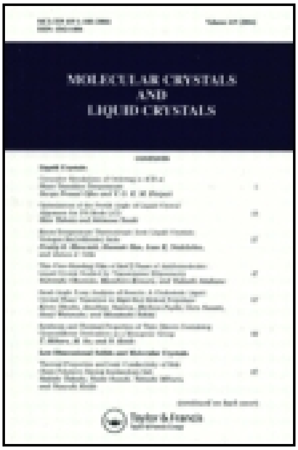

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Dependency of the Photo-Charge Generation Efficiency on the Photoconductivity and on the Space-Charge Field in Photorefractive Polymeric Composites

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Space-charge field is considered as an important factor determining photorefractive efficiency of polymer composites. Recently, we proposed a simple method which can measure the space-charge field built in photorefractive materials. Six polymeric photorefractive composites with different electron acceptor as a photosensitizer were prepared to vary the photo-charge generation efficiency and consequently to vary the space-charge field only. We investigated the dependency between photo-charge generation efficiency, photoconductivity, and space-charge field.

Keywords: charge generation efficiency; space charge field; photoconductivity; photorefractive composite

1. INTRODUCTION

The interference of the two coherent beams creates a light pattern in the material, with regions of high and low intensity. In the regions where the light is intense, absorption can generate both positive and negative charges, which separate and rearrange themselves, aided by the application of an external electric field. As the charges separate, they give rise to an internal space charge field. The field in turn causes changes in the index of refraction. The net result is the creation of a refractive-index grating in the material (a hologram), with the

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periodicity of the grating reflecting the interference pattern of the laser beams [1]. These materials should possess two important properties, which are photoconductivity and electro-optic property.

The formation and erasure of space charge field in photoconductive polymers have not been as thoroughly studied as in inorganic photorefractive crystals. Recently, Schildkraut and coworkers [2] developed a theoretical model in which the space charge field was solved both numerically and analytically (zero- and first-order). The more recently, the photorefractive model was further developed by Ostroverkhova and Singer [3] who introduced in the model two kinds of traps: shallow and deep. However, this phenomenon of formation of the space charge field was not understood until now.

We recently reported the high performance photorefraction of poly[methyl-3-(9-carbazoly)propylsiloxane] (PSX-Cz)-based photorefractive composite [4] and proposed a new method which is capable of measuring the magnitude of space charge field in the low glass transition temperature (T_g) organic photorefractive materials for the first time [5]. We have found that a space charge build-up process and an electro-optic modulation are crucial parts governing the efficiency and response time of photorefractivity.

In this paper, we investigate the dependence of photo-charge generation efficiency on the formation of space charge field in low T_g polymer photorefractive composites. The photo-charge generation efficiency can be altered using various electron acceptors with different electron affinities.

2. EXPERIMENTS

2.1. Materials and Device Fabrications

Photorefractive polymer composites were prepared by doping the optically anisotropic chromophore, 2-{3-[(*E*)-2-(dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexenyliden} malononitrile (DB-IP-DC), into photoconducting polymer matrix, poly[methyl-3-(9-carbazolyl) propylsiloxane] (PSX-Cz) sensitized by various electron acceptors. PSX-Cz and DB-IP-DC chromophore were synthesized by the previously described methods [4]. Electron acceptors (Kanto Chem. Co. Inc.) was used after purification. The composition of polymeric composite was PSX-Cz: DB-IP-DC: acceptor = 79:20:1 by wt%. The chemical structures of polymeric photorefractive composites are described in Figure 1. A predetermined mass of the components was dissolved in 1,1,2,2,-tetrachloroethane, and the resulting solution filtered through a 0.2 μm filter. The composite was cast on indium tin oxide (ITO) glass

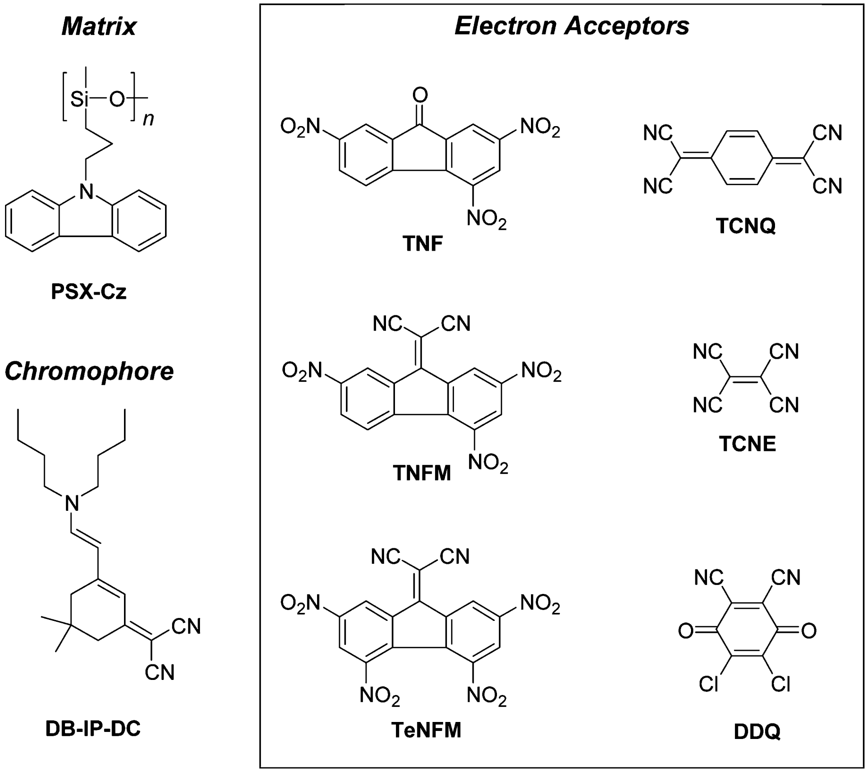

FIGURE 1 Chemical structures of photoconducting polymer matrix (PSX-Cz), electro-optic chromophore (DB-IP-DC) and electron acceptors (TNF, TNFM, TeNFM, TCNQ, TCNE, DDQ).

plates, dried for 12 h at ambient temperature, and subsequently heated in an oven at T = 50°C for 24 h to remove any residual solvent. Then, the composite was softened by placing it on a hot plate at T = 100°C. This was then covered with second ITO-coated glass. The thickness of the film was controlled using a Teflon spacer between the two ITO glass plates.

2.2. Measurements

The glass transition temperature (T_g) of the composite was determined by differential scanning calorimetry (Perkin Elmer DSC7). Table 1 summarizes UV absorption maxima of the polymer composites prepared.

TABLE 1 Absorbance Maxima and Glass Transition Temperatures of the Composites Prepared[a]

Code	Electron acceptor	$\lambda^{b}_{\max}$ (*nm*)
Co-A	TNF	277
Co-B	TNFM	300
Co-C	TeNFM	292.5
Co-D	TCNE	263
Co-E	TCNQ	396.5
Co-F	DDQ	241

[a] composition; PSX-Cz:DB-IP-DC:electron acceptor = 79:20:1.
[b] in toluene.

The photo-charge generation efficiencies of the polymeric composites were determined using the xerographic discharge technique [6]. The photon flux density was a 8.48×10^{14} photon $\cdot$ m^{-2} $\cdot$ s^{-1} at a wavelength of 632.5 nm. The magnitude of space charge field measurements was performed on about 80 μm-thick samples sandwiched between ITO electrodes using a our previous method [5]. The diffraction efficiency of the photorefractive materials was determined using a degenerated four-wave mixing (DFWM) experiment. Two coherent laser beams with $\lambda = 632.5$ nm were irradiated on the sample in the tilted geometry at an incident angle of $\theta = 15^\circ$ and 45° with respect to the sample's normal axis. The writing beams were both *s*-polarized, and had equal intensities of 30 mW/cm^2. The recorded photorefractive grating was read by a *p*-polarized counter-propagating beam. An attenuated reading beam with a very weak intensity of 0.06 mW/cm^2 was used. The magnitude of diffraction efficiency was determined from the measured transmitted and diffracted intensities of the reading beam, using the relation:

$$\eta = \frac{I_{R,\text{diffracted}}}{I_{R,\text{diffracted}} + I_{R,\text{transmitted}}}$$

.

3. RESULTS AND DISCUSSION

It is well known that the refractive index modulation of a low-T$_g$ photorefractive material can be enhanced by the orientation of a NLO chromophore in response to the space-charge [7]. At normal temperature, all composites are stable amorphous glassy materials which exhibit T_g around room temperature and no crystallization or degradation, based on DSC experiments.

The characterization of the photoconductive properties of a given photorefractive polymer are important since they control the formation of the internal space charge field that is responsible for the refractive index modulation through the electro-optic effect. Photo-charge generation efficiency were obtained using the xerography discharge technique, which is based on the measurement of the decay rate of the surface potential of a sample under illumination of He-Ne laser. Photo-charge generation efficiency and absorption coefficient of the devices at the wavelength of 632.5 nm were plotted in Figure 3.

Co-B, composite with TNFM, exhibits the best photo-charge generation quantum yield and Co-D, composite with TCNE, exhibits the worst one as seen at Figure 2. It seems that photo-charge generation efficiency is closely related to absorption coefficient of the composites. The photo-charge generation quantum yield depends not on the electron affinity of the electron acceptors but on their molecular configuration.

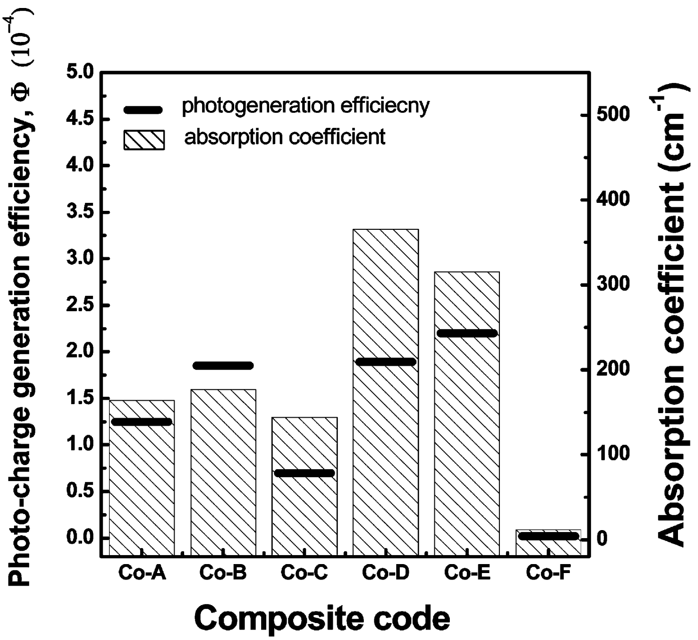

FIGURE 2 Photo-charge generation efficiency and absorption coefficient of polymeric PR composites at 632.5 nm.

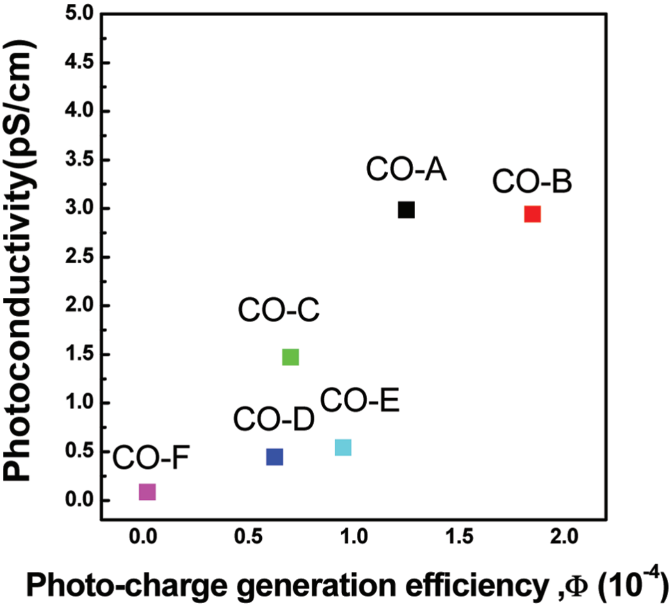

FIGURE 3 Plot of photoconductivity against photo-charge generation efficiency. Photoconductivity were measured under 60 V/μm at 3°C above T_g.

Photoconductivity is an important factor to be measured for the characterization of photorefractive performance, since it is a combined feature of the photo-charge generation and the charge carrier mobility. Photoconductivity is found to be linearly dependent of photo-charge generation efficiency as expected, since we varied only the electron acceptor part so that the charge carrier mobility can be assumed constant (Fig. 3).

Large index contrast in the polymeric photorefractive composites can be explained by molecular reorientation of the optically anisotropic chromophores induced by the internal space charge field. We measured the space charge field formed in the composites by the interference pattern of two He-Ne laser beams while applying external electric field which can facilitate the charge separation in the CT complex and accelerate the charge drift (Fig. 4).

Photoconductivity shows a quadratic dependency on external fields, because the external electric field affects both charge mobility and the charge separation process. On the other hand, space charge field shows linear relationship with electric field.

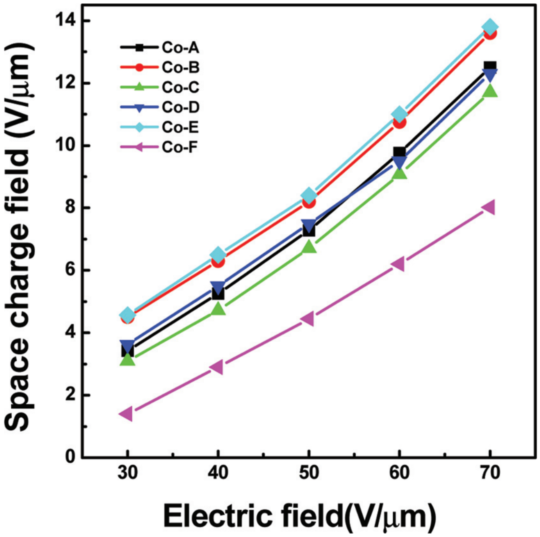

FIGURE 4 Space charge field formed by the interference pattern of two He-Ne laser beams while applying external field.

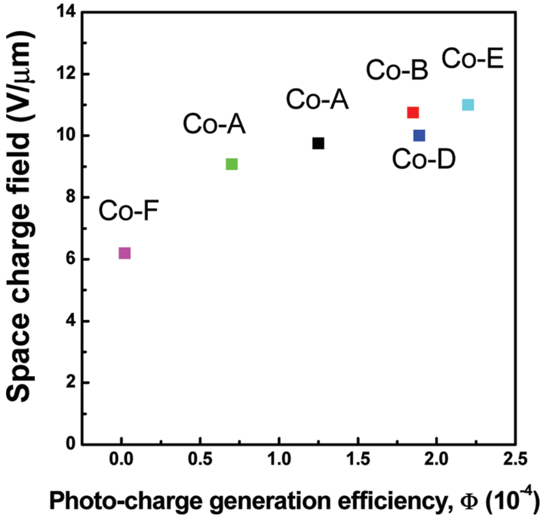

FIGURE 5 Relationship between the space charge field and photo-charge generation efficiency of polymeric photorefractive composites.

The space-charge field of composite is varied in the order of DDQ < TeNFM < TNF < TCNE < TNFM < TCNQ which is same order with photo-charge generation efficiency (Fig. 5).

4. SUMMARY

We successfully characterized the space charge field formed upon shining the interference pattern of two coherent beams in the photorefractive polymer composites which have low glass transition temperature. Photo-charge generation quantum yield depends on the molecular configuration not on the electron affinity of the electron acceptors. Photoconductivity is closely related to the photo-charge generation efficiency which, in the same way, related to the space charge field.

REFERENCES

[1] Moerner, W. E. & Silence, S. M. (1994). Polymeric photorefractive materials. *Chem. Rev.*, *94*, 127.

[2] Schildkraut, J. S. & Buettner, A. V. (1992). Theory and simulation of the formation and erasure of space-charge gratings in photoconductive polymers. *J. Appl. Phys.*, *72*, 1888.

[3] Ostroverkhova, O. & Singer, K. D. (2002). Space-charge dynamics in photorefractive polymers. *J. Appl. Phys.*, *92*, 1727.

[4] Chun, H., Moon, I. K., Shin, D.-H., Song, S., & Kim, N. (2002). The effect of the molecular structure of the chromophore on the photorefractive properties of the polymer systems with low glass transition temperatures. *J. Mater. Chem.*, *12*, 858.

[5] Joo, W.-J., Kim, N.-J., Chun, H., Moon, I. K., Kim, N., & Oh, C.-H. (2002). Determination of the space-charge field in polymeric photorefractive material. *J. Appl. Phys.*, *91*, 6471.

[6] Scott, J. C., Pautmeier, L. Th., & Moerner, W. E. (1992). Photoconductivity studies of photorefractive polymers. *J. Opt. Soc. Am. B*, *9*, 2059.

[7] Moerner, W. E., Silence, S. M., Hache, F., & Bjorklund, G. C. (1994). Orientationally enhanced photorefractive effect in polymers. *J. Opt. Soc. Am. B*, *11*, 320.