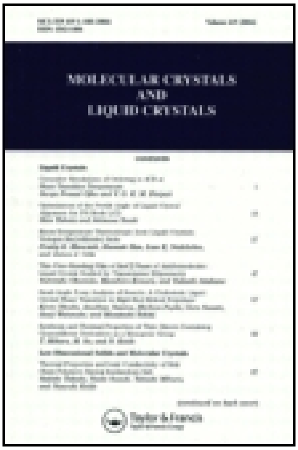


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Effect of the Electrical Field on the Phase Transition in Solutions of Rod-Like Particles I: Optical Observations

Yoshinorl Toyoshima [a] , Naokl Minami [a] & Mitsunori Sukigara [a]
[a] Institute of Industrial Science, University of Tokyo, Roppongi. Minato-Ku, Tokyo, 106, Japan

To cite this article: Yoshinorl Toyoshima , Naokl Minami & Mitsunori Sukigara (1976): Effect of the Electrical Field on the Phase Transition in Solutions of Rod-Like Particles I: Optical Observations, Molecular Crystals and Liquid Crystals, 35:3-4, 325-335

To link to this article: http://dx.doi.org/10.1080/15421407608083681

Mol. Cryst. Liq. Cryst., 1976, Vol. 35, pp. 325–335

Printed in Holland

Effect of the Electrical Field on the Phase Transition in Solutions of Rod-Like Particles I

Optical Observations

YOSHINORI TOYOSHIMA, NAOKI MINAMI and MITSUNORI SUKIGARA

Institute of Industrial Science, University of Tokyo, Roppongi, Minato-Ku, Tokyo 106, Japan

(*Received January 1, 1976*)

Effect of electrical field on the temperature of phase transition between the isotropic liquid phase and liquid crystal phase in dioxane solution of poly-γ-benzyl-L-glutamate (PBLG), ranging in concentration from 11.0 to 15.0 wt % was examined by means of polarizing microscope measurements.

Shift of the transition temperature, ΔT was found to be essentially proportional to square of the field strength applied in the range of less than 500 volts/cm. A semi-empirical equation which gives a linear relationship between the transition temperature and square of the field strength is derived taking the structure of the solution into consideration and compared with the experiments.

INTRODUCTION

It was shown by Helfrich that at temperature slightly above the normal phase transition between liquid crystal (nematic) and isotropic liquid, it is possible to observe a field induced phase transition from the isotropic phase to the nematic phase by applying an electric field.[1] According to a thermodynamic consideration, the shift in the transition temperature caused by the electric field, E is given by

$$\Delta T = E^2(T_0/q)(\varepsilon_2 - \varepsilon_1)/8\pi\rho \qquad (1)$$

as a first approximation. Here T_0 is the transition temperature in the absence of the electric field, q is the heat of transition per unit mass, ρ is the density and ε_2 and ε_1 are the dielectric constants of the solution below and above the transition temperature. In most phase transition $(\varepsilon_2 - \varepsilon_1)/q$ is too small to detect a shift at practicable field strengths. However, for the transition between liquid crystal and isotropic liquid phases of materials whose molecules possess a large dielectric anisotropy, the component ε_{1c} of dielectric constant of the oriented liquid crystal parallel to the electric field is expected to be remarkably larger than the dielectric constant of the isotropic liquid phase, ε_{iso}. Furthermore, the transition of a nematic phase to the isotropic liquid state is often associated with an extraordinarily small heat of transition of order of kT or less per molecules[2] which is much smaller than the heat of fusion of the ordinary organic compounds. This appears to be the case for *p*-ethoxybenzylidene-*p*′-aminobenzonitorile, investigated by Helfrich.[1] It was found that the transition temperature was raised by nearly 1°C by a field of 10^5 V/cm at 400°k, in approximate agreement with Eq. (1) using the values $\varepsilon_{1c} - \varepsilon_{iso} = 10$ (Ref. 3) and $q = 150$ cal/mole (Ref. 2).

Synthetic polypeptides such as poly-γ-benzyl-L-glutamate (PBLG) which exist in the form of an α-helix in some solvents have been known to be in a liquid crystal phase above a certain polymer concentration.[4-7] In the system of PBLG-dimethyl formamide, the heat of transition of the isotropic to choresteric liquid crystal phase transition was estimated to be maximum of 5 cal/mole of solution from the data of differential scanning calorimetric measurements.[8] The value of the dipole moment of PBLG molecule was determined to be 3.5 Debye per residue which gives very large values such as 1750 Debye per molecule parallel to the long axis of the helix of PBLG with a degree of polymerization of 500.[9] Although a part of the PBLG molecules in a solution may exist as dimers and/or clusters in which their dipole moments are cancelled out, a number of dipole moments may remain in a form susceptible to polarization by an electric field. From these data it can be expected that the effect of the electric field on the transition temperature is much larger in the rod-like polypeptide systems than the *p*-ethoxybenzylidene-*p*′-aminobenzonitorile system.

In this paper, we report the result of the shift of the transition temperature caused by an electric field on the system of PBLG in dioxane and compare them with a theory derived semiempirically.

EXPERIMENTS

Materials

PBLG synthesized by NCA method was fractionated into three parts with methanol-dichloroethane system and the center fraction was submitted to the experiments. Its molecular weight, M was estimated as 13.5×10^4 from the limiting viscosity number, $[\eta]$ in dichloroacetic acid at 25°C, according to the equation,[10]

$$[\eta] = 2.78 \times 10^{-5} M^{0.87}$$

and the axial ratio of the polymer in α-helix was calculated as 59.6 by using equation,[10]

$$X \text{ (axial ratio)} = (1.5\ \text{Å}/15.5\ \text{Å})(M/219)$$

Methanol, dichloroethane and dichloroacetic acid were redistilled prior to use. *m*-Cresol and dioxane were dehydrated by calcium chloride, followed by distillation and kept in ampoules.

Phase transition experiments

The phase transition was investigated by means of polarizing microscope measurements. A microscope (Olympus POM 2203) with temperature controlled stage was employed for all studies. A measured amount of PBLG was dissolved in a given volume of dioxane or *m*-cresol. The soution was kept at 25°C for more than 24 hrs under stirring to establish the helical structure of the polymer. This solution was injected into a sandwich type glass cell with the dimensions of 2.0 × 2.0 × 0.01 mm. The temperature of the sample was controlled within ±0.1°C during measurement and monitored with a thermocouple connected to a recorder (Type 3406 Yokogawa Electric Works Ltd.).

Placed between crossed nicols a liquid crystalline phase transmits light unless its optical axis is completely in parallel to the optical path; the isotropic phase does not. Upon cooling a sample in the cell the temperature at which light began to be transmitted was taken as the isotropic to liquid crystal equilibrium temperature.

In the absence of the electric field, with decrease in temperature a biphasic system was produced at a temperature, T_a where some areas of the sample transmitted light. This biphasic system was stable over a temperature range T_a down to T_b and below T_b only the cholesteric liquid crystal phase existed. However in our observation, it was found difficult to determine the critical point T_b when no dark area remained. Therefore, in the absence of the electric field only the isotropic to biphasic transition temperature, T_a was determined. Cycling the temperature through this point, the transition of the system was confirmed to be reversible within ±0.5°C.

Figure 1 shows the cell constructed for the purpose of observing the phase transition with an applied electric field almost perpendicular to the line of vision. One half of the inner surface of each window of the cell was rendered electrically conductive by a transparent layer of evaporated Au. The transparent electrodes do not overlap and have a gap of 1.0 mm between their edges. (See Figure 1.) In this cell the electric field was applied practically

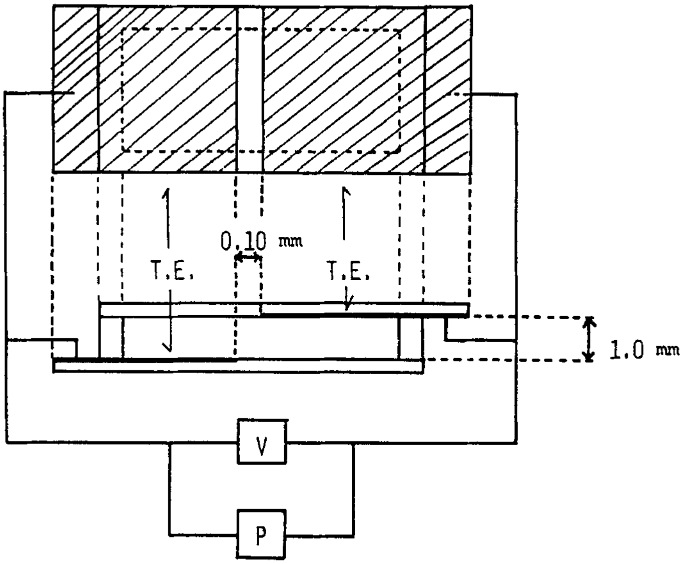


FIGURE 1 Cell for observing the phase transition with an applied electric field almost perpendicular to the line of vision.

V: Electrometer, *P*: Regulated power supply, T.E.: Transparent electrodes.

perpendicular to the line of view through the microscope. This type of cell was used because the field induced liquid crystal phase has its optical axis in direction almost parallel to the field and it transmits light most when the optical axis is perpendicular to the line of vision.

When the temperature of an isotropic solution was decreased in the presence of an electric field, a homogeneous phase which transmitted light suddenly appeared at a certain temperature without passing through any biphasic system. By repeating of cooling and heating a sample through this temperature under a constant field applied with a regulated power supply (Model G. P. 1001-1 Takasago Seisakusho, Ltd.), the temperatures at which light began to be transmitted and ceased being transmitted were determined. These temperatures were in agreement with each other ±0.5°C and their average was taken as the transition temperature corresponding to a given field strength.

RESULTS AND DISCUSSION

In Figure 2 the isotropic to biphasic equilibrium temperature, T_a in the absence of the electric field is plotted against the concentration of PBLG, C_p (wt. fraction) in dioxane and *m*-cresol and compared with the results obtained

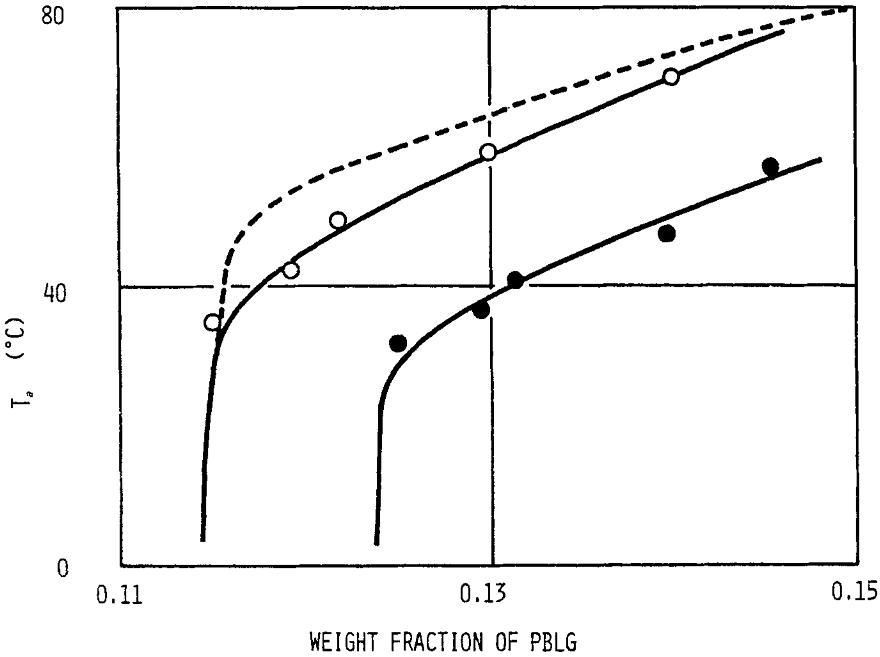
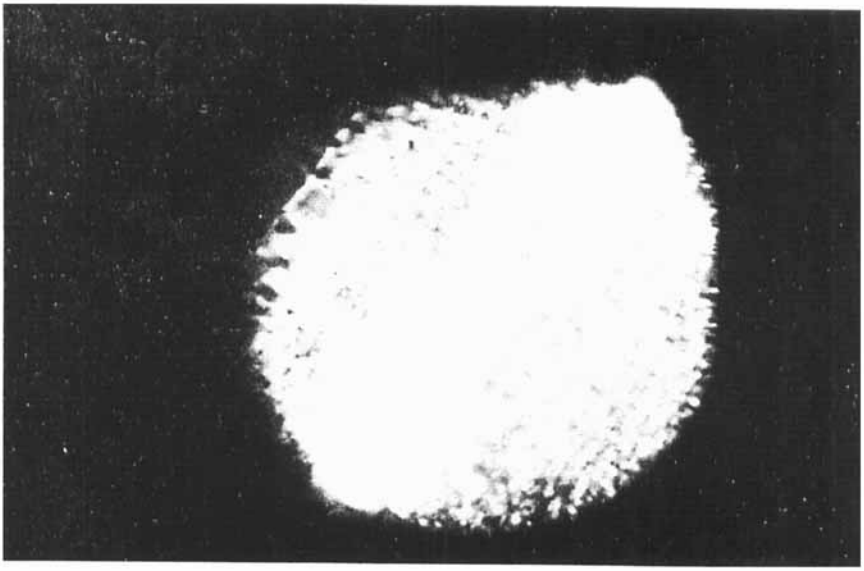


FIGURE 2 The isotropic to biphasic equilibrium temperature, T_a plotted against the concentration of PBLG, C_p in three solvents.

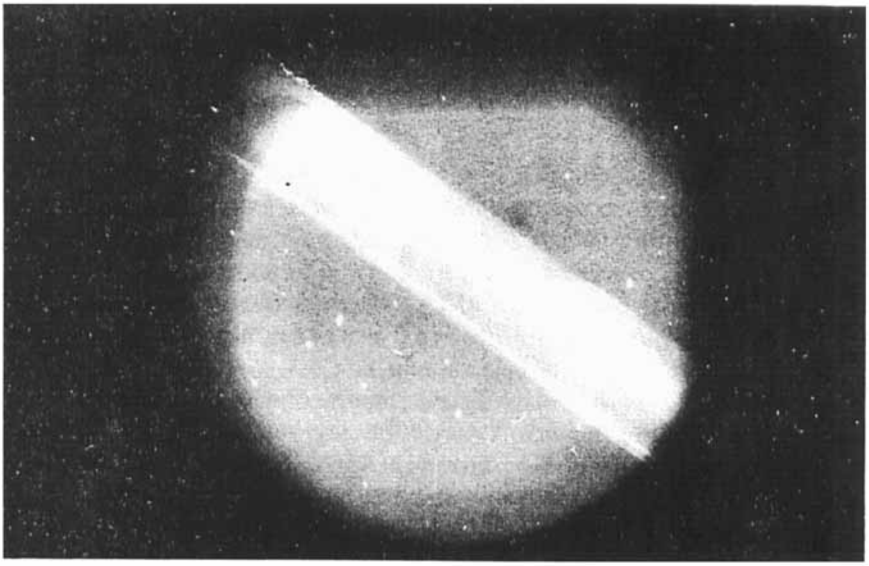
○: in dioxane, ●: in *m*-cresol, ---: in DMF[8]

in dimethyl formamide by Miller *et al.*[8] The behavior of T_a versus C_p was very similer in the three systems. Each curve had a critical concentration at which the discontinuous sharp dip in T_a appeared with a decrease in C_p. Below the critical concentration, T_a in dimethyl formamide was found to be about 10°C almost independent of C_p. But the biphasic system below the critical concentration was not observed in dioxane nor *m*-cresol solution, because both solutions froze below about 11°C.

A few examples of the polarizing microscope observation in the presence of an electric field are shown in Figure 3. Photograph (a) in Figure 3 shows a 11.87 wt % solution of PBLG in dioxane at 40.0°C. The bright part in a belt is a birefringent phase which appeared on application of an electric field of 350 V/cm perpendicular to the line of vision for one hour. The two-phase region at both sides in which the choresteric mesophase appears in the isotropic phase is the no field region. When the temperature of the system was increased up to 48.0°C and allowed more than one hour at the setting, the cholesteric mesophase disappeared from the no field region as shown in photograph (b), while no significant change in appearance of the part under



(a)



(b)

FIGURE 3 11.87 wt % PBLG in dioxane viewed between crossed polarizers in the presence (belt zone) and absence of electric field.
(a): $T = 40.0°C$ and $E = 350v/cm$ (in belt zone),
(b): $T = 48.0°C$ and $E = 350v/cm$ (in belt zone).

the electric field except a considerable decrease in the light transmittance. When the electric field was removed at this temperature, the bright part was getting dim gradually and became indistinguishable from the no field region. Applying the field of 350 V/cm to the system again, the intensity of transmitted light was increased monotonically with time to reach saturation at about one hour after setting the field. Rotating the sample between the crossed nicols, the part under the electric field exhibited a continuous change in the light transmittance as a bright and dark angles appeared each 90 degrees in turn, but the view of the no field region was practically dark at all angles. The light transmittance of the part under the field was diminishing with further increase in temperature until 55°C, at which it suddently became indistinguishable from the no field part. Cycling the temperature through this point, a 11.87 wt % PBLG solution in dioxane was confirmed to have a reversible critical temperature, 55.0 ± 0.5°C at which light began to be transmitted under the electric field of 350 V/cm. The value of the critical temperature, T_c was found to depend on the field strength and PBLG concentration. In Figure 4, T_c for PBLG solutions in dioxane at various con-

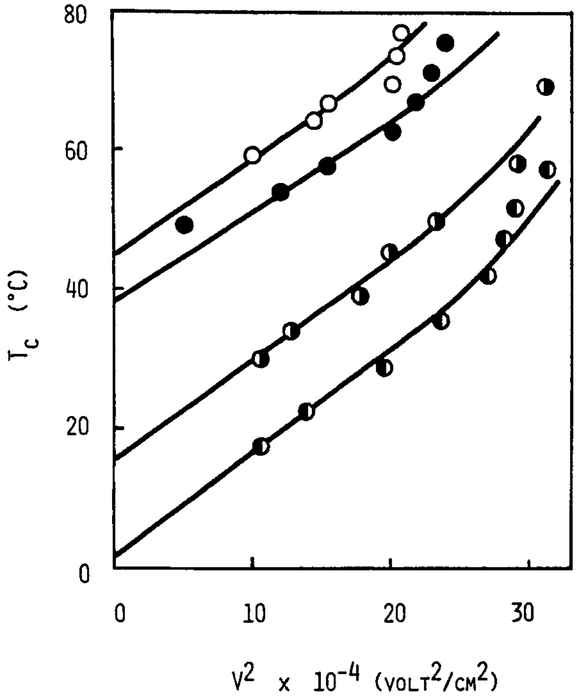


FIGURE 4 T_c plotted against E^2 for PBLG solutions in dioxane with various concentrations. ○: C_p = 12.28 wt %, ●: C_p = 11.87 wt %, ◑: C_p = 11.39 wt %, ◐: C_p = 10.73 wt %.

centrations are plotted against square of the field strength, E^2. In each concentration studied, the plots fall on a straight at a field strength lower than about 500 V/cm. The existance of the field dependent, reversible, discrete change in the light transmittance at T_c suggests that a cooperative change in molecular orientation of PBLG in the solution is induced by the electric field. This fact, together with a comparison of the linear relation experimentally obtained between T_c and E^2 with Eq. 1 derived from the thermodynamic consideration of the phase transition may lead to the conclusion that the appearance of the ordered state at T_c corresponds to a phase transition of the isotropic solution to a certain liquid crystal state. Here we consider the linear relationship between T_c and E^2 in the present system. In the derivation of Eq. (1) a field induced liquid crystal phase was assumed to be same to the liquid crystal phase which appears in the absence of the electric field at lower temperature, however it is not applicable to the present system. In the presence of an electric field above a threshold value, E_{th}, the PBLG system preferred an aligned nematic phase, with the optical axis parallel to the direction of the electric field rather than a cholesteric mesophase.[11-13]

We confine ourselves to cases where the electric field is higher than E_{th} and start from the thermodynamic relation

$$\partial \Delta g(E_0)/\partial T = -q/T_c(E_0) \tag{2}$$

valid in the presence of an electric field E_0 ($> E_{th}$) at the transition temperature, $T_c(E_0)$, where q is the heat of transition per unit mass between the isotropic phase and the aligned nematic phase and $\Delta g(E_0) = g_{1c}(E_0) - g_{iso}(E_0)$ is the difference between the Gibbs free energies per unit of the two phases under the electric field E_0. Since $\Delta g(E_0) = 0$ at $T = T_c(E_0)$

$$\Delta g(E_0) = -[T - T_c(E_0)]q/T_c(E_0) \tag{3}$$

unless T is far from $T_c(E_0)$. In the electric field E, $\Delta g(E)$ may differ from $\Delta g(E_0)$ by the difference in the polarization energy, $[(\varepsilon_{1c} - \varepsilon_{iso})/8\pi\rho](E^2 - E_0^2)$:

$$\Delta g(E) = \Delta g(E_0) + [(\varepsilon_{1c} - \varepsilon_{iso})/8\pi\rho](E^2 - E_0^2) \tag{4}$$

Introducing Eq. (3) to Eq. (4) and equating $\Delta g(E)$ to zero at the transition temperature $T_c(E)$, the temperature shift as a function of E at constant pressure is in contrast with Eq. (1) given by

$$T_c(E) - T_c(E_0) = [T_c(E_0)/q][(\varepsilon_{1c} - \varepsilon_{iso})/8\pi\rho](E^2 - E_0^2) \tag{5}$$

Since PBLG in a helical molecular structure is associated with a very large dipole moment along its long axis, in a calculation of ε only a molecular polarizability which arises from the preferred orientation of PBLG molecules along the direction of the field is taken into consideration and the simplifying assumption is made that the molecule has cylindrical symmetry about its long axis. If there are N molecules of PBLG per unit volume, the effective polarization would be given by

$$p = \frac{Np_0 \int_{-0}^{\pi} \cos\theta f(\theta) \sin\theta \, d\theta}{\int_{-0}^{\pi} f(\theta) \sin\theta \, d\theta} \equiv Np_0 \langle \cos\theta \rangle \tag{6}$$

where p_0 is an intrinsic dipole moment of PBLG molecule and $f(\theta)$ is its distribution function with respect to the angle between the direction of the field and the long axis of the molecule. We consider only uniaxial liquid crystals with the symmetry axis parallel the electric field. Under the condition of thermal equilibrium, the distribution function would be expressed in term of the potential of average force $U(\theta)$ as

$$f(\theta) = A \exp[-U(\theta)/kT] \tag{7}$$

where k is the boltzmann constant and A is a normalization constant to give $\int f(\theta) \sin\theta \, d\theta = 1$. If we assume that in the liquid crystal phase $U(\theta)$ is given by a linear combination of the potential due to the liquid crystal formation, $U(\theta)_{1c}$ and the energy induced by the field to the dipole moment, $-p_0 E \cos\theta$, $\langle \cos\theta \rangle$ is calculated by the following equation

$$\langle \cos\theta \rangle = \frac{\int \cos\theta \exp[\{-U(\theta)_{1c} + p_0 E \cos\theta\}/kT] \sin\theta \, d\theta}{\int \exp[\{-U(\theta)_{1c} + p_0 E \cos\theta\}/kT] \sin\theta \, d\theta} \tag{8}$$

Under the assumption of $p_0 E/kT \ll 1$, which is satisfied in the present system, Eq. (8) becomes to the first approximation,

$$\begin{aligned} \langle \cos\theta \rangle &= (p_0 E/kT) \frac{\int \cos^2\theta \exp[-U(\theta)_{1c}/kT] \sin\theta \, d\theta}{\int \exp[-U(\theta)_{1c}/kT] \sin\theta \, d\theta} \\ &= (p_0 E/kT) \langle \cos^2\theta \rangle_{1c} \end{aligned} \tag{9}$$

$\langle \cos^2\theta \rangle_{1c}$ defined in Eq. (9) is related to the extrapolated value of an order parameter with respect to θ, $S(\theta)$ in the liquid crystal state at $E = 0$ as

$$S(\theta) = (1/2)(3\langle \cos^2\theta \rangle_{1c} - 1) \tag{10}$$

A combination of Eqs. (6) and (9) gives for the effective polarization in the liquid crystal state, p_{1c}

$$p_{1c} = (Np_0^2/kT) \langle \cos^2\theta \rangle_{1c} E \tag{11}$$

The corresponding value in the isotropic phase may be given as

$$p_{\text{iso}} = (Np_0^2/3kT) E \tag{12}$$

by taking into consideration that $U(\theta)$ is given by $-p_0 E \cos\theta$ in the isotropic phase. Eqs. (11) and (12) together with Eq. (10) give for the difference between the dielectric constants of the liquid crystal state and of the isotropic liquid state, $\varepsilon_{1c} - \varepsilon_{\text{iso}}$ at the transition temperature:

$$\varepsilon_{1c} - \varepsilon_{\text{iso}} = (2/3)[Np_0^2/kT_c(E)]S(\theta) \tag{13}$$

Introducing Eq. (13) into Eq. (5), one gets

$$T_c(E) - T_c(E_0) = (Np_0^2/12\pi\rho qk)S(\theta)(E^2 - E_0^2) \tag{14}$$

In the derivation of Eq. (14), N had been regarded as the number of PBLG molecules per unit volume, but it should be a number of the molecules which contribute to the polarization induced by the field. This may not be the stoichiometric number, since a part of PBLG molecules in dioxane exists in the form of dimers and/or cluster in which their dipole moments are cancelled out.[9] Now we consider the case that a chemical equilibrium between the individual molecule associated with an effective dipole moment and the dimer of the molecules in which their dipole moments are cancelled out in a lateral aggregated configuration of the helices is maintained with the equilibrium constant K, in both the isotropic and liquid crystal phase. Under this assumption, N is given by

$$N = (1/4)(\sqrt{K^2 + 8N_0K} - K) \tag{15}$$

where N_0 is the stoichiometric number of PBLG per unit volume. The data of the dielectric constant obtained in the present systems suggested N to be sufficiently smaller than N_0.[9] In this case, Eq. (15) may be approximated to

$$N = \sqrt{K/2}\sqrt{N_0} \tag{16}$$

Using Eq. (16), Eq. (14) may be finally rewritten in the form

$$[T_c(E) - T_c(E_0)]/\sqrt{N_0} = (\sqrt{K}p_0^2/12\sqrt{2}\pi\rho qK)S(\theta)(E^2 - E_0^2) \tag{17}$$

Eq. (17) indicates that T_c data for the PBLG solutions with different concentrations collect to a single straight line if they are substituted into the left-hand side of Eq. (17) and the resulting values are plotted against $(E^2 - E_0^2)$ with the assumptions that K and $S(\theta)$ are independent of the temperature. This prediction is demonstrated in Figure 5 with data on all systems shown in Figure 4. In the calculation of the left-side of Eq. (17), the extrapolated value of $T_c(E)$ at $E = E_0$ for each curve in Figure 4 was chosen as the reference value, $T_c(E_0)$. The points at high field strength seem to deviate systematically from the predicated line. This feature is a manifestation of the failure of our crude approximations particularly of the assumption that K and $S(\theta)$ are independent of temperature. Unfortunately, it is impossible to discuss the value of

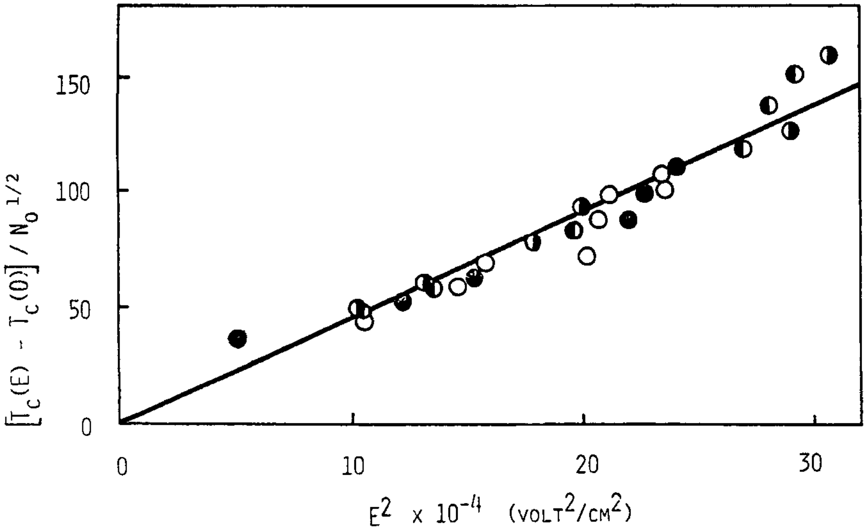


FIGURE 5 Linear relation between $[T_c(E) - T_c(0)]/\sqrt{N_0}$ and E^2 with data on all systems shown in Figure 4.

○: C_p = 12.28 wt %, ●: C_p = 11.87 wt %,
◑: C_p = 11.39 wt %, ◐: C_p = 10.73 wt %.

the coefficient $(\sqrt{K}p_0^2/12\sqrt{2}\rho\pi qk)S(\theta)$ at this stage, since it is composed of various unknown parameters. It, however will be discussed in the succeeding paper by comparing it with the results obtained in the change of dielectric constant induced by phase transition in the present systems.

References

1. W. Helfrich, *Phys. Rev. Letters*, **24**, 201 (1970).
2. E. M. Barral, R. S. Porter, and J. F. Johnson, *Mol. Cryst.*, **3**, 299 (1968).
3. L. A. Zanoni and J. E. Goldmacher, 158th Natl. Meeting Am. Chem. Soc., Sept. 1969, Abstr. Papers, Coll. No. 58.
4. C. Robinson, *Trans. Faraday Soc.*, **52**, 571 (1956).
5. E. L. Wee and W. G. Miller, *J. Phys. Chem.*, **75**, 1446 (1971).
6. C. Robinson, *Mol. Crystals*, **1**, 467 (1966).
7. P. J. Flory, *Proc. Roy. Soc. (London)*, **A234**, 73 (1956).
8. J. H. Rai and W. G. Miller, *J. Phys. Chem.*, **76**, 1081 (1972).
9. A. Wada, *J. Polymer Sci.*, **33**, 822 (1960).
10. P. Doty, *J. Am. Chem. Soc.*, **79**, 3961 (1957).
11. W. J. Toth and V. Tobolsky, *Polymer Letters*, **8**, 531 (1970).
12. E. Iizuka, T. Keira and A. Wada, *Mol. Crystals and Liq. Crystals*, **23**, 13 (1973).
13. R. W. Duke and D. B. DuPre, *Macromolecules*, **7**, 374 (1974).