$

When an applied voltage, V, is larger than the threshold, V_{th}, a change in θ at any z point can be computed from equation (12) which is mathematically transformed from equations (10) and (11):

$$\frac{V}{V_{th}} = \frac{2}{\pi}\int_0^{\theta_{\max}}\left(\frac{1 + \kappa\sin^2\theta}{\sin^2\theta_{\max} - \sin^2\theta}\right)^{1/2}\mathrm{d}\theta$$
$$= 1 + \frac{1}{4}(\kappa + 1)\theta_{\max}^2 + \cdots, \quad (12)$$

where $\kappa = (K_3 - K_1)/K_1$. It is clear from equation (12) that a sharper change in $\theta_{\max}$ with V/V_{th} can be achieved in the case of a smaller value of κ. Namely, a smaller value of the K_3/K_1 ratio might give a sharper reorientation characteristic of the liquid crystalline molecules upon application of an electric field in the homogeneous cell. In the case of the twisted nematic cell, it has been also reported that a sharper response can be realized for a smaller value of K_3/K_1 [3, 16].

3.2. *Phase transition behaviour of the composite system*

Figure 5 shows a phase diagram of the composite system of PS6EC and E7. Phase transition temperatures were determined by DSC and POM studies. PS6EC and E7 exhibit a smectic and nematic phase respectively. The PS6EC/E7 composite system across the whole range of concentration exhibited a mesophase between the isotropic and crystal phases. The mesophase in this region was in a miscible state; the endothermic peak for the mesophase–isotropic phase transition of the composite system was single and homogeneous textures observed for the mesophase under POM. Figure 6 shows polarizing microscopy textures for the PS6EC/E7 composite system. In the E7 fraction range below 49 mol % (see figure 6(*c*)), a focal-conic or fan-shape texture, being characteristic of the smectic phase, was observed. On the other hand, in the E7 fraction range above 59 mol %

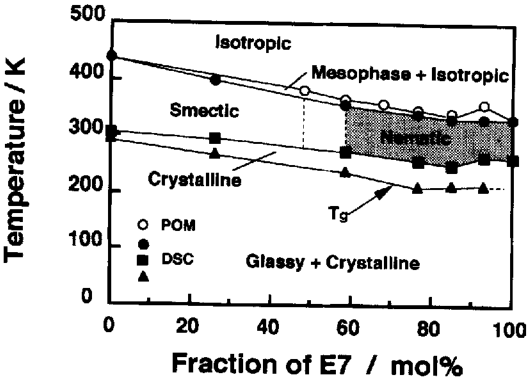

Figure 5. Phase diagram of the PS6EC/E7 composite system.

(see figures 6(*a*) and (*b*)), a schlieren texture with a disclination strength of ±1/2 was observed. Though a schlieren texture is generally observed for a planar alignment of nematic or a homeotropic alignment of a smectic C phase, the presence of disclinations of strength ±1/2 is forbidden in the smectic C phase. Therefore, it is reasonably concluded from the polarizing optical microscopic observation that the PS6EC/E7 composite system above 59 mol % of E7 is a nematic phase and below 49 mol % of E7 is a smectic phase.

3.3. *Smectic-like short range ordering in the nematic composite system*

Meer *et al.* [5], calculated the elastic constants of a nematic liquid crystal as a function of the strength of the smectic-like local ordering on the assumption that distributed harmonic forces act among the molecules so that the neighbours have some preference for their centres to be in the same plane. Based on their theory, equation (13) can be derived:

$$\frac{K_3}{K_1} \propto \frac{L^2}{D^2}\langle\alpha^2\rangle \qquad (13)$$

where α is the normalized positional displacement between the nearest neighbours of the mesogenic side chain groups in the LCP and LC molecules along a direction parallel to **n** as shown in figure 7. The distribution of α is assumed to be Gaussian. Since an increase in the local ordering corresponds to an increase in the sharpness of the Gaussian distribution, the magnitude of $\langle\alpha^2\rangle$ might be decreased. It is then apparent from equation (13) that a reduction in K_3/K_1 corresponds to both a decrease in L/D and an increase in the smectic-like local ordering, $\langle\alpha^2\rangle$. Equation (13) is approximately transformed into equation (14) [6]:

$$\frac{K_3}{K_1} \propto \frac{L^2}{D^2}(\ln(C|F|^2) - \ln I) \qquad (14)$$

where F, I and C are the structure factor of an ideal smectic layer structure, the integrated intensity of X-ray diffraction from the smectic layers, and the constant, respectively. Equation (14) was confirmed by the linear relationship between K_3/K_1 and $-\ln I$ for several kinds of nematogen. This apparently shows a strong

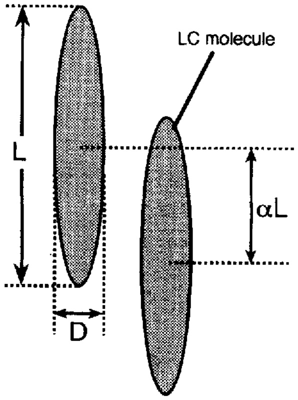

Figure 7. Schematic representation of the normalized positional displacement between the molecules in a direction parallel to *n*.

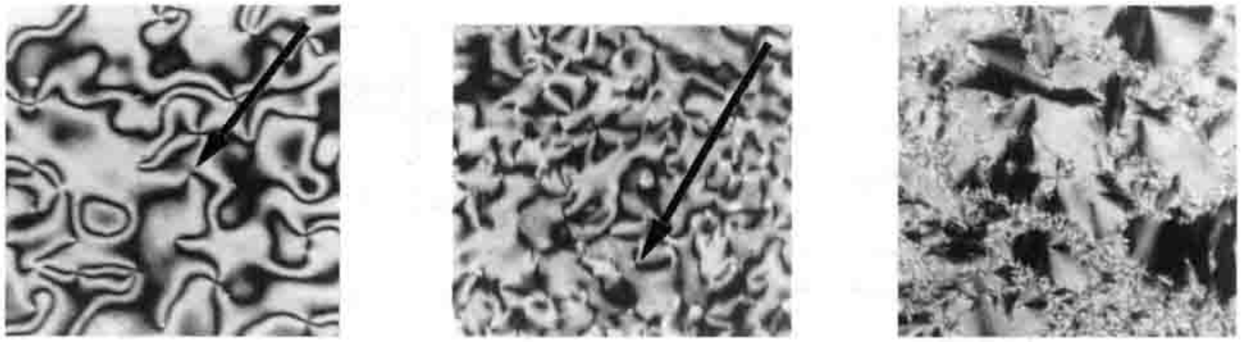
(*a*) (*b*) (*c*)

Figure 6. Polarizing microscopy textures for the PS6EC/E7 composite system. (*a*) PS6EC/E7 = 15/85 mol %, (*b*) PS6EC/E7 = 41/59 mol % and (*c*) PS6EC/E7 = 52/48 mol %.

correlation between K_3/K_1 and the strength of the smectic-like local ordering.

A second kind of lattice distortion exists for isotropic or nematic liquid crystals due to a broad statistical distribution of the intermolecular distance. In this case, only amorphous hallows can be observed on the X-ray scattering pattern. On the other hand, in the case of a smectic liquid crystal, the sharp X-ray scattering pattern might be obtained due to the sharp distribution of a well-defined interlayer spacing. The two scattering maxima were detected at around 1·4–1·5 and 10 degrees of the Bragg angle for the PS6EC/E7 composite system in the mesophase. When the X-rays were incident perpendicular to **n** with a uniaxial orientation, the small and wide angle X-ray diffractions were detected along the directions parallel and perpendicular to **n**, respectively. The diffused diffraction at around 10 degrees corresponds to the intermolecular distance along the direction perpendicular to the molecular axes. The SAXS peak profiles for the PS6EC/E7 composite system are shown in figure 8 as a function of the different compositions. As mentioned above, the observed SAXS peaks correspond to long spacings for the smectic or the smectic-like layer structure in the composite system. The intensity of the SAXS peaks decreased with an increase in the mole fraction of E7. Since even in the case of the nematic phase, the obvious SAXS peak was discernible, it seems reasonable to conclude that a smectic-like short-range ordering is formed even in the nematic phase of the composite system.

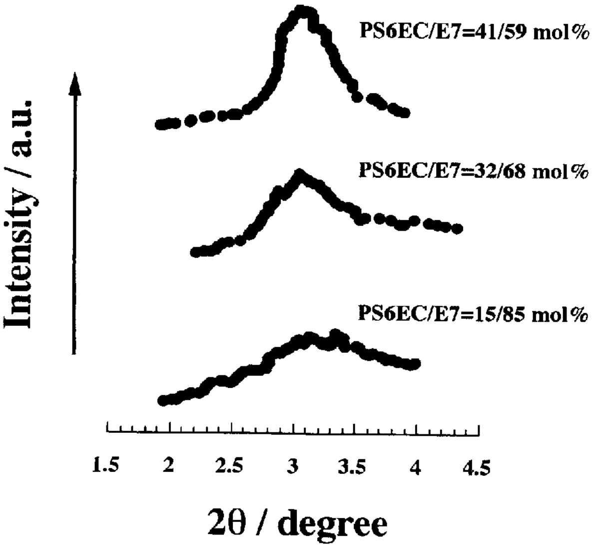

Figure 8. Small angle X-ray scattering profiles of the PS6EC/E7 composite system.

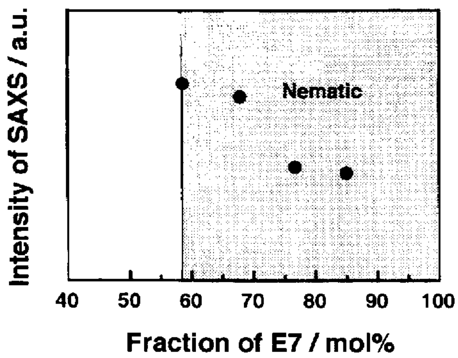

Figure 9. E7 mole fraction dependence of the integrated intensity of SAXS peak for the PS6EC/E7 composite system.

Figure 9 shows the integrated intensity for the SAXS peak in the nematic phase for the PS6EC/E7 composite system. The integrated intensity and the intensity distribution of the SAXS peak increased and became sharper with an increase in the fraction of PS6EC respectively, as shown in figure 8. This result apparently indicates that the short-range ordering, i.e., the flatness of the smectic-like layer structure, increases with an increase in the mole fraction of PS6EC. The half width of the SAXS peak profile reflects a regularity and lateral continuity of the smectic layer structure because the X-ray diffraction peak profile is strongly related to the interference and shape factors of the scattering objects consisting of an assembly of molecules. The interference factor depends on the second kind of disposition of scattering molecules. The shape factor is expressed by a Fourier transform of the geometry of the scattering object, that is directly related to the number of scattering molecules and the continuity of their ordering. Therefore, the half width of the X-ray scattering peak should become narrower with an increase in the regularity and the continuity of the scattering lattice. The half width of the SAXS peak decreased with an increase in the fraction of PS6EC as shown in Figure 10. Figures 9 and 10 indicate that the short-range ordering of the smectic-like layer structure increases with increasing fraction of PS6EC. Therefore, it seems reasonable to consider that

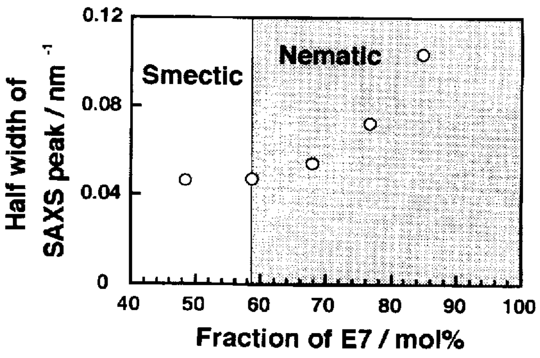

Figure 10. E7 mole fraction dependence of the half width SAXS peak for the PS6EC/E7 composite system.

a side chain-type liquid crystalline polymer enhances formation of the smectic-like layer structure because the mesogenic side groups are connected laterally along the main chain. If such a molecular aggregation entity was molecularly dispersed in the low molecular weight nematics, it is also reasonable to conclude that a local smectic-like ordering might be induced in the composite system.

3.4. *Relationship between smectic-like short range ordering and* K_3/K_1 *ratio*

Based on the theoretical prediction given by equation (11), it is expected that the magnitude of K_3/K_1 depends on the degree of smectic-like short-range ordering in the PS6EC/E7 composite system. The value of K_3/K_1 was measured on the basis of the electric capacitance method as shown by figure 3 and equation (1). Figure 11 shows the E7 mole fraction dependence of the K_3/K_1 ratio for the composite system. The value of K_3/K_1 decreased with an increase in the PS6EC fraction. Figures 9–11 reveal that the smectic-like short-range ordering and the magnitude of K_3/K_1 have a similar tendency with the E7 mole fraction. The magnitude of K_3/K_1 was anomalously small at an intermediate region between the smectic and nematic phases (59 mol % of E7). Such a small value of K_3/K_1, nearly zero, has never been reported in the case of low molecular weight liquid crystals.

Why the presence of smectic-like short-range ordering causes the decrease in the value of K_3/K_1 is supposed as follows: K_3/K_1 might be related to the ratio of molecular length to width, L/D. K_3/K_1 decreases with a decrease in L/D. Considering that the molecules which constitute the smectic-like short-range ordering behave as a single molecule as shown in figure 12, its width, D' is apparently larger than D. Consequently, it is supposed that the addition of PS6EC into E7 results in a decrease in K_3/K_1 due to an apparent decrease in L/D' of the molecules.

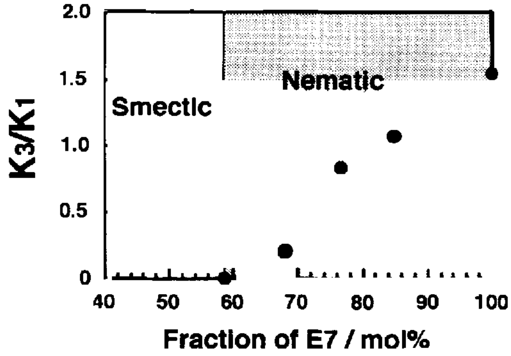

Figure 11. E7 dependence of the K_3/K_1 ratio for the PS6EC/E7 composite system.

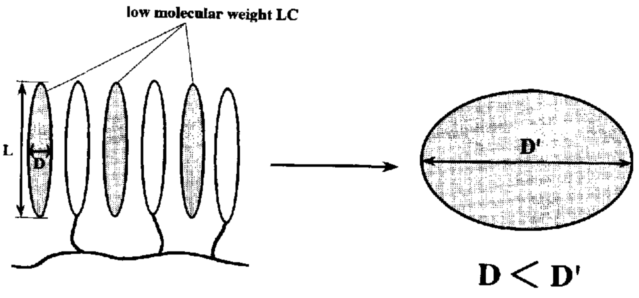

Figure 12. Schematic representation of the molecular width (D) with the larger width (D').

3.5. *Steepness of LC molecular reorientation in the composite system*

Figures 13 (*a*)–(*d*) show the electric voltage dependence of the electric capacitance for the homogeneous cells of E7 and the PS6EC/E7 composite systems in the vicinity of the Freedericksz transition. The change in the electric capacitance corresponds to the degree of reorientation of the liquid crystalline molecules. The capacitance for the E7 cell (see figure 13 (*a*)) gradually increased above the threshold voltage, and on the other hand, especially in the case of figure 13 (*d*) for the PS6EC/E7 : 41/59 composite system, the magnitude of capacitance increased discontinuously at the applied voltage of 2·2 V. These results reveal that the steepness of the molecular reorientation upon application of an electric field is remarkably enhanced by adding PS6EC to E7.

The steepness of the electro-optical response for the TN cells of the PS6EC/E7 composite system was investigated as shown in figure 14. Figure 14 shows the applied voltage dependence of the normalized intensity of transmitted light through the polarizer–TN cell–analyser optical path under crossed nicols. The steepness of electro-optical response, γ_s is defined by equation (15):

$$\gamma_s = \frac{V_{90}}{V_{10}} \qquad (15)$$

where V_{90} and V_{10} are the applied voltages at transmittance of 90 per cent and 10 per cent respectively. As the steepness is higher, the value of γ_s approaches 1·0. The table shows the values of γ_s for E7 and the PS6EC/E7 composite systems. In general, the magnitude of γ_s for LC materials ranges 0·66–0·8. On the other hand, the magnitude of γ_s for the PS6EC/E7 : 41/59

Table. γ_S for the PS6EC/E7 composite system

Sample	γ_s
E7	0·70
PS6EC/E7 = 32/68	0·77
PS6EC/E7 = 41/59	0·96

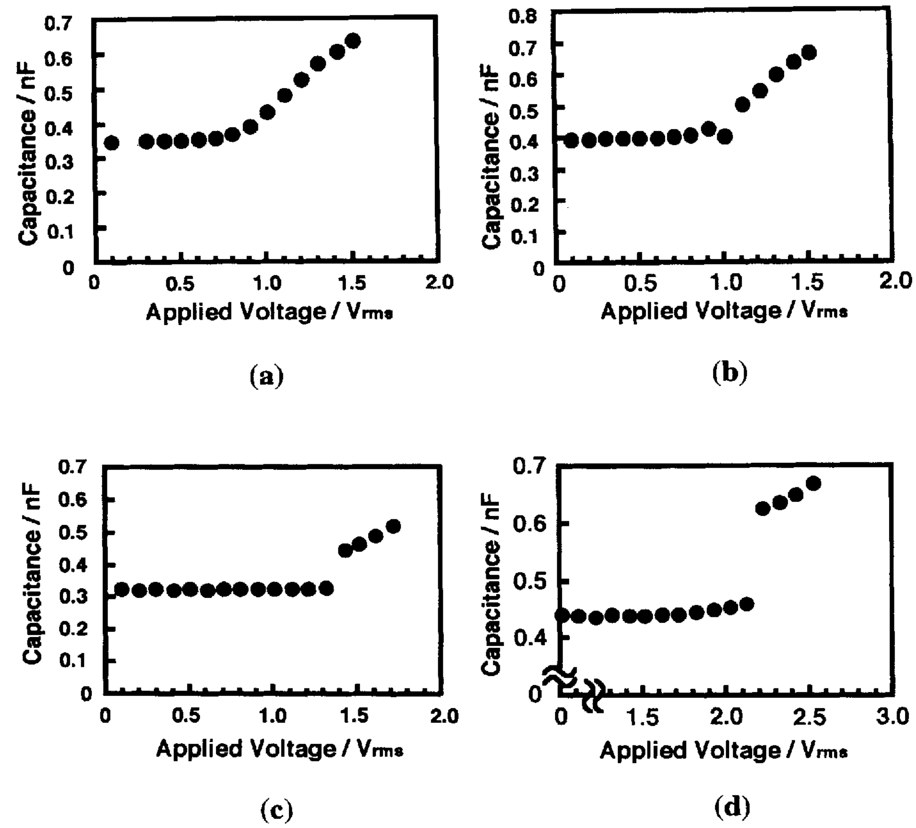

Figure 13. Applied electric voltage dependence of the electric capacitance around the Freedricksz transition for the homogeneous cell of (*a*) E7, (*b*) PS6EC/E7 = 15/85, (*c*) 32/68 and (*d*) 41/59 mol % composite systems.

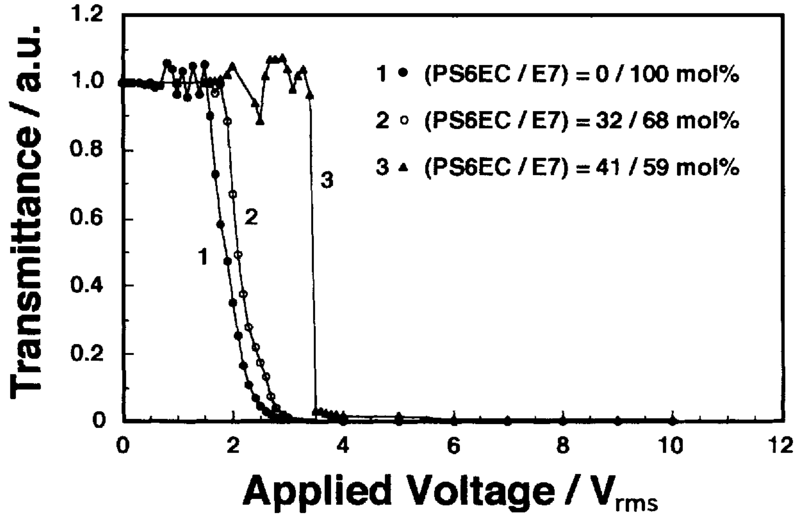

Figure 14. The electric voltage dependence of the normalized intensity of the transmitted light through the polarizer, TN cell and analyser under crossed nicols.

composite system was 0·96. This result reveals that a remarkably steeper response characteristic was successfully achieved for the PS6EC/E7 : 41/59 composite system by control of the short-range ordering for the alignment of the liquid crystalline molecules.

4. Conclusions

The phase diagram of the PS6EC/E7 composite system revealed that the system has a miscible mesophase of nematic and smectic phases above 59 mol % and below 49 mol % of E7 content, respectively. From the small angle X-ray scattering study, the presence of smectic-like short-range ordering was suggested in the nematic phase of the PS6EC/E7 composite system. With increasing the E7 mole fraction in the composite system, the smectic-like short-range ordering decreased and K_3/K_1 increased. An anomalously small value, nearly zero, of K_3/K_1 was observed at an intermediate region between the smectic and the nematic phases (E7 : 59 mol %). A remarkable improvement in the steepness for the molecular reorientation was successfully achieved for the PS6EC/E7 composite system.

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References

[1] Gruler, H., Scheffer, T. J., and Meier, G., 1972, *Z. Naturf*, (a), **27**, 966.

[2] Pieranski, P., Brochard, F., and Guyon, E., 1972, *J. Phys.*, **33**, 681.

[3] Baur, G., 1981, *Mol. Cryst. liq. Cryst.*, **63**, 45.

[4] Leenhouts, F., Roebers, H. J., Dekker, A. J., and Jonker, J. J., 1979, *J. Phys.*, **40**, C3-291.

[5] van der Meer, B. W., Posma, F., Dekker, A. J., and de Jeu, W. H., 1982, *Mol. Phys.*, **45**, 1227.

[6] Bradshaw, M. J., Raynes, E. P., Fedak, I., and Leadbetter, A. J., 1984, *J. Phys.*, **45**, 157.

[7] Kajiyama, T., Kikuchi, H., Miyamoto, A., Moritomi, S., and Hwang, J. C., 1989, *Chem. Lett.*, **1989**, 817.

[8] Kajiyama, T., Kikuchi, H., Miyamoto, A., Moritomi, S., and Hwang, J. C., 1990, *Mat. Res. Soc. Symp. Proc.*, **171**, 305.

[9] Kikuchi, H., Moritomi, S., Hwang, J. C., and Kajiyama, T., 1991, *Polym. Adv. Tech.*, **1**, 297.

[10] Kajiyama, T., Kikuchi, H., and Mori, Y., 1991, *Chem. Lett.*, **1991**, 925.

[11] Kikuchi, H., Kibe, S., and Kajiyama, T., 1995, *Proc. SPIE*, **2408**, 141.

[12] Finkelmann, H., Ringsdorf, H., and Wendorf, J. H., 1978, *Makromol. Chem.*, **179**, 273.

[13] Uchida, T., and Takahashi, Y., 1981, *Mol. Cryst. liq. Cryst. Lett.*, **72**, 1339.

[14] Deuling, H. J., 1972, *Mol. Cryst. liq. Cryst.*, **12**, 123.

[15] de Gennes, P. G., 1975, *The Physics of Liquid Crystals* (Oxford Univ. Press).

[16] Leslie, F. M., 1970, *Mol. Cryst. liq. Cryst.*, **12**, 57.