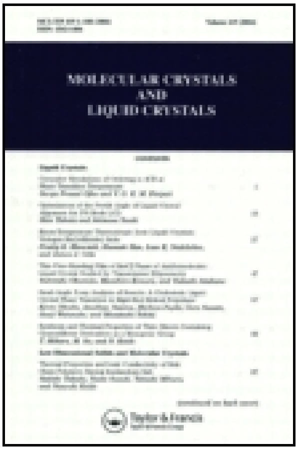

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 22 Sep 2010

To cite this article: Jin-Woo Oh, Chil-Sung Choi, Choongkeun Lee & Nakjoong Kim (2007): The Effect of the Electro Optic Chromophore on the Space Charge Field Formation in Polymeric Photorefractive Composites, Molecular Crystals and Liquid Crystals, 471:1, 373-379

To link to this article: http://dx.doi.org/10.1080/15421400701549009

Mol. Cryst. Liq. Cryst., Vol. 471, pp. 373–379, 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701549009

The Effect of the Electro Optic Chromophore on the Space Charge Field Formation in Polymeric Photorefractive Composites

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We investigated the effect of the electro-optic chromophore concentration on the space charge field formation in polymeric photorefractive composites. For polymeric photorefractive materials, the electro optic chromophore is one of the most substantial components, because it is to provide a refractive index modulation in response to the electric field and probably can act as trap which is essential part to promote space charge field inside the material. The photoconductivity was decreased as the chromophore ratio increased. However, the space charge field measured by our characterized method remains unchanged. This result can be explained that presence of chromophore may reduce the photoconductivity, but also facilitate the charge trapping process.

Keywords: chromophore concentration; magnitude of space charge field; photoconductivity; trap

INTRODUCTION

The photorefractive (PR) effect refers to the spatial modulation of the refractive index of material due to redistribution of photo-charge carriers [1]. Under the illumination of nonuniform light formed by the interference of two coherent laser beams, a spatially oscillating space charge field is formed arising from the generation and the redistribution of photoinduced charges. The refractive index of material is

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subsequently modulated via an electro-optic (EO) effect by space charge field [2].

The EO chromophore is one of the most substantial components deciding the photorefractive property of the polymeric PR composite, since chromophore is to provide a refractive index change in response to the space charge field. Chromophore also can participate in photoconducting processes, such as photo-charge generation, transport, and trapping. Diaz-Garcia *et al.* [3] studied poly(N-vinylcarbazole) (PVK, 49.5%)/dicyanostyrene(DCST, 35%)/(butyl benzyl phthalate (BBP, 15%)/C_{60}(0.5%) composites, in which different DCST derivatives with various I_P were utilized as EO chromophores. And Ostroverkhova and Singer [4] varied the concentration of a chromophore complementary to that of a plasticizer (BBP) (PVK(49%)/EO(x%)/BBP(50-x%)/C_{60}(1%)). It was confirmed that chromophores with I_P lower than that of the transport molecule can create deep traps in the PR material, while shallow traps form due to impurities and defects in the transport molecule itself [5].

In this work, we investigated the effect of the chromophore concentration on the magnitude of the space charge field formation. To measure the magnitude of space charge field, we used the characterization method presented recently in our previous article [6].

EXPERIMENTAL

In this study, low T_g PR materials were prepared by doping the optically anisotropic chromophore, 2-{3-[(*E*)-2-(dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexenyliden} malono-nitrile (DB-IP-DC), into a photoconducting polymer matrix, poly[methyl-3-(9-carbazoly)propylsiloxane] (PSX-Cz) sensitized by 2,4,7-trinitro-9-fluorene (TNF) as shown in Figure 1. The composition of the samples is shown in Table 1. By varying the BBP ratio, the T_g of all sample was adjusted to (26 ± 1)°C.

The photoconductivity of samples was measured at a wavelength of 632.8 nm using a simple photocurrent method. The current flowing through the sample was measured during the illumination of light with an intensity of 20 mW/cm^2 at an applied field of 30 V/μm. We measured the magnitude of the space charge field using the method that had been reported in our previous article [6]. The basic scheme of the method can be summarized as follows. The chromophore group that is previously aligned along external electric field is reoriented by newly-formed space charge field. The variation of the birefringence is induced by the reorientation and is closely associated with the space charge field. Using numerical analysis based on the oriented gas

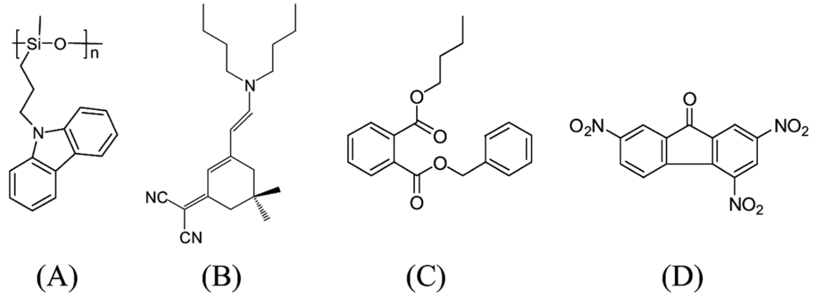

FIGURE 1 Chemical structure of components of photorefractive composite: (A) PSX-Cz, (B) DB-IP-DC, (C) BBP, and (D) TNF.

model and the index ellipsoid method, we can determine the magnitude of the space charge field from the variation. Details on this method were well described in Ref. [6].

RESULTS AND DISCUSSION

Polymeric composite systems with a T_g around room temperature exhibit excellent photorefractive properties due to the in situ reorientation of the birefringent chromophore molecule under a spatially modulated space charge field [7]. As shown in Table 1, all the samples had a T_g in the range of 25.0–26.6°C and formed a stable amorphous glassy material with no crystallization or degradation.

Figure 2 shows the field dependence of the photocurrent of samples. The photocurrent increased distinctly with increasing electric field. The electric field dependence on the photocurrent resulted from

TABLE 1 Photoconducting Polymer, Chromophore, BBP Concentration (wt%), Glass Transition Temperature (T_g), Photoconductivity (σ_{ph}), and Space Charge Field (E_{sc}).

Sample	PSX-Cz (wt%)	jDB-IP-DC (wt%)	BBP (wt%)	T_g(°C)^a	σ_{ph} (pS/cm)^b	E_{sc} (V/μm)^a
1	69	22	8	26.3	16.29	5.80
2	69	24	6	26.6	15.00	5.92
3	69	26	4	26.6	12.80	6.95
4	69	28	2	25.0	11.06	6.68
5	69	30	0	26.5	10.46	6.07

^{*a}Determined by differential scanning calorimetry.
^{b}Measured at $E_0 = 30\,V/\mu m$.

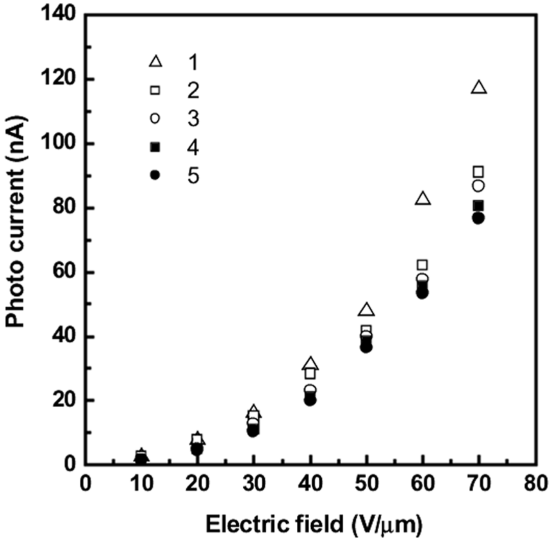

FIGURE 2 Field dependence on the photo current (σ_{ph}) for samples 1–5.

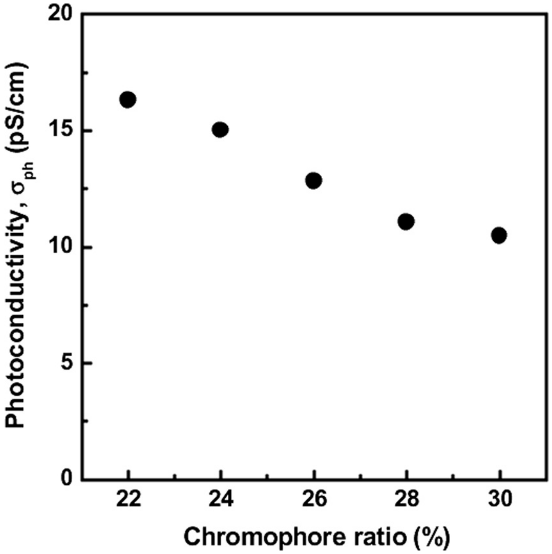

FIGURE 3 Correlation between the photo-conductivity (σ_{ph}) and the chromophore ratio (%) at 30 V/µm for samples 1–5.

electric-field-assisted separation of charge from the electron-hole pair with a high energy distribution. Figure 3 shows the photoconductivity of the samples as a function of the chromophore concentration. The photoconductivity is considerably decreased with increasing the chromophore concentration. The photoconductivity, which is crucial to the space charge field formation, is dependent on the photocharge generation, charge transport, and trap as follow [8]:

$$\sigma_{ph} = ne\mu = \left(\frac{\phi\alpha I\tau}{h\nu}\right)e\mu \tag{1}$$

where n is the density of carriers produced at a light intensity, I, e is the elementary charge, ϕ is the photocharge generation efficiency, α is the absorption coefficient at frequency ν, h is Plank's constant, τ is the carrier lifetime, and μ is the hole mobility. The diminishment of photoconductivity with chromophore concentration as shown in Figure 3 can support that chromophore may act as a trap.

The field dependence of the space charge field of samples 1–5 was studied. The formation of the space charge field that is phase-shifted with respect to the illumination pattern is an important step in the photorefractive effect. The space charge field measured by our characterized method was linearly increased with increasing electric field, as shown Figure 4. The magnitude of the space charge field is related to

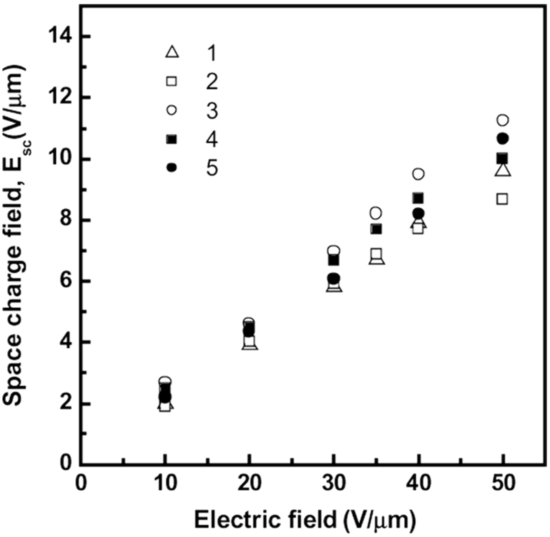

FIGURE 4 Field dependence on the space charge field (E_{sc}) for sample 1–5.

the density of charge carriers and traps by Poisson's equation [9].

$$\frac{\partial E}{\partial x} = \rho - N^{-} + T^{+} \tag{2}$$

where ρ is the hole density, N^{-} is the ionized sensitizer density, and T^{+} is the ionized trap density. The space charge field increases with the hole density and the trap density. Figure 5 shows the space charge field of the samples measured as a function of the chromophore ratio. In chromophore concentration ranging from 22 to 26 wt%, the space charge field is somewhat increased with increasing the chromophore ratio, although the conductivity is decreased in the same range as shown Figure 3. In this range, the increased trap density with increasing chromophore has a favorable influence to achieve the space charge field, although it leads to decreasing of photoconductivity by reduced hole density. In ranging from 26 to 30 wt%, however, the space charge field is decreased with increasing the chromophore ratio similar to the trend of photoconductivity. In this range, the decreased hole density is larger than the increased trap density which affect space charge field formation. From this result, we can confirm that the presence of traps is necessary for achieving high space charge field in the polymeric PR

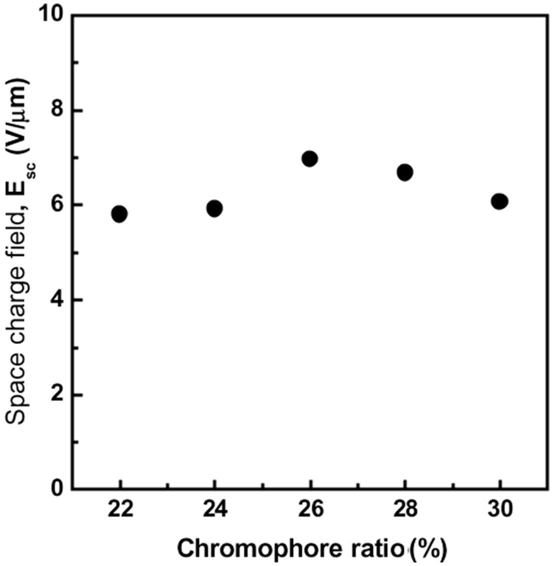

FIGURE 5 Correlation between the space charge field (E_{sc}) and chromophore ratio (%) 30 V/μm for samples 1–5.

composite, but excessive amounts of traps could be detrimental for PR dynamics such as photoconductivity.

CONCLUSION

The space charge field might be formed through a multiple process such as charge generation, charge transport, and charge trapping process. As expected, the photoconductivity was decreased with increasing the chromophore density. However, the space charge field was not changed much as the chromophore concentration was increased. This means that the chromophore may act as a trap to reduce the photoconductivity and also it helps to enhance the space charge formation process.

REFERENCES

[1] Gunter, P. (Ed.). (2000). *Nonlinear Optical Effects and Materials*, *Springer Series in Optical Sciences*, Springer: Heidelberg, Vol. 72, 301–304.

[2] Chun, H., Moon, I. K., Shin, D. H., Song, S., & Kim, N. (2002). *J. Mater. Chem.*, *12*, 858–862.

[3] Diaz-Garcia, M. A., Wright, D., Casperson, F. D., Smith, B., Glazer, E., Moerner, W. E., Sukhomlinova, L. I., & Twieg, R. J. (1999). *Chem. Mater.*, *11*, 1784.

[4] Ostroverkhova, O. & Singer, K. D. (2002). *J. Appl. Phys.*, *92*, 1727.

[5] Daubler, T. K., Bittner, R., Meerholz, K., Cimrova, V., & Neher, D. (2000). *Phys. Rev. B*, *61*, 13515.

[6] Joo, W. J., Kim, N. J., Chun, H., Moon, I. K., & Kim, N. (2002). *J. Appl. Phys.*, *91*, 6471–6475.

[7] Nalwa, H. S. & Miyata, S. (1997). An introduction to photorefractive polymers. *In: Nonlinear Optics of Organic Molecules and Polymers*, CRC Press: New York, London, Tokyo, 480.

[8] Moerner, W. E., Grunnet-Jepsen, A., & Thompson, C. L. Annu. (1997). *Rev. Mater. Sci.*, *27*, 585.

[9] Schildkraut, J. S. & Buettner, A. V. (1992). *J. Appl. Phys.*, *72*(5), 1888.