Photorefractivity and Transmission-Type Holograms of a Poly(N-vinylcarbazole)-Based Composite with N-4-nitrophenyl-(*l*)-prolinol as Chromophore

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ABSTRACT: The photorefractivity of a poly(N-vinylcarbazole)/2,4,7-trinitro-9-fluorenone/N-4-nitrophenyl-(*l*)-prolinol/N-ethylcarbazole composite was investigated by two-beam coupling and degenerate four-wave mixing experiments. The composite in a weight ratio 35 : 1 : 50 : 15 exhibited a 22% steady-state diffraction efficiency and 70 cm^{-1} two-beam coupling coefficient at the applied external field of 55 V/μm. Zero applied field transmission-type holograms were observed in the photorefractive sample as well as the spin-coated thin film. The dynamic decay of diffraction light indicated that there existed two contributors with different phase-shift, and the slow decay time can be as long as several h under continuous illumination by the readout beam. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 447–451, 2000

Key words: photorefractivity; hologram; PVK; NPP

INTRODUCTION

The photorefractive (PR) effect can be observed in materials that are both electro-optic and photoconductive. The effect arises when charge carriers, photogenerated by spatially modulated light intensity, migrate by drift or diffusion processes and eventually get trapped to produce a nonuniform space-charge distribution. The resulting internal space-charge electric field then modulates the refractive index to create a so-called PR holograms.[1]

Since the first observation of the PR effect in a polymer in 1991,[2] tremendous progress has been made in the development of polymeric PR materials. These materials possess many advantages over inorganic PR crystals in applications of high-volume information storage and data processing because of their large nonlinear optical properties, high optical damage thresholds, low dielectric constants, and good film-forming capabilities. Composite PR materials are of particular interest because the nature and concentration of each component can be independently varied to meet specific application requirements. A series of poly(N-vinylcarbazole) (PVK)-based PR composites have been investigated,[3,4] and it was found that the superior performance of these materials arises from an enhancement mechanism which relies on the ability of the nonlinear chromophores to reorient under the influence of the space charge field. This enhancement can be optimized with efficient plasticization and, as a result, several PR composites with diffraction efficiency approaching 100% have been reported.[5–7]

In this article, we report on the investigation of photorefractivity by two-beam coupling (2BC) and

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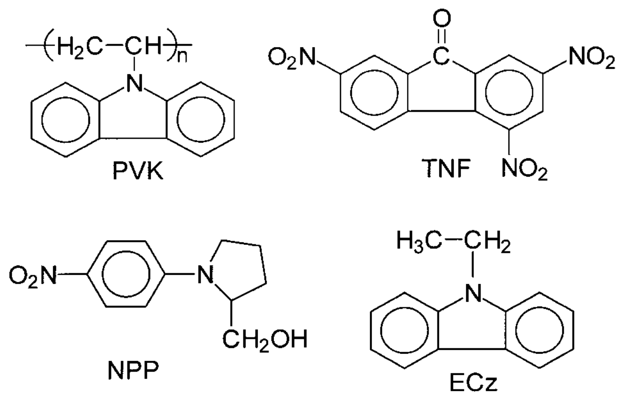

Figure 1 Chemical structures of the components in our PR sample.

degenerate four-wave mixing (DFWM) experiments in a PVK-based polymeric composite containing 2,4,7-trinitro-9-fluorenone (TNF) as photosensitizer, N-ethylcarbazole (ECz) as plasticizer, and N-4-nitrophenyl-(l)-prolinol (NPP) as electro-optic (EO) chromophore (Fig. 1). The composite of PVK/TNF/NPP/ECZ in a weight ratio 35 : 1 : 50 : 15 exhibited a 70 cm^{-1} 2BC coefficient and 22% steady-state diffraction efficiency at an approximate applied external field of 55 V/μm. The amplitude of the grating reached 0.66 $\times 10^{-3}$. In addition, transmission-type holograms were observed in this PR composite at zero applied field. The dynamic decay of diffraction light indicated that there exist two contributors with different phase-shift, and the slow decay time τ_{slow} can be as long as several h under continuous illumination by the readout beam (Fig. 1).

EXPERIMENTAL

Preparation of the PR Sample

PVK was synthesized in our laboratory (average M_w ca. 400,000) and purified by dropping 100 mL of 5% solution of PVK in toluene in 400 mL of methanol while stirring. NPP, ECz, and TNF were synthesized in our laboratory and purified twice by recrystallization. The sample was prepared by dissolving 200 mg of purified PVK, TNF, ECz, and NPP in 10 mL of chloroform. The solution was filtered through a PTFE(polytetrafluoroethylene) membrane with 0.45 μm pore size and the solvent was evaporated with a rotary evaporator. The mixture was dried in a vacuum oven at 60°C overnight to completely remove the solvent. After that, the film sandwiched between two ITO-coated glass slides was formed according to the method described in Hendrickx et al.[8] High optical quality films were obtained with PVK/TNF/NPP/ECz in a weight ratio of 35 : 1 : 50 : 15 and the thickness of the films was controlled to 130 μm by using spacers.

2BC Experimental Setup

A typical titled geometry[5,9] was used in our 2BC measurements as shown in Figure 2. Two coherent 632.8 nm laser beams separated from a cw single model (TE M_{00}) He-Ne laser were incident upon the sample film. The diameter of the beams was 2.0 mm on the surface of the sample and their intensities were reduced to ~ 1 mW/cm^2. During the measurement, an external dc electric field was applied perpendicularly to the sample surface. The tilt angle was $\phi_{exp} = 60°$ and the angle between two incident beams was $2\theta_{exp} = 20°$ in air.

DFWM Experimental Setup

The DFWM experiment was performed with the so-called SSP geometry.[10] Two s-polarized beams, beam E1 and beam E2 with the same incident angles as in the 2BC experiments, wrote a grating inside the sample. A third p-polarized beam E3, which was counter-propagating to beam E2 with a much weaker intensity, was used as the recording beam. The intensity of the diffraction beam E4, which is counter-propagating to beam E1, was detected.

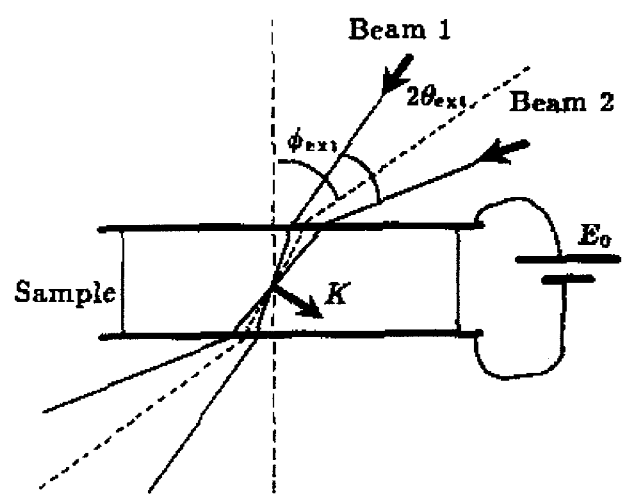

Figure 2 Experimental setup for 2BC. K is the grating wave vector.

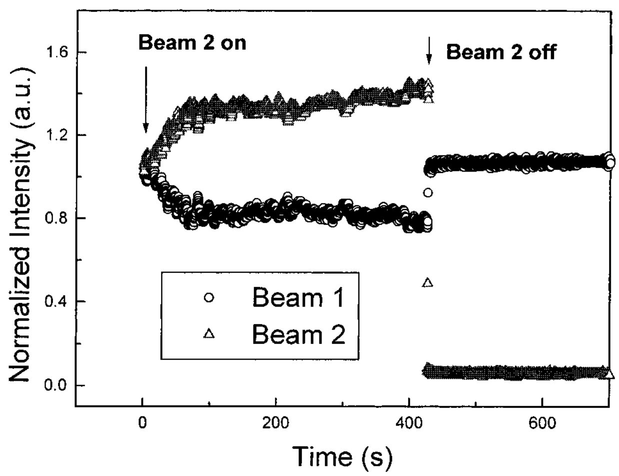

Figure 3 Energy transfer in a 2BC experiment at a dc external field 55 V/μm for the NPP doped sample.

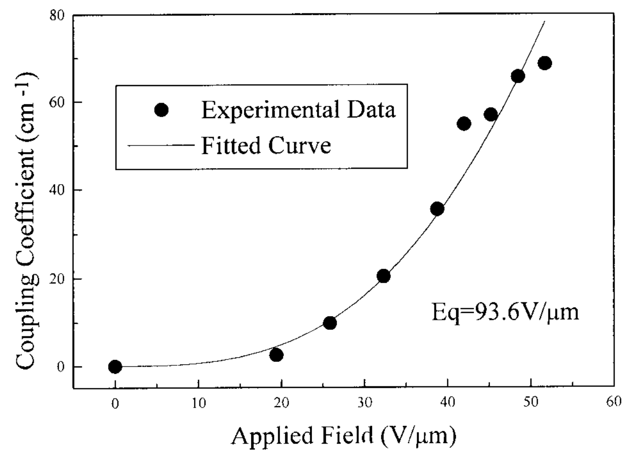

Figure 4 The dependence of the 2BC gain coefficient with the applied field.

RESULTS AND DISCUSSION

2BC Characterization of the PR Sample

The nonlocal nature of the PR grating is the main feature for PR effect to distinguish itself from many other mechanisms that may result in refractive index gratings. Therefore, the asymmetric energy transfer in 2BC experiments was usually used for direct adjustment of PR gratings.[11] Typical two-beam coupling behavior of the NPP doped PR film is shown in Figure 3, in which a significant energy transfer between the two beams can be observed. This proves that the PR effect occurred in the NPP doped sample and a coupling gain of ~ 70 cm^{-1} was obtained at a bias applied field of 55 V/μm. The electric field dependence of the coupling gain of the NPP doped sample is shown in Figure 4 and the experimental results fit eq. (1) according to the standard band transport model[12]:

$$\Gamma = K\frac{E_0E_0^G}{\sqrt{1+(E_0^G/E_q)^2}}\sin[\tan^{-1}(E_0^G/E_q)] \quad (1)$$

where E_0^G is the component of E_0 along the direction of the grating wave-vector, E_q is the trap-limited saturation space-charge field. The diffusion field effect has been neglected because it is always very small in polymers.[10,13]

DFWM Characterization of the PR Sample

Figure 5 shows the typical result of the dynamic grating formation and decay in PVK/TNF/NPP/ECz. The writing beams are turned on at I ($t = 0$), and the diffraction efficiency grows slowly, reaching a steady-state after ~ 800 s of writing. The fluctuations in the signal as it rises to its steady-state value are due to slow changes in the optical paths of the writing beams.[2,14] When the external field and writing beams are turned off at II, the signal first decays to zero rapidly, followed by a significant recovery and then a slow decay. This phenomenon suggests that more than one grating is formed during the writing period. Similar decay phenomena can be observed when the applied field is again turned on and then turned off.

Figure 6 shows the electric field dependence of DFWM diffraction efficiency (η) and grating amplitude (Δ) of the NPP doped sample. The exper-

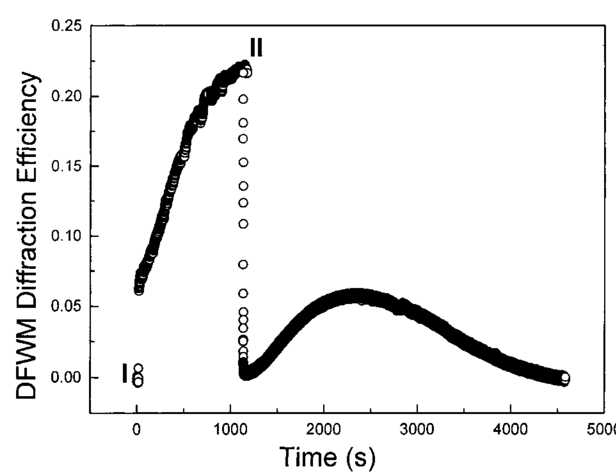

Figure 5 FWM result of NPP doped PR sample.

imental diffraction efficiency data are fitted very well by the eq.[15]:

$$\eta \sim \sin^2\left(k\frac{E_0^G E_0}{\sqrt{1 + E_0^G/E_q}}\right) \qquad (2)$$

where k is a constant relating to the effective EO response including both EO effect and orientational birefringence effect in the experimental geometry. The amplitude of the grating Δn was calculated using the expression of[15]:

$$\eta = \sin^2\left(\frac{\pi \Delta n d}{\lambda(\cos\,\theta_1\,\cos\,\theta_2)^{1/2}}\right) \qquad (3)$$

where d is the thickness of the sample, θ_1 and θ_2 are the incident angles of writing beams E1 and E2 inside the sample and λ is the operating wavelength. At an applied field of 58 V/μm, the amplitude of the grating reached 0.66×10^{-3}.

Transition-Type Hologram Characterization at Zero Applied Field

A photoinduced refractive index change in our PR sample was also observed without an applied field. The holographic reading experimental setup was the same as with the 2BC experiment at zero external field. After writing for ~ 5 min, beam 1 was blocked, and beam 2 acted as a pass through the sample to form a transmission-type hologram. The decay of the diffraction signal intensity was fitted to a biexponential decay process (Fig. 7):

$$I_d = A_{\text{fast}}\exp(-t/\tau_{\text{fast}}) + A_{\text{slow}}\exp(-t/\tau_{\text{slow}}) \qquad (4)$$

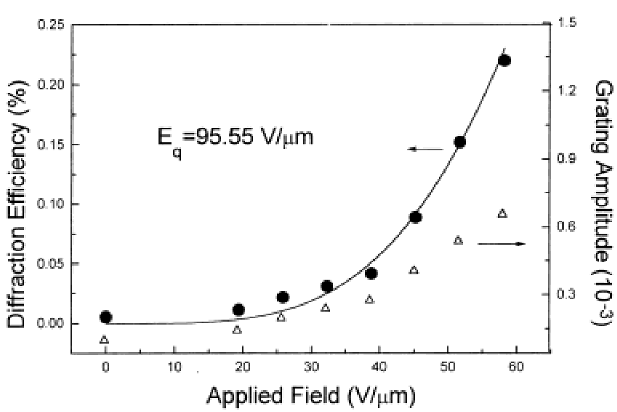

Figure 6 Diffraction efficiency and grating amplitude as function of applied field.

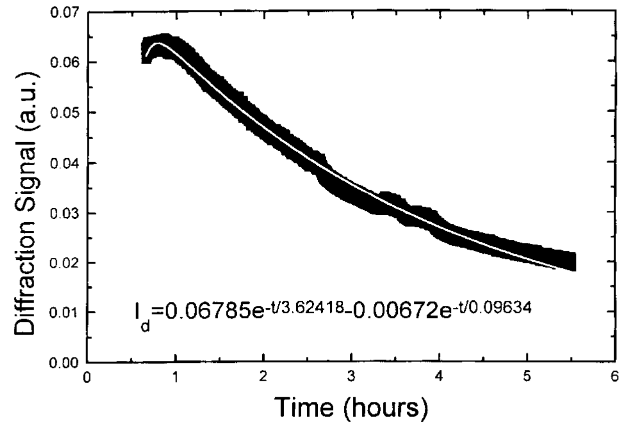

Figure 7 Decay of the diffraction signal intensity formed at zero external field.

The slow decay time can be as long as several h under continuous illumination and can be expected to be longer in a dark condition. Furthermore, a thin hologram that produced multiple diffraction orders was determined in a spin-coated sample that had the same component parts with the PR sample for ~ 1 μm on optical glass slide. Because NPP does not show any photochromic properties, the reason for the formation of the grating is still under investigation.

CONCLUSIONS

We have investigated the photorefractivity of a PVK/TNF/NPP/ECZ composite by 2BC and DFWM experiments. The composite in a weight ratio of 35 : 1 : 50 : 15 exhibited a 22% steady-state diffraction efficiency and 70 cm^{-1} 2BC coefficient at the applied external field of 55 V/μm. The amplitude of the grating reached 0.66 $\times 10^{-3}$. During the DFWM experiment, abnormal decay behavior was observed, and this suggests there exists more than one grating during the writing period. We also observed transmission-type holograms at zero applied field in our PR sample as well as the spin-coated thin film. The slow decay time of diffraction light can be as long as several h under continuous illumination by the readout beam.

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