High Performance in Photorefractive Polymers and Their Application to Transient Hologram

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Abstract

As a new target following xerographic photoreceptor in the research of organic opto-electronic materials, photorefractive polymers have been investigated focusing on the PVK/TNF photoconductive polymer. The serious problem of thermal instability of the PVK-based PR polymer reported by Arizona Univ. group has been solved by replacing EtCz added as a hole transportable plasticizer with BisCzPro (dimeric compound) or their mixture. We have succeeded in fabricating a highly stable photorefractive polymeric system and high-speed response of less than 100 ms has been achieved, which seems to promise a future application for the real-time hologram. This paper will describe the molecular design for high performance and demonstrate the state-of-arts in real-time hologram using the present photorefractive polymer.

Introduction

Organic opto-electronic materials including photoconductive polymers have succeeded in practical use as xerographic photoreceptors, which play an important role for the current information-oriented society. With the advance of technology in this field, a great progress has been achieved in developing many prominent materials as well as understanding the electronic processes used in there. On the other hand, it is often said that the technology of this field has been reaching full growth. Thus, it is to be desired to find a new avenue for making full use of much worthwhile knowledge developed there so far.

Recently, photorefractive polymers are of growing interest as a new class of organic opto-electronic materials for constructing the advanced imaging and recording devices[1,2]. Photorefractive (PR) effect, i.e., photo-induced refractive index change, is appeared only in the material that exhibits both photoconductivity and electro-optic effect. In a different light, this phenomenon seems to provide a new avenue for further application of organic photoreceptor materials since the photoconductivity is definitely required. Actually, in the well-known PVK/TNF photoconductive polymer incorporating NLO (Non-linear optic) compound, high performance of almost 100% diffractivity has been reported from Arizona Univ. group[3]. Such high diffractivity in organic photorefractive polymers, however, has been found later to be attributed to the "orientational enhancement effect", in which NLO molecules incorporated reorientate toward the space charge filed built-in by photoconductivity to result in enhancing refractive index change. Indeed, they added the third compound of EtCz (N-ethylcarbazole), which is a monomeric compound of PVK, as a hole transportable plasticizer to ensure low Tg (glass transition temperature) without deterioration of the hole transport ability for the "orientational enhancement". This system, however, has had a serious problem that EtCz added is easy to crystallize and results in an optically opaque film.

In this paper, we would like to report that we have succeeded in fabricating a highly stable photorefractive polymeric system and high speed response of less than 100 ms has been performed by replacing EtCz to be added to PVK with BisCzPro (a dimeric model compound of PVK).

Experimental

The present photorefractive polymers are also composed of PVK/TNF (2,4,7-trinitro-fluorenone) charge transfer complex photoconducting polymer, EtCz and/or BisCzPro as hole transportable plasticizers, and NLO compound. The NLO compounds used in this study, DBMNA(Schiff-base type), DMNAA(azo-tpe) and NPP, are shown in Fig. 1.

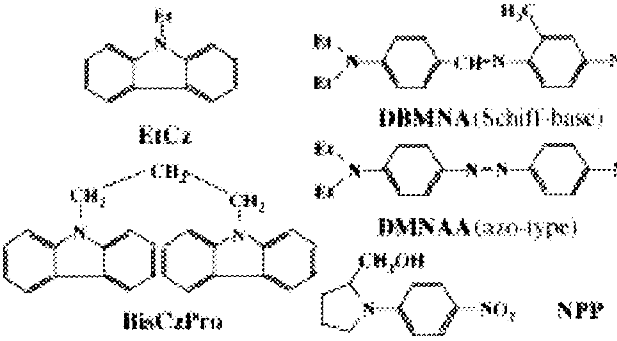


Fig. 1. Hole transportable plasticizers and NLO used in this study.

The samples were prepared in a sandwiched structure by hot press of the cast film at 130 °C with two optically transparent ITO electrodes with a spacer of 100 μm thickness. The typical dispersion ratios of TNF, plasticizer and NLO were 1 ~ 3%, 30%, 30 ~ 40% by weight, respectively. Measurements were carried out under applying DC voltage externally to the sample for ensuring electro-optic effect of the polymers, by which originally randomly oriented NLOs are aligned to make the film non-centrosymmetric.

The evaluation of the photorefractivity was made by four-wave mixing (FWM) and two-beam coupling experiments (Fig. 2). Holographic gratings were written in the polymers using two beams of equal intensity from 10 mW He-Ne laser (633 nm) overlapped in the sample film at incidence angles of 60° and 30° to the normal direction, respectively. In FWM experiments, the reading beam (0.5 mW) was aligned so as to propagate in the opposite direction to one of the writing beam. The electro-optic coefficients, r_{33}, an effective component for PR effect, were obtained according to the method reported by J. Schildrauk[4].

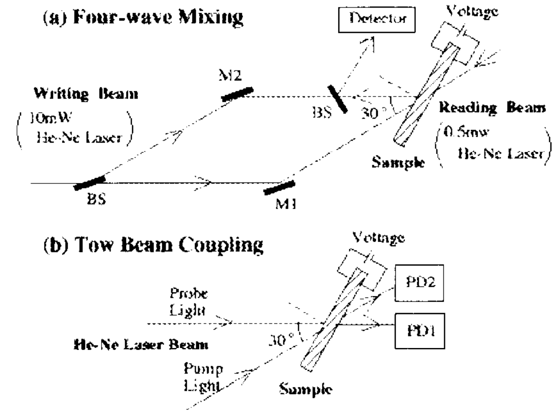


Fig. 2. Experimental setup of (a) Four wave mixing and (b) Two beam coupling.

Results and Discussion

1. Photorefractive effect in organic PR polymers

In Fig. 3 is shown the basic principle of photorefractive effect in organic PR polymers. When the two coherent lights are focused in a PR media, the light fringe pattern of alternating bright and dark sequence is formed. In the bright portion, the charge photogeneration occurs due to photoconductivity, i.e., the first nature of the PR polymers. If only hole carriers photogenerated are mobile, holes can migrate from bright fringe to dark leaving negative charges. The accumulation of holes and electrons in the dark and bright portions, respectively, gives rise to the spatially distributed space charges. The resulting space charge field modulates the refractive index of the PR media through the electro-optic effect, i.e., Pockels effect, due to the second nature of the PR polymers. Thus, the phase-shifted refractive index grating is formed as a replica of the light fringe pattern in the media. This is the reason for the PR media to be applicable to the hologram recording system, but in addition, the generation of phase-conjugated wave characteristic of the PR media, is very useful for various optical data processing.

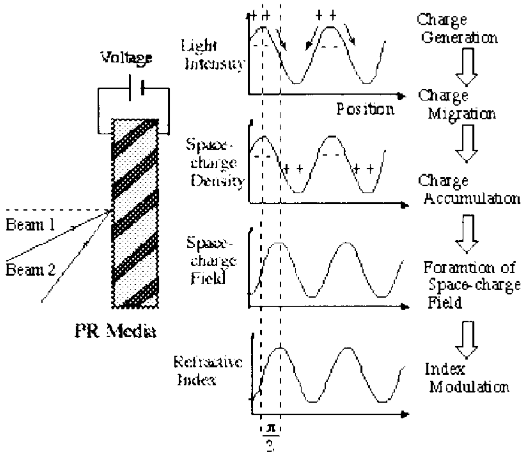
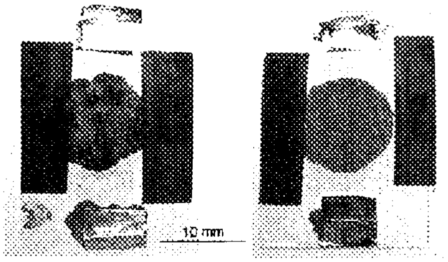


Fig. 3. The principle of PR effect in organic PR polymers.

2. Thermal Stability of PVK-based PR Polymers

Based on our previous investigations[3] on hole transport in PVK, we have already had a knowledge that PVK added with BisCzPro (a dimeric compound) provides very stable amorphous polymer film with low Tg and well-defined hole transport nature even in heavy loading. By replacing EtCz with BisCzPro, therefore, we tried to prepare PVK-based PR polymers. In Fig. 4 are compared the thermal stability of two samples doped with EtCz and BisCzPro as hole transportable plasticizers, respectively. If EtCz was added with PVK:EtCz = 1:0.5, the sample showed low Tg of –12 °C, but crystallization occurred immediately within a short period. On the other hand, the film doped with PVK/BisCzPro=1:1 was thermally very stable and no crystallization occurred even after more than 1 month, although Tg was comparatively high (about 10 °C). Figure 5 shows the field dependence of diffraction efficiency in these PR polymers with a composition of PVK/TNF/Plasticizer/DBMNA=22/1/22/55 in wt%. Reflecting Tg effect for "orientational enhancement", the doping of EtCz gave higher diffraction efficiency than that of BisCzPro. Next, in order to obtain high diffractivity in a thermally stable polymer, we have tried to use the mixture of both plasticizers with keeping the doping ratio of PVK/plasticizer=1:1. As shown in Fig. 6, Tg is lowered linearly with increasing EtCz ratio and until EtCz:BisCzPro=3:1 the sample was stable without crystallization. At 3:1 ratio, the PR polymer gave almost the same diffraction efficiency to the case of EtCz alone, as shown in Fig. 5. It should be noted here that the Tg of the sample changeable with changing the mixing ratio is useful and important because the maximum diffraction efficiency relating to the orientational enhancement is found to obtain at the temperature of about 10° higher than Tg in molecularly doped PR polymers, so it will be adjustable to the condition employed. Thus, we obtained good diffractivity and thermal stability with keeping low Tg enough for "orientational enhancement" even at ambient temperature.



PVK/EtCz
(1:0.5)
after 1 hr

PVK/BCzPro
(1:1)
after more than 1 month

Fig. 4 Comparison of the sample stability of the PVK-based PR polymers. PVK/EtCz(Left) and PVK/ BisczPro (Right).

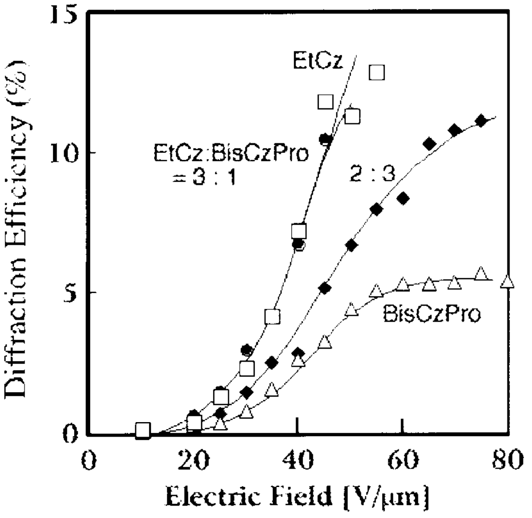


Fig. 5. Applied field dependence of diffraction efficiency for various BisCzPro: EtCz ratios. Sample composition: PVK/ Plasticizer/ DBMNA/ TNF= 22/ 22/ 55/ 1wt%.

3. Photorefractivity of the PVK/BisCzPro-based PR polymers

Undoubted evidence for photorefractivity is given by demonstrating phase-shifted refractive index grating formation. To do this, the asymmetric-energy transfer in two beam coupling experiment was performed. Figure 7 shows the intensity changes of probe and pump beams in the PR polymer (PVK:22wt%/BisCzPro:22/DBMNA:55/

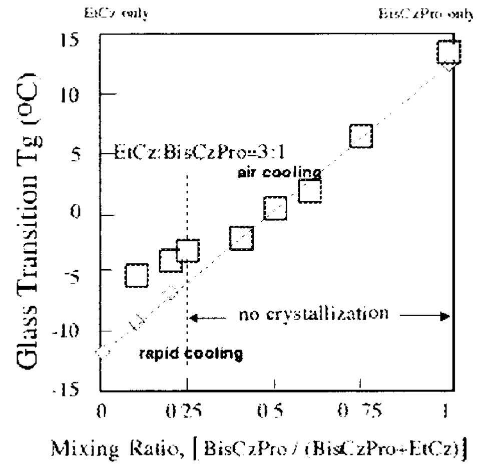


Fig. 6. Grass transition temperature, Tg with EtCz: BisCzPro mixing ratio in PVK-based PR polymer.

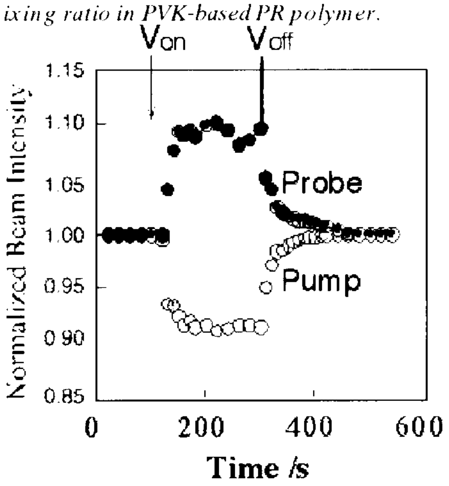


Fig. 7. Asymmetric energy transfer in two beam coupling in a PVK/BisCzPro-based PR polymer.

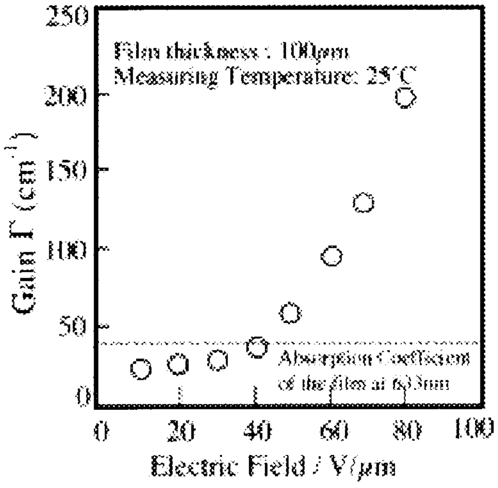


Fig. 8. Electric field dependence of beam-coupling gain coefficient Γ.

TNF:1), which gave diffraction efficiency of about 5% at 80V/μ. With applied voltage turned on, the probe beam intensity increased, while that of the pump beam decreased, and both beam intensities are restored with voltage turned off. This result apparently indicates that refractive index grating induced by space charge field due to photogenerated charge carriers phase-shifted from the interference fringe pattern. As shown in Fig. 8, the 2BC gain coefficient Γ calculated was found to be 200 cm^{-1} at 80V/m, which exceeds the absorption coefficient α of the polymer (40 cm^{-1} at 633 nm) and is large enough for the light amplification.

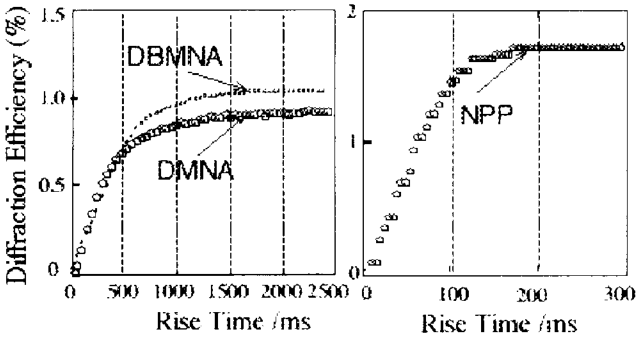


Fig. 9. Typical response upon applying external voltage for three kinds of NLO.

4. Response of PVK/BisCzPro-based PR polymers

Since the PR effect in organic PR materials wes largely to the "orientational enhancement" due to reorientation of NLO molecules toward inner built-in space charge field in addition to Pockels effect, the response is said to be slow if compared with inorganic PR materials. The PVK-based PR polymers doped with plasticizers shows relatively high speed than others. The refractive index grating formation speed was evaluated using thermally stable PVK/BisCzPro-based PR polymers incorporating several types of NLOs shown in Fig. 1. In Fig. 9 are shown the typical response upon applying external voltage. Response depends on the kind of NLO molecules. The case of NPP, the most small compound among those, gave fairly high response of less than 100 ms, whereas both cases of DBMNA and DMNAA gave relatively slow response of about 1 s, The origin of the deference is not clear at this moment, although it seems dependent on the size and shape. It should be pointed out that the response time is also strongly dependent on the operating temperature . Actually, even in DBMNA of high loading of more than 30 wt% and at warmer room temperature, the high speed response time of about 100 ms was observed with 6% diffractivity, by which the video-rate real time hologram (Fig. 10) was successfully demonstrated in a PVK:25wt%/BisCzPro:24/DBMNA:50 /TNF:1 composition.

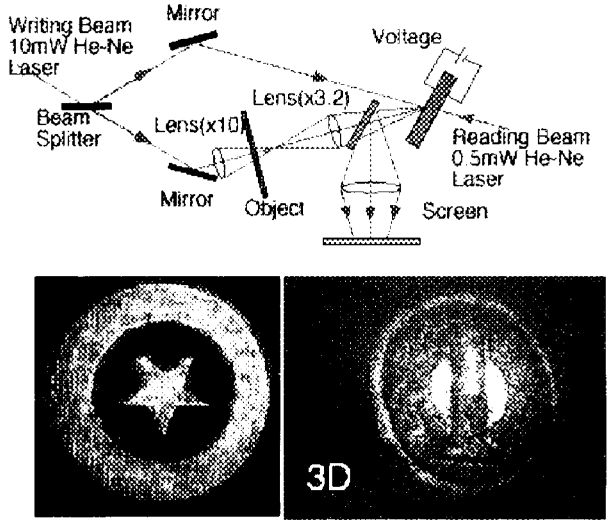


Fig. 10 Experimental setup for real-time hologram recording and a reproduced image.

Conclusion

As a new target following xerographic photoreceptor for organic opto-electronic materials, photorefractive polymers have been investigated. We have succeeded in fabricating a highly stable photorefractive polymeric system and high-speed response of less than 100 ms was achieved, which seems to promise a future application for the real-time hologram.

References

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Biography

Prof. Masaaki Yokoyama received the B.Sc. in 1966, the M.Sc. in 1968 and the Ph. D. in 1971 from Osaka University in polymer science. Since 1971 he worked in the Faculty of Engineering, Osaka University, and in 1987 became professor. His current interests involve photo-conducting materials and their application to novel opto-electronic devices. He is an active member of ISJ (The Imaging Society of Japan) . He received the Journal Award of SEPJ in 1987 and 1998, the Journal Award of IS&T in 1990, and IS&T Fellowship Award in 1994.