Stability of Photoinduced Orientation of Poly (methyl methacrylate)/ Solvent Red 23Thin Films

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Abstract

The effect of the reversible photo-orientation of the Solvent Red 23 dye incorporated in Poly (methyl methacrylate) thin films has been investigated. A probe-pump optical system was used to investigate the dichroic behavior of the samples. Orthogonal polarized laser light induces a smaller increase in the transmitted beam intensity. A stronger polar order was induced using a parallel pump-probe laser light compared to that of the perpendicular state. It was found that the dichroic ratio value of the Poly (methyl methacrylate) / Solvent Red 23 thin film is 4.952, which indicates that the net orientation of Solvent Red 23 molecules is orthogonal to the applied beam field. The dynamic evolution of the dichroic ratio showed that the relaxation is rather slow, and it deteriorates in a slow logarithmic fashion, which may take a very long time in order to reach the isotropic state.

Keywords: Photoinduced orientation, Solvent Red 23, Poly (methyl methacrylate), Dichroic ratio, Polarized light.

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استقرارية التوجيه المحثوث ضوئياً في الأفلام الرقيقة لبولي ميثيل ميثاكريليت/سولفنت رد 23

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الملخص

استكشف تأثير التوجيه المحثوث ضوئياً العكوس لصباغ سولفنت رد 23 (Solvent Red 23) المتحد مع بوليمر البولي ميثيل ميثاكريليت ((Poly(methyl methacrylate) في الأفلام الرقيقة. استخدمت منظومة ضخ-سبر لاستقصاء السلوك اللوناني للعينات. يولد الضوء الليزري المستقطب عمودياً ازدياداً أصغرَ في شدة الشعاع النافذ. جرى توليد بنية قطبية أقوى باستخدام أشعة ضخ-سبر ليزرية متوازية، مقارنة بحالة الأشعة المتعامدة. وجد أن قيمة نسبة اللونانية للمنظومة البوليميرية تبلغ 4.952 التي تشير إلى أن التوجة المحصَّل لجزيئات الصباغ العضوي معامدة لاتجاه شعاع حقل حزمة ضوء الليزر. يظهر التطور الحركي لنسبة اللونانية أن استرخاءها بطيء، و يتدهور بشكل لوغاريتمي بطيء، و الذي يمكن أن يستمر وقتاً طويلاً جداً للوصول إلى الحالة المتناحية.

الكلمات المفتاحية: التوجيه المحثوث ضوئياً، سولفنت رد 23، بولي ميثيل ميثاكريليت، الضوء المستقطب.

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1. Introduction

Photosensitive materials such as compounds containing azobenzene and its derivatives may become dichroic under the action of linearly polarized light [1].The studies performed on dichroic-dyes dispersed in polymer matrix predicted that it is a useful technique to enhance the optical response of the device. Such dyes dispersed into polymer matrix are known as guest–host polymer systems [2]. Research has centered on the potential applications of the polymers doped with azobenzene-based dyes[3]. 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. The photoalignment has been studied in a number of polymer systems including dye doped polymer [5-6].The role played by azobenzene-containing polymers in the modern photonic, electronic and opto-mechanical applications cannot be underestimated[7]. The novel and intriguing optical phenomenon, photoinduced orientation in azopolymers have been reviewed[8-10]. Orientation could be defined as ordering of the absorbing molecules' dipoles in directions in which light affects them less [11]. The implementation of photoinduced orientation in molecular-based optical materials represents a promising approach for the synthesis of high-contrast, high-resolution photosensitive materials, high-density (holographic), data storage andreal-three-dimensional (holographic) displays [12]. Moreover,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 [13].When a thin polymer film is exposed to linearly polarized light (LPL), photo-orientation of the dye molecules produces dichroic films [3].

In this paper, our own involvement in this area of research will be summarized and our contributions will emphasize to the basic understanding of the physics of this phenomenon, by studying the photoinduced orientation of Solvent Red 23 molecules that have been incorporated in Poly (methyl methacrylate) polymeric network.

2. Experimental

The Solvent Red 23 dye (95% dye content, from Aldrich) was dissolved in the Poly (methyl methacrylate) (MW: 36000, from Acros Organics) with the concentration of 5 wt % of the Poly (methylmethacrelate) polymer. Figure 1 depicts the chemical structure of Solvent Red 23, while figure 2 shows the chemical structure of poly(methylmethacrylate) polymer.

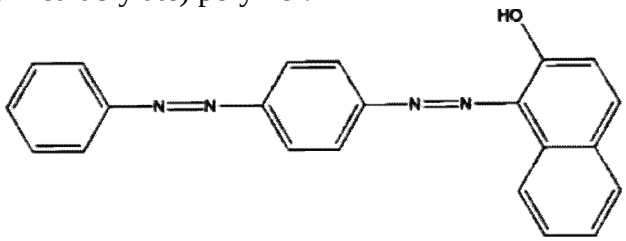

Figure 1: The chemical structure of Solvent Red 23 molecule.

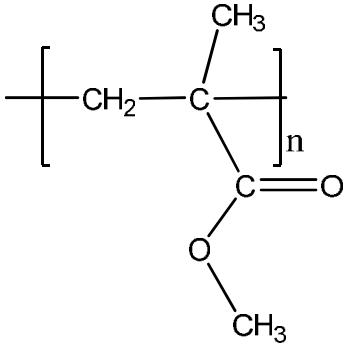

Figure 2: The chemical structure of poly(methylmethacrylate) polymer.

The nonionic diazo dye-doped polymer films were prepared at room temperature conditions.Thin films were dip-coated on transparent glass substrates. The thickness of the film was controlled to be in the range of 1–2μm, which is measured by the Prism Coupling technique. After dried in vacuum oven for 24 hours, the amorphous films with good optical quality were obtained and stored in a desiccator for further studying.

The absorption spectrum of Solvent Red 23 exhibits a broadband absorption in the range of 300–600 nm with an absorption peak of

508.4 nm, as it is illustrated in Figure 3. A UV-visible spectrophotometer (Photodiode Array Photospectrometer (PDA) Specord S100, Analytik Jena) was used to measure the films' absorption. This spectrum confirms that the wavelength of 514 nm provided by the multi-line Ar-ion laser (543-MAP-A02, MellesGriot) is quite appropriate for pumping.

To detect the optical photoinduced response of the Solvent Red 23 dye contained in the Poly (methyl methacrylate) polymer, the setup shown in Figure 4 was used. This setup enabled the analysis of changes in the absorption of the Poly (methyl methacrylate) / Solvent Red 23 thin films, which were induced by optical irradiation with a 1 mW intensity of laser light.

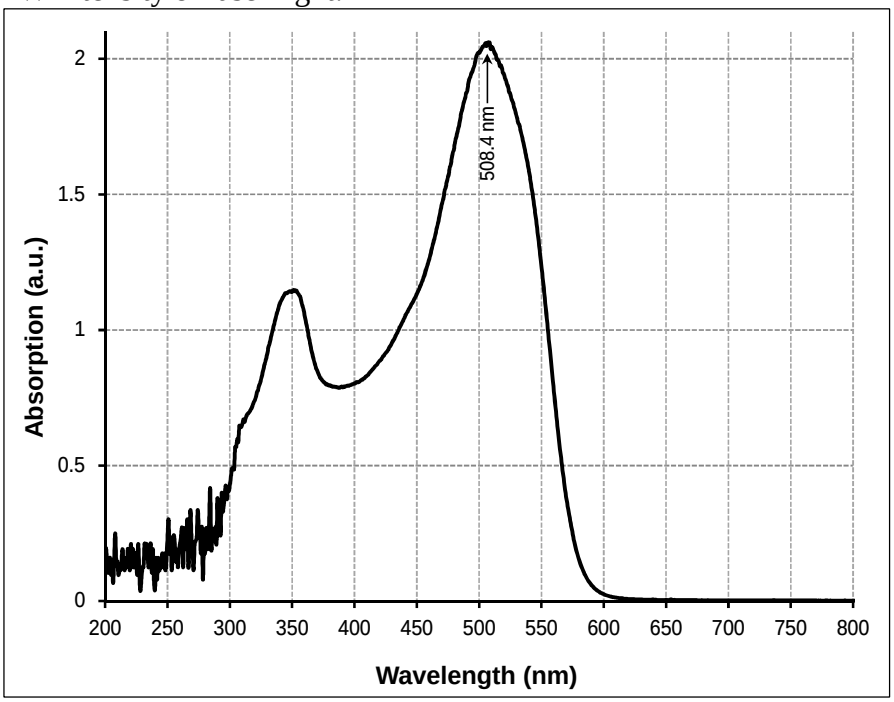

Figure3:UV-Visible absorption spectrum of Solvent Red 23 doped poly(methylmethacrylate) thin film.

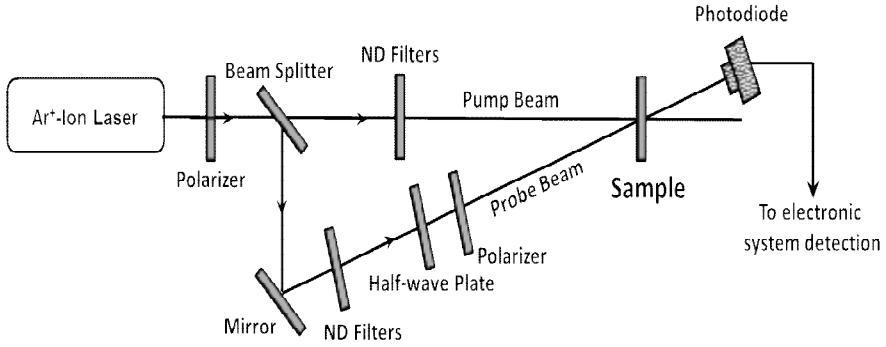

Figure. 4: The experimental setup of photoinduced orientation of Poly(methyl methacrylate)/ Solvent Red 23.

The probe signal of the beam falling onto the sample and subsequently onto 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++.

The probe beam absorbance parallel ($A_{||}$) (the pump and probe polarization vectors are parallel) and the absorbance perpendicular ($A_{\perp}$) (the pump and probe polarization vectors are perpendicular) become different. The absorbances were then calculated from [14]:

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

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

Poly (methyl methacrylate)/Solvent Red 23 samples were pumped with Ar^+ laser at λ=514 nm at 1 mW intensity and the transmitted probe beam was recorded. Figure5 shows the photoinduced changes in the parallel absorption polarized laser beam intensity.

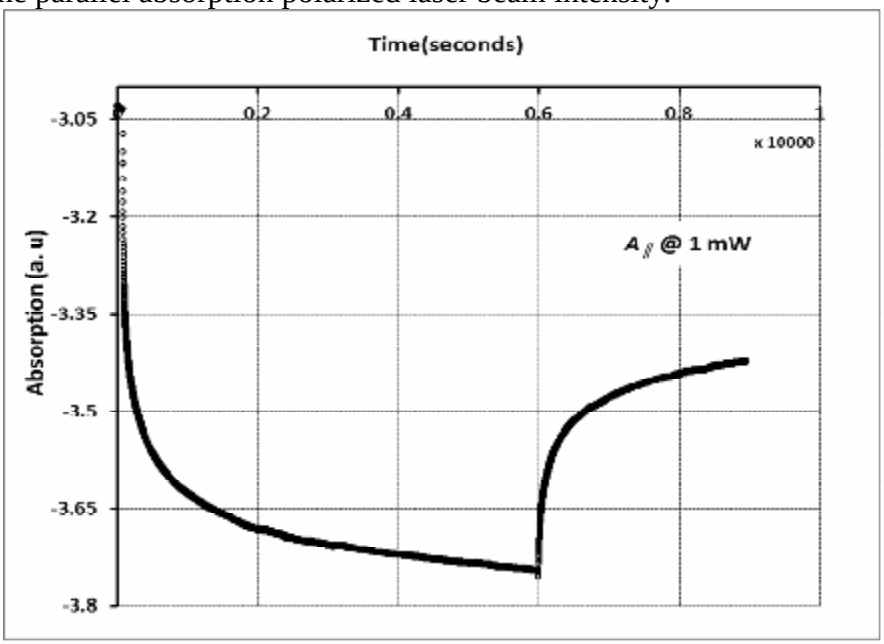

Figure 5: Absorption spectrum of Poly(methyl methacrylate) /Solvent Red 23 at 1mW parallel polarized laser intensity.

Absorption decreases rapidly, in Poly (methyl methacrylate) /Solvent Red 23 thin films, when the pump beam is switched on, as it is illustrated in Figure 5. Saturation state is reached when the absorption becomes stable. Cutting off the pump beam leads to a major increase in the absorption. This is becausea part of the aligned Solvent Red 23 azo molecules will tend to return to the random arrangement, leading to a loss of photo-orientation. However, depending on the thermal properties of the Poly (methyl methacrylate)/ Solvent Red 23 polymer film and the experimental conditions, a significant amount of aligned azo molecules will be frozen in the oriented position for a period of time, a state which could persist for a long time reaching the isotropic state, which is called the relaxation state. A similar trend was observed for the absorption

spectrum of Poly (methyl methacrylate)/ Solvent Red 23 at the perpendicular polarized laser light (Figure 6). Analyzing Figures 5 and 6 reveals that the absorption induced by parallel polarized laser light is smaller than that induced by perpendicular polarized laser light. This result could be attributed to the contribution of the dipole moments of the Solvent Red 23 molecules upon orientation, where parallel laser light induces a stronger polar order in the samples than in the direction perpendicular to it.

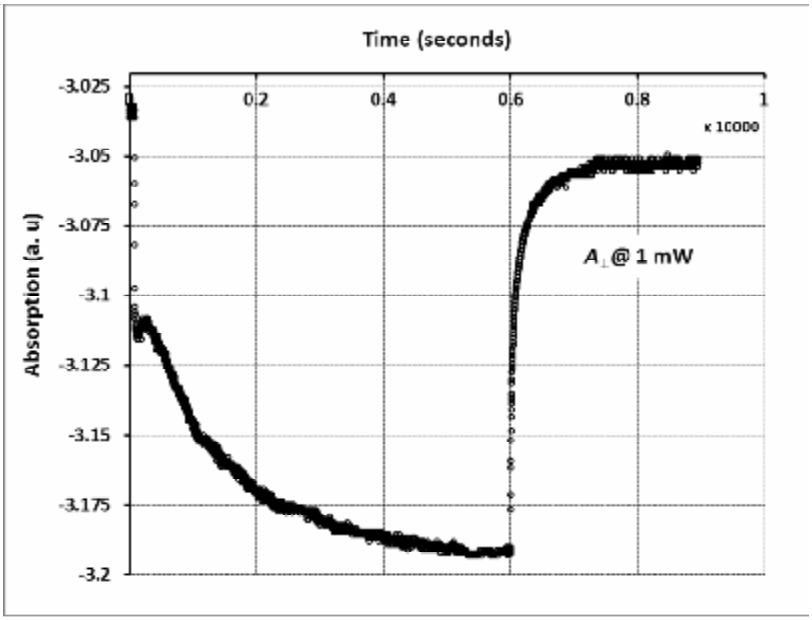

Figure 6: Absorption spectrum of Poly(methyl methacrylate) /Solvent Red 23 at 1 mW perpendicular polarized laser intensity

3.1. Dichroic Ratio

The dichroic ratio is a measure of the stability of photoinduced orientation as a function of time after the light was cut-off.This ratio is calculated by using the absorption spectra at polarized parallel ($A_{\parallel}$)and perpendicular ($A_{\perp}$) to the polarization state of the laser pump beam, using[2],

$$DR = \frac{A_{\parallel}}{A_{\perp}} \qquad (3)$$

The dichroic ratio calculated here was 4.952, which indicates that the net orientation of Solvent Red 23 molecules is orthogonal to the applied beam field.

The dynamic evolution of the dichroic ratio during irradiation, and relaxation, shows a consistent increase with the pumping time until a photostationary state is reached. Cutting-off the pumping radiation does not cause the dichroic ration to deteriorate rapidly. As Figure 7 shows, a slow decrease in this ratio is observed, which may take a very long time in order to reach the isotropic state.

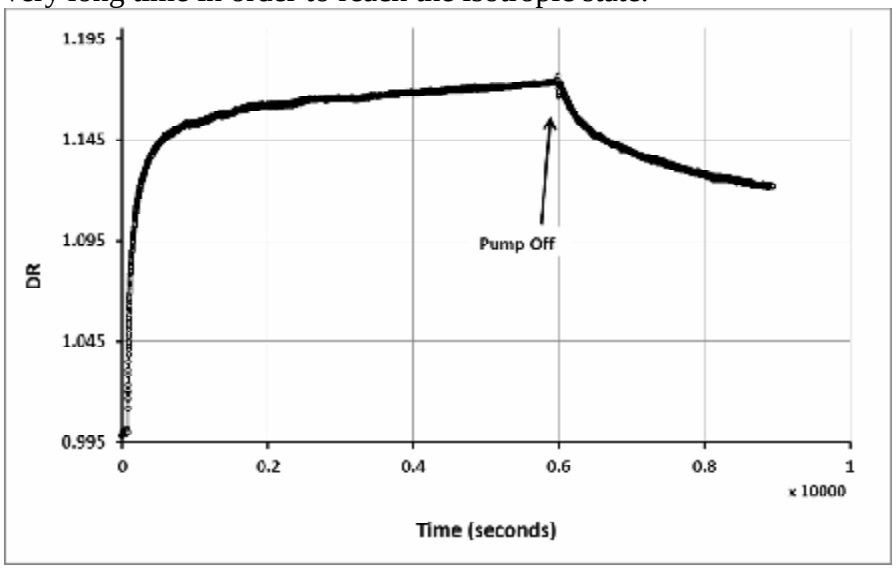

Figure 7: The dynamic evolution of the dichroic ratio.

4. Conclusion

Solvent Red 23 dye is one of the best candidates for the optical induced ordering. It absorbs in the visible range of the spectrum (300 nm- 600 nm), and low-power lasers can be used for photoinduced optical applications. Dichroic ratio was about 5, which reveals that the net orientation of Solvent Red 23 molecules is orthogonal to the applied beam field and exhibits more stability of photoinduced orientation.

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