Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Minoru Tohnoe[a]; Shoichi Kai[a]; Masahide Imasaki[a]
[a] Department of Electrical Engineering, Kyushu Institute of Technology, Kitakyushu, Japan

To cite this Article Tohnoe, Minoru , Kai, Shoichi and Imasaki, Masahide(1989) 'Surface effects on the polarization reversal of the ferroelectric liquid crystal 8SI*', Liquid Crystals, 5: 4, 1149 — 1157
To link to this Article: DOI: 10.1080/02678298908026419
URL: http://dx.doi.org/10.1080/02678298908026419

LIQUID CRYSTALS, 1989, VOL. 5, NO. 4, 1149–1157

Surface effects on the polarization reversal of the ferroelectric liquid crystal 8SI*

by MINORU TOHNOE, SHOICHI KAI and MASAHIDE IMASAKI
Department of Electrical Engineering, Kyushu Institute of Technology,
Tobata Kitakyushu 804, Japan

The activation field for the switching time ($\tau_{1/2}$) in the truly ferroelectric liquid crystal 8SI* (CE8; ΔS-(+)-4-(2′-methylbutyl) phenyl-4′-*n*-octylbiphenyl-4 carboxylate) has been studied for various surface conditions of the transparent electrode (SnO_2), in order to understand the memory effect, the polarization reversal mechanism and its surface effect. We prepared five different surfaces, namely one coated with polyvinyl alcohol (PVA) and the other four by scratching N-times ($N = 0, 10, 20$ and 30) with a paste made of Cr_2O_3 powder (about 0·1 μm). The number and the area of scratches on the electrode surface obviously increase with N. The polarization reversal processes are influenced by this treatment. $\tau_{1/2}$ decreases with increasing N, but no change is observed in the contrast of the light transmittance. Two different activation fields, E_{a1} for the applied field $E > E_0$ and E_{a2} for $E < E_0$ are observed, where E_0 is a certain field depending on the sample. Here E_{a1} is much larger than E_{a2}; typically $E_{a1} = 260\,\mathrm{kV\,cm^{-1}}$ and $E_{a2} = 144\,\mathrm{kV\,cm^{-1}}$ for $N = 0$. This means that nucleation for the higher field needs a large activation energy which therefore has strong barriers. In contrast with this, nucleation for the low field occurs easily. Changing a surface condition, E_{a2} clearly decreases with increasing N although E_{a1} is almost independent of the surface scratching. This may suggest that E_{a1} corresponds to the activation field for the bulk pinning and nucleation, and E_{a2} for the surface pinning. The PVA treatment gives an intermediate influence between $N = 0$ and 10.

1. Introduction

Recently Brand and Cladis have found that the smectic phase appearing in the lowest temperature range of 8SI* (CE8; ΔS-(+)-4-(2′-methylbutyl) phenyl-4′-*n*-octylbiphenyl-4 carboxylate) shows true ferroelectricity and named it the smectic X ($\tilde{G}$) because of unknown phase before [1, 2]. They have suggested that the structure of S_X is similar to that of S_G; that is, it has in-plane rectangular lattice ordering [2, 3]. There is, however, no helical rotation of layers in S_X and long range interlayer correlations exist. When an applied field is switched off after the reversal there are then no restoring elastic forces. The S_X phase shows, therefore, pure bistability in the bulk on application of an electric field without surface anchoring [2, 3]. This is essentially different from the S_C^* phase where bistability results from the surface anchoring. Brand and Cladis have also reported the ferroelectric switching which exhibited a switching time exponentially proportional to an applied voltage with activation energy [1, 2]. The direct observation of the spontaneous polarization in S_X, however, such as the D–E loop and the polarization reversal current, is not yet achieved unlike those in S_G^*, S_I^* and S_C^*, although several researchers have tried [2, 4–6]. We have recently reported that the memory effect of S_X due to multistability can be controlled by the pulse width of an applied electric field because of surface pinning [6, 7]. A similar memory effect was observed in a lower temperature phase of DOBAMBC (4-*n*-decyl-oxybenzylidene-4′-amino-2′-methylbutylcinnamate) than S_C^* and in the surface stabilized cell (SSFLC) whose thickness must be thinner than the helical pitch [8].

It should be noted that the memory effect means not only bistability (binary memory) but also multistability. Although a bulk S_X shows bistability, under a surface effect with various pinnings it will be possible to achieve multistability, i.e. arbitrary memory effect. This actually occurs in S_X [7].

Here the polarization reversal process and its surface dependence are studied in order to understand the memory effect and the reversal mechanism in S_X. The polarization reversal process in SSFLC of S_C^* of DOBAMBC has been investigated in detail by Orihara and Ishibashi [9, 10] from the analogous point of view to that of ordinary ferroelectric crystals and a first order phase transition such as crystal growth, based on Avrami's idea [11]. We take our position for the reversal process in S_X similar to them, but contain the surface effect by changing the surface conditions.

2. Experimental

2.1. *Preparation*

The compound used in the present study is the material 8SI* which on cooling shows the sequence of phase transitions I–N* (141°C)–S_A (135°C)–S_C^* (81°C)–S_I^* (71°C)–$S_{G'}^*$ (66°C) and S_X (60°C). The thickness d of the sandwiched cell was prepared in the range from 2 to 30 μm. The dielectric and the electro-optic measurements were carried out in the S_X phase mainly at $\Delta T = T_{S_X S_{G'}^*} - T = 1$°C, where $T_{S_X S_{G'}^*}$ is the transition temperature from the $S_{G'}^*$ to the S_X phase (60°C). For $\Delta T > 1$°C, the reversal dynamics are too slow to be studied. No surface treatment including rubbing was done. The domain reversal process was detected via the light transmittance under a D.C. electric field. The temperature was controlled to within $\pm 0{\cdot}02$°C using a copper container with double wall and with a feedback power controller. In order to investigate the reversal dynamics in space, image processing techniques were used [6, 7]. The intensity of the light transmitted through the sample was obtained by a photodetector. When a D.C. field was applied to the S_X phase, the reversal area was proportional to the change of light transmittance $\Delta I_0(t)$ [6]. The experimental set-up has already been reported in detail elsewhere [6, 7, 12]. The D–E hysteresis loop was measured by a D.C. bias method using a lock-in amplifier (NF Co. LI-574) [13]. The frequency of the A.C. field used to measure the dielectric constant was 1 kHz with an amplitude of 1 V. To obtain different surface states, a glass substrate was scratched with a Cr_2O_3 polisher, whose grain size was about $0{\cdot}1$ μm, and rubbed on with a different number of repetitions N under a constant pressure (see figure 1). The scratching machine was constructed by the authors. No quantitative information concerning the size and the number of scratches on the glass plate is yet available. Instead, however, we have confirmed the change in the surface due to the scratching with a scanning electron microscope (JOEL Ltd, JCXA733), as shown in figure 2. The different scratching treatments certainly changed the number and the size of surface scratches. We made three different surface conditions in one identical cell, for example $N = 0$, 10 and 20, by scratching one part of the glass substrate while masking others, as shown in figure 1. Several sample cells were prepared by this procedure. Thus, the surface effect could be studied for identical thicknesses. We have also used polyvinyl alcohol (PVA) as another surface coating to understand the effect of the surface condition on the dynamic behaviour of the polarization reversal. PVA is a widely used polymer for homogeneous alignment of nematic liquid crystals.

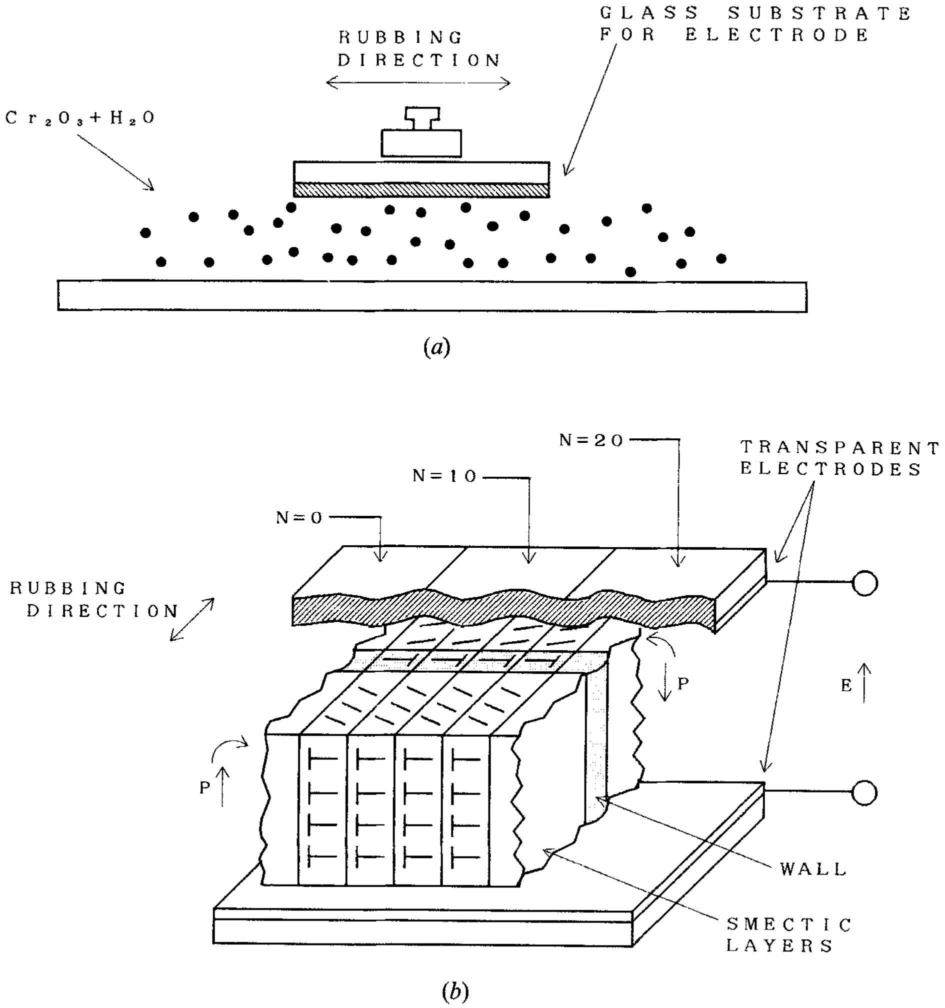

Figure 1. (*a*) The scratching procedure and (*b*) an example of a sample scratched with three different values of *N*.

2.2. *Result and discussion*

Figure 3 shows the D–E hysteresis of the S_X phase obtained by a D.C. bias method. To check the experimental set-up we also measured the D–E hysteresis loop of the S_C^* phase of DOBAMBC and obtained the well known ordinary loop [13]. In contrast, the hysteresis of the S_X^* phase of 8SI* is very unusual. Evaluation of the spontaneous polarization is not possible because there is no saturating tendency. Instead, however, the remanent polarization can be determined from the figure, it is estimated to be about $0{\cdot}3\,\mathrm{nC\,cm^{-2}}$. The cusp of the loop in the first and the third quadrants shows a linear dielectric constant at very high electric field, while it seems to show ferroelectric properties at relatively low fields. Other methods for dielectric measurements, the Pepinsky bridge (double Sawyer–Tower method) and the triangular wave methods, were also tried, but they were not applicable here, unlike the case of DOBAMBC [13].

A typical example of polarization reversal behaviour for the cell treated with PVA is shown in figure 4. Increasing the field increases the response. The universality for

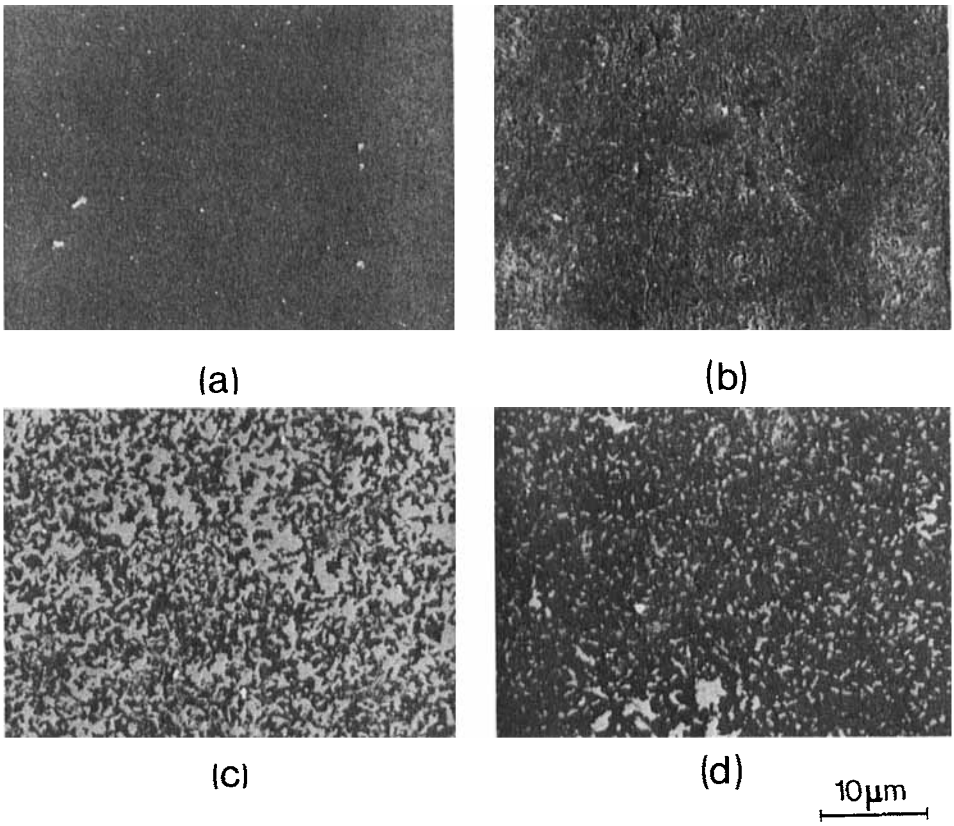

Figure 2. Photographs of the surface observed by a scanning electron microscope. (*a*) $N = 0$, (*b*) $N = 10$, (*c*) $N = 20$ and (*d*) $N = 30$.

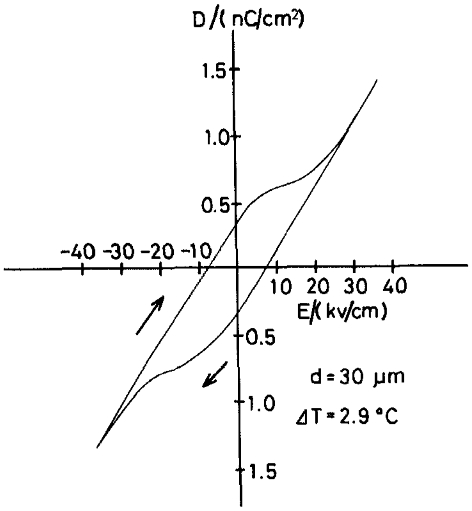

Figure 3. The *D*–*E* hysteresis loop obtained in S_X at 57·1°C using a D.C. bias method.

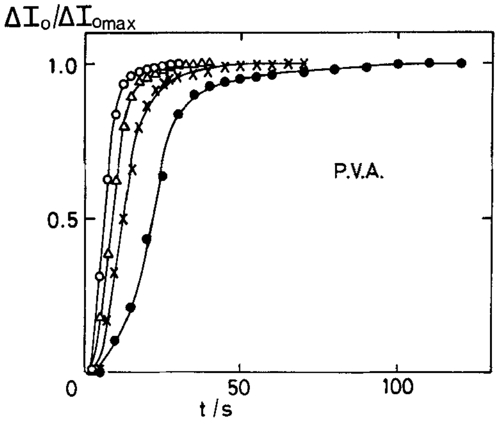

Figure 4. The time evolution of the light transmittance, corresponding to the fraction of the reversed area for the sample with the PVA treated surface. (○) $E = 100\,\mathrm{kV\,cm^{-1}}$, (△) $E = 89\,\mathrm{kV\,cm^{-1}}$, (x) $E = 78\,\mathrm{kV\,cm^{-1}}$ and (●) $E = 67\,\mathrm{kV\,cm^{-1}}$.

this time evolution has already been discussed elsewhere [6]. The time dependence in figure 4 can be described by the law $(1 - \exp At^n)$ with $n = 2{\cdot}3$ for the PVA treated cell, where A is a constant [6]. This suggests the validity of the Avrami theory for the reversal process in the S_X phase [9, 11]. The growth velocity of nucleus in this reversal process does not show a simple behaviour and oscillates in time [6].

Figure 5 shows the field dependence of the transmittance which is proportional to the reversed area [6] for the cell with scratching repetition $N = 30$, under a step-like electric field. The step height is always fixed at the initial value. One should note that the results in figure 5 were obtained as a steady state value by applying a constant field in a step-like fashion. For $E < E_c$ ($= 1{\cdot}8\,\mathrm{kV\,cm^{-1}}$ in this sample) no reversal process can be observed, even maintaining the field for a period longer than for 6 h. For $E > E_c$ the reversed area increases with an applied field. For $E > E^*$ ($= 8{\cdot}6\,\mathrm{kV\,cm^{-1}}$) the whole area is always reversed. Thus, there are two kinds of threshold fields; that is, E_c characterizing the onset of partial reversal and E^* characterizing complete reversal. When the field is removed, the memory effect is observed for $E > E_c$. E^* depends systematically on N (see table 1). For the PVA treated cell E^* is $16{\cdot}7\,\mathrm{kV\,cm^{-1}}$;

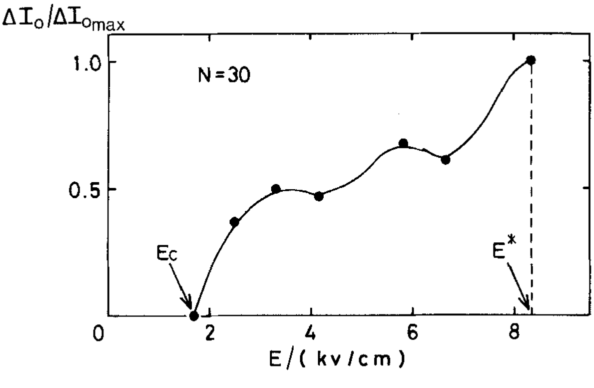

Figure 5. The field dependence of the light transmittance obtained by applying a step-like field for $N = 30$.

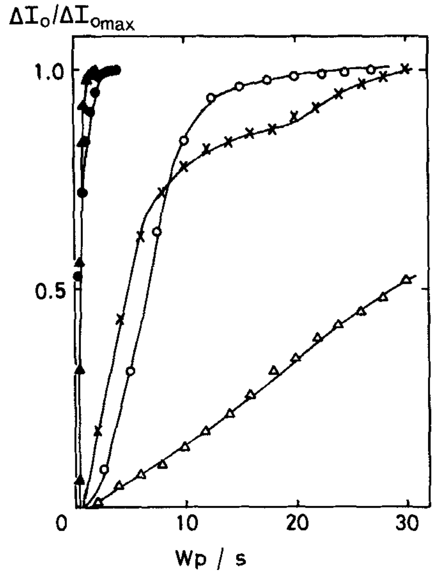

Figure 6. The memory effect for the various surface treatments ($d = 7\,\mu$m); W_p is the pulse width of field. The field intensity, E, is 100 kV cm^{-1}. (○) PVA coated surface; scratching (△) $N = 0$, (x) $N = 10$, (●) $N = 20$ and (▲) $N = 30$.

Table 1. Dependence of E^* on the scratching number.

Scratching number, N	0	10	20	30
100 per cent threshold field, E^*/kV cm^{-1}	33	14	14	8·6

this value is between those for $N = 0$ and 10. Such a dependence of E_c is difficult to evaluate and no systematic surface effect is obtained.

Figure 6 shows the dependence of the light transmittance $\Delta I_0/\Delta I_{0\max}$ on the pulse width of the applied field for the various surface conditions. Applying a field higher than E_c with a pulse width, W_p, longer than W_{pth}, the memory effect can be observed in the transmittance. As seen in figure 6, the response becomes slower as N is decreased from 30 to 0. In particular, for $N = 30$ and 20 the reversal response can be led by a very narrow W_p. We note the linear relationship between the memory of the transmittance and W_p for $N = 0$. A similar dependence can be seen in figure 7 which shows $\Delta I_0/\Delta I_{0\max}$ versus W_p for various field intensities [7]. The W_p needed to saturate ΔI_0 becomes shorter with an increase in E.

Figure 8 shows the normalized switching time $\tau_{1/2}/\tau(\infty)$ plotted against $1/E$ using a semilogarithmic scale as abscissa, where $\tau_{1/2}$ is the time required for ΔI_0 (proportional to the reversed area) to become half the value of $\Delta I_{0\max}$ and $\tau(\infty)$ the time for infinite E

$$\tau_{1/2}/\tau(\infty) = \exp(E_a/E). \tag{1}$$

$\tau_{1/2}$ has an important physical meaning and is sometimes also called the onset time [14]. The slope of the switching time in figure 8 becomes smaller with increasing N. It means that the activation field E_a decreases with N, and therefore nucleation occurs more easily. Another fact also seen in figure 8 is the existence of two different slopes for the same sample. That is, E_{a1} in the high field regime is larger than E_{a2} in the low

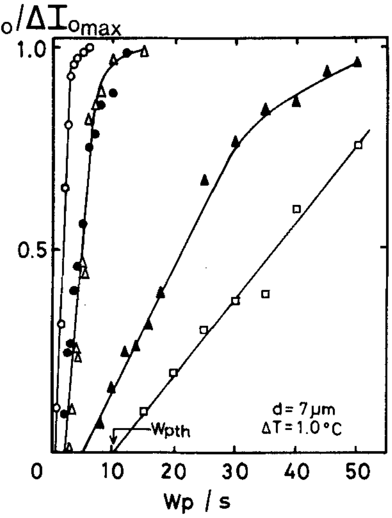

Figure 7. The memory effect for various field intensities E with no surface treatment ($N = 0$). W_{pth} is the threshold pulse width. (○) $E = 100\,\mathrm{kV\,cm^{-1}}$, (●) $E = 60\,\mathrm{kV\,cm^{-1}}$, (△) $E = 50\,\mathrm{kV\,cm^{-1}}$, (▲) $E = 40\,\mathrm{kV\,cm^{-1}}$ and (□) $E = 30\,\mathrm{kV\,cm^{-1}}$.

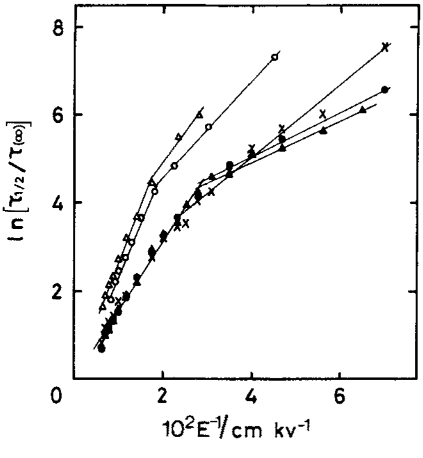

Figure 8. The field dependence of the switching time for the various surface treatments. $\tau(\infty)$ is the value of $\tau_{1/2}$ extrapolated to $E = \infty$. (○) PVA coated surface; scratching (△) $N = 0$, (x) $N = 10$, (●) $N = 20$ and (▲) $N = 30$.

field regime. This can be seen more clearly for the large-N sample. The values of the activation fields, E_{a1} and E_{a2}, are summarized in table 2. Two facts are clear here. One is that E_{a1} is almost independent of the surface treatment, but E_{a2} depends strongly on it. Secondly, the PVA treatment shows intermediate values between those for $N = 0$ and 10.

We now discuss briefly the background to the discussion of our results for the switching time. When the field E is applied against the polarization direction P, the reversal process starts from nucleation of the stable phase with P parallel to E. According to a theory for ferroelectric crystals, we can discuss the dynamical behaviour of the polarization reversal by use of the Gibbs free energy, ΔG, consisting of the

Table 2. Activation field for various surfaces.

	PVA	$N = 0$	$N = 10$	$N = 20$	$N = 30$
$E_{a1}/\mathrm{kV\,cm^{-1}}$	235	260	159	159	159
$E_{a2}/\mathrm{kV\,cm^{-1}}$	109	144	89	51	44

electrostatic energy and the domain wall energy containing an elastic distortion part. The depolarization energy may also be important, but we neglect it here. Then the nucleation rate J is given by [6]

$$J = J_\infty \exp(-\Delta G^*/kT), \tag{2}$$

where ΔG^* is the free energy for the critical nucleus (activation energy). The characteristic time (the switching time) $\tau_{1/2}$ for the reversal process is then proportional to $(Jv^2)^{-1/3}$, i.e.

$$\tau_{1/2} \propto v^{-2/3} \exp(E_a/E), \tag{3}$$

where E_a $(= \pi d \Delta \mu_w^2/6kTP)$ is an activation field [6] and v is the growth velocity. We have here replaced the characteristic time with $\tau_{1/2}$ for comparison with the experimental results. The field dependence of v is neglected compared with the exponential dependence of J, when $E \lesssim E_a$. At $E \gg E_a$, on the other hand, the field dependence of v is dominant for the switching time behaviour. The first case shows an exponential dependence of $\tau_{1/2}$ in agreement with the experimental results. The second case shows a power law dependence of $\tau_{1/2}$ because v is expected to be proportional to the field E^α,

$$\tau_{1/2} \propto E^{-2\alpha/3}. \tag{4}$$

According to equation (3) the exponential dependence of $\tau_{1/2}$ on the applied field as shown in figure 8 indicates the dominant role of J and the negligible effect of v. This suggests that the growth of domains occurs as secondary nucleations. Furthermore, the two activation fields suggest the two different activation energies, ΔG^*, which control two different nucleation sites. According to their dependences on the surface treatment, E_{a1} is probably related to the bulk nucleation because of the weak dependence on the surface treatment. On the other hand, E_{a2} should be related to surface nucleation.

3. Conclusion

In the present study the D–E hysteresis loop for the S_X phase of 8SI* was obtained but showed a very unusual form. The cause for this is not well understood and it will be necessary to study it further. One reason might be the insufficient intensity of the applied field necessary to saturate the polarization [15]. We have determined the dependence of the switching time on the applied field and the activation field E_a. The exponential dependence suggests that the nucleation rate J is more dominant in the switching of the S_X phase than the growth velocity v. Two activation fields, E_{a1} and E_{a2}, were observed in the higher field region and in the lower field region, respectively. This fact also suggests the existence of two different kinds of nucleation sources. E_{a1} is almost independent of the surface conditions while E_{a2} has a strong dependence on the surface treatment. The scratching procedure makes E_{a2} smaller. It is suggested therefore, that E_{a1} is the activation field for the bulk nucleation site and E_{a2} is for the surface site. The PVA treatment gives an intermediate influence between that for $N = 0$ and 10. Finally we mention that the power law dependence of $\tau_{1/2}$ could be observed by choosing a sample with a very small E_a, as seen in equation (4).

This study was supported in part by a Grant in Aid for Scientific Research from the Ministry of Education, Science and Culture in Japan.

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[15] We confirmed that it was not the case. For even very high field ($E > 200$ kV/cm) we found the similar D–E hysteresis loop to figure 3.