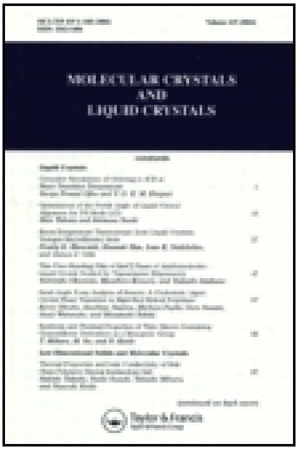

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Stabilization of Epoxy-Based Polymer-Dispersed Liquid Crystal Films by Addition of Excess Hardener

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Stabilization of Epoxy-Based Polymer-Dispersed Liquid Crystal Films by Addition of Excess Hardener

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Polymer-dispersed liquid crystal (PDLC) films whose matrices consist of two-component epoxy resins have been studied. Their driving voltage and response time depend on the epoxy oligomer/hardener ratio in the epoxy resin. When an excess of the hardener (polythiol) is mixed in the epoxy resin, PDLC films which have the following superior properties have been successfully fabricated. 1) The driving voltages are lower than that of the PDLC film which contain an equal amount of the epoxy oligomer and the hardener. 2) The driving voltage and response time do not change with time. On the other hand, when an equal amount of the oligomer and the hardener are mixed in the epoxy resin, the driving voltage and response time of the PDLC film vary with the time. The driving voltage change of the PDLC films is related to the change of their admittance by the use of a two-phase model, in which spherical droplets are dispersed in the matrix.

Keywords: polymer-dispersed liquid crystal, epoxy resin, admittance, driving voltage, response time

1. INTRODUCTION

Polymer-dispersed liquid crystal (PDLC) films can be switched between a light-scattering state and a transparent state by the use of applied voltage. PDLC films offer the advantages of high contrast and excellent brightness, since they require no polarizer.[1-3]

Several PDLC fabrication methods have previously been reported. In one, capsulated liquid crystal forms an emulsion with a solution of water and water soluble polymers, and a PDLC remains after the water has been evaporated.[4] In another, polymerization, thermal quenching or solvent evaporation are applied to homogeneous liquid crystal mixtures to achieve the phase separation from which a PDLC is produced.[5]

In another method applying phase separation, an epoxy resin is used as a PDLC matrix.[6] Here, heating induces polymerization in the epoxy resin, which results in phase separation. Because this method requires no evaporation, it avoids some of the disadvantages such as volume shrinkage, the remaining solvent resulting from incomplete evaporation. It also has advantages over UV curing methods because it avoids both the changes in liquid crystal properties produced by UV irradiation, as well as the contamination of radical initiator reagents.

While previously reported epoxy based PDLC films are promising, they also have a serious disadvantage in that their driving voltage and response times change spontaneously with time.[7,8] That is a serious problem when the PDLC films are to be used as light valves for display devices. G. Chidichimo *et al.*[8] have attributed such a change in driving voltage of an epoxy PDLC to the continuing reaction of unreacted epoxy oligomer over time. In an attempt to avoid any lingering unreacted epoxy oligomer in our own PDLC film, we added an excess of hardener to the resin, on the theory that polymerization would then proceed more rapidly and thus be completed by the end of the curing process. This approach has, in fact, proved successful.

In this paper we describe the fabrication method and discuss the properties of the PDLC film produced. We also discuss the change of the driving voltage by the use of a two-phase model, with which it is possible to confirm that the change in the driving voltages can be explained in terms of changes in admittance.

2. EXPERIMENTAL

A commercially available epoxy adhesive "Hi Super 5" made by Cemedine was used as a polymer matrix of PDLC films. The epoxy adhesive is a two-component epoxy resin, which consists of an epoxy oligomer and a hardener. The epoxy oligomer is diglycidyl ether of bisphenol A oligomer, whose epoxy equivalent is about 180. The hardener is a polythiol. Relative dielectric constants of the epoxy oligomer and the hardener are 5.19 and 17.6, respectively.

A liquid crystal used in our experiment is a mixture of cyanobiphenyl and triphenyl liquid crystals, E7 (Merck), whose ordinary and extraordinary refractive indexes are 1.746 and 1.522 (at 589 nm, 298 K), respectively. The mixing weight ratios of liquid crystal/epoxy resin (epoxy oligomer + hardener) was fixed at 1/2. The mixing weight ratios of epoxy oligomer/hardener are varied from 2/8 to 6/4. The hardener is an equivalent mixture to the epoxy oligomer, then the weight ratios are almost the same to the theoretical reaction ratio.

A mixed solution which consists of the epoxy oligomer, the hardener and the liquid crystal was sandwiched between a pair of glass substrates with transparent ITO-electrodes. 10 μm polymer films were used as spacers. The curing temperature for making the PDLC films were room temperature, 60°C, 80°C and 100°C, and the curing time was 30 minutes.

Transmittance and response time of the PDLC films were measured with a He-Ne laser (NEC GLG5321) and a photodiode, whose diameter was 10 mm. The photodiode was connected to a storage oscilloscope (LeCroy 9400A). The distance between the sample and the photodiode was 30 cm. A rise time was defined as the time needed for the change of a transmittance from 0% at time zero to 90% of its maximum value. A decay time was defined as the time needed for the change of transmittance from 100% at the time zero to 10% of its maximum value. The signal applied in our measurements was a 100 Hz square-wave ac voltage. All electro-optic properties were measured at room temperature.

Admittances of PDLC films were measured with an impedance analyzer (Hewlett Packard 4192A). The PDLC films which were used in the admittance measurement were the same as that used in transmittance measurements. The area for the admittance measurement was 1 cm^2. Applied voltage used in the measurement was a 100 Hz sin wave ac voltage.

3. RESULTS

Applied voltage dependence of the epoxy PDLC transmittance is shown in Figure 1. Driving voltages strongly depend on epoxy oligomer/hardener ratios. As the ratio decreases, the driving voltage decreases.

In ordinary usage of the epoxy adhesive, which was used as a PDLC matrix in our experiments, an equal amount of an epoxy oligomer and a hardener are mixed with each other. In this case, an amount of the hardener is almost the same to the theoretical amount for the polymerization reaction. However, the best result, which is low transmittance at 0 V and low driving voltage, was obtained, when more of the hardener was mixed in the epoxy resin, i.e. 4/6 or 3/7.

But when the ratio is very small, e.g., 2/8, the transmittance under no applied voltage is rather high. On the other hand, when the epoxy oligomer is rich, e.g., 6/4, incident light is not scattered enough by the PDLC, and the change of the transmittance is small.

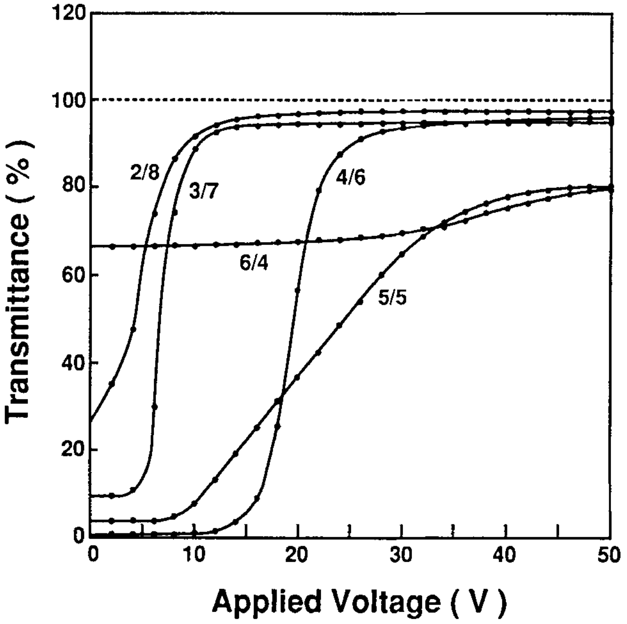
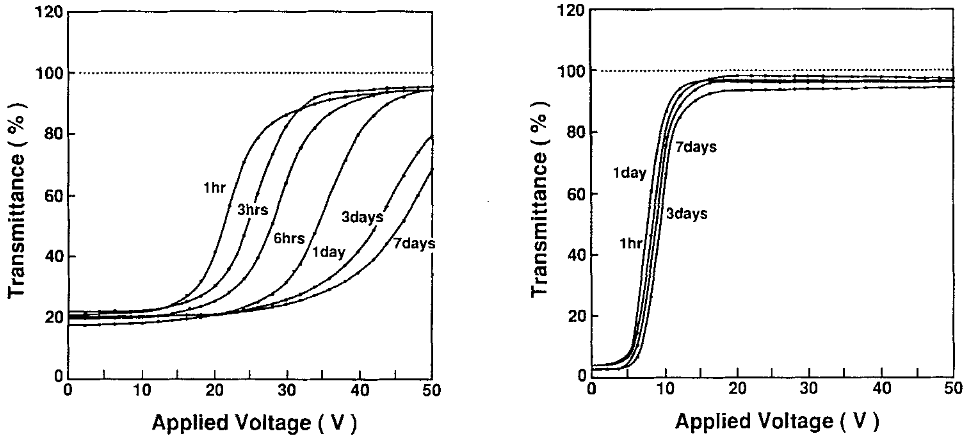


FIGURE 1 Dependence on applied voltage of transmittance, as a function of epoxy oligomer/hardener ratios. The epoxy oligomer/hardener ratio was changed from 2/8 to 6/4.



(a) (b)

FIGURE 2 Change of PDLC driving voltage with standing time. (a) epoxy oligomer/hardener = 5/5, (b) epoxy oligomer/hardener = 4/6.

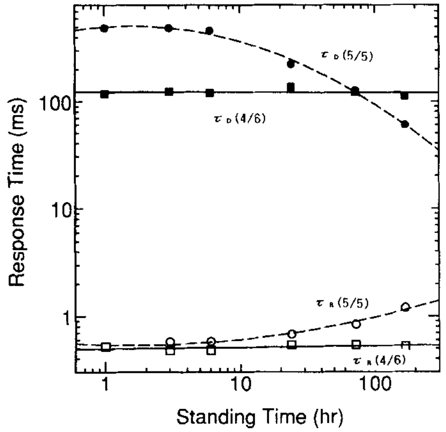


FIGURE 3 Dependence on standing time of response time, at room temperature. τ_R, rise time; τ_D, decay time. Numbers in the parentheses indicate epoxy oligomer/hardener ratios.

As has been reported before, driving voltages of PDLC films whose matrices are epoxy resin increase with the lapse of time.[7] This is a serious problem for usage of these PDLC films as display devices. G. Chidichimo *et al.*[8] have attributed such a change in driving voltage of an epoxy PDLC to the continuing reaction of unreacted epoxy oligomer over time and they observed an increase of electrical resistivity of the PDLC film with time. Figure 2 shows the change of driving voltage with the lapse of time at room temperature. The change of driving voltage for the epoxy oligomer/hardener (*o*/*h*) = 5/5 PDLC is drastic (Figure 2(a)). On the other hand, the driving voltage for the *o*/*h* = 1/2 PDLC is almost independent of time.

Figure 3 shows the change of response times with standing time at room temperature. Response times for the *o*/*h* = 5/5 and 4/6 PDLC are in the same order.

But for the *o*/*h* = 5/5 PDLC, the driving voltage changes remarkably with the lapse of time. The rise time increase and the decay time decrease with the lapse of time. On the other hand, for the *o*/*h* = 4/6 PDLC, the driving voltage does not change with standing time.

As reported before by Yamaguchi *et al.*,[7] decay times depend on voltage applied time. The longer the applied time, the larger is the decay time. In our experiments, the decay time depends similarly on the voltage applied time. But for the *o*/*h* = 4/6 PDLC, the magnitude of dependence of the decay time is much smaller than that for the *o*/*h* = 5/5 PDLC as shown in Figure 4.

4. DISCUSSION

Driving voltages of PDLC films depend on the liquid crystal droplet diameter. Therefore, we must compare the driving voltages of PDLC films whose droplet diameters are almost the same. In a method that makes a PDLC film from a liquid crystal and a prepolymer solution by phase separation, liquid crystal droplet diameters of the PDLC depend on phase separation speed.[9] For a PDLC film whose matrix consists of heat curing resin the droplet diameter decreases as the curing temperature increases.

Figure 5 shows applied voltage dependence of transmittance as a function of the curing temperature. As the curing temperature increases, the driving voltage decreases. As shown in Figure 6, the mean diameters of the liquid crystal droplets become smaller as the curing temperature increases. The mean diameters were measured from SEM photographs. When the mixed solution was cured at room temperature, the liquid crystal phase became a continuous phase. Then droplet diameters of PDLC which were cured at room temperature are plotted as more than 5 μm. These results show that the liquid crystal droplet diameter becomes smaller as the curing temperature becomes higher. Comparing in the same curing

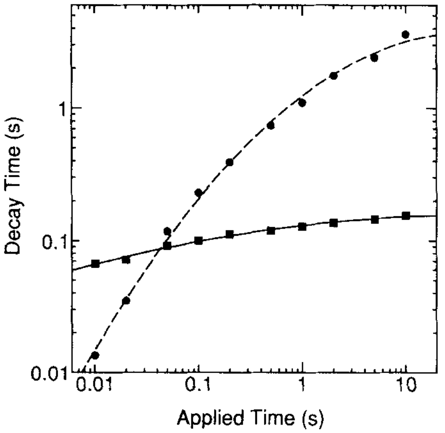


FIGURE 4 Dependence of decay time on time of voltage application. Applied voltage was 50 V, 1 kHz. ●, epoxy resin/hardener = 5/5; ■, epoxy resin/hardener = 4/6.

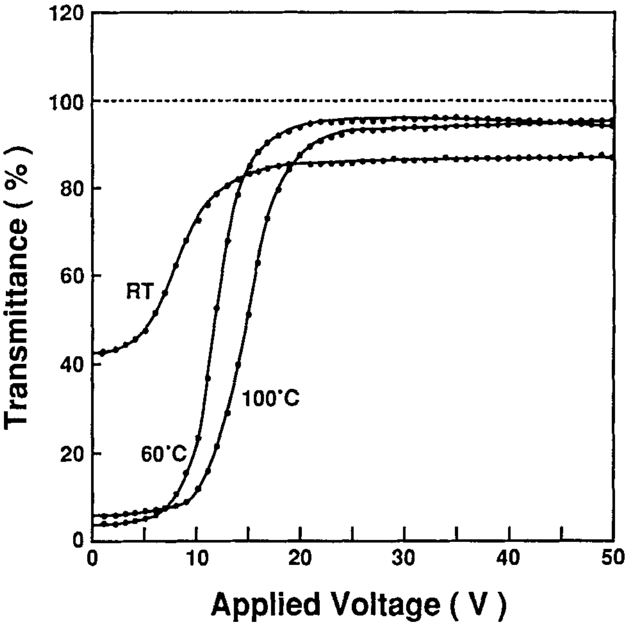


FIGURE 5 Dependence on applied voltage of transmittance, as a function of curing temperature. Epoxy oligomer/hardener ratio is 4/6.

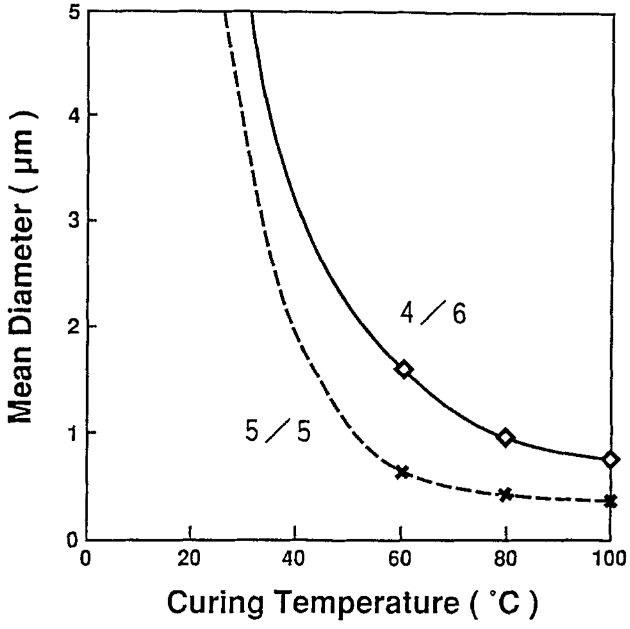


FIGURE 6 Dependence of liquid crystal droplet diameters on curing temperature. ×, epoxy resin/hardener = 5/5; ◇, epoxy resin/hardener = 4/6.

temperature, the mean diameters for the *o*/*h* = 4/6 PDLC films are larger than those of the 5/5 PDLC films. The liquid crystal and the hardener are insoluble to each other. Therefore, as the hardener becomes larger, the phase separation becomes easier.

Figure 7 shows the relationship between the mean diameter of the liquid crystal droplet and the driving voltage of the PDLC films for 10% and 90% transmittance (V_{10}, V_{90}). When the voltages are compared with the same diameter, about 0.7 μm, the driving voltage of the *o*/*h* = 4/6 PDLC film is smaller than that of the 5/5 PDLC. This result shows that the lower driving voltage of the 4/6 PDLC is caused not only by the droplet diameter but by other factors.

In order to discuss the change of the driving voltage, admittances (= 1/impedance) of the epoxy resin and the PDLC films were measured. Figure 8 shows epoxy resin composition dependence of the admittances. The smaller the epoxy oligomer content, the larger the admittances of the epoxy resin and the PDLC films. This result may be attributed to the presence of active hydrogen coming from the hardener, polythiol.

To investigate the composition dependence of the PDLC driving voltage and the change of the PDLC driving voltage with the standing time, we discuss the driving voltage on the basis of a two-phase model, in which sphere phases (liquid crystal phase) disperse in a continuous phase (epoxy resin matrix). The electric field in the sphere phase E_{lc} can be expressed using the voltage applied to the PDLC film (V_P) and the PDLC film thickness (d) as,[10]

$$E_{lc} = \frac{3Y_m}{Y_{lc} + 2Y_m - \delta(Y_{lc} - Y_m)} \times \frac{V_P}{d} \qquad (1)$$

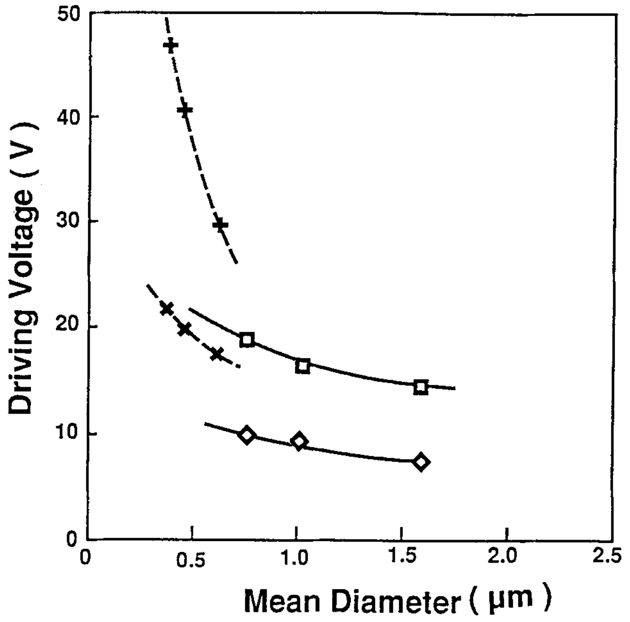


FIGURE 7 Dependence on droplet diameter of PDLC driving voltage. +, V_{90}, 5/5; ×, V_{10}, 5/5; □, V_{90}, 4/6; ◇ V_{10}, 4/6.

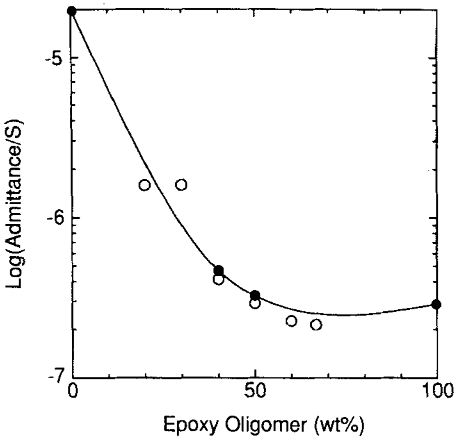


FIGURE 8 Dependence of admittance on epoxy resin composition. ●, Resin only; ○, PDLC.

TABLE I

Calculated and experimental PDLC driving voltage ratio (epoxy oligomer/hardener = 5/5, 4/6)

	Calculated	Experimental		
		V_{10}	V_{50}	V_{90}
$\frac{V_P(5/5)}{V_P(4/6)}$	1.43	1.64	1.48	1.40

where *Ys* are admittances, δ is a volume fraction of the sphere phase (a liquid crystal), and subscripts *P*, *lc*, *m* indicate values for PDLC, liquid crystal, matrix, respectively. The admittances can be related to each other by the following equation,[11]

$$\frac{Y_P}{Y_m} = 1 + \frac{3\delta(Y_{lc} - Y_m)}{Y_{lc} + 2Y_m - \delta(Y_{lc} - Y_m)} \tag{2}$$

From Equation (2) and Equation (1), we obtain

$$E_{lc} = \frac{(Y_P - Y_m)}{\delta(Y_{lc} - Y_m)} \times \frac{V_P}{d} \tag{3}$$

Another equation which relates the admittances to each other was introduced by Böttcher,[11]

$$\frac{Y_P - Y_m}{3Y_P} = \frac{\delta(Y_{lc} - Y_m)}{2Y_P + Y_{lc}} \tag{4}$$

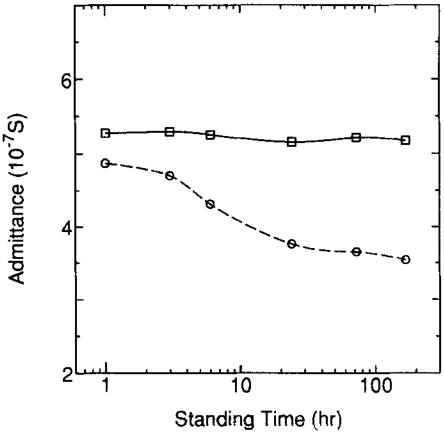


FIGURE 9 Dependence on standing time of admittance at room temperature. ○, epoxy resin/hardener = 5.5; □, epoxy resin/hardener = 4/6.

From Equation (3) and Equation (4), we can obtain

$$E_{lc} = \frac{3Y_P}{2Y_P + Y_{lc}} \times \frac{V_P}{d} \tag{5}$$

Under the assumption that the driving voltage and the admittance of the liquid crystal is not affected by the epoxy oligomer/hardener ratio, the driving voltage for different composition PDLC films can be expressed as

$$\frac{V_{P2}}{V_{P1}} = \frac{Y_{P1} \times (2Y_{P2} + Y_{lc})}{Y_{P2} \times (2Y_{P1} + Y_{lc})} \tag{6}$$

where subscript 1 and 2 show values for different composition PDLC films. Y_{P1}, Y_{P2} and Y_{lc} can be obtained from experiments.

Table I shows a comparison of the calculated driving voltage ratio with experimental values. The calculated value was obtained from data in Figure 8 using Equation (6). Taking into account the reliability of the experiments, the calculated value is in agreement with the experimental values.

Figure 9 shows the admittance change with the lapse of time at room temperature. The admittance of the *o*/*h* = 5/5 PDLC decreases with time but those of the 4/6 PDLC are almost constant. The PDLC driving voltage changes can be calculated from data in Figure 9 using Equation (6), in which subscripts 1 and 2 indicate values at standard time (=1 hr) and at any other time, respectively. Figure 10 shows the time dependence of the PDLC driving voltages expressed in relative values to 1 hr. The calculated value roughly agrees with the experimental values. However, after 10 hr, the calculated driving voltages are smaller than the experimental ones. These results show that most parts of the change of the PDLC driving voltage are attributed to the change of the admittance, but all of the change can

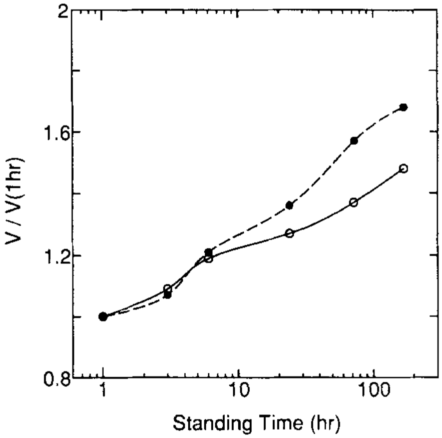


FIGURE 10 Change with respect to standing time in the ratio in PDLC driving voltage to the driving voltage at 1 hr. ○, calculated; ●, experimental.

not be explained by the change of the admittance. It may be presumed that the unreacted hardener, which was added in excess, affects the movement of the liquid crystal molecules.

5. CONCLUSION

We have investigated PDLC films whose matrices consist of two-component epoxy resin. When an excess of the hardener (polythiol) was mixed in the epoxy resin, which constitute a PDLC matrix, PDLC films which have the following superior properties have been obtained. 1) Driving voltages are low. 2) Driving voltages and the response time do not depend on time. 3) Dependence of the decay time of voltage application is small. 4) The admittance of the PDLC films do not depend on the lapse of time.

By the use of a two-phase model, in which liquid crystal droplets are dispersed in a polymer matrix, most parts of the change of the PDLC driving voltage are attributed to the change of the admittance.

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