The Determination of the Coloring Centers through Casting (C-DCPF)5% - (PMMA) Film and New Optical Comparative Studying With its E-isomer.


1. Thin film laboratory, Physics Department, Faculty of Education, Ain Shams University, Roxy, Cairo, 11757, Egypt.
2. Physics Department, Faculty of Science, Minia University, Minia, Egypt.

Abstract

Films of 5% E-dicycloprenyl-methylene-(2,5-dimethyl-3-furylethylidene-succinic anhydride (E-DCPF) doped in PMMA polymer films, [E - (DCPF) - (PMMA) films], were prepared by casting method and then were irradiated with UV light (360 nm) for different exposure time (2-38 min). The color of the films turned to deep pink after 38 min. The photo-bleaching time was 670 min. The absorbance spectrum was studied in the range from 190 nm up to 650 nm, where that spectrum showed four peaks. The onset one was related to the photo coloration effect at 516.44 nm, where it was increased in height and decreased in its width by the increasing of the exposure time of UV-Irradiation. The other three peaks were at 363 nm, 272.85 and 218 nm respectively. The spectra have an isosbestic point at (417 nm). The optical properties of the films were investigated using the spectrophotometric measurements of both the transmittance and reflectance in the spectral range from 400 to 1500 nm. Both the refractive index, n, and the absorption index, k, were calculated before and after coloration. For the first time, the parameters of the molar extinction coefficients (εmolar) of oscillators energy (E0), oscillator strength (f), electronic dipole strength (q2) and the concentration of the coloring centers were evaluated. The analysis of the absorption coefficient (α) revealed three indirect transitions and only one direct transition for photo-bleached films, while two indirect transitions and only one direct transition for colored films.

Introduction:

Dicycloprenyl fulgide (DCPF) has attracted a great attention because it is an important one of the organic photochromic compounds. These compounds are considered as promising candidates in photoswitchable system which require high reversibility [1-11] and in optical memory devices which depending on non-destructive readout stability [5-7]. Through all photochromic candidates; Fulgides showed a reversible photochromism with minimum photochemical fatigue [2,8], thermal stability [9] and nondestructive readout stability. The photochromism of fulgide occurs between the open E-isomer and the photocycle colored form (C-isomer) [2,5-7]. The molecular structure for E&C (isomers) of DCPF is shown in Fig.1(a).
The present work is to introduce a new optical comparative study of casting (C-DCPF)-PMMA film with its E-isomer, determine the concentration of the coloring centers, and many other important optical parameters for more promising photochromic application.

**Experimental Technique:**

Films of (5% E-DCPF) doped in (PMMA), with 37.5 µm thickness, were prepared using casting technique. The polystyrene methacrylate (PMMA), was obtained from Aldrich chemical company, while dicyclopropyl-methylene-(2,5-dimethyl-3-furyl)ethyldiene-succinic anhydride (E-DCPF) was obtained from TCI company, Japan. Pure chloroform was used as a common solvent for both DCPF and PMMA. The solutions were then mixed by using a magnetic stirrer for about 4.5 hours and under vacuum to reach a suitable viscosity and homogeneity. The solution was casted on a glass plate and kept in a dry atmosphere at room temperature for 24 hours. UV-VIS absorption spectra of the unirradiated and irradiated films were carried out at room temperature in the wavelength range (190-650 nm). In addition, both the transmittance (T) and the reflectance (R) were measured at normal incidence in the spectral range from 190 to 1500 nm, using a double beam spectrophotometer (JASCO model V-670 UV-VIS-NIR) attached with constant angle specular reflection attachment (5°). The analysis of the obtained data of T, R and A were carried out in a similar manner as published before [10,12]. The relative uncertainty in the transmittance and reflectance given by the manufacturer was 1%. Transmittance scans were performed using the air in the reference compartment of the same type as the one used for film deposition. The reflectance was measured at the incidence angle of 5° with an aluminum reference mirror. The absolute values of measured transmittance and reflectance, after correcting for the absorbance and reflectance of the substrates, are given by the following equations:

\[ T = \left( \frac{I_f}{I_a} \right) (1 - R_a) \]  
\[ R = \left( \frac{I_f}{I_m} \right) R_m \left[ 1 + (1 - R_a)^2 \right] - T^2 R_a \]

From the measured T, R and film thickness, d, the value of the refractive index (n) and the absorption index (k) were computed by a special computer program based on minimizing \((\Delta T)^2\) and \((\Delta R)^2\) simultaneously, where

\[ (\Delta T)^2 = | T_{n,k} - T_{exp} |^2 \] 
\[ (\Delta R)^2 = | R_{n,k} - R_{exp} |^2 \]
where \( T_{n,k} \) and \( R_{n,k} \) are the calculated values of T and R using the Murmann's exact equations taking into account the experimental error in measuring the film thickness to be \( \pm 2.5\% \) and in T and R to be \(+1\%\), the error in the calculated values of n and k are estimated to be \( \pm 3\% \) and \( \pm 2.5\% \), respectively.

**Results and Discussion**

Fig. 1(b) showed the experimental pictures of the bleached (E-isomer) and colored (C-isomer) (DCPF) \(_5\%\) (PMMA) films, while Fig. 2(a&b) represents the obtained patterns for NMR \(-\text{H}^1\) & \(\text{C}^{13}\) estimations for both E and C- DCPF films under our estimation.

**Fig. 1(b):** The colour of the obtained E and C- (DCPF) \(_5\%\) - (PMMA) isomers in the film form.

**Fig. 2(a):** The patterns of NMR- \(\text{H}^1\) & \(\text{C}^{13}\) estimations of (E-DCPF) \(_5\%\) - (PMMA) film.
Fig. 2(b): The patterns of NMR- H¹ & C¹³ estimations of (C-DCPF )₅% - (PMMA) film.

Fig. 3 shows the effect of the exposure times to UV light on absorbance spectrum of (E-DCPF )₅% - (PMMA) films. The exposure time ranged from 2 to 38 min, where the absorbance reached a saturation and stability in its value. The absorption in VIS region increased with increasing of the exposure time up to 38 min then leave off, with photochromic absorption peak at 516.44 nm, see Fig. 4(a). The spectra of absorbance in Fig. 3 illustrated an isosbestic point at 417.079 nm, where the second absorption band was mentioned with an inverted response to light. The amplitude of the absorption peaks increased with exposure time to UV light. Fig. 4(b) represents a comparison between the absorption spectrum of the saturated photo-colored and photo-bleached of (DCPF )₅% - (PMMA) films at room temperature in the wavelength range (190-650 nm), while Table.1 involved a comparison between E and C of (DCPF )₅% - (PMMA) films. The isosbestic point revealed the presence of only one product in photoreaction[13]. C-isomer product was then photobleaching using a white light. The photo-colored was gradually started disappeared after 670 min, where it returned to the original color which related to E-isomer. This behavior was found to obey a first order reaction with a rate constant, \( k = 0.158 \text{ s}^{-1} \) and a half-life time \( t_{1/2} = 40 \text{ s} \).
Fig. 3: The absorbance spectra of (DCPF)$_{35\%}$ - (PMMA) films at room temperature in the wavelength range (190 -750 nm) at different exposure time (2-38 min).

Fig.4(a): The time dependence of the absorbance spectra of the coloration peak through (DCPF)$_{35\%}$ - (PMMA) film in the wavelength range (400-650 nm).
Fig.4 (b): A comparison between the absorbance spectra of the photo-colored and photo-bleached (DCPF)\textsubscript{5}\% - (PMMA) film.

Table 1: The values of the energies(E) of the peaks in the absorbance spectra of both E and C- (DCPF)\textsubscript{5}\% - (PMMA) film.

<table>
<thead>
<tr>
<th>No., of the peak</th>
<th>E-isomer</th>
<th>E(eV)</th>
<th>C-isomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>2.401</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.44</td>
<td>3.416</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4.129</td>
<td>4.545</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5.602</td>
<td>5.668</td>
<td></td>
</tr>
</tbody>
</table>

The spectral distribution of the molar extinction coefficient (ε\textsubscript{molar}) was also determined and it is shown in Fig.5. ε\textsubscript{molar} and its companion parameters meanly, oscillator energy(E\textsubscript{os}), oscillator strength (f) and the electric dipole strength (q\textsuperscript{2}) were determined using the following equations [14].

\[ \alpha = 2303(\frac{\rho}{M})\varepsilon_{\text{molar}} \quad (5) \]
\[ f = 4.38 \times 10^{-9} \int \varepsilon_{\text{molar}} \, d\nu \quad (6) \]
\[ q^2 = \frac{1}{2500} \varepsilon_{\text{molar}} \Delta \lambda / \lambda \quad (7) \]

Where \( \rho \) is the solid's mass density, \( M \) is molecular's weight and \( \alpha \) is absorption coefficient. These parameters have been listed in Table 2.
Fig.5: The molar extinction coefficient ($\varepsilon_{\text{molar}}$) vs. the wave number ($\nu$) for both E and C (DCPF)$_{5\%}$ - (PMMA) films.

Table 2: The calculated spectral parameters, $f$ and $q^2$ of the different peaks for both E and C (DCPF)$_{5\%}$ - (PMMA) films.

<table>
<thead>
<tr>
<th>No., of the peak in Fig.(5)</th>
<th>F</th>
<th>$q^2$(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C-isomer</td>
<td>E-isomer</td>
</tr>
<tr>
<td>1</td>
<td>0.689</td>
<td>1.3</td>
</tr>
<tr>
<td>2</td>
<td>1.681</td>
<td>1.75</td>
</tr>
<tr>
<td>3</td>
<td>0.456</td>
<td>0.94</td>
</tr>
<tr>
<td>4</td>
<td>0.73</td>
<td>--------</td>
</tr>
</tbody>
</table>

Also, the concentrations of the coloring centers were calculated by the analysis of the peak of coloration and depending on approximate Smakula's equation, which can be represented by the following formula [15]:

$$N_f = 0.99 \times 10^7 \left[ \frac{n}{(n^2+2)^{3/2}} \alpha \mu \right]$$ (8)

Where $N$ is the density of the coloring centers, $n$ is the refractive index of the films, $\mu$ is the width at the half maximum of the absorption peak. The calculated centers were increased from ~ 4.57x10$^{10}$ to 9.18 x10$^{12}$/cm$^3$ as the time of coloration increased from 2 to 38 min.

On the other side, the spectral distribution of both T and R in the wavelength (400 to 1500 nm) for bleached, and colored films are shown in Fig.6. The analysis of both T and R gave us the ability to calculated the mean optical constants, the refractive index, $n$, and the absorption index, $k$. 

\begin{align*}
\text{ISSN: 2320-5407} & \quad \text{Int. J. Adv. Res. 5(1), 838-848} \\
\text{Fig.5: The molar extinction coefficient ($\varepsilon_{\text{molar}}$) vs. the wave number ($\nu$) for both E and C (DCPF)$_{5\%}$ - (PMMA) films.} \\
\text{Table 2: The calculated spectral parameters, $f$ and $q^2$ of the different peaks for both E and C (DCPF)$_{5\%}$ - (PMMA) films.} \\
\begin{tabular}{|c|c|c|c|c|}
\hline
\text{No., of the peak in Fig.(5)} & \text{F} & \text{$q^2$(Å)} \\
\hline
\text{C-isomer} & \text{E-isomer} & \text{C-isomer} & \text{E-isomer} \\
\hline
1 & 0.689 & 1.3 & 0.59 & 0.79 \\
2 & 1.681 & 1.75 & 0.37 & 0.48 \\
3 & 0.456 & 0.94 & 8.002 & 11.90 \\
4 & 0.73 & -------- & 14.63 & -------- \\
\hline
\end{tabular}
\end{align*}
Fig. 6: $T\%$ and $R\%$ vs. $\lambda$(nm) for both E and C - (DCPF)$_{5\%}$ - (PMMA) isomers in the film form.

The refractive index, $n$, was analyzed using the single oscillator model in the transparent region and all the optical data could be described to a very good approximation, by the following equations[16-17].

$$n^2 = 1 + \frac{E_0E_d}{(E_0^2 - (h\nu)^2)^2}$$ (9)

$$n^2(e_x) = \varepsilon_l - \frac{(e_x^2N)}{(4\pi\varepsilon_0 \frac{e^2}{c^2 m^*})} \lambda^2$$ (10)

where $h\nu$ is the photon energy, $E_0$ is the oscillator energy, $E_d$ is the dispersion energy, $\varepsilon_x$ is the high frequency dielectric constant, $\varepsilon_l$ is the lattice dielectric constant, $N/m^*$ is the ratio of the free carrier concentration to the effective mass, $c$ is the speed of light, and $e$ is the electronic charge. The dispersion parameters were obtained by plotting $(n^2 - 1)^{-1}$ vs $(h\nu)^2$ and $n^2$ vs. $\lambda^2$ (see Fig.7(a&b)) and the obtained results are listed in Table 3.

Fig.7(a): $(n^2 - 1)^{-1}$ vs $(h\nu)^2$ for both E and C - (DCPF)$_{5\%}$ - (PMMA) isomers in the film forms.
Table 3: Some Dispersion parameters for both E and C-(DCPF)$_{5\%}$-(PMMA) isomers in the film form.

<table>
<thead>
<tr>
<th>The dispersion parameters</th>
<th>E-isomer</th>
<th>C-isomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$, eV</td>
<td>5.107</td>
<td>3.397</td>
</tr>
<tr>
<td>$E_d$, eV</td>
<td>8.626</td>
<td>5.9327</td>
</tr>
<tr>
<td>$\varepsilon_\infty$</td>
<td>2.689</td>
<td>2.7465</td>
</tr>
<tr>
<td>$\varepsilon_L$</td>
<td>2.794</td>
<td>2.927</td>
</tr>
<tr>
<td>$\varepsilon_L - \varepsilon_\infty$</td>
<td>0.105</td>
<td>0.181</td>
</tr>
<tr>
<td>N/m* , /Kg.m$^2$</td>
<td>$3.345 \times 10^{46}$</td>
<td>$4.084 \times 10^{46}$</td>
</tr>
</tbody>
</table>

After the analysis of the dispersion curves we converted to determine both the type and the values of the energy gaps depending on the analysis of the absorption coefficient and according to Baradeen et al equation[16] for E and C-(DCPF)$_{5\%}$-(PMMA) isomers in the thin film forms. The results are listed in Table 4 and shown in Fig.8(a&b). These results supported the presence of three indirect transitions with 1.669, 2.61 and 2.787 eV for E-isomer, while two with 1.967 and 2.787 eV for C-isomer respectively and only one direct transition for the both isomers, in the thin film forms, with a value equal to 2.937 eV.
Fig. 8: (a) $(\alpha h\nu)^{1/2}$ vs. $(h\nu)$ and (b) $(\alpha h\nu)^2$ vs. $(h\nu)$ for both E and C-(DCPF)$_{5\%}$-(PMMA) isomers in the film form.

Table 4: The values the optical energies of both direct and indirect transitions for both E and C-(DCPF)$_{5\%}$-(PMMA) isomers in the film form.

<table>
<thead>
<tr>
<th>The type of the optical transitions</th>
<th>The values of the</th>
<th>Optical energies (E$_g$) in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E-isomer</td>
<td>C-isomer</td>
</tr>
<tr>
<td>Indirect</td>
<td>$E_{g_1}^{in}$</td>
<td>1.669</td>
</tr>
<tr>
<td></td>
<td>$E_{g_2}^{in}$</td>
<td>2.61</td>
</tr>
<tr>
<td></td>
<td>$E_{g_3}^{in}$</td>
<td></td>
</tr>
<tr>
<td>Direct</td>
<td>$E_g^{d}$</td>
<td></td>
</tr>
</tbody>
</table>
Conclusion:
Casting E-(DCPF)$_{5\%}$ - (PMMA) isomer in the film form was prepared and then was irradiated with UV light (360 nm) for different exposure time. The film turned to deep pink color after 38 min. The photo-bleaching time was 670 min. The absorbance spectra showed four peaks. The onset one was related to the photo coloration effect at 516.44 nm, where it was increased in height and decreased in its width by exposure time of UV-Irradiation. The other three peaks were at 363.04 nm, 272.848 and 218.819 nm respectively. The spectra have an isosbestic point at (417.079 nm). The photo-coloring effect was gradually disappeared and return to the original color after 670 min, which related to E-isomer. This behavior was found to obey a first order reaction with a rate constant, k = 0.158 s$^{-1}$ and a half-life time, $t_{1/2} = 40$ s. The analysis of both the transmittance and reflectance in the spectral range from 400 to 1500 nm revealed the presence of three indirect transitions with 1.669, 2.61, and 2.787 eV for E-isomer, while two with 1.967 and 2.787 eV for C-isomer respectively and only one direct transition for the both isomers, in the thin film forms, with a value equal to 2.937 eV. The application of Smakula’s equation indicated the increasing of the concentration of the coloring centers from ~ $4.57 \times 10^{10}$ to $9.18 \times 10^{12}$/cm$^3$ as the time increased from 2 to 38 min.

References: