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Orientation-enhanced nonlinear optical properties and phase-conjugate reflective system of a novel Azobenzene doped polymer film*

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This paper reports that the nonlinear refractive index of a novel organic optical storage film doped azo-diphenylamine polymer is measured by using the Z-scan technique. The nonlinear refractive index up to 3.7×10^{-6} cm^2/W induced by thermo-optical effect is obtained. It indicates that the sample has excellent optical nonlinear properties. The physical mechanism of the great nonlinear optical effect is analysed and the optical conjugate characteristic is also discussed with degenerate four-wave-mixing. The phase conjugate wave diffracted from the formative refractive index grating in the sample is acquired and its equivalent reflectivity reaches about 22%. On this basis, the reflective wave phase-conjugated mirror system was designed, and the image aberration experienced in propagation in the storage experiment is corrected by using the system.

Keywords: phase conjugated mirror, azo-diphenylamine, nonlinear refractive index, orientation-enhanced, Z-scan

PACC: 4265F, 4278, 4280, 4270J

1. Introduction

In recent years, azo-polymer, including doped organic glass polymer with azo-dye, have been developed in the field of optics because of their particular optical properties. Azo-aromatic compounds have longer π electron conjugate system than other compounds. When different electron-accepting and electron-donating groups are imported into the both sides of the aromatic ring, charge migration of molecule strengthens, the dipole moment increases and nonlinear optical effects are enhanced.[1,2] Azo-compound, especially doped in photo-refractive (PR) polymer, has received more and more attention due to its larger optical nonlinear coefficient and lower dielectric constant.[3−5] At present, the studies of developing orientation-enhanced PR materials are very important for achieving a high-efficiency refractive index grating by only optical-action. It means that materials must have high order optical nonlinear effect and molecular orientation effect. Yu *et al*[6] and Zheng *et al*[7] have already reported the observation in organic polymer in this aspect. Up to now however, investigations on the nonlinear property of azo polymer have been mainly focused on the photo-induced birefringence, with few on the nonlinear refractive index.

This paper reports on the novel doped azo-diphenylamine (ADPA) polymer film and a Z-scan technique measuring the film's nonlinear refractive index. The Z-scan method for measuring the film was applied by using the self-effect[8,9] with high sensitivity. A degenerate four wave mixing (DFWM) for exploring the optical conjugate specialty of doped dye polymer is also reported. We found that the forward or the reflected conjugate phase wave occurred from the medium in the DFWM experiment. The conjugate reflector system called phase-conjugate mirror built by us has the capability to correct the distorted image, which is formed due to phase distortion experienced during input wave transmission. The results indicate that the ADPA polymer is a well-developed nonlinear optical material.

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2. Sample, nonlinear measure and discussion

We obtained the film of doped ADPA with the polymer of poly (N-Vinylcarbazole)-Polybutylacrylate (PVK-PBA), and 2,4,7-trinitro-9-fluorenone (TNF) using the hot-press method. Figure 1 presents the chemical structure of each component and Fig.2 shows the absorption spectrum of the film.

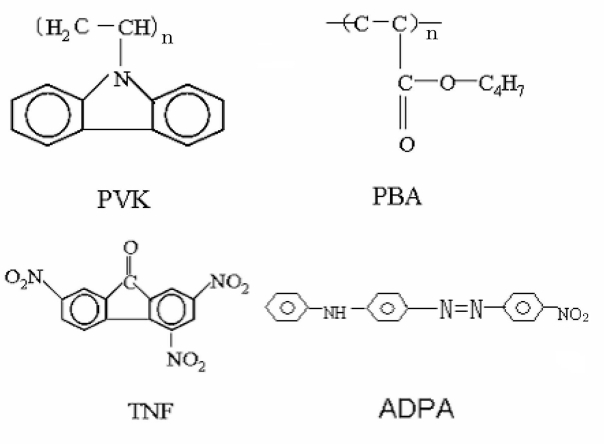


Fig.1. The structure of PVK–PBA–ADPA–TNF.

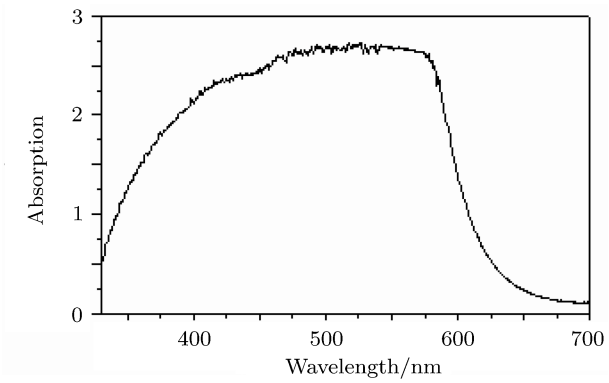


Fig.2. Absorption spectrum of the PVK–PBA–ADPA–TNF film.

It is well known that the nonlinear refractive index γ of inorganic optical nonlinear materials is normally about 10^{-13} to 10^{-15} cm^2/W. But for one of the excellent optical biology materials–bacteriorhodopsin (BR), the optical nonlinear refractive index γ (at 633 nm) reaches 10^{-6} to 10^{-5} cm^2/W.[10,11] Wang *et al*[12] measured azo-disperse red polymer film (at 633nm) by Z-scan, γ is over 10^{-6}cm^2/W. Our experimental setup of Z-scan is shown in Fig.3, where a Gaussian laser beam is focused by lens (L), and the beam waist is taken as zero point of z axes; the sample is placed near the zero point of axes and R is limitative aperture, D is a detector. As the sample with the thickness of 25 μm moving along the z axis, the input intensity on the sample changes with the z. The laser wavelength of 633 nm locates in the sample's low absorption area, the power and radius ω_0 of laser beam is 5.2 mW and 0.87×10^{-3} cm respectively. The data measured from the Z scan with a closed-aperture of 3 mm diameter were disposed by the symmetry method,[13] from which each contribution of nonlinear refractive index and nonlinear absorption were separated.

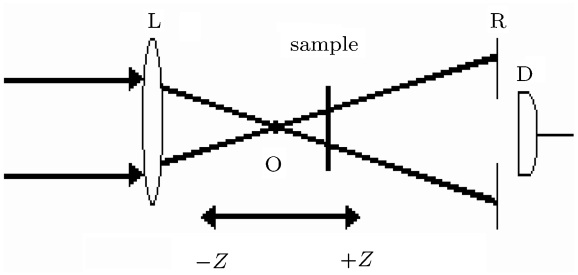


Fig.3. The experimental setup of Z-scan.

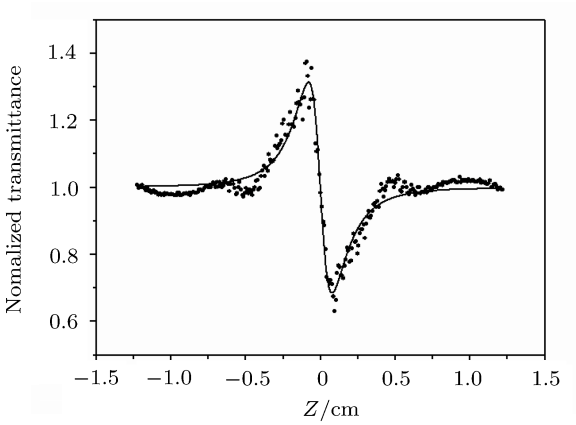


Fig.4. Normalized transmittance curve with the closed-aperture Z-scan. The solid line is the theoretical fit to the data.

The closed-aperture experimental data of nonlinear refractive index are shown in Fig.4, the normalized transmittance T versus Z curve $(T-Z)$ is of peak–valley $(P-V)$ shape, so the nonlinear refractive index γ induced by thermo-optical effect should be negative. The theoretical formula of the $T-Z$ curve for closed-aperture measurement can be shown as[8]

$$T = 1 + \frac{4\Delta\phi_0(z/z_0)}{[(z/z_0)^2+9][(z/z_0)^2+1]}, \qquad (1)$$

where $\Delta\phi_0$ is the effective phase-shift of sample on the axis, defined as

$$\Delta\phi_0 = \gamma k I_0 L_{\text{eff}} \qquad (2)$$

and $z_0 = \pi\omega_0^2/\lambda$, $L_{\rm eff} = 1 - {\rm e}^{-\alpha L}/\alpha$. L is thickness of the sample, α is absorption coefficient. According to formula (2) we gained $\gamma = 3.7 \times 10^{-6}$ cm^2/W. Here $\Delta\phi_0 = -1.55$ was achieved from the curve of theoretical simulation.

We can see that the sample has great nonlinear refractive index γ from the above results. Afterwards we shall analyse the mechanism of the nonlinear optical response of the film. First of all, ADPA chromophore has a longer stick shape group due to its one side connection with two benzene rings by amine linkage, which makes the medium change from glassy state to liquid crystal phase (LCP) state by isomerous process of trans-cis-trans at light irradiation. In the process of isomerism, tropism state of molecule is changed constantly until molecule trends to array in the vertical direction of pump light, thus it produces anisotropism phenomenon. The response of azo-benzene molecule is similar to LCP molecule, in which the molecules associate with each other under the irradiation of linear polarization laser. The tropism of molecules is a collectivity for response to the light field, so it has great nonlinear response. Secondly, ADPA is an azo-benzene molecule with 'push–pull' D-Π-A structure: having electron-accepting group and electron-donating group in both sides of the azo-benzene amine long axis, which makes the molecule possess great dipole moment and enhanced polarity. It will produce second- or third-order nonlinear optical phenomenon and conjugate effect by polarization of light field. Consequently, the π electron cloud is much more fluid and the -N=N- becomes a perfect channel for charge transfer. It is easy for realizing the photo-induced cis-trans isomerism which is excited by laser, and results in further enhanced orientation of the molecule. Thirdly, the doped element PVK of the sample is carrier transport medium not only because carbazolyl has good conductivity for cavity or electron, but also because it can form transfer-complex with TNF for charge transport. A photo-voltage can be produced by irradiation of incident laser, which speeds up charge drift and change of refractive index in the sample. Fourthly, PBA acts as a plasticizer to decrease effectively the glass-transition temperature $T_{\rm g}$, which enables the polymer to be poled and orientated at room temperature in the optical-field. So the sample can achieve great optical nonlinear polarizability at non-resonant absorption range according to the mechanism analysed above.

3. DFWM and conjugate specula system

In the following we discuss the optical conjugate property by DFWM. As we know, in the DFWM the two of three incident beams with same frequency form a static grating or a motive grating inside the sample, thus the third incident wave was diffracted by the grating, and it results in the fourth wave. In general, we should consider the phase match of input waves. If in the case of wave vector $\boldsymbol{k}(I)_2 = -\boldsymbol{k}(I_3)$, the output wave vector $\boldsymbol{k}(I_4) = -\boldsymbol{k}(I_1)$ is phase-suited.[14] So the fourth beam I_4 is produced at the opposite direction of writing beam I_1 in the same axis. According to DFWM theory, the signal relies on the third-order nonlinear polarizability of the sample. The ratio of the signal to the probe beam (I_4/I_3) reflects the diffractive efficiency of the grating formed. The experimental setup of DFWM is shown in Fig.5. The thickness of sample is 50 μm; the He–Ne laser was divided into three beams I_1, I_2, I_3 through BS$_1$ and BS$_3$ to irradiate the sample and I_3 is just at the opposite direction of I_2 in the same axis. The DFWM phenomenon was detected by the photomultiplier and disposed by a computer. The tilt angle of sample with respect to the bisector of I_1, I_2 is 20°, and the angle between I_1 and I_2 is 15°, the optical power of I_1 or I_2 is 33.6 mW/cm^2. The detected signal I_4 reflects from BS$_2$ and it changes with I_3 intensity. The diffractive efficiency η of refractive index grating ($\eta = I_4/I_3$) is shown in Fig.6. We find that diffractive efficiency increases firstly and then decreases slowly with enhancement of intensity I_3. The optimal intensity is about 20 mW/cm^2 for diffractive efficiency reaching 12.7%.

The relation of nonlinear polarizable intensity versus optical field is

$$\boldsymbol{P} \propto \chi^{(3)} \boldsymbol{E}_1 \boldsymbol{E}_2 \boldsymbol{E}_3. \tag{3}$$

As the polarization intensity increases with enhancement of I_3, the diffractive light intensity and diffractive efficiency increase accordingly. But when I_3 reaches up to the saturation absorption intensity of sample, the diffractive efficiency reduces accordingly when the existence of particulate and micro-bladder in the sample results in the light dispersion and the grating interference modulation.

As we know, the technique of phase conjugation is such a process that the output wave is complex conjugate to the phase of input.[15] In other words, the process reverses the phase of input accurately by us-

ing nonlinear optical effect. Accordingly, the following experimental setup likes the Fig.5 with little change of omitting the I_3 and using a mirror M reflecting the I_2 passed through sample back in the original route. The back beam symbolized by $I_{\rm P}$ is shown in Fig.7. When reflected-light $I_{\rm P}$ is adjusted by the mirror just in the contrary direction of I_2, the reflected-conjugation signal $I_{\rm PC}$ can appear at the contrary direction of pump beam I_1 and a part of it can be detected by using a semi-transparent mirror (BS). The reflected conjugation signal can be explained through nonlinear optical effect produced by the real-time holographic grating in refractive medium.

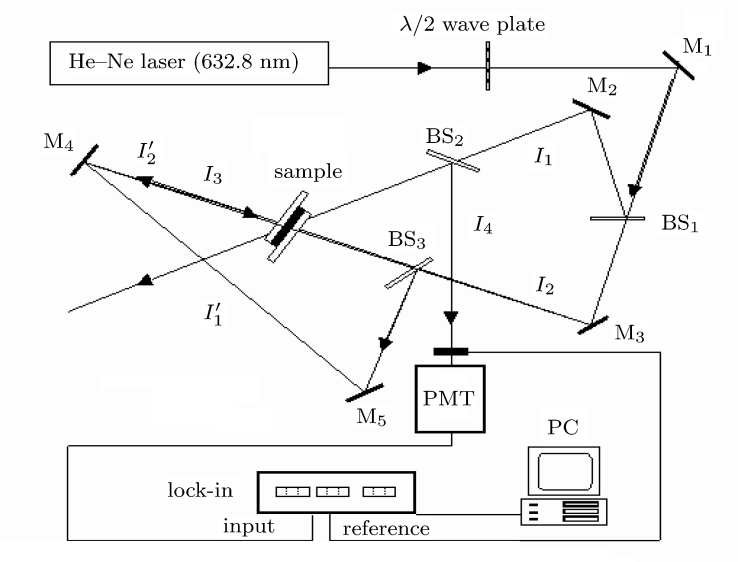


Fig.5. The experimental setup for DFWM.

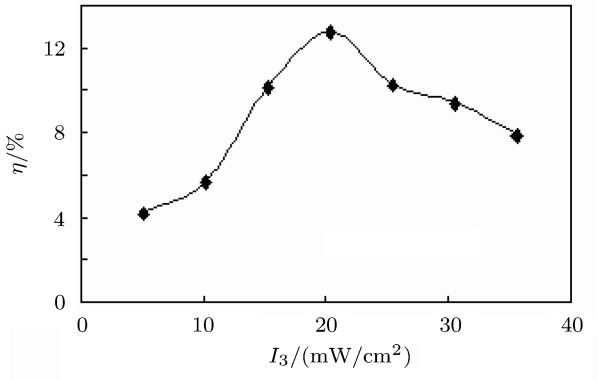


Fig.6. Diffraction efficiency versus beam intensity of I_3.

As shown in Fig.7, the interference of I_1 wave and I_2 wave forms a suit of grating with space between stripes as

$$D_{12} = \lambda/(2\sin(\alpha/2)). \tag{4}$$

The interference of I_1 wave and $I_{\rm P}$ wave forms another suit of grating with space as

$$D_{1\rm P} = \lambda/(2\cos(\alpha/2)). \tag{5}$$

Where, α is the angle between I_1 and I_2, λ is the wavelength of light in the medium. These different gratings can diffract the third incident wave $I_{\rm P}$. Because the design of the light-arrangement satisfied automatically the phase matching condition, the output phase conjugated wave can be observed.

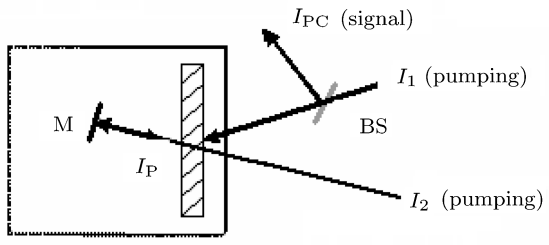


Fig.7. The experimental principle for PCM system.

Suppose R the ratio of the signal $I_{\rm PC}$ to the incident light I_1 is the nonlinear reflective rate

$$R = I_{\rm PC}/I_1. \tag{6}$$

The R measured by us is about 22%. It is a very

high value for such a thin sample.

The third experiment for image storage and correction of aberration based on the above experiment is shown in Fig.8. Where, the $\lambda/2$ wave plate is used to adjust the polarization direction of laser beam, Ex is a beam expander, M is a reflector, L1 and L2 are focus lens, BS is semi-transparent mirror. The He-Ne laser beam is expanded and divided into two beams and then impinge on the sample, where I_1 is the beam writing the mark image cyclostyle 'R' and going through a fragment of glass bottom to the sample. The intensity of image light on sample surface is about 40.8mW/cm^2. Behind the fragment of glass, the image wave front is distorted seriously because the phase is disturbed badly. But as the phase conjugation system reflects wave back through the fragment again, the wave-front distortion is completely removed. As illustrated in Fig.9, (a) is an unperturbed image imported, (b) is the distortion image behind fragment of glass, (c) is the phase conjugation image through reflection of phase-conjugated mirror (PCM) system and the fragment again. From Fig.9, we see that the distorted image was corrected to the original. It indicates that the system has strong capabilities of removing distortion and information processing.

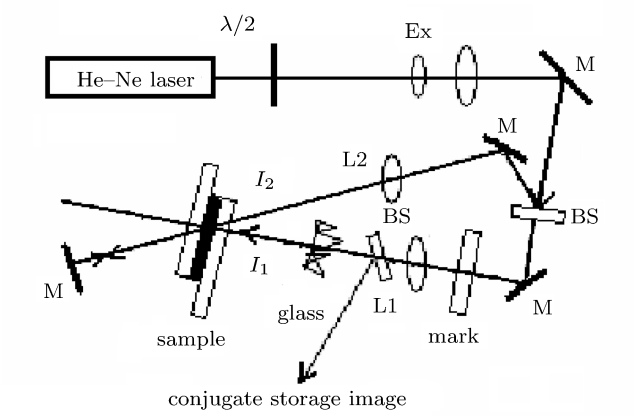


Fig.8. The experimental setup for phase conjugate.



(a) (b) (c)

Fig.9. The ability of removing distortion of PCM system. (a) the unperturbed image imported, (b) the distortion image behind fragment of glass, (c) the phase conjugation corrected image.

4. Summary

From the absorption spectrum of sample ADPA–PVK–PBA–TNF film we know that 632.8nm wavelength is in the trail of absorption area with very few absorption. We choose laser with this wavelength as illuminant to reduce the influence of the thermal-effect to optical nonlinearity in measurement. The nonlinear refractive index induced by thermo-optical effect of 3.7×10^{-6} cm^2/W was obtained by Z-Scan method. It is much more than those of inorganic nonlinear materials in magnitude. Through primary analysis, we consider that molecules of doped ADPA sample are similar with LCP being well collective for each other. The orientation response of the molecules to the external perturbation is a group effort and can be expected to be extremely large. In addition, ADPA molecules have great dipole moment which leads to high orientation-enhanced under the irradiation of the linear polarizing laser and strong change in nonlinear refractive index. A high diffractive efficiency of phase conjugate wave was obtained in the DFWM. By using the reflective wave conjugate mirror system, we corrected the aberration of image in which the phase was seriously distorted in propagation. These indicate that it may have great potential in optoelectronic device such as three-dimensional hologram storage, optical information transfers and processing, optical filters and so on.

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