Appl. Phys. B 73, 35–37 (2001) / Digital Object Identifier (DOI) 10.1007/s003400100594

Applied Physics B
Lasers
and Optics

Photorefractive properties in homogeneous and heterogeneous polymer / liquid crystal composites*

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Received: 6 December 2000/Revised version: 5 March 2001/Published online: 9 May 2001 – © Springer-Verlag 2001

Abstract. The photorefractivity of a photorefractive composite consisting of poly(N-vinylcarbazole) (PVK) doped with a non-room-temperature liquid crystal, 4-butyloxy-4'-cyanobiphenyl (4OCB), and C_{60} was studied by means of measuring the two-beam coupling coefficients. The results show that the photorefractivity is enhanced by phase separation.

PACS: 42.65; 61.30; 61.40

Interest in materials that exhibit photorefractivity has been intense. More than 10 years ago, studies of the photorefractive effect were focused on inorganic crystals, such as $LiNbO_3$, $BaTiO_3$ and several others [1]. Since the first photorefractive effect in polymers was reported in 1991 [2], rapid progress has been made in the exploration of new materials and investigation of the mechanisms accounting for photorefractivity in this class of materials. In 1994, Meerholz et al. studied photorefractive composites with low glass transition temperature (T_g) and found that the two-beam coupling coefficient (Γ) was over 220 cm^{-1} [3]. Later investigations proved that the high two-beam coupling coefficient was attributed to the orientational enhancement effect [4]. From then on, highly anisotropic non-linear chromophores have become important components in the photorefractive polymer composites [5, 6].

Liquid crystals are long rod-shaped molecules that can produce large birefringence, which would maximize the orientational enhancement effect. Thus, liquid crystals became other chromophores for photorefractive materials. Khoo et al. found that low-molar-mass nematic liquid crystals doped with fullerene show orientational photorefractive effects and presented a detailed discussion of the mechanism [7, 8]. In order to improve the resolution of the photorefractive low-molar-mass liquid crystal, polymer dispersed liquid crystals (PDLCs) and high- and low-molar-mass liquid-crystal mixtures were also investigated [9–13]. Zhang and Singer reported a homogeneous photorefractive composite consisting of poly(N-vinylcarbazole) (PVK) doped with a low-molar-mass liquid crystal and C_{60} [14]. Gain coefficients over 100 cm^{-1} were observed at high electric field (150 V/μm). However, the liquid crystals used as photorefractive chromophores up to now have been room-temperature liquid crystals. In fact, the number of non-room-temperature liquid crystals is much larger than that of room-temperature liquid crystals and many of the non-room-temperature liquid crystals are highly anisotropic. Thus, it is possible for the non-room-temperature liquid crystals to become another kind of photorefractive chromophores. On the other hand, phase separation is a common problem in low-T_g photorefractive polymeric composites [15] and should be avoided. But for a polymer/liquid crystal system, such as a polymer-dispersed liquid crystal, the phase separation is induced purposely. As far as we know, there is no report on effects of phase separation on photorefractive properties in a polymer/liquid crystal composite. In this study, we have chosen a non-room-temperature liquid crystal, 4-butyloxy-4'-cyanobiphenyl (4OCB), as the non-linear chromophore, PVK as the photoconductive agent and matrix and C_{60} as a sensitizer. By controlling the sample-making process, two samples were obtained: one heterogeneous and one homogeneous. The effect of phase separation on photorefractive properties is discussed.

1 Experimental

4-butyloxy-4'-cyanobiphenyl (4OCB) and poly(N-vinylcarbazole) (PVK) were synthesized in our laboratory. C_{60} ($>$ 99.9% pure) was provided by the College of Chemistry, Peking University. 4OCB is a monotropic liquid crystal. The melt temperature is 78 °C and its clear temperature is 73 °C. The average-molecule weight (M_n) of PVK is about 10 000 and the dispersion of a distribution of PVK is 2.25. The glass transition temperature is 207 °C (measured by DSC (Differential Scanning Calorimeter)). The structures of the compounds used in the photorefractive composite are shown in Fig. 1. The composition of our samples is $PVK : 4OCB : C_{60} = 49.8 : 50 : 0.2$ wt %. For the preparation of samples, proper amounts of PVK, 4OCB (dissolved in

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*This work was supported by the National Natural Science Foundation of China (59873001)

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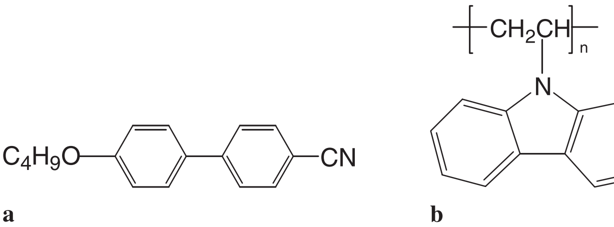

Fig. 1a,b. The chemical structures of **a** 4OCB and **b** PVK

chloroform) and C_{60} (dissolved in toluene) were mixed. The mixture was subsequently dripped onto indium tin oxide-coated glass plates. After 12 h in an oven at 60 °C, the plates were assembled at 100 °C with proper spacers. If the plates were then quenched to 0 °C, a homogeneous sample can be obtained. On the other hand, if the plates were cooled slowly, we can get a heterogeneous sample. Figure 2 exhibits a photograph obtained from atomic force microscopy (AFM) and many micro domains of about 100–200 nm in size can be seen in the heterogeneous sample. The homogeneous sample is transparent and the absorption coefficient α is $12\,\text{cm}^{-1}$. The heterogeneous sample is semitransparent and the total loss (including α and the scattering loss) is $79\,\text{cm}^{-1}$. The thickness of the samples was 95 μm.

The photorefractive properties were evaluated by the two-beam coupling experiment. A linearly polarized (*s*-polarized or *p*-polarized) beam from a He-Ne laser (632.8-nm, 0.2-mW output) was divided into two beams by a beam splitter and refocused onto the sample. A schematic illustration of the two-beam coupling experimental geometry is shown in Fig. 3. The tilted angle ϕ_{ext} was set to be 60°. The fringe spacing was varied by controlling the incident angle $2\theta_{\text{ext}}$ between the two writing beams. An electric field was applied to the sample by a high-voltage supply unit (made by the Factory of the Chinese Academy of Science) and the change in transmitted intensity was monitored by a power meter and recorded by a computer.

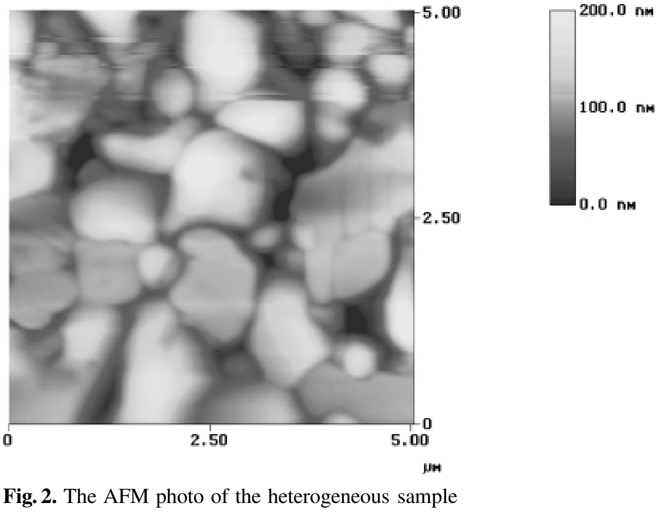

Fig. 2. The AFM photo of the heterogeneous sample

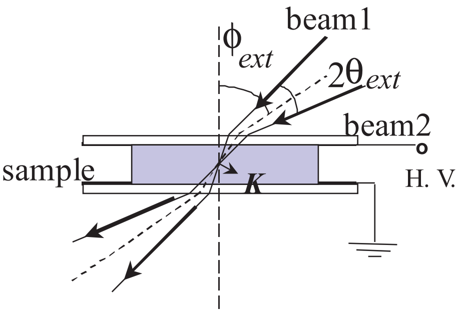

Fig. 3. Schematic illustration of the two-beam coupling experimental geometry. The sample is tilted at the angle $\phi_{\text{ext}} = 60\,°\text{C}$ relative to the bisector of the two writing beams

2 Results and discussion

To characterize the photorefractive properties of PVK : 4OCB : C_{60}, we performed a series of two-beam coupling (2BC) experiments. A 2BC experiment is the simplest experiment to verify the photorefractive effect and the results are convincing. In the 2BC experiment the change in the transmitted intensity of either of the write beams is recorded as the other write beam is switched on and a grating is formed. Each write beam is partially diffracted in the direction of the other write beam by the grating. Then, the 2BC coefficient Γ is calculated as [16],

$$\Gamma = \frac{1}{L}(\ln(\gamma_0\beta) - \ln(\beta + 1 - \gamma_0))\,, \tag{1}$$

with

$$\gamma_0 = P_{\text{signal, with pump}}/P_{\text{signal, without pump}}\,, \tag{2}$$

where P_{signal} is the measured power of the write beam under consideration, β is the ratio of the write powers before the sample and L is the optical path length.

Figure 4 illustrates the dependence of Γ on the applied electric field for the heterogeneous sample and the homogeneous one. The 2BC coefficients increased with the applied electric field and fit well with the equation given by Moerner and co-workers [5, eq.(8)]. For the heterogeneous sample the gain coefficient of $42\,\text{cm}^{-1}$ was obtained for a *p*-polarized beam at the applied field of 57.4 V/μm, while Γ was $25\,\text{cm}^{-1}$ under the same field for the homogeneous one. The gains for *s*-polarized light are consistently smaller than those for *p*-polarized light and the direction of energy transfer is opposite for the two cases for the same applied field. Regarding the gains obtained for the *p*-polarized beam, the gains for the heterogeneous sample are bigger than the values for the homogeneous one (negative gains for the *s*-polarized beam denote the opposite direction of energy transfer).

We studied the role of the orientational effect in PVK : 4OCB : C_{60} when the grating spacing is 5 μm. Using the theory of orientational enhancement [5]

$$\frac{\Gamma^{(p)}}{\Gamma^{(s)}} = \frac{1}{2}\cos\theta_{\text{int}}\left[\left(\frac{C}{A} - 1\right) + \left(\frac{C}{A} + 1\right)\cos\theta_{\text{int}}\right]\,, \tag{3}$$

where $\Gamma^{(p)}$ and $\Gamma^{(s)}$ are the gain coefficients for *p*- and *s*-polarized beams. θ_{int} is the internal interbeam angle, the material constant $A = C_{\text{EO}}/3 - C_{\text{BR}}/2$ and $C = C_{\text{EO}} + C_{\text{BR}}$. C_{EO}

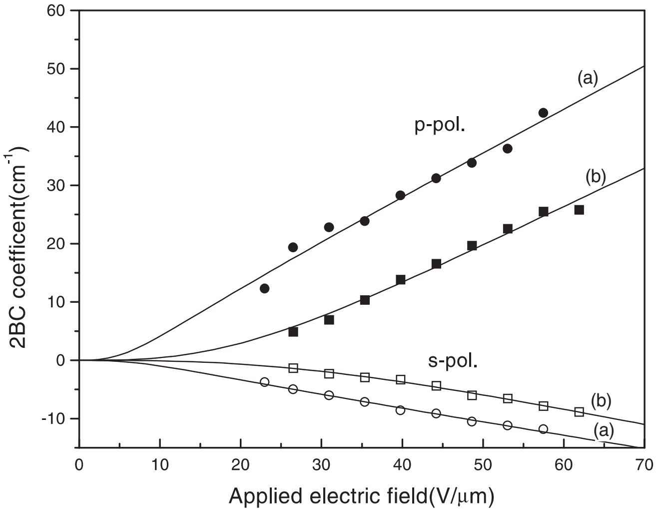

Fig. 4. The dependence of 2BC coefficients on applied field at $\Lambda = 4\,\mu$m. The *curves* are the theoretical fits to Γ. (a) heterogeneous sample (b) homogeneous sample

and C_{BR} are the coefficients from contributions of the electro-optic (EO) and the induced birefringence (BR) effects [5]. These are given by

$$C_{\mathrm{EO}} = \frac{1}{5} N \beta_{333} \left(\frac{\mu}{k_{\mathrm{B}} T} \right) \tag{4}$$

$$C_{\mathrm{BR}} = \frac{2}{45} N (\alpha_{\parallel}^{\omega} - \alpha_{\perp}^{\omega}) \left(\frac{\mu}{k_{\mathrm{B}} T} \right)^2 , \tag{5}$$

where N is the density of the chromophore, μ the ground-state dipole moment, $\alpha_{\parallel}$ and $\alpha_{\perp}$ the linear optical polarizabilities of the chromophore molecule parallel and perpendicular to the molecular axis and β_{333} the hyperpolarizability of the chromophore.

We obtain the ratio for the heterogeneous sample $\Gamma^{(p)}/\Gamma^{(s)} = -3.00$, while $\Gamma^{(p)}/\Gamma^{(s)} = -3.43$ for the homogeneous one. Using the definitions of A and C above, we find that $C_{\mathrm{BR}}/C_{\mathrm{EO}} = 4.0$ for the heterogeneous sample, which is larger than that for the homogeneous one ($C_{\mathrm{BR}}/C_{\mathrm{EO}} = 3.0$). This leads the heterogeneous sample to show a larger photorefractive effect. On the other hand, phase separation increases the scattering loss. In our case, the total loss (including the absorption and the scattering losses) of the heterogeneous sample (79 cm^{-1}) is six times as large as that of the homogeneous one (12 cm^{-1}).

3 Conclusion

The preliminary result of this study has shown that PVK/4OCB/C$_{60}$ is a photorefractive system. The 2BC coefficients depend not only on the composition but also on the morphology of the film. The phase separation and the formation of the low-molar-mass liquid crystal component domains were found to enhance the 2BC coefficients, but phase separation also increased the light loss because of scattering. Therefore, morphology control forms a key issue in the study of photorefractive materials.

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