Photo-Induced Optical Density in Poly(Methyl Methacrylate) /Brilliant oil scarlet BThin Films

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Abstract: The photo-induced optical density of Brilliant oil scarlet /BPMMA thin films has been investigated using the pump-probe method. The results showed the dynamic evolution of the optical density where it increased rapidly in an exponential fashion, a photostationary state was reached and the relaxation phase decreased exponentially in a slow manner. Existence of the Angular Hole Burning (AHB) and the Angular Redistribution (AR) effects in the Brilliant oil scarlet Bmolecules in the PMMA polymeric host was proved. Finally, the results showed the behavior of the optical density as a function of the pump beam intensity of the Brilliant oil scarlet B/PMMA sample and the predominance of the photostationary state.

Keywords: Photo-Induced, Optical Density, Photoisomerization, Angular Hole Burning (AHB), Angular Redistribution (AR), Brilliant oil scarlet B.

1. Introduction

The photoinduced optical density (POD) in polymer/organic dye systems has been the subject of intensive investigations in the recent years. Materials with POD properties are very promising for use in many photonic applications [1-2], such as production of optical elements for polarization holographic [3-5], fabricating high quality aligning substrates[6-7] and molecular strain sensors for polymer films [8-11], etc.

Research has centered on the potential applications of the polymers doped with azobenzene-based dyes [12].The studies performed on dichroic-dyes dispersed in polymer matrix predicted that it is a useful technique to enhance the optical response of the devices[13].The formation of such highly dichroic polarizing films may be used for the fabrication of anisotropic non-linear optical devices [14-17]. The assembly of organic molecules into polymeric thin films has potential applications for miniaturized optoelectronic devices [18-19].

The presence of azo groups in Brilliant oil scarlet Band their symmetry suggest the possibility of isomerization. Due to the highly anisotropic nature of azobenzenes, polarized light activates the photoisomerization in a selective manner [20].The photoisomerization induced in the azo-polymer leads to conformational changes in the polymer chains, which, in turn, leads to macroscopic variations in the chemical and physical properties of their surroundings and media. Incident light on an organic dye containing polymer induces an important property; photochemical *trans* →*cis* →*trans* isomerization [21].In Brilliant oil scarlet B/ PMMA thin film, photoisomerization activity is induced constantly and rapidly by polarized light through the excitation of the Brilliant oil scarlet Bdye molecules. This process results in a series of motions leading to optical density. Such phenomenon could be exploited in photonic applications [22].

To the best of our knowledge, the photoinduced optical density in PMMA/ Brilliant oil scarlet Bthin films has never been studied separately and in depth. In this paper we describe our investigation of the dynamic behavior of the photoinduced optical density of Brilliant oil scarlet Bazoaromatic structure incorporated into a poly(methyl methacrylate) (PMMA) polymeric matrix.

2. Experimental

Brilliant oil scarlet Bazobenzene dye incorporated into a PMMA matrix as a guest-host system was prepared. 8gr of PMMA (MW: 36000, from Acros Organics) was dissolved in 80ml of tetrahydrofurane (THF, C_4H_8O, 95.5%, from Merck) and Ethanol(CH_3CH_2OH, 95.5%, from Merck). Brilliant oil scarlet B(95% dye content, from Aldrich),equivalent to 3 % of PMMA by weight was added to the clear dissolved solution of PMMA. The mixture was stirred for 12 hours at room temperature until the chromophore molecules were fully dissolved. Thin films were dip-coated on transparent glass substrates. The Samples were baked in an oven and held at 70 ^{o}C for 4 hours in order to eliminate the residual solvent. Film thicknesses were measured by a Prism Coupling technique, and were of the order of 1μm. Finally, samples were kept in a desiccator at 22 ^{o}C in a dark environment for later investigation.

A UV-visible spectrophotometer (Photodiode Array Photospectrometer (PDA) Specord S100, from Analytik Jena) was used to record absorption spectra of Brilliant oil scarlet B/PMMA thin film samples.
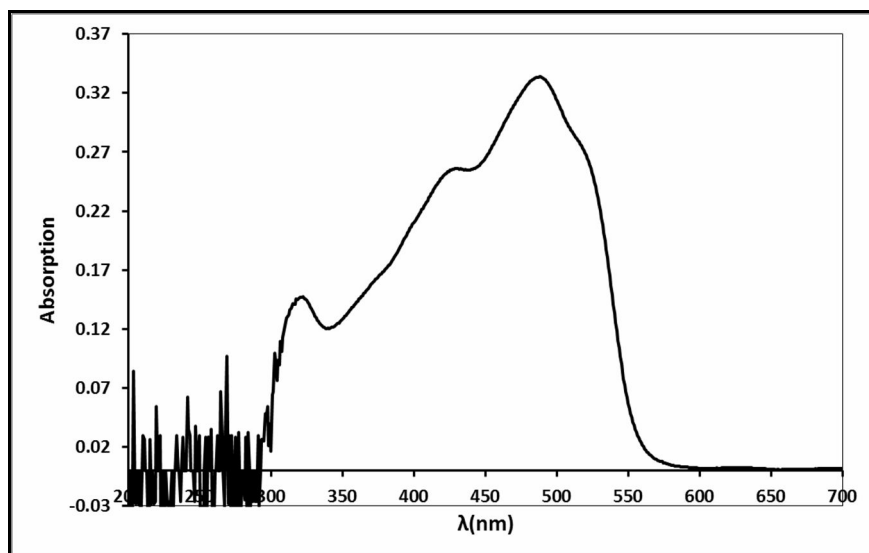

Figure 1.UV-Visible absorption spectrum of Brilliant oil scarlet B/PMMA samples.

Figure 1 shows the UV-Vis absorbance of the thin films; where the absorption maximum of Brilliant oil scarlet Bin PMMA prepared samples was at 484 nm.The photoinducedoptical density was measured via an experimental set up shown in Fig. 2. An Ar^+ laser (543-MAP-A02, from MellesGriot) with 488 nm wavelength was used to pump the samples. The probe beam passing through the sample was incident on a photosensor and fed to a personal computer through a low noise current preamplifier (SR570, from Stanford Research Systems), and a DSP lock-in amplifier (SR850, from Stanford Research Systems). An IEEE 488.2 GPIB (from National Instruments) card was used to control and record the experimental data along with a special program written in Borland C++.
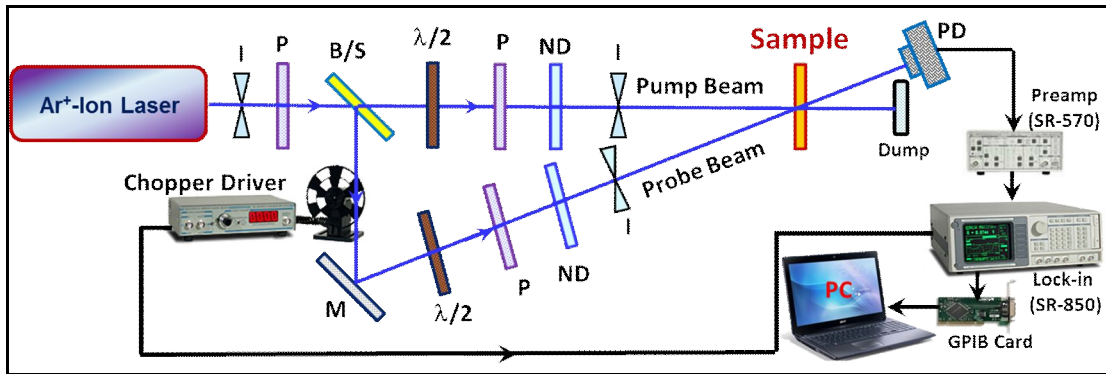
Figure 2.The experimental setup: P: polarizer, ND: neutral density filter, B/S: beam splitter, $\lambda/2$ half-wave plate, and PD: photodiode.

The photoinduced optical density of Brilliant oil scarlet B/PMMAthin film was calculated from the recorded spectra as[22]

$$OD_m = \frac{1}{3}\left(OD_{\parallel} + 2OD_{\perp}\right) \qquad (1)$$

Where $OD_{\parallel}$ and $OD_{\perp}$ are the optical densities parallel and perpendicular to the electric vector of the pump, respectively. They were calculated using [23]

$$OD_{\parallel} = -logT_{\parallel} \qquad (2)$$
and
$$OD_{\perp} = -logT_{\perp} \qquad (3)$$

Where $T_{\parallel}$ and $T_{\perp}$ are the transmitted beam intensities in the parallel and perpendicular states with respect to the electric vector of the pump, respectively. They are given by [24]

$$T_{\parallel} = \frac{I_{\parallel}}{I_0} \qquad (4)$$
and
$$T_{\perp} = \frac{I_{\perp}}{I_0} \qquad (5)$$

Where I_0 is the intensity of the probe beam when there is no sample. $I_{\parallel}$ and $I_{\perp}$ 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

The photoinduced optical density in Brilliant oil scarlet B/PMMA thin film is plotted in Fig. 3. This figure depicts the dynamic evolution of the optical density in the sample.

This figure showed that optical density increased rapidly in an exponential fashion in the first seconds of pumping, so that a photostationary state was reached as a result of the photoisomerization process cycles. The optical density relaxation phase decreased exponentially in a slow manner, which means that the optical density did not disappear instantaneously when the irradiation was switched off.

The fast increasing of the optical density in the first stage means that most *trans* molecules has drifted to the *cis* state[25] which is an evidence of the angular hole burning (AHB) predominance.

The angular redistribution (AR) effect accumulates *trans* molecules perpendicular to the pump polarization direction [26]. Reaching saturation reveals the balance between the AHB and AR effects. The

exponential decrease in optical density after cutting-off the pump indicates the sudden collapse in *cis* population in the first seconds as well as the collapse of the photoinduced polar order.
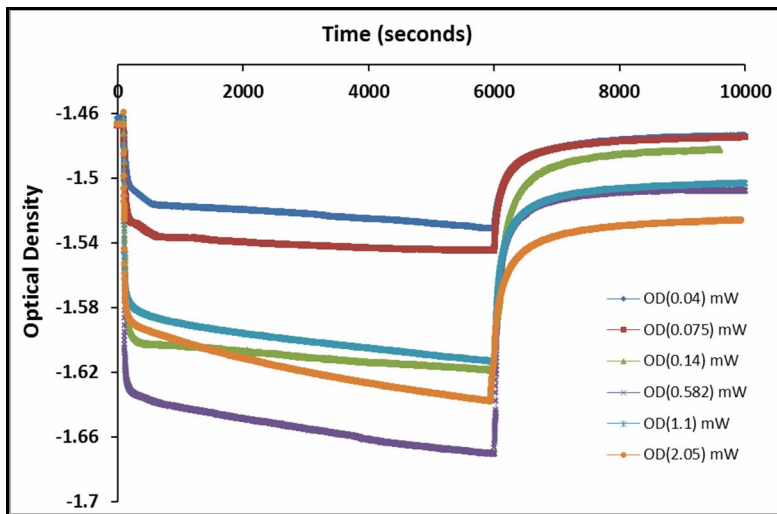

Figure 3. The photoinduced optical density in Brilliant oil scarlet B/ PMMA thin films at pump intensities (0.04), (0.075), (0.14), (0.582), (1.1) and (2.05) mW respectively.

The optical densities growth and relaxation spectrum curve (Fig. 3) reveals that the photoinduced optical densities was stable for the guest-host Brilliant oil scarlet B/PMMA thin films at the photostationary state. Furthermore, the transmitted light intensity did not decay completely to the original level after cutting off the pump beam. It is a proof of a strong AR and a very slow angular diffusion in *trans*.

Figure 4depicts the relation between the optical density and the pump beam intensity of the Brilliant oil scarlet B/PMMAsample. This figure showsthe optical density in both; average and stationary states. Both lines increased, reached a maximum and then decreased slowly. This behavior indicates the evolution stages of the photoisomerization process during irradiation of the sample and after cutting off the pump beam. We can deduce from figure 4 that the stationary state is a predominant state since it is greater than that of the average one.
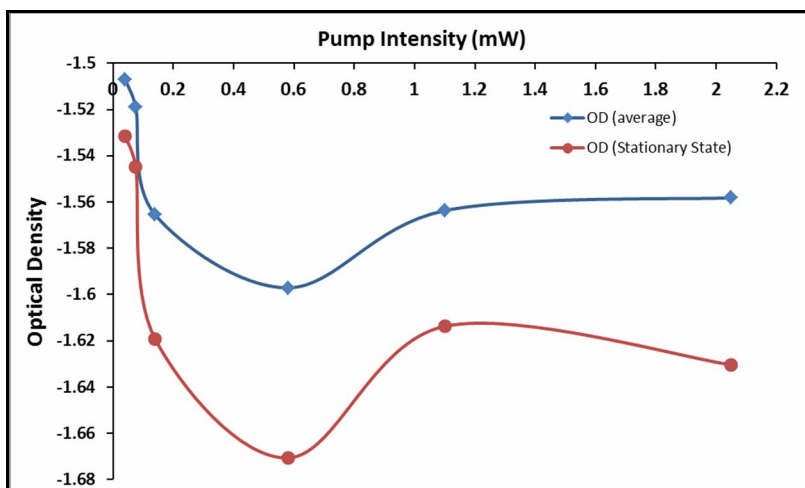

Figure 4.The optical density as a function of the pump beam intensity in the Brilliant oil scarlet B/PMMA samples

The behavior of the optical density of the samples is another evidence of the dynamic evolution of the photoisomerization processes.

4. Conclusions

The predominance of AHB, in the first 1000 seconds, and the emergence of AR in the following minutes are particularly clear with Brilliant oil scarlet B/PMMA thin film illuminated with polarized laser light.

The photoinduced optical density of Brilliant oil scarlet B/PMMA thin film is shown to be the result of the competition of the angular hole burning (AHB) by polarized light, and the angular redistribution (AR) during the photoisomerization processes.

The optical density vs the pump beam intensity of the Brilliant oil scarlet B/PMMA sample increased, reached the maximum and decreased.

The illustrated results prove the potential usefulness of the Brilliant oil scarlet B/PMMA thin films in optoelectronic and photonics applications.

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