All-Optical Photorefractive Effect in Carbazole-Based Azo-Side Group Polymer *

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We observe the photorefractivity without bias voltage or prepoling in a bifunctional photorefractive polymer. The maximum two-beam coupling gain is measured to be 126 cm^{-1} at zero bias voltage. The sample is considered to be poled by the photoinduced longitudinal electric field, which is formed due to the light intensity gradient along the light path. The expression of the electric field was deduced. The energy transfer direction between two writing beams and light intensity dependence of the two-beam coupling gain coefficient is predicted to be consistent with the experimental results. Furthermore, the dependence of the two-beam coupling gain coefficient on external applied electrical field is measured and this experiment verifies the existence of the photoinduced longitudinal electric field.

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Intense interest in photorefractive (PR) materials and devices has been stimulated by the potential applications in data storage, image processing and nondestructive testing, etc. The PR effect in polymer is defined as the spatial modulation of the refractive index by the following processes: first photos generate anion–hole pairs, then holes drift toward the dark region and are trapped, finally a space charge field is formed because the anions remain the original region. The space charge field modifies the refractive index through electro-optic effect and orientation enhancement effect.[1−3] Nonzero effective electro-optic (EO) coefficient requires orientation of chromophores, which is usually achieved by high external applied electric field.[4] However, some research groups have reported two-beam coupling in photorefractive polymer without external electric field or prepoling.[5−11] Such an effect is termed as the 'all-optical photorefractivity' in this study. The mechanism of the all-optical photorefractivity is assumed such that the PR chromophores are oriented by the photoinduced electric field.[5−10] In this Letter, we report the all-optical PR effect in an azo-carbazole polymer and the formation of photoinduced longitudinal electric field. The PR process have been analysed.

The PR composite was composed of bifunctional carbazole-based azo-side group polymer poly[nitrophenyl-3-[N-[10′-(methacryloxy)alkyl]] carbazolyl diazene] (PAC-10)(99 wt.%) and photosensitizer trinitrofluorenone (TNF) (1 wt.%). TNF was purchased and used without further purification. PAC-10 was obtained by reacting a precursor polymer bearing carbazole group with a long alkylene chain with diazonium salt in nitrobenzene.[10] Figure 1 shows the chemical structure of PAC-10 and the UV-vis absorption spectrum. The glass transition temperature T_g of the polymer was measured to be 36°. The blend of PAC-10 and TNF was sandwiched between two pieces of indium tin oxide (ITO) coated glass to fabricate the PR sample. The absorption coefficient of the sample was measured to be about 80 cm^{-1} at 633 nm.

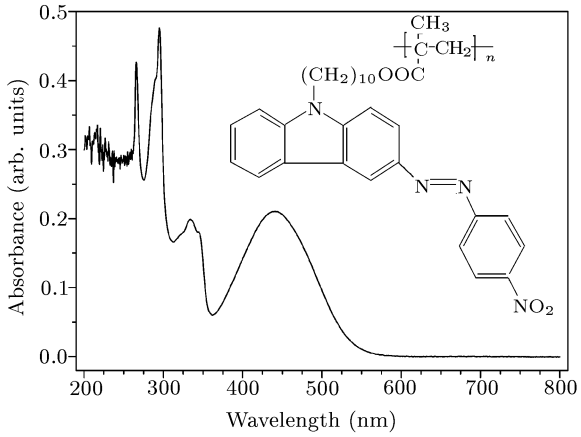


Fig. 1. The chemical structure and absorption spectra of the bifunctional PR polymer PAC10.

The usual tilt geometry for the two-beam coupling (TBC) experiment is not adopted in this study. The

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geometry is depicted in Fig. 2(a), the angle between two writing beams in the air is 20°, and the bisector of the two beams is collinear with the normal of the sample. A nonzero and stable TBC signal can be observed when two coherent p-polarized He–Ne laser beams with intensity ratio of $I_{10}/I_{20} = 11/18$ interfered in the sample, as shown in inset of Fig. 3, and energy is transferred from the weaker beam to the more intense one. The TBC gain coefficient is calculated by

$$\Gamma = \frac{1}{d/\cos\theta}[\ln(\gamma_0\xi + 1 - \gamma_0)],$$

where ξ is the ratio of the beam intensities; d is the thickness of the sample; $\gamma_0 = I/I_i$ is the beam coupling ratio; I_i and I are the detected signal when the pump beam is on and off, respectively; $\theta = (\theta_1 + \theta_2)/2$ is the bisecting angle of the incidence angles of two writing beams inside the sample, here $\theta = 0$. The TBC gain coefficient is related to the total intensity $I_t = (I_{10} + I_{20})$ of the two writing beams, as shown in Fig. 3. The maximum TBC gain coefficient is 126 cm^{-1} at a total intensity of 486 $\mathrm{mW/cm^2}$. In addition, the TBC between the incident beam and the reflected beam has been observed in the absence of the external electric field. The intensity of reflective beam increases with time and the dynamic process is shown in Fig. 4.

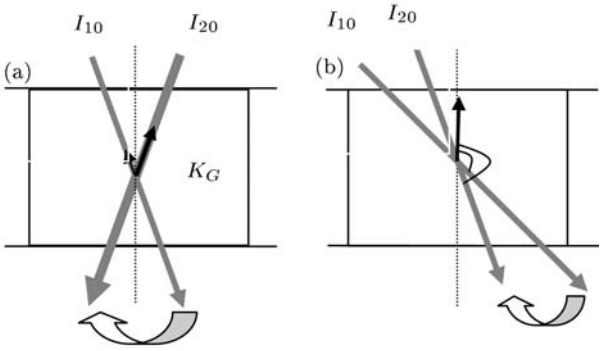


Fig. 2. (a) Geometry adopted for our TBC experiment in all-optical photorefractivity. The grey arrows denote the writing beams and the dark arrows denote the longitudinal electric field. The incident angles of the two writing beams are equal. (b) Geometry adopted for the conventional TBC experiment. The curved arrow denotes the direction of energy transfer.

In the previous work,[8] we have proposed a qualitative description of the all-optical PR process, in which the gradient of light intensity along the light path is formed due to light absorption, and the mobile holes diffused from brighter regions to darker regions, and then a longitudinal electric field is formed. Here we present a quantitative expression of the photoinduced longitudinal electric field.

When the laser beam propagates along the z direction, the growth rate of holes or anions in illuminated areas can be described by[12]

$$\frac{\partial n^{\pm}}{\partial t} = \alpha I(z) - \frac{n^{\pm}}{\tau} + D^{\pm}\frac{\partial^2 n^{\pm}}{\partial z^2} \mp \mu^{\pm}\frac{\partial(En^{\pm})}{\partial z}, \quad (1)$$

where n^+ is the density of holes, n^- is that of anions; α is a constant related to the absorption cross section of the sensitizer; τ is the mean life time of the anions; D and μ are the diffusion coefficient and drift coefficient of the carriers respectively. There is no external electric field applied on the sample, i.e. $E \approx 0$, hence the drift of the carriers can be neglected in the zeroth order approximation. In an equilibrium state, the density of holes and anions are invariable with time, Eq. (1) can be reduced to

$$0 = \alpha I(z) - \frac{n^{\pm}}{\tau} + D^{\pm}\frac{\partial^2 n^{\pm}}{\partial z^2}, \quad (2)$$

Taking the absorption into account, light intensity along the light path reads

$$I(z) = I_0 \exp(-\beta z), \quad (3)$$

where β is the absorption coefficient and I_0 is the initial intensity of the laser beam before entering the sample.

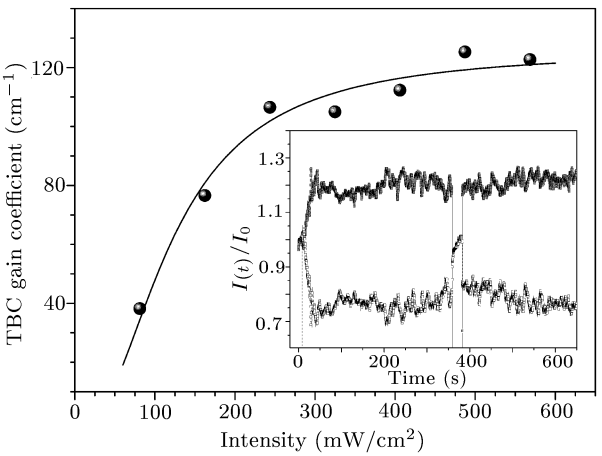


Fig. 3. Dependence of the TBC gain coefficients on the total beam intensity. The solid line is fitted theoretically. Inset: TBC traces in PAC-10 at zero electric field, in which beam I_2 is blocked from 360 s to 380 s.

Combining Eqs. (2) and (3) we can obtain the densities of holes and anions:

$$n^{\pm}(z) = \frac{\alpha I_0 \tau}{1 - \tau D^{\pm}\beta^2}\exp(-\beta z). \quad (4)$$

Thus the net charge at position z is

$$\begin{aligned}\rho(z) &= en^+ - en^- \\ &= \frac{e\alpha I_0 \tau^2 \beta^2 (D^+ - D^-)}{(1 - \tau D^+\beta^2)(1 - \tau D^-\beta^2)}\exp(-\beta z).\end{aligned} \quad (5)$$

The electric field is related to charge density by $\nabla \cdot \boldsymbol{E} = \rho/\varepsilon$, where ε is the dielectric constant of the polymer.

When the charge density distribution is described by Eq. (5), we can reach

$$\boldsymbol{E}(z) = -\frac{e\alpha I_0 \tau^2 \beta (D^+ - D^-)}{(1-\tau D^+ \beta^2)(1-\tau D^- \beta^2)\varepsilon} \exp(-\beta z)\boldsymbol{e}_z. \tag{6}$$

The minus sign indicates that the electric field is opposite to the light propagation direction, moreover the electric field intensity is proportional to the light intensity I_0. When two writing beams with intensity I_{10} and I_{20} are incident on the sample, two electric fields $\boldsymbol{E}_1$ and $\boldsymbol{E}_2$ are produced. The resultant electric field is the superposition of the two electric fields,

$$E_r = \sqrt{E_1^2 + E_2^2 + 2E_1 E_2 \cos(\theta_1 - \theta_2)}. \tag{7}$$

The intensities of writing beams, I_{10} and I_{20}, are related to total intensity by

$$I_{10} = aI_t, \quad I_{20} = bI_t, \tag{8}$$

where $a = 11/29$ and $b = 18/29$ are taken in our experiment. From Eqs. (6)–(8), the relation between the resultant electric field and total intensity I_t is

$$E_r \propto I_t \sqrt{(a^2 + b^2 + 2ab\cos(\theta_1 - \theta_2)} \propto I_t. \tag{9}$$

The projection of the electric fields along the grating vector $\boldsymbol{K}_G$ is

$$E_G = E_1 \cos\theta_1 - E_2 \cos\theta_2 \propto (a-b) I_t \cos\theta_1 \propto I_t. \tag{10}$$

Based on the above theory, we can obtain some conclusions and compare them with the experimental results.

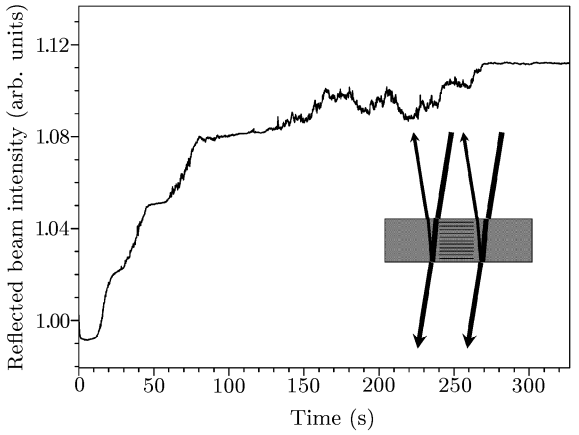


Fig. 4. The dynamic process of the growth of the reflected beam intensity. Inset: the scheme used for demonstrating the interference of the incident beam with the reflected beam.

Firstly, we consider the energy transfer direction. In the conventional TBC experiments with transmission grating geometries,[13] PR chromophore is poled by an external electric field, the energy is transferred from one beam to the other, where the angle between the propagation direction of the former and the direction of the external electric field is smaller than that of the latter, as shown in Fig. 2(b). In the all-optical PR experiment, the polymer is poled by the resultant electric field $\boldsymbol{E}_r$ that is in the direction close to the more intense writing beam and far away from the weaker beam. It is expected that the energy is transferred from the weaker beam to the more intense beam according to analysis in conventional TBC experiments. This agrees with the experimental results. Moreover, the incident beam and the corresponding reflected beam can form the TBC with reflection grating geometries. In the conventional TBC the reflected beam gains energy from the incident beam when the applied external electric field is opposite to the propagation direction of the incident beam.[14] This is consistent with our experimental result shown in Fig. 4.

Secondly, the dependence of the TBC gain coefficients on the total writing beam intensity can be explained theoretically. In the conventional PR theory, dependence of the TBC gain coefficient on the external electric field is[6]

$$\Gamma = CE_0 E_0^G [1 + (E_0^G/E_q)^2]^{-1/2} \sin[\tan^{-1}(E_0^G/E_q)], \tag{11}$$

where C is a constant related to the effective electro-optic coefficient; $\boldsymbol{E}_0$ is the external applied field; E_0^G is the component of $\boldsymbol{E}_0$ along the direction of the grating wave-vector $\boldsymbol{K}_G$; and $\boldsymbol{E}_q$ is the internal saturation field. In all-optical photorefractivity, $\boldsymbol{E}_r$ plays the role of $\boldsymbol{E}_0$. From Eqs. (9)–(11), we can obtain relation between the total intensity and the TBC gain coefficient,

$$\Gamma = P_1 I_t^2 [1 + (I_t/P_2)^2] \sin[\tan^{-1}(I_t/P_2)], \tag{12}$$

where P_1 and P_2 are constant. The solid line in Fig. 3 is the fitting curve based on Eq. (12). The theoretical analysis is in agreement with the experimental data.

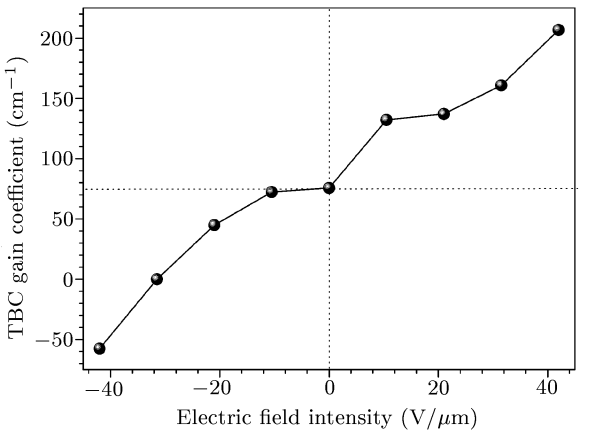


Fig. 5. Dependence of TBC gain coefficients on applied external electric field.

In order to prove the existence of photoinduced longitudinal electric field further, the dependence of

the TBC gain coefficient on the applied external electric field was measured in the sample. In this experiment, the propagation direction of the more intense beam was collinear with the normal of the sample. The result is shown in Fig. 5. When the external electric field is almost with the same polarity of $\boldsymbol{E}_r$, it will reinforce poling strength and increase the TBC gain coefficient, whereas the polarity of the external electric field is almost opposite to that of $\boldsymbol{E}_r$, it will weaken the poling strength and decrease the TBC gain coefficient, and even the TBC energy transfer direction will reverse when the effect of external electric field outstrips that of $\boldsymbol{E}_r$. The experimental data obey the rule discussed above, indicating that a longitudinal electric field cannot exist in the sample and this plays a role in removing the centrosymmetry of the sample and makes the sample EO active.

In summary, TBCs without an external electric field or prepoling have been observed in a PR polymer. The reason for the all-optical PR effect is presumed that the centrosymmetry of the sample is removed by the photoinduced longitudinal electric field, which is induced by light intensity attenuation along the light propagation path. All the experimental results are consistent with the PR theory.

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