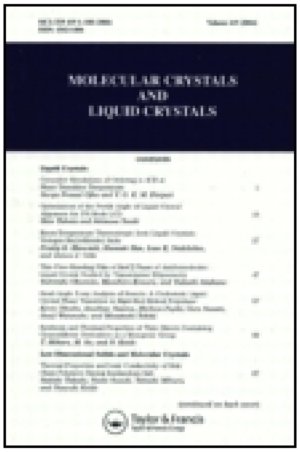

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Effect of Dopants on Characteristics of Polypyrrole as a Liquid Crystal Alignment Layer

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Effect of Dopants on Characteristics of Polypyrrole as a Liquid Crystal Alignment Layer

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Electrochemically polymerized polypyrrole (PPy) films with different dopants showed different surface energies. The films were used as alignment layers of liquid crystal displays (LCDs). The PPy films doped with ClO_4^- (PPy/ClO_4) and PF_6^- (PPy/PF_6) showed surface energies of 43.2 and 32.3 mJ/m^2, respectively, while the pretilt angles of 4-cyano-4′-pentylbiphenyl on the films were 5.6 ± 0.3 and 14.0 ± 2.2 degrees, respectively. The electro-optic response time measured by light transmittance through the twisted nematic (TN) LCDs on switch-on was shorter for the display with PPy/PF_6 than for that with PPy/ClO_4. However, the turn-off response time was shorter for the display with PPy/ClO_4 than for that with PPy/PF_6. The total response time, which is the sum of the turn-on and turn-off response times, was 75 and 120 msec at 3.0 V_{pp} for the displays with PPy/ClO_4 and PPy/PF_6, respectively.

Keywords: Polypyrrole; liquid crystal alignment layer; surface energy; pretilt angle; electro-optic response

INTRODUCTION

Electro-conductive materials have recently attracted some attention as a promising liquid crystal (LC) alignment layer because a thin film is obtained by a relatively simple process and the surface is expected to easily dissipate electrostatic charges generated by the rubbing process [1-4]. It was reported

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that a polyimide (PI) film doped with a charge transporting material improved the legibility of highly multiplexed super-twisted nematic (STN)-liquid crystal displays (LCDs) [1]. A polypyrrole (PPy) film formed electrochemically on an indium tin oxide (ITO)-glass plate was found useful especially for ferroelectric liquid crystal (FLC) displays since the depolarization field generated by the spontaneous polarization of the FLC was effectively suppressed by the film [2]. It was also reported that conductive polymer films such as PPy and polythiophene rendered different pretilt angles of an LC on changing counter ions [3] or alkyl side-chain lengths [4]. Polyaniline (PAn) and its blends with other polymers have been tried as an LC alignment layer which also served as the electrode [5]. Electro-optic response characteristics of a twisted nematic (TN)-LCD with a PAn blend film as the LC alignment layer were controllable by changing the composition of the blend. Precursor polymers of poly(*p*-phenylene) and poly(*p*-phenylene vinylene), which were converted to the desired conductive polymers after the Langmuir-Blodgett deposition, have been utilized in order to replace both the PI alignment layer and the ITO electrode at the same time [6].

In the present work we have used electrically conductive PPy as an LC alignment layer for TN-LC cells. PPy films were electrochemically deposited on ITO-glass plates with two different dopants (counter ions). The surface energies of the two PPy films were measured. The effect of the dopants on the electro-optic response characteristics of the TN-LC cells as well as on the LC pretilt angles have been investigated.

EXPERIMENTAL

A PPy film was deposited on an ITO-glass plate by electrochemical polymerization of pyrrole as described in the literature [7]. Acetonitrile was used as a solvent and tetrabutylammonium (TBA) salts of two different anions, ClO_4^- and PF_6^-, were used as electrolytes. The polymerization mixture comprised of 40 mL of 0.036 mol electrolyte solution in acetonitrile and 1 mL of the monomer was kept in a constant temperature bath maintained at 0°C. An ITO-glass plate was used as the working electrode (anode) and a platinum plate was used as the counter electrode (cathode). The thickness of the PPy film was controlled by adjusting the charge density galvanostatically. A 400 Å-thick PPy film was obtained by applying a current of $0.4\,mA/cm^2$ for 25 seconds and the film was washed with fresh methanol and dried at 80°C for 30 min.

The surface energy of the PPy film doped with ClO_4^- (PPy/ClO_4) or PF_6^- (PPy/PF_6) was determined by the method described in the literature [8] using four polar liquids; water, glycerol, formamide, and diiodomethane, of which the surface energies are known [9]. In order to employ the Wilhelmy plate method [10], PPy films were deposited on both sides of a 0.1 mm-thick carbon foil supplied by Goodfellow Cambridge Ltd., using two platinum counter electrodes facing each side of the foil. A WET-TEK dynamic contact angle balance was employed to record the force exerted on the specimen at 25°C at an immersing speed of 2.0 mm/min. The advancing contact angle was calculated after extrapolating the advancing force slope to the zero-immersion depth.

4-cyano-4′-pentylbiphenyl (5CB) from Merck was used as a nematic LC in this work. 50 μm-thick cells with PPy films rubbed antiparallelly with each other were prepared for the measurement of the pretilt angles of 5CB on the PPy films. The pretilt angles were measured by the crystal rotation method [11, 12] at 25°C.

A sandwich cell with the rubbing directions of the two PPy film plates being at right angles to each other was assembled. A 4.6 μm-thick poly(ethylene terephthalate) film was used as the spacer. The cell was filled with 5CB by capillary action and followed by sealing. The working area of the cell was $1.5 \times 2.0\,cm^2$.

The TN-LC cell was placed between two parallel polarizers for the dark- mode operation. A bias potential with a 100 Hz square wave was generated by a function generator, Philips PM 5139, and applied to the cell with an interval of 100 msec-on and 200 msec-off. The optical response of the LC cell at a given bias potential was displayed on a Kikusui Digital Storage Oscilloscope, Model 5521U, and the data were transferred to a personal computer. The schematic diagram of the set-up was shown elsewhere [5].

RESULTS AND DISCUSSION

Light transmittance of an ITO-glass plate coated with a 400Å-thick PPy film was measured to be 75%. The surface resistivity of the PPy film on ITO-glass was as low as that of ITO($\sim 30\Omega/\square$) due to the influence of the ITO layer underneath the film. The PPy film was insoluble in common solvents or in the LC used. Atomic force microscopic (AFM) observations on the PPy film surface doped with ClO_4^- or PF_6^- gave no characteristic difference in morphology before and after rubbing.

Table I summarizes the surface energies of the ClO_4^-- and PF_6^--doped PPy films ($\gamma_s(PPy/ClO_4)$ and $\gamma_s(PPy/PF_6)$, respectively), and the pretilt angles of 5CB on the films. $\gamma_s(PPy/ClO_4)$ was measured to be 43.2 while $\gamma_s(PPy/PF_6)$ was 32.3 mJ/m^2. Electrochemically polymerized PPy has been known to have 0.25 to 0.33 counter ion per pyrrole unit [13]. It has been also reported that an incorporation of fluorine-containing additives to a polymer or fluorination of a polymer reduces the surface energy of the polymer [14]. PPy/PF_6 seems to show the same effect as an addition of fluorines on the surface energy.

The pretilt angle of 5CB on a PPy/ClO_4 film was measured to be 5.6 ± 0.3 degrees while the angle on a PPy/PF_6 film was as high as 14 ± 2.2 degrees. It has been reported that the surface energy contributes to controlling the pretilt angle [15] and the introduction of fluorine-containing groups to PI increases the pretilt angle by lowering the surface energy of the PI surface [16–18]. The measured pretilt angles of 5CB seem to support the result that the PPy/ClO_4 film has a higher surface energy than the PPy/PF_6 film.

The relative transmittance of the TN-LC cells prepared with each of the PPy films were plotted against the bias potential as shown in Figure 1. V_{10},

TABLE I Surface energies of the ClO_4^--and PF_6^--doped PPy films and the pretilt angles of 5CB on the films

	PPy/ClO$_4$	*PPy/PF$_6$*
Surface energy, γ_s(mJ/m^2)	43.2	32.3
Pretilt angle of 5CB (degree)	5.6 ± 0.3	14.0 ± 2.2

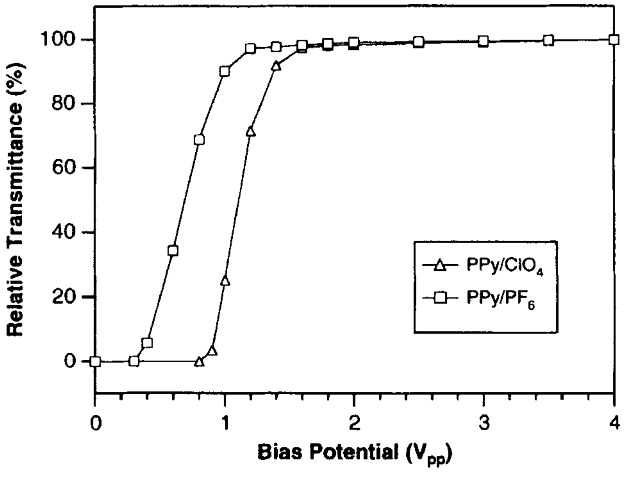

FIGURE 1 Bias potential dependence of relative transmittance.

the bias potential required to get 10% of the ultimate transmittance, was 0.4 and 0.9 V_{pp} for the cells with PPy/PF_6 and PPy/ClO_4 films, respectively. V_{90}, the bias potential required to get 90% of the ultimate transmittance, was 1.0 and 1.4 V_{pp} for the cells with PPy/PF_6 and PPy/ClO_4 films, respectively. Both V_{10} and V_{90} of the PPy/PF_6 film cell were lower than those of the PPy/ClO_4 film cell. This implies that the PPy/ClO_4 film with higher surface energy holds the LC molecules more tightly during the cholesteric-to-nematic transition of the TN-LC layer on applying an electric field.

The two TN-LC cells were compared with each other in terms of the electro-optic response characteristics *vs* bias potential as shown in Figure 2. The rate of increase in transmittance of the PPy/PF_6 film cell on switch-on is faster than that of the PPy/ClO_4 film cell at the same bias potential. The difference in the increase rate of transmittance may be attributed to the difference in the interaction energy between the LC and the alignment layer surface. It must be much easier for the LC molecules bound by the PPy/PF_6 film to orient to the external electric field on switch-on than those bound by the PPy/ClO_4 film.

A bounce in the light transmittance was observed immediately after switching-off the applied electric field whenever the bias potential was over 2.0 V_{pp}. This phenomenon has been attributed to a shear flow (back-flow) effect induced by the fast fluid motion of LC molecules near the substrates on switch-off, which causes a temporary reverse twist of the LC directors in the middle of the cell where the elastic torque is very small [19 ∼ 21]. The time interval between the end of the driving pulse and the bounce maximum was observed to increase with an increase of the driving potential [19]. It was noticed that the cell with the PPy/ClO_4 film generated a deeper bounce with a longer interval than the one with the PPy/PF_6 film on switch-off at the same applied potential. The stronger interaction between the LC and the alignment layers seems to be responsible for the deeper bounce with a longer interval.

The rate of decrease in transmittance on switch-off demonstrated an opposite trend. The cell with the PPy/ClO_4 film shows a steeper decrease in transmittance than that with the PPy/PF_6 film, which is feasible since the stronger interaction between the LC and the PPy/ClO_4 alignment layer pulls the LC into the twisted state faster than in the case of the PPy/PF_6 film. It was also observed that the decay rates (the slopes of decay curves) are the same regardless of the bias potential although the higher the potential, the longer the time for the bounce maximum. A larger elastic energy seems to be stored in the LC molecules when a higher potential is applied resulting in a larger bounce on switching-off.

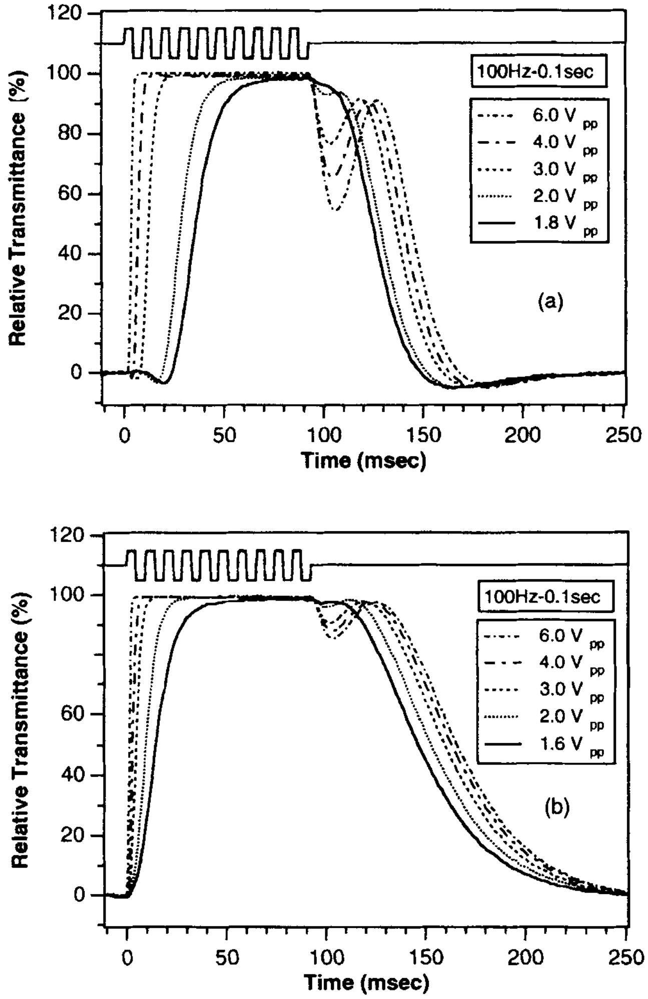

FIGURE 2 Electro-optic response patterns as a function of driving potential for the 4.6 μm-5CB TN cells with (a) PPy/ClO$_4$ and (b) PPy/PF$_6$ films.

The electro-optic response characteristics were analyzed in detail by examining different components of response times. The delay time, τ_d, defined as the time to reach 10% transmittance on switch-on, is inversely proportional to the square of the bias potential [20] as in Eq. (1),

$$\frac{1}{\tau_d} = K \cdot V^2 + C \tag{1}$$

where K and C are constants independent of the applied potential V. It is observed in Figure 3 that τ_d of the PPy/ClO$_4$ film cell is longer than that of the PPy/PF$_6$ film cell regardless of the applied bias potential and the difference becomes much higher with an increase of the bias potential.

The rise time, τ_r, defined as the time for an increase in transmittance from 10 to 90% on switch-on, is also inversely proportional to the square of the bias potential as in Eq. (1). However, it is very interesting to observe in Figure 4 that there is little difference between the rise times of the two cells. The slope of Eq. (1) is theoretically expressed as $K(\tau_R)$ [21] in Eq. (2) without differentiating τ_d and τ_r:

$$K(\tau_R) = \frac{\varepsilon_0 \Delta\varepsilon}{4\pi\eta d^2} \tag{2}$$

where ε_0 is the dielectric constant *in vacuo*, $\Delta\varepsilon$ the dielectric anisotropy of the LC, η the viscosity of the LC, and d the cell thickness. It is shown in Eq. (2) that $K(\tau_R)$ is a function of the bulk properties of an LC and the cell geometry. Therefore, the alignment layer gives no effect on K for τ_r. However, the interaction between the LC molecules and the polymer surface appears to play an important role with regard to K for τ_d because the static interaction at the interface should be overcome [21]: a stronger interaction produces a smaller K for τ_d.

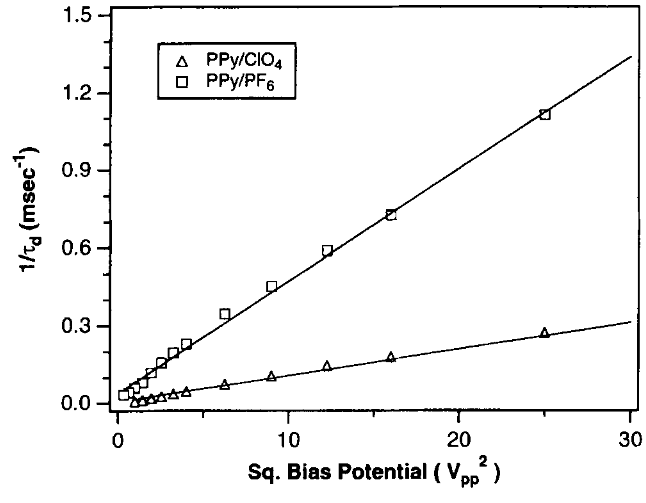

FIGURE 3 Bias potential dependence of the delay time, τ_d, of 4.6 µm-5CB TN cells with PPy/ClO$_4$ and PPy/PF$_6$ films.

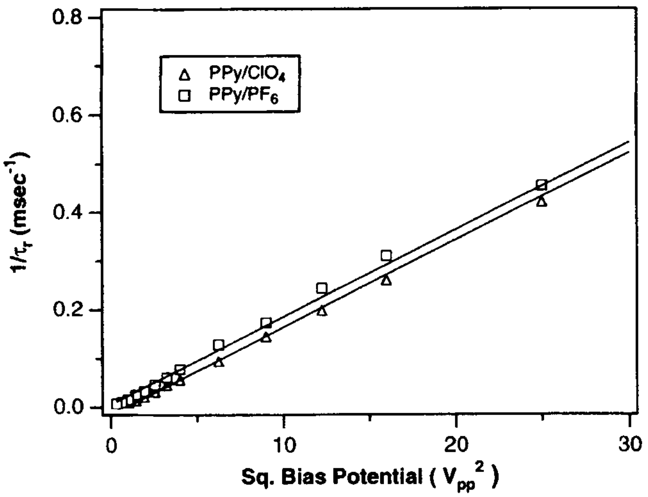

FIGURE 4 Bias potential dependence of the rise time, τ_r, of 4.6 μm-5CB TN cells with PPy/ClO$_4$ and PPy/PF$_6$ films.

The turn-off response time, τ_{off}, is defined as the time for a transmittance decrease to 10% on switch-off. The τ_{off} of the PPy/PF$_6$ film cell was about twice as long as that of the PPy/ClO$_4$ film cell as shown in Figure 5, probably due to a weaker interaction of the PPy/PF$_6$ film with the LC. The τ_{off} of both cells are small at a low bias potential and increase fast with an

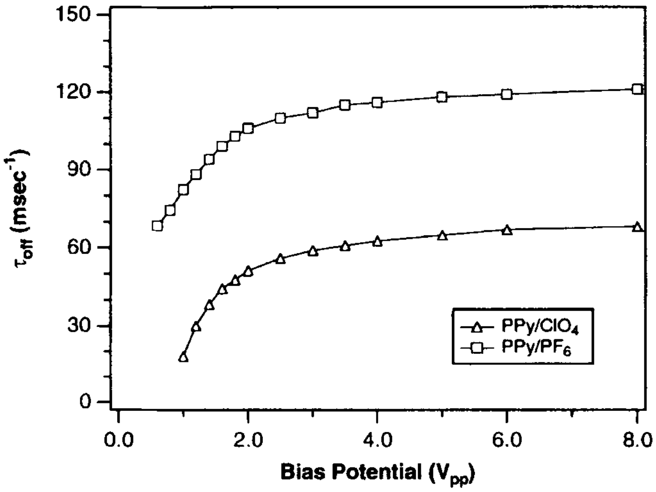

FIGURE 5 Bias potential dependence of the turn-off response time, τ_{off}, of 4.6 μm-5CB TN cells with PPy/ClO$_4$ and PPy/PF$_6$ films.

TABLE II Electro-optic response times of 4.6 μm-5CB TN-LC cells with electrochemically deposited PPy alignment layers measured at different driving potentials*

Potential	*LC Alignment Layer*	*Response Times (msec)* τ_d	τ_r	τ_{on}	τ_{off}	τ_{tot}
2.0 V_{pp}	PPy/ClO$_4$	22.0	18.0	40.0	51.0	91.0
	PPy/PF$_6$	4.4	13.0	17.0	106.0	123.4
3.0 V_{pp}	PPy/ClO$_4$	9.5	6.9	16.5	59.0	75.5
	PPy/PF$_6$	2.2	5.8	8.0	112.0	120.0
6.0 V_{pp}	PPy/ClO$_4$	2.9	1.6	4.5	67.0	71.5
	PPy/PF$_6$	0.8	1.4	2.2	119.0	121.2

* $\tau_{on} = \tau_d + \tau_r$ and $\tau_{tot} = \tau_{on} + \tau_{off}$.

increase of the bias potential up to 2.0 V_{pp}. The elastic energy stored in the LC molecules on switch-on seems to be saturated beyond the applied potential of 2.0 V_{pp}. It is observed in Figure 3 that the low applied potential failed to generate the bounce on switch-off.

Table II summarizes the electro-optic response times of the two TN-LC cells measured at different driving potentials. τ_{on}, the sum of τ_d and τ_r, decreased while τ_{off} increased with an increase of the bias potential. The total response time ($\tau_{tot} = \tau_{on} + \tau_{off}$) of the PPy/PF$_6$ film cell was practically constant since the decrease in τ_{on} was balanced with the increase in τ_{off} as the bias potential increased. In the case of the PPy/ClO$_4$ film cell, however, τ_{on} was very long at low bias potentials and its decrease rate is faster than the increase rate of τ_{off}, resulting in a decrease in τ_{tot} with increasing bias potential. It is apparent that the difference in τ_{tot} between the two TN-LC cells is mainly due to the difference in τ_{off}.

CONCLUSION

The surface energy of an electrochemically synthesized PPy film was affected by the counter ion with which the polymer is neutralized electronically. γ_s(PPy/ClO$_4$) was higher than γ_s(PPy/PF$_6$). However, the surface morphology of the two PPy films was neither much different from each other nor altered by the rubbing process. The surface energy played an important role in determining the characteristics of the PPy film as an LC alignment layer and, accordingly, in the performance of the TN-LC cell fabricated with the PPy film. The PPy/ClO$_4$ film with a higher surface energy had a stronger interaction with the LC than the PPy/PF$_6$ film, which resulted in a smaller pretilt angle of 5CB, a higher threshold voltage, slower turn-on response times, and faster turn-off response times of the PPy/ClO$_4$ film cell.

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