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The crosslinkable polymer matrices and NLO chromophores containing alkoxysilyl groups are used in this system to increase the stability of NLO property for sustaining photorefractive effect. The polymer systems with or without crosslinkable groups were prepared from PMMA, poly(MMA-co-TMSM), poly(VK-co-MMA) and poly(VK-co-TMSM) doped with modified DR1 (DRS) and modified carbazole (CzS). The photoconductivity and second harmonic generation measurements for poled thin films were carried out to manifest the photorefractive effect. The d_{33} values were high (about 40 pm/V) and the temporal stability for crosslinkable polymer system was reasonably high (without UV-absorption change for 90 hrs). The electric field dependence of the photoconductivity was obtained by negative discharging method. Furthermore, photorefractivity was confirmed from two-beam coupling (2BC) measurements. It follows a value of the normalized gain coefficient Γ' of 2~13 cm^{-1} at 633nm.

Keywords: photorefractive materials; crosslinkable polymer system

INTRODUCTION

The photorefractive effect, that is, the change of refractive index of the material has been observed almost three decades ago[1]. Most of researches have been focused exclusively on inorganic crystals[2]. However, inorganic crystals have a lot of problems such as a difficulty in fabrication and

processability. Recently, both organic single crystals and pold polymers have been emerged in this field because of their useful properties and unique advantages, e.g., ease of preparation for large-area samples, a low dielectric constant, high optical performance, and low cost.

In view of the poled polymer systems, the thermal crosslinking is promising for stability, such as crosslinked epoxy host polymeric system ; bisA-NPDA : DEH[3]. However, they have serious disadvantages such as optical loss and poor film quality due to phase separation. More recently, most of the researches focused on the multifunctional polymeric or monolithic material system[4]. Though the multi-component systems with low T_g have been studied, the crosslinked system can be considered for thermally stable photorefractive materials as well.

In this work, a crosslinkable polymer system was selected in order to obtain thermally stable multifunctional system. The matrices and NLO chromophores containing alkoxysilyl group were used in this system to increase the stability of NLO property for sustaining photorefractive effect.

EXPERIMENTAL

Modified disperse red 1 (DRS) was used as a nonlinear optical chromophore. Modified carbazole (CzS) was used as a charge transporting molecule, especially in the cases of PMMA and Poly(MMA-co-TMSM). The 3-nitril carbazole (67%) was prepared from solution of carbazole (3.0g, 0.018 ㏖), nitric acid (0.9mL, 0.018 ㏖), and acetic acid (1.0mL, 0.018 ㏖) in *N,N*-dimethylformamide (DMF) (50 ㎖). CzS (yield 75%) was prepared from 3-nitril carbazole, 2-chloroethanol and tri-ethoxysilylpropylisocynate at room temperature in THF for 5 hrs using sodium hydride. Modified DR1 (DRS) was prepared following previously reported method[5].

Four kinds of polymers were used as matrices : PMMA, poly(MMA-co-TMSM), poly(VK-co-MMA), and poly(VK-co-TMSM), where TMSM is 3-(trimethoxy silyl)propyl methacrylate, and VK is 9-vinylcarbazole. The thermal properties of polymers were determined by DSC and TGA (Thermal analyst 2100, TA Instrument). The molecular weights of polymers were determined by light scattering (S 4700 Marvern) analysis.

Precursor solution was prepared from matrix polymer and dopants such as DRS (10wt%) and CzS (10wt%) in THF (2 g), and spin-coated onto micro

slide glass. Each sample was poled at 7kV and 80 ℃. UV-VIS spectroscopy (Shimadzu UV-3100) was used to measure the absorption change before and after poling. The wavelength for photoconductivity and two beam coupling (2BC) measurements were determined using UV/VIS spectroscopy as well. Second harmonic generation (SHG) was measured using a rotational Maker fringe method at a fundamental wavelength of 1064 ㎚ Nd:YAG laser. The films were coated on the ITO coated glasses for the photoconductivity measurement due to xerographic discharge method.

For measuring photorefractivity, the films were prepared by casting onto the slide glasses, and dried more than one day. The thickness of the resulting films were 50 ㎛~180 ㎛. Each film was poled at 7kV by corona poling apparatus. The 2BC gain for each system was measured at 633nm. Since all the samples have a weak absorption at 633nm, then it was suggested that the absorption act as the charge generation, and the traps are assumed to be inherent in the polymer.

RESULTS AND DISCUSSION

Table I summarizes decomposition temperature (T_d), glass transition temperature (T_g), d_{33} and molecular weight of polymers introduced in this work. Generally, UV-VIS spectra and SHG coefficient were introduced to confirm the orientation of molecules after poling. The temporal stability is estimated from the time evolution of the optical absorbance. A normalizes with that of t=0 (A_0). The value of A/A_0 for crosslinked polymer was reasonably high.

TABLE I. Characterization of polymers, absorption properties, SHG (d_{33}'s) and 2BC gain coefficients of the PR composites.

Polymer	T_d(℃)	Tg(℃)	Mw[a]	λ_{max} (nm)[b]	d_{33} (pm/V)[b]	α (cm^{-1})[b),c)]	Γ (cm^{-1})[b),d)]
PMMA	263	108.5	85,000	486	126	7.5	2.6
Poly(MMA-co-TMSM)	240	23.7	150,000	487	21	17.5	2.0
Poly(VK-co-MMA)	345	137.0	31,000	494	57	14.7	12.8
Poly(VK-co-TMSM)	267	50.2	360,000	493	41	-	-

[a] by Light Scattering (g/mol), [b] doped with DRS and CzS, [c] absorption coefficient at 633nm, and [d] 2BC gain coefficient

Figure 1 shows the electric field dependence of photoconductivity for photorefractive systems. The photoconductivities are at least one order of

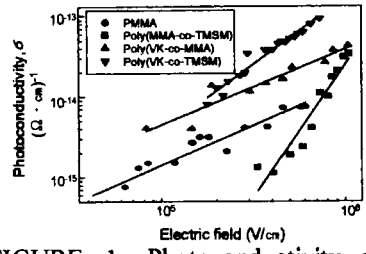

FIGURE 1. Photoconductivity vs. electric field strength by photo-induced discharge method.

magnitude smaller than PVK system. However, the results reveal a relatively strong dependence for the electric field.

The photorefractive properties were confirmed from 2BC measurements. A value of the normalized gain coefficient Γ' was 2~13cm^{-1} at 633nm, whereas the absorption coefficient α was 7.5~17.5 cm^{-1} at the same wavelength (see Table 1). In fact, to achieve a real application, the net gain ($\Gamma' - \alpha$) must be positive, which are not achieved yet for our systems. This might be due to the absorption of exciting light by DRS chromophore. It follows that the design of optical windows for CT complex formation is strongly required. Further investigation is in progress.

CONCLUSIONS

In summary, second order nonlinear optical properties have been observed each system. In addition, photoconductivity, and asymmetric energy transfer in the two-beam coupling have been observed in a poly(N-vinylcarbazole) copolymer composite. This system is suitable for long-term information storage application.

REFERENCES

[1]. Ashkin, A., Boyde, G. D., Dziedzic, J. M., Smith, R. G., Ballman, A. A., Levenstein, J. J. and Nassau, K., Appl. Phys. Lett., **9**, 72 (1966)
[2]. Coodman, J. W., International trends in optics, *Academic press*, chap. 8 (1991)
[3]. Dücharme, S., Scott, J. C., Twieg, R. J., and Moerner, W. E., Phys. Rev. Lett., **66**, 1846 (1991)
[4]. Zhang, Y., Wada, T., and Sasabe, H., Chem. Commun., 621 (1996)
[5]. J.-S. Lee, Y.-S. Cho, G. Cho, K. T. Jung, Y. S. Shul, and M.-G. Choi, Mol. Cryst. Liq. Cryst., **280**, 53 (1996)