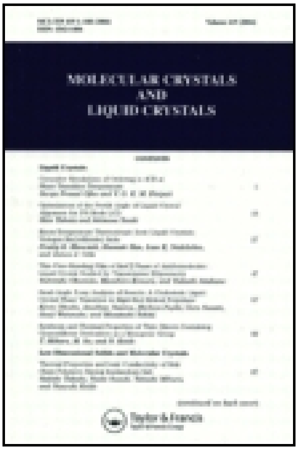


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

ORIENTATIONAL BEHAVIOR OF POLY (γ-BENZYL L-GLUTAMATE) IN A CHOLESTERIC LIQUID CRYSTALLINE SOLUTION UNDER A DYNAMIC ELECTRIC FIELD NEAR THE NEMATIC TEMPERATURE

Toshinori Imai [a], Mitsuru Masui [a], Nobuyori Matsui [a], Kazuyuki Hiraoka [a], Takuhei Nose* [a], Munehiro Date [a] & Yoshiko Uematsu [a]

[a] Department of Applied Chemistry, 1583 Iiyama, Atsugi, Kanagawa, Japan, 243-0297

Version of record first published: 02 Sep 2010

To cite this article: Toshinori Imai, Mitsuru Masui, Nobuyori Matsui, Kazuyuki Hiraoka, Takuhei Nose*, Munehiro Date & Yoshiko Uematsu (2004): ORIENTATIONAL BEHAVIOR OF POLY (γ-BENZYL L-GLUTAMATE) IN A CHOLESTERIC LIQUID CRYSTALLINE SOLUTION UNDER A DYNAMIC ELECTRIC FIELD NEAR THE NEMATIC TEMPERATURE, Molecular Crystals and Liquid Crystals, 423:1, 37-50

To link to this article: http://dx.doi.org/10.1080/15421400490494418

Mol. Cryst. Liq. Cryst., Vol. 423, pp. 37–50, 2004
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490494418

ORIENTATIONAL BEHAVIOR OF POLY (γ-BENZYL L-GLUTAMATE) IN A CHOLESTERIC LIQUID CRYSTALLINE SOLUTION UNDER A DYNAMIC ELECTRIC FIELD NEAR THE NEMATIC TEMPERATURE

Toshinori Imai, Mitsuru Masui, Nobuyori Matsui, Kazuyuki Hiraoka,
Takuhei Nose, Munehiro Date, and Yoshiko Uematsu*
Department of Applied Chemistry, Tokyo Institute of Polytechnics,
1583 Iiyama, Atsugi, Kanagawa, 243-0297 Japan

We investigate the cholesteric texture of a poly(γ-benzyl L-glutamate) liquid crystalline solution in 1,1,2,2-tetrachloroethane as a function of temperature and the strength of alternating electric filed (10 Hz) to see the effects of that field on cholesteric twisting. The solution under no electric field has a nematic temperature, T_N, at which the cholesteric pitch diverges with changing the cholesteric sense. We have discovered cholesteric-to-nematic-to-cholesteric changes with no change in the cholesteric sense as the electric voltage is progressively increased at a fixed temperature above T_N. Below T_N, only the cholesteric-to-nematic change takes place with increasing the voltage.

Keywords: poly(γ-benzyl L-glutamate); dynamic electric field; nematic point; cholesteric pitch

INTRODUCTION

Poly(γ-benzyl L-glutamate) (PBLG) forms a liquid crystal (LC) in helicogenic organic solvents above a certain concentration [1,2]. The cholesteric liquid crystalline texture formed by PBLG [1,2] has been shown to be the norm due to the optical activity of the PBLG molecule, and the nematic textures under some particular conditions are rather exceptional [3–6]. For instance, we have found for PBLG in a 1,1,2,2 tetrachloroethane solution that, as the temperature is raised, the cholesteric pitch increases, becomes infinitely large, and then decreases, showing the opposite cholesteric sense with a further increase of temperature. That is, the liquid crystalline solution passes through a nematic state at a particular temperature, which

---

*Corresponding author. E-mail: nose@chem.t-kougei.ac.jp is referred to as the *nematic point*. In other words, the thermal fluctuation can affect the twisting force of a cholesteric structure, and realize a nematic texture, even bringing about a change in the cholesteric sense [7]. On the other hand, since a PBLG molecule in helical conformation has a large permanent dipole moment along the helical axis [8], the electric field may also change the cholesteric twist pitch. The application of a strong electric field exceeding the threshold value is expected to align the rodlike molecules in the direction of the electric field, resulting in a trasitional change from a cholesteric to a nematric state [9]. Actually, we observed the transition in PBLG in a 1,1,2,2-tetrachloroethane (TCE) solution under an electrostatic field of several hundred kilovolts per centimeter [10]. Recently, we found a similar transition to the nematic state from the cholesteric state under alternating electric field instead of a strong electrostatic field for a PBLG solution in TCE. In this study, we investigate the liquid crystalline texture as a function of temperature and the strength of an alternating electric field for the PBLG solution in TCE, a helicogenic solvent, to understand the effects of that field on the cholesteric twisting behavior of PBLG as well as those on the thermal force with changing temperature. We have discovered a novel cholesteric-to-nematic-to-cholesteric change in texture as the alternating voltage is progressively increased at a fixed temperature. In the following, we will describe the details of experimental observations and discuss them in terms of the effects of an external alternating electric field on the cholesteric twisting force, which are different from those of thermal perturbations.

EXPERIMENTAL

Materials and Samples

PBLG was synthesized by the N-carboxyanhydride method in dioxane with n-buthylamine as the initiator and was subsequently precipitated in methonal. The crude PBLG was repeatedly precipitated by cooling a dilute solution of the polymer in a mixed solvent of TCE and hexane. The viscosity-average molecular weight was 6×10^4. TCE was a product of Wako-Junyaku Co. (Tokyo, Japan) and used as received. The concentration of the sample solution was fixed at 0.30 g/ml.

Measurements

The liquid crystalline texture was observed by a polarizing microscope on which a hot stage was mounted and controlled at a desired temperature. The polarizing plates of a polarizer and an analyzer were always set to be crossed at right angles. The cholesteric pitch was evaluated from the polarizing microscopic images of the finger-print texture. The cholesteric sense was determined by circular dichroism (CD). The sample cell used for these observations by applying an electric field was constructed of two glass plates coated with thin-film Au as electrodes. The direction of the electric field was perpendicular to the cell surface. The sample thickness was either 130 μm or 200 μm. The frequency of the alternating electric field ranged from 0.01 Hz to 10 Hz but was fixed at 10 Hz in most cases. The electric field strength ranged from 0.1 to 2.0 kV/cm.

We adopted two procedures for scanning the temperature and the strength of the alternating electric field: Procedure (1) was to increase the strength of the applied electric field at the rate of 0.1 kV/cm per 30 min at a fixed temperature after increasing the temperature to the set value with no electric field. Procedure (2) was to increase the temperature at the rate of 5°C per 20 min at a fixed electric field strength after elevating the voltage to the desired value at the room temperature.

RESULTS AND DISCUSSION

Temperature Dependence of Cholesteric Pitch under no Electric Field

Figure 1 shows the temperature dependence of an inverse cholesteric pitch, 1/P, for the PBLG solution under no electric field. It clearly demonstrates the presence of the nematic point at about 80°C, where the pitch, P, diverges to be infinitely large, implying that the solution is nematic. CD measurements indicate that the cholesteric sense changes from right to left at the nematic point as the temperature is increased. In other words, the twisting force to the left direction seems to monotonically increase with increasing temperatures.

Molecular Orientation as Observed by Intensity of Transmitted Light through Crossed Polarizer and Analyzer

At the frequency of 10 Hz of an applied alternating electric field, we have stationary transmittance of light in polarizing microscopic observations with no change with time, seeing static textures of molecular axis orientations. Figure 2 shows changes of the intensity of transmitted light through the crossed polarizer and analyzer with increasing the strength of the electric field following Procedure (1) at various fixed temperatures. As is shown in Figure 2(a), sufficiently below the nematic temperature, T_N, the transmittance vanishes above about 0.3 kV/cm up to 2.0 kV/cm, indicating a change from a cholesteric to a nematic texture. It is noteworthy

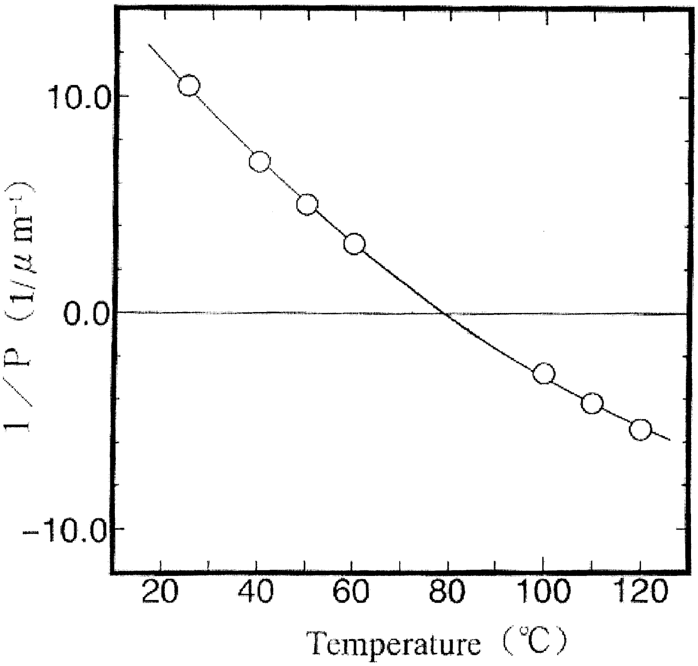
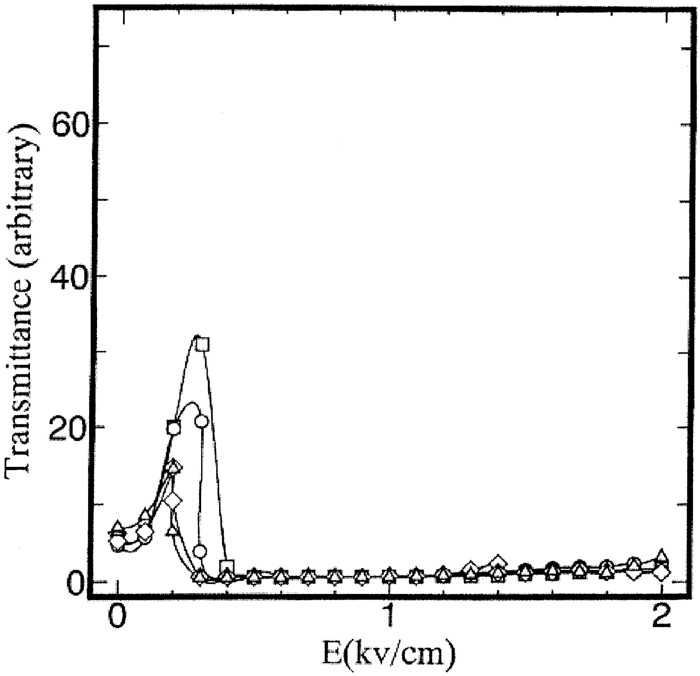


FIGURE 1 Plots of inverse cholester pitch, 1/P, against temperature for PBLG solution of 0.30 g/ml in TCE. Positive and negative values of pitch correspond to right-hand and left-hand twist, respectively.

that the transmittance exhibits a peak right before vanishing, probably reflecting orientation motions of PBLG molecules taking place at the transition point from twisting alignments to nematic alignments. Around T_N, as in Figure 2(b), the transmittance easily disappeared by applying an electric field of very low strength, exhibiting peaks right before the disappearance, as is in the case below T_N. This is understandable because the temperature is closer to T_N, so that the orientation easily changes to be nematic. With a further increase of the electric field strength, however, the transmitted light appears again around 1 kV/cm with a peak at the start of the bright region. Above T_N, the appearance of the light-transmitted region at higher voltages is clear, as is shown in Figure 2(c), where no peaks are observed near the onset of increasing transmittance. These behaviors at higher voltages near and above T_N suggest the presence of another cholesteric region at higher voltages in the higher-temperature region. Polarizing microscopic observations and CD measurements confirm that it is of a cholesteric texture with the same cholesteric sense as that under no electric field.



(a)

FIGURE 2 Transmitted light intensity against electric field strength at various temperatures for the PBLG solution with the thickness of 130 μm (a) below, (b) near, and (c) above the nematic temperature. Temperatures for (a) (□) 25°C, (○) 30°C, (◇) 40°C, (△) 50°C ; (b) (□) 60°C, (○) 70°C, (◇) 80°C, (△) 90°C; (c) (□) 100°C, (○) 110°C, (◇) 120°C, (△) 130°C.

Figure 3 shows the polarizing microscopic images at 110°C under intermediate electric fields of 0.5 kV/cm and 0.6 kV/cm, as well as those at 80°C and 110°C under a higher electric field of 2.0 kV/cm. The image at 110°C under 0.5 kV/cm (Figure 3(a) is just dark, suggesting the homeotropic nematic texture. On the other hand, the images (Figures 3(b), 3(c), and 3(d)) at higher voltages clearly exhibit the fingerprint texture, which indicates the cholesteric molecular orientations. Coexisting Grandjan textures allow us to measure the CD spectra, which can indicate the cholesteric sense. In Figure 4 are shown the CD spectra as a function of the voltage at a fixed temperature in the higher-temperature region. When the voltage is increased, a peak is observed at lower voltages, becomes lower at 0.2 kV/cm, disappears at the voltages of 0.3 kV/cm and 0.4 kV/cm, and then appears again with a further increase of the voltage. The

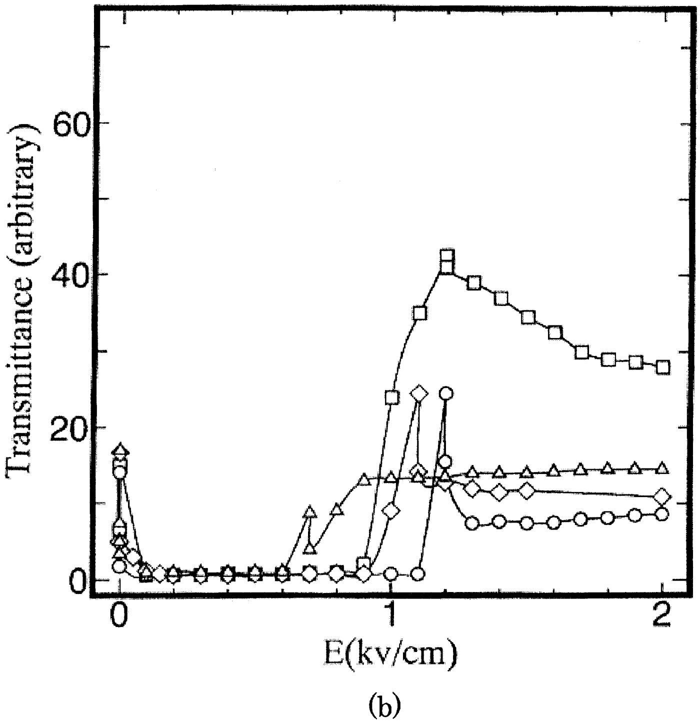


FIGURE 2 Continued.

transition voltages are consistent with those observed in the transmittance illustrated in Figure 2. The peaks observed at higher voltages are negative, having the same sign as that at lower voltages. These results of CD and polarizing microscopic measurements show that the changes observed at higher temperatures with an increase of the voltage are the cholesteric-to-nematic-to-cholesteric transitions with no change of the cholesteric sense. The peaks and enhanced transmittance at higher voltages observed around T_N but not above T_N may be due to the transitional unstable orientation behavior in changing to the cholesteric texture. The appearance of transmittance peaks around the transition from the cholesteric to the nematic state implies that the transitional motions of molecular orientation include motions with molecular axes shifting their direction from the light direction; that is, it suggests that the cholesteric texture passes through the planar cholesteric texture to change to the homeotropic nematic texture.

The above-mentioned kinds of behavior of molecular orientation are all observed for a different sample thickness of 0.20 mm as well.

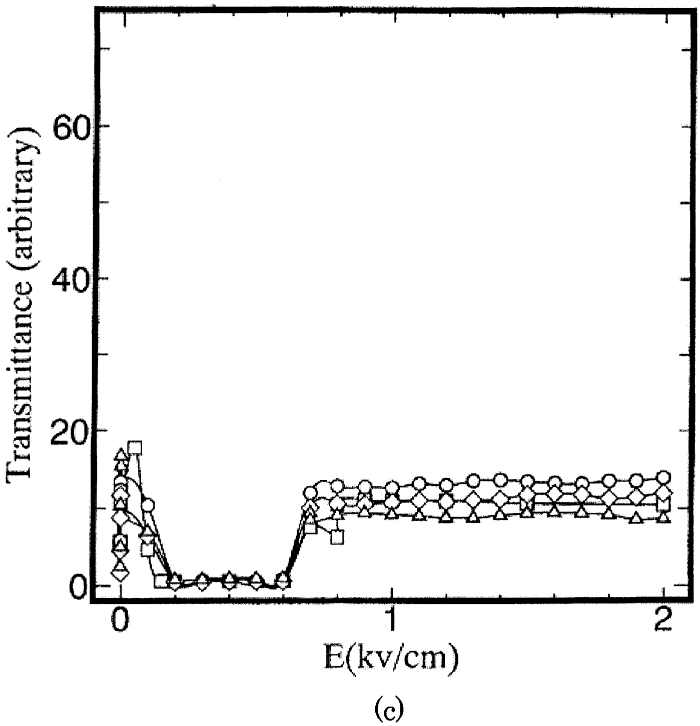


FIGURE 2 Continued.

Summarizing the above results, we have drawn a diagram of temperature vs. electric field strength of the liquid crystalline texture for the present system, which is shown in Figure 5. In conclusion, we have found for the first time a cholesteric region at higher alternating voltage above T_N as well as a homeotropic nematic region located at intermediate strengths of an electric field, and even at higher voltages below T_N.

Temperature Dependence of Cholesteric Pitch under Elevated Alternative Electric Field

Figure 6 illustrates the temperature dependence of an inverse cholesteric pitch, 1/P, in the cholesteric region appearing in an alternating electric field at higher temperatures. The results are under an electric field of 2.0 kV/cm with a frequency of 10 Hz, including those with different sample thicknesses and different experimental procedures. The inverse cholesteric pitch, i.e., the magnitude of cholesteric twist, appears at a temperature slightly lower than T_N, which is consistent with Figures 2(b) and 3, and

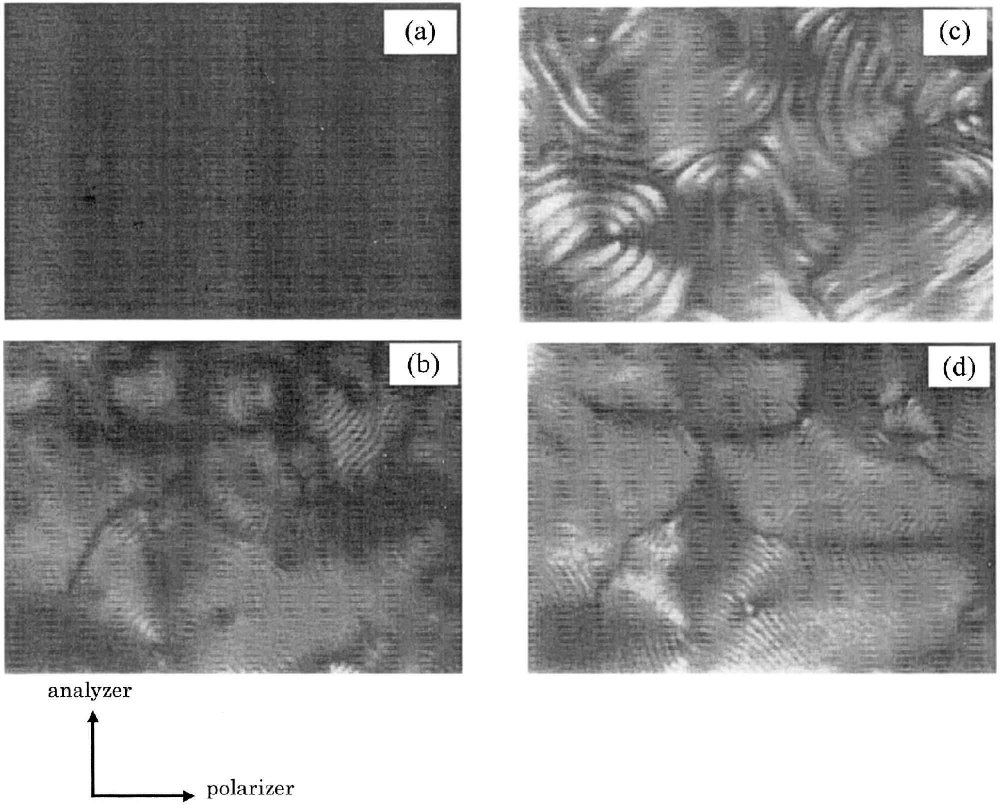


FIGURE 3 Polarizing microscopic photos taken at 110°C under intermediate electric fields of (a) 0.5 kV/cm and (b) 0.6 kV/cm, and those taken at (c) 80°C and (d) 110°C under a higher electric field of 2.0 kV/cm.

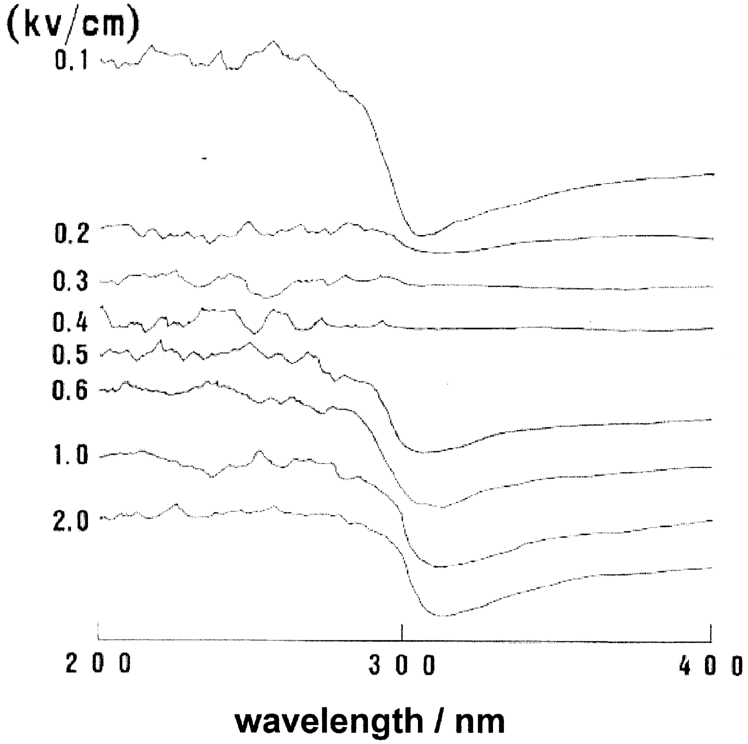


FIGURE 4 CD spectra as a function of the voltage indicated at a fixed temperature in the higher temperature region.

increases with increasing temperature. The twisting magnitude represented by 1/P is much smaller than that under no electric field at the same temperature (cf. Figure 1), although the cholesteric sense is the same. It is also noted that the results show neither process dependence nor cell-thickness dependence. The phase behavior illustrated by Figure 5 is confirmed to be independent of the process and sample thickness. It should be noted here that the cholesteric pitch is substantially independent of the strength of applied electric field in this cholesteric region, as seen by comparing the fingerprint textures between 0.6 and 2.0 kV/cm in Figures 3(b) and 3(d).

Effects of Frequency of Alternating Electric Field

The frequency of 10 Hz used above seems to be unique to the appearance of the new cholesteric region. At frequencies higher than 10 Hz, we see more complicated textures, depending on the voltage by polarizing

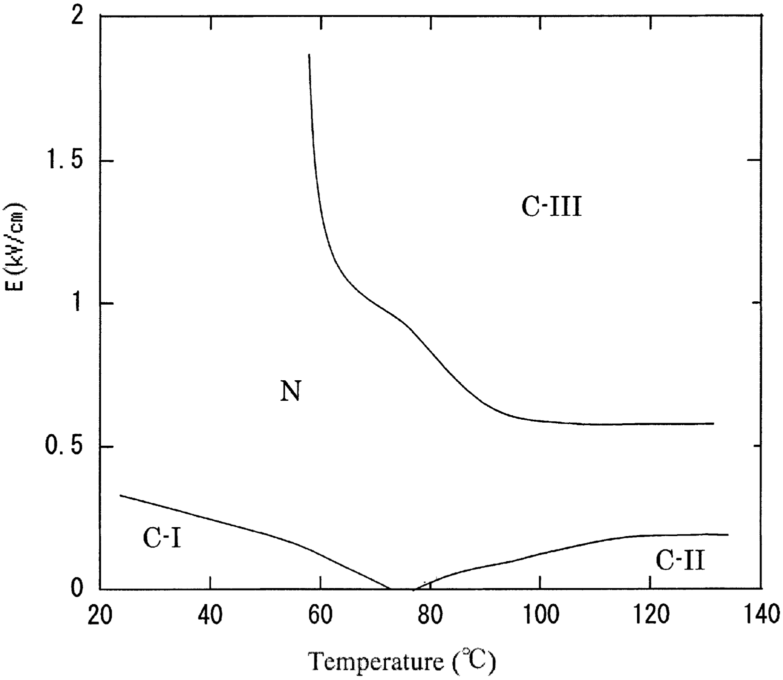


FIGURE 5 A diagram of temperature versus electric field strength for the liquid crystalline texture of PBLG solution in TCE at 10 Hz of the alternating electric field. N, homeotropic nematic region; C-I, right-hand cholesteric region; C-II, left-hand cholesteric region; C-III, left-hand cholesteric region.

microscopic observations. At lower frequencies, the transmitted light in polarizing microscopy alternatively changes from dark to bright with time under an alternating electric field, as shown in the drawn transmittance patterns for 1 Hz at 25°C in Figure 7. The dark-and-bright response of transmittance must be due to orientational motions of PBLG molecules driven by an external alternating electric field. In other words, this suggests that the orientated molecular axes sinusoidally wave following the alternating electric field. At voltages below 1.4 kV/cm, the response of transmitted light synchronizes with a sinusoidal electric field with the same frequency. As the voltage increases to 1.7 kV/cm or more, the vibrational frequency of transmittance becomes twice the electric field frequency. It should be noted that the appearance of bright peaks is supposed to come from the same origin as the peak observed at the transition between cholestric and nematic textures in Figure 2. The molecular axes must deviate from the light direction and may be waving around the light axis as the axis of rotation. The change in the direction of waving molecular axes is supposed

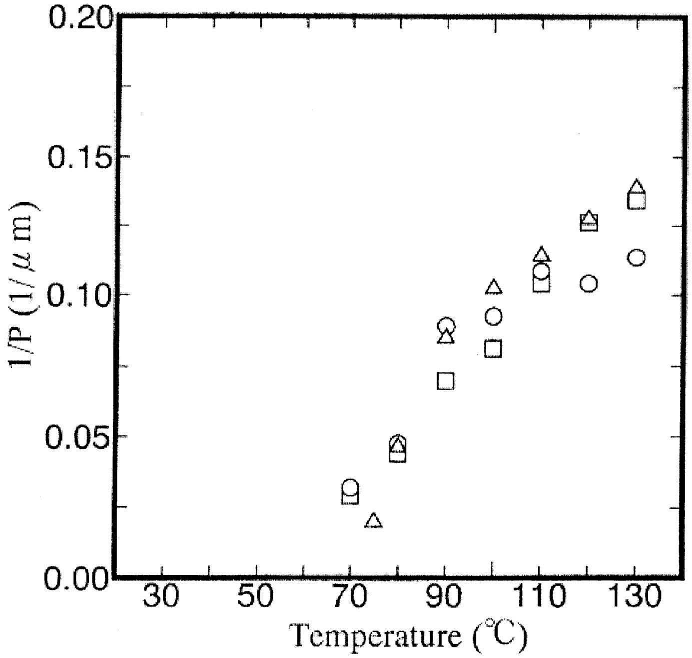


FIGURE 6 Plots of inverse cholesteric pitch, 1/P, against temperature under electric field of 2.0 kV/cm with a frequency of 10 Hz for the PBLG solution in TCE: (□) sample thickness = 130 μm and Procedure (1); (○) sample thickness = 200 μm and Procedure (1); and (△) sample thickness = 200 μm and Procedure (2).

to give the dark-and-bright pattern. Even at a low frequency of 1 Hz, the orientation of PBLG molecular axes may not always follow the direction of an alternating electric field and instead be waving with the finite amplitude at low voltages, since the PBLG molecules are giant rods. Therefore, the change in frequency of the pattern with voltage may be due to a change in the amplitude of the vibrational waving motions: the larger amplitude of motion could take two positions of bright angle in an electric period at higher voltages, while the smaller motion could take one per period.

Similar changes of a pattern that are consistent with the above explanation are observed when the frequency of electric field is increasing at higher voltages. At a low frequency, e.g., 1 Hz, we observe two peaks of the dark-and-bright pattern in a period of electric field as is mentioned above. Then we see a change in the pattern to one peak per period as the frequency is further increased and eventually reach a region of a stationary transmittance of light with no change with time at higher frequencies around 10 Hz. In this region, the molecular axes cannot move

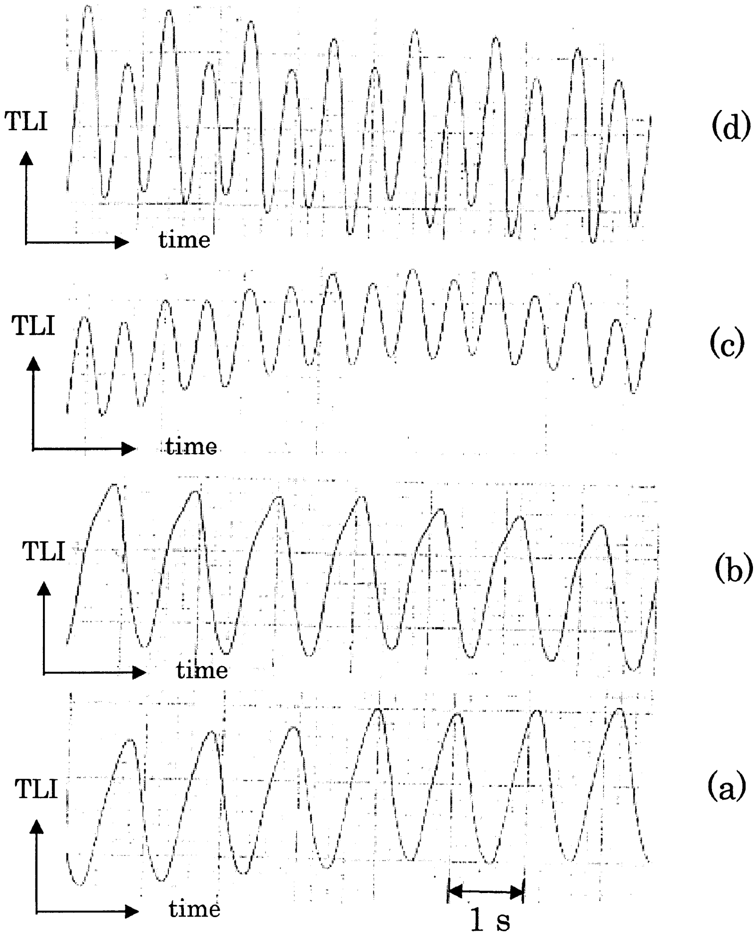


FIGURE 7 Dependency of transmittance patterns [transmitted light intensity TLI/(a.u.) against time] of polarizing microscopic observations on alternating voltage under electric field of a low frequency (1 Hz) for the PBLG solution in TCE at 25°C. Voltages are (a) 1.1 kV/cm, (b) 1.4 kV/cm, (c) 1.7 kV/cm, and (d) 2.0 kV/cm.

so fast as to follow the external alternating electric field and may take stationary positions with thermal fluctuations. The frequency of 10 Hz in the present study is in this frequency range.

General Discussion

Summarizing the experimental results, we may say the following: Homeotropic nematic texture is realized by applying an "alternating" electric field for a PBLG solution in TCE at 10 Hz under appropriate voltages above 0.5 kV/cm. A new cholesteric phase is found with further increasing voltage at temperatures higher than T_N. The important findings and conditions for the appearance of the cholesteric texture, which may be keys to understanding it, are described below.

The cholesteric region at higher voltage does not appear at low temperatures but does appear at temperatures slightly lower or higher than T_N. This may alternatively imply that not the right-hand but the left-hand cholesteric twist is a necessary condition. This cholesteric sense is the same as that under no electric field. The frequency of electric field should be reasonably high but not too high, i.e., around 10 Hz. These results obviously show that cholesteric-to-nematic-to-cholesteric changes with increasing voltage of an alternating electric field are totally different from the change with the nematic temperature induced by increasing temperature under no electric field.

The following possible explanation can tentatively be deduced. At lower voltages, an alternating electric field of an appropriate frequency aligns the orientation of PBLG molecular axes and/or domain axes parallel to the direction of the electric field, resulting in a homeotropic nematic texture. Usually the nematic phase must be more stable under a higher electric field. The experimental fact observed here is not the case. As long as the intrinsic molecular characteristics for molecular interactions such as the permanent dipole moment and/or twisting force (quadrupole moment) are not changed by an electric field, the experimental finding is quite unexpected. PBLG may not behave as simple molecules under an alternating electric field. The PBLG molecule is a giant rodlike molecule having many side chains that yield a large overall permanent dipole moment and strongly affect the intermolecular (i.e., interrod) interactions. The thermal motion of the side-chains is considered to be active enough to change their conformations, which has been detected by dielectric measurements [11,12]. Therefore, an external electric field can be presumed to easily alter the side-chain conformations, which may lead to changes in the interrod interactions, while the PBLG molecule cannot easily change its orientation because of a large rodlike molecule. Therefore, a strong electric field may change both the aligning force and the cholesteric twisting force of rodlike PBLG molecules. In the higher-temperature region of left-hand twist, the enhancement of the twisting force and/or the reduction of the aligning force are brought about to recover the left-hand cholesteric texture, while in the lower-temperature region of right-hand twist, the aligning force by the electric field is still stronger than the twisting force. The experimental finding that the cholesteric region starts to appear slightly below T_N may suggest that the enhancement of the left-hand twisting force is more or less induced by the electric field around T_N, at the least.

A more explicit mechanism based on the chemical structure of PBLG, including chirality, should be revealed to understand this phenomenon.

CONCLUSION

For a rodlike PBLG lyotropic liquid crystal, a new cholesteric region under an alternating electric field has been discovered beyond the homeotropic nematic texture by further increasing voltage. The cholesteric region does not appear at lower temperatures, but it does at temperatures higher than T_N. The cholesteric sense is the same as that under no electric field. The frequency of the electric field should be reasonably high—that is, around 10 Hz—where the axial motions of PBLG cannot follow changes in the electric field and are stationary. At lower voltages, an alternating electric field aligns the PBLG molecular axes and/or domain axes to the electric field direction. An alternating electric field of high voltage is presumed to enhance the twisting force and/or to reduce the aligning force of PBLG molecules by intensively moving the dipoles in the side chains. This may result in the recovery of the cholesteric twisting that the PBLG solution possesses originally.

REFERENCES

[1] Robinson, C. (1956). *Trans. Faraday Soc.*, *52*, 571–592.
[2] Robinson, C., Ward, J. C., & Beevers, R. B. (1958). *Discuss. Faraday Soc., 25*, 29–42.
[3] Sobajima, S. (1967). *J. Phys. Soc. Japan*, *23*, 1070–1078.
[4] Samulski, E. T. & Tobolsky, A. V. (1968). *Macromolecules*, *1*, 555–557.
[5] Robinson, C. (1961). *Tetrahedron*, *13*, 219–234.
[6] Duke, R. W., Dupre, D. B., Hines, W. A., & Samulsky, E. T. (1976). *J. Am. Chem. Soc., 98*, 3094–3101.
[7] (a) Keating, P. (1969). *Mol. Crys. Liq. Cryst., 8*, 315–326.
(b) Lin-Liu, Y. R., Shih, Y. M., Woo, C., & Yang, H. T. (1976). *Phys. Rev., A14,* 445–450.
[8] Wada, A. (1959). *J. Chem. Phys.*, *30*, 328–329.
[9] Duke, R. W. & Dupre, D. B. (1974). *Macromolecules*, *7*, 374–376.
[10] Imai, T., Mizunoya, T., Hiraoka, K., Nose, T., Date, M., & Uematsu, Y. (2004). *Polymer J.*, *36*, 167–170.
[11] Hikichi, K., Saito, K., Kaneko, M., & Furuichi, J. (1964). *J. Phys. Soc. Japan*, *19*, 577.
[12] Yamashita, Y., Tsutsumi, A., Hikichi, K., & Kaneko, M. (1976). *Polymer J.*, *8*, 114–120.