Impurity Effect on Domain Formation in a Nematic Liquid Crystal

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(Received February 19, 1973)

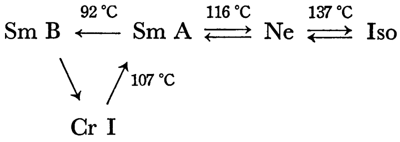
The effect of impurity on domain formation in an ethyl anisal-*p*-aminocinnamate nematic liquid crystal was investigated. With the decrease of the content of ionic impurities, the threshold voltage of the domain formation increases and the size of the domain patterns becomes larger. With blocking electrodes, the domain patterns could not be seen, although molecular orientation was still observed. When a negative electrode is coated partly with Nesa and partly with gold, the domain patterns appear first in the Nesa (*n*-type) part. When an electric field is cut and applied within one second intervals, the domains reappear at the same places. The mechanism of domain formation is discussed.

It is well-known that the optical properties of nematic liquid crystals are remarkably altered when electric fields are applied. Anomalous alignment called "domain" occurs at a low field strength. This phenomenon was first found by Williams in the nematic state of a *p*-azoxyanisole liquid crystal,[1] and has since been studied by many investigators.[2-6] Helfrich[7] proposed a quantitative theory describing the behavior of nematic liquid crystals with DC electric field near the critical field strength of domain formation. With DC electric field, ionic impurities influence the electro-optical properties of a liquid crystal.[7,8] However, there are few reports on the effect of impurities. We thought it of interest to elucidate the effect of impurities in a liquid crystal on the process of domain formation.

The present report deals with the effect of impurities on domain formation in a nematic liquid crystal. Our results for ethyl anisal-*p*-aminocinnamate (EAPAC) show that the current, probably due to ionic impurities, considerably contributes to the size and shape of the domain patterns.

Experimental

EAPAC was synthesized according to the literature.[9-11] EAPAC was purified by recrystallizations from absolute ethanol, and was dried sufficiently under reduced pressure. Three EAPAC samples (I, II, and III) each having different electrical conductivity, were obtained by recrystallization once, twice, and three times, respectively. Phase transition temperatures were determined with a differential scanning calorimeter (Rigaku Model 8001). Heating and cooling rates were controlled to within 5 °C/min.



There is no conspicuous difference in phase transition temperature between samples I, II and III. Although Vorländer reported the presence of another crystal phase II with transition at 83 °C from Sm B,[11] no such phase could be observed. Other phase transition temperatures showed good agreement with those reported by Vorländer.

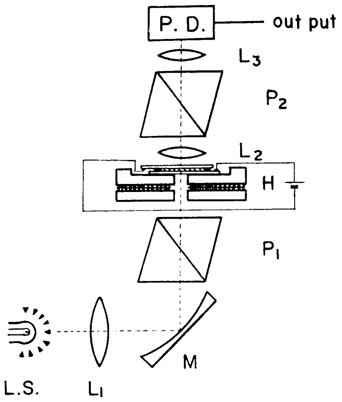


Fig. 1. Experimental alignment for observing the optical behavior of EAPAC in the nematic state. L.S: light source, M: mirror, L_1: condensing lens, L_2,L_3: objective and ocular lenses, P_1,P_2: polarizer and analyzer, P.D.: photodiode, H: heater plate.

All measurements were made in a nematic region. The domain patterns were observed under a Leitz polarizing microscope in the transmission mode with crossed nicols. The experimental alignment for observing the optical behavior is shown in Fig. 1. An EAPAC sample held between two Nesa-coated glass electrodes with a Teflon spacer (50 μ thickness), was set on a heater plate, which was then placed on the stage of a microscope. The optical response when the electric field was applied, was detected with a photodiode (NEC PD32) equipped at the top of a microscope and displayed on an oscilloscope (National VP517A). The DC current-voltage characteristics were measured by using a sandwich type cell with temperature control within 0.5 °C.

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[1] R. Williams, *J. Chem. Phys.*, **39**, 384 (1963).

[2] E. F. Carr, *Mol. Cryst. Liquid Cryst.*, **7**, 253 (1969).

[3] H. Gruler and G. Meier, *ibid.*, **12**, 289 (1971).

[4] G. H. Heilmeier, *J. Chem. Phys.*, **44**, 644 (1966).

[5] H. Koelmans and A. M. von Boxtel, *Phys. Lett.*, **32A**, 32 (1970).

[6] R. B. Beyer, *Phys. Rev. Lett.*, **22**, 918 (1969).

[7] W. Helfrich, *J. Chem. Phys.*, **51**, 4092 (1969).

[8] G. H. Heilmeier, *Proc. IEEE*, **59**, 442 (1971).

[9] J. J. Broomfield and R. Fuchs, *J. Org. Chem.*, **26**, 2991 (1961).

[10] E. D. Bergmann, S. Berkovic, and R. Ikan, *J. Amer. Chem. Soc.*, **78**, 6037 (1956).

[11] D. Vorländer, R. Wilke, U. Haberland, K. Thinius, H. Hempel, and J. Fisher, *Ber.*, **71**, 501 (1938).

Results and Discussion

The threshold voltage of domain formation was determined from the change of the transmitted light intensity as a function of the applied voltage by a similar method to that reported by Williams.[1] The threshold field strengths of the domain formation in I, II, and III were about 560, 600, and 700 V/cm, respectively. These critical points correspond to the applied voltage for the appearance of extinction crosses which are observed by a polarizing microscope.

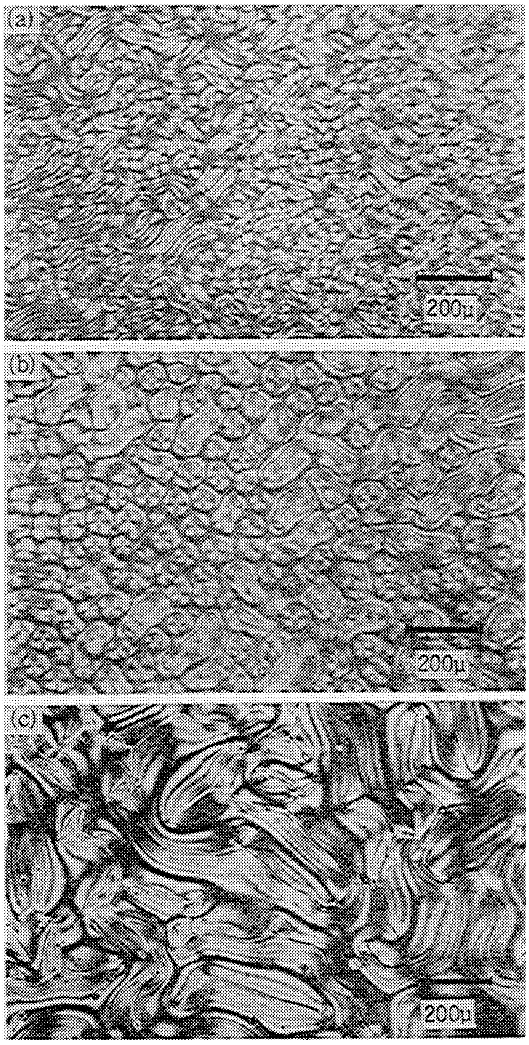

Fig. 3. The typical domain patterns of EAPAC (a) Sample I (applied voltage 4V, 50 μ thickness, 128 °C), (b) Sample II (4 V, 50 μ, 128 °C), and (c) Sample III (4.5 V, 50 μ, 128 °C).

Figure 2 shows the DC current-voltage characteristics for I, II, and III. Their conductivities are of the order 10^{-7}, 10^{-8}, and $10^{-9}\ \Omega^{-1}\text{cm}^{-1}$, respectively. These rather high values of conductivity at DC electric field indicate that ionic conduction is predominant. A difference in DC electrical conductivity was, however, clearly observed with the number of recrystallization times. Taking this difference in conductivity into consideration, the difference in the threshold voltage of domain formation for the samples is considered to be due to the different degree of contribution of ionic impurities. Thus, ionic impurities to some extent

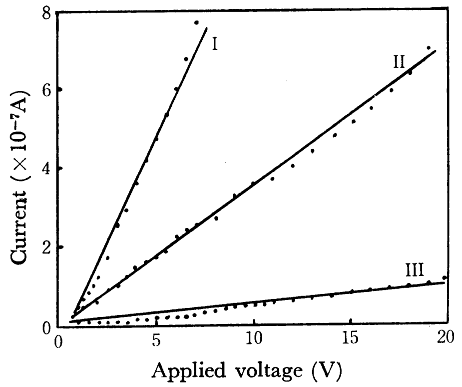

Fig. 2. Current-voltage characteristics of the EAPAC samples I, II, and III measured at 128 °C. The separation of electrodes is 50 μ.

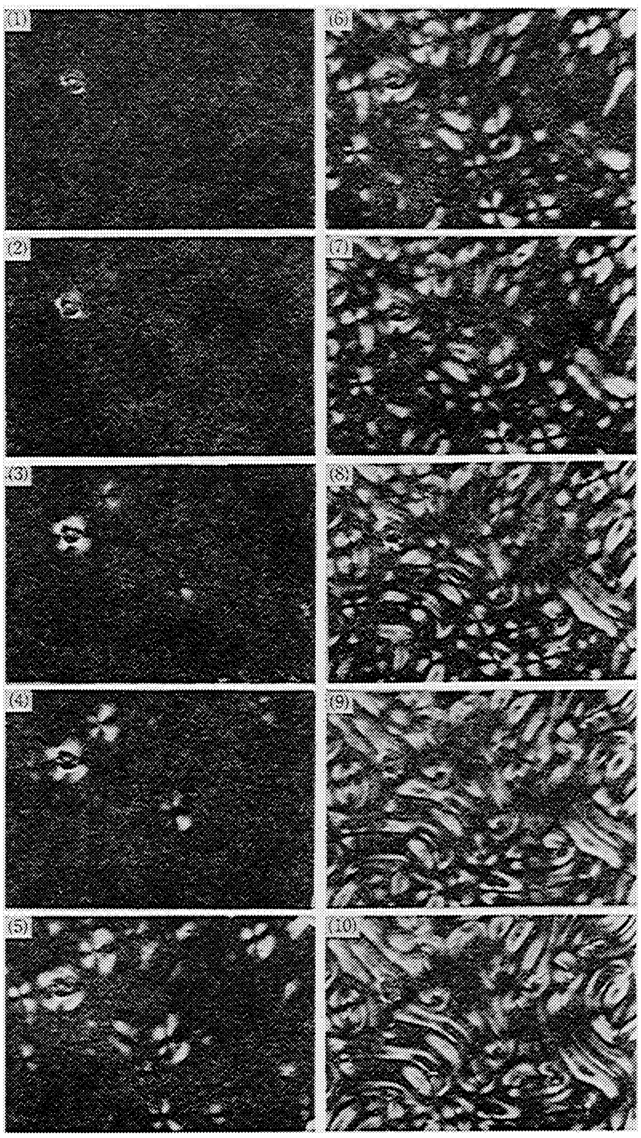

Fig. 4. The process of the domain formation of EAPAC Sample III (5 V, 50 μ, 130 °C) observed by a 16 mm moving camera. The 10 frames shown here are selected in the order of the process with appropriate intervals, 0.3 s for 1)—7) and 1 s for 7)—10).

influence the domain formation. Typical domain patterns of I, II, and III are shown in Fig. 3. The process of domain formation for III observed by a 16 mm moving camera with a crank speed of 64 frames per second is shown in Fig. 4. At the threshold voltage, Maltese cross-like extinction crosses of spherulites appear and then increase in number. As the voltage increases further, some of the crosses link with each other and gradually grow independently into long stripes everywhere, and finally form the characteristic cellular domain patterns of EAPAC. The size of the cellular domain becomes larger with the number of recrystallization times, *viz.*, with the decrease of impurities (Fig. 3). The domain patterns of III appear at slightly higher applied voltage (4.5 V) than those of the other two samples (4 V). The outer domain wall, shown in the figure as a dark obscure part with the pattern of a slightly stretched circle occurs in the neighborhood of the negative electrode. On the other hand, the inner wall which had been produced by the linking of the extinction crosses can be observed near the positive electrode by focusing a microscope in sharp focus. Penz[12] reported that even at the domain formation voltage the hydrodynamic flow of a *p*-azoxyanisole liquid crystal occurred. In the case of EAPAC it was also found that a dust particle in a domain moves in a circular motion between the two electrodes through these inner and outer domain walls. When observed carefully, a dust particle moves from the negative electrode to the positive electrode through the inner domain wall and inversely through the outer domain wall. This phenomenon may imply that the hydrodynamic flow of a liquid crystal is necessary to produce the domain pattern.

In order to examine the effect of the contact of an electrode and a liquid crystal, experiments were made with blocking electrodes, Nesa electrodes being covered with thin mica sheets ($10\ \mu$ thickness). In the case of both positive and negative blocking electrodes, the domain pattern could not be observed even in the voltage region of the dynamic scattering mode. However, a transient increase of transmission was still observed under the crossed polarizers at the instant of applying an electric field, the transmission decreasing gradually to a final steady state value (Fig. 5). The transient increase of transmission may be caused by the orientation of the dipoles of EAPAC molecules to the direction of an electric field, and then the back field due to these ordered dipoles may decrease the effect of the external field, and a final arrangement of dipoles in a steady state may be attained with decreasing transmission. Thus, only the molecular orientation is observable and the domain pattern does not appear in the case of blocking electrodes. This suggests that not only the orientation of molecules but also the stationary current is necessary for the domain formation with DC electric field. Since an electron injection or electron transfer to EAPAC molecules, if any, is possible only in the case of direct contact to the electrodes and not in blocking electrodes, the electron transfer to EAPAC molecules from the negative electrode may play an important role in the domain formation.

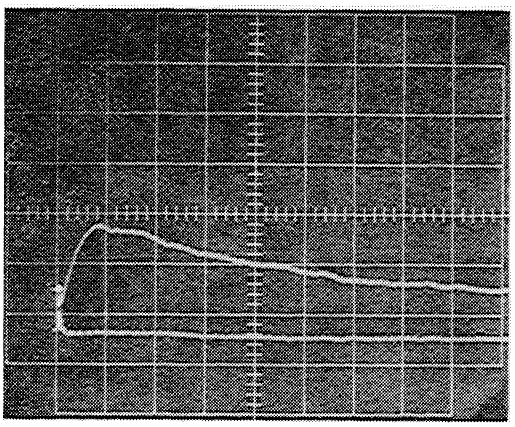

Fig. 5. Transient transmission change with blocking electrodes observed under the crossed polarizers. The upper and lower curves indicate the changes at the instant of switching on and off electric field (4×10^4 V/cm), respectively. Vertical axis: arbitrary transmittance, sweep: 100 ms/division.

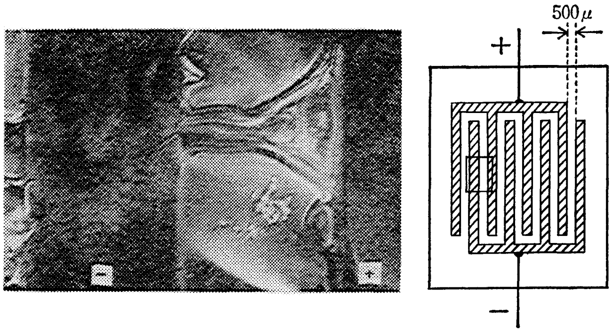

Fig. 6. The domain patterns of EAPAC observed with a gold surface cell on glass plate (10^3 V/cm, 127 °C). The place corresponding to the photograph is indicated by square in the schematic figure of the electrode.

Furthermore, in the case of the negative electrode plate coated half with Nesa and half with gold, the domain patterns appear first in the Nesa-coated part and subsequently in the gold part as the field strength increases. Provided that electron injection is required for the domain formation, this phenomenon is easily understood because an electron injection occurs more easily from the *n*-type Nesa part than from gold. The result of the optical measurement under a surface cell with the separation of $500\ \mu$ between two electrodes is shown in Fig. 6. The measurement with surface type electrodes corresponds to the case of viewing transversely the domain pattern between two sandwich type electrodes. In this case, the striped structure due to hydrodynamic flow of EAPAC molecules was observed, and the source point of the hydrodynamic flow was considered to coincide with the site of electron injection at the negative electrode.

Another experimental result suggests that the ionic impurities in a liquid crystal have an influence on the initial process of the domain formation. The extinction crosses or domain patterns reappear in the same

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[12] P. A. Penz, *Mol. Cryst. Liquid Cryst.*, **15**, 141 (1971).

position for the quick switching (about 1 s intervals) of the applied field, while the position as well as the shape of the domain patterns change when an electric field is applied again after an interval long enough for the ionic impurities stuck to the electrodes to diffuse. The domain patterns in the nematic state are still memorized even if the temperature once rises to the isotropic region or once falls to the crystal region keeping the applied field.

Taking all the measurements into account collectively, the process of EAPAC domain formation may be considered as follows. When an electric field is applied, ionic impurities in a liquid crystal are attracted and migrate to the negative electrode. Here, ionic impurities sticking to the electrode lower the electrode potential, and the electron transfer from the electrode to EAPAC molecules as an electron acceptor, *i.e.*, electron injection, may easily occur as Heilmeier has suggested.[8] This injection site corresponds to the place where the extinction crosses can be observed with a polarizing microscope at the threshold voltage of the domain formation. The injected electrons are captured by EAPAC molecules and cause the hydrodynamic flow of a liquid crystal and finally produce the characteristic domain pattern. Thus, (1) the domain inner wall gushes out from the negative electrode as the injection site, and (2) with a smaller amount of ionic impurities, the number of injecting sites becomes smaller and hence the size of the domain becomes larger.