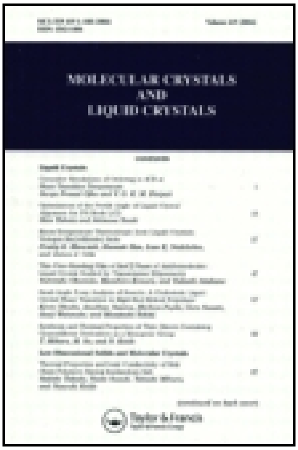

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Photovoltaic Effects in Liquid Crystal Cells Containing Organic Dyes

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Photovoltaic Effects in Liquid Crystal Cells Containing Organic Dyes†

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Dye sensitization on photovoltaic phenomena under visible light stimulation are described in smectic, nematic, and isotropic phases of *p*-cyano-*p'*-*n*-octylbiphenyl cells with a symmetrical electrode arrangement. Methyl red is used as a sensitizer. The dependence of short-circuit photocurrents on excitation light intensity, light pulse width, temperature, and the cell thickness are measured. The photocurrent consists of three components, that is, the small negative peak with a fast response, the second positive peak following after the first peak, and the third negative peak with a slow response. The second and the third components of the photocurrents cannot be observed in the solid crystalline state. Both of them decrease with an increase in the cell thickness, and their response time becomes shorter as the temperature rises. These two components are induced by the diffusion processes of the carriers produced by the light stimulation.

INTRODUCTION

The photovoltaic effects in nematic liquid crystals were first published by Kamei *et al.*[1] They were using nematic cells with an asymmetric electrode arrangement; that is, one electrode was partially coated with tin oxide and the other was completely coated. The polarity of the photovoltage on the illuminated electrode was negative and the maximum photovoltaic effect was obtained at the boundary of the electrode when the cell was illuminated with a spotlight. A similar photovoltaic effect was also reported by Kurita *et al.*[2] in nematic cells with a symmetrical electrode arrangement. They assumed that this photovoltaic effect was induced by the difference of mobility between the positive ions and the negative ions produced by the

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uv stimulation. Since the excitation spectra of the photovoltaic effect correspond with the absorption of the liquid crystals, this effect is induced by the excitation of the liquid crystal molecules.[3] These photovoltaic effects are inefficient under visible light stimulation, since the absorption by the liquid crystal itself is very weak in the visible wavelength region.

Recently, we observed a remarkable dye sensitization effect under visible light stimulation on the photovoltaic phenomenon in MBBA and other liquid crystal cells.[4] In this report, we will describe in detail the sensitized photovoltaic effects, that is, the measurements of the dependence of short circuited photocurrents on excitation light intensity, light pulse width, sample temperature, and the thickness of the cell in the liquid crystal cells containing organic dyes.

EXPERIMENTAL

Liquid crystal cells with transparent symmetrical electrodes were prepared using COB (*p*-cyano-*p*'-*n*-octylbiphenyl) and spacers of a suitable thickness. Indium-tin oxide coated glass plates, 1 mm in thickness, were used and no further electrode surface treatment to orient the liquid crystal molecules were made. Methyl red was used as a sensitizer. The excitation light source used was a combination of a tungsten lamp (Color Cabin Model II Projector, 150 W) and a camera shutter, or a Xe strobo-flashlamp. The effective area for the light stimulation was about 1.1 cm^2. Induced photocurrents were amplified by a current-to-voltage converter made with MOS-IC (CA3140) and recorded by a digital wave memory (minimum sampling time was 1 μs). The polarity of the photovoltage was defined for the illuminated electrode. A uv-cut glass filter (VY 45) was used to remove the uv component of the light source. Except where specially noted, the thickness of the spacer was 25 μm, the temperature of the cell was 26°C, and the dye concentration was 1.51 wt.%.

RESULTS AND DISCUSSION

Figure 1 shows a typical waveform of photocurrents under visible light stimulation. The photocurrent usually consists of three components. The first component is a small negative peak with a quick response observed at the moment of light stimulation. Since this first peak is so small under the projector stimulation, the measurements of the exact value of this peak are made only for the flashlamp stimulation. The second peak with a positive polarity is observed following immediately after the first peak. The third

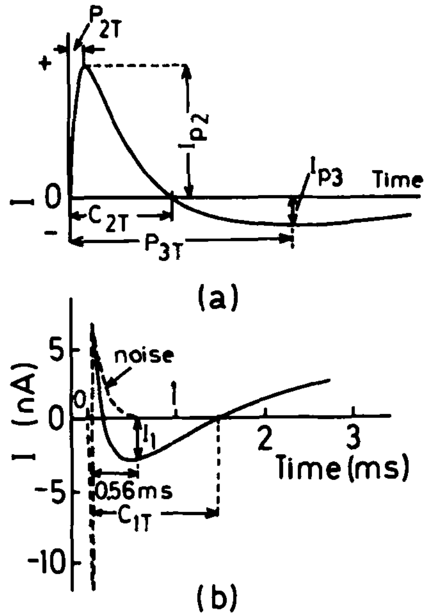

FIGURE 1 Waveforms of photocurrents. (a) projector stimulation, (b) flashlamp stimulation.

peak is negative and has a slow response characteristic. This third negative component seems to correspond to the photocurrent previously observed in the pure liquid crystals, stimulated by the uv light source.[1,2] These three components are also observed in the open circuit photovoltaic properties. The effective excitation spectra of them correspond with the absorption of methyl red.

The value of each peak photocurrent and the time intervals are defined as follows. I_1 is defined as the peak value of the first component that is measured at 0.56 ms after the onset of the stimulation light, because the intense noise components of the flashlamp discharge are superimposed on the signal of the first peak. I_{p2} is the maximum value of the second component and I_{p3} is that of the third component. P_{2T} is defined as the interval of time between the onset of light stimulation and the second peak's maximum point. P_{3T} is defined as that of the third peak's maximum point. C_{1T} is defined as the interval of time between the onset of light stimulation and the first crosspoint of the photocurrent from negative to positive. C_{2T} is that for the second crosspoint from positive to negative.

The transient properties of the photocurrents stimulated by the projector light are shown in Figures 2a and b. The first peak is so small that the exact value cannot be obtained in this case. The second peak's maximum value

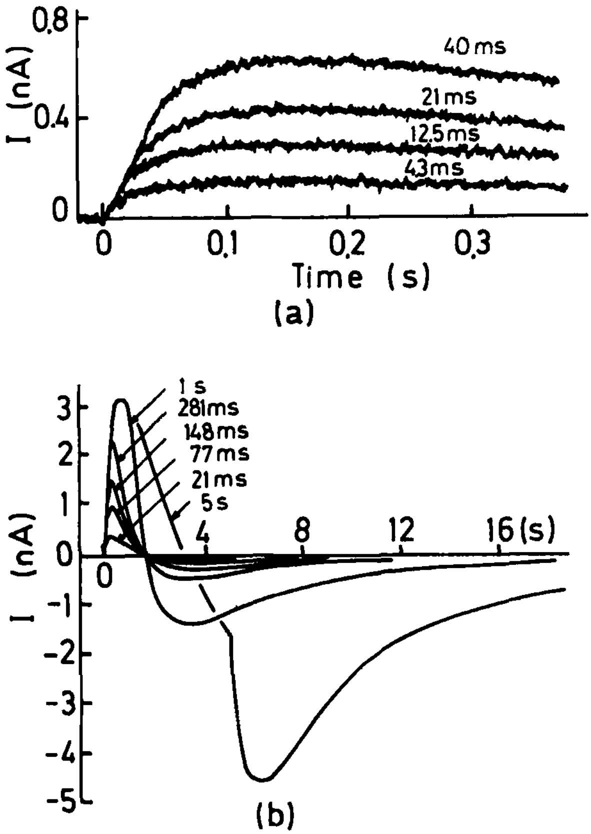

FIGURE 2 Transient properties of the photocurrents stimulated by the projector light.

tends to saturate with an increase in the light pulse width. The polarity of the photocurrent changes from positive to negative while the light stimulation continues for a long time; for example, in the case where the pulse width is 5 s. The third peak enlarges immediately after the cessation of light stimulation. Both the second and the third peak photocurrents increase with an increase in the concentration of methyl red.

The relationship between the maximum values of the photocurrent and the stimulation light pulse width is shown in Figure 3. It is seen that the second peak photocurrent tends to saturate with an increase in the pulse width. Of course, the third peak also has a tendency to saturate, but at a somewhat longer pulse width region.

The stimulation light intensity dependence of the photocurrent for the constant pulse width (148 ms) is shown in Figure 4a and that for the flash-

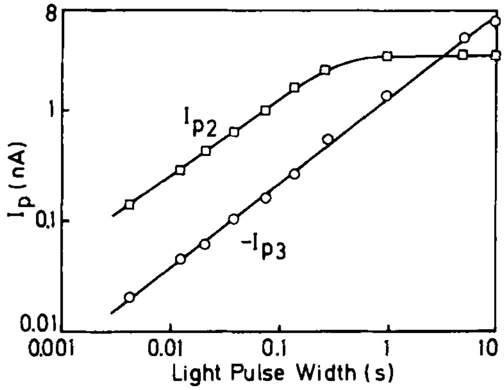

FIGURE 3 Maximum values of the photocurrents as a function of the light pulse width.

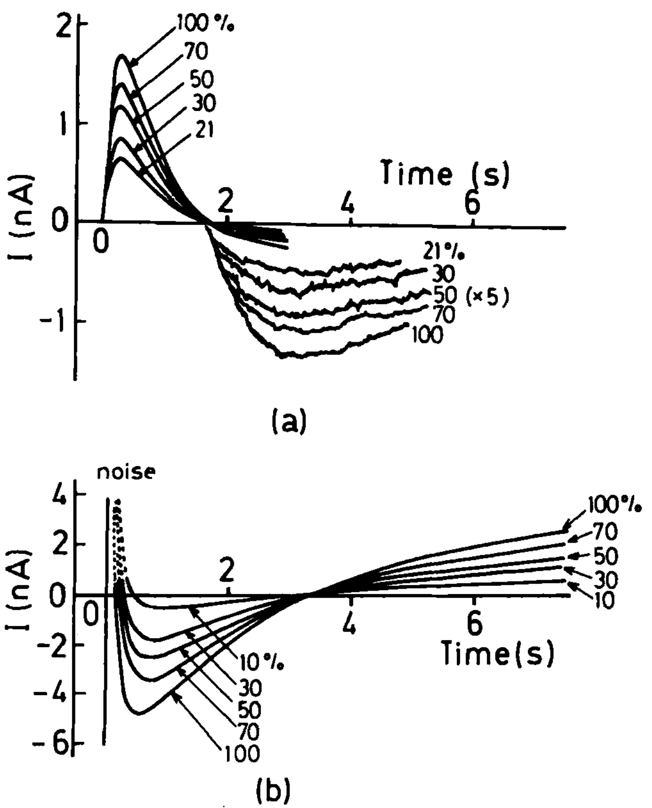

FIGURE 4 Transient properties of the photocurrents as a function of the light intensities. (a) projector stimulation, (b) flashlamp stimulation.

lamp stimulation is shown in Figure 4b, respectively. The maximum light intensity, that is 100% in Figure 4a, corresponds to about 10 mW/cm^2. As the light intensity increases, the peak value of the photocurrent becomes large but the interval of time between the light stimulation and the maximum point does not depend on the light intensity. Figure 5 shows the photocurrent as a function of light intensity for the flashlamp stimulation where the first peak photocurrent can be measured. Both the second peak and the third peak have the tendency to saturate. On the other hand, the first peak photocurrent has linear dependence in a logarithm plot up to the higher light intensity. The same results are obtained in the case of the projector stimulation except for the property of the first peak photocurrent that cannot be measured.

Figure 6 shows the temperature dependence of the photocurrents stimulated by the projector light. Open circles correspond to the second peak and triangles to the third peak photocurrents. The activation energy of the photocurrents for the smectic phase is nearly equal to that for the nematic phase; however, it becomes smaller in the isotropic phase. Dashed lines show the photocurrents for the supercooling state. In the solid crystalline state, neither the second peak nor the third peak component can be detected. That is, only the first peak is observed. The second and the third component of the photocurrents increase and the interval of time between the light stimulation and the maximum point becomes shorter with an increase in the sample temperature. On the other hand, in the case of the

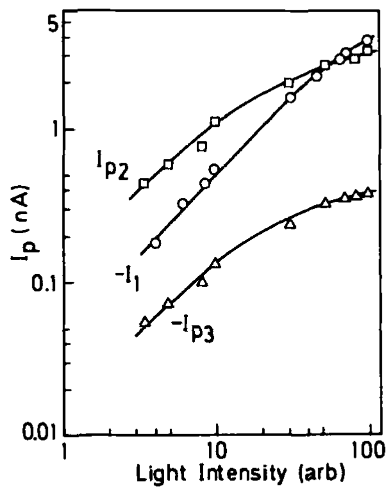

FIGURE 5 Relationship between the photocurrents and the light intensities under the flashlamp stimulation.

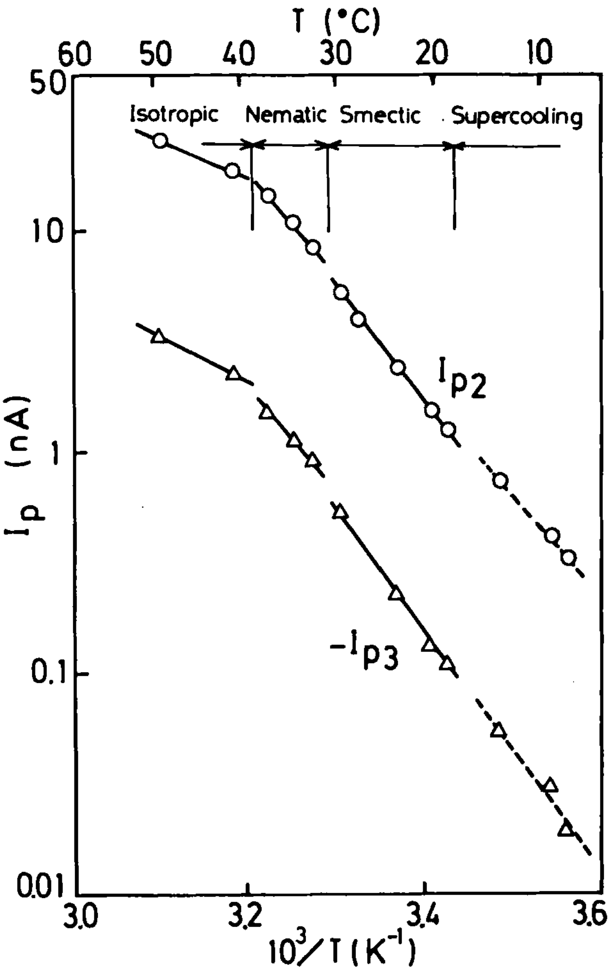

FIGURE 6 Arrenius plots of the photocurrents under the projector stimulation (light pulse width is 148 ms).

flashlamp stimulation, the response time of the first peak component seems to be independent of the sample temperature. These experimental results suggest that both the second peak and the third peak component of the photocurrents are controlled by the diffusion processes.

Figure 7 shows the relationship between the photocurrent and the spacer thickness for the projector stimulation. The temperature of 26°C corresponds to the smectic phase, 36°C to the nematic phase, and 46°C to the isotropic phase. Both the second peak and the third peak in all phases

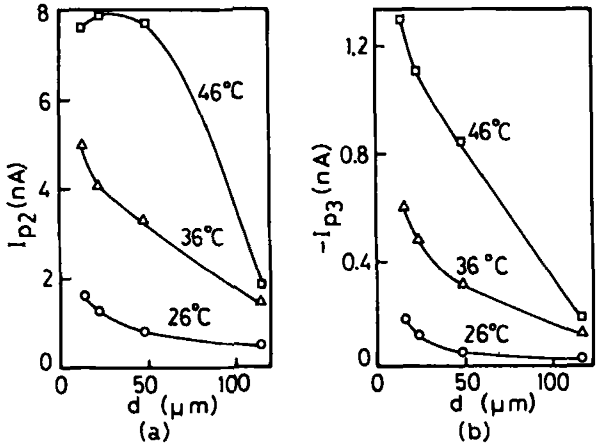

FIGURE 7 Relationship between the photocurrent and the spacer thickness for the projector stimulation. (a) I_{p2}, (b) $-I_{p3}$.

decrease with an increase in the thickness of the spacer. The light pulse width used in this case is 281 ms. In the case of the flashlamp stimulation, the first peak photocurrent as well as the second and the third peak decreases with an increase in the thickness of the spacer. These decreases of the photocurrents with an increase in the thickness of the spacer are presumably caused by the increase of the effective electrical series resistance of the liquid crystal cell. The transient properties of the photocurrents under the flashlamp stimulation are shown in Figures 8a, b, c, and d, respectively. The first cross time C_{1T} does not have an apparent tendency on the thickness of the spacer. On the other hand, the interval of time between the onset of light stimulation and the second peak's maximum point, P_{2T}, becomes longer with an increase in the thickness of the spacer, and with a decrease in the sample temperature. The same tendencies are observed in the case of the second cross time C_{2T}, and the interval of the time for the third peak maximum P_{3T}.

Figure 9 shows the integration effect of the photocurrent stimulated by the repetitive light pulses produced by a combination of a rotating mirror and the camera shutter. The light source used is a 500 W Xe-lamp and the shape of the pulse is shown in the figure. The repetition frequency of the light pulses is 50 Hz. Transient properties are the same as those obtained for the single pulse stimulation by the projector light. Then the photovoltaic effect has the integration characteristics for light stimulation. Saturation tendencies for the photocurrents are observed with an increase in the irradiation pulse width.

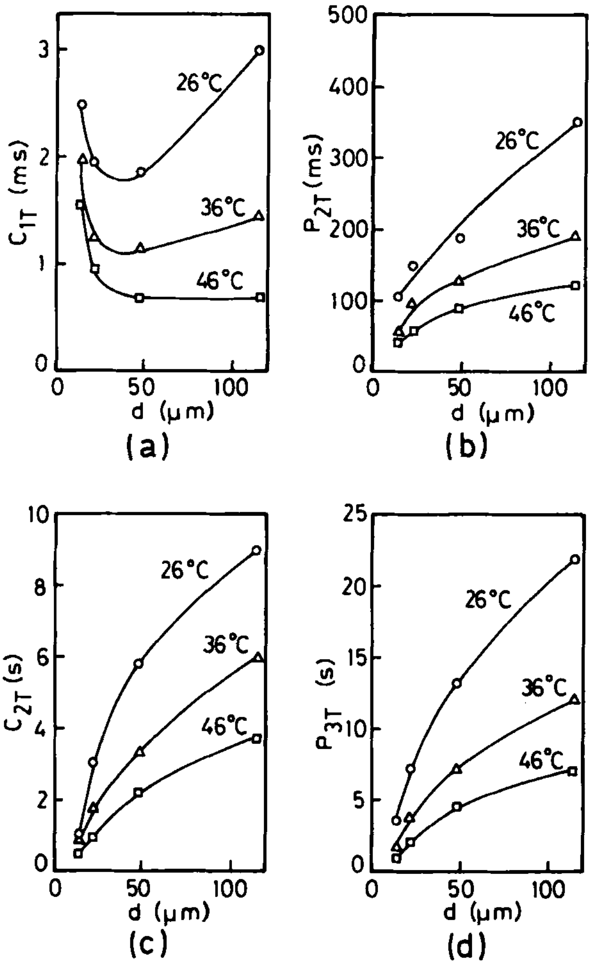

FIGURE 8 Transient properties of the photocurrents as a function of the cell thickness under the flashlamp stimulation. (a) C_{1T}, (b) P_{2T}, (c) C_{2T}, (d) P_{3T}.

CONCLUSION

The dye sensitization effect on the photovoltaic phenomena in liquid crystal cells is observed for visible light stimulation. The sensitized photocurrents consist of three components. The first is a small negative peak observed at the moment of light stimulation. The second peak is with a positive polarity following immediately after the first peak and the third negative peak is with a slow response.

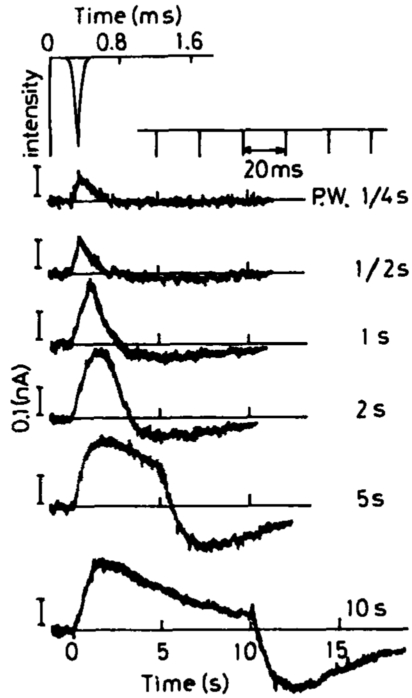

FIGURE 9 Transient properties of the photocurrents under repetitive light pulse stimulation.

The maximum values of the second peak and the third peak photocurrent increase and tend to saturate with an increase in the light pulse width and the light intensity. They can be observed only in the smectic, the nematic and the isotropic phases. The intervals of time between the light stimulation and the second peak and the third peak maximum point increase with an increase in the thickness of the spacers and with a decrease in the sample temperature. Then the second and the third components of the photocurrents are controlled by the diffusion of the ionized charge carriers.

Since there are cases where the maximum open circuit voltage in the photovoltaic phenomena described in this paper becomes more than a hundred millivolts, it may affect some influences upon the operating characteristics of guest-host type displays using some special dyes under very intense illumination.

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