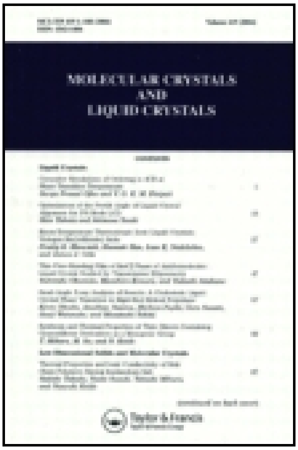

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Effect of Electrical Field on the Phase Transition of Rod-like Polymer Solution†

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The effect of external electrical field on the phase transition from isotropic to liquid crystalline phase in rod-like polymer solution was discussed by applying the lattice model. Free energy of each phase and the chemical potential of rod-like molecule and that of solvent in each phase were calculated. With these results a phase diagram was obtained. Application of an electrical field resulted in narrowing the region of phase separation and shifting the phase transition concentration to a lower value.

1 INTRODUCTION

It has been known that a solution of rod-like particles of sufficiently large axial ratio takes an ordered phase, or liquid crystalline phase[1, 2] when its concentration exceeds a certain critical value. There have been two approaches for theoretically explaining the existence of liquid crystalline phase, the mean field approximation[3] and the exclusion volume approach with a hard rod model.[4] The theory of Maier and Saupe[3] expressed the interaction between molecule *i* and the rest of the whole molecules by averaging the dispersion force depending upon the direction of long axes of molecules *i* and *j*. In the lattice model, one molecule occupies several lattice sites according to its shape,[5] and intermolecular interaction is considered as the van Laar type interaction.[6–8] Onsager,[9] Zimm,[4] and Ishihara[10] treated a hard rod system by calculating second virial coefficients, so the results obtained are restricted to low

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concentrations. Flory[8] carried out calculation which is capable of describing portions of a hard rod solution of any concentration by adopting the lattice model. An experimental study on the phase transition in a solution of rod-like particles was first undertaken by Robinson.[11] He reported that, increasing the concentration of a solution, transition from an isotropic phase to an anisotropic phase took place through a phase separation region. α-Helix polypeptide, particularly poly (γ-benzyl-L-glutamate) has been frequently employed as a model of rod-like particles.[12] In the Flory's lattice model, a rod-like particle was considered undistinguishable in its head and tail. However, in real case a rod-like molecule sometimes has polarization along its long axis. For example, α-helix polypeptide has an electric dipole moment of about 3.5 Debye per residue along its axis, so that the total dipole moment of the polymer rod becomes considerably large value.[13] In such a case, it is possible to align polymer molecules with an external electrical field. We reported an experiment on the effect of external electrical field on the transition between isotropic and liquid crystalline phases in PBLG-dioxane solution.[14] The present paper shows the effect of an external electrical field on the phase transition of a solution of rod-like molecules with electrical polarization on the basis of the lattice model.

2 FREE ENERGY OF SOLUTION

In the lattice model we assume that there are N sites of cubic lattice with lattice constant a. Each solvent occupies one site and a rod-like solute molecule with axial ratio l and an electrical dipole moment P along its long axis occupies linearly connecting l sites as shown in Figure 1. The total number of the rod-like molecules is assumed n. The direction of the external electrical field, which is the same as the preferred axis of liquid crystalline phase is chosen as z direction.

Number of states

Let j molecules be already placed in the lattice and solvent molecules are not placed yet. In this case, the probability, p_h^j, that a site neighboring in the z direction to one site is not occupied is given as,[15]

$$p_h^j = \frac{n_{hj}}{n_{hj} + \sum_{i=1}^{j} m_i} \tag{2}$$

Here, n_{hj} represents the number of empty site after j molecules are already placed, $n_{hj} \equiv N - lj$, and m_i $(i = 1, 2, \ldots j)$ represents the degree of inclination of i-th molecule from the preferred axis as $m_i = l \sin \theta_i$, here θ_i is an angle be-

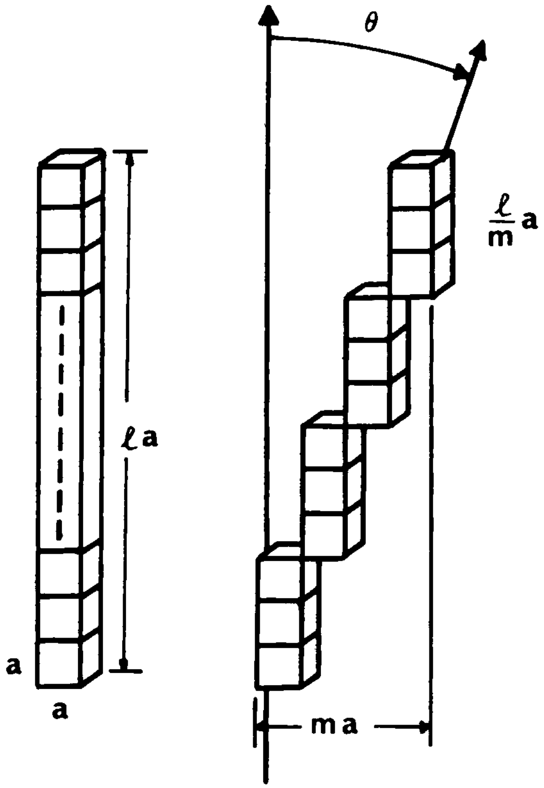

FIGURE 1 A model for configuration of a rod-like particle in solution. l: axial ratio, m: disorientation parameter.

tween the preferred axis of i-th molecule. Under this condition, the number of ways for placing the $(j+1)$ th molecule is[8]

$$\nu_{j+1} = n_{hj}(p_h^j)^{(l/m_{j+1})-1}\left[\frac{n_{hj}}{N}(p_h^j)^{(l/m_{j+1})-1}\right]^{m_{j+1}-1}$$
$$= \frac{n_{hj}^l}{\left(n_{hj}+\sum_{i=1}^{j} m_i\right)^{l-m_{j+1}} N^{m_{j+1}-1}} \tag{3}$$

By using the disorientation parameter m,

$$m = \frac{\sum_{i=1}^{j} m_i}{j} \tag{4}$$

(3) is rewritten as,

$$\nu_{j+1} = \frac{n_{hj}^{l}}{(n_{hj} + jm)^{l-m_{j+1}} N^{m_{j+1}-1}} \tag{3'}$$

The number of states for the n rod-like molecules with average alignment, $m = \sum_{i=1}^{n} m_i/n$, is

$$\Gamma = \frac{\prod_{j=0}^{n-1} \nu_{j+1}}{\prod_k n_k!} = \frac{(n_h + nm)!}{n_h! n! N^{n(m-1)}} \frac{n!}{\prod_k n_k!} \tag{5}$$

Here $n_h = N - nl$ and n_k is the number of molecules whose axes are within the solid angle $\delta\omega_k$. When the inclination of the molecules from z axis is small, the quantity $n!/\Pi n_k!$ will be given by Eq. (6) by taking into account the asymmetry in the molecular axis direction of a rod-like molecule.

$$\frac{n!}{\prod_k n_k!} = (2m^2)^n \tag{6}$$

Therefore, the number of states in the liquid crystalline phase is given by

$$\Gamma_L = \frac{(n_h + nm)!}{n_h! n! N^{n(m-1)}} (2m^2)^n \tag{7}$$

Eq. (6) can not be used in case where the inclination of molecular axis from the preferred direction is large.

In the case of an isotropic phase, where $m = (\pi/4)l$, ν_{j+1} is given by

$$\nu_{j+1} = \frac{(N - lj)}{N^{l-1}} \gamma \tag{8}$$

where γ is the orientation number. Therefore, the number of states in an isotropic phase is given as

$$\Gamma_I = \frac{\prod_{j=1}^{n} \nu_j}{n!}$$

$$= \frac{N!}{n_h! n! N^{n(l-1)}} \gamma^n \tag{9}$$

By the similar consideration as Flory,[8] γ will be given as

$$\gamma = 2l^2 \tag{10}$$

then,

$$\Gamma_l = \frac{(n_h + nl)!}{n_h!n!N^{n(l-1)}}(2l^2)^n \tag{11}$$

Comparing Eq. (11) with Eq. (7), it is recognized that Eq. (7) can also be used in the isotropic phase by replacing m by l instead of $(\pi/4)l$. Therefore, Eq. (12) can describe both the anisotropic and isotropic phases if the meaning of m in the isotropic phase is changed as above.

$$\Gamma = \frac{(n_h + nm)!}{n_h!n!N^{n(m-1)}}(2m^2)^n \tag{12}$$

Thus, the entropy of a solution of rod-like molecules with disorientation parameter m is given by

$$\begin{aligned} S &= k \log \Gamma \\ &= -Nk\Bigg[(1-c)\log(1-c) + \frac{c}{l}\log c \\ &\qquad - \left\{1 - \left(1 - \frac{m}{l}\right)c\right\}\log\left\{1 - \left(1 - \frac{m}{l}\right)c\right\} \\ &\qquad + \frac{c}{l}\{-\log(2lm^2) + m - 1\}\Bigg] \end{aligned} \tag{13}$$

Here, c represents the volume fraction of the rod-like molecules, $c = nl/N$.

Solute-solvent interaction

There are three types of nearest neighbor interaction: interaction between solvent molecules, ϵ_{ss}, interaction between a solvent and a rod-like molecule, ϵ_{ps}, and interaction between segments of two rod-like molecules, ϵ_{pp}. Let the number of neighboring sites of solvents be n_{ss}, that of a solvent and a segment of rod-like molecule be n_{ps} and that of segments of two rod-like molecules be n_{pp}, then the total interaction energy E is given by

$$E = n_{ss}\epsilon_{ss} + n_{ps}\epsilon_{ps} + n_{pp}\epsilon_{pp} \tag{14}$$

As the total number of neighboring sites between two segments in a rod-like molecule is $n(l-1)$, then

$$3N - n(l-1) = n_{ss} + n_{ps} + n_{pp} \tag{15}$$

since the number of neighboring sites to a rod-like molecule is $4l + 2$, then

$$n(4l + 2) = n_{ps} + 2n_{pp} \tag{16}$$

Therefore Eq. (14) is rewritten as,

$$E = E_p + E_s + n_{ps}\Delta\epsilon \tag{17}$$

Here,

$$E_p \equiv n(2l + 1)\epsilon_{pp}$$

$$E_s \equiv 3(N - nl)\epsilon_{ss}$$

$$\Delta\epsilon \equiv \epsilon_{ps} - (\epsilon_{pp} + \epsilon_{ss})/2$$

Thus, the energy change, ΔE, by mixing is given as

$$\begin{aligned}\Delta E &= n_{ps}\Delta\epsilon \\ &= nJ - 2\Delta\epsilon n_{pp}\end{aligned} \tag{18}$$

Here, J is the exchange energy defined by

$$J \equiv (4l + 2)\Delta\epsilon$$

The number n_{pp} is approximately replaced by an average value which is given as

$$n_{pp} = \frac{1}{2} n(4l + 2) \frac{nl}{N}$$

Using the above relation in Eq. (18), average solute-solvent interaction energy is given by

$$\Delta E = NJc(1 - c)/l \tag{19}$$

Interaction with electrical field

From Eq. (3′), the number of ways in which a rod-like molecule is oriented with the angle Θ from the preferred axis of liquid crystal is given by,

$$\nu(\Theta) = N\left(\frac{n_h}{M}\right)^l \left(\frac{M}{N}\right)^{l \sin \Theta} \tag{20}$$

Here, $M = n_h + nm$ and $N = n_h + nl$, therefore, the distribution function for the orientation of rod-like molecules with a disorientation parameter m is given by,

$$f(\Theta) = \frac{\left(\frac{M}{N}\right)^{l \sin \Theta}}{\int_0^\pi \left(\frac{M}{N}\right)^{l \sin \Theta} \sin \Theta d\Theta} \tag{21}$$

The probability of the state where a rod-like molecule with an electric dipole moment p along the molecular axis makes an angle Θ from the electric field is written as,

$$\rho(\Theta) = \frac{f(\Theta)\exp\left(\frac{pE}{kT}\cos\Theta\right)}{\int_0^\pi f(\Theta)\exp\left(\frac{pE}{kT}\cos\Theta\right)\sin\Theta d\Theta}$$

Therefore, the average value of the dipole moment along the field is approximately given under the condition, $pE \ll kT$, by

$$\begin{aligned} \langle p\rangle &= \int_0^\pi p\cos\Theta\,\rho(\Theta)\,d\Theta \\ &= \frac{p^2E}{kT}\langle\cos^2\Theta\rangle \qquad (22) \end{aligned}$$

Here,

$$\begin{aligned} \langle\cos^2\Theta\rangle &= \frac{\int_0^\pi \left(\frac{M}{N}\right)^{l\sin\Theta}\cos^2\Theta\sin\Theta\,d\Theta}{\int_0^\pi \left(\frac{M}{N}\right)^{l\sin\Theta}\sin\Theta\,d\Theta} \\ &= 1-\left(\frac{m}{l}\right)^2 - \langle(\sin\Theta-\langle\sin\Theta\rangle)^2\rangle \qquad (23) \end{aligned}$$

The last term of the right hand side of Eq. (23) will be small since the last term is the mean square of fluctuation of sin Θ. Thus, in a liquid crystalline phase,

$$\langle\cos^2\Theta\rangle = \frac{l^2-m^2}{l^2}$$

And in an isotropic phase,

$$\langle\cos^2\Theta\rangle = \frac{1}{3}$$

Therefore, the interaction energy of the liquid crystalline phase with an electrical field is given as,

$$E_e^A = -N\frac{cp^2(l^2-m^2)E^2}{2l^3kT} \qquad (24)$$

and the interaction between the isotropic phase and an electric field is given as,

$$E_e^I = -N\frac{cp^2E^2}{6l\,kT} \qquad (25)$$

3 THE DEGREE OF ORDER AT EQUILIBRIUM

The free energy of a solution of rod-like molecules under an electric field is represented by the sum of the three terms which were discussed above: In the liquid crystalline phase,

$$\frac{G^A}{N} = kT\left[(1-c)\log(1-c) + \frac{c}{l}\log c - \left\{1 - \left(1 - \frac{m}{l}\right)c\right\} \times \log\left\{1 - \left(1 - \frac{m}{l}\right)c\right\} + \frac{c}{l}\{-\log(2lm^2) + m - 1\}\right] + Jc(1-c)/l - \frac{cp^2(l^2 - m^2)}{2l^3kT}E^2 \qquad (26)$$

and in the isotropic phase,

$$\frac{G^I}{N} = kT\left[(1-c)\log(1-c) + \frac{c}{l}\log c + \frac{c}{l}\{-\log(2l^3) + l - 1\}\right] + Jc(1-c)/l - \frac{cp^2}{6lkT}E^2 \qquad (27)$$

Under the condition of constant pressure, the disorientation parameter is obtained as the value which minimizes G^A, or as the solution of the following equation.

$$c = \frac{l}{l-m}\left[1 - \exp\left\{-\frac{2}{m} + \frac{mp^2E^2}{l^2k^2T^2}\right\}\right] \qquad (28)$$

The dependence of the disorientation parameter m on the volume fraction c in equilibrium is demonstrated in Figure 2. On applying the electrical field to the system, the curve shifts to the lower concentration side and in the case where the field strength exceeds the value, $E_c = \sqrt{2}\ k\ T/p$, the disorientation parameter takes a value smaller than l, and the system begins to have an orientational order. Since the high temperature approximation is not applicable in the region, $E > E_c$, only the case where $E < E_c$ is considered here. In the case, $E < E_c$, there exists the minimum concentration, c_m, for the existence of a finite value of m as the solution of Eq. (28). Since the free energy of this system decreased monotonously with the increase of disorientation parameter m at a concentration below c_m, the liquid crystalline phase does not exist in this concentration range. From Eq. (28), c_m is given by,

$$c_m = \frac{4}{l}\left(1 + \sqrt{1 - \frac{p^2E^2}{2k^2T^2}}\right) \simeq c_m^0 - \frac{p^2E^2}{lk^2T^2} \qquad (29)$$

Here, c_m^0 is the critical concentration for an orientational ordering in the absence of an electrical field, and equal to $8/l$ which is identical as the critical value given by Flory.[8]

4 CHEMICAL POTENTIAL

The free energy of a liquid crystalline phase and that of an isotropic phase in equilibrium are rewritten as follows by applying Eq. (28) in Eqs. (26) and (27). Then the free energy of a liquid crystalline phase, G^A, is expressed as,

$$\frac{G^A}{N} = kT\left[(1-c)\log(1-c) + (1-c)\left(\frac{2}{m} - \frac{mp^2E^2}{l^2k^2T^2}\right) + \frac{c}{l}\{\log c - \log(2lm^2) + m + 1\}\right] + Jc(1-c)/l - c\,\frac{(l^2+m^2)p^2E^2}{2l^3kT} \quad (30)$$

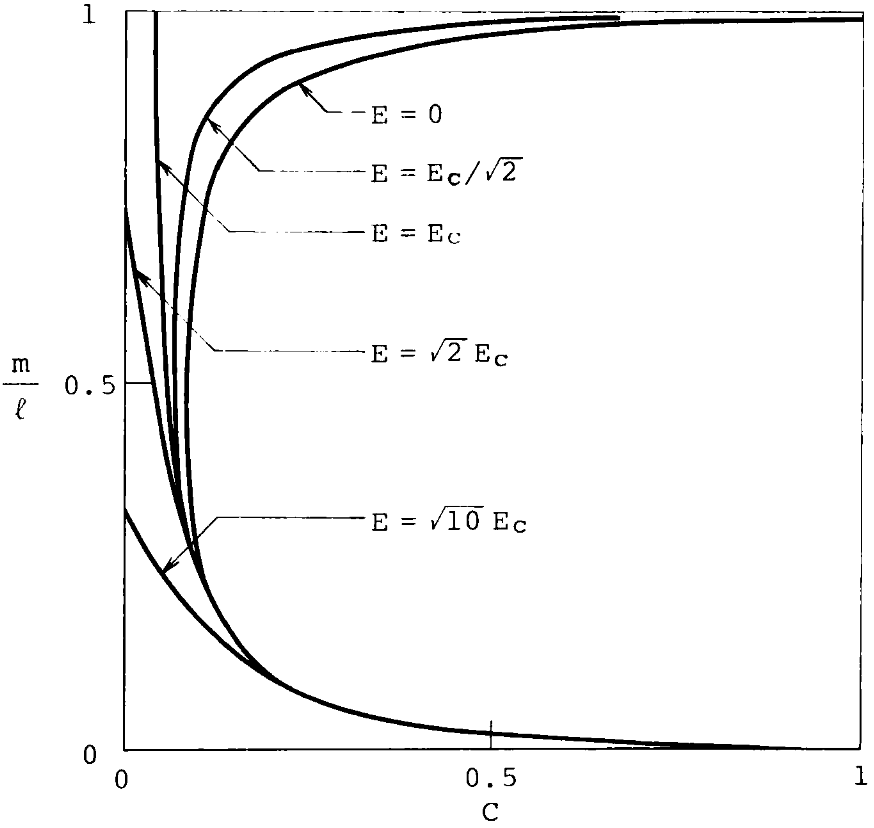

FIGURE 2 Dependence of disorientation parameter on the volume fraction of solute particles, c, at various electric fields. The axial ratio, l, was assumed to be 100.

Thus, the chemical potential of rod-like molecule, $\Delta\mu_P^A$, and solvent, $\Delta\mu_s^A$, are given by,

$$\Delta\mu_p^A = RT[\log c + (m-1)c - \log(2lm^2) + 2] + N_A\left[J(1-c)^2 - \frac{p^2E^2(l^2+m^2)}{l^2kT}\right] \tag{31}$$

$$\Delta\mu_s^A = RT\left[\log(1-c) + (m-1)\frac{c}{l} + \frac{2}{m}\right] + N_A\left[J\frac{c^2}{l} - \frac{mp^2E^2}{l^2kT}\right] \tag{32}$$

Here, N_A is Avogadro's number. The free energy of an isotropic phase, G^I is expressed as,

$$\frac{G^I}{N} = kT\left[(1-c)\log(1-c) + \frac{c}{l}\{\log c - \log(2l^3) + l - 1\}\right] + Jc(1-c)/l - \frac{cp^2E^2}{6lkT} \tag{33}$$

In this case the chemical potential of rod-like molecule, $\Delta\mu_p^I$, and of solvent, $\Delta\mu_s^I$, are given by,

$$\Delta\mu_p^I = RT[\log c + (l-1)c - \log(2l^2)] + N_A\left[J(1-c)^2 - \frac{p^2E^2}{6k^2T^2}\right] \tag{34}$$

$$\Delta\mu_s^I = RT\left[log(1-c) + \left(1-\frac{1}{l}\right)c\right] + N_AJc^2/l \tag{35}$$

The phase diagram calculated for the case where $J = 0.174$ eV and $l = 100$ is shown in Figure 3. It is clear that, when an external electrical field exists, the region of phase separation becomes narrower and shifts to the lower concentration side.

5 COMPARISON WITH EXPERIMENT

An experiment using poly(γ-benzyl L-glutamate) (PBLG) was carried out for examining the variation of phase transition concentration c_c of rod-like molecule by an external electrical field. The molecular weight of PBLG was determined as 135,000 and its axial ratio as 60 from the viscosity.[16] As the dipole moment of a residue of PBLG is 3.5 Debye, the total dipole moment of PBLG is about 2000 Debye. The phase transition was observed with a polarizing microscope.[14] In this observation, only the change of phase separation from an isotropic phase was determined without ambiguity. The change in the transi-

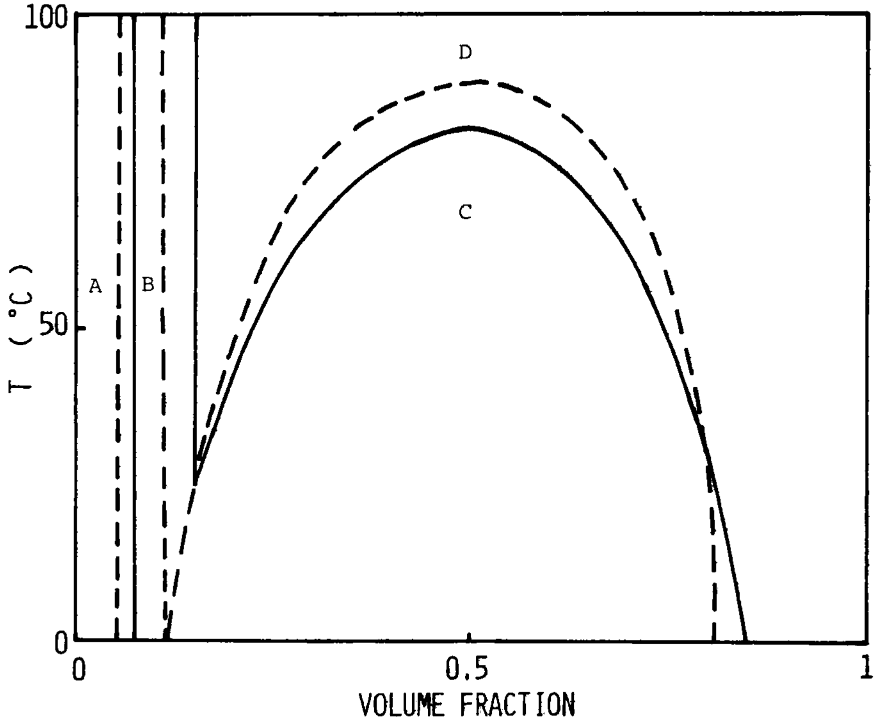

FIGURE 3 Phase diagram of the solution of rod-like particles. Solid line: $E = 0$ V/cm; Broken line: $E = 2.7$ kV/cm. A: Isotropic region; B, C: Phase separation regions; D: Liquid crystal region.

tion concentration, Δc_c, was plotted against square of the external electrical field in Figure 4. The minimum concentration, c_m^0, in the absence of electrical field has been known to be very close to the transition concentration on the isotropic phase side.[8] Therefore, c_m should be almost equal to the observed transition concentration, c_c. Thus, the change of transition concentration, $\Delta c_c = c_c - c_m^0$, by an external electrical field is given by,

$$\Delta c_c = -\frac{p^2 E^2}{l k^2 T^2} \tag{36}$$

The plots of observed Δc_c against E^2/T^2 in Figure 4 showed a good linearity and its slope was -6.7×10^{-3} (deg^2.cm^2/V^2). Applying the value, $p = 2000$ Debye and $l = 60$, in Eq. (36) results in the slope of -9.0×10^{-4} (deg^2.cm^2/V^2), which is somewhat smaller than the experimental value. It was shown in this paper that the change in transition concentration c_c is proportional to the square of an external electrical field likewise the change in the transition temperature.[14]

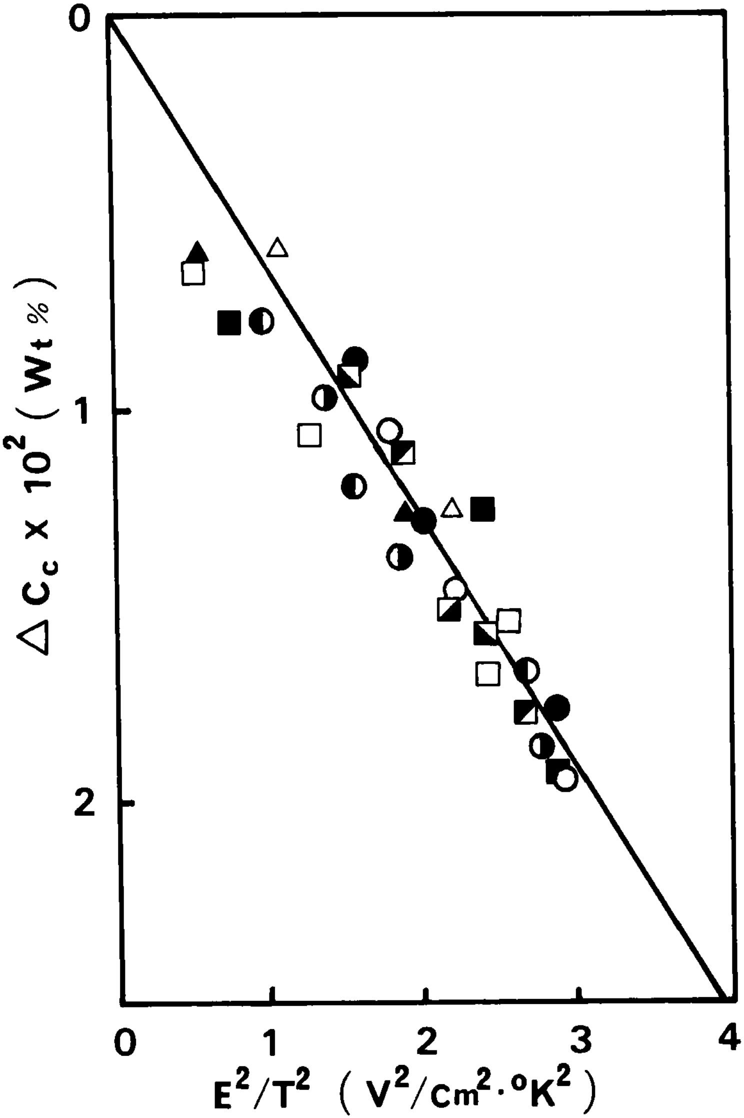

FIGURE 4 Plots of the phase transition concentration against E^2/T^2.
○: $T = 75°C$, ●: $T = 70°C$, ◕: $T = 65°C$, ◐: $T = 60°C$,
□: $T = 55°C$, ■: $T = 50°C$, ◪: $T = 45°C$, ◩: $T = 40°C$,
⬔: $T = 35°C$, △: $T = 30°C$, ▲: $T = 25°C$.

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