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ELECTROSTATIC FIELD-INDUCED TRANSFORMATION IN THE HOMEOTROPICALLY ALIGNED LIQUID CRYSTALLINE POLYMER.

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Abstract For the liquid crystalline(LC) solution of Poly(γ -benzyl L-glutamate),(PBLG), / 1,1,2-trichloroethane, which gives a nematic texture aligned homeotropically at a glass surface, the effect of DC field applied perpendicularly to the director in a homeotropic texture was investigated by microscopic optical measurements. An increase of the DC field above a threshold generates some planar texture at the negative electrode and the texture develops with a distinct boundary between the homeotropic and the planar ones. After the field direction was inverted, the boundary begins to move backward into the electrode, and at the same time, the planar texture to develop slowly from the another electrode. Under a fixed strength of the field, the ratio of the homeotropic and the planar areas is kept constant during transforming process after an inversion and the value depends on the field strength. The phenomenon may be qualitatively associated with the balance between some electrostatic interaction of the polar terminal groups of polymer with the ionic charges on the glass surface and the dielectric instabilities due to the large dipole along the molecular axis.

INTRODUCTION

A kind of polypeptide, poly(γ -benzyl L-glutamate),(PBLG), holds the familiar α -helix itself in many organic solvents and forms generally a cholesteric liquid crystal in concentrated solution due to the stiff helical nature. However it frequently gives a nematic texture aligned homeotropically when the solution is confined into the very thin cell constructed of two glass plates. The origin of the phenomenon to provide excellent homeotropic alignment of PBLG even without application of any external field may lie in the electrostatic interaction of polar terminal groups of polymer with the ionic charge on the glass surface.[1]

A prominent characteristic of PBLG is the large dipole along the molecular axis.

The dipole moment of PBLG which is α-helical had been measured in various solutions and confirmed that it is directly proportional to the degree of polymerization.[2] The value of the dipole moment per residue for PBLG was estimated as 3.4 Debye and accumulated along the helix. Our recent work for this system suggests that the behavior of molecular orientation in a DC field is very complicated.

We should be interested to investigate the rotational behavior due to the electric field induced switching of the director under the strong anchoring and to advance our understanding of the phenomena at an interface between a polymer and a solid substrate. In this study, the electrostatic behavior with applying a DC field across the cell under the strong anchoring condition was investigated through the local Frederiks transition by microscopic optical measurements, for a liquid crystalline solution of PBLG.

EXPERIMENTS

The solution of PBLG (Mw=48000) / 1,1,2-trichloroethane(TriCE) (concentration:0.18V/V) is confined into the sandwich type of very thin cell(thickness:0.22 μ m) which structure is shown in fig.1. After leaving it for several hours at room temperature, the anchoring transition from the cholesteric grandjean texture to the homeotropic orientation gradually occurs and the perfect homeotropic alignment is performed after c.a. 2 hours. A DC field is applied transversely crossed a cell(parallel to the cell surface), in which the homeotropic alignment has been performed. The structural transformation induced by an electric field is observed by means of an optical microscope and simultaneously the current response is measured.

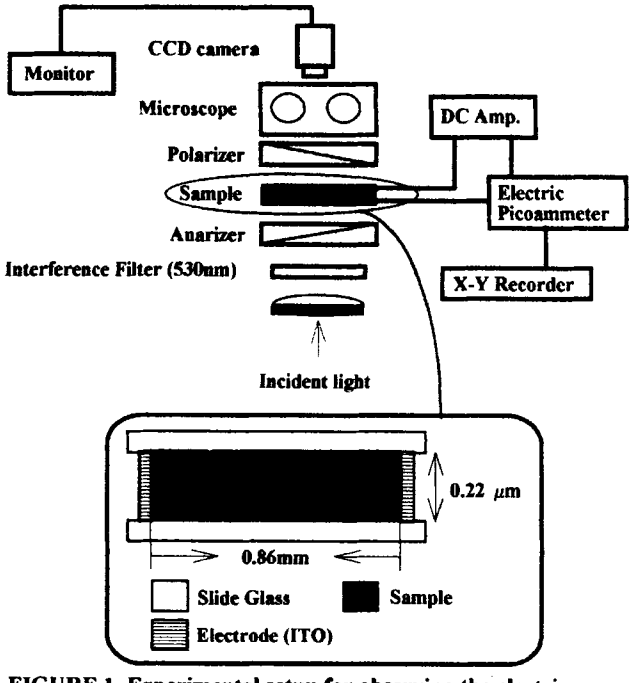

FIGURE 1 Experimental setup for observing the electric field induced tranformation and Cell structure.

RESULTS AND DISCUSSION

As shown in the photograph(fig.2(1)), the homeotropic alignment is well performed in the cell, filled with PBLG solution, without any field. When a DC electric field is applied to the cell, the homeotropic texture does not change until the field strength exceeds a threshold value. The first threshold exists around at 0.34 kV/cm. Applying a field above the first threshold value, a planar texture appears at the surface of the negative electrode, as a belt with a distinct boundary in the homeotropic texture which was previously performed (fig.2(2)(3)). It was clearly seen that the boundary parallel to electrodes moves toward the positive electrode from the negative one and arrived at an equilibrium position under the experimental condition after a while. The equilibrium distance, finally attained, between the boundary and the negative electrode depends on the field strength applied to the cell. The distance from the negative electrode to the boundary as a measure of transformed area was measured. The value increased with the stepwise increase of the voltage as shown in fig.3. The ordinate(R) is scaled by the relative

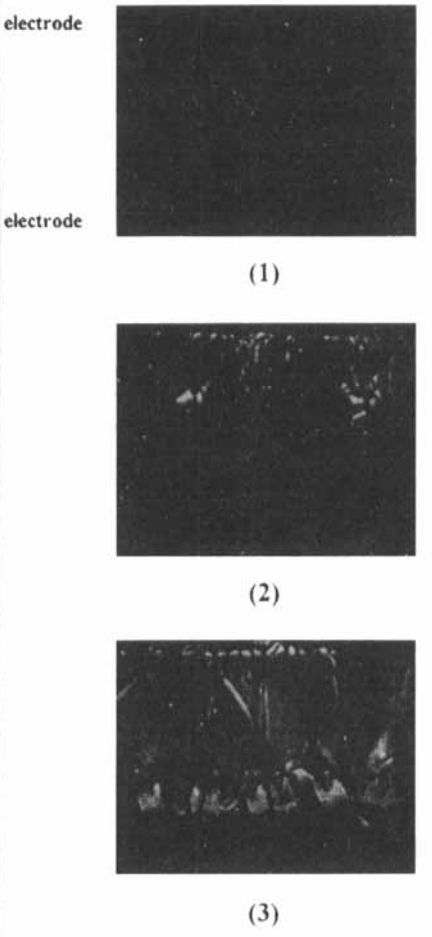

FIGURE.2 Photomicrographs taken under crossed polars(× 40). (1) The homeotropic texture in the cell filled with PBLG solution without any field. The planar textures appeared from the negative electrode(top) with applied voltages (2) 0.407 and (3) 0.93 (kV/cm), respectively, are seen as the bright region.

distance from the negative electrode to the boundary. The secondary threshold voltage(ca 0.7 kV/cm) can be seen apparently. The homeotropic area remains unvanished under the present experimental condition even at the ultimate voltage. The variation of the electric current in the process of transformation from the homeotropic to the planar texture is also pursued. Here, fig.4 is one of the results with a fixed voltage applied at a stroke. The value of the electric current is kept at constant at a stop of boundary movement under a moderate voltage. However, the system used for the stationary current measurement with stepwise increase of field strength is little different from that for transient current. The results are shown in fig.3. The increment of transformation area leads to the increase of the electric current with the stepwise increment of voltage.

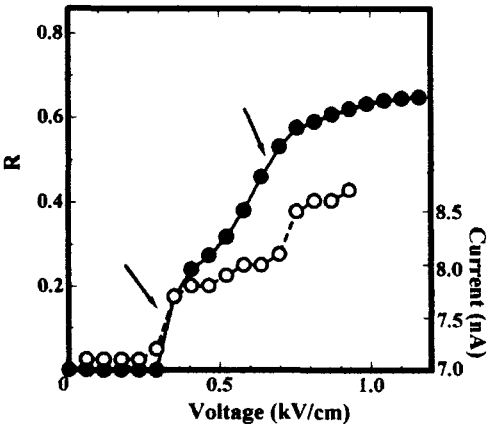

FIGURE 3 The transformed area(close circles) and stationary electric current(open cirles) vs applied voltages.

(The relative distance from the negative electrode to the boundary refered to the interelectrode distance, R, is taken as a measure of transformed area.)

When the field direction has been inverted between two threshold voltages, the boundary begins to move backward into the newly positive(originally negative) electrode, and at the same time, the new planar phase develops slowly from the opposite side(newly turned to the negative electrode). The phenomenon occurs reversibly and under a fixed strength of the field, the homeotropic area is kept constant with several repeated inversions of field

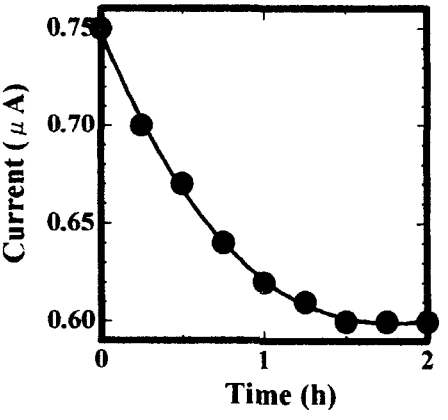

FIGURE 4 The variation of electric current through the LC cell following application of DC field much higher than the threshold voltage at room temperature.

direction. However, at a field strength above the second threshold(ca 0.7kV/cm), the repeated inversions of the field direction make the homeotropic area decrease and achieve ultimately the entire transformation of the homeotropic texture to the planar one. The backward movement of the boundary between the homeotropic and planar textures following an inversion of the electric field direction may be explained as follows : the charges initially injected from the negative electrode and accumulated on the glass surface may be carried away with inverting the field direction and then the specific interaction of N-terminal with the polar groups on the glass surface will be regenerated. In the newly developed planar texture, regular strips perpendicular to the field direction can be observed in the process of realignment following a field inversion and however no strip appears in the homeotropic area.

This fact suggests that the planar rotation of director with regular domain structure in the planar texture takes the lead and then the boundary movement follows after that. Along with the fact that the homeotropic texture is performed without any external field, the strong stabilization of the texture under the applied voltage implies the existence of strong interaction between polymer terminals and glass surface. If the origin of the interaction is electrostatic one, the dielectric constant of the used solvent should affect the anchoring strength. In order to change the dielectric constant of the solvent, a few amount of propionic acid is added to 1,1,2-trichloroethane. The values of the dielectric constant , ε , for mixtures of them are summarized in table.1.

Table.1 Dielectric constant of Solvents

Sample	Dielectric Constant (ε)
TriCE	7.182
Propionic acid	3.405
X_5	6.891
$X_{7.5}$	6.720
X_{10}	6.582

(X : The mixed solvent[a small amount of propionic acid is added to TriCE]. The subscripts[5,7.5,10] represents the volume fraction of propionic acid in the mixed solvents.)

As mentioned above, for the TriCE solution of PBLG, the perfect transformation to the planar texture over the entire area could not performed with the stepwise increment of voltage without the inversions of the field direction under the present experimental condition. However, the addition of small amount acid makes the threshold voltage extremely lower. Nevertheless, it bring to decrease the dielectric constant of solvent.

The voltage transforming the homeotropic texture to the planar over the whole region , Vc, is plotted against the composition of solvent in fig.5. The acidic molecule may easily associate with N-terminal of polymer and then the interaction between the polar groups on the glass surface and the terminal groups will become weak. The phenomenon suggests that the origin of the strong anchoring(tendency to perform homeotropic orientation) of PBLG may be rather in the specific electrostatic interaction of N-terminal than in the overall electrostatic interaction of the polar terminal residues with ionic charges on the glass surface.

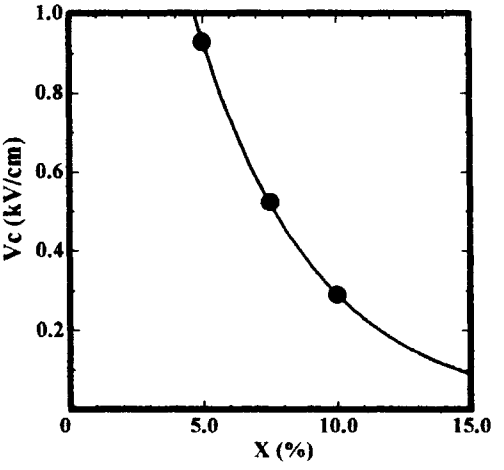

FIGURE 5 Vc vs the composition of the mixed solvents.

(Vc : A kind of critical field at which the homeotropic texture is transformed to the planar texture over the whole region in the cell.
X : The volume % of propionic acid in TriCE.)

CONCLUSION

The transformation of the homeotropic texture to the planar one could be observed in the LC solution of PBLG with applying an DC field across the cell as a kind of Frederiksz transition with a clear inversion wall. It is evident from the experimental result that there is the existence of the strong interaction between N-terminal of PBLG and the polar group on the glass surface.

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