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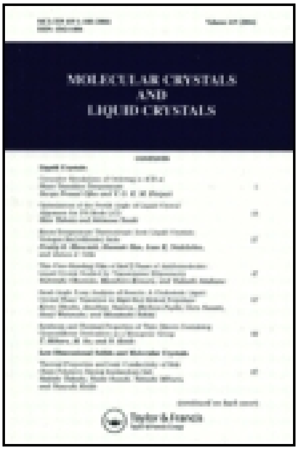

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MECHANISM OF ELECTRO-OPTICAL EFFECT IN POLY(γ-[2-(9-CARBAZOLYL)ETHYL]-L-GLUTAMATE) LYOTROPIC LIQUID CRYSTAL

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Lyotropic liquid crystalline cell composed of polypeptide having carbazolyl groups (poly(γ-[2-(9-carbazolyl)ethyl]-L-glutamate) (PCLG) was studied to analyze the novel electro-optical effect, in which the transparent cell became scattering under applying d.c. bias voltage. The absorption at 350–600 nm was increased under d.c. bias application, leading to the scattering behavior. Effect of hole transport properties of PCLG on the scattering behavior was discussed. Direct observation was also examined to clarify this scattering behavior.

Keywords: charge transport property; electro-optical effect; liquid crystal; poly(glutamate)

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INTRODUCTION

Polymer dispersed liquid crystal (PDLC) is prepared by mixing guest liquid crystal with an appropriate host-matrix polymer. This PDLC is applicable to optical shutter and polymer blinder because scattering PDLC turned to transparent state by applying a voltage [1,2]. The cell does not need alignment film, polarizer, which are employed in common LC display, and should be a display device with low electricity, no surface treatment nor complex twisted nematic processes. Scattering state is produced by the difference in refractive indices between guest LC particles and host polymer matrix. Application of electric field makes the LC domain orient, and if the refractive index of guest LC is adjusted to that of host-polymer, then the cell becomes transparent. However, removing the electric field makes guest LC domains return their initial orientation because of surface force etc. In this electro-optical effect, bias-off state is the scattering state and bias-on state is transparent. The cell is commonly driven under a.c. bias voltage.

Polypeptide shows a character of lyotropic LC when it is mixed with suitable solvent [3,4]. This is because polypeptide has rigid rod-like α-helical structure. The side chain shows an ordered structure along main chain. Effective energy or electron transfer along main chain is expected and has been collecting keen interest in a viewpoint of fundamental science and its application [5,6]. In the lyotropic LC, the polypeptide main chain should align along one direction by applying bias voltage because of large dipole moment along α-helical main chain. On this basis, we have studied charge transport properties of polypeptide having carbazolyl groups (poly(γ-[2-(9-carbazolyl)ethyl]-L-glutamate) (PCLG). Carbazolyl groups at the side chain ordered along a main chain should work as effective carrier hopping sites. PCLG amorphous film showed the hole mobility of ca. $10^{-8}\,\mathrm{cm^2/Vs}$ [7]. This mobility was not remarkable compared with common charge-transporting polymers. However, when a lyotropic LC cell was prepared by mixing PCLG with suitable amount of 1,4-dioxane, the PCLG LC cell showed relatively high carrier mobility of ca. $10^{-3}\,\mathrm{cm^2/Vs}$. This is possibly due to higher ordered intermolecular alignment in the LC state [5,6]. When bias voltage was applied to the cell to measure electrical properties, we found that the cell became scattering. Its scattered state immediately changed to transparent by turning off the bias voltage. This character seems to be novel and different from PDLC. Furthermore, its character was enhanced by adding 2,4,7-trinitrofluorenone (TNF) in the PCLG LC cell.

In this paper, the study was focused on this electro-optical behavior of the PCLG LC cell. Effects of bias voltage and materials on this effect were analyzed, and its mechanism was estimated.

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EXPERIMENTAL

PCLG was prepared and purified according to procedures similar to those described by Nomori *et al.* [8] PCLG was obtained by ester exchange reaction of poly (γ-methyl-L-glutamate) (PMLG, Kyowa Hakko Kogyo Co., Ltd.) with N-(2-hydroxyethyl carbazole (HECz) in monochlorobenzene in the presence of *p*-toluensulfonic acid as a catalyst. The polymer obtained was identified by FT-IR and ^{1}H-NMR spectra. Substitution ratio of carbazolyl groups was calculated to be approximately 100%. PCLG LC was prepared by mixing PCLG with 1,4-dioxane to be the PCLG concentration of 20 wt.%. The LC was placed between ITO electrodes keeping the inter-electrode distance of 10 μm with a Teflon spacer. PCLG LC cell with polyethylene (1μm thickness insulator) coated ITO electrode, PMLG LC cell and PMLG containing carbazole (Cz) (Cz:MLG monomer unit = 1 : 1) LC cell were also prepared by the same method. In the experiment with TNF, TNF was added into PCLG LC with the molar ration of (Cz on PCLG)/TNF = 1/0.01. Surface-type cell with inter-digitated electrodes was also employed to carry out direct observation near the electrode in PCLG LC cell. The inter-electrode distance was 250 μm. The d.c. voltage was applied between a pair of ITO electrodes with ultra high resistance meter (ADVANTEST R8340A). The change in the transmittance was measured using a spectrophotometer (JASCO V-570, monitored at 600 nm).

RESULT AND DISCUSSION

The polarized optical micrograph of the cell composed of 1,4-dioxane solution containing 20 wt.% of PCLG showed fan-shape like texture. By applying an electric field about 10^4 V/cm, the micrograph was gradually changed, and consequently turned to dark field after 30 sec. This indicates that PCLG molecules are oriented along electric field similar to the homeotropic alignment of nematic liquid crystal. This is due to a large dipole moment of PCLG along α-herical main chain. This observation clearly suggests that the cell composed of PCLG/1,4-dioxane solution shows liquid crystalline behavior. We found that PCLG lyotropic LC cell became scattering when high d.c. bias voltage was applied as shown in Figure 1 (a) and (b). The scattering state immediately turned to transparent by turning off the bias voltage. The change between scattering and transparent states was found to be considerably fast as shown in Figure 1 (c). This does not indicate that the scattering behavior is attributed to electrochemical reaction and/or long-range migration of PCLG molecules.

Figure 2 shows the UV-vis. spectra of PCLG LC cell at various applied bias voltages of 0-1000 V. The absorption assignable to terminal carbazolyl

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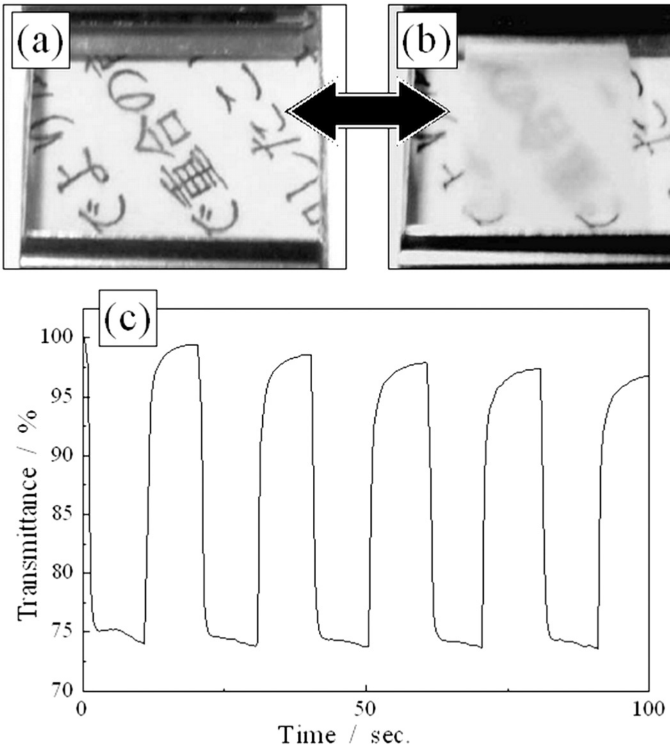

FIGURE 1 Photographs of PCLG LC cells when d.c. bias voltage of 600 V was off (a) and on (b), and time dependence of transmittance for PCLG LC cell by alternating turn-on and -off of d.c. bias voltage of 600 V (c).

groups of PCLG was observed at 300–350 nm. The absorption at 300–350 nm decreased, but that at 350–600 nm increased with increasing bias voltage. Interestingly, the decrease at 300–350 nm was found even below the applied voltage of 300 V, but the increase at 350–600 nm and the scattering behavior were not found in this range. The increase at 350–600 nm was found above the voltage of 300 V, having considerable relation with the scattering behavior. The decrease at 300–350 nm is probably attributed to the change in the alignment of terminal carbazolyl groups due to the homeotropic alignment of PCLG. When dichroic dye was dissolved in the present LC and the bias voltage below 300 V was applied, the color corresponding to the dichroic dye was bleached. This indicates that the application of bias voltage below 300 V makes PCLG molecules aligns along the electric field. This also supported the result of the polarized optical macrograph.

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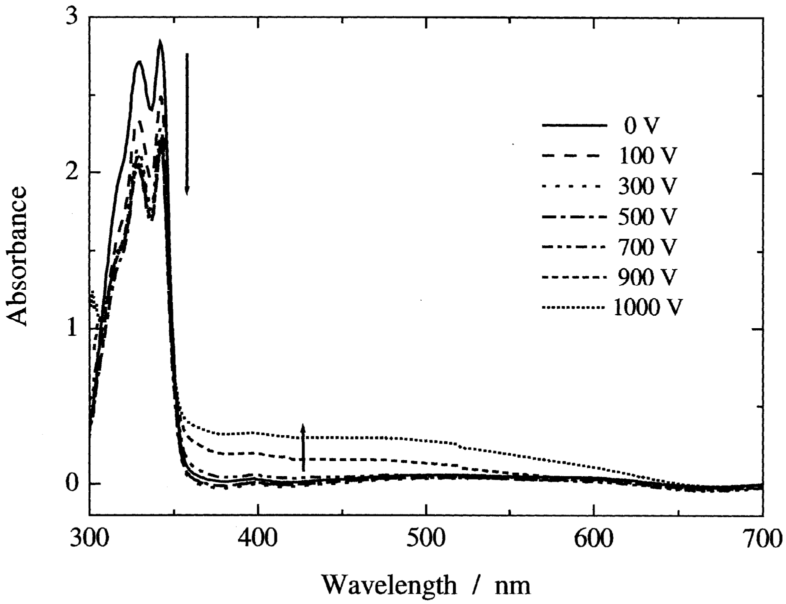

FIGURE 2 UV-vis. spectra for PCLG LC cell under the applied bias at 0 ~ 1000 V.

The scattering behavior was not found in PMLG lyotropic LC cell or PMLG containing low-molecular weight Cz lyotropic LC cell. Further, the scattering behavior was not also observed in PCLG LC cell with polyethylene (1 μm thickness insulator) coated ITO electrode. These results were summarized in Figure 3. If the present scattering behavior is originated from dynamic scattering mode (DSM), scattering should be observed even in the polyethylene coated ITO cell. This is because DSM is driven under electric field but not current. However, only coating the polyethylene on either electrode (anode and/or cathode) prevented the scattering behavior. These results clearly show that the present scattering behavior is different from well-known DSM behavior. The experimental fact seems to indicate that the scattering correlates with current flow. Actually, the steady-state current flowing the cell decreased four orders by coating the polyethylene. The polyethylene on the ITO prevents carrier transport and/or injection. Charge transport properties through carbazolyl groups along PCLG α-helical chain effect the present scattering behavior considerably. This explanation may be also supported by the result that the current flowing the PCLG LC cell is one order higher than that in PMLG containing Cz LC cell.

Figure 4 shows polarized micrographs of PCLG LC cell when d.c. bias voltage of 500 V was turned-on and -off. This measurement was carried out with surface-type cell composed of inter-digitated electrodes. The interface

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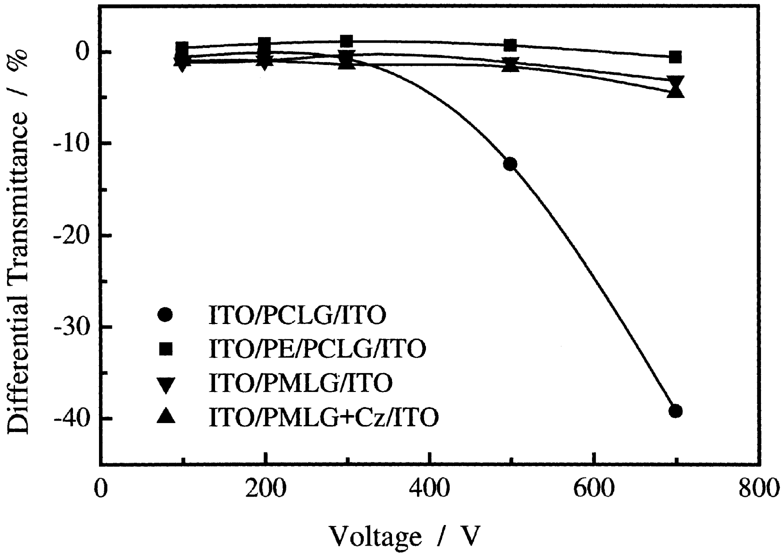

FIGURE 3 Applied voltage dependence of differential transmittance for ITO/PCLG/ITO, ITO/PE/PCLG/ITO, ITO/PMLG/ITO and ITO/PMLG+Cz/ITO LC cells.

pointed by the arrow in Figure 4 was observed by turning-on the bias voltage. The interface was generated near the only anode side and was not found near the cathode, and it disappeared immediately when the voltage

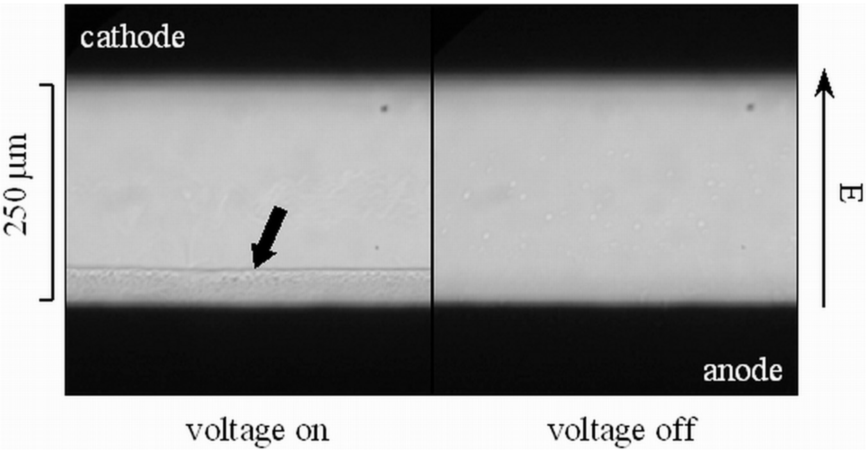

FIGURE 4 Micrographs of PCLG LC surface-type cell when d.c. bias voltage of 500 V was turned-on and -off.

was turned-off. This suggests that the generation of interface correlates with the scattering behavior observed in the PCLG LC cell. Further, when applied voltage was increased, the interface was emphasized clearly and the scattering of the LC cell became enhanced. The appearance of the interface near only anode reminds us the hole injection from electrode to PCLG. This may results in the local concentration difference or micro-phase separation in PCLG LC cell, leading to scattering behavior.

TNF was added to the present PCLG LC cell to increase the current flowing the cell, because the charge transfer (CT) complex is expected to be formed in PCLG/TNF LC cell due to the donor-acceptor interaction between carbazolyl group and TNF [9]. This was confirmed by the color change of the LC cell by adding TNF. The ratio of PCLG and TNF was determined to be 1 : 0.01 so as to keep the LC cell homogeneous. As a result, the differential transmittance between scattering and transparent state was found to be enhanced from about 30% to about 70% by adding TNF to PCLG LC cell when the applied voltage was 600 V, and the change of transmittance repeats more than 150 times without any remarkable decrease. This result supports that charge transfer in PCLG probably plays an important role in the present scattering behavior. These interpretations must be regarded as preliminary. Further analysis must be done to clarify the detail mechanism of the scattering, the appearance of the interface near the anode as well as the role of charge transport properties of PCLG in detail.

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