SECURITY CLASSIFICATION OF THIS PAGE

AD-A252 641

DOCUMENTATION PAGE

1a. REPOR
Un

2a. SECUR

2b. DECLA... JUL 07 1992

1b. RESTRICTIVE MARKINGS
None

3. DISTRIBUTION / AVAILABILITY OF REPORT
Unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
18

5. MONITORING ORGANIZATION REPORT NUMBER(S)
Office of Naval Research

6a. NAME OF PERFORMING ORGANIZATION
Univ. of Nebraska-Lincoln

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)
632 Hamilton Hall
University of Nebraska
Lincoln, NE 68588-0304

7b. ADDRESS (City, State, and ZIP Code)
Chemistry Division, Code 111 3PO
800 N. Quincy Street
Arlington, VA 22217-5000

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
Office of Naval Research

8b. OFFICE SYMBOL (If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS (City, State, and ZIP Code)
800 N. Quincy Street
Arlington, VA 22217-5000

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)
The Electric Field Dependence of the Laser Induced Holographic Grating Relaxation of a Photorefractive Polymer

12. PERSONAL AUTHOR(S)
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13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM _____ TO _____		

16. SUPPLEMENTARY NOTATION
SPIE Proceedings

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

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20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Dr. Joanne Millikan	(202) 696-4409	

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

The Electric Field Dependence of the Laser Induced Holographic Grating Relaxation of a Photorefractive Polymer

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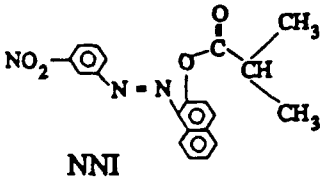
ABSTRACT

Laser induced holographic grating relaxation (HGR), electro-optical (EO) and second harmonic generation (SHG) studies have been carried out in a guest/host system subject to an external electric field with and without the presence of a hole transport agent. The guest is NNI, which has moderate second order nonlinear optical (NLO) coefficient, the host is PMMA and the hole transport agent is DEH. (See the text for the exact names of the acronyms.) In the presence of DEH, the lifetime of the cis isomer of NNI detected by using the HGR technique is lengthened by the application of an electric field of moderate strength. The field dependence effect is not observed when DEH is absent in the sample. The result is interpreted as due to the stabilization of the cis-isomer by the electric field polarized DEH. The data obtained from SHG and EO measurements appear to corroborate the HGR result.

1. INTRODUCTION

Laser induced holographic grating relaxation (HGR) is a powerful technique for the investigation of the dynamic processes involving the photochromous dye molecules dispersed in a polymer host. The technique involves first creating amplitude or phase gratings (holograms) by the interference of two intersecting coherent laser beams in the photochromous material. The gratings are induced and recorded (and subsequently altered or erased) in "real time" without intermediate development steps as is required for hologram recording in photographic emulsions. The state of holograms can be read out simultaneously by one of the original recording beams or by an additional beam. These holograms are persistent in the absence of illumination for a time which is proportional to the lifetime or the time associated with translational or rotational diffusion of the long-lived photoexcited dye molecules.

In this report we present results of a preliminary study of the dynamic process of 1-(4-nitrophenyl-azo) 2-naphthyl isobutyrate (NNI) doped in poly(methyl methacrylate) (PMMA) with and without the presence of p-diethylamino-benzaldehyde diphenylhydrazone (DEH). The motivation for conducting this study is to search for a method with which one can perturb the holographic grating in a controllable manner by an external means, e.g. through the application of an electric field. Upon irradiation of NNI, whose formula is given by

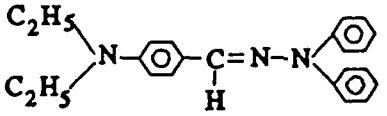


NNI

it undergoes the trans-cis isomerization through the azo bond.[1] The change in the electronic configuration due to isomerization results in a change in the real and imaginary parts of the refractive index. The refractive index change gives rise to holographic gratings, when the sample is irradiated with coherent laser beams.

One of the advantages of utilizing the azo dye as an active medium for generating holographic gratings is the capability of manipulating the duration of the lifetime of the cis-isomer via the selection of the various wavelengths of the reading laser. For example, the life-time of the cis-isomer of methyl red is considerably shortened by using the 488.0 nm radiation of an argon ion laser in comparison with using the 632.8 nm line of an He-Ne laser.[2] Recently, the conversion of the cis-isomer electrochemically to a stable third species (hydrazobenzene), which is then oxidized back to the trans isomer by an electron-chemical means has also been realized.[3] By combining the photo with the electrochemical process, the azo system forms a three state system for high density storage, multi function memory and non-destructive information read out.

The reason for adding DEH, whose chemical formula is given by



DEH

is that DEH is an effective hole transport agent and when DEH is added to a nonlinear optical (NLO) epoxy polymer, bisphenol-A-diglycidyleher 4-nitro-1,2-phenylenediamine (BisA-NPDA),[4] it produces electro-optic response and photoconduction sufficient for photorefraction.[4] Besides being a suitable holographic medium, we have shown in the second harmonic generation (SHG) study that NNI is also a moderate NLO chromorphore. It is thus of interest to find out whether or not the NNI-DEH/PMMA system also gives rise to a photorefractive response.

2. EXPERIMENTAL

The samples used in the holographic grating relaxation (HGR), electro-optical (EO) and SHG studies are guest host systems. The guest is NNI chromophore whose chemical formula is given above; the host is PMMA with molecular weight (Mw = 20,000). Two types of samples are prepared for experiments. One sample contains 5 wt% of NNI and 95 wt % of PMMA; the other has 5 wt % NNI, 9.5 wt % DEH and 85.5 wt % PMMA. Thin films for the SHG measurements were fabricated by first mixing the PMMA, NNI and DEH in chloroform and filtered through a 0.2 micron size microfilter to remove the undissolved particulate. The solution was adjusted to a suitable viscosity and then spin coated on soda lime glass slides, which were precoated with 300 Å SiO_2 and 250 Å ITO

films for electrical conduction. The sample was then dried in a vacuum oven at 40°C to remove the solvent and pressed together at 100°C to form a sandwich of slide-polymer-slide and cooled to room temperature. The sample thickness was about 3 μm. Thick films were fabricated by first spreading the mechanically blended solid mixture of dust free NNI, DEH and PMMA each with an appropriate amount on an ITO coated glass slide. Another ITO slide was then placed on the top of the mixture. The assembly was then compressed in a heated press to a uniform sample thickness of 220 μm. Thin spacers placed between the slides at the edges of the film were used to obtain uniform film thickness.

The UV-VIS absorption spectra of PMMA host, DEH/PMMA, and NNI-DEH/PMMA are shown in Fig. 1.

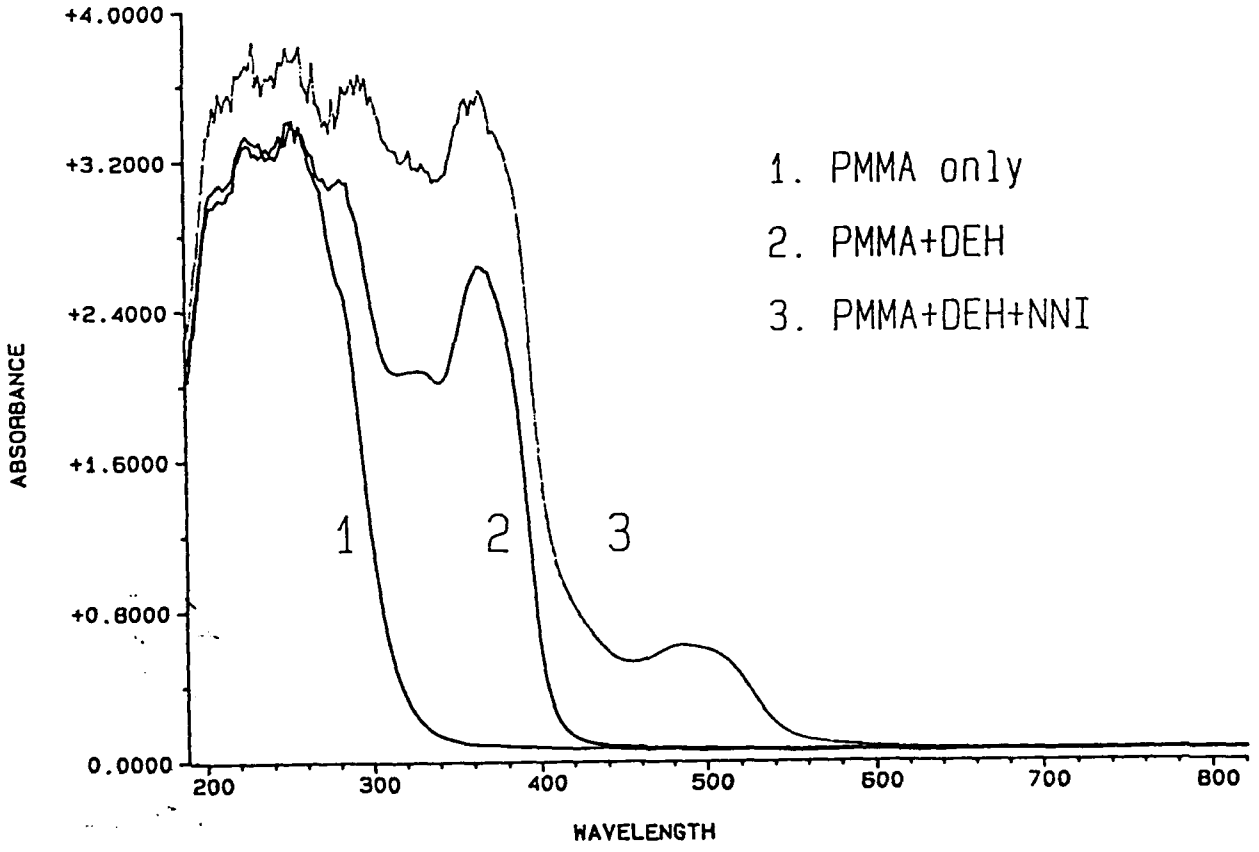


Fig. 1: The UV-VIS absorption spectra of PMMA, DEH/PMMA, and NNI-DEH/PMMA films on the IT glass slide.

For the HGR measurement, the holographic gratings were induced by crossing two equal intensity coherent beams at 501.7 nm emitted from an argon ion laser. The 501.7 nm radiation falls near the maximum of the NNI absorption band (Fig. 1). The power of each laser beam was 50 mW. The writing time was 1-3 controlled by a shutter. The crossing angle was 13.25 degrees. The state of holographic gratings was read by an He-Ne laser beam at 632.8 nm or by one of the attenuated argon ion laser beams. The HGR study was carried out at room temperature (21°C).

The electro-optical response was measured by using a Mach-Zehnder interferometer described elsewhere,[5] and the SHG signal was measured with a Nd:YAG laser (Spectra-Physics GCR-11, λ = 1.06 μm, Q-switched at 10 Hz and 250 mJ per pulse) as the fundamental beam. The sample was mounted on a computer controlled goniometer stage. The signal of the sample (poled at 90°C with an electric field of 5 x 10^4 v/cm) was detected by a photomultiplier tube, followed by a preamplifier, and averaged by a boxcar integrator (EG & G 4422). Comparing the signal with that of a single crystal quartz plate, d_{33} was estimated to be 0.07 pm/V for the thick sample containing DEH, which is about 7 times smaller than d_{11} of quartz.

3. Results and Discussion

The time dependence of the HGR curve for the sample without containing DEH can be fit to

$$I(t) = (A + Be^{-t/\tau})^2 \quad (1)$$

where A and B are optical constants.[6] The relaxation time τ obtained is 330.0 s which does not change with the crossing angle of the two coherent beams and thus is not associated with the translational diffusion process. As shown in ref. 6, the reciprocal of the relaxation time τ^{-1} corresponds to the conversion rate of the cis isomer back to the more stable trans isomer, and A corresponds to the coherent background associated with the scattering intensity from the trans isomer.

For the sample containing DEH, the HGR curve changes considerably from that without DEH. It has two decay processes. Shown in Fig. 2a are the decay curves at the short time region obtained with several electric fields applied. At zero voltage, the time constant for the fast decay is 0.38 s. Shown in Fig. 2b are the decay curves at the long time region obtained with different voltages applied. At E = 0, the time constant for the slow decay is about 172.03 s, which is smaller by a factor of 2 compared with the one without containing DEH.

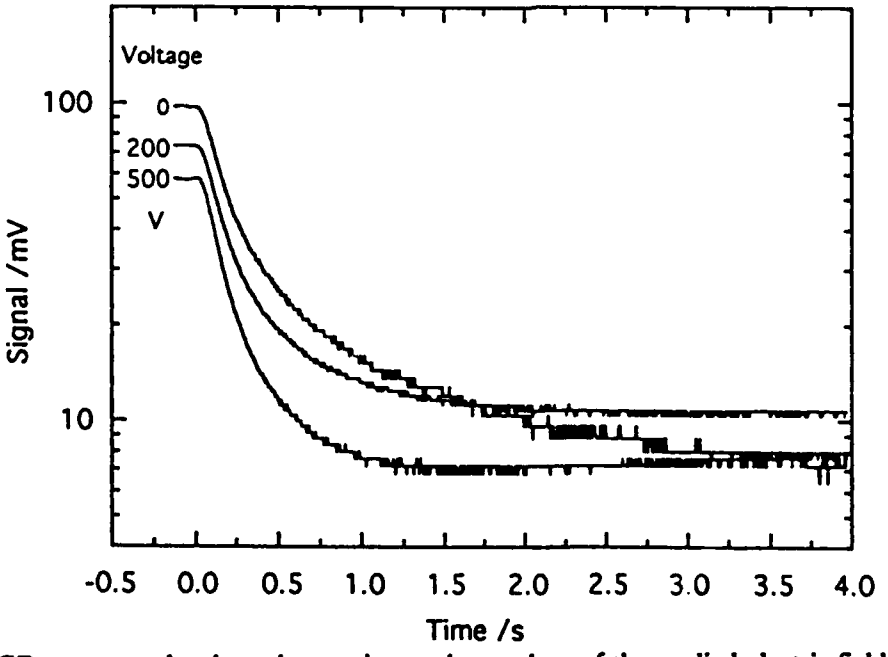


Fig. 2a: The HGR curves at the short time region at three values of the applied electric field.

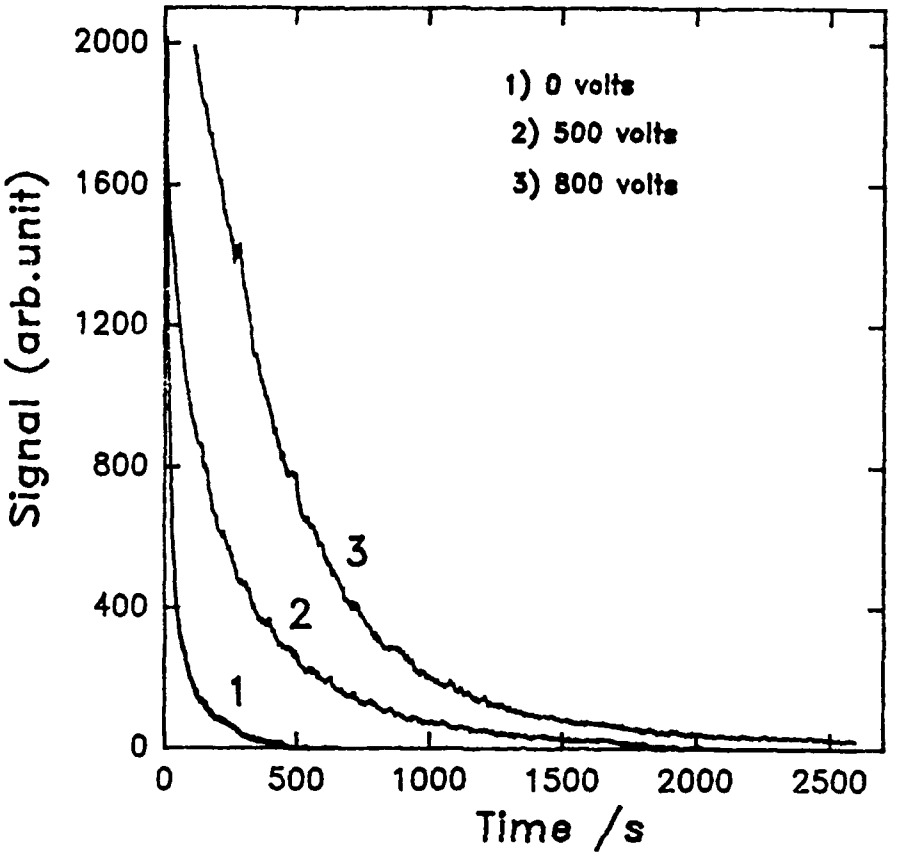


Fig. 2b: The HGR curves at the long time region at these values of the applied electric field.

Except for having a greater value of τ, the variation of τ with concentration for the samples not containing DEH is quite similar to other azobenzenes already reported in ref. 6. Also, the value of τ does not appear to depend on the applied electric field. Basically τ corresponds to the lifetime of the cis-isomer, which reverts back to the more stable trans from by overcoming the energy barrier. Thus, for the subsequent discussion, we shall focus on the sample containing DEH.

While the relaxation time obtained for the NNI/PMMA system does not depend on the electric field, the electric field dependence is quite pronounced for the sample containing DEH. Shown in Figs. 3a and 3b are the field dependence of the fast and slow relaxation times. The fast relaxation time first decreases with increasing electric field, reaching a minimum of 0.16 s for the field of 1.6 V/μm, and whence it appears to increase slightly with an increasing electric field. The holographic grating signal (or the diffraction efficiency) appears to behave similarly with the fast relaxation time. That is, it first decreases, reaching a minimum, and then increases. However, the increase in the diffraction efficiency is not as strong as that observed in DEH/BisA-NPPA system. Thus, the NNI-DEH/PMMA system does not behave as a true photorefractive material.

The field dependence of the slow relaxation time is considerably more pronounced (Fig. 2b). It increases from 172.03 s at E = 0 to a plateau value of 750.12 s at E = 4.5 V/μm, an increase of more than 4 fold. While considerable more work is needed to elucidate the nature of the fast and slow decays, we may speculate on the nature of the two decays. The fast decay is absent in the

sample without containing DEH. Adding about 10 wt % of DEH to the sample considerably lowers the glass transition temperature (Tg) and thus enhances the mobility of the NNI chromophore. Although in the time window of the experiment, the relaxation times are not due to translational diffusion, it is possible that the fast component is associated with the reorientation of the NNI chromophore and the slow component is with the lifetime of the cis-isomer.

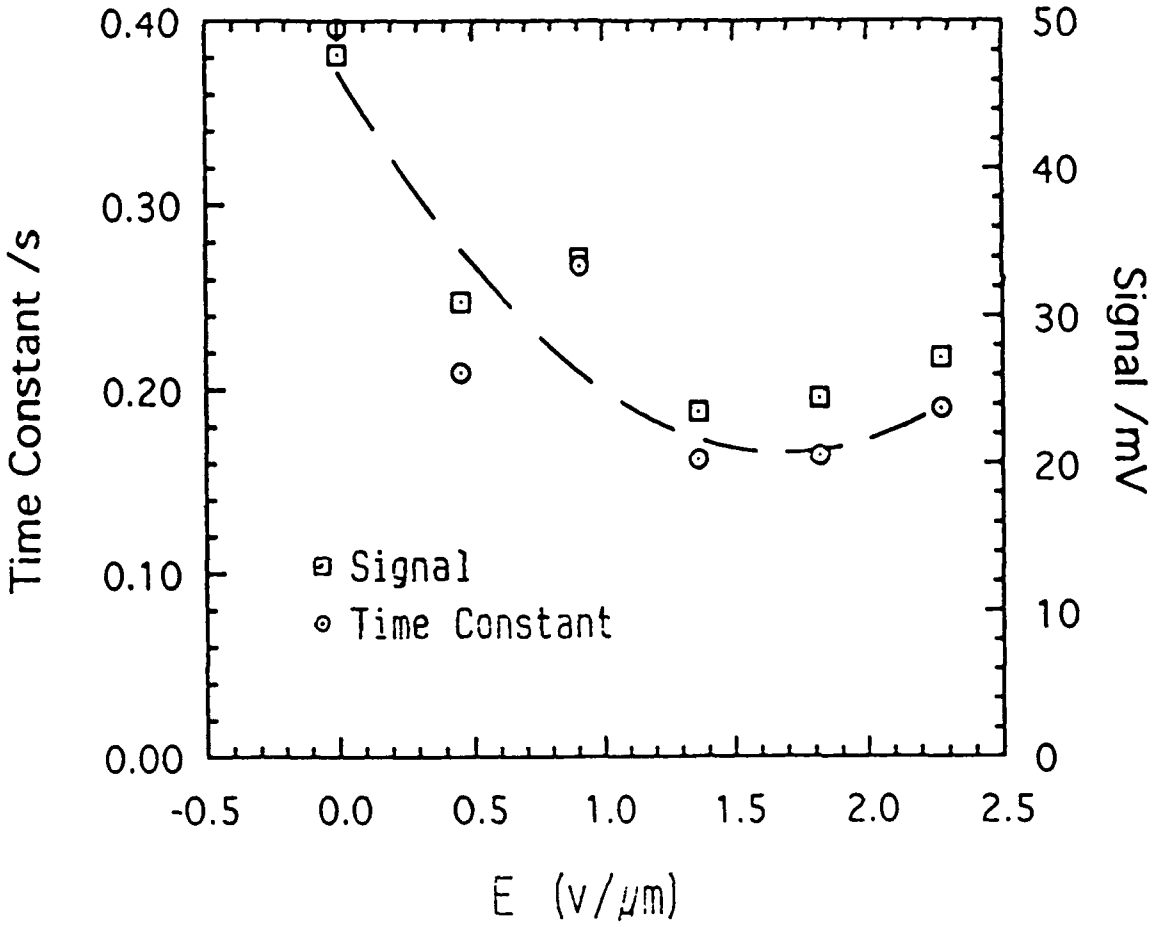


Fig 3a: The relaxation time dependence of the fast component & the diffraction efficiency on the applied electric field.

In the absence of DEH, the NNI chromophore reorientation is frozen because the polymer system is not plasticized and it has a higher glass transition temperature. In the presence of DEH, the polymer is more mobile and NNI chromophore reorientation can now take place. The reorientational dynamics is affected by the applied electric field due to the interaction of the NNI dipole with the field.

The lengthening of the lifetime with increasing applied electric field suggests that through DEH the cis-isomer is stabilized. The stabilization is presumably due to the interaction of DEH with the external field.

Because of the hydrazone functional group

DEH is well known for use as polymer plasticizers, stabilizers in industrial applications.[7] More interesting is the use of DEH as a hole transporting agent in organic layered photoconductors.[8,9] In order to facilitate hole transport through an organic solid in the presence of an electric field, the hole transport agent must at least have a low ionization potential. In the molecularly doped polymer, such as DEH doped into bisphenol-A-polycarbonate (PC), the mobility study of the photogenerated carriers in the DEH/PC system has suggested that the interaction of the hoping particle (presumably the photogenerated carriers associated with the ionized DEH) with phonons which results in an associated lattice (or molecular) distortion. The lengthening of the lifetime of the cis-isomer may be associated with a similar mechanism. However, due to the fact that no ionizing radiation (such as UV) is utilized in the present work, the interaction with DEH and the cis-isomer of NNI cannot be due to charge carriers in the system. This is also evidenced by low photoconduction current. Nevertheless, considering the fact that due to the p-π conjugation of the hydrazone functional group, the electron density in DEH is rather polarizable. Upon the application of the electric field, the induced dipole of DEH is expected to interact more effectively with the cis azo isomer than with the trans isomer as the cis form has a larger dipole moment. Therefore, a stabilized cis isomer is obtained through the interaction of the polarized DEH.

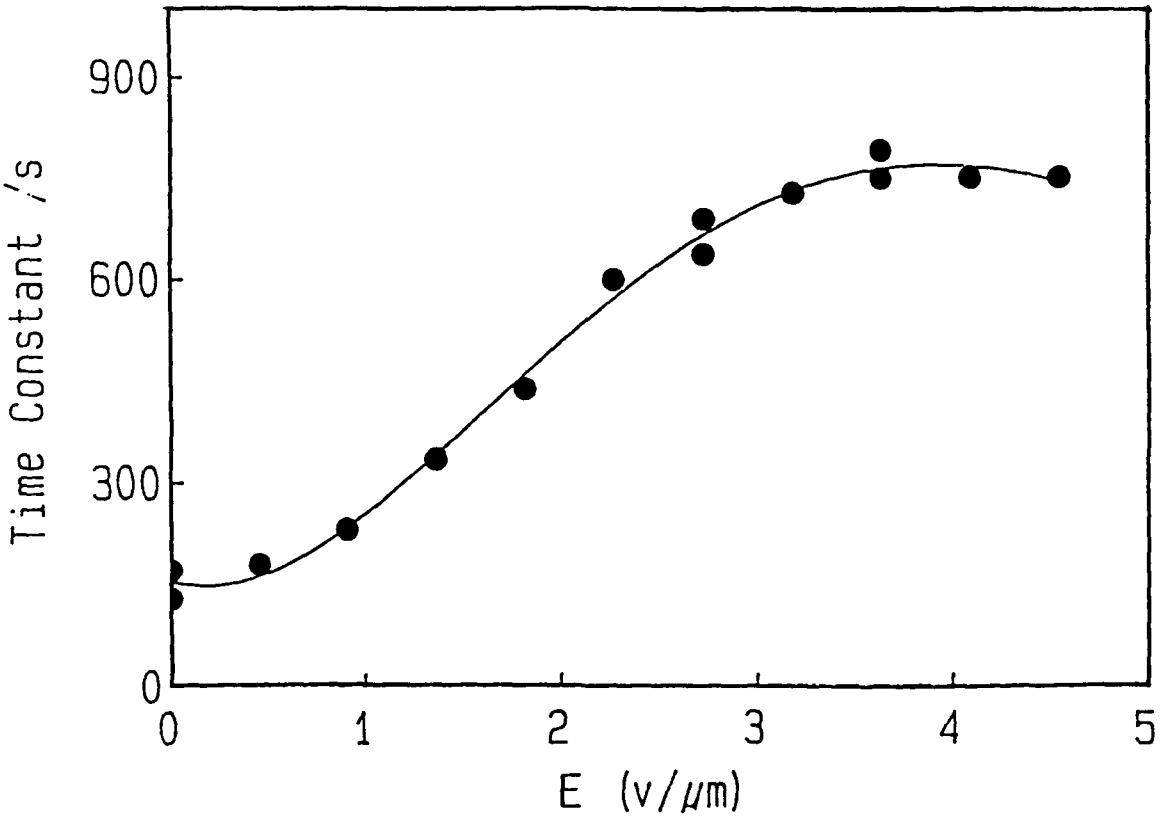


Fig. 3b: The dependence of the relaxation time of the slow component on the applied electric field.

This picture is plausible considering the fact that the signal from second harmonic generation (SHG) of the NNI/PMMA at 530 nm is negligibly small, whereas, its intensity is readily detectable when 10 wt % DEH is added to the NNI/PMMA system. The increase in the SHG intensity for the DEH-NNI/PMMA system is presumably also associated with the stabilized cis-form owing to the presence of DEH, which facilitates the orientation of the NNI chromophore to allow for SHG.

Fig. 4 shows the effect of the wavelength of the reading beam on the relaxation time of the slow decay. At the wavelengths in the vicinity of 480.0 nm, the relaxation time of the slow decay becomes rather short; the relaxation time becomes progressively longer as the reading laser wavelength moves outwards toward longer wavelength, reaching a limit of 173 s at 632.8 nm. The wavelength effect is associated with the absorption band of the cis isomer, which shifts toward shorter wavelength than that of the trans isomer (Fig. 1). Away from the absorption region of the cis-isomer, the photo conversion back to the trans form from the cis-isomer is avoided.

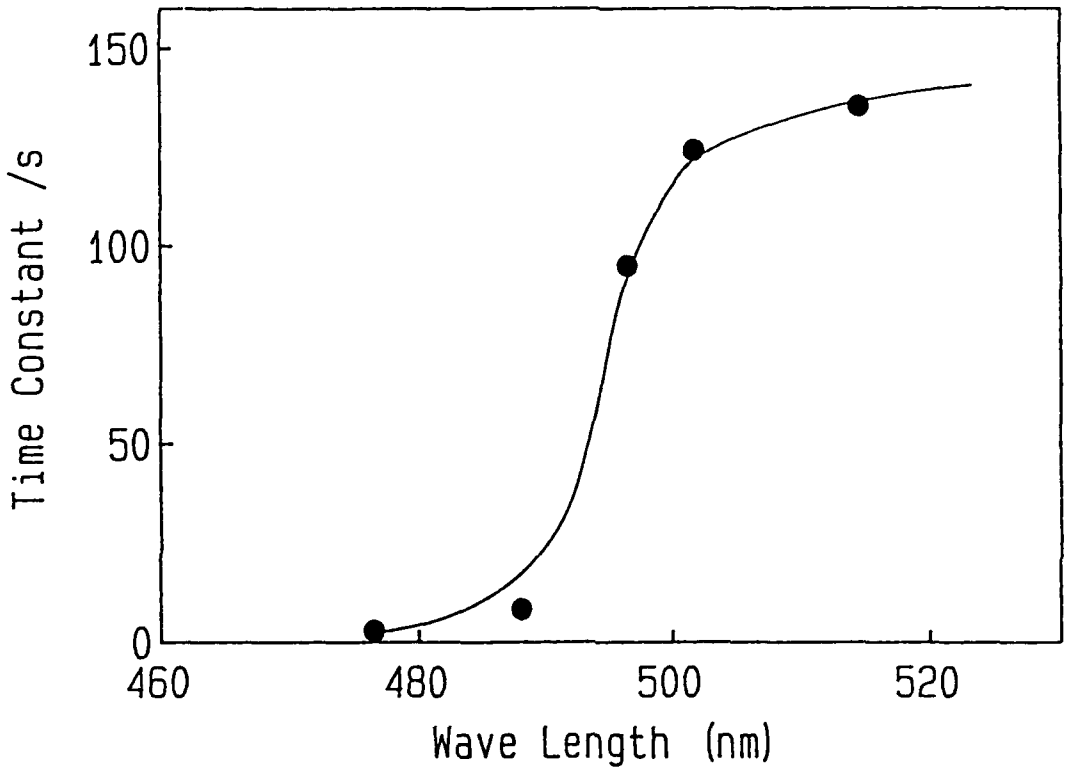


Fig. 4: The dependence of the slow relaxation time τ/n the wavelength of the reading laser beam for the NNI-DEH/PMMA sample. The power of the writing laser is kept at 40 mW and writing time is 1 s.

The electro-optical (EO) coefficients of the samples were measured at 10 KHz by using a Mach-Zehnder (MZ) interferometer. The optical layout of the MZ interferometer apparatus used in this measurement is given in ref. 5. The incident beam is s-polarized, and the change in the refractive index n in the present experimental configuration is related to the electro-optical coefficient by [5]

$$\Delta n = n^3 r_{13} E_{ac}/2 \qquad (2)$$

where E_{ac} is the applied AC electric field oscillating at 10 KHz. The result for $n^3/r_{13}/E_0$ obtained for $E_0 = 2.27$ V/μm is 26×10^{-20} m^2/V^2. Comparing with BisA-NPDA where $n^3/r_{13}/E_0 \sim 40 \times 10^{-20}$ m^2/V^2, we have found the value for the present NNI-DEH/PMMA system to be rather respectable. However, there is a possible contribution from the pizo-electric and electrode attraction effects that may contribute to the Mach Zehnder output signal. It is necessary in the future work to examine possible artifacts that may be present in the EO experiment.

In conclusion, we have observed effects of the applied electric field on the NNI-DEH/PMMA guest/host system in the HGR, EO, and SHG experiments. When DEH is introduced, a fast relaxation component is present. The fast decay is tentatively assigned to be due to the reorientation of the cis isomer. The slow relaxation component is due to the lifetime of the cis form which is stabilized by the applied electric field due to the interaction with the polarized DEH. The stabilization of the cis isomer is also corroborated by the SHG experiment. Although the field dependence of the diffraction efficiency from holographic gratings does not meet the requirements of a true photorefractive medium, the lengthening of the lifetime of the cis isomer may offer a realistic approach to non-destructive reading of the information stored in the azo-system, as the information stored by the writing beam can be read by monitoring the spectral change of the cis form, which is not destroyed by the reading process. The stored information can be erased by the reading beam with the wavelength falling in the region of the absorption band of the cis form.

4. ACKNOWLEDGEMENTS

We thank the Office of Naval Research and the Center for Research and Analysis at the University of Nebraska-Lincoln for financial support. We also thank Theodore Goodson for performing the second harmonic generation experiment and Rajan Athalye for the preparation of NNI.

5. REFERENCES

1. G. Zimmerman, L. Y. Chow, U. J. Paik, *J. Am. Chem. Soc.* **80**, 3258 (1958).

2. S. S. Gong, D. Christenson, J. Zhang and C. H. Wang, *J. Phys. Chem.* **91**, 4504 (1987).

3. Z. F. Lin, K. Hashimoto and A. Fujishima, *Nature* **347**, 658 (199).

4. S. Ducharme, R. W. Twieg, J. C. Scott and O. W. E. Moerner, *Phys. Rev. Lett.* **66**, 1846 (1991).

5. C. H. Wang, H. W. Guan and J. F. Zhang, SPIE Proceedings, Polymer Device Physics, Chemistry & Application II; **1559**, 39 (1991).

6. C. H. Wang and J. L. Xia, *J. Phys. Chem.* **46**, 190 (1992).

7. J. Kern Sears and J. R. Darby, The Technology of Plasticizers, John Wiley and Sons, New York, 1982.

8. H. W. Anderson and M. T. Moore, U. S. Patent **4**, 150, 987 (1989).

9. J. Mort and G. Pfister, Electronic Properties of Polymers, ed. by J. Mort and G. Pfister (Wiley, New York) 1982.

10. J. X. Mack, L. B. Schein and A. Peled, *Phys. Rev. B.* **39**, 7500 (1989).