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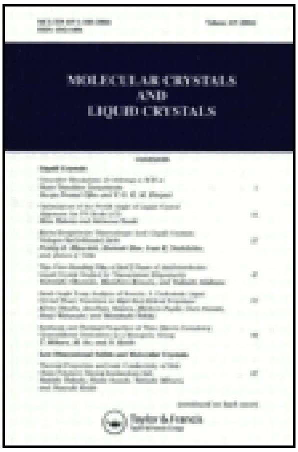

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Monitoring of the Changes of Dynamic Viscoelastic Properties of Liquid Crystals-During the Orientation with Voltage Pulses Using a Quartz Crystal Resonator

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Monitoring of the Changes of Dynamic Viscoelastic Properties of Liquid Crystals-During the Orientation with Voltage Pulses Using a Quartz Crystal Resonator

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The change of dynamic viscoelastic properties of liquid crystals was monitored using the quartz crystal resonator by measuring the resonant frequency and the resonant resistance of the quartz crystal during impression of voltage pulses. The viscoelastic change showed different responses as the effects of the applied voltage amplitude, an alignment film and the anisotropy of dielectricity. The higher applied voltage and a cell with alignment films gave larger responses than lower applied voltage and a cell without alignment film, respectively, and the positive and negative anisotropy of dielectricity gave opposite responses. The diagramed resonant frequency and resonant resistance for the voltage pulses showed hysterisis, and these changes are understood as the hysterisis of the dynamic orientation processes of liquid crystal molecules.

Keywords: Liquid crystal, quartz crystal, resonant frequency, resonant resistance, viscoelastic property.

INTRODUCTION

The viscosity and elasticity of liquid crystals are important properties for driving a liquid crystal cell because these properties affect the response of the cell. The steady viscosities can be determined by viscometry with a uniformly oriented sample,[1,2] absorption of ultrasonic shear waves[3–5] and spectroscopy of the light scattered by the long wavelength function of the director.[6] The elasticities can be determined from the critical magnetic field for the Freédericksz transition[7] or the critical electric field for the molecular orientation transition.[8] However, the changes of dynamic viscoelastic properties of liquid crystals during the application of a voltage pulse have reported a little.

An AT-cut quartz crystal has been used as a sensing device for viscoelasticity as well as a micro balance.[9–11] The resonant frequency change of the quartz crystal in contact with a Newtonian liquid can be derived from the mass change equation;[12]

$$\Delta F = -\Delta m F^2/(\mu \rho_Q)^{1/2} A, \tag{1}$$

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and the viscous penetration depth of the shear vibration of the contacting liquid;

$$l = (\eta/\pi\rho_L F)^{1/2}, \tag{2}$$

using the relation of $\Delta m = \rho l A$ as [11];

$$\Delta F = -F^{3/2}(\rho_L \eta/\pi\mu\rho_Q)^{1/2}, \tag{3}$$

where ΔF is the resonant frequency shift, F is the resonant frequency, Δm is the surface mass change, μ is the shear modulus of the quartz, ρ_Q is the density of the quartz, ρ_L is the density of the liquid, η is the viscosity of the liquid, and A is the surface area of the quartz crystal electrode. This equation corresponds to the equation which was derived by the shear vibration model directly.[13] This correspondence means that the resonant frequency reflects the effective mass for the shear vibration on the quartz crystal surface.

The penetration depth changes not only with the viscosity change but also with the elastic change in case a viscoelastic material is coated on the quartz crystal surface. This means that both changes of viscosity and elasticity change the resonant frequency. The effect of viscosity and elasticity can distinguish to estimate the energy loss in the vibrating material because this energy loss is mainly induced by the viscosity on the quartz crystal. The equation for the resonant resistance of the quartz crystal in contact with a Newtonian liquid has been derived as;[14]

$$R = (2\pi F\rho_L \eta)^{1/2} A/K^2, \tag{4}$$

where R is the resonant resistance, and k is the electro-mechano coupling factor.

Although we do not have a complete equation for in-contact-with-viscoelastic fluid such as liquid crystal to define a relation between the resonant parameters of quartz crystal and the dynamic viscosity of the fluid: $\eta^*(=\eta' - i\eta'')$, the shear vibration model of the quartz crystal suggests that the resonant resistance reflects mainly η', and the resonant frequency change includes both changes of η' and η''.[11] The increase of η' brings an increase of the resonant resistance and a decrease of the resonant frequency. The increase of η'' brings a decrease of the resonant frequency.

Simultaneous measurement of the resonant frequency and the resonant resistance is useful to observe the viscoelastic change of the contacting materials on the quartz crystal directly.[15] This technique has already been applied to the phase transition determination of liquid crystals and Langmuir–Brodgett films by temperature sweep.[11,16] Especially, the viscoelastic property of the Langmuir–Brodgett films was discussed by diagramming the resonant frequency and the resonant resistance. Also the change of viscoelastic properties of the coated films on the electrode was studied with the intercalation phenomena in the electrochemical cell.[15,17] These studies showed that the quartz crystal is a useful tool for studying the viscoelastic phenomena of thin films or layers.

The purpose of this study is to monitor the change of the dynamic viscoelastic properties of liquid cyrstals during orientation with voltage pulses to study the orientation process of the liquid crystals. The conformation change of the liquid crystals is discussed using the resonant frequency and the resonant resistance of the quartz crystal.

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EXPERIMENTAL

Apparatus and Materials

Figure 1 shows the experimental system. A liquid crystal cell is composed of an AT-cut, 9 MHZ quartz crystal ($8 \times 8 \times 0.18\,\mathrm{mm}^3$) with Pt electrodes, a 80 μm thickness Teflon sheet spacer and a glass plate with an ITO electrode. Polyimide films were coated on the Pt electrode and the ITO electrode as an alignment film. The liquid crystal to be tested was inserted between the quartz crystal and the glass plate with the Teflon spacer. The two electrodes of the quartz crystal were connected to an instrument for analyzing the quartz crystal (model QCA 917, Seiko EG&G) which monitored the resonant frequency and resonant resistance simultaneously. The electrode of the quartz crystal on the liquid crystal side and the ITO electrode were connected to the pulse generator (model 8165A, Yokogawa Hewlett Packard) for applying the voltage pulse.

E-8 (BDH) and ES-E001 (Chisso) were used as the liquid crystals which have positive and negative anisotropy of dielectricity, respectively. E-8 is a mixture of cyano-pentylbiphenyl, cyano-octylbiphenyl, cyano-propylbiphenyl, cyano-alcoxybiphenyl and p-terphenyl, and has values of NI transition point: 72°C, viscosity at 20°C: 54 cP, viscosity at 0°C: 270 cP, anisotropy of reflective index (Δn): 0.249 and anisotropy of dielectricity: 15.6. ES-E001 is a mixture based on the tolane type of liquid crystal and the phenylpyridin type of liquid crystal, and includes 2,3-dicyano-4-pentyloxy-phenyl = 4-(trans-4-ethylcyclohexyl) benzoate, 2,3-dicyano-4-pentyloxy-phenyl = trans-4-propyl-1-cyclohexancarboxylate and 2,3-dicyano-4-butoxy-phenyl = trans-4-butyl-1-cyclohexancalboxylate which makes the anisotropy of die-lectricity negative. The NI transition point of ES-E001 is 36.5°C.

Polyimide (PSI-A-2402-D01, Chisso) was dissolved with dimethyl formamide to be 2% and coated on the Pt and ITO electrodes. The coated electrodes were treated at 200°C for 90 min.

The experimental cell was treated at 80°C for 5 min before the experiments. The resonant frequency and resonant resistance were measured by applying 50 to 100 mHz and 5 to 10 V DC pulse.

RESULTS AND DISCUSSION

Effect of Rubbing Layer

Figure 2(a) shows the responses of the resonant frequency (the value is the change from the value before inserting the liquid crystal) and the resonant resistance for E-8 by

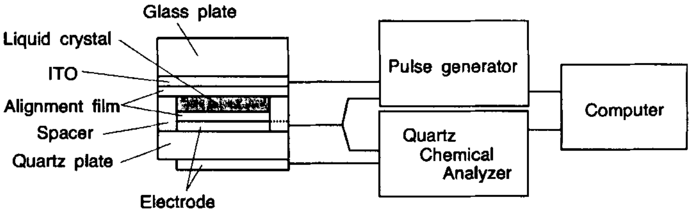

FIGURE 1 Schematic diagram of experimental system.

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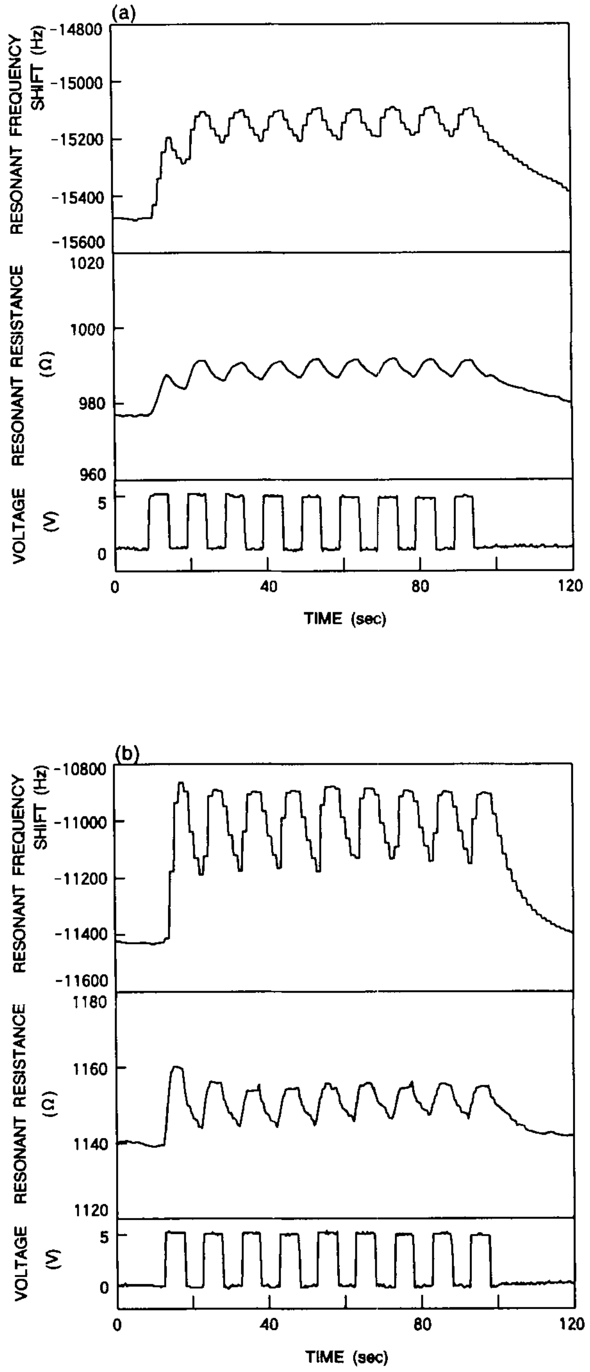

FIGURE 2 Responses of the resonant frequency change and the resonant resistance for (a) E-8 by 5 V pulse without the alignment film, (b) E-8 by 5 V pulse without the alignment film, (c) E-8 by 10 V pulse without the alignment film and (d) ES-E001 by 10 V pulse without the alignment film.

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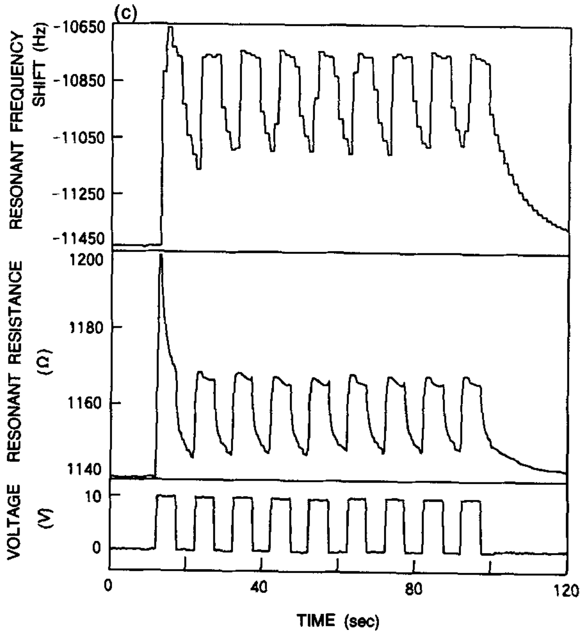

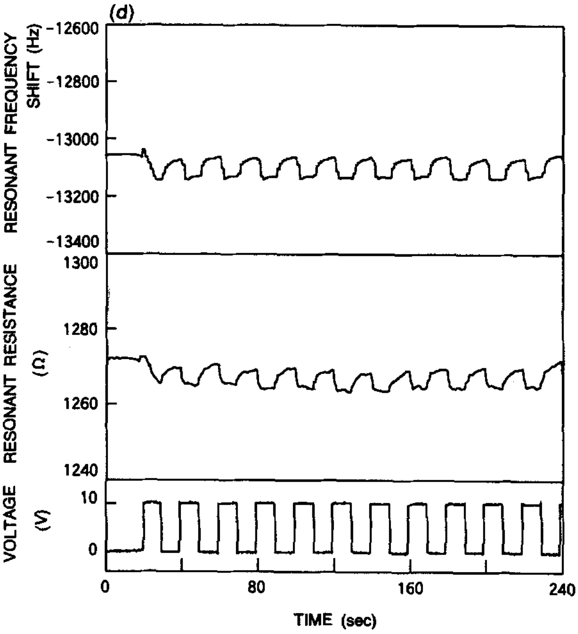

FIGURE 2 (*Continued.*)

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applying 5 V pulse without the polyimide film. In Figure 2(a), both the resonant frequency and the resonant resistance increased by applying the voltage. This change shows that the quartz crystal can detect the orientation change of liquid crystal molecules because there was no change in the resonant frequency and resonant resistance without inserting the liquid crystal. Figure 2(b) is the response for E-8 with the alignment film. The response of Figure 2(b) is larger than that of Figure 2(a). One of the reasons for this change is the difference of response of the liquid crystal with the arrangement film because a longer relaxation time against the driving frequency makes the response smaller. This can be understood by comparing the responses for the first pulse between Figures 2(a) and 2(b). The response of the first pulse in Figure 2(a) is smaller than that in Figure 2(b). The alignment film makes the orientation of the liquid crystal molecule quicker. Another reason for the response amplitude change is the difference of the liquid crystal orientation. As shown in Figure 3, the rubbing layer puts the liquid crystal molecule in a horizontal orientation without applying voltage (Figure 3(a)), and in a vertical orientation with applying voltage (Figure 3(c)). In cases without the alignment film, the liquid crystal molecules orient randomly without applying voltage (Figure 3(b)) and orient vertically with applying voltage (Figure 3(c)). Because the difference of the horizontal orientation and the vertical orientation greatly contrast and the difference of the random orientation and the vertical orientation is medium, the alignment film makes a larger change in the resonant frequency and resonant resistance than the case without the alignment film.

Figure 2(c) shows the response for E-8 by applying a 10 V pulse with the rubbing layer. By comparing Figures 2(b) and 2(c), it can be seen that the higher voltage makes the resonant frequency and resonant resistance changes larger. In this case, also the higher voltage makes the molecular orientation quicker and clearer because the force for the orientation is larger.

EFFECT OF ANISOTROPY OF DIELECTRICITY

Figure 2(d) shows the response for ES-E001 by applying a 10 V pulse. In Figure 2(d), the resonant frequency and resonant resistance decreased by applying the voltage. This change is the opposite of the change for the E-8 liquid crystal. This is easily understood as ES-E001 has negative anisotropy of dielectricity and orients horizontally by applying voltage and stays random without applying voltage.

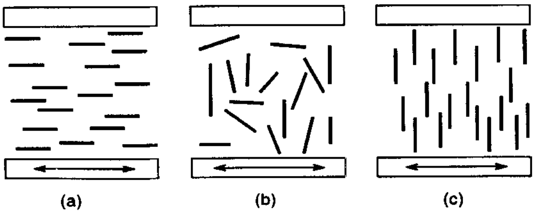

FIGURE 3 Schematic diagram of liquid crystal orientation for (a) the vertical orientation, (b) the random orientation and (c) the horizontal orientation.

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MECHANISM OF RESONANT FREQUENCY AND RESONANT RESISTANCE CHANGE

Figure 4 shows diagrammed resonant frequency and resonant resistance change (F-R diagram) for Figure 2(c). In Figure 4, Point A shows the base point before inserting the liquid crystal, B shows the value for Figure 2(c), the dashed line shows the F-R relation for the elastic film coating because the elastic film never gives energy loss, and the solid line shows the F-R relation for the contacting liquid because of the common relations of $R \propto (\rho_L \eta)^{1/2}$ and $\Delta F \propto (\rho_L \eta)^{1/2}$, as shown in Eqs. (3) and (4). The position of plots for the liquid cyrstal in F-R diagram indicates the liquid crystal is nearer to the liquid state rather than the elastic state.

Normally, increasing of the viscosity of the contacting liquid makes the resonant resistance increase and the resonant frequency decrease. To the contrary, as seen in Figure 2(c), both of the resonant resistance and the resonant frequency increase by applying voltage. This implies that the change of properties of the liquid crystal can not be explained by a change of the viscosity alone. As the resonant resistance reflects the energy loss on the quartz crystal surface and the resonant frequency reflects the effective mass loading on the quartz crystal surface, the result of Figure 2(c) indicates that the energy loss was increased and the effective mass was decreased by applying voltage. These phenomena can be discussed with the structure of molecular orientation of the liquid crystal. Figure 5 shows the schematics of oriented liquid crystal molecules being vibrated by shear force. In the case of horizontally arranged liquid crystal molecules (Figure 5(a)), the molecules get the shear force horizontally against the molecular axis, and the shear vibration is converted to the friction of the molecular sides. In the case of vertically arranged molecules (Figure 5(b)), the shear force works on the molecules not

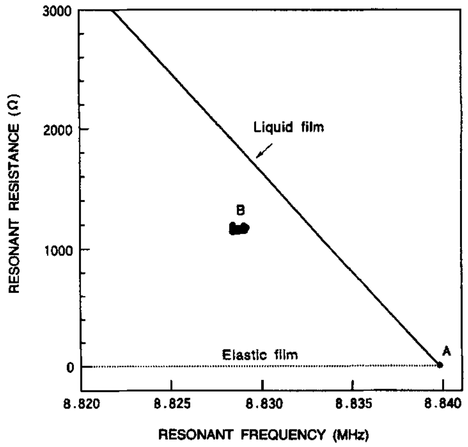

FIGURE 4 Diagrammed resonant frequency change and resonant resistance (F-R diagram). Point A shows the base point for the value before inserting the liquid crystal. Point B shows the value for Figure 2(c). The dashed line shows the value for the coated elastic film and the solid line shows the value for in-contact-with-liquid.

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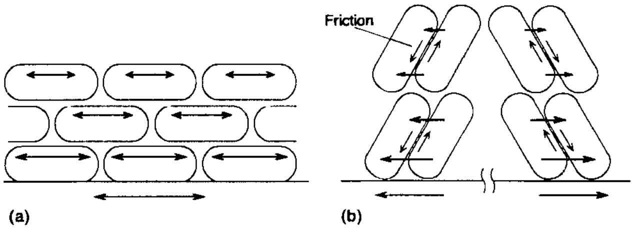

FIGURE 5 Shear vibrating models for the horizontally oriented (a) and vertically oriented (b) liquid crystal molecules.

only to vibrate horizontally but also to rotate the molecules. The rotating force makes the friction with side by side molecules which does not affect the shear force transfer. This indicates that the vertical orientation gives a larger energy loss than the horizontal orientation. This can explain the resonant resistance increase in Figure 2(c) by applying voltage. The rotating movement of vertical orientation gives less transferring movement to the next layer of liquid crystal molecules. This indicates that the effective mass for the vertical orientation is less than that for the horizontal orientation. Namely, the horizontal orientation has more elastic property than the vertical orientation against the shear force. This can explain the resonant frequency increase in Figure 2(c) by applying the voltage. These values of the resonant frequency change and resonant resistance change reflect the anisotropic viscosity and elasticity of liquid crystals.

The magnified F-R diagram gives additional information as shwon in Figures 6(a)–(d) which shows the F-R diagrams for the result of Figures 2(a)–(d), respectively. Figure 6(a) shows the F-R diagram for E-8 without the alignment film. The F-R relation changed almost linearly between Points A to F. To the contrary, the change for E-8 with the alignment film showed no linear change. For example, in Figure 6(c), the F-R relation changes from point A to H according to the applied voltage pulses. For the first pulse, the values moved thus: Point A→B→C→D→E→F, and for the steady pulse, the values moved thus: Point F→G→D→E→F. These changes can be summarized as the resonant resistance increases at first and next the resonant frequency increases during the applied voltage pulse, also the resonant resistance decreases at first and next the resonant frequency decreases during the releasing of the voltage pulse. This hysteresis indicates that the dynamic orientation processes of the liquid crystal take place in different ways for the on- and off-processes with the alignment film because of the electrical field affect on the whole of the liquid crystal molecules in the cell in the on-process, and that the liquid crystal molecules start to orient from the interfacial layer of the alignment films in the off-process. Figure 7 shows these images. Namely, Figure 7(a) for Point F has low viscosity and high mass effect, Figure 7(b) for Point C has high viscosity and high mass effect, Figure 7(c) for Point D has high viscosity and low mass effect, and Figure 7(d) for Point E has low viscosity and low mass effect.

Further experiments using this technique will make the dynamic properties of the orientation of liquid crystals more clear.

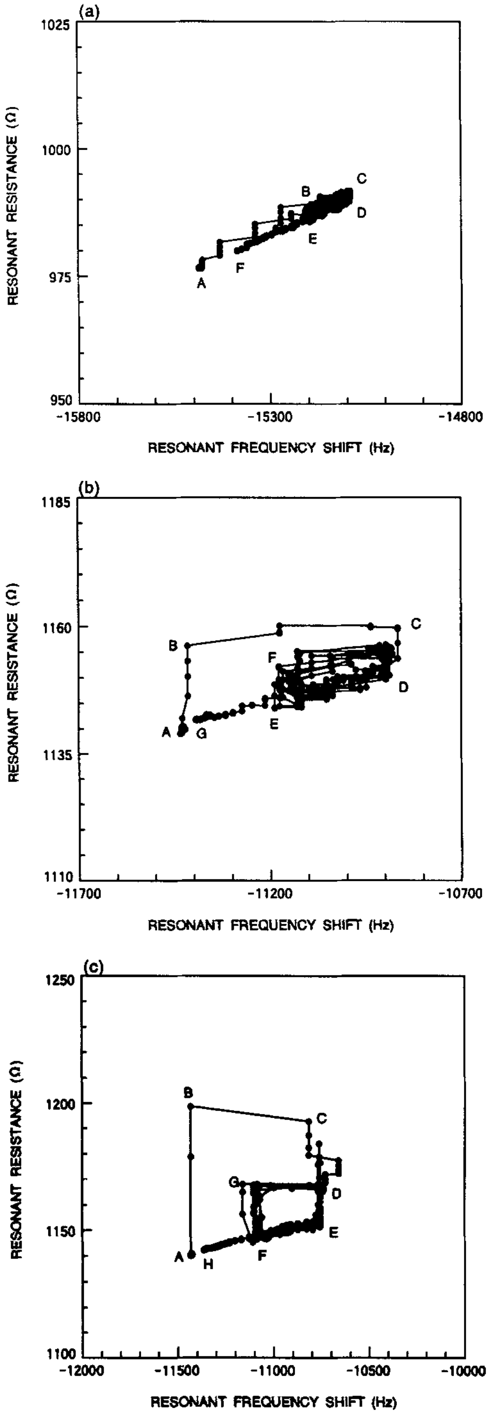

FIGURE 6 Magnified F-R diagram from Figures 2(a)–(d), respectively.

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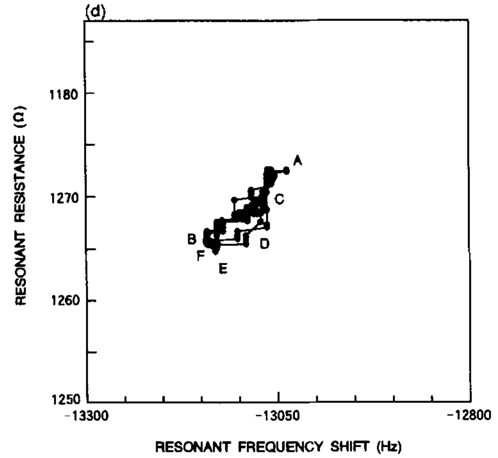

FIGURE 6 (*Continued.*)

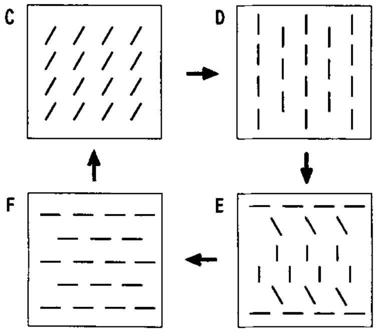

FIGURE 7 Images of liquid crystal orientation for Points F, C, D and E in Figure 6(b).

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