

Optical and Thermal Spectroscopic Studies of Luminescent Dye Doped Poly(methyl methacrylate) as Solar Concentrator

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ABSTRACT: A luminescent solar concentrator was prepared that was based on a bulk sheet of poly(methyl methacrylate) doped with different luminescent dyes (K1, K27, and Lpero) during the polymerization process. Photo- and thermal-stability studies revealed that the Lpero dye system is the most stable one. The electronic transition mechanism for the concentrator systems was obtained by the darktrap and phototrap spectroscopy technique. The results were correlated with the outdoor test measurements over 1 year. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3316–3323, 1999

Key words: optical and thermal spectroscopy; luminescent dyes; poly(methyl methacrylate); solar concentrator

INTRODUCTION

Luminescent dye doped transparent materials such as glasses or polymers are of growing interest because of their potential use as solid-state lasers and luminescent solar concentrators (LSCs).¹ These LSCs offer the possibility of concentrating both direct and diffuse radiation and thus considerably reducing the cost of solar electric energy (i.e., less photovoltaic cell area) and increasing overall solar conversion efficiency. Very high efficiencies have been predicted theoretically² in a solar cell attached to the edge of the LSCs doped with different types of luminescent dyes. Many experimental efforts have been made for a large plate area of LSCs.³ The effect of the geometrical shape of the bulk concentrators doped with different luminescent dyes on the conversion coefficient and the principles of LSCs in

yearly, monthly, and daily correlations for dye photodegradation and optical efficiency have been discussed.^{4–7}

In the present work we study the transition mechanism within the wide band gap of LSC materials to attain the best conditions under which these LSCs will have high thermal stability and photostability and enhance the solar cell conversion efficiency. UV absorption and the thermal stimulated current (dark and photo) were discussed as the most effective tools to study both optical and trap-level spectroscopy. The practical realization of our LSC systems were investigated using data analysis of outdoor test measurements.

EXPERIMENTAL

Polymerization of methyl methacrylate (MMA) was performed using azobisisobutyronitrile as a catalyst (1 wt %) at 323 K for 2 days in the dark and then drying in a vacuum at 383 K for 6 h.

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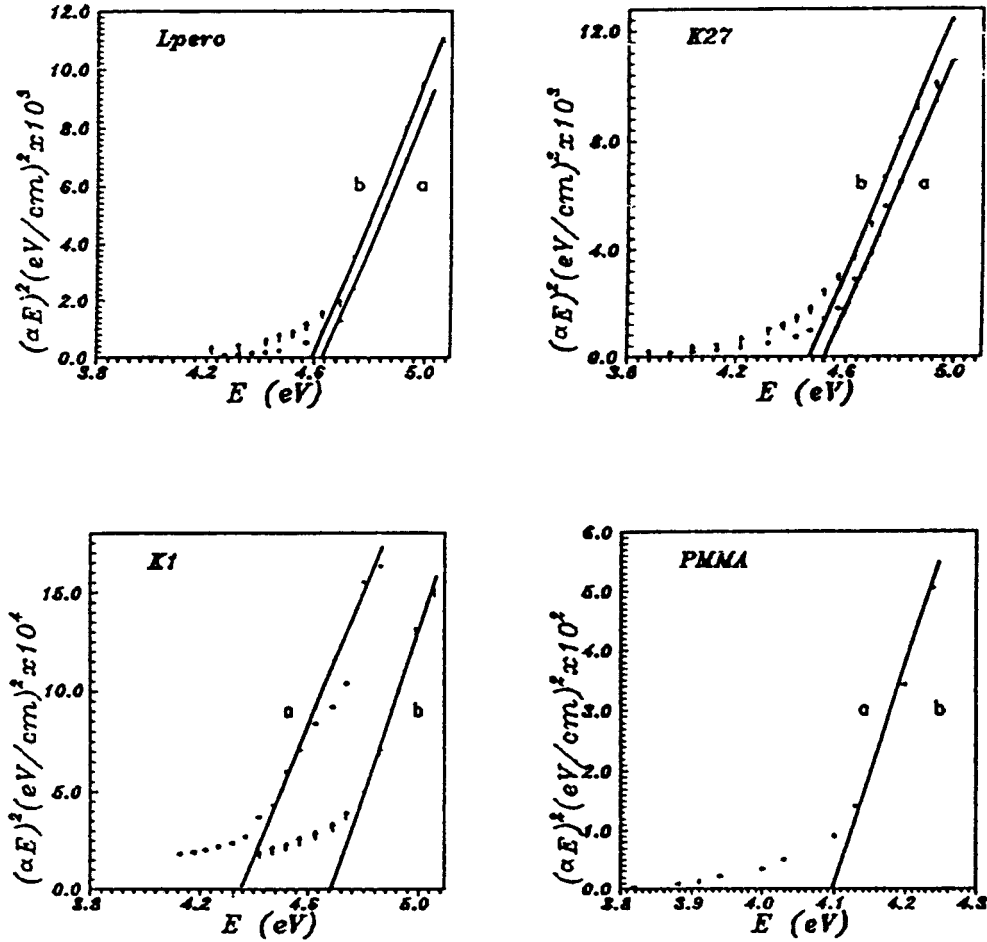


Figure 1 The dependence of $(\alpha E)^2$ on photon energy (E) at room temperature (a) before and (b) after exposure to daylight for 1 year for pure and doped PMMA with different luminescent dyes.

Doping with the luminescent dyes Lpero, K27, and K1 (BASF, Germany) was carried out during the polymerization processes. Sheets of bulk sam-

ples with $5 \times 10 \text{ cm}^2$ surface areas and different thicknesses (0.8–3.3 mm) were obtained. A silicon solar cell with an efficiency of $\sim 12\%$ was at-

Table I Optical Parameters (E_g and E_u) for Pure and Doped PMMA with Different Luminescent Dyes at Different Temperatures and after 1-Year Sunlight Exposure

Optical Parameters and Temps. (K)	PMMA		Lpero		K27		K1	
	Before	After	Before	After	Before	After	Before	After
E_g (eV)								
303	4.1	4.1	4.64	4.6	4.53	4.47	4.35	4.68
323	4.05	4.06	4.62	4.59	4.51	4.45	4.3	4.55
353	4.04	4.05	4.6	4.58	4.5	4.42	4.22	4.4
E_u (eV)								
303	0.19	0.192	1.0	0.7	0.55	0.5	1.5	1.5
323	0.188	0.19	0.95	0.68	0.52	0.48	1.45	1.44
353	0.185	0.19	0.93	0.66	0.51	0.47	1.43	1.42

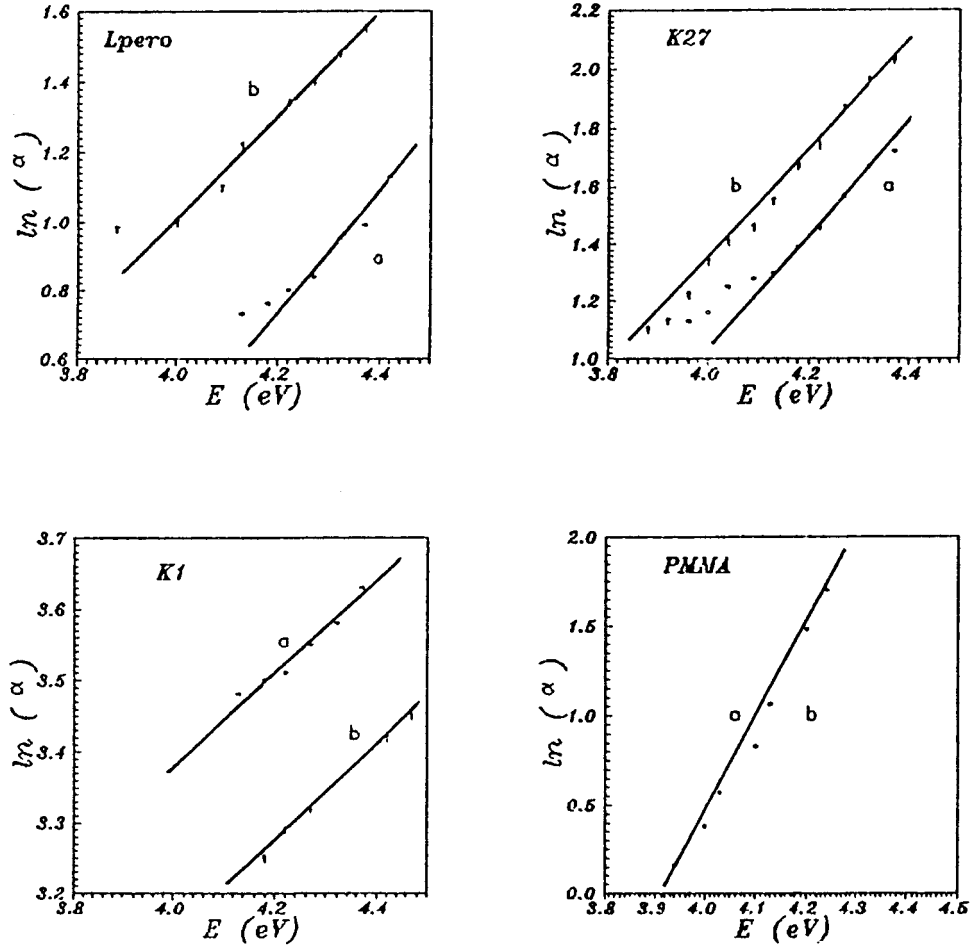


Figure 2 The variation of $\ln \alpha$ versus photon energy (E) for pure and doped PMMA with Lpero, K27, and K1 dyes (a) before and (b) after 1-year daylight exposure.

tached to one side edge of the sheet using silicon oil as a good optical matching. The other side edges were blackened and the lower plate surface, which was not directly exposed to the sunlight, was coated with silver as a good reflective layer. The LSC systems were maintained on a glass box covered with a thin quartz sheet in a horizontal position at about 27 m.

The outdoor and photostability measurements were carried out considering day 22 as a reference day from each month and the average values were taken through each season. Absorption measurements were done by using an Ati Unicam spectrophotometer at different temperatures up to 353 K in the wavelength interval of 200–900 nm.

For dark-thermal and photothermal stimulated current (DTSC, PTSC) experiments the samples were first polarized by heating to a specific poling temperature (T_p) of 323 K. Then an electric field (E_p) of 2×10^6 V/m was applied for

a time (t_p) of 1 h. The sample was then rapidly cooled under the applied field to a lower temperature (room temperature). After removing the field the DTSC (in the dark) and PTSC (sample optically excited with a white light lamp under a 10-V bias) were measured under the short-circuit condition at a constant heating rate (β) of 3 K/min. The current was measured using a Keithly electrometer (type 485).

RESULTS AND DISCUSSION

In thin film materials the absorption coefficient can be expressed by the relation⁸

$$\alpha(h\nu) = 2.3 \log(I_0/I)/d = 2.3A/d \quad (1)$$

where I_0 and I are the intensity of the incident and transmitted light, A is the absorbance, and d

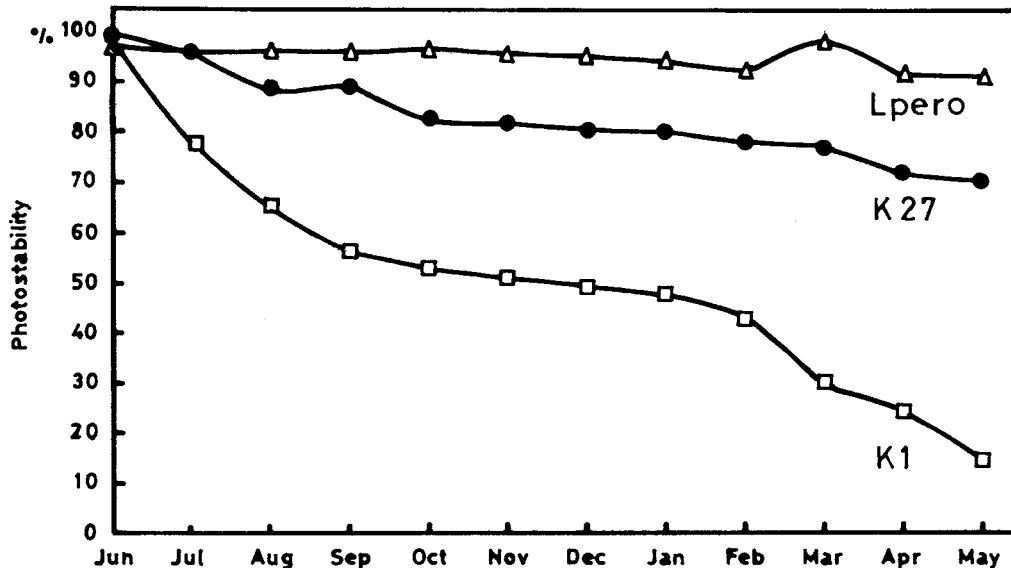


Figure 3 Yearly photostability of PMMA doped with different luminescent dyes.

is the film thickness. In our case, for the bulk samples the problem is somewhat different. We considered two samples with different thicknesses,⁹ so eq. (1) can be modified to

$$\alpha_1(h\nu) = \left[\ln \frac{T_2}{T_1} + \ln \frac{A_1}{A_2} + \Delta\alpha(h\nu)d_2 \right] / \Delta d \quad (2)$$

where $\Delta d = d_1 - d_2$; $\Delta\alpha(h\nu) = \alpha_2(h\nu) - \alpha_1(h\nu)$; and T_1 , T_2 , and α_1 , α_2 are the transmission and the absorption coefficients, respectively, of the samples of thicknesses d_1 and d_2 . Assuming that

$$\ln \frac{T_2}{T_1} \gg \ln \frac{A_1}{A_2} + \Delta\alpha(h\nu)d_2$$

the absorption coefficient of the samples under investigation can be simply written in the form

$$\alpha_1(h\nu) = \ln \frac{T_2}{T_1} / \Delta d = \ln \frac{A_1}{A_2} / \Delta d \quad (3)$$

The UV absorption spectra at room temperature for pure and doped poly(MMA) (PMMA) before and after sun exposure for 1 year was measured in the wavelength range of 200–350 nm. When a quantum of radiation is absorbed by a film material the absorption coefficient α , using eq. (3), as a function of photon energy $h\nu$ for a simple parabolic band can be expressed as^{10,11}

$$\alpha E \sim (E - E_g)^n \quad (4)$$

where n depends on the transition type and E_g is the optical gap. Figure 1 shows the dependence of $(\alpha E)^2$ versus the photon energy (E). The relation has a linear behavior that can be considered as evidence of the direct transition (i.e., for $n = \frac{1}{2}$).^{12,13} The approximate value of the bandgap energy can be determined from the extrapolation of the straight line part to zero photon energy. The values of E_g obtained for the samples under investigation are listed in Table I. These values indicate that there is no significant variation in the bandgap near the absorption edge for Lpero and K27 samples upon exposure to sunlight. From the above observation one can consider that PMMA is a good matrix for the dyes under investigation and could act as an inert medium.

On the other hand, the absorption spectra show an extending tail for lower photon energies below the bandedge, which can be described by Urbach's formula,^{14–16}

$$\alpha(h\nu) = \alpha_0(h\nu)\exp(E/E_u) \quad (5)$$

corresponding to the transition from the localized state in the valance-band tail, which forms because of the extrinsic origins arising from defects or impurities, to extended states in the conduction band. The Urbach energy (E_u) values, which were calculated as the reciprocal gradient of the

obtained straight line, from the relation between $\ln \alpha$ versus the photon energy (E) (Fig. 2) are listed in Table I. An equal and/or small value difference of the localized band tail width before and after sun ray exposure were obtained for pure PMMA. On doping the polymer with different dyes, the band tail width varied to an intermediate value for the Lpero and K27 dyes and a high value for the K1 type.

The dependence of $(\alpha E)^2$ and/or $\ln \alpha$ on the photon energy for the samples at temperatures ranging from room temperature to 353 K were studied, and the corresponding bandgap (E_g) and Urbach's energy (E_u) were calculated and recorded in Table I. These data show that there was no major thermal effect on both the E_g and E_u , except in the case of the polymer matrix doped with the K1 dye. The values of E_g and E_u for the polymer-dye structure were found to be higher than those for the pure PMMA. This may be attributed to the nature of the dye structure.

The photodegradation studies for Lpero, K27, and K1 dye-doped PMMA through 1-year exposure to daylight are illustrated in Figure 3. It is clear that the photodegradation rates of the different samples are increased from the lower rate degradation (9%) for the Lpero dye system, passing through the K27 samples (30%), and finally to a large degradation rate value for the K1 system (70%).

The UV spectra in the range of 400–600 nm at different temperatures for the samples under investigations are indicated in Figure 4. The variations of the maximum absorption coefficient α_m as a function of temperature up to 353 K are shown in Figure 5 for Lpero and K27 dye-doped samples.

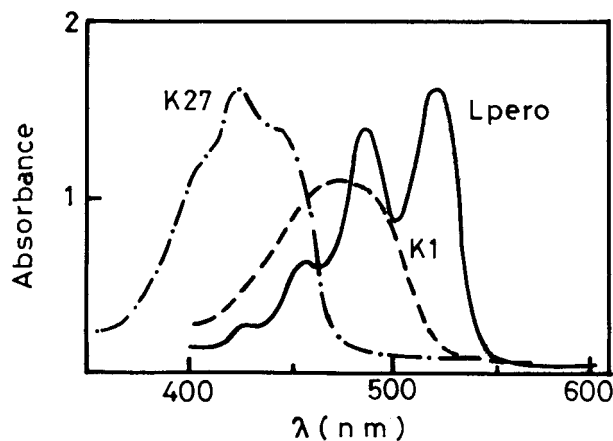


Figure 4 UV-vis absorption spectra for doped PMMA with K27, K1, and Lpero dyes.

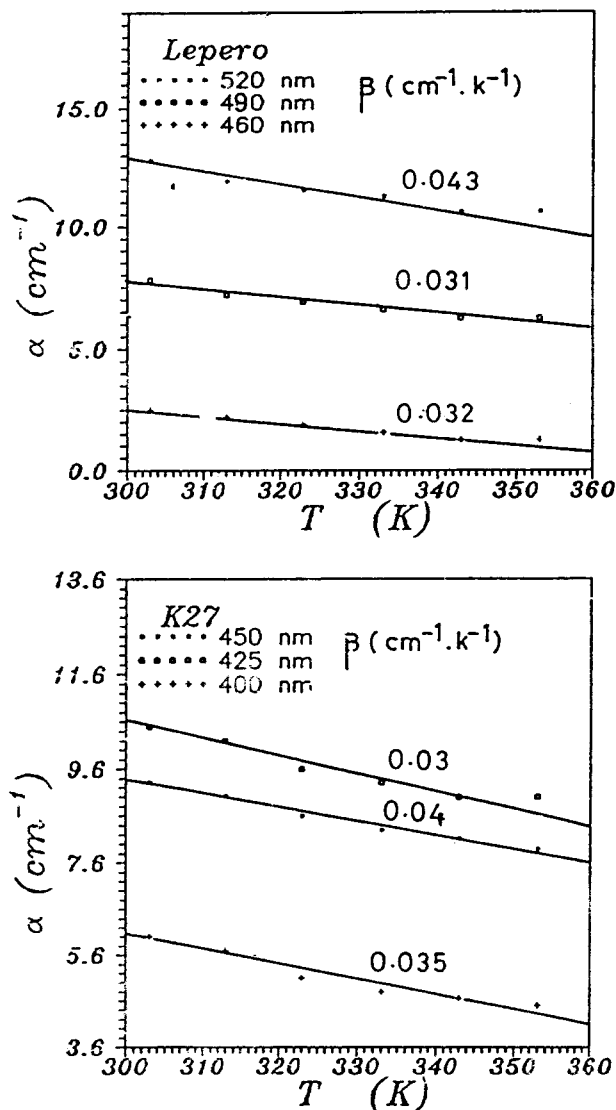


Figure 5 The temperature dependence of the maximum absorption coefficient for Lpero and K27 luminescent dyes.

A linear behavior was obtained that obeys the relation

$$\alpha_m(T) = \alpha_m(o) - \beta T \quad (6)$$

where $\alpha_m(o)$ is a constant representing the maximum absorption coefficient at a constant wavelength at 0 K and β ($\text{cm}^{-1} \text{K}^{-1}$) is the slope of the straight line, depending on the material under investigation, and can be taken as a measure of the thermal degradation of the dye in the polymeric matrix. The values of β obtained for the Lpero and K27 samples are illustrated in Figure 5.

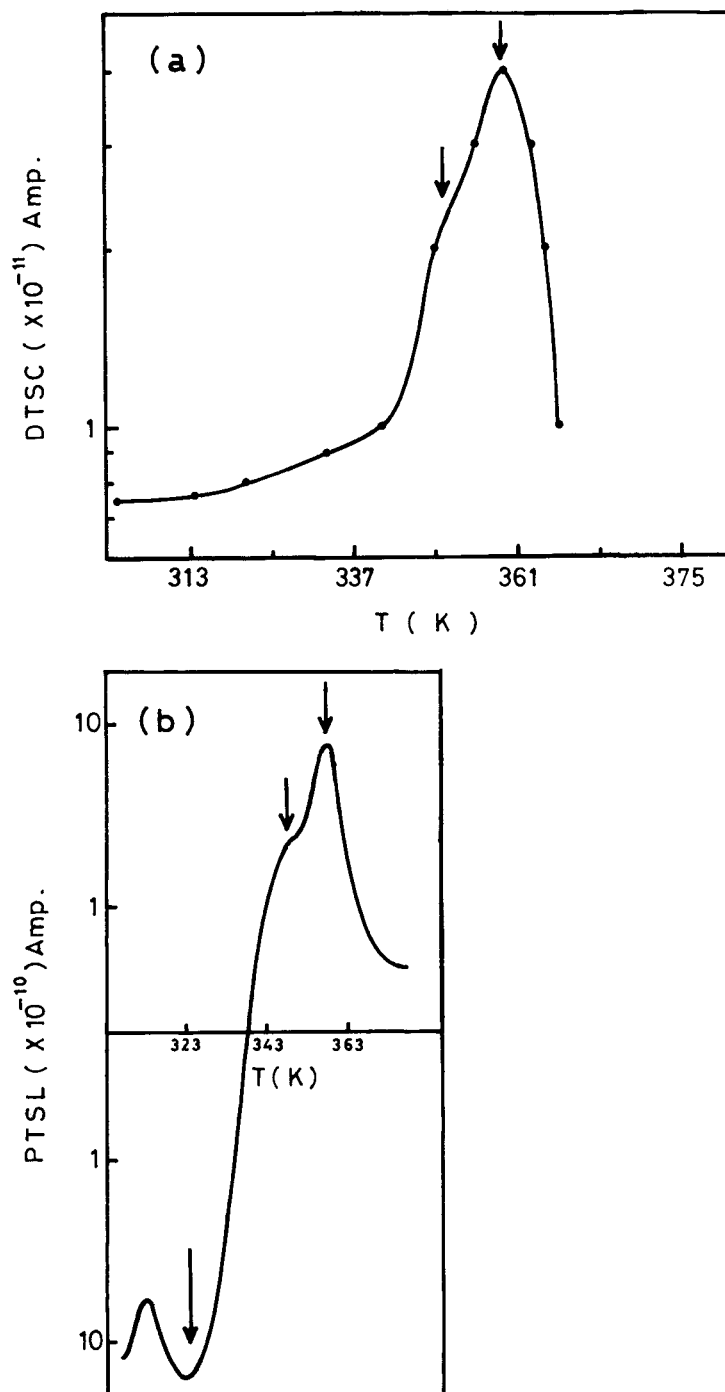


Figure 6 (a) Dark-thermal and (b) photothermal stimulated current spectra for PMMA doped with Lpero dye.

From the above discussion we conclude that the Lpero dye concentrator system has a higher stability for both photo- and thermal excitation (i.e., losses in the activity are very small).

More studies were done to investigate the nature of the transition mechanism as a result of

doping PMMA with the luminescent dyes. The appearance of a number of a very fine structures in the spectrum for the Lpero dye system and their overlapping and broadening for the K27 and K1, respectively, were observed as shown in Figure 4. It is clear that the spectra of the Lpero and

K27 dyes consist of a series of nearly equidistant narrow peaks near the bandedge of the fundamental absorption. The energy interval between these lines corresponds to ~ 0.14 and 0.17 eV for Lpero and K27 doped samples, respectively. These energies cannot be considered as lattice phonons, but they may be due to the localized modes associated with the impurity centers.

The global DTSC and PTSC spectra for PMMA doped with Lpero dye are shown in Figure 6. For the dark measurement a broad band was observed [Fig. 6(a)], which was composed of two overlapping peaks. A permanent and intense peak was observed at a temperature of 353 K, which can be attributed to the superposition of the segmental motion of the polymer around its glass transition temperature, T_g ,¹⁷ and/or the local relaxation of the attached side (ester) group to the main polymer chain. The second peak was recorded at a lower temperature of 343 K. This peak represents the possibility of the formation of electron trapping centers that could have originated from the surface state of the polymer, the polymer-dye interfaces, molecular disorder, and impurities in the material.¹⁸

On the other hand Figure 6(b) shows the PTSC glow curve under the same conditions as in Figure 6(a). Two peaks, which are similar to that obtained in the dark one, can be identified at nearly the same temperature positions. This implies that the origins of these peaks are the same for both dark and photomeasurements. At the low temperature region we can observe the appearance of a new negative thermally stimulated current minimum located at 323 K. This negative current can be attributed to the hole-trap process,¹⁹ which is only produced by optical illumination.

The activation energies for both dark-thermal and photothermal currents, corresponding to electron and hole traps, can be evaluated by using the initial rise method.²⁰⁻²² By this analysis, we deduced two different traps originating by illumination: the electron-trap center with 1.0 eV below the conduction band and the hole-trap level with 0.47 eV above the valence band.

An outdoor test on the LSC of the Lpero dyed PMMA over 1 year under daylight illumination was carried out. These data can be replotted in the form of the relation between the average optical efficiency values versus the year seasons at different daylight times as shown in Figure 7. Observe that the output efficiencies of the LSC systems are generally lowered at sunrise

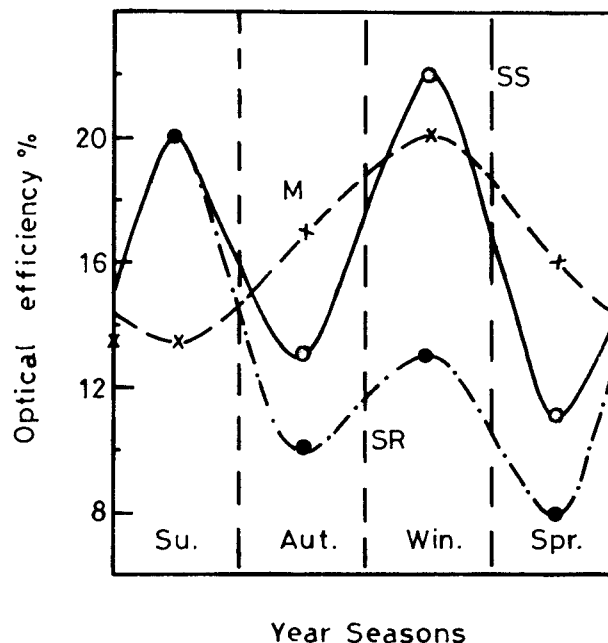


Figure 7 The average optical efficiency as a function of year seasons for PMMA/Lpero concentrator system (SR, sunrise; M, midday; SS, sunset).

for the autumn, winter, and spring seasons. The higher efficiency values are for the summer. The decrease in efficiency in autumn and spring can be attributed to the humidity, dust, wind, and clouds that scatter solar radiation.⁶ For both midday and sunset times the resulting optical efficiency of the solar collector system at all seasons increased and attained its maximum value in summer and winter by about 80%, which may be due to the concentrator operation itself.

CONCLUSION

From this study we can conclude that the efficiency of some solar cells that do not need high technological preparation and that are cheap in price can be improved by using some type of concentrator doped with different luminescent dyes with specific properties. This was proven, especially in the cold seasons. This phenomena happened when we chose the polymer matrix as a concentrator with a large bandgap compared to the absorption edges of the selected dyes. Adding these dyes (with low concentration) introduced energy levels in the concentrator bandgap that produced electron-hole pairs (exciton-like state) followed by the annihilation process through a set

of equidistant energy levels that accordingly produced sets of very specific wavelengths. In other words, an advantage of this type of concentrator is the possibility of concentrating the diffuse radiation and division of the incoming solar spectrum into different wavelength fractions. Each part can be converted by solar cells optimized for a narrow photon energy range. Surprisingly, the results of the outdoor efficiency measurements showed a remarkable increase in the winter season, especially in the morning and evening periods.

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