JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY • Volume 43, Number 3, May/June 1999

Carrier Transport in Molecularly Diluted Liquid Crystalline Photoconductor

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The carrier transport properties of a molecularly diluted smectic liquid crystalline photoconductor, 2-(4'-octylphenyl)-6-dodecyloxynaphthalene (8-PNP-O12) and 2-(4'-hexyoxy)-6-octypbiphenyl (6O-BP-8) system, were investigated by time-of-flight technique, in order to clarify the nature of electronic conduction in the liquid crystalline mesophases. The mobility in the diluted liquid crystals was ambipolar, independent of both electric field and temperature in SmA and SmB phase as in the pure 8-PNP-O12, and continuously reduced with an increase in the diluent concentration. The reduction, however, remained within a small range of one third of that of pure material even in 60 mol%. The carrier transport in the diluted liquid crystals was described by the relation of a $\mu/\rho^2 \propto \exp(-2\,\rho/\rho_0)$, where μ is the mobility, ρ the average hopping distance, and ρ_0 a wavefunction decay constant of molecular orbital, indicating the 2-dimentional random hopping mechanism. The fairly large ρ_0 of 2.3 ~2.4 A characterizes a fast mobility gently decreasing with an increase in the diluent concentration. The molecular ordering within a smectic layer did not affect the carrier transport properties at all except the initial difference of the mobility, as far as comparison of those in SmA and SmB phases were concerned. In addition, the effect of self-organization of hopping site is discussed in terms of carrier transport in disorded materials system.

Journal of Imaging Science and Technology 43: 237–241 (1999)

Introduction

In these past two decades, organic photoconductors including molecularly doped polymers were well established for xerographic applications and have been increasing their importance as industrial materials.[1] This is due to the increasing demand in non-impact printing technologies for computer outputs, i.e., the emergence of a new business of laser printers and to the recent increasing activity in organic light emitting diodes.[2] All these are backed up by the unique nature of organic materials, i.e., variety of materials and their feasibility of designing and manufacturing new materials for increasing requirements in photoelectrical properties, in addition to feasibility of preparing large-area and uniform thin films in low cost.

In contrast to outstanding advances in their practical application, the nature of carrier transport properties in organic disordered systems have remained to be fully understood for a long time. In this decade, however, there was significant advance in its theoretical understanding, which owes to establishment of analytical method for abstracting the essence of carrier transport properties in various disordered systems, i.e., the disorder formalism proposed by Bässler[3] and to the recognition of the importance of carrier-dipole interaction in the carrier transport.[4,5] This must have never been brought without earnest and steady efforts to understand the nature made by the late Dr. Borsenberger and his co-workers.[1] Now, our understanding is coming up to the origin of the specific nature in the disordered carrier transport on the theoretical basis.[6–9]

At the same time, this understanding provides us with a guiding principal and a new idea for upgrading the present properties of organic photoconductors. Indeed, Bosenberger and co-workers demonstrated that the hole mobility is improved up to 10^{-3} cm^2/Vs even in conventional molecularly doped polymers by appropriate choice of a polymer matrix and a carrier transport material.[10] On the other hand, there was a coincidence in the different direction with his demonstration. That is, it is the discovery of a fast electronic conduction in discotic and smectic liquid crystalline mesophases, which is characterized by a high mobility over 10^{-3} cm^2/Vs independent of electric field and temperature.[11–15] This can be an alternative way to take for upgrading photoconductive properties outside of the conventional organic photoconductors.

The liquid crystalline photoconductors exhibit some kind of *crystal-like* self-organizing molecular alignments and *liquid-like* fluidity.[16] This unique feature provides us with a good basis of their practical application to large-area electronic devices. Thus, liquid crystalline photoconductors is a promising material for making a break-through in device applications of organic photoconductors currently limited by electrical properties of the materials.[17] Indeed, the conventional organic photoconductors have been practically used in xerographic drums and more recently in organic light emitting diodes as mentioned above, but their electrical properties characterized by a small mobility of 10^{-5} ~ 10^{-6} cm^2/Vs that depends on electric field and temperature are rather poor from electronic materials point of

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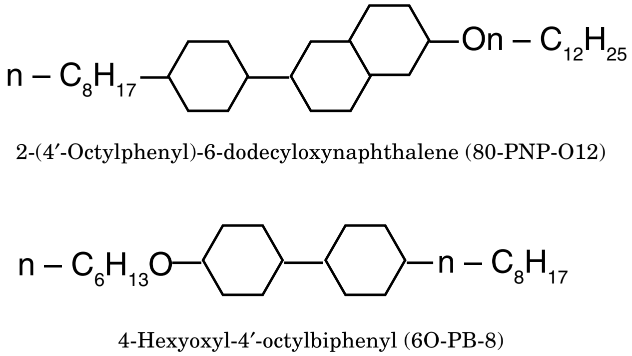
Original manuscript received December 11, 1998



2-(4′-Octylphenyl)-6-dodecyloxynaphthalene (80-PNP-O12)

4-Hexyoxyl-4′-octylbiphenyl (6O-PB-8)

Figure 1. Chemical structures of 8-PNP-O12 and 6O-BP-8.

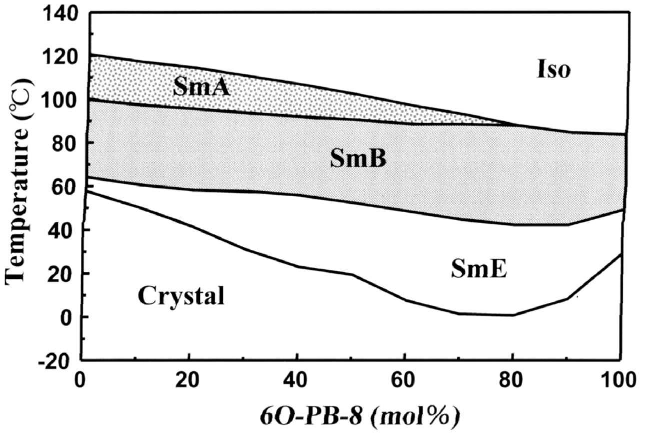


Figure 2. Phase diagram of 6O-BP-8 and 8-PNP-O12 system.

view. This inferior property, however, is covered well in the present application by specific device structures and performance: in xerographic applications, the drums are illuminated at a high electric field of $10^5 \sim 10^6$ V/cm and accessed at a very slow frequency of 0.1~1 Hz (6 ~ 60 ppm); on the other hand, the cell thickness is thinned down to less than 0.1 μm in order to establish a high electric field of $10^5 \sim 10^6$ V/cm and a fast response in the light emitting diodes.[2]

There is another reason why the liquid crystalline photoconductor is an important material deserving our attention. That is, it is likely that their carrier transport characteristics provide us with a new insight into the nature of carrier transport in disordered systems ever established. This is because liquid crystalline materials are a unique materials system just between ordered and disordered materials, with which we can test and confirm our established understanding: the liquid crystals exhibit a variety of molecular alignment, where each molecule is thermally fluctuated; for example, in smectic liquid crystals where all the molecules sit in layers and are oriented in a direction with thermal fluctuation, the molecular alignment in the layer are ordered from “liquid-like” in SmA phase to “almost crystal” in SmE phases, and so on.[16]

In this work, we have investigated the carrier transport in molecularly diluted liquid crystalline photoconductors in order to characterize their carrier transport properties by transient photocurrent measurements. Here, we describe the effect of molecular dilution on the carrier transport in liquid crystalline photoconductors elucidated and discuss self-organization in the molecular system in comparison with the conventional diluted carrier transport system, i.e., molecularly doped polymers.

Experimental

A photoconductive smectic liquid crystal, 2-(4'-octylpheny)-6-dodecyloxynaphthalene (8-PNP-O12) was prepared by a cross coupling reaction of corresponding benzene and naphthalene derivatives with a palladium catalyst described elsewhere[14] and purified by recrystallization from *n*-hexane. 8-PNP-O12 exhibits phase transitions from Crystal to SmB phase at 79°C, from SmB to SmA phase at 100°C, and from SmA to isotropic phase at 121°C. A diluent liquid crystal, 2-(4'-hexyloxy)-6-octypbiphenyl (6O-BP-8) was prepared similarly from corresponding benzene derivatives, which exhibit SmE phase between 30°C and 49°C, and SmB phase between 49°C and 83°C. The chemical structures of these materials are shown in Fig. 1. These two smectic liquid crystals were miscible without phase separation in the present experimental conditions up to ~60 mol%.

The liquid crystal cells were prepared by capillary-filling the mixed liquid crystals in isotropic phase into the glass cells made of indium-tin oxide coated glass plates (electrode area: 16 mm^2) and a silica spacer. The resulting molecular orientation was parallel to the electrode surface in terms of longitudinal axis of the liquid crystal molecule, i.e., homogeneous alignment. This was never affected by the electric field applied.

The conventional time-of-flight setup, equipped with a N$_2$-laser and digital oscilloscope, was used in order to measure transient photocurrents. The mixed liquid crystals exhibited optical absorption at 337 nm high enough to ensure the one carrier condition for carrier transit. The transit time was determined with an inflection point in double logarithmic plots of the transient photocurrents as a function of time.

Result and Discussion

6O-BP-8 used as a diluent is a calamitic (rod-like) liquid crystal and has similarity to a host material, 8-PNP-O12 in its chemical structure. This is beneficial to the suppression of phase separation and the maintenance of liquid crystalline phases in a wide concentration range, which enables us to establish a wide variation of the hopping distance while keeping their microscopic molecular circumstances unchanged. Thus, it exhibited complete compatibility when mixed with 8-PNP-O12 and gave a liquid crystalline mixture in the whole range of concentration studied up to ~60 mol%. The mixture exhibited a new smectic phase at the lower temperature region, which is never seen in pure 8-PNP-O12, probably SmE. SmB and SmA phases were well maintained in the lower concentrations less than 80 mol%. SmA phase was sensitive to 6O-BP-8 concentration and its temperature range was decreased with an increase in the concentration and finally disappeared more than 80 mol%, as shown in Fig. 2.

To clarify true effects of the dilution on the carrier transport, the transient photocurrent measurement was focused on SmB, SmA and isotropic phases that appear in pure 8-PNP-O12.[14] The photocurrents tended to be reduced as the diluent concentration was increased. As is expected from the ambipolar nature of carrier transport in pure 8-PNP-O12 reported previously, the mixed liquid crystals also exhibited the ambipolar carrier

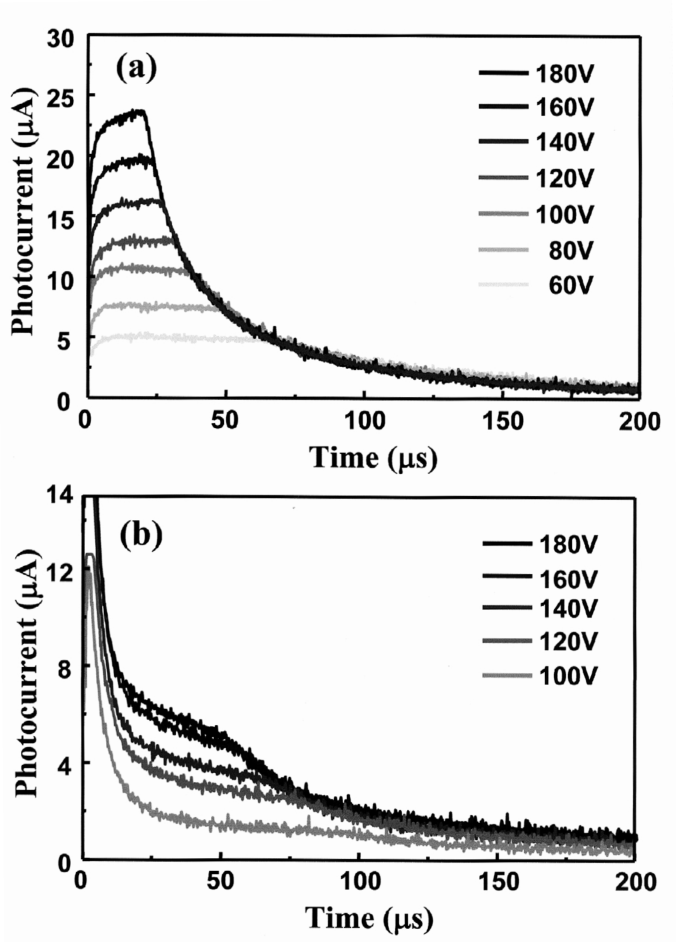


Figure 3. Transient photocurrents of 50 mol% diluted 8-PNP-O12 with 6O-BP-8 in SmB phase illuminated with a N_2-laser pulse of 337 nm; (a) For positive carriers; (b) for negative carriers. The cell thickness was 15 μm at 80°C (SmB phase).

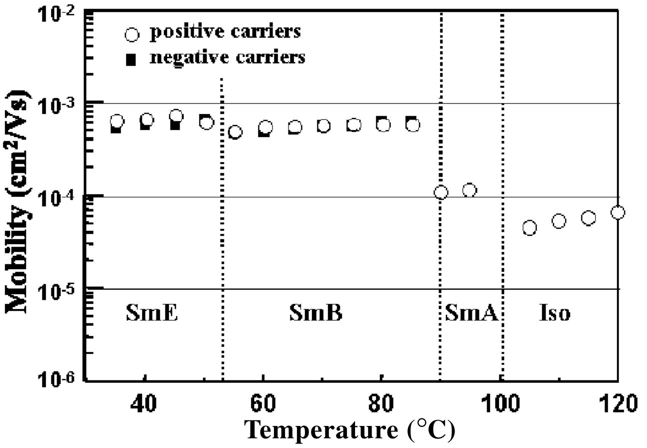


Figure 4. Carrier mobility in 50 mol% diluted 8-PNP-O12 with 6O-BP-8 as a function of temperature. The squares and circles indicate positive carriers and negative carriers, respectively. The mobility was measured at 1 × 10^4 V/cm.

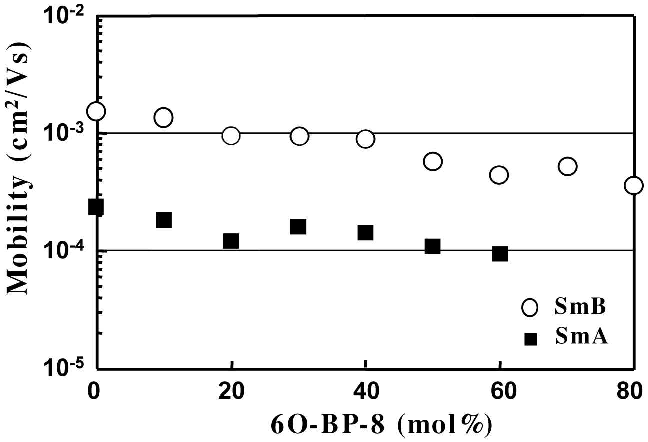


Figure 5. Carrier mobility of diluted 8-PNP-O12 as a function of 6O-BP-8 concentration in SmB (80°C) and SmA (110°C) 1 × 10^4 V/cm.

transport basically. In SmA and isotropic phases, however, the transient signals for negative carriers were too small to determine the transient time when the diluent concentration was more than 40 mol%.

Figure 3 shows typical transient photocurrents in SmB phase of 50 mol% diluted 8-PNP-O12. The transient photocurrents were non-dispersive irrespective of the carrier sign. There was initial delay for positive carriers probably due to carrier trapping at surface states on the ITO electrode and initial decay for negative carriers. The μ/τ_t plot as a function of V/d^2 gave a well-defined line starting from zero, where μ is the mobility of carriers, τ_t the transit time, V the applied voltage, and *d,* a cell thickness, indicating that the mobility does not depend on the applied electric field. The carrier mobility was determined from a slope of the line and was 6 × 10^{-4} cm²/Vs irrespective of carrier signs. This mobility was one-third of that in pure 8-PNP-O12. This transport is reasonably attributed to the electronic conduction as discussed previously because of high viscosity in the present mixed liquid crystals. In SmA and isotropic phases, the mobility for positive carriers was determined to be 1.1 × 10^{-4} cm²/Vs and 5 × 10^{-4} cm²/Vs, respectively. These mobilities were corresponding to 40 ~ 50% of those in the pure 8-PNP-O12, while the mobility could not be determined for negative carriers because of small signals as described.

The mobilities at 1 × 10^4 V/cm are plotted as a function of temperature in Fig. 4. In smectic phases, the mobility was independent of temperature, while Arrhenius type of temperature dependence was observed in isotropic phase. The ionic conduction is most likely in isotropic phase as is the case of pure 8-PNP-O12.[14]

The present experimental results were summarized in Fig. 5, where the mobilities in SmA and SmB phases were plotted as a function of the 6O-BP-8 concentration in 8-PNP-O12. The mobilities were almost equal for positive and negative carriers and gave no difference in the figure. In fact, the mobility was continuously decreased with an increase in the 6O-BP-8 concentration irrespective of the phases, but its reduction remained within one-third of corresponding mobilities of pure 8-PNP-O12.

In smectic phases, all the molecules align in layers with an orientation in one direction. The distance between the smectic layers is about 36A, which is very far compared with 4A for the average distance between liquid crystalline molecules within a smectic layer. Therefore, it is reasonable that the photogenerated carriers hop among the molecules in the smectic layer to reach the counter electrode when the electric field is applied parallel to the layer. This is the case of the present experiments, i.e., the homogeneous alignment.

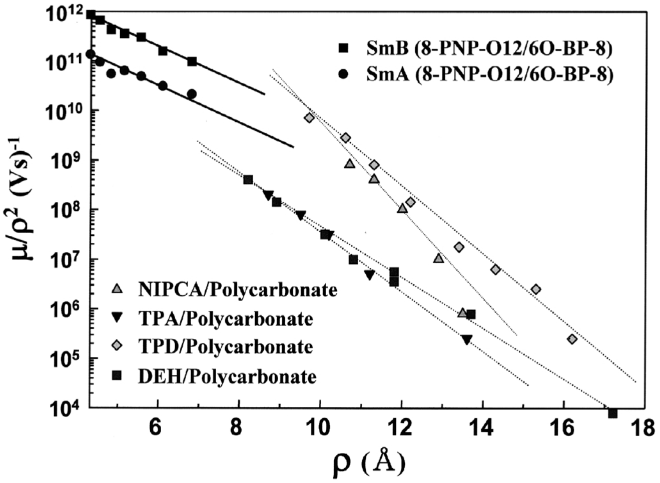


Figure 6. Concentration dependence of carrier mobility in molecularly diluted 8-PNP-O12 and typical molecularly doped polymers.

Let us consider the effect of dilution semi-quantitatively. The HOMO level of 6O-BP-8 is higher than that of 8-PNP-O12, because of small molecular-orbital of biphenyl moiety. Therefore, 6O-BP-8 is expected to be electronically inactive as an impurity as far as 6-PNP-O12 molecules contribute as the major hopping passway. Therefore, 6O-BP-8 can be an ideal diluent for 8-PNP-O12. The average distance between 8-PNP-O12 molecules for each concentration can be calculated and range from 4A to 6.8A in the range of 0~60 mol%. This is very different from more than 8A in the molecularly doped polymers. It should be noted that the reduction of mobility remained within 40~50% in spite of this large change in the hopping distance.

Assuming 2-D random hopping of carriers in the smectic layer, the experimental data were plotted as a function of the average hopping distance caluculated, according to the relation,[18] $\mu \propto \rho^2 \exp(-2\rho/\rho_0)$ as is the case of the carrier transport in disordered systems, where μ is the mobility, ρ the average hopping distance, and ρ_0 a wavefunction decay constant of molecular orbital. In fact, in the fluid media exhibiting a high mobility over 10^{-3} cm^2/Vs, it is reasonable that the contribution of translational molecular motion is negligible to the carrier transport or hopping, because of a very short estimated residence time of ~10^{-9} s at each hopping site. As shown in Fig. 6 accompanied by representative results for the molecularly doped polymers,[19–21] log μ/ρ^2 gives a linear relation with ρ. This result indicates that the carrier transport in smectic mesophases can be described by the 2-D random hopping model within the smectic layers. It is clear from Fig. 6 that in the diluted liquid crystals, the average hopping distance of 4~6.8A is fairly small compared with these of molecularly doped polymers of > 8A. This results from a closed packing of the molecules due to the self-organization in the mesophase. In addition, the slopes of lines for the diluted liquid crystals are gentler than those of the molecularly doped polymers, indicating larger ρ_0 in the diluted liquid crystals. In fact, ρ_0 was determined to be 2.3A and 2.4A for SmB and SmA phases, respectively. These values are fairly large comaperd with a typical value of 1 ~ 2A in the molecularly doped polymers, which characterizes the fast carrier transport and explains a small reduction of mobility, i.e., 50 ~ 60%, when the diluent concentration was increased.

As far as molecular ordering within the smectic layer is concerned, there is a big difference between SmA and SmB phases: in SmA phase, all the molecules sit at random in the smectic layer; on the other hand, the molecules sit in hexatic order in SmB phase. Therefore, it is likely that microscopic circumstance of molecules in the smectic layer is different in these phases in terms of energetic and spatial disorder. In the pure 8-PNP-O12, however, there is no difference in the carrier transport behaviors except a fairly big difference in the mobility of one-order of magnitude. This is true in the present diluted liquid crystals as well. As described, no difference is observed even in the ρ_0 characterizing the hoping site. This indicates that the basic physical process is the same in SmA and SmB phases in terms of determining hopping rate. Therefore, the mobility difference between these mesophases including those in the pure 8-PNP-O12 is attributed to the difference in the pre-factor mobility, μ_0.

Disorder formalism as described in the following equation, where μ is the mobility, μ_0 a prefactor mobility, σ the density of states, Σ a parameter characterizing the degree of positional disorder, *k* the Boltzman constant, *E* the electric field, *T* the temperatrure, and *C* an empirical constant of 2.9×10^{-4} (cm/V)$^{1/2}$, specifies the the carrier transport characteristics in individual materials systems.

For $\Sigma \geq 1.5$,

$$\mu(\sigma, \Sigma, E, T) = \mu_0 \exp[-2\sigma/3kT)^2] \exp[C\{(\sigma/kT)^2 - \Sigma^2\}E^{1/2}]$$

For $\Sigma < 1.5$,

$$\mu(\sigma, \Sigma, E, T) = \mu_0 \exp[-2\sigma/3kT)^2] \exp[C\{(\sigma/kT)^2 - 1.5^2\}E^{1/2}]$$

In this formalism, if the disorder manifolds become zero, the temperature and electric field dependences disappear as is the case of the molecular crystals. In the liquid crystals however, the molecular alignment is not fixed and thermally fluctuated, so that there exist the disorder to any appreciable extent. Therefore, we cannot understand these unique carrier features of liquid crystalline photoconductors in the framework of disorder formalism. There is a need for ample experimental data to describe a total view of the carrier transport before its formalism.

Conclusion

The electronic carrier transport properties in a diluted liquid crystalline photoconductor, i.e., 6O-BP-8 and 8-PNP-O12 system, was investigated by transient photocurrent measurements. The mobility was ambipolar, independent of electric field and temperature, and continuously reduced with an increase in the diluent concentration studied up to 60 mol%, but the reduction remained within the range of one-third of that of pure 8-PNP-O12. In isotropic phases, however, the transport was ionic whose mobility was on the order of 10^{-5} cm^2/Vs and depended on temperature.

It is revealed that the carrier transport characteristics in the mesophase can be described by a 2-D random hopping model, which is characterized by a relatively small average hopping distance, of 4~7A and a large ρ_0 of 2.4A. This explained an apparently gentle dependence of the mobility on the diluent concentration.

There remain many interesting experimental results to be explained, including no mobility dependence on electric field and temperature, and no effect of molecular ordering in intra-smectic layer on the mobility. The liquid crystalline system is a very unique materials system enjoying both macroscopic molecular alignment and microscopic molecular disorder. The experimental and theoretical understanding of carrier transport in this system gives us a new insight into the understanding of that in conventional disordered systems and re-inforce its framework of our understanding. ▲

Acknowledgements. We thank M. Funahashi for guiding material preparation and TOF measurements. This work was partly supported by Grant-in-Aid for Scientific Research on Priority Area on Basic Research from Ministry of Education, Sport, and Culture of Japan.

References

1. P. M. Borsenberger and D. S. Weiss, Organic Photoreceptors for Xerography, Marcel Dekker, Inc. New York, 1998.
2. C. W. Tang and S. A. van Slyke, *Appl. Phys. Lett.* **51,** 12 (1987).
3. H. Bässler, *Phys. stat. sol. (b)* **175,** 15 (1993).
4. P. M. Bosenberger and H. Bässler, *J. Chem. Phys.* **95,** 5327 (1991).
5. M. Sugiuchi and H. Nishizawa, *J. Imag. Sci. Technol.* **37,** 245 (1993).
6. H. Nishizawa, M. Sugiuchi and T. Uenohara, *Proc. Mat. Res. Soc.* **227,** 33 (1992).
7. A. Dieckman, H. B. H. Bässler, and P. M. Borsenberger, *J. Chem. Phys.* **99,** 8136 (1993).
8. A. Hirao and H. Nishizawa, *Phys. Rev. B* **56**, R2904 (1997).
9. D. H. Dunlap, P. E. Parris and V. M. Kenkre, *Phys. Rev. Lett.* **77**, 542 (1996).
10. P. M. Borsenberger, W. T. Gruebaum, L. J. Serriero, and N. Zumbulyadis, *Jpn. J. Appl. Phys.* **34,** L1597 (1995).
11. D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schumacher, and K. Siemensmeyer, *Phys. Rev. Lett.* **70,** 457 (1993).
12. D. Adam, P. Schuhmacher, J. Simmerer, L. Haussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf, and D. Haarer, *Nature* **371**, 141 (1994).
13. M. Funahashi and J. Hanna, *Phys. Rev. Lett.* **78**, 2184 (1997).
14. M. Funahashi and J. Hanna, *Appl. Phys. Lett.* **71**, 602 (1997).
15. M. Funahashi and J. Hanna, *Appl. Phys. Lett.* **73**, 3733 (1998).
16. Handbook of Liquid Crystals, D. Emus, J. W. Goodby, G. W. Spiess, and H. W. VillP, Eds., Wiley-VCH, 1998.
17. A. Miller and A. Abrahams, *Phys. Rev.* **120,** 745 (1960).
18. K. Kogo, T. Gouda, M. Funahashi, and J. Hanna, *Appl. Phys. Lett.* **73,** 1595 (1998).
19. G. Pfister, *Phys. Rev. B* **16,** 3676 (1977).
20. J. X. Mack. L. B. Schein and A. Peled, *Phys. Rev. B* **11,** 39 (1989).
21. G. Pfister, *Phys. Rev. B* **16,** 3676 (1977).