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Non-linear dielectric spectra of ferroelectric liquid crystals

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The non-linear dielectric relaxation spectroscopy has been recently developed and applied to soft materials such as polymers. We have applied this new method to the S_C^* phases of some ferroelectric liquid crystals. Under a weak AC electric field, the original and third order harmonic frequency components of electric displacement are proportional to the first and third powers of the applied electric field, respectively. The linear spectrum obtained from the original frequency component shows the relaxation of Debye type and the third order non-linear spectrum shows the relaxation with an extended form of Debye type to the non-linear case. The third order non-linear dielectric increment is found to be negative, which implies that the dielectric non-linearity of the liquid crystal in the S_C^* phase is due to the saturation of molecular dipole moments induced by the applied electric field. The temperature dependence of the linear and third order non-linear spectra in the S_C^* phase are also studied. Both spectra do not change their forms much through the whole temperature range of the S_C^* phase. In the vicinity of the S_A - S_C^* transition temperature, the critical behaviour is more remarkable in the third order spectrum than in the linear one.

1. Introduction

Dielectric relaxation spectroscopy in the linear regime is one of the most useful methods to investigate the dynamics of soft materials such as polymers and liquid crystals. In the case of ferroelectric liquid crystals, there are many theoretical [1-5] and experimental studies [6-17] on dielectric behaviour mainly close to the S_A - S_C^* transition. Two relaxational modes have been observed in the lower frequency range (several Hz to MHz) corresponding to the thermal fluctuation of molecular directors. One is called the soft mode which is due to the fluctuation of the director tilt angle and is observed both in the S_A and S_C^* phases. The increment and relaxation time of this mode increase as the temperature approaches the S_A - S_C^* transition. The other is called the Goldstone mode which corresponds to the fluctuation of the director azimuthal angle around the helical axis. This mode is observed in the dielectric relaxation measurement as a twisting-untwisting motion of the helix induced by the applied electric field. In the S_C^* phase, except in the vicinity of the phase transition temperature, the Goldstone mode is predominant in the dielectric spectrum compared to the soft mode.

Recently, non-linear dielectric relaxation spectroscopy has been developed and applied to solid state polymers, such as ferroelectric polymers [18-20] and polymers with large dielectric permittivity [21]. Non-linear dielectric relaxation is the higher order effect on the thermal fluctuation in substances induced by applied electric field. Therefore, non-linear dielectric spectroscopy is expected to give more detailed information on the microscopic environment of the dipoles than linear spectroscopy.

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Non-linear spectra of dielectric relaxation are often analysed in terms of the phenomenological non-linear response theory proposed by Nakada [22]. According to this theory, if the after-effect function is assumed to be a product of single exponential decay functions, the non-linear spectra are given by extended forms of the Debye type relaxation spectrum to the non-linear case.

In this paper, the linear and non-linear dielectric relaxation spectra for ferroelectric liquid crystals measured under a weak applied electric field are analysed by using Nakada's phenomenological theory.

2. Non-linear dielectric relaxation spectroscopy

The phenomenological treatment of the non-linear dielectric relaxation spectroscopy proposed by Nakada is briefly summarized as follows [22]. The electric displacement $D(t)$ is phenomenologically given by a sum of the multi-convolution integrals which are the superposition of the effects due to the applied electric field $E(t)$ at past multi-time points t_1, t_2, \dots, t_n given by

$$D(t) = \sum_{n=1}^{\infty} \int_0^{\infty} dt_1 \int_0^{\infty} dt_2 \dots \int_0^{\infty} dt_n \varepsilon_n(t_1, t_2, \dots, t_n) E(t-t_1) E(t-t_2) \dots E(t-t_n), \quad (1)$$

where $\varepsilon_n(t_1, t_2, \dots, t_n)$ is the multi-time after-effect function which characterizes the non-linear response studied. In the following discussion, the applied field $E(t)$ is limited to the sinusoidal one, $E(t) = E_0 \operatorname{Re} [\exp(i\omega t)]$, with the amplitude E_0 and the angular frequency ω . By using the symmetrical nature of $\varepsilon_n(t_1, t_2, \dots, t_n)$ with respect to the time variables (t_1, t_2, \dots, t_n) , equation (1) can be rewritten as,

$$D(t) = \sum_{n=0}^{\infty} \operatorname{Re} [D_n^*(\omega) \exp(in\omega t)], \quad (2)$$

where $D_n^*(\omega)$ is the complex amplitude of the n th order harmonic component in $D(t)$ appearing at the angular frequency $n\omega$. For example, $D_1^*(\omega)$ and $D_3^*(\omega)$ are given as

$$D_1^*(\omega) = E_0 \varepsilon_1^*(\omega) + \frac{3}{4} E_0^3 \varepsilon_3^*(\omega, \omega, -\omega) + \dots, \quad (3)$$

$$D_3^*(\omega) = \frac{1}{4} E_0^3 \varepsilon_3^*(\omega, \omega, \omega) + \frac{5}{16} E_0^5 \varepsilon_5^*(\omega, \omega, \omega, \omega, -\omega) + \dots \quad (4)$$

The complex function $\varepsilon_n^*(\omega_1, \omega_2, \dots, \omega_n)$ is the Fourier transform of $\varepsilon_n(t_1, t_2, \dots, t_n)$ defined as,

$$\begin{aligned} \varepsilon_n^*(\omega_1, \omega_2, \dots, \omega_n) &\equiv \int_0^{\infty} dt_1 \int_0^{\infty} dt_2 \dots \int_0^{\infty} dt_n \varepsilon_n(t_1, t_2, \dots, t_n) \\ &\times \exp[-i(\omega_1 t_1 + \omega_2 t_2 + \dots + \omega_n t_n)]. \end{aligned} \quad (5)$$

As is seen from equations (3) and (4), $D_n^*(\omega)$ is expressed as a summation of the terms which are proportional to the powers E_0^k ($k \geq n$) of the amplitude E_0 of applied electric field. When E_0 is small enough, $D_n^*(\omega)$ is almost proportional to E_0^n and the effects of higher order terms ($k > n$) are negligibly small. Then, we can define the n th order non-linear dielectric constant $\varepsilon_n^*(\omega)$ by using the coefficient of the predominant term proportional to E_0^n as,

$$\varepsilon_n^*(\omega) \equiv \varepsilon_n^*(\omega, \omega, \dots, \omega) = \varepsilon_n'(\omega) + i\varepsilon_n''(\omega), \quad (6)$$

which is experimentally obtained from the complex amplitude $D_n^*(\omega)$ of the n th order harmonic component by the following equation:

$$\epsilon_n^*(\omega) = \lim_{E_0 \rightarrow 0} \frac{D_n^*(\omega)}{E_0^n} 2^{n-1}. \tag{7}$$

It is further assumed by Nakada [22] that the after-effect function $\epsilon_n(t_1, t_2, \dots, t_n)$ is given by a product of single exponential decay functions as,

$$\epsilon_n(t_1, t_2, \dots, t_n) = (\Delta\epsilon_n/\tau_n^n) \exp\left(-\sum_{i=1}^n t_i/\tau_n\right), \tag{8}$$

where $\Delta\epsilon_n$ is the increment of the n th order non-linear dielectric spectrum and τ_n is its relaxation time. The spectra obtained by introducing equation (8) into equation (5) become the extended forms of the Debye type relaxation spectrum ($n = 1$) to the non-linear case ($n > 1$) as,

$$\epsilon_n^*(\omega) = \frac{\Delta\epsilon_n}{(1 + i\omega\tau_n)^n}. \tag{9}$$

This formula or its modified form is utilized to analyse the experimentally obtained non-linear dielectric spectrum.

3. Experimental

The sinusoidal electric field $E(t)$ with the angular frequency ω and the amplitude E_0 is generated by the synthesizer (Hewlett–Packard HP3325A) and applied to the sample. The electric displacement signal $D(t)$ detected by a charge amplifier is digitized and averaged on the storage oscilloscope (Yokogawa DL3120B). The signal is then transferred to a personal computer and transformed into complex spectrum data (the amplitude and phase shift) by the FFT algorithm. The complex amplitude $D_n^*(\omega)$ of the n th order harmonic component of $D(t)$ is obtained for various ω and E_0 of the applied electric field.

The ferroelectric liquid crystal sample is sandwiched between two glass plates with ITO as electrodes and spin-coated with polyimide. The glass plates are rubbed unidirectionally for attaining the homogeneous alignment of the ferroelectric liquid crystal. In the following discussion, we limit ourselves to the results for DOBAMBC as a typical example. The thickness of the cell used is about 13 μm .

4. Linear and non-linear dielectric relaxation spectra of ferroelectric liquid crystals

The applied electric field dependences of the complex amplitudes of the linear and third order non-linear components of $D(t)$, $D_1^*(\omega)$ and $D_3^*(\omega)$, obtained at 70°C for DOBAMBC in the S_C^* phase are shown in figures 1 and 2, respectively. The real and imaginary parts of $D_n^*(\omega)$ are plotted against the n th power E_0^n of the applied electric field amplitude E_0 ($n = 1, 3$). As seen from the figures, $D_n^*(\omega)$ has a linear relationship to E_0^n within the range of E_0 used. Therefore, we can calculate $\epsilon_n^*(\omega)$ from $D_n^*(\omega)$ by using equation (7). The calculated spectra $\epsilon_1^*(\omega)$ and $\epsilon_3^*(\omega)$ are shown in figures 3 and 4, respectively.

4.1. Linear dielectric relaxation spectrum

It is found that the linear spectrum $\epsilon_1^*(\omega)$ shows a relaxation profile of slightly distorted Debye type which is similar to that obtained by other authors [3, 7, 13]. This

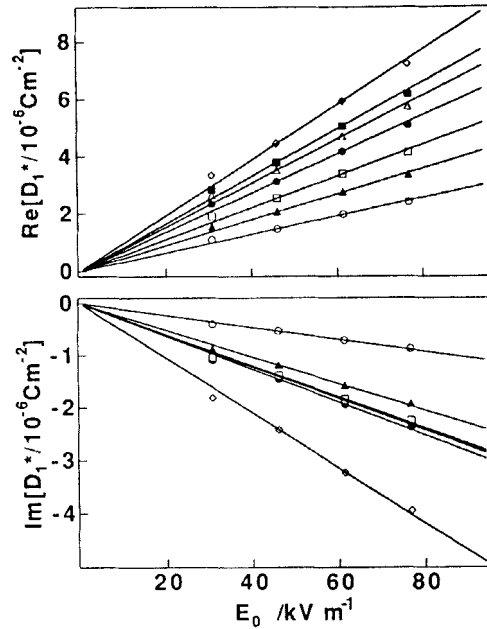


Figure 1. The applied electric field dependence of the real and imaginary parts of linear electric displacement component D_1^* at 70°C . Real part: \diamond , 12 Hz; \blacksquare , 55 Hz; \triangle , 80 Hz; \bullet , 120 Hz; \square , 200 Hz; \blacktriangle , 320 Hz; \circ , 1000 Hz. Imaginary part: \diamond , 12 Hz; \blacksquare , 55 Hz; \triangle , 80 Hz; \bullet , 120 Hz; \square , 200 Hz; \blacktriangle , 320 Hz; \circ , 1000 Hz.

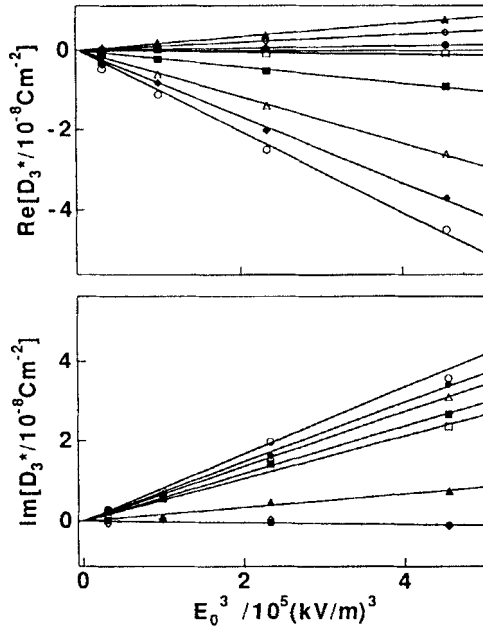


Figure 2. The applied electric field dependence of the real and imaginary parts of non-linear electric displacement component D_3^* at 70°C . Real part: \circ , 8 Hz; \blacklozenge , 12 Hz; \triangle , 20 Hz; \blacksquare , 40 Hz; \square , 55 Hz; \blacktriangle , 120 Hz; \diamond , 200 Hz; \bullet , 320 Hz. Imaginary part: \circ , 8 Hz; \blacklozenge , 12 Hz; \triangle , 20 Hz; \blacksquare , 40 Hz; \square , 55 Hz; \blacktriangle , 120 Hz; \diamond , 200 Hz; \bullet , 320 Hz.

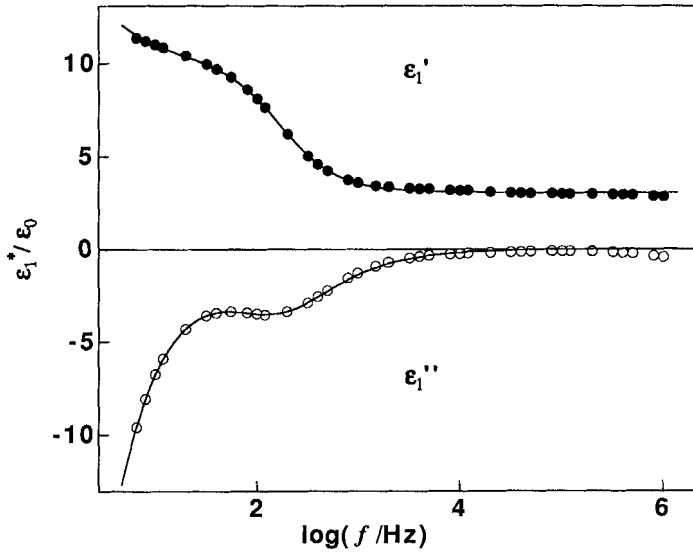


Figure 3. The comparison between the observed values (open and filled circles) and the best fitted curves (solid lines) for the linear dielectric spectrum $\epsilon_1^*(\omega)$ in the S_C^* phase at 70°C .

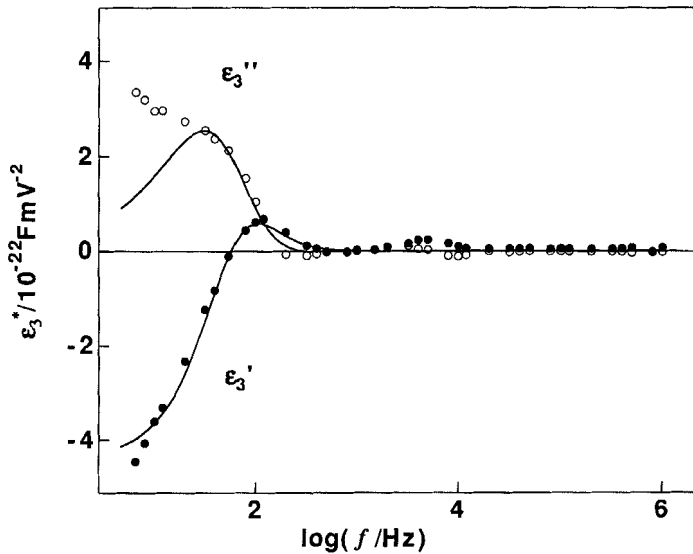


Figure 4. The comparison between the observed values (open and filled circles) and the best fitted curves (solid lines) for the third-order non-linear dielectric spectrum $\epsilon_3^*(\omega)$ in the S_C^* phase at 70°C .

relaxation mode observed in the S_C^* phase only and not in the S_A phase is regarded as the Goldstone mode. We can fit the relaxation formula with a distribution of relaxation times given by,

$$\frac{\epsilon_1^*(\omega)}{\epsilon_0} = \epsilon_\infty + \frac{\Delta\epsilon_1}{1 + (i\omega\tau_1)^{\beta_1}} + \frac{A_1}{(i\omega)^{\gamma_1}} \tag{10}$$

to the measured spectrum $\epsilon_1^*(\omega)$. In equation (10), $\Delta\epsilon_1$ is the first order dielectric increment, τ_1 the apparent relaxation time, ϵ_∞ the dielectric constant at sufficiently high

frequencies, ϵ_0 the dielectric permittivity in a vacuum. The Cole–Cole parameter β_1 which represents the broadness of the relaxation time distribution is also introduced ($0 < \beta_1 \leq 1$). Here, the last term with the exponent γ_1 on the right hand side of equation (10) is added to represent the effects of conductivity and electrode polarization which are not negligible in the low frequency region. If we set γ_1 to 1, A_1 is reduced to the DC conductivity of the sample divided by ϵ_0 . We find the best fitted curve of equation (10), drawn as a solid line in figure 3, is in good agreement with the measured spectrum. The best fitting values of parameters for figure 3 are $\Delta\epsilon_1 = 7.11$, $\tau_1 = 0.94$ ms, $\beta_1 = 0.88$ and $\gamma_1 = 0.90$. The value of β_1 is not too far from unity, which indicates a narrow distribution of relaxation times.

4.2. Third order non-linear dielectric relaxation spectrum

The profile of the third order spectrum $\epsilon_3^*(\omega)$ is more complicated than the linear one. The real part of $\epsilon_3^*(\omega)$ is nearly zero at high frequencies and becomes negative after taking the positive maximum value with decreasing frequency. It is found that $\epsilon_3^*(\omega)$ shows a similar profile to equation (9) for $n = 3$. The measured spectrum $\epsilon_3^*(\omega)$ can be fitted better by introducing a distribution of relaxation times into equation (9) as,

$$\epsilon_3^*(\omega) = \frac{\Delta\epsilon_3}{\{1 + (i\omega\tau_3)^{\beta_3}\}^3}, \quad (11)$$

where $\Delta\epsilon_3$ is the third order dielectric increment, τ_3 the apparent relaxation time, β_3 the Cole–Cole parameter. We find the fitted curve from equation (11), drawn as a solid line in figure 4, is in good agreement with the measured spectrum except at lower frequencies. The best fitting values of parameters for figure 4 are $\Delta\epsilon_3 = -4.46 \times 10^{-22}$ Fm V⁻², $\tau_3 = 1.73$ ms and $\beta_3 = 0.87$. The real part of $\epsilon_3^*(\omega)$ at low frequencies is negative and its absolute value amounts to 4.0×10^{-22} Fm V⁻², which is much larger than that obtained for other organic materials, for example 3.5×10^{-27} Fm V⁻² for PVDF as a ferroelectric polymer [18]. Thus, the dielectric response in the ferroelectric liquid crystal easily becomes non-linear for a rather weak electric field, which implies it is one of the most suitable materials for investigating non-linear dielectric relaxation phenomena. The negative sign of the third order non-linear dielectric increment indicates that the observed non-linearity in this case is caused by the saturation of the dipole moment under a strong electric field. This kind of dielectric non-linearity is observed also for amorphous polymers with a large dipole moment but its magnitude is much smaller by five to nine decades [21]. The large non-linearity of the ferroelectric liquid crystal is ascribable to the cooperativeness of the molecular motion concerning this relaxation, which is characteristic of ferroelectric materials in general.

5. Temperature dependence of linear and non-linear dielectric constants at a low frequency

The temperature dependences of the real parts of $\epsilon_1^*(\omega)$ and $\epsilon_3^*(\omega)$ at a low frequency (12 Hz) are shown in figures 5 (a) and (b), respectively. The real part of ϵ_1^* increases close to 87°C and then becomes almost constant through the S_C^* range. The real part of ϵ_3^* shows a sharp peak around the transition temperature and then monotonously decreases in magnitude with decreasing temperature. The corresponding anomaly is

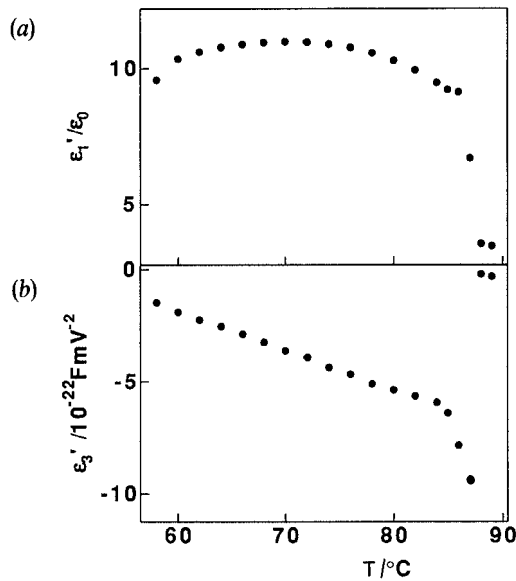


Figure 5. The temperature dependences of dielectric constants ϵ_1^* and ϵ_3^* at 12 Hz. (a) the real part of ϵ_1^* , (b) the real part of ϵ_3^* .

not observed in ϵ_1^* . This peak seems to correspond to the extraordinary increase in helical pitch just below the transition point. The detailed profiles of the temperature dispersions of ϵ_1^* and ϵ_3^* are not similar for various ferroelectric liquid crystals and will be treated in a forthcoming paper.

6. Conclusion

We have applied the new technique of non-linear dielectric relaxation spectroscopy to ferroelectric liquid crystals in the S_C^* phase. The non-linear dielectric spectrum has been obtained from the electric field dependence of the n th order harmonic frequency component of the electric displacement for a weak electric field. It is found from the sign of the third order non-linear increment that the dielectric non-linearity of the ferroelectric liquid crystal is caused by saturation of the orientation of dipole moments due to the applied electric field and is not ascribable to strong interactions between dipoles. This is consistent with a conventional view that the ferroelectric liquid crystal belongs to ferroelectrics of improper type.

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References

- [1] MICHELSON, A., BENGUIGUI, L., and CABIB, D., 1977, *Phys. Rev. A*, **16**, 394.
- [2] BLINC, R., and ZEKS, B., 1978, *Phys. Rev. A*, **18**, 740.
- [3] OSTROVSKII, B. I., RABINOVICH, A. S., SONIN, A. S., and STRUKOV, B. A., 1978, *Sov. Phys. JETP*, **47**, 912.
- [4] MARTINOT-LAGARDE, PH., and DURAND, G., 1981, *J. Phys., Paris*, **42**, 269.
- [5] LEVSTIK, A., CARLSSON, T., FILIPIC, C., LEVSTIK, I., and ZEKS, B., 1987, *Phys. Rev. A*, **35**, 3527.

- [6] YOSHINO, K., UEMOTO, T., and INUISHI, Y., 1977, *Jap. J. appl. Phys.*, **16**, 571.
- [7] BENGUIGUI, L., 1982, *J. Phys., Paris*, **43**, 915.
- [8] MARUYAMA, N., 1984, *Ferroelectrics*, **58**, 187.
- [9] YOSHINO, K., OZAKI, M., SAKURAI, T., SAKAMOTO, K., and HONMA, M., 1984, *Jap. J. appl. Phys.*, **23**, L175.
- [10] OZAKI, M., YOSHINO, K., SAKURAI, T., MIKAMI, N., and HIGUCHI, R., 1987, *J. chem. Phys.*, **86**, 3648.
- [11] CAVA, R. J., PATEL, J. S., COLLEN, K. R., GOODBY, J. W., and RIETMAN, E. A., 1987, *Phys. Rev. A*, **35**, 4378.
- [12] YOSHINO, K., NAKAO, K., TANIGUCHI, H., and OZAKI, M., 1987, *J. phys. Soc. Jap.*, **56**, 4150.
- [13] LEVSTIK, A., CARLSSON, T., FILIPIC, C., and ZEKS, B., 1988, *Molec. Crystals liq. Crystals*, **154**, 259.
- [14] FILIPIC, C., CARLSSON, T., LEVSTIK, A., ZEKS, B., BLINC, R., GOUDA, F., LAGERWALL, S. T., and SKARP, K., 1988, *Phys. Rev. A*, **38**, 5833.
- [15] OZAKI, M., HATAI, T., and YOSHINO, K., 1988, *Jap. J. appl. Phys.*, **27**, L1996.
- [16] BIRADAR, A. M., WROBEL, S., and HAASE, W., 1989, *Phys. Rev. A*, **39**, 2693.
- [17] GOUDA, F., SKARP, K., ANDERSSON, G., KRESSE, H., and LAGERWALL, S. T., 1989, *Jap. J. appl. Phys.*, **28**, 1887.
- [18] FURUKAWA, T., NAKAJIMA, K., KOIZUMI, T., and DATE, M., 1987, *Jap. J. appl. Phys.*, **26**, 1039.
- [19] IKEDA, S., SUZUKI, H., KOYAMA, K., and WADA, Y., 1986, *Polymer J.*, **19**, 681.
- [20] IKEDA, S., KOMINAMI, H., KOYAMA, K., and WADA, Y., 1987, *J. appl. Phys.*, **62**, 3339.
- [21] FURUKAWA, T., TADA, M., NAKAJIMA, K., and SEO, I., 1988, *Jap. J. appl. Phys.*, **27**, 200.
- [22] NAKADA, O., 1960, *J. phys. Soc. Jap.*, **15**, 2280.