Photorefractive Effect of Liquid Crystal Polymer Poly 4-methacryloyloxyhexyloxy(4'-nitrobenzylidene)aniline

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The photorefractive effect of the liquid crystal polymer, poly 4-methacryloyloxyhexyloxy(4'-nitorobenzylidene)aniline doped with (diethylamino)benzaldehyde diphenylhydrazone (DEH) and 2,4,7-trinitro-9-fluorenone (TNF), was investigated using a two-beam coupling experiment. A diffraction efficiency of ~5% was obtained under an applied electric field of 20~30 V/μm.

Photorefractive polymers have been attracting great interest from both fundamental and practical viewpoints.[1] Especially with regard to photonic applications, photorefractive polymers with high sensitivity, high transparency and high stability are required. The photorefractive effect of glassy materials has been investigated in which a high concentration of NLO compounds was doped in the photoconductive polymers.[2-6] They showed a diffraction efficiency (η) of 30~80% under application of a 50 V/μm electric field, however, they were rather unstable because of dopant aggregation. Recently, the photorefractive effect of low-molecular-weight nematic liquid crystals has been investigated.[7,8] It was reported that the change in the refractive index was enhanced in a nematic liquid crystal phase due to a quadratic electrooptic effect.[9] In this study, the photorefractive effect of a liquid crystal polymer (Figure 1) doped with 10~30 wt% of a photoconductive dopant was investigated.

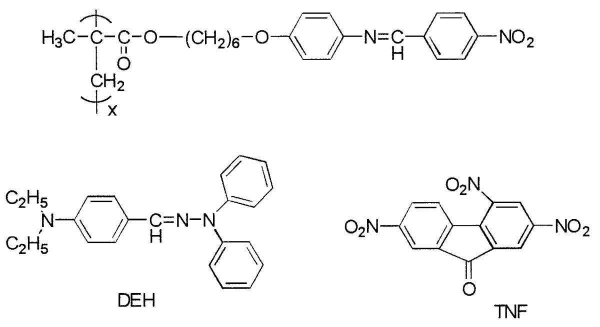

Figure 1. Structures of compounds used in this study.

The liquid crystal polymer was synthesized according to ref. 10. The photoconductive compound, DEH, was synthesized via the reaction of diphenylhydrazine and diethylamino-benzaldehyde in pyridine. TNF (sensitizer) was obtained from Tokyo Kasei Co. and purified by recrystallization from a mixture of hexane-ethylacetate. The polymer film exhibited a liquid crystal phase. A schlieren texture was observed under a polarizing microscope. The phase transition temperature was determined by DSC to be 118℃ and the phase transition enthalpy was estimated at 369 J/mol. The phase was attributed to a nematic phase. The photorefractive sample was prepared by casting of the dichloroethane solution of the polymer mixed with DEH and TNF on an ITO patterned glass. The ratio of DEH in the film ranged from 0 to 30 wt% with the concentration of TNF maintained at 3 wt%. No phase separation was observed under the polarizing microscope and during the DSC measurements. In order to obtain a flat film, the casting solution was prepared at a rather high concentration (about 200mg in 1 ml). The film was dried under vacuum for 6 h and sandwiched between two ITO glasses at 70 ℃. The film was softened at this temperature and was completely filled between the ITO electrodes. The film thickness was 100 μm as determined by a Teflon spacer.

Table 1. Phase transition temperature and photorefractive properties of LC polymer/DEH mixtures

DEH / %	Tg^a	T_{NI}^a	η^c / %	$\tau_E^{c,d}$ / s
0	50	118	-	-
10	37	64	< 0.1	7.3
20	29	52	0.4	5.1
30	23	44^b	0.8	4.3

[a]Measured by DSC. [b]Only a weak birefringence was observed under the polarizing microscope. [c]Electric field of 10 V/μm was applied to the sample. [d]τ_E is the response time to an applied electric field required to change the transmittance intensity from the initial value to 90% of the maximum change.

The photorefractive effect was measured using a two-beam coupling experiment. A P-polarized beam from a He-Ne laser (633 nm, 7 mW output) was separated by a half mirror and refocused at the sample film. The sample was tilted 30° and the angle between the two incident beams was 40° which gave a grating spacing of 0.17 μm. An electric field of 10~30 V/μm was applied to the sample and the change in transmitted beam intensity was monitored by a power meter and recorded by a computer.

Prior to the optical experiments, a DSC analysis of the prepared films was conducted because the thermal property of the optical materials generally affects the appearance of the photorefractive effect. The temperatures of the glass transition (Tg) and of the nematic to isotropic phase transition (T_{NI}) are shown in Table 1. Both the Tg and T_{NI} decreased as the DEH concentration increased. One can readily assume that at a higher dopant concentration, the polymer matrix was plasticized and the NLO chromophore (mesogen) effectively rearranged along the direction of the applied electric field.

A typical example of the result of the two-beam coupling experiment is shown in Figure 2. When an electric field of 10 V/μm was applied to the sample, the transmitted intensity of one beam increased while that of the other beam decreased. An energy exchange of about 1% was observed under these conditions. When the field was turned off, the intensities of the two beams gradually returned to their original values. The dependence of the intensity of the electric field on the diffraction efficiency is shown in Figure 3. The diffraction efficiency was increased as the intensity of the applied electric field increased. The gain coefficient at 33 V/μm was calculated to be 9.02 cm^{-1}.

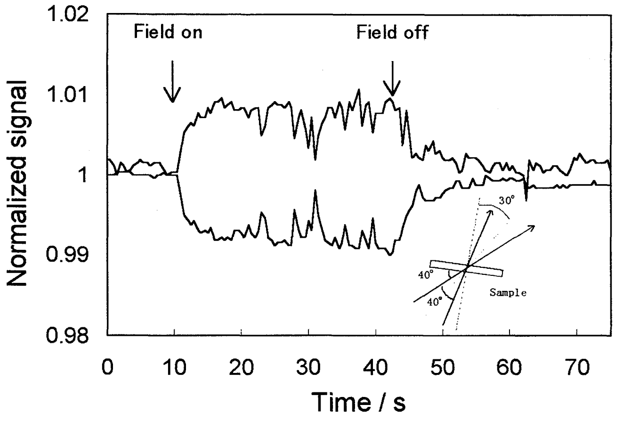

Figure 2. Example of asymmetric energy exchange between laser beams. Electric field (10 V/μm) was switched on at t=10 s and off at t=42 s. Sample composition: Polymer:DEH:TNF = 67:30:3 wt%.

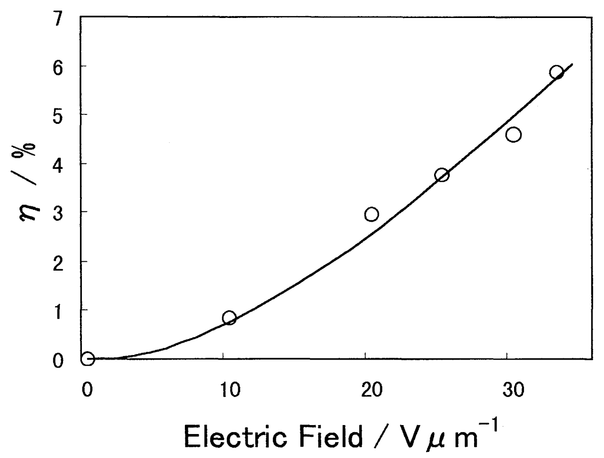

Figure 3. Dependence of diffraction efficiency on electric field. Sample composition: Polymer:DEH:TNF = 67:30:3 wt%.

In our experimental set-up, only a weak electric field with a maximum of 33V/μm could be applied to the sample. If a higher electric field was applied, a higher optical gain could have appeared. The diffraction efficiency of this sample was relatively large compared to those of other photorefractive amorphous polymers previously reported under the same electric field of 20~30 V/μm.[1] We also examined the effect of the concentration of DEH. As we already mentioned, with increasing concentration of the dopants, the diffraction efficiency was increased and the response time to an applied electric field (τ_E) was shortened. The flexibility for rearrangement of the NLO molecules would play a crucial role in the large Pockels effect within a short period.

The photorefractive effect of the liquid crystal polymer, poly 4-methacryloyloxy hexyloxy-n-(4'-nitorobenzylidene) aniline, was investigated. The photorefractive gain coefficient of 9.02 cm^{-1} was obtained under application of the weak external electric field of 33 V/μm on the composite of LC polymer:DEH:TNF with a 67:30:3wt% ratio. Further measurements of the photorefractive effect of liquid crystal polymers are now in progress.

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