

## Nonlinear Photoinduced Transmission in Polymeric Poly (methyl methacrylate) Doped Cerasin Red Thin Films

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Received 23/03/2014

Accepted 26/08/2014

### ABSTRACT

Investigation of nonlinear photoinduced transmission in polymeric Poly (methylmethacrylate) doped Cerasin Red thin films was performed with visible polarized parallel and perpendicular laser light. The change of transmission in Poly (methyl methacrylate) doped Cerasin Red samples is observed upon illumination. Results showed that the level of transmission and the time to achieve the saturation level increased with respect to pump beam intensity. Transmission increased in an exponential fashion with increasing the pump intensity. Transmitted parallel polarized laser light is greater by one order of magnitude than that of the transmitted perpendicular polarized laser light. Photobleaching effect was observed at 4 mW of pump beam intensity, which was attributed to the degradation of the chromophore molecules.

**Keywords:** Cerasin Red, Transmission, Thin film, Polarized laser light, Photobleaching.

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## النفوذية اللاخطية المحرّضة ضوئياً في الأغشية البوليميرية لبولي ميثيل ميثاكريليت الرقيقة المشابهة بالسيرازين الأحمر

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تاريخ الإيداع 2014/03/23

قبل للنشر في 2014/08/26

### الملخص

استُقصيت النفوذية اللاخطية المحرّضة ضوئياً في أغشية البولي ميثيل ميثاكريليت البوليميرية الرقيقة والمُشابهة بالسيرازين الأحمر، بواسطة ضوء الليزر المرئي المستقطب بشكل مواز ومتعامد. بيّنت النتائج أن مستوى النفوذية والزمن اللازم للوصول إلى مستوى الاشباع يتزايد بتزايد كثافة حزمة الضخ. كذلك تبين أن النفوذية تتزايد بشكل أسي بتزايد كثافة الضخ. وجدنا أيضاً أن ضوء الليزر النافذ والمستقطب بشكل مواز أكبر بنحو عشرة أضعاف من الحزمة النافذة والمستقطبة بشكل معامد. لوحظ كذلك مفعول الابيضاض الضوئي من أجل كثافة حزمة ضخ 4 ميلي واط التي تعزى إلى تخرب جزيئات الكروموفور.

**الكلمات المفتاحية:** السيرازين الأحمر، النفوذية، أغشية رقيقة، ضوء ليزر مستقطب، الابيضاض الضوئي.

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## 1. Introduction

The importance of nonlinear optical (NLO) materials for applications are quite obvious in many fields [1], such as polarization holography, optical data storage, integrated optics, all-optical modulation, second-order nonlinear optical (NLO) effects, optical recording, optically-controlled optical elements, and optical switches [2]. One of the most powerful methods for studying the structure and physical behavior of nonlinear optical polymeric systems is the measurement of the transmission of linearly polarized light by an ensemble of oriented molecules [3]. Chromophore molecules are well known for their properties of photochromism, which is a reversible change between two species having different transmission spectra, which can be induced by photoirradiation [4]. Optical methods have been developed for ordering chromophore molecules in polymer films, for nonlinear optics and photonics applications. Photoinduced transmission (PIT) is induced by a polarized resonant light excitation [5]. Research has centered on the potential applications of the polymers doped or functionalized with azobenzene-based [6]. The presence of azo groups in Cerasin Red and their symmetry suggest the possibility of isomerization. Due to the highly anisotropic of azobenzenes, polarized light activates the photoisomerization in a selective manner [6]. The motion results at molecular level is the chromophore motion that results from the interaction between Cerasin Red azo molecules and polarized laser light [6]. Owing to the azobenzene derivatives' reversible isomerization by photo irradiation, one can manipulate the optical properties, and the optical transmission as well [7]. Photoinduced optical transmission (POT) is of primary importance in the development of tools dealing with the light-controlled transmission and the materials that exhibit POT are very promising for use in many photonic applications [8]. In this work, we investigate the optical nonlinear photoinduced transmission effect of polymeric Poly (methyl methacrylate) doped Cerasin Red thin, which has never been studied (to our knowledge) in this polymeric thin films.

## 2. Experimental

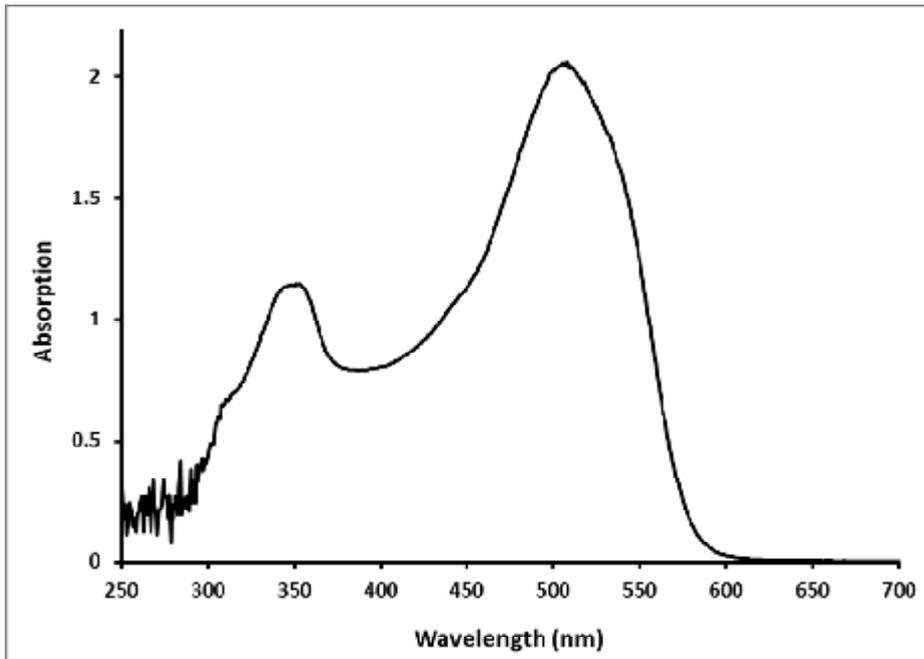
### 2.1. Sample Preparation

The prepared sample was the polymeric film made of poly (methyl methacrylate) and Cerasin Red molecules. Poly (methyl methacrylate) possesses the features of high transparency, and good mechanical properties, which make it an ideal polymeric material for fabrication of composite films with active chromophores included[9].

2grams of poly (methyl methacrylate) (MW: 36000, from Acros Organics), was dissolved in 20ml of dichloromethane. Cerasin Red (95% dye content, from Aldrich) was then added to the clear dissolved solution of poly (methyl methacrylate) (equivalent to 5% of poly (methyl methacrylate) by weight). The mixture was stirred for 24 hours until the clear solution was obtained with dye molecules fully dissolved. Thin films were dip-coated on transparent glass substrates (film thicknesses of the order  $1\mu\text{m}$  were measured by Prism Coupling technique and the absorption maximum was at 508.4 nm). Samples were baked in an oven and held at  $70\text{ }^{\circ}\text{C}$  for 5 hour in order to eliminate the residual solvent. Finally, samples were kept in a desiccator at  $22\text{ }^{\circ}\text{C}$  in a dark environment.

The samples' absorption was measured using an UV-visible spectrophotometer (Photodiode Array Photospectrometer (PDA) Specord S100, Analytik Jena).

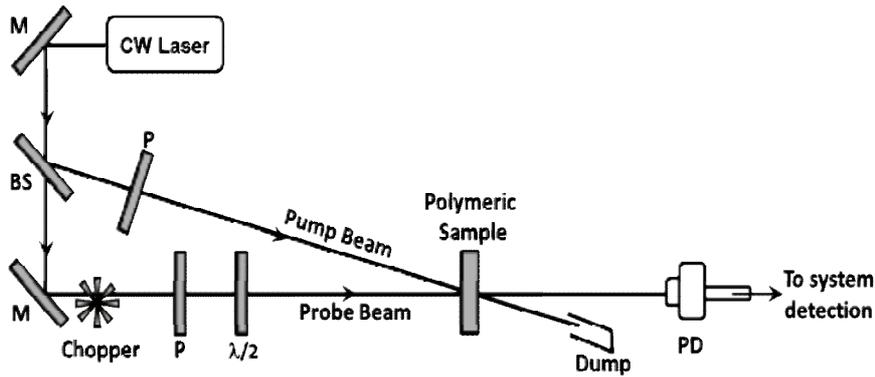
Fig. 1 shows that a wavelength of  $\lambda=514\text{ nm}$  from a multi-line Ar-ion laser (543-MAP-A02, Melles Griot) is quite appropriate since it's inside the maximum absorption region of the poly (methyl methacrylate) doped Cerasin Red prepared samples.



**Fig. 1. UV-Visible absorption spectrum of poly (methyl methacrylate) doped Cerasin Red thin film.**

### **2.2. Experimental Set up**

Polymeric thin films were pumped with linearly polarized beams from an Ar<sup>+</sup> laser at  $\lambda=514$  nm. 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 shows the experimental arrangement of the setup.



**Fig. 2** The experimental setup of nonlinear photoinduced transmission in poly(methyl methacrylate)doped Cerasin Red thin films.

Transmission is measured by a probe beam linearly polarized passing through the sample while it is being subject to the pump beam. In this manner, the probe beam transmittance parallel ( $I_{\parallel}$ ) and perpendicular ( $I_{\perp}$ ) to the electric vector of the pump beam become different. The transmittance was then calculated from [10]:

$$T_{\parallel} = \frac{I_{\parallel}}{I_0} \quad (1)$$

and

$$T_{\perp} = \frac{I_{\perp}}{I_0} \quad (2)$$

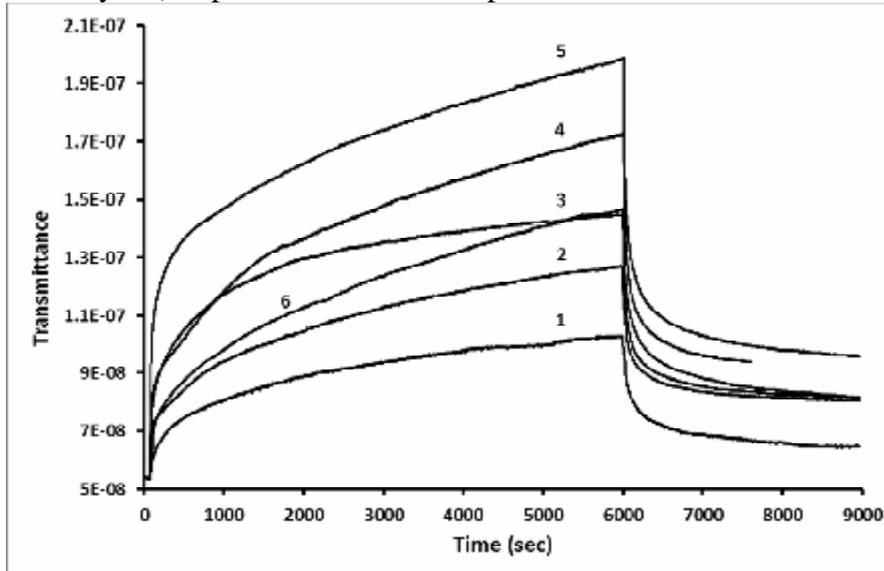
Where  $I_0$  is the intensity of the probe beam when there is no sample, and  $I_{\parallel}$  &  $I_{\perp}$  are the intensities of the probe beam transmitted through the sample when it is polarized parallel and perpendicular to the pump beam polarization, respectively.

### 3. Results and Discussion

A series of experiments was carried out in order to elucidate the influence of linearly polarized light on the transmission. Samples were pumped at several intensity levels at which the transmitted probe beam intensities were recorded simultaneously. The experimental

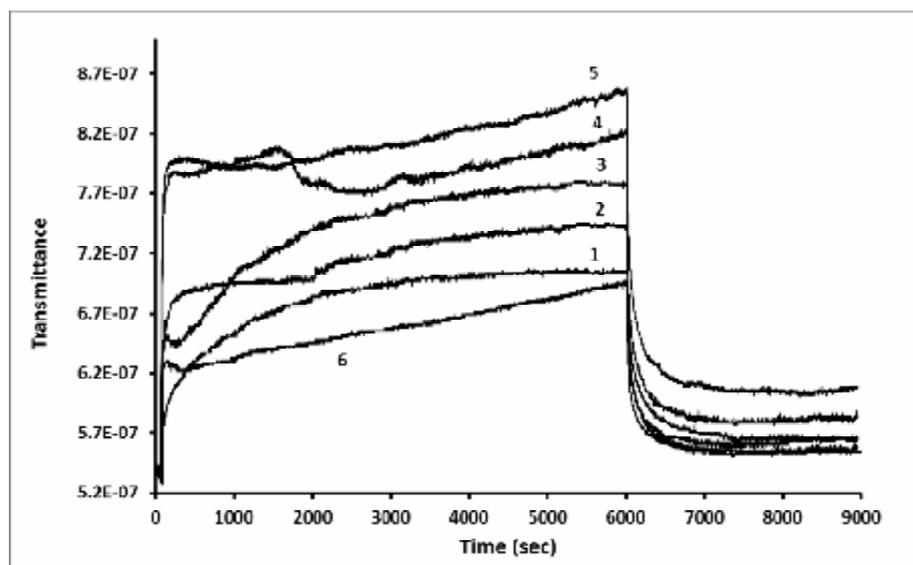
results are shown in Fig. 3 and Fig. 4. Photoinduced changes in the transmitted probe beam intensities are plotted. From Fig. 3 one can see that the transmission spectra of poly (methyl methacrylate) doped Cerasin Red thin films at different parallel polarized laser intensities, and the increasing of transmitted light intensity as a function of the pump intensity. The level of the transmission and the time to achieve the saturation level can change with the intensity of the pump beam[6].

The geometrical change of the molecules upon photoisomerization could be a source of nonlinearity in the transmission in Poly (methyl methacrylate) doped Cerasin Red compounds.



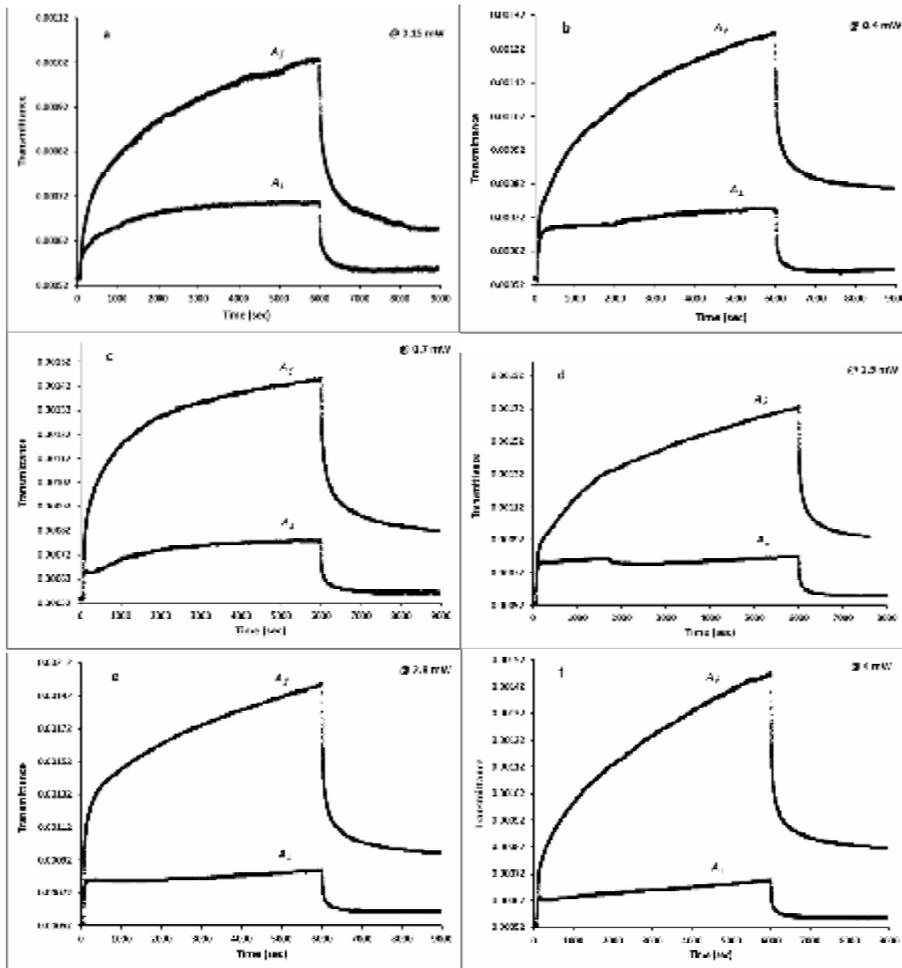
**Fig.3** Transmission spectra of polymeric Poly (methyl methacrylate) doped Cerasin Red thin film at different parallel polarized laser intensities ((1): 0.15, (2): 0.4, (3): 0.7, (4): 1.5, (5): 2.8 and (6): 4 mW).

Fig. 4 shows the observed transmission spectra of Poly (methyl methacrylate) doped Cerasin Red at different perpendicular polarized laser intensities, which has a similar trend to the parallel polarization state.



**Fig.4 Transmission spectra of polymeric Poly methyl methacrylate) doped Cerasin Red thin film at different perpendicular polarized laser intensities ((1): 0.15, (2): 0.4, (3): 0.7, (4): 1.5, (5): 2.8 and (6): 4 mW).**

Comparing transmission spectra of both parallel and perpendicular laser polarization states reveal that the intensities of the transmitted parallel polarized laser light are greater by one order of magnitude than those of the transmitted perpendicular polarized laser light as illustrated in Fig. 5. This may be attributed to the contribution of the dipole moments of the dye molecules upon orientation. This contribution is largely affected by the laser light polarization state, in which parallel laser light induces a stronger polar order in the samples along the direction perpendicular to it. This leads progressively to a greater increase in the transmitted probe light with parallel polarization.

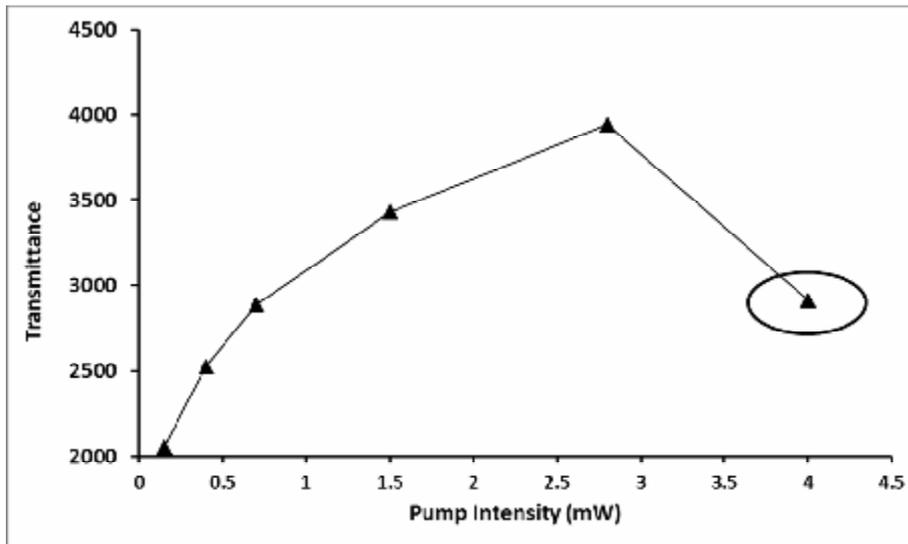


**Fig. 5** Transmission spectra of polymeric Poly(methyl methacrylate) doped Cerasin Red thin film at different parallel and perpendicular polarized laser intensities ((a): 0.15, (b): 0.4, (c): 0.7, (d): 1.5, (e): 2.8 and (f): 4 mW).

Fig. 5 indicates that  $T_{||} - T_{\perp}$  is positive when the transition was polarized in the direction of the long molecular axis, and considered as parallel transitions (i.e.  $\pi - \pi^*$ ). In other words, during the  $\pi - \pi^*$  transition, a net displacement of charge occurs parallel to the molecular plane [7].

An interesting behavior for the pumping intensity at 4 mW was noticed in curves 6 Figs. (3) and (4), where the transmittance level of the probe beam decreased instead of increasing with respect to the pump intensity. This behavior may be attributed to an irreversible photobleaching processes accompanying the chromophore orientation[6]. The latter is -in turn- due to destruction of the chromophore molecules.

Fig. 6 depicts the relationship between the probe beam transmitted intensity and the pump beam intensity, which shows an increase in the probe beam transmission with respect to the pump intensity. However, at pump intensity 4 mW the photobleaching effect becomes clear.



**Fig. 6: Transmission intensity of the probe beam as a function of the pump intensity with parallel polarized beams scheme.**

A similar interesting behavior of the probe beam transmission at 4 mW perpendicular polarized laser pump intensity was also observed as it is illustrated in Fig. 7.

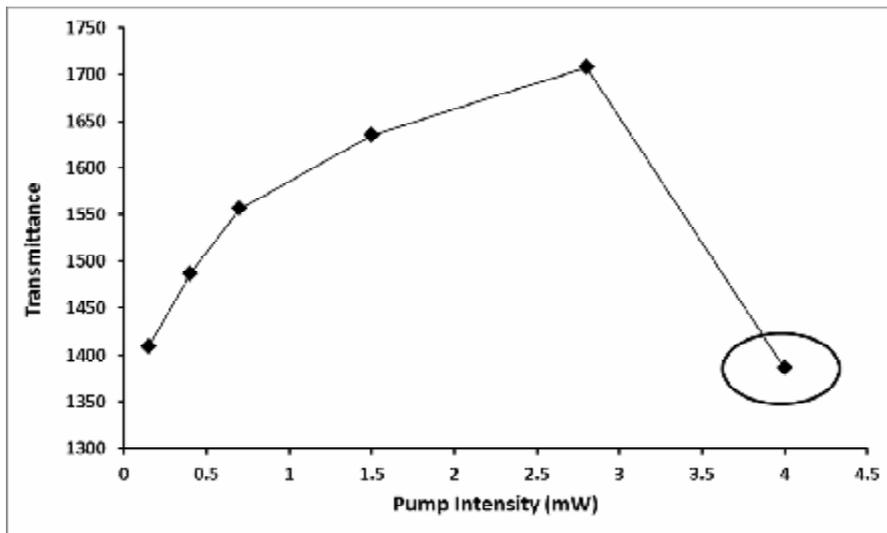


Fig. 7: Transmission of the probe beam as a function of the pump beam intensity at perpendicular polarized beams scheme.

#### 4. Conclusion

The transmission of the Poly (methyl methacrylate) doped Cerasin Red thin films was induced under irradiation with linearly polarized laser light. The transmitted probe beam intensity increased as the pump laser beam intensity did. However, higher pump intensities ( $\geq 4$  mW) induced a photobleaching effect in the samples. Photobleaching led to the deterioration of the intensity of the probe beam, which may attributed to the chemical structure destruction of the chromophore molecules, which is – on the other hand - a permanent effect.

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