

OPTICAL STORAGE MECHANISM AND HIGH-ORDER DIFFRACTION PROPERTIES OF NITROAZOBENZENE-CONTAINING POLYESTER FILMS

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Abstract Using Nd:YAG second harmonic pulse (100 ps), the optical storage properties of two novel polyesters, poly [4'-bis (N, N-oxyethylene) imino-4-nitroazobenzene succinyl] and poly [2'-chloro-4'-bis (N, N-oxyethylene) imino-4-nitroazobenzene succinyl] have been studied by multiwave mixing. The high-order diffractions of the orientation gratings induced by anisotropy via the reorientation of nitroazobenzene groups and optical information storage with long-term stability have been realized by multiwave mixing in their films. Up to 3rd order forward diffraction was detected in two wave mixing, while up to 4th order backward diffraction was observed in degenerated four wave mixing. The recording mechanism was explained by the *trans-cis-trans* isomerization cycles of azobenzene groups. The isomerization of these azobenzene groups probably undergoes with inversion mechanism under the experimental conditions. The information recorded in these films has been kept for more than 6 months.

Keywords Azobenzene-containing polyester; Multiwave mixing; Optical storage; Photoinduced anisotropy; High-order diffraction of orientation grating

INTRODUCTION

Polymers functionalized by azobenzene derivatives have attracted much attention due to their potential applications in a number of photonic and optoelectronic technologies^[1]. During the last decade, a variety of polymers have been used as recording media. The storage mechanism which is related to the high optical sensitivity, photoinduced anisotropy and photodichroism of polymers have been elucidated by a number of different techniques, but many investigations for these optical recording media seem to emphasize the use of birefringence and holography techniques^[2,3]. Studies on optical storage in these polymer films by multiwave mixing are very few^[4]. Recently, the azobenzene-containing polyesters are particularly

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interesting, for the variability of main-chain tailoring and high performance of film forming. Shi et al. reported that the photoinduced birefringence was monitored over 1000 h without obvious decrease in a polyester film at the temperature below its glass transition temperature^[5]. Hvilsted et al. synthesized a series of side chain liquid crystalline polyesters containing cyanoazobenzenes as mesogens and obtained long-term stability, high resolution and high diffraction efficiencies of holography gratings at the temperature near their glass transition temperature^[6]. In this work, investigation on the optical storage properties of poly [4'-bis (N, N-oxyethylene) imino-4-nitroazobenzene succinyl] (PINS) and poly [2'-chloro-4'-bis (N, N-oxyethylene) imino-4-nitroazobenzene succinyl] (PCINS) has been carried out. The high-order diffractions of orientation gratings formed in these polyester films were observed in degenerated four wave mixing (DFWM) and two wave mixing (TWM) experiments. The gratings formed in these polyester films are all stable after removing pump beams. The recorded information has been remained without obvious decrease in these films for more than 6 months at ordinary conditions.

EXPERIMENTAL

Materials

The preparation of PINS and PCINS (Fig.1) was reported in our previous paper^[7]. Their dioxane solutions were cast on 1 mm thick polished glass slides and vacuum dried for 6 h at 60°C, thin homogeneous films were obtained. These films possess about 3 μm and 5 μm thickness, and a maximum absorption at 454 nm and 466 nm for PINS and PCINS, respectively.

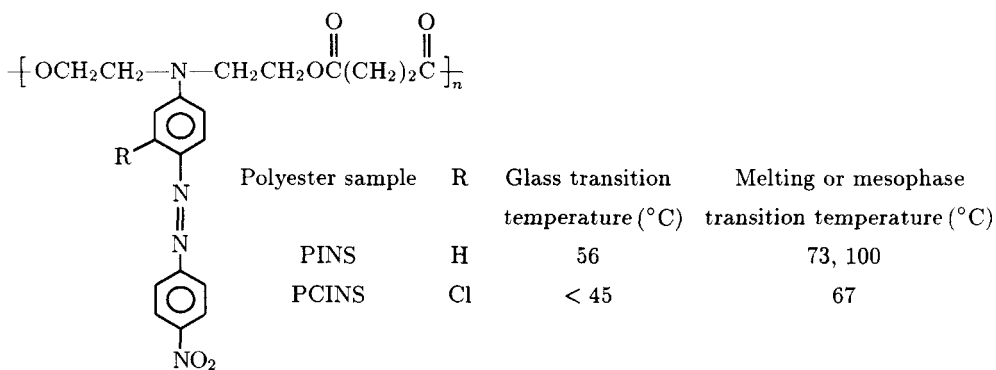


Fig. 1 Structures of PINS and PCINS.

Setup of multiwave mixing systems

A typical experimental arrangements for degenerated four wave mixing (DFWM) and two wave mixing (TWM) was set up utilizing polarized Nd:YAG second har-

monic pulse of 100 ps duration and 7 kHz repetitive frequency. In the arrangement of DFWM, two counter propagation pump beams, I_1, I_2 and a probe beam I_p interacted with each other in the film, the angle between I_p and I_1 is 12.7° . In the setup of TWM, two pump beams, I'_1 and I'_2 ($I'_1 > I'_2$) with an angle of 12.7° , intersected in the film. The signals of phase conjugated beam and high-order diffractive beams were detected by photomultiplier and recorded by a X-Y recorder^[7-9]. Fig. 2 shows the scheme of high-order diffraction in DFWM and TWM.

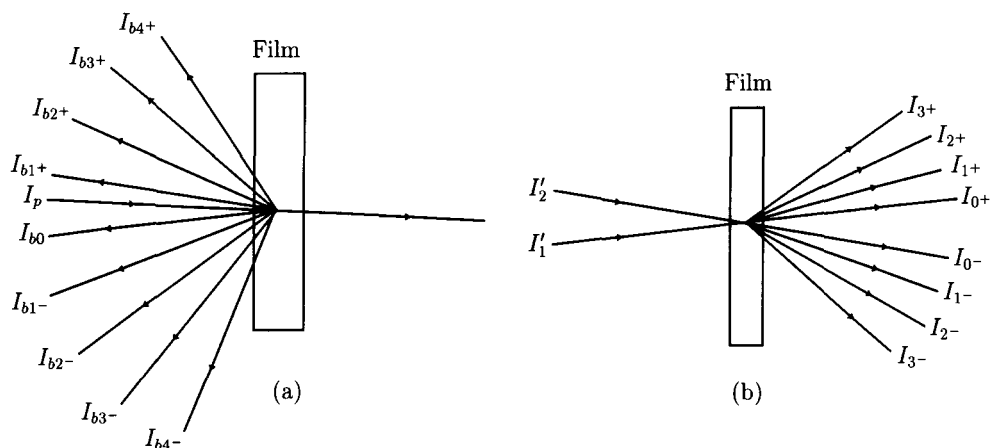


Fig. 2 Scheme of high-order diffraction in DFWM and TWM

(a) backward diffraction beams produced by I_p in DFWM, (b) high-order diffraction in TWM

RESULTS AND DISCUSSION

Optical recording via photoinduced isomerization

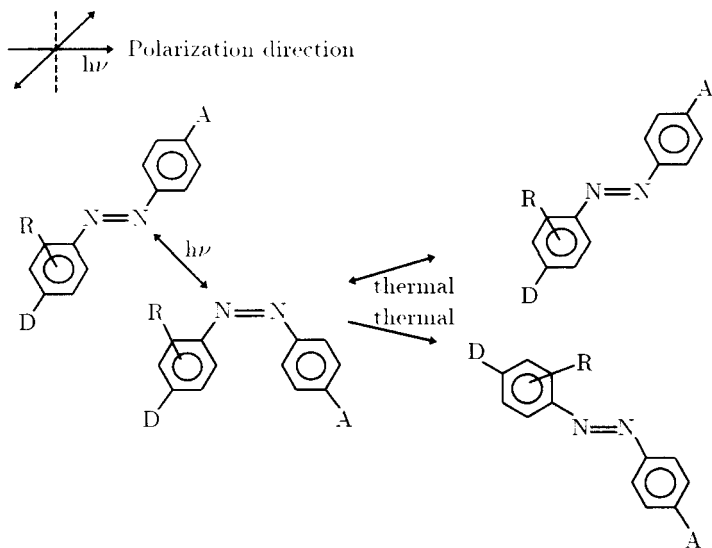
In recent years, optical storage through photoinduced dichroism and birefringence in azobenzene-containing polymers has been studied extensively by many research groups. The isomerization of azobenzene groups induced by polarized beam undergoes a reorientation through an isomerization cycle, *trans-cis-trans* cycle, which can create optical anisotropic domains in the polymer film^[2,10]. Since the effect factors of isomerization are numerous, recording mechanism is still difficult to be elucidated.

Rau et al. classified the isomerization of azo dyes in different surroundings in a polymeric matrix as two types, of which one is the environment with enough free volume to isomerize and the other is that without enough free volume to isomerize^[11,12]. In many functionalized polymers, these two cases may be existed. In this work, the nitroazobenzene with "push-pull" structure is covalently linked to the mainchains by its donor groups. There is a small free volume for the thermal motion of each nitroazobenzene group, i.e. the thermal motion of the nitroazobenzene group will

be inhibited by the mainchain. Thus, it is favorable for the isomerization of azobenzene group to undergo with inversion mechanism compared to rotation mechanism which needs a larger free volume arrounding the azo bond^[12]. In addition, the $\pi - \pi^*$ transition of the nitroazobenzene in these polyesters is overlapping its $n - \pi^*$ transition. Thus a wide structure band which depends strongly on solvent polarity has been observed in the absorption spectrum of the *trans* isomer (Table. 1). Such an azobenzene may be regarded as the pseudostilbene type molecule according to Rau^[12]. Under irradiation with 532 nm writing beams, the $n - \pi^*$ transition of these azobenzene groups will be excited easily, and inversion isomerization will be induced with more possibility.

Table 1 Absorption of 4'-(N, N-dihydroxyethyl) imino-4-nitroazobenzene (INA) and 2'-chloro-4'-(N, N-dihydroxyethyl) imino-4-nitroazobenzene (CINA) in different solvents

	INA				CINA			
	λ_1/nm	$\varepsilon_1/\times 10^{-4}$	λ_2/nm	$\varepsilon_2/\times 10^{-4}$	λ_1/nm	$\varepsilon_1/\times 10^{-4}$	λ_2/nm	$\varepsilon_2/\times 10^{-4}$
N, N-Dimethylformamide	503	2.74	290	1.06	495	3.69	298	1.14
Chloroform	469	2.69	252	3.40	455	3.47	262	2.83
1, 4-dioxane	468	2.50	285	1.06	462	3.53	293	1.26



Scheme 1 Isomerization of azobenzene group induced by linear polarized laser at 532 nm

Therefore, the mechanism of photoisomerization of nitroazobenzenes in these polyester films could be simply described as inversion isomerization under the present conditions, and hence the optical recording process may be illustrated by Scheme 1. In this case, the optical anisotropic domains in which the optical information storage could be created through some isomerization cycles of azobenzene groups induced by polarized beams. The extent of the reorientation of the azobenzene groups depends

on many factors: the intensity, repetition rate and duration of the exciting pulse, time constants of the thermal isomerization, the properties of the matrices and the inversion angle of an azobenzene nucleus from *trans*- to *cis*-form, etc. Here, effects of the structure, the properties of the matrix and the glass transition temperature of the matrix must be emphasized. The process of *trans-cis-trans* isomerization can continue until all azobenzene groups lie on the direction which is perpendicular to the polarization direction^[2,10]. These were reflected on the changes of the efficiencies of the conjugated signal with the change of the intensities of the writing beams and with the writing process^[7,8].

Characteristics of diffraction of grating formed by multiwave mixing in the polyester films

With a low-intensity pump beams in DFWM, the isomerization cycle will be controlled by the photochemical process alone, the thermal effect may be negligible, and the process of *cis-to-trans* isomerization is very slow. Therefore, the intensity gratings formed by the interaction of the low-intensity pump beams are the gratings of *trans* and *cis* isomer populations, and the gratings of amplitude or phase modulation by the triplet state formed by the exciting of both isomers, and no orientation grating exists. In both films, the phase conjugated signal produced by I_2 which diffracts with grating formed by low-intensity beams (I_1 and I_p) in the order of a few W/cm² is easy to saturate and disappear when I_1 or I_p was turn off. However, when the intensity of writing beams increases to the order of 10 W/cm², the phase conjugated signal in the film will not disappear but decreases to some extent after turning off I_1 or I_p ^[7]. These results all indicated that the gratings formed in these films are not stable when using low-intensity writing beams. Both films may be regarded as a four-level saturable absorber with two saturation intensities, I_{s1} and I_{s2} ($I_{s1} < I_{s2}$)^[7,8]. I_{s1} and I_{s2} of them were measured to be 14.7 W/cm² and 119 W/cm², 44.0 W/cm² and 239 W/cm² for PINS and PCINS, respectively. The effective third-order nonlinearities were elucidated to be 1.5×10^{-2} esu and 1×10^{-2} esu by the methods of Maloney et al. for PINS and PCINS, respectively^[13].

Once the intensities of writing beams reach the order of 10³ W/cm², the phase conjugated signal will remain without obvious decreasing after turning off the writing beams in each polyester film. We considered that the thermal effect of the writing beams has an effect on the thermal process of *cis-to-trans* isomerization, the isomerization could complete quickly, and on the end of the *trans-cis-trans* cycle, a long-term stable anisotropy appears in the film. In other words, the stable grating of reorientational azobenzene groups was formed under the reaction of intense writing beams in the DFWM experiment. In the view of holography, there are three groups of gratings formed by DFWM: 1) the grating formed by I_1 and I_p , 2) the grating formed by I_1 and I_2 , and 3) the grating formed by I_2 and I_p . Each group is only

detected by one of the three beams. Among the backward diffraction beams, phase conjugated beams produced by I_2 have up to 3rd and 2nd order diffraction in PINS and PCINS, respectively. Among the backward diffraction beams produced by I_1 or I_p interacting with the grating the 4th order diffraction beam is observed in the two films (Table 2).

Table 2 Characteristics of high-order diffraction of the polyester films when the intensities of incident beams were in the order of 10^3 W/cm^2

	The highest diffraction beams in DFWM						The highest forward	
	Forward diffraction			Backward diffraction			diffraction beams in TWM	
	for I_1	I_2	I_p	for I_1	I_2	I_p	for I'_1	I'_2
PINS	3rd	3rd	3rd	4th	3rd	4th	3rd	3rd
PCINS	3rd	3rd	2nd	4th	4th	2nd	2nd	2nd

In addition, the directions of these beams change with the change of angle between the incident beam (I_1 or I_p) and the film. The efficiency of backward diffraction produced by I_p with the reflective grating is the largest among all of diffraction produced by I_1 , I_2 and I_p , i.e. the diffraction efficiency of reflective grating is higher than that of transmissive grating (Table 3).

Table 3 The efficiencies of high-order diffraction beams produced by probe beam on PINS film in DFWM experimetns

High-order diffraction beams	Forward diffraction beams			Backward diffraction beams			
	1st	2nd	3rd	1st	2nd	3rd	4th
Efficiency (%)	7.6	2.9	0.7	7.7	4.5	3.0	1.0

When two of the three beams are switched off, there is always one group of diffraction beams detected without obvious decreasing for any order diffraction in each polyester films. Fig. 3 shows the changes of backward diffraction beams with the probe beam in the films when I_1 and I_2 are switched off. The properties of high-order diffraction in TWM employing intensive writing beams with order of 10^3 W/cm^2 have been also investigated. Both beams diffract with the grating of orientation and produce up to the 3rd order diffraction in PINS, and the 2nd order in PCINS, when I'_1 and I'_2 is either turned on or turned off (Table 3). These indicate that the orientation grating formed by photoinduced anisotropy in the film is very stable, i.e. after turning off one of the two beams, the azobenzene groups lay on an anisotropic state formed through reorientation. Information can be recorded in the film by TWM completely and will not be lost. Through monitoring the diffraction efficiency, a long-term stability of the storage information is obtained at ordinary conditions.

Thanks to the differences of the azobenzene dyes, the effective third-order non-linearities and the thickness between the both films, there are some differences of

the photoinduced processes between them, such as in photoresponsive time, optical amplifier, wave coupling and some results described above, which will be studied in detail in our later work.

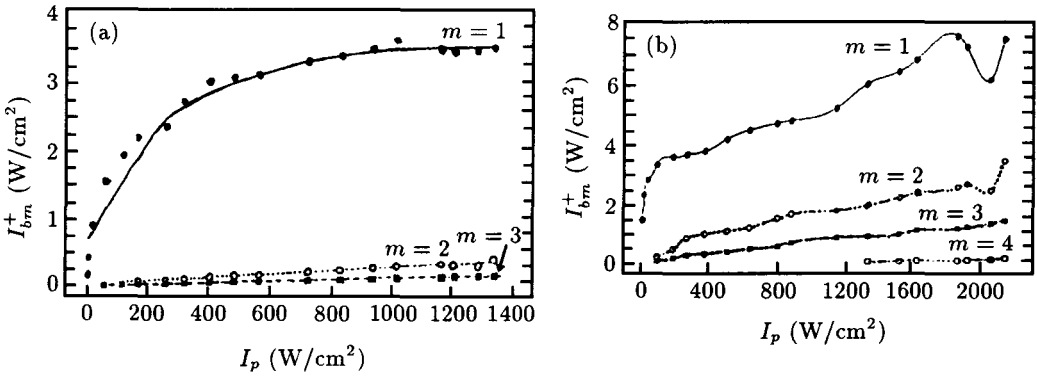


Fig. 3 Change of high-order backward diffraction beams, I_{bm}^+ (I_{b1}^+ , I_{b2}^+ , I_{b3}^+ and I_{b4}^+) vs. I_p when pump beams are turned off, (a) PINS, (b) PCINS

Stable anisotropic state and photodichroism for the films

After writing in DFWM and TWM, brilliant hologram spots were observed in the films, which had remained for more than 6 months without obvious change under ordinary condition. There is obvious difference between the absorption spectra of the film with hologram spots and that of the origin film without writing^[8,9]. It can be also considered that there is photodichroism brought about by the bleaching of writing beams, as discussed by Natansohn et al.^[1,2,10]. This indicates that the decrease of the absorbance of the films is due to the anisotropy of the reorientation of the azobenzene groups, and the new stable anisotropic states is formed by the linear polarized writing beams in the films.

CONCLUSION

In conclusion, the azobenzene-containing polyesters synthesized in this work have good properties of optical information storage, and the information can be recorded in their films without any obvious loss for a long time. The stable optical storage and high order diffraction show that these azobezene-containing polyesters are apt to be ideal media for their application in photonic devices.

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