Effect of Polarization State of Laser Irradiation on Absorption in 1-((4-(phenyldiazenyl)phenyl) azonaphthalen-2-ol Doped in Poly(methyl 2-methylpropenoate) Polymeric Thin Films

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Received 02/02/2014
Accepted 25/05/2014

Abstract

The excitation of the dye molecules by polarized light induces an anisotropy in Poly (methyl 2-methylpropenoate)/1-((4-(phenyldiazenyl) phenyl) azonaphthalen – 2 - ol polymeric thin films. The orientation of the 1-((4-(phenyldiazenyl) phenyl) azonaphthalen-2-ol molecules was controlled by the polarization of the laser electric field, which enabled the contrast ratio of the dye to be obtained by photooptically switching. The maximum absorbance (parallel and perpendicular to the polarization state of the laser beam), contrast ratio of nonionic diazo 1-((4-(phenyldiazenyl) phenyl) azonaphthalen-2-ol dye in Poly (methyl 2-methylpropenoate) polymeric host were investigated using Ar-ion polarized laser light. Results showed that the parallel probe beam absorbance ($A_{||}$) is much greater than that of the perpendicular ($A_{\wedge}$) one. The high value of the contrast ratio reveals that Poly (methyl 2-methylpropenoate) / 1- ((4- (phenyldiazenyl) phenyl) azonaphthalen-2-ol is a promising candidate for photoswitching applications.

Keywords: Poly (methyl 2- methylpropenoate), 1- ((4 - (phenyldiazenyl) phenyl) azonaphthalen-2-ol, parallel absorbance, perpendicular absorbance, contrast ratio, photoswitching.

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تأثير حالة استقطاب ليزر التشعيع في الامتصاص في أفلام البولي ميثيل 2- ميثيل بروبينوات البوليميرية الرقيقة المشوبة بـــ 1- ((4-(فينيل دايآزينيل) فينيل) آزونفثالين-2-أول

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تاريخ الإيداع 2014/02/02

قبل للنشر في 2014/05/25

الملخص

تُنتج إثارة جزيئات الصباغ بواسطة الضوء المستقطب لا تناحٍ في أفلام البــولي ميثيــل 2- ميثيــل بروبينـــوات Poly(methyl 2-methylpropenoate) البوليميريـــة الرقيقـــة المـــشوبة بـــصباغ 1- ((4-(فينيل دايآزينيل) فينيــل) آزونفثـــالين – 2 - أول 1 - ((4 - (phenyldiazenyl) phenyl) azonaphthalen -2-ol. أمكن التحكم بتوجيه جزيئات1-((4-(فينيل دايآزينيل) فينيل) آزونفثالين-2-أول 1-((4-(phenyldiazenyl)phenyl) azonaphthalen-2-ol بواســـطة الحقـــل الكهربـــائي المستقطب لليزر. جرى استقصاء الامتصاص الأعظم (الموازي والمعامد لاستقطاب حزمة الليزر)، وكـــذلك نـــسبة التبـــاين للـــصباغ 1- ((4-(فينيـــل دايآزينيـــل) فينيـــل) آزونفثـــالين-2-أول 1-((4-phenyldiazenyl)phenyl) azonaphthalen-2-ol) ثنائي الآزو في المضيف البوليميري البـــولي ميثيل 2 ميثيل بروبينوات؛ وذلك باستخدام ضوء الليزر المستقطب. بيّنت النتـــائج أن امتـــصاص شـــعاع السبر الموازي ($A_{\parallel}$) أكبر بكثير من الشعاع المعامد ($A_{\perp}$). و تـــوحي القيمـــة العاليـــة لنـــسبة التبـــاين contrast ratio أن 1- ((4-(فينيل دايآزينيل) فينيل) آزونفثالين-2-أول في البولي ميثيـــل 2 ميثيـــل بروبينوات مرشحاً واعداً في تطبيقات المفاتيح الضوئية (photoswitching).

الكلمات المفتاحية: البولي ميثيل 2- ميثيل بروبينوات، 1- ((4-(فينيـــل دايآزينيـــل) فينيل) آزونفثالين-2-أول، الامتصاص المـــوازي، الامتـــصاص المعامد، نسبة التباين، المفتاح الضوئي.

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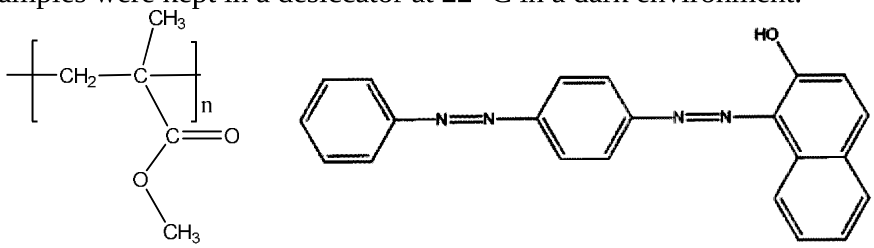
1. Introduction

Linearly polarized visible light is known to have a profound effect on the physical properties of some photosensitive materials such as compounds containing azobenzene and its derivatives like 1-((4-(phenyldiazenyl) phenyl) azonaphthalen-2-ol [1]. These materials are of great importance for applications in many fields, such as, optoelectronics, photonics, signal processing, data storage, holography, integrated optics, all-optical modulation, optical recording, and optical switches [2-3]. Moreover, dye molecules are well known for their properties of photochromism [4], which is a reversible change between two species having different absorption spectra, which can be induced by photoirradiation. One of the most powerful methods for studying the structure and physical behavior of nonlinear optical guest-host polymeric systems is the measurement of the absorption of linearly polarized light by an ensemble of oriented molecules [5]. To the best of our knowledge, absorption properties of 1-((4-(phenyldiazenyl) phenyl) azonaphthalen-2-ol doped Poly (methyl 2-methylpropenoate) polymeric thin films has never been studied before. In this work we report the results of absorption properties of 1-((4-(phenyldiazenyl) phenyl) azonaphthalen-2-ol molecules that have been incorporated in Poly (methyl 2-methylpropenoate) polymeric network.

2. Experimental

2.1. Synthesis of 1-((4-(phenyldiazenyl)phenyl) azonaphthalen-2-ol doped poly(methyl 2-methylpropenoate) Samples

There are several techniques for the synthesis of 1-((4-(phenyldiazenyl) phenyl) azonaphthalen-2-ol/ Poly (methyl 2-methylpropenoate) thin films [6-11]. Guest-host system was chosen to synthesize the samples. The starting materials for preparing the guest-host polymeric thin films were poly (methyl 2-methylpropenoate) (Poly (methyl 2-methylpropenoate, MW: 36000) from Acros Organics, and 1-((4-(phenyldiazenyl) phenyl) azonaphthalen-2-ol (95% dye content), from Aldrich (their molecular structures are shown in Fig.1). 3 gr of poly (methyl 2-methylpropenoate) was dissolved in 30 ml of dichloromethane($C_2H_2Cl_2$). 1-((4-(phenyldiazenyl) phenyl) azonaphthalen-2-ol was added to the solution of poly(methyl 2-methylpropenoate). The mixture was stirred for 24 hours until the clear solution was obtained with 1-((4-(phenyldiazenyl) phenyl) azonaphthalen-2-ol molecules fully dissolved. Thin films were dip-coated on transparent glass substrates. Film thicknesses of the order of 1µm were measured by the Prism Coupling technique (PCT). Samples were baked in an oven and held at 70 ^{o}C for two hours in order to eliminate the residual solvent. Finally, samples were kept in a desiccator at 22 ^{o}C in a dark environment.



(a) **(b)**

Fig.1.The chemical structure of poly(methyl 2-methylpropenoate) polymer (a), and 1-((4-(phenyldiazenyl)phenyl) azonaphthalen-2-ol molecule (b).

2.2. Set up Arrangement

Fig. 2 shows the experimental arrangement of the experimental setup. Guest-host polymeric thin films were pumped with linearly polarized beams from an Ar^+ laser at λ=514 nm from a multi-line Ar-ion laser (543-MAP-A02, Melles Griot). The probe signal of the beam falling on the sample and subsequently on a photosensor is fed to a personal computer through a low noise current preamplifier (SR570, Stanford Research Systems), and a DSP lock-in amplifier (SR850, Stanford Research Systems). An IEEE 488.2 GPIB (National Instruments) card was used to control and record the experimental data along with a special program written in Borland C++.

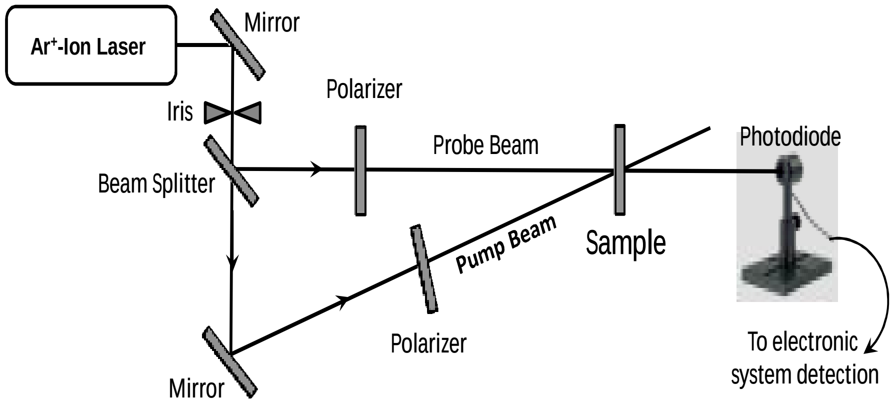


Fig. 2: The schematics of the experimental setup.

The linearly polarized probe beam passes through the sample while it is being subject to the pump beam. The probe beam intensity was kept at about 0.01% of the pump beam intensity and with a wavelength identical or very close to the absorption maximum of the dye molecules where changes in the absorption will be greatest, without influencing the pumping effect of the sample. The samples' absorption spectrum was measured using a UV-visible spectrophotometer (Photodiode Array Photospectrometer (PDA) Specord S100, Analytik Jena). Fig. 3 shows that the maximum absorption wavelength for the 1-((4-(phenyldiazenyl) phenyl) azonaphthalen-2-ol doped poly (methyl 2-methylpropenoate) prepared samples is at λ=508.4 nm.

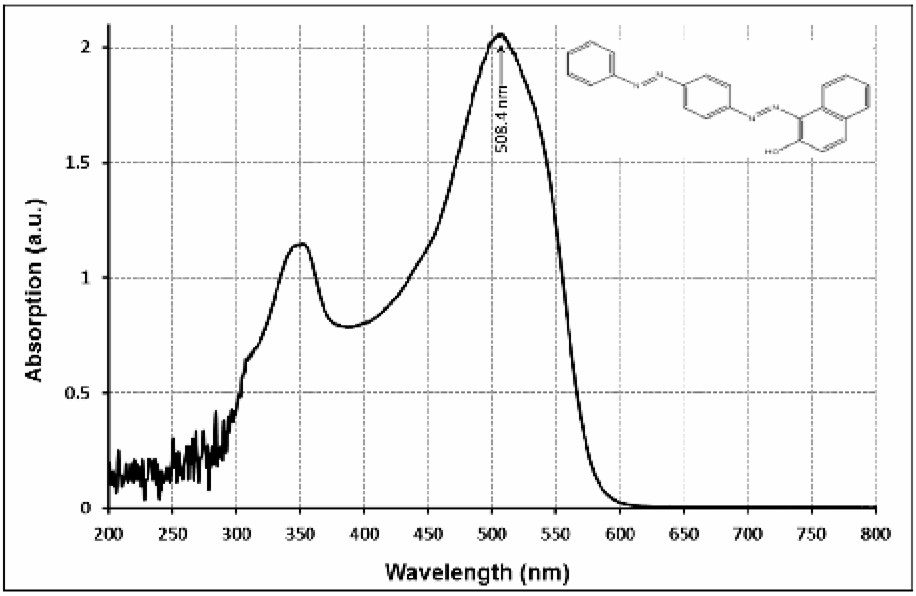


Fig. 3. UV-Visible absorption spectrum of **1-((4-(phenyldiazenyl)phenyl) azonaphthalen-2-ol doped poly(methyl 2-methylpropenoate) thin film. The chemical structure of 1-((4-(phenyldiazenyl)phenyl) azonaphthalen-2-ol is shown in the inset.**

The probe beam absorbance parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the electric vector of the pump beam become different. The absorbances were then calculated from [12]:

$$A_{//} = -\log\left(\frac{I_{//}}{I_0}\right) \qquad (1)$$

and

$$A_{\perp} = -\log\left(\frac{I_{\perp}}{I_0}\right) \qquad (2)$$

Where I_0 is the intensity of the probe beam when there is no sample, and $I_{//}$ & $I_{\perp}$ are the intensities of the probe beam transmitted through the sample when it is polarized parallel and perpendicular to the pump beam polarization, respectively.

3. Results and Discussion

A series of experiments was carried out in order to elucidate the influence of linearly polarized light. Samples were pumped at an intensity level, at which the transmitted probe beam intensities were recorded simultaneously. Initially, the 1-((4-(phenyldiazenyl) phenyl) azonaphthalen-2-ol doped poly (methyl 2-methylpropenoate) thin film is isotropic owing to the random distribution of the anisotropic photosensitive molecules. When the film is illuminated by a linearly polarized laser light, those 1- ((4 - (phenyldiazenyl) phenyl) azonaphthalen-2-ol molecules best aligned along the light polarization direction are bleached, while those with perpendicular orientation are spared, leading to the macroscopic optical anisotropy [13].

Photoinduced changes in the absorption probe beam intensity are plotted in Fig.4. This figure shows the absorption spectrum of Poly (methyl 2-methylpropenoate) / 1-((4-(phenyldiazenyl) phenyl) azonaphthalen-2-ol thin films at 2.5 mW in both cases parallel and perpendicular polarized laser intensities of the pump, and depicts the increasing of the signal after the pump is switched on, and then reach to the saturation. When the pump is switched off, the absorption relaxed exponentially.

Looking at figure 4, one can see that the intensity of the absorption parallel polarized laser light is greater than that of the absorption perpendicular polarized laser light. This could be understood by knowing that irradiation laser light induces a strong polar order in the samples in the plane perpendicular to its polarization direction. This leads to a greater increase in the absorption of the probe light whose polarization direction is parallel to that of the pump light.

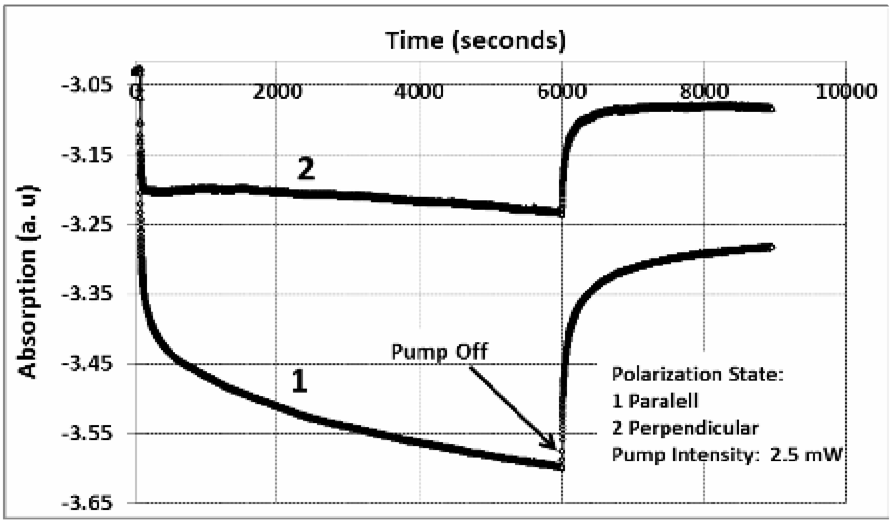


Fig. 4: Absorption spectra of Poly(methyl 2-methylpropenoate)/1-((4-(phenyldiazenyl)phenyl) azonaphthalen-2-ol at 2.5 mW parallel and perpendicular polarized laser intensities.

One of the most important applications of the photoinduced optical anisotropy was observed in Poly (methyl 2-methylpropenoate)/1-((4-(phenyldiazenyl) phenyl) azonaphthalen-2-ol thin films. As soon as switching off the irradiation the photoinduced optical anisotropy deteriorates in a fast fashion. This behavior is illustrated in Figure 5. which shows that such ensemble of guest-host systems are a promising candidate for photo-switches, which are used to rapidly and reversibly control the material properties [14].

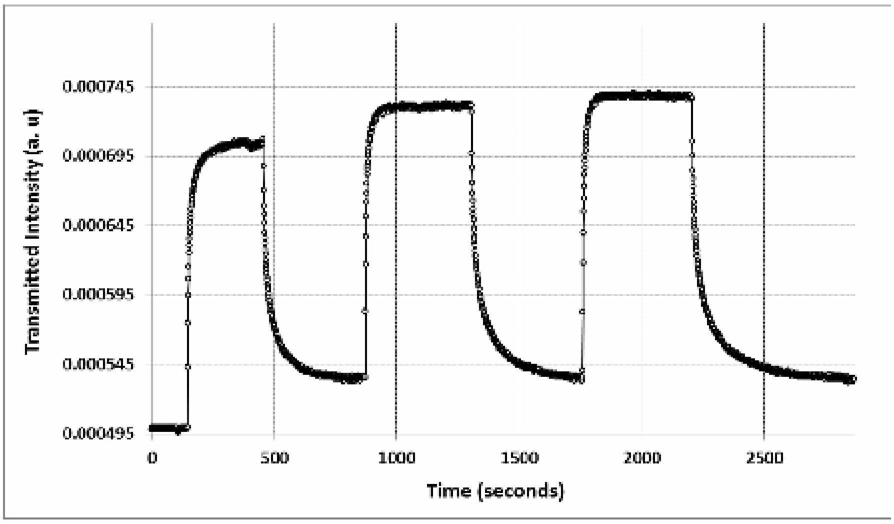


Fig.5: The optical switching results of Poly (methyl 2-methylpropenoate) / 1- ((4-(phenyldiazenyl) phenyl) azonaphthalen-2-ol at pump beam of 1mW parallel polarized laser intensity.

3.1. Contrast Ratio

The contrast ratio is defined as the ratio between maximum absorption at switching-on and -off states, which was calculated as [12]:

$$CR = \frac{A_{off}}{A_{on}} \qquad (3)$$

Where A_{off} and A_{on} are the absorbance at the maximum absorption wavelength at the off- and on-states, respectively. Contrast ratio is an important parameter to measure the performance of any electro-optic display [15]. To measure the contrast ratio, the polarized parallel and perpendicular absorption spectra of the Poly (methyl 2-methylpropenoate) / 1- ((4- (phenyldiazenyl) phenyl) azonaphthalen-2-ol, before starting the irradiation process, and after reaching the photostationary state of the samples' absorption were measured. Evolution of the absorption during irradiation was estimated via Eqs.1 and 2, as well as after cutting-off irradiation. The change of the transmitted signal through the 1- ((4- (phenyldiazenyl) phenyl) azonaphthalen-2-ol / Poly (methyl 2- methylpropenoate) thin film is large, resulting in a high contrast ratio (0.9113 and 0.9542 for parallel and perpendicular polarized laser). The orientation of the 1-((4-(phenyldiazenyl) phenyl) azonaphthalen-2-ol dye molecules was controlled using laser light, and this enabled the contrast ratio of the 1-((4- (phenyldiazenyl) phenyl) azonaphthalen-2-ol dye to be obtained by optically switching [16]. For photoactivated switching applications, it is particularly desirable that the contrast ratio is high [13]. Figure5 demonstrates such a photonic switching behavior using our Poly (methyl 2-methylpropenoate)/1-((4-(phenyldiazenyl) phenyl) azonaphthalen-2-ol thin films.

4. Conclusion

Absorption of 1- ((4- (phenyldiazenyl) phenyl) azonaphthalen-2-ol azobenzene dye doped in Poly(methyl 2-methylpropenoate) polymeric thin films were investigated by means of optical irradiation. The relationship between the probe beam absorbance parallel ($A_{||}$) and perpendicular ($A_{\perp}$) indicates that the latter is much smaller than the former. The change of the absorbance in 1- ((4- (phenyldiazenyl) phenyl) azonaphthalen-2-ol / Poly (methyl 2-methylpropenoate) thin film was large, resulting in a high contrast ratio which is desirable in photooptical switching.

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