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Effect of sensitizer on photorefractive nonlinear optics in poly(*N*-vinylcarbazole) based polymer composites

Naoto Tsutsumi *, Yuki Ito, Wataru Sakai

Department of Macromolecular Science and Engineering, Kyoto Institute of Technology Matsugasaki, Sakyo, Kyoto 606-8585, Japan

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Abstract

In organic photorefractive systems, photo-carrier generation of photoconductive polymer with sensitizer is important process, but no systematic study with the series of sensitizer on photorefractivity has been done yet. In this paper, the effect of sensitizer on photorefractivity is investigated for poly(*N*-vinylcarbazole) (PVCz) composites. Five types of quinones, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), 2,3,5,6-tetrachloro-*p*-benzoquinone (Chloranil), 2,5-dichloro-*p*-benzoquinone (Cl_2Q), *p*-benzoquinone (BQ), and 2,6-dimethyl-*p*-benzoquinone (MQ), and 1,2,4,5-tetracyanobenzene (TCNB), as well as 2,4,7-trinitrofluorenone (TNF) were used as sensitizer. Higher diffraction efficiency was measured for the samples of TCNB and Cl_2Q with lower photocurrent and lower absorption coefficient. This suggests that uniform photorefractive gratings in the direction of thickness was formed for the sample with lower absorption coefficient and couples to the resultant higher diffraction efficiency. Optical gain was in the range of $18.5 \pm 5\ cm^{-1}$ irrespective of kinds of acceptor except for Cl_2Q. Cl_2Q gave the largest optical gain of $43\ cm^{-1}$ and thus net optical gain of $33.3\ cm^{-1}$. Larger number density of traps was related to the larger photocurrent. Faster grating build-up speed for diffraction was significantly related to the larger number density of traps.

Keywords: Poly(*N*-vinylcarbazole) photorefractive composite; Sensitizer; Optical gain; Diffraction efficiency

1. Introduction

Photorefractive (PR) effect is based on the spatial modulation of refractive index, upon interfered beams illumination, via the Pockels effect (linear electro-optic effect) which is induced by the space-charge-field created by the photogenerated charge carriers. Thus, the photoconductive properties including photo-carrier generation and electro-optic nonlinearity are required for the PR response. In the photorefractive medium, index grating due to purely diffusive or purely drift-induced charge motion is spatially shifted by $\pi/2$ relative to the intensity pattern, and thus a unique phenomenon of two-beam coupling, when two-beams propagate through the medium, is observed in addition to the holographic recordings. Two-beam coupling optical gain can be employed for many applications, beam clean-up, self-pumped phase conjugators, optical interconnection, etc. [1].

Organic polymer composites with photoconductive material, nonlinear optical (NLO) chromophore and sensitizer have been typically used for PR materials. To seek the high-speed photorefractive polymer composites, several NLO chromophores based on the amino-styrene derivatives was investigated in poly(*N*-vinylcarbazole) (PVCz) composites [2]. Influence of ionization potential in NLO chromophore on speed and magnitude of photorefractive effects was investigated for PVCz based composites [3]. The photorefractive studies in the past have been well summarized in recent reviews [4]. We have investigated the photorefractivity of the molecular glass based materials [5,6] and the photoconductive materials with pendant triphenylamine moiety [6,7].

It is well-known that the charge transfer (CT) complex between photoconductor and sensitizer plays an important

* Corresponding author. Tel.: +81 75 724 7810; fax: +81 75 724 7805.
E-mail address: tsutsumi@kit.ac.jp (N. Tsutsumi).

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role for the creation of electron–hole pairs, their separation to electron and hole, and thus the generation of hole photo-carriers. In the past studies of organic photorefractive material, a couple of sensitizers of 2,4,7-trinitro-9-fluorenone (TNF) and fullerene derivatives were only investigated [4], but no systematic studies of the series of sensitizer on photorefractive properties have been done yet. Current organic photorefractive researches have focused on the applications of recording media with high video rate, optical devices with fast response time and usage in optical communications.

We think that it is important to examine the essential role of sensitizer for developing new photorefractive systems. In this study, we focus and discuss the role of the sensitizer on the overall photorefractive performances.

2. Experimental

2.1. Materials

Samples were composed of PVCz as a charge transporting matrix, 4-azacycloheptylbenzylidene-malonitrile (7-DCST) as a NLO chromophore, diphenylphthalate (DPP) as a plasticizer and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), 2,3,5,6-tetrachloro-*p*-benzoquinone (Chloranil), 2,5-dichloro-*p*-benzoquinone (Cl_2Q), *p*-benzoquinone (BQ), 2,6-dimethyl-*p*-benzoquinone (MQ), 1,2,4,5-tetracyanobenzene (TCNB) and TNF as a sensitizer (an electron acceptor). Except for TCNB and TNF, the chemical structure of sensitizer is based on quinone molecule, which is substituted by cyano, chloro or methyl group.

2.2. Sample preparation

Composites with a given weight ratio of PVCz, 7-DCST, DPP and sensitizer were dissolved in tetrahydrofuran (THF). Then the composite films were cast from THF solution followed by drying at 70 °C for 24 h and in vacuum at 60 °C for 24 h. Finally, the film is sandwiched between two indium tinoxide (ITO) plates at an elevated temperature up to 140 °C. The weight ratio of PVCz/7-DCST/DPP/acceptor (49/15/35/1 by wt%) was used.

2.3. Four wave mixing diffraction measurement

A degenerate four-wave mixing (DFWM) technique was used to measure the diffraction grating of the sample film. The holographic gratings were written in the sample by two p-polarized beams of a He–Ne laser (632.8 nm, 10 mW) with intersected. The s-polarized reading (probe) beam from the same source propagating in the direction opposite to the writing beam is diffracted by the refractive index gratings in the sample film, and the diffracted signal propagates in the direction opposite to another writing beam and is reflected off by a beam splitter. The diffracted signal is then detected by a photodiode detector.

2.4. Two-beam coupling measurement

A two-beam coupling (2BC) technique was used to measure the coupling gain coefficient (optical gain) of the sample film. The gain coefficient (optical gain) is due to the two-beam coupling from one beam to the other. The same geometric configuration of two *p*-polarized beams crossing as DFWM was used, except that no probe beam was used, and the intensity of two crossing beams were measured using photodiode detectors to evaluate the coupling gain coefficient (optical gain).

2.5. Characterization

The UV–Vis absorption spectrum was recorded on a Shimadzu UV-2101PC spectrophotometer. Differential scanning calorimetry was carried out on a TA Instruments DSC 2920 differential scanning calorimeter with a heating rate of 10 °C min^{-1} to determine the glass transition temperature of the samples. The m-line method, in which an evanescent field is responsible for the guided-wave mode at discrete mode angle, was employed to determine the refractive indices of sample films. Laser source is a polarized He–Ne laser (632.8 nm). A prism of TaFD21 (HOYA Glass) with high refractive index (1.92588 at 632.8 nm) was coupled to film with an air gap. Photoconductivity was measured using an electrometer at applied voltage of 400 V under an illumination of monochromated Xenon light (slit width: 10 nm). Electro-optic measurement was performed with a He–Ne laser to determine Pockels coefficient at 632.8 nm.

3. Results and discussion

Table 1 summarizes the thermophysical properties of glass transition temperature (T_g) and fundamental optical properties of refractive index (n), absorption coefficient (α), photocurrent (I_p) and Pockels coefficient (r_{33}) with film thickness (d). All optical parameters were measured at 632.8 nm. The glass transition temperatures measured by DSC for the samples with various sensitizers are in the range between −5 and −7 °C. We measured higher photoconductivity due to larger absorption coefficient for DDQ, Chloranil and TNF with PVCz. Larger absorption coefficient related to the absorption due to strong CT complex of these sensitizers with PVCz.

Photocurrent is the product of the number of the photogenerated charge carriers per unit volume and drift mobility, and the number of carriers strongly depends on the photophysical processes of photo excitation through absorption, followed by the generation of ion-pair between PVCz and sensitizer, and the electric field dependent carrier generation efficiency from the ion-pair. Thus, we think that the photocurrent is the over-all properties of photophysical and carrier mobile processes significantly related to the photorefractivity. Action spectrum (wavelength dependence of photocurrent) and absorption spectrum are shown