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# Photochromic materials sensitive for UV recording

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We report a spectrophotometric investigation of the photoprocesses in different polymer films containing stilbene and stilbenecarboxaldehyde. The films are sensitive to UV light. We have observed considerable photoinduced changes in the absorption spectra of the samples due to *trans-cis* photoisomerization of the stilbene-type molecules. The influence of different chemical sensitizers on the photochromic process is observed. If the UV- illumination is done with linearly polarized light, the induced changes in the absorption spectra are anisotropic.

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*Keywords*: Photochromic materials, Photoinduced dichroism, Stilbene-type molecules, UV recording

## 1. Introduction

The photochemical and spectral properties of *trans*-stilbene have been studied experimentally [1-3]. The stilbene-type molecules have a double carbon bond. They are olefin-type compounds [4] and have two isomeric forms: *trans*-stilbene and *cis*-stilbene. Illumination with UV light induces *trans-cis* isomerization of the stilbene-type molecules, accompanied by considerable changes in the absorption spectra both of the longer-wavelength and the shorter-wavelength band [3]. Similar results have been reported by Imamura *et al* for PMMA films doped with *trans*-4-methoxystilbene [5].

The aim of this work is the investigation of the photoinduced processes in chemically sensitized photochromic materials incorporated in a polymethylmethacrylate (PMMA) matrix. These materials are sensitive to UV light and transparent in the visible.

## 2. Experimental

In these experiments, we have used six types of polymers film:

- type 1 – PMMA containing *trans*-stilbene (S/PMMA);
- type 2 – PMMA containing *trans*-stilbene sensitized with dibenzyl ketone (ESt/PMMA);
- type 3 – PMMA containing *trans*-stilbene sensitized with diphenyl diketone (FSt/PMMA);
- type 4 – PMMA containing *trans*-4-stilbenecarboxaldehyde (SCA/PMMA);
- type 5 – PMMA containing *trans*-4-stilbenecarboxaldehyde sensitized with dibenzyl ketone (ESCA/PMMA);
- type 6 – PMMA containing *trans*-4-stilbenecarboxaldehyde sensitized with diphenyl diketone (FSCA/PMMA).

Sensitizers were added in order to obtain faster photoinduced changes in the absorbance.

The stilbene-type materials were dissolved in 1,2 - dichlorethane together with the polymer. Their concentration with respect to the PMMA was 13 wt%. Films with thickness about 4 μm were obtained by solution casting onto clean quartz plates for the spectrophotometric investigation.

The spectral investigation was carried out with a Cary 5A spectrophotometer. A 50 W mercury lamp was used to induce isomerization of the stilbene-type molecules in the polymer films. The illumination was done through 333 or 313 nm interference filters. The light intensity at the sample surface was 32.4 μW $cm^{-2}$ with the 333 nm filter and 2.7 μW $cm^{-2}$ with the 313 nm filter. The polarization of the beam was at 45° with respect to the horizontal. In order to calculate the photoinduced dichroism, we measured the absorbance spectra of the samples through a polarizer oriented parallely and perpendicularly to the exciting light polarization direction.

## 3. Results

The absorption maximum of the *trans*-stilbene molecules in the PMMA was at 296 nm and for the *trans*-4-stilbenecarboxaldehyde film was about 330 nm [3] i.e. the films were sensitive to UV light.

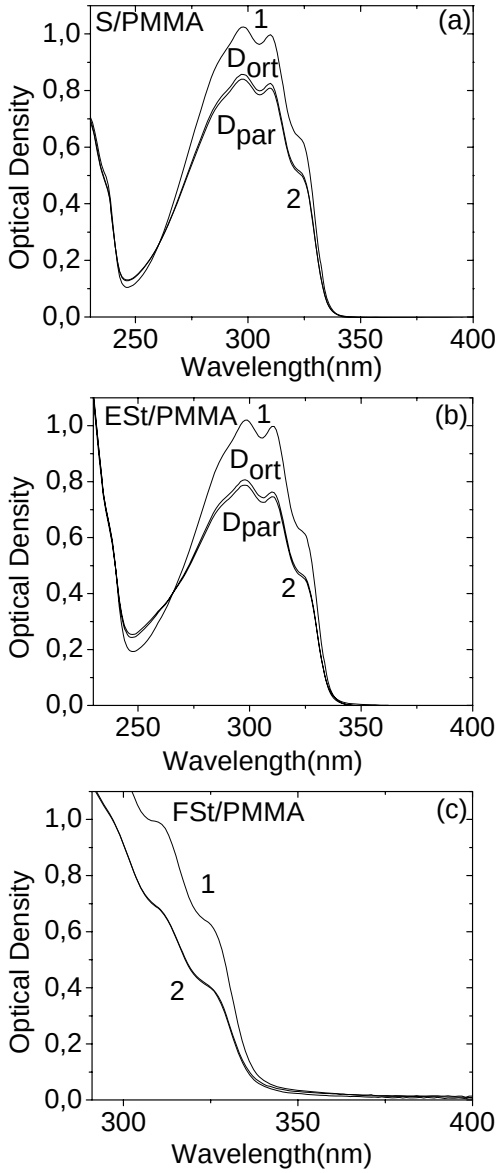


*Fig. 1. Absorption spectra of the S/PMMA films (a), the ESt/PMMA films (b) and the FSt/PMMA films (c). The graphs show the optical density before illumination (1) and the optical density after 2 min illumination (2) at 333 nm.*

The samples were illuminated through the 333 nm interference filter for 2, 5, 10, 20, 30 and 60 minutes (for the samples type 4, 5 and 6). In Fig. 1, the normalized absorption spectra of the type 1 (S/PMMA), type 2 (ESt/PMMA) and type 3 (FSt/PMMA) films is shown. Curves 1 in Fig. 1 (a), (b) and (c) correspond to the absorption spectra of the type 1, type 2 and type 3 films before illumination and curves 2 after 2 min illumination at 333 nm. We measured the absorbance spectra of the samples through a polarizer oriented parallely and perpendicularly to the exciting light polarization direction. $D_{ort}$ and $D_{par}$ are the optical densities for light polarized orthogonal and parallel to the exciting light polarization. After 30 min illumination, there were considerable photoinduced changes in the absorption spectra of these samples.

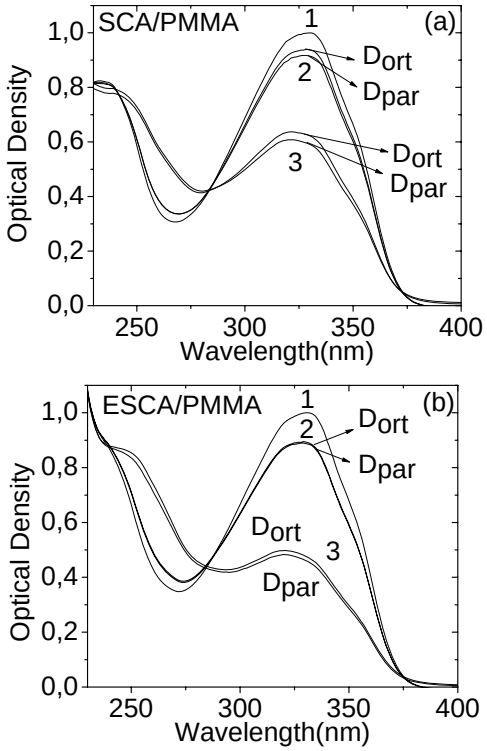


*Fig. 2. Absorption spectra of the SCA/PMMA films (a) and the ESCA/PMMA films (b). The graphs show the optical density before the illumination (1) and the optical density after 10 min. (2) and 60 min. (3) illumination at 333 nm.*

In Fig. 2 (a) and (b), the normalized absorption spectra of the type 4 and 5 films before and after 10 and 60 minutes illumination through the 333 nm interference filter is shown. The bleaching of the sample FSCA/PMMA was practically the same as that in the SCA/PMMA. The bleaching in *trans*-stilbene sensitized with dibenzyl ketone (ESt/PMMA) was very large in comparison to *trans*-4-stilbenecarboxaldehyde sensitized with dibenzyl ketone (ESCA/PMMA).

In Fig. 3, the experimental results for the average optical density $\Delta D_{av} = D^{non} - D_{av}^{illum}$ as a function of time are presented ($D_{av}^{illum} = (D_{ort}^{illum} + D_{par}^{illum})/2$). If we compare the results for the average optical density for 2 minutes illumination with wavelength $\lambda$ = 333 nm, we notice that the processes of bleaching in the sensitized polymer films is faster. Significant changes are seen – faster bleaching of the *trans*-stilbene sensitized with diphenyl diketone in comparison to samples sensitized with dibenzyl ketone. The average optical density for samples of types 1, 2 and 3 increased slowly, approaching saturation and afterwards $\Delta D_{av}$ was stable in time, as seen in Fig. 3.

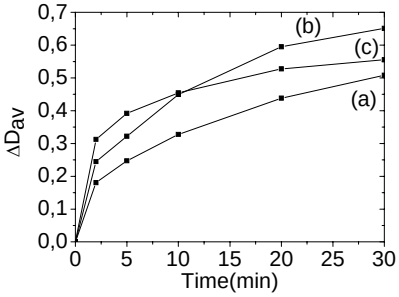


*Fig. 3. The average optical density of the type 1 (S/PMMA) (a), the type 2 (ESt/PMMA) (b) and the type 3 (FSt/PMMA) (c) after 2, 5, 10, 20 and 30 minutes illumination through the 333 nm interference filter.*

The processes of bleaching of the polymer films of types 4, 5 and 6 were relatively slow. This is shown in Fig. 4. The average bleaching is smaller in comparison to Fig. 3, but photoinduced dichroism was observed only in PMMA containing *trans*-4-stilbenecarboxaldehyde.

We illuminated the samples: S/PMMA, ESt/PMMA and FSt/PMMA through the 313 nm interference filter for 5, 10, 20 and 30 minutes and obtained results for the average optical density as a function of time (Fig. 5).

If we compare the results for average optical density for 5 minutes illumination with wavelength 313 nm, we notice that the processes of bleaching in the *trans*-stilbene sensitized with dibenzyl ketone is faster than that for *trans*-stilbene sensitized with diphenyl diketone.

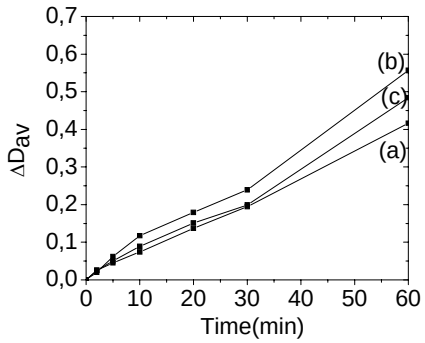


*Fig. 4. The average optical density of the type 4 (SCA/PMMA) (a), type 5 (ESCA/PMMA) (b) and type 6 (FSCA/PMMA) (c) after 2, 5, 10, 20, 30 and 60 minutes illumination through the 333 nm interference filter.*

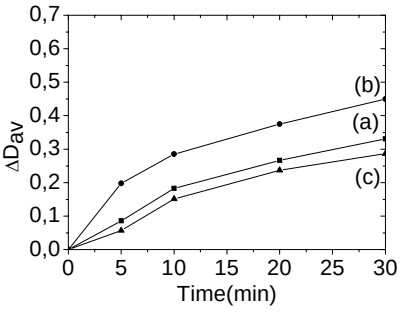


*Fig. 5. The average optical density of the type 1 (S/PMMA) (a), type 2 (ESt/PMMA) (b) and type 3 (FSt/PMMA) (c) after 5, 10, 20 and 30 minutes illumination through the 313 nm interference filter.*

We measured the spectra through a polarizer oriented parallel and perpendicular to the exciting light polarization direction. A small dichroism was measured in the SCA/PMMA. Fig. 6 shows the spectrum of $D_{ort}$–$D_{par}$, where $D_{ort}$ and $D_{par}$ are the optical densities for light polarized orthogonal and parallel to the exciting light polarization.

We used the ratio $r$ of the dichroism value at its maximum to the corresponding induced change in the absorption. It was calculated by the expression:

$$r = \frac{D_{ort} - D_{par}}{D_0 - (D_{ort} + D_{par})/2} \approx 0.08 \qquad (1)$$

Here $D_0$ is the maximal optical density of the film before the illumination.

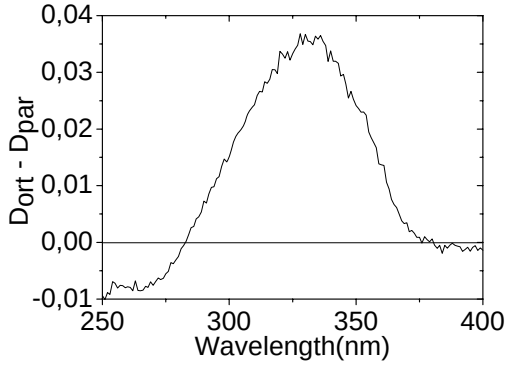


Fig. 6. *Spectrum of the dichroism induced in the SCA/PMMA films after 60 min illumination at 333 nm, 32.4 $\mu W\ cm^{-2}$.*

## 4. Discussion

In this paper, we presented the results from an investigation of photoinduced processes in photochromic materials. We observed considerable photoinduced changes in the absorption spectra of the four types of polymer film sensitized with dibenzyl ketone or diphenyl diketone. The chemically sensitized photochromic materials incorporated in a PMMA matrix were used to obtain faster photoinduced changes in the absorbance.

Significant changes were seen – faster bleaching of the *trans*-stilbene sensitized with dibenzyl ketone and sensitized with diphenyl diketone in comparison to *trans*-stilbene, if the illumination was done with a wavelength absorbed by both the *trans*- and *cis*- isomers. Similar results were observed for sensitized *trans*-4-stilbenecarboxaldehyde.

When illuminating a SCA/PMMA film with UV light for 60 minutes we observed photoinduced dichroism, but it was small compared to the isotropic bleaching. Contrary to our expectation, the dichroism measured in sensitized polymer films of types 5 and 6,

was very small in comparison to that in the sample of type 4.

## 5. Conclusions

In summary, our experiment involved measurements of the sensitized photoisomerization kinetics of photochromic materials. We observed considerable changes in the absorption spectra in different polymer films containing *trans*-stilbene and *trans*-4-stilbenecarboxaldehyde, on illumination with UV light. The influence of different chemical sensitizers on the photochromic process was observed. Sensitizers were used to obtain faster photoinduced changes in the absorbance. The results for samples sensitized with dibenzyl ketone and with diphenyl diketone *trans*-stilbene in PMMA matrix showed that bleaching is larger in comparison to that in sensitized *trans*-4-stilbenecarboxaldehyde, but the photoinduced dichroism in sensitized polymers films of types 2 and 3 is very small. The induced changes in the absorption spectra for *trans*-4-stilbene-carboxaldehyde are anisotropic, if the illumination is done at a wavelength absorbed by both the *trans*- and *cis*- isomers, but is small compared to the isotropic bleaching.

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