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Memory Effect of Liquid Crystals Dispersed in Ferroelectric Copolymer of Vinylidene Fluoride and Trifluoroethylene

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We constructed PDLC film of ferroelectric polymer P(VDF/TrFE) and nematic liquid crystal 5CB. Results of measurement of electro-optical response show that electric poling of P(VDF/TrFE) imposed effective bias to liquid crystal. This bias was memorized at least for 10 hours.
Key words: P(VDF/TrFE), 5CB, ferroelectric, memory

1. INTRODUCTION

Polymer dispersed liquid crystal (PDLC) film of droplet type consists of matrix polymer which contains liquid crystal droplets. External electric field changes alignments of directors of droplets causing change in light transmission. PDLC is a candidate of light valve that does not need a polarizer[1,2].

In this study, we prepared PDLC film that was composed of nematic liquid crystals dispersed in random copolymer of vinylidene fluoride and trifluoroethylene [P(VDF/TrFE)]. P(VDF/TrFE) is a ferroelectric polymer having spontaneous polarization that can be reversed by electric field[3]. We discuss a memory effect that is imposed by a spontaneous polarization to dispersed liquid crystals.

2. EXPERIMENTAL

2.1 Sample preparation

We dissolved P(VDF/TrFE) and nematic liquid crystal 4'-n-pentil-4-cyanobiphenyl (5CB) into solvent N,N-dimethylformamide (DMF). Nematic droplets in P(VDF/TrFE) matrix were constructed by phase separation due to removal of DMF in vacuum at room temperature.

Ferroelectricity of P(VDF/TrFE) originates from β crystal composed of molecules of all-trans conformation[3]. Electric property[4,5] and phase transition temperature [5,6] depend on copolymerization fraction. Present copolymer contained 78 mol % VDF.

2.2 Differential scanning calorimetry (DSC)

We used DSC6200(Seiko Instruments) to obtain overview of phase transitions. Heating ratio was 5°C/min. Fractions of 5CB for DSC measurement were 0, 10, 30, 50, 80 and 100 wt%.

2.2 Measurement of electric displacement

Effect of annealing at 130°C for the ferroelectricity was examined using Sawyer-Tower circuit that detects relation between electric displacement (D) and electric field (E). Triangular electric field of amplitude 100MV/m and frequency 0.05Hz was used.

2.3 Electro-optical measurement

Electro-optical measurement was performed for PDLC of 10wt% 5CB. Sample cell was made of pare of ITO glass plates in which PDLC film was put with the help of UV-curable adhesive. Fig. 1 shows experimental system used to measure electro-optical property. Sawyer-Tower circuit monitored electric displacement of sample cell. Change in intensity of scattered laser beam was detected by photodiode. Electro-optical measurement was performed at room temperature.

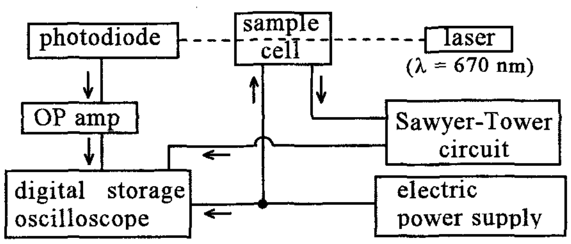

Fig. 1 Experimental system for electro-optical measurement.

3. RESULTS AND DISCUSSION

Fig. 2 shows DSC data of the second heating for PDLC films of various weight fractions of 5CB. Three endothermic peaks are shown in Fig. 2. The peak about 30°C corresponds to nematic-isotropic phase transition of 5CB. The peak about 125°C corresponds to ferroelectric-paraelectric transition of P(VDF/TrFE), and peak about 140°C to melting transition of P(VDF/TrFE).

Fig. 3 summarizes transition temperature calculated from DSC data. Fig. 3 indicates decrease of melting temperature due to the addition of liquid crystal. It is known that annealing at temperature of paraelectric phase reinforces ferroelectricity of P(VDF/TrFE)[3,5,7]. We selected annealing temperature as 130°C for the present case.

Fig. 4 shows dependence of D-E hysteresis loop on annealing period at 130°C. It shows that spontaneous polarization increased due to the annealing. To study memory effect that was imposed to electro-optical property of liquid crystal by polarization of P(VDF/TrFE), we used sample annealed for 2 hours.

Using experimental system of Fig. 1, we monitored scattered light intensity simultaneously with D-E relation. Fig. 5 shows D and photodiode output voltage depending on E. This was obtained using triangular electric field of 0.05 Hz.

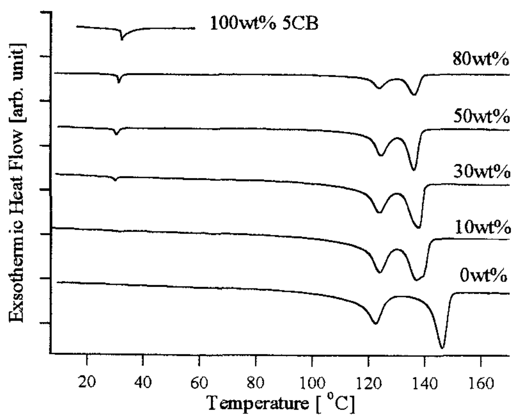

Fig.2 DSC data of the second heating for PDLC of various weight fraction of 5CB.

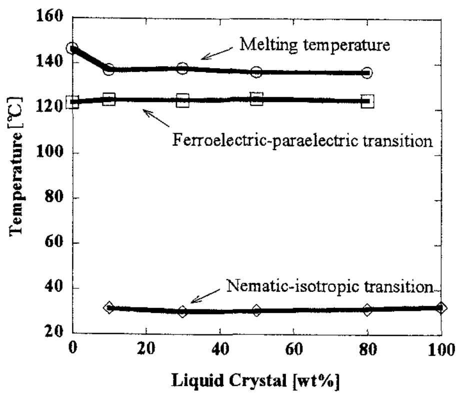

Fig. 3 Transition temperature of PDLC of P(VDF/TrFE) and 5CB.

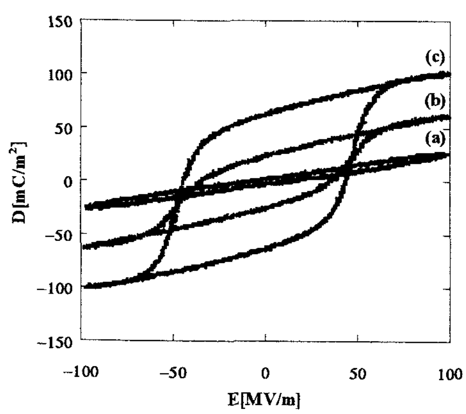

Fig. 4 D-E relations after annealing for (a) 5 minutes, (b) 30 minuets, and (c) 5 hours.

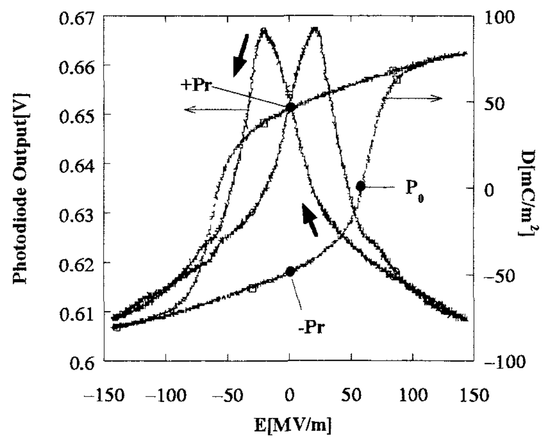

Fig. 5 Photodiode output and D that show hysteresis for E. The sample were PDLC of 10wt% 5CB annealed for 2 hours at 130°C.

In Fig. 5, three points +Pr, -Pr and P_0 are indicated at D-E loop. When we turn off electric field at +Pr, -Pr, and P_0 of Fig. 5, we can prepare three different states of polarization. The state +Pr and –Pr take spontaneous polarization signs of which are opposite to each other. For the state P_0, macroscopic polarization cancels.

For the three polarization states, we detected response of scattered light intensity using sinusoidal electric field which is too small to reverse the polarization. We show results in Figs. 6, 7, and 8. The amplitude of the sinusoidal wave was 10MV/m, and the frequency was 100Hz.

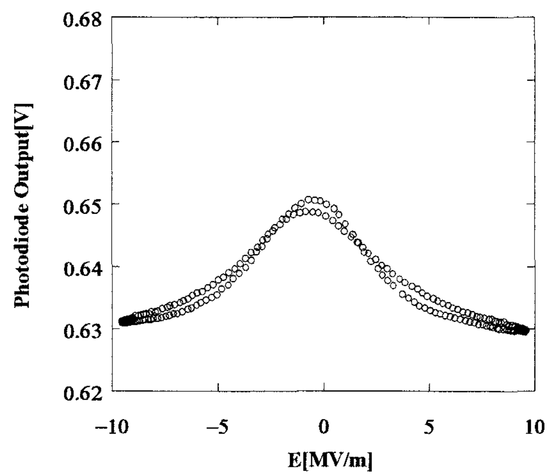

Fig. 6 Electro-optical response using sinusoidal electric field for polarization state P_0.

Fig. 6 shows peaks about zero electric field. Depending on frequency, these peaks split due to dielectric delay.

The peaks shift to negative direction in the case of Fig. 7, while on the other hand they shift to positive direction in the case of Fig. 8. The shift to negative (positive) direction indicates existence of positive (negative) bias electric field. Hence the present results indicate that positive polarization effectively imposed positive bias electric field on liquid crystal. Reverse of the polarization reverses the direction of the bias field.

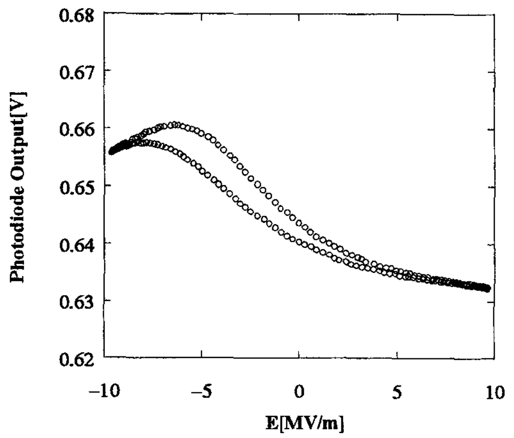

Fig. 7 Electro-optical response using sinusoidal electric field for polarization state +Pr.

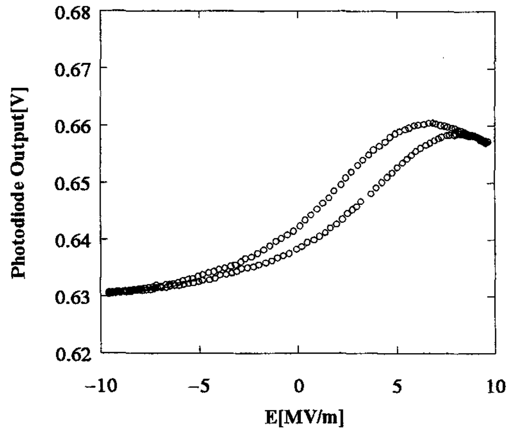

Fig. 8 Electro-optical response using sinusoidal electric field for polarization state -Pr.

Peak shift in the cases of Figs. 7 and 8 is about 6MV/m. This quantity depended on the amplitude of sinusoidal electric field and elapsed time after electric poling.

As Fig. 9 indicates the peak shift decayed but it lasted at least for 10 hours.

4. CONCLUSION

We constructed PDLC film of ferroelectric polymer P(VDF/TrFE) and nematic liquid crystal 5CB. Results of measurement of electro-optical response show that electric poling of polarization of P(VDF/TrFE) imposed effective bias to liquid crystal. We concluded existence of the bias from the peak shift of Figs. 7 and 8 comparing the peak position of Fig. 6. The fact that the polarization of P(VDF/TrFE) was poled was memorized as the peak shift at least for 10 hours.

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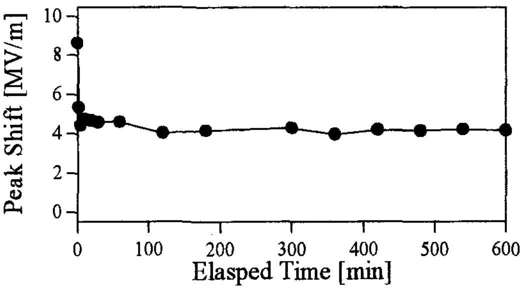

Fig. 9 Peak shift depended on elapsed time after poling procedure

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