

# Synthesis and characterization of bi-functional photorefractive polymers

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## Abstract

A novel bi-functional photorefractive acrylate polymer with pendant carbazolyl groups and azo derivatives as side chains was synthesized, in which azo derivatives as electro-optic chromophores and carbazolyl as photoconductive moiety were covalently linked on the acrylate backbone. Photorefractive experiments showed that a high two-beam coupling gain coefficient of  $93 \text{ cm}^{-1}$ , diffraction efficiency of 12% and electro-optic coefficient of 26 pm/V were obtained. With increasing writing beam's intensity, the two-beam coupling enhanced gradually, and then reached saturation. Using the method of four-wave mixing, the photoisomerization grating was observed. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Acrylate polymer; Bi-functional polymer; Photorefractive material

## 1. Introduction

Photorefractive (PR) polymer is a new class of photorefractive materials, which has been investigated widely in the past few years [1–5]. Since 1990, PR studies have been extended into organic polymer materials [6–12]: host-guest polymer composites [6–9] and fully-functional polymers [10–12]. Host-guest polymer composites exhibit an obvious disadvantage: low stability due to phase separation; while fully-functional polymers are difficult to be synthesized due to complex synthesis routes and very low content of photosensitizer being difficult to be linked to the fully-functional polymer. The driving force to pursue research on semi-fully-functional photorefractive polymers, which possess both photoconductivity and electro-optic (EO) effect, comes from their high stability and easy synthesis.

Based on the above knowledge, a novel semi-fully-functional photorefractive polymer was designed and synthesized, whose structure was shown in Scheme 3. It is expected that this kind of polymer could exhibit PR property or an improved performance. Designing this kind of PR system is based on the facts that alkoxy azo dyes/poly(N-vinyl carbazole)/2,4,7-trinitrofluorenone (TNF) composite systems are well-known photorefractive systems and exhibit high EO response and large asymmetric optical energy

exchange, as verified by Peyghambarian's group [5] and our research group [13–15]. In this article, we report the detailed results on the synthesis and characterization of this new photorefractive polymer, in which an azo derivative as the EO chromophore and carbazolyl as photoconductive moiety are covalently linked on an acrylate backbone.

## 2. Experimental

### 2.1. Materials

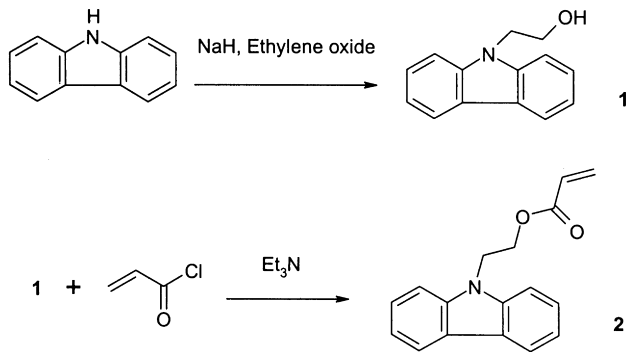
All materials were purchased from Acros and Aldrich, respectively. TNF was purified by recrystallization before use.

### 2.2. Characterization

The samples were characterized by means of IR spectroscopy on a Nicolet Magna FT-IR 750, by elemental analysis on Elementar Vario EL, UV-Vis spectroscopy on Shimadzu 2100, and by <sup>1</sup>H-Nuclear Magnetic Resonance (<sup>1</sup>H NMR) recorded on a ARX 400. Gel permeation chromatography (GPC) was performed with tetrahydrofuran (THF) as a solvent and UV/RI detection versus polystyrene standards. Thermogravimetry (TG) was performed under nitrogen with a Shimadzu DT-30 (heating rate 20 °C/min, sample size 4–6 mg). A TA DSC 2010 was used for

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Scheme 1.

differential scanning calorimetry (DSC) with a sample size of 4–6 mg at a heating rate of 10 °C/min.

### 2.3. Sample preparation

It has been known that PR materials are multifunctional materials which combine EO effect and photoconductivity to manifest a new property: photorefractivity. To make the thick samples (100 μm) be poled in situ at room temperature to obtain the contribution of the large birefringence, we modified the polymeric system to obtain low  $T_g$  by adding a plasticizer, 9-ethyl carbazole (ECZ). The composite sample consisted of copolymer 7-3 at a weight ratio of 65%, in which carbazole groups act as photoconductive moieties and azo derivatives moieties provide EO property, ECZ at weight ratio of 34% and TNF at weight ratio of 1% acted as the plasticizer and the photosensitizer, respectively. According to the method reported in our previous paper [15], the sample was sandwiched by two ITO-coated glass slides and a Teflon film was used as a spacer to control the thickness of the sample film.  $T_g$  of the composite was measured to be 20°C by DSC and thus poling can be carried out by applying a d.c. electric field directly at room temperature.

### 2.4. Photorefractive measurements

To detect the photorefractive properties of our low  $T_g$  samples, the EO measurements, two-beam coupling (TBC) experiments and four-wave mixing (FWM) experiments were performed. The TBC experimental setup is shown in the insert of Fig. 4. Two-coherent p-polarized He–Ne laser beams overlapped on the sample. The intensity of beam was  $I_1 = I_2 = 2 \text{ mw/cm}^2$ . The sample was tilted at an angle  $\phi_{\text{ext}} = 60^\circ$  (in air) relative to the bisector of the incident beams, and the angle between incident beams  $2\theta_{\text{ext}} = 20^\circ$  (in air). TBC gain was calculated in the formula [16]:

$$\Gamma = \frac{\cos \phi_{\text{in}}}{d} \ln \left( \frac{br}{b+1-r} \right), \quad (1)$$

where  $d = 100 \mu\text{m}$  is the thickness of the sample,  $\phi_{\text{in}}$  is the tilting angle inside the sample,  $b = I_2/I_1 = 1$ ,  $\gamma = I_{12}/I_1$ ,  $I_1$  ( $I_2$ ) and  $I_{12}$  ( $I_{21}$ ) are the intensity of beam 1 (beam 2) after the sample in the absence and in the presence of beam 2 (beam

1), respectively. The experiment was carried out under room temperature.

FWM experiment has also been performed to determine grating amplitude in the way of the steady-state diffraction efficiency of holograting recorded in the polymer composite. In these experiments, writing beams were s-polarized to minimize coupling effect so as to maximize the effective modulation of the grating. A much weaker beam with p-polarized acted as the probe beam.

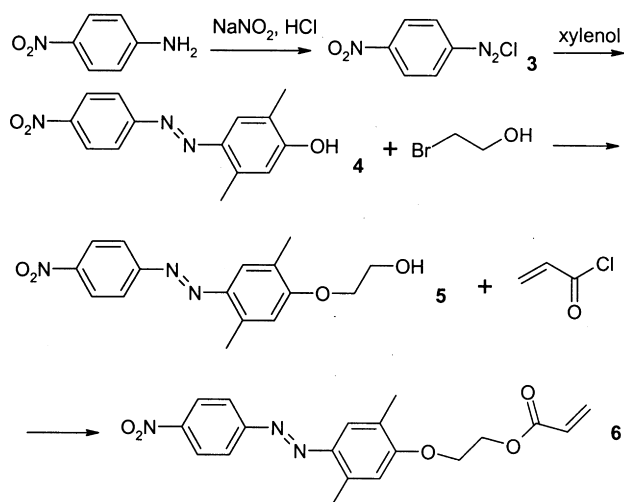
EO properties of the composite were measured by using a compensation EO modulation technique [17]. A linear polarized 632.8 nm He–Ne laser beam (power 0.2 mW) with a polarization angle of 45° with respect to the plane of incidence, propagated through the sample film at an incident angle of 60° in air and then a KD\*P crystal. A dc voltage was applied to the sample film through the two ITO electrodes. The transmitted beam then passed through an analyzer, whose polarization direction was oriented at 90° with respect to the initial polarization of the incident beam. The phase-difference  $\Delta\Phi$  of p- and s-polarized components of the beam from both voltage-induced anisotropy and the EO effect of sample was compensated by using another variable d.c. voltage on the KD\*P crystal. With the measured value of  $\Delta\Phi$ , we may deduce the effective EO coefficient  $\gamma_{\text{eff}}$  through

$$\Delta\Phi = \frac{\pi n_0^3 r_{\text{eff}} V \sin^2 \theta_{\text{in}}}{\lambda \cos \theta_{\text{in}}}, \quad (2)$$

where  $\lambda$  is the wavelength of laser beam,  $V$  the dc voltage applied on the sample, and  $n_0$  the refractive index of the polymeric composite film.

### 2.5. Preparation of carbazolylethyl acrylate (2)

As shown in Scheme 1 N-hydroxyethyl carbazole (1) was synthesized by the approach developed in our laboratory with reaction of sodium carbazole and ethylene oxide. This approach could avoid the disadvantages of rigorous synthesis condition of potassium carbazolate in the method of Ref. [18] and low yield by etherization of bromoethanol in the method of Ref. [19]. Sodium carbazolate was obtained by dropping 10 g (60 mmol) of carbazole into 1.56 g (65 mmol) NaH solution in 60 ml tetrahydrofuran. To the above solution, 2.64 g (60 mmol) ethylene oxide in 10 ml tetrahydrofuran was dropped slowly, and then stirred overnight. The products were extracted with ether, and recrystallized by benzene/petroether (50/50). Yield 80%, m.p.: 79–80°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/TMS):  $\delta$ (ppm) = 1.595 (s, 1H, OH); 3.970 (t, 2H,  $J = 5.8 \text{ Hz}$ , NCH<sub>2</sub>); 4.409 (t, 2H,  $J = 5.8 \text{ Hz}$ , OCH<sub>2</sub>); 7.227 (d, 2H,  $J = 8.1, 1.8\text{-H}$ ); 7.426 (t, 4H, 2,3,6,7-H); 8.070 (d, 2H,  $J = 7.8 \text{ Hz}$ , 4,5-H). Carbazolylethyl acrylate (2) was synthesized from 5.27 g (25 mmol) of N-hydroxyethyl carbazole and 2.9 ml of acrylic chloride with 4.2 ml triethyl amine as catalyzer. The products were purified by chromatogram with dichloromethane as diluent. Yield 70%, m.p.: 75–76°C,



Scheme 2.

elemental analysis: found C, 76.98%, H, 5.66%, N, 5.28%, O, 12.08%; calculated C, 77.08%, H, 5.66%, N, 5.39%, O, 12.36%,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ ):  $\delta(\text{ppm}) = 4.545$  (t, 2H,  $J = 5.9$  Hz,  $\text{NCH}_2$ ); 4.578 (t, 2H,  $J = 5.9$  Hz,  $\text{OCH}_2$ ); 5.749 (d, 1H,  $=\text{C}-\text{H}$ ); 5.961 (d, 1H,  $=\text{C}-\text{H}$ ); 5.238 (t, 1H,  $J_1 = 10.4$ ,  $J_2 = 17.2$  Hz,  $=\text{C}-\text{H}$ ); 7.246 (d, 2H,  $J = 8.0$  Hz, 1,8-H); 7.444 (m, 4H, 2,3,6,7-H); 8.085 (d, 2H,  $J = 7.6$  Hz, 4,5-H).

## 2.6. Preparation of 1-(acryloxyethoxy-2,5-dimethyl-4-(nitrophenylazo) benzene (6)

As shown in Scheme 2, 1-hydroxyethoxy-2,5-dimethyl-4-(nitrophenylazo) benzene was synthesized from 15 g (76 mmol) of 2,5-dimethyl-4-nitrophenylazo phenol (5) prepared in our laboratory and 5.4 ml (76 mmol) of bromoethanol with 30 g potassium carbonate as catalyzer in acetone, and recrystallized by ethylacetate. Yield 50%, m.p.: 179–180°C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ ):  $\delta(\text{ppm}) = 2.260$  (s, 3H,  $\text{CH}_3$ ); 2.747 (s, 3H,  $\text{CH}_3$ ); 4.049 (t, 2H,  $J = 6.9$  Hz,  $\text{OCH}_2$ ); 4.211 (t, 2H,  $J = 6.9$  Hz,  $\text{OCH}_2$ ); 6.782 (s, 1H, arom. H); 7.651 (s, 1H, arom. H); 7.976 (d, 2H,  $J = 8.2$  Hz, arom. H); 8.354 (d, 2H,  $J = 8.2$  Hz, arom. H). Monomer (6) was obtained from 3 g (12.5 mmol) compound (5) and 1 ml acrylic chloride according to the method above, and purified by chromatography

with dichloromethane as diluent. Yield 76%, m.p.: 130–131 °C, elemental analysis: found C, 61.79%, H, 5.15%, N, 11.38%, O, 21.68%; calculated C, 61.70%, H, 5.10%, N, 11.32%, O, 21.70%,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3/\text{TMS}$ ):  $\delta(\text{ppm}) = 2.229$  (s, 3H,  $\text{CH}_3$ ); 2.742 (s, 3H,  $\text{CH}_3$ ); 4.322 (t, 2H,  $J = 7.1$  Hz,  $\text{COOCH}_2$ ); 4.596 (t, 2H,  $J = 7.1$  Hz,  $\text{OCH}_2$ ); 5.881 (d, 1H,  $=\text{C}-\text{H}$ ); 6.189 (t, 1H,  $J_1 = 10.4$ ,  $J_2 = 17.3$  Hz,  $=\text{C}-\text{H}$ ); 6.494 (d, 1H,  $=\text{C}-\text{H}$ ); 6.765 (s, 1H, arom. H); 7.657 (s, 1H, arom. H); 7.965 (d, 2H,  $J = 8.2$  Hz, arom. H); 8.362 (d, 2H,  $J = 8.1$  Hz, arom. H).

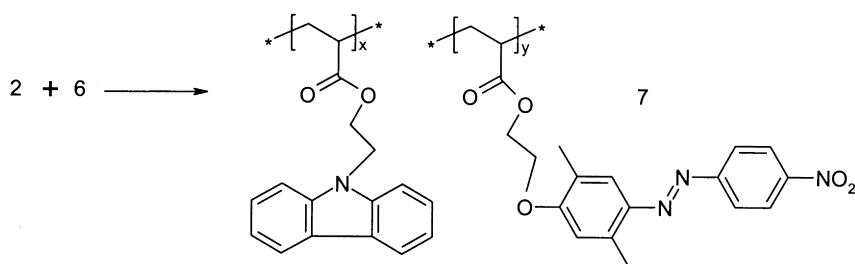
## 2.7. Preparation of copolymers (7)

As shown in Scheme 3, the polymerizations were carried out with various proportions of monomer (2) and (6) in purified toluene with a 0.5% AIBN as initiator at 60°C for 48 h in sealed vacuum tube. The resulted polymers were precipitated out in methanol and were purified by redissolving in chloroform and re-precipitation in methanol. The feed ratio of the monomers and yield for each polymerization reaction were presented in Table 1. The compositions ( $x/y$ ), shown in Table 2, were deduced from the UV data. The average molecular weight ( $\overline{M}_w$ ), the polydispersity ( $\overline{p_d}$ ), the decomposition temperature ( $T_d$ ) and the glass transition temperature ( $T_g$ ) of the copolymers were also presented in Table 1, and the result of the elemental analysis was listed in Table 2.

## 3. Results and discussion

### 3.1. Synthesis and molecular structure of the copolymer

The basic concept is the combination of carbazole moieties and azo derivative moieties. From the nonlinear optics point of view the content of nonlinear optical chromophore moieties ought to be high in order to keep the EO effect high, and able to enhance diffraction efficiency consequently. However, the intensity of anisotropy of chromophore still deserves particular attention with the monomers selected here. From the chemical point of view the reactivity of the comonomers has to be similar in order to obtain good copolymerizability, a uniform molecular structure, and high molecular weights. From the physical point of view the copolymer should have a homogeneous morphology in order to gain on good optically transparent properties.



Scheme 3.

Table 1  
The composite and physical properties of the copolymers

Polymers	Feed (2/6) molar ratio	Yield (%)	$\overline{M}_w \times 10^{-4}$	$\overline{pd}$	$T_g$ (°C)	$T_d$ (°C)
7-1	1:0.7	90	0.653	2.10	227	360
7-2	1:1	86	0.471	1.77	231	345
7-3	1:1.2	92	0.330	1.59	250	357

In view of these demands we decided to synthesize copolymers by copolymerization of carbazolyethyl acrylate and 1-(acryloxyethoxy-2,5-dimethyl-4-(nitrophenylazo) benzene with several ratios of photoconductive moiety to nonlinear optical chromophore moiety (Scheme 3).

As proved by UV–Vis spectroscopy, the copolymers contain the typical absorption peaks of both the carbazole moiety ( $\lambda_{\max} = 342$  nm) and the azo derivative moiety ( $\lambda_{\max} = 390$  nm) (Fig. 1). The relative height of the peaks at 342 and 390 nm for copolymers was used for calculating the composition of monomers in the polymers.

The IR spectra showed the typical peaks of 1521, 1341 (aromatic nitro), 1255 (aromatic ether), 1376 (C–N) and 1735  $\text{cm}^{-1}$  (carbonyl). The relative intensities of these peaks were also identical with the results of UV data (Fig. 2).

As proved by  $^1\text{H}$  NMR spectroscopy, the copolymers contain the typical peaks of both the azo derivative moiety ( $\delta = 2.15$  ppm,  $\text{CH}_3$ ; 6.75 ppm, arom. H) and the carbazole moiety units (part of arom. H of 7.20–7.70 and 7.94–8.41 ppm). The NMR spectra of copolymers (7) are almost identical and differ only in relative signal intensities. For example, copolymer 7-3:  $\delta = 1.50$ –2.02 ppm (m,  $-\text{CH}_2-$ ); 2.15 (m,  $\text{CH}_3$ ); 2.60–2.80 (m,  $\text{CH}_3$ ,  $-\text{CH}-$ ); 4.30–4.70 (m,  $\text{OCH}_2$ ,  $\text{NCH}_2$ ); 6.75 (m, arom. H); 7.20–7.70 (m, arom. H); 7.94–8.41 (m, arom. H).

This corresponds to the analysis of GPC curves that shows a monomodal distribution, and there is no evidence for the presence of homo-polymer fractions any more. The molecular weights ( $\overline{M}_w$ ) are between 6530–3300 with polydispersities of 2.10–1.59 (Table 1). Molecular weights drop systematically with increasing content of azo derivative moiety. This can be attributed to higher chain transfer reactivity of azo moieties.

### 3.2. Thermal properties and morphology

The thermogravimetical analysis showed the decomposition temperature of the copolymers at about 350°C. Their glass transition temperatures were found between 227–

250°C by DSC. Single glass transition steps were detected which are typical for random copolymers. Surprisingly, compared to the glass transition temperature of homopolymer poly(carbazolyethyl acrylate) ( $T_g \approx 85^\circ\text{C}$ ), the glass transition temperatures of the copolymers did shift considerably towards high temperature. This may be attributed to the big bulk of azo derivative moieties. The copolymer film with certain amount of ECZ and TNF have good optically transparent property observed by optical microscopy.

### 3.3. Photorefractive properties

As a low  $T_g$  polymer film, the nonlinear optical chromophore side-chain of host copolymer in the film could be also effectively aligned at room temperature by applying an additional electric field. To confirm this point, we measured the effective EO coefficients at different applied electric fields, and the result was showed in Fig. 3. A linear dependence of the effective EO coefficient on the applied electric field was obtained, and an effective EO coefficient of 26 pm/V was proved at a field of 92.4 V/ $\mu\text{m}$ . Notice that this EO coefficient contained contributions from both the orientational birefringence and Pockels effect.

It is well known that the nonlocal nature is the only feature to distinguish PR grating from index gratings caused by other mechanisms and thus the asymmetric energy transfer between two writing beams, so-called two-beam coupling is the most direct evidence for the occurrence of the PR effect. Fig. 4 illustrated the TBC coefficients of the polymer film as a function of the applied electric field. At the applied electric field of 92.4 V/ $\mu\text{m}$ ,  $\Gamma$  was measured to be 93  $\text{cm}^{-1}$ . According to the relationship of  $\Delta n \propto E_0 E_{sc}$  [20,14], the applied electric field dependence of the TBC coefficient should be

$$\Gamma = K \frac{E_0 E_0^G}{\sqrt{1 + (E_0^G/E_q)^2}} \sin(\tan^{-1}(E_0^G/E_q)), \quad (3)$$

where  $\Delta n$  is the index grating amplitude,  $E_0$  the applied

Table 2  
The elemental analysis of copolymers

Polymers	$x/y$	C %		H %		N %	
		Found	Calcd.	Found	Calcd.	Found	Calcd.
7-1	63.6/36.4	69.95	70.23	5.49	5.47	7.90	7.98
7-2	60/40	69.31	69.66	5.40	5.45	8.21	8.21
7-3	45/55	66.94	67.40	5.66	5.38	8.58	9.11

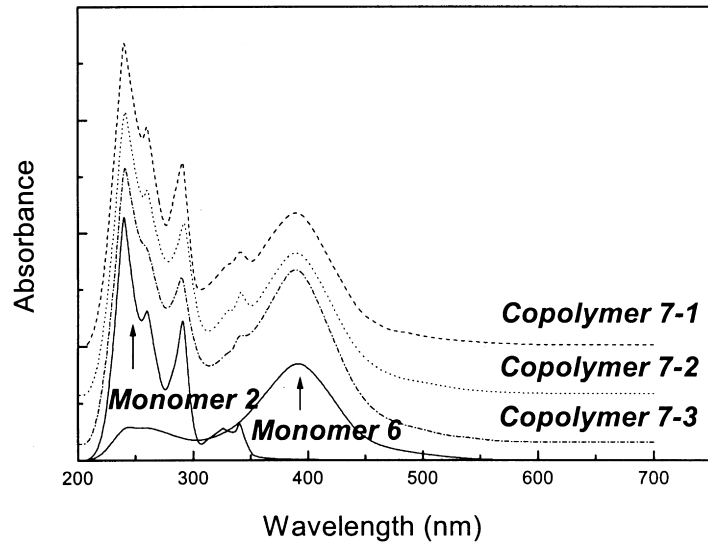


Fig. 1. UV-Vis spectroscopies of monomers and copolymers.

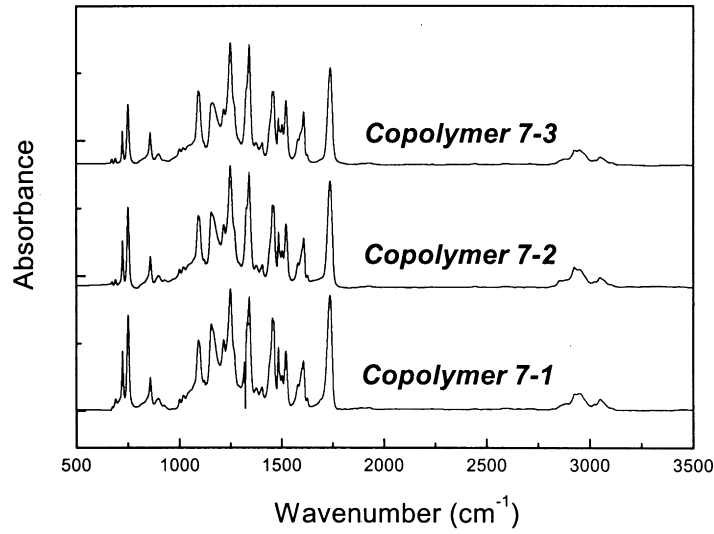


Fig. 2. IR spectroscopies of copolymers.

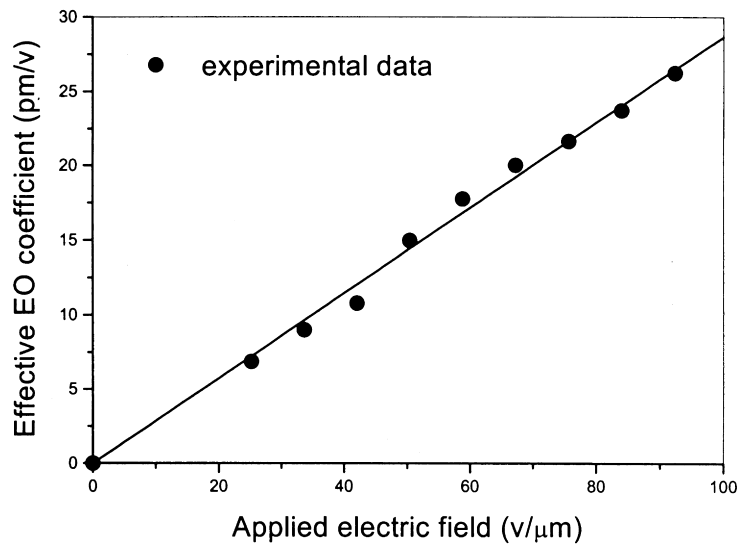


Fig. 3. The measured effective EO coefficient of the composite film.

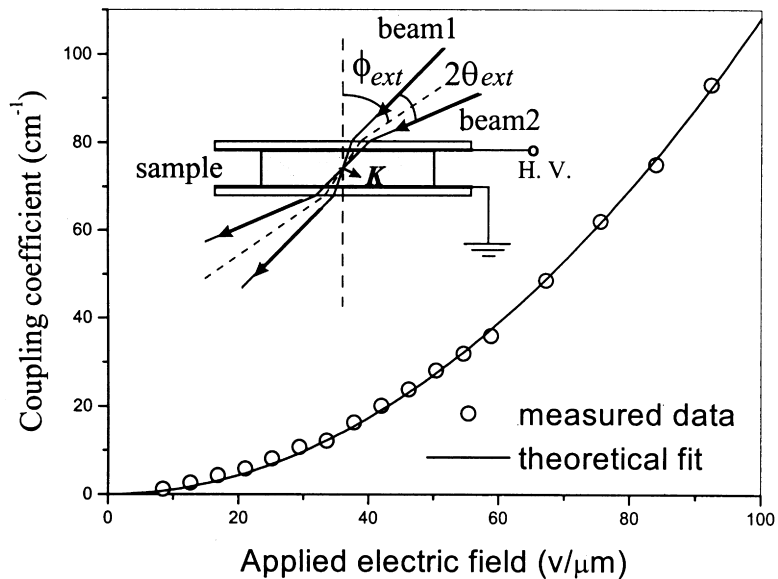


Fig. 4. Two-beam coupling coefficient as function of applied electric field. The insert shows the typical tilted geometry for the two-beam coupling experiment.

electric field,  $E_{sc}$  the internal space-charge electric field,  $E_0^G$  the component of  $E_0$  along the direction of the grating wave-vector, and  $E_q$  the trap limited saturation space-charge field. We used Eq. (3) to fit two-beam coupling process, and the theoretical fitting curve is also presented in Fig. 4.

We detected the diffraction efficiency  $\eta$  as a function of the applied electric field and the result was presented in Fig. 5. Limited by the reflection and absorption losses, a maximum of only  $\sim 12\%$  was obtained at the applied electric field of  $92.4 \text{ V}/\mu\text{m}$ . It should be pointed out that at zero electric field, the diffraction was  $\sim 1.4\%$  instead of zero. This was contributed from the photoisomeric grating caused by the intensity pattern through the photoisomerization.

We have also studied the intensity-dependence of the coupling coefficient containing the same intensity modulation depth as shown in Fig. 6. It was clear that with the increasing of the intensity, the two-beam coupling coefficient increased quickly and then slowly tended to a saturation value.

This point is different from the case of inorganic PR crystals, in which the  $I$  was almost independent on the illumination intensity. Our experiments also proved a similar phenomenon on the PR grating in a polymeric composite which Volodin et al. had earlier reported [21].

#### 4. Conclusions

A novel copolymer with carbazole moieties as photoconductive agent and azo derivative moieties as nonlinear optical chromophore was synthesized. Doped with TNF, the polymer film was proved to have PR effect by two-beam coupling measurement. Electric-optic experiments showed that nonlinear optical chromophore could be aligned by an applied d.c. electric field. It could be imaged that the copolymer doped without plastisizer but only with photosensitizer also exhibited excellent photorefractive performance. It

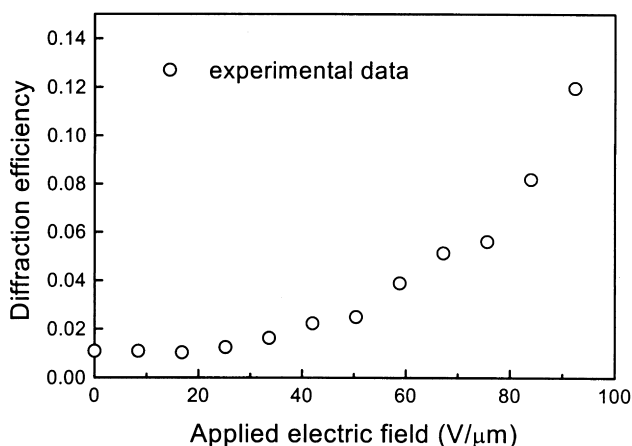


Fig. 5. Diffraction efficiency as a function of applied electric field.

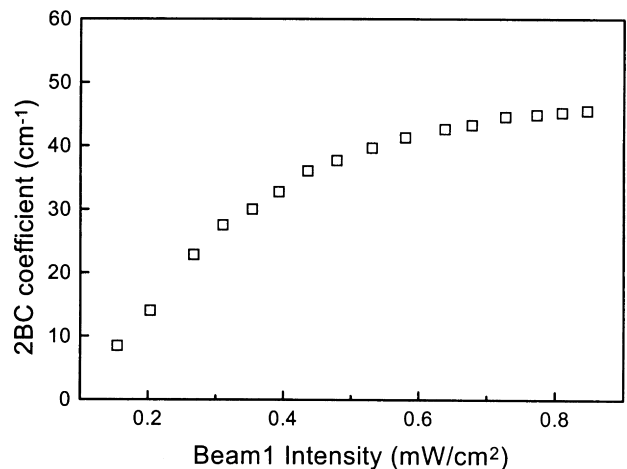


Fig. 6. The intensity-dependence of the two-beam coupling coefficient.

has become an important trend to synthesize photorefractive polymer with both photoconductive moieties and electric optic moieties but doped with few photosensitizer, due to its more advantages over other polymer photorefractive materials.

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