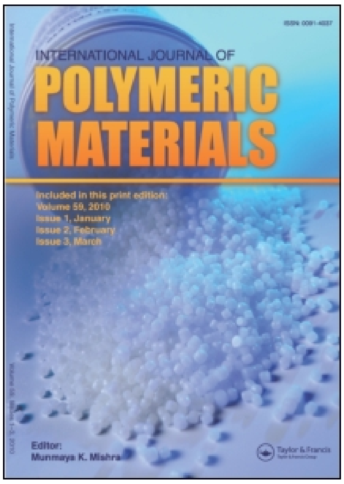

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CHARACTERIZATION OF POLYMER FILMS FOR FLUORESCENT SOLAR-CONCENTRATOR APPLICATIONS

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Films for fluorescent solar concentrators applications were prepared by doping different organic dyes in PMMA. The products were characterized spectroscopically using FTIR. The optical energy gap and the band tail width were calculated. A simple but effective method is used to determine the optical constants (n and k) for the films from combination of transmission and specular reflection in a wide range of wavelengths (200–2400 nm). The results of these measurements show that the value of the refractive index increases with dye concentration in the PMMA. Also, three films of Rh-6G/PMMA, perylene/PMMA, and K1/PMMA were prepared with the same optical density and the optical constants of these films were determined.

Keywords: poly(methyl methacrylate), rhodamine 6G, perylene, fluorescent solar collectors

INTRODUCTION

The possibility of collecting diffuse radiation [1] and the division of the incoming solar spectrum into different wavelength fractions can be done by fluorescent solar concentrators (FSCs) and thus reducing considerably the cost of solar electric energy [2–4]. (FSCs) convert the absorbed radiation of the sun by the organic fluorescent dyes to fluorescence radiation, which is trapped inside the collector and

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guided to the edges of the plate where it can be converted, for example, to heat or electricity by thermal absorbers or photovoltaic cells (solar cells) [5]. Various substrate materials have been studied including poly(methyl methacrylate) (PMMA) as an FSC basic matrix. This material is a transparent amorphous polymer with high strength, also known as "Plexiglas" or organic glass.

The physical properties of this material have led to its extensive use in outdoor electrical and optical applications [6–7]. These properties are: crystal clarity, lightweight, outstanding weather resistance, formability, and mechanical strength. However, this material has a number of deficiencies, as it is brittle, has high moisture uptake, and causes swelling [8].

The study of the optical constants of material is interesting for many reasons. First, the use of materials in optical applications such as interference filters, optical fibers, and reflective coating requires accurate knowledge of their optical constants over a wide range of wavelengths. Second, the optical properties of all materials may be related to their atomic structure, electronic band structure, and the electrical properties. Thus, the study of optical constants together with their variation with frequency, enables correlation to be made with the band structures derived by other methods. There are some reports [9–11] for the optical constants n and k of rhodamine 6G.

In this article the authors have prepared some films of FSCs. The films are optically transparent and were characterized spectroscopically using FTIR. The optical band–gap value and band tails were determined. The authors decided to undertake refractive index investigation on some FSC samples for two reasons, the first being that a necessary requirement for a FSC system is a large stokes shift, which is known to be a function of the dielectric permittivity (ε^1) and the refractive index (n) of the substrate material [12–13]. The second reason is for the purpose of calculating the optical efficiency of FSC (μ_{opt}) theoretically.

EXPERIMENTAL

Perylene($C_{20}H_{12}$) and Rhodamine 6G ($C_{28}H_{31}$ N_2O_3Cl) were obtained from Sigma, and poly(methyl methacrylate)(PMMA) from Aldrich. K1 from BASF, Germany (K1 is the factory code for a dye developed specifically for fluorescent solar collectors). The samples were prepared by casting method as grains of both PMMA and dyes were dissolved in chloroform. The mixture was poured in a glass container; after the films were dried, they were taken off the glass. The thickness of the samples was in the range of 18 μm – 25 μm.

FTIR Spectra were measured on a Bruker Vector 22 spectrometer in the wave number range 400–4000 cm^{-1}.

TABLE 1 The Wave Number (cm^{-1}) of the Characteristic Groups in PMMA and Dye/PMMA

Groups	PMMA	Rh-6G/PMMA	Perylene/PMMA	K1/PMMA
C=O (ester)	1725	1741.2	1742	1740.7
C−O (ester)	1064.8	1065.7	1065.5	1067.8
C−H (aliphatic)	2995.4	2995.7	2951.4	2953.4
$-C-CH_2-C-$	2841.9	2842.7	2842.8	2845.1
$-C-CH_3$	2950	2951.3	2951.4	2953.5
C−C1	666.7	666.8	666.6	667.5
−N−H	—	3568.4	—	—
C=NH	—	1608.6	—	—
C−H (aromatic)	—	—	3090	—
C=C (aromatic)	—	—	1559.6	—
C=O || O	—	—	—	2365.2

Transmission and reflectance spectra were recorded with an UV-Vis-NIR Spectrometer (UV-3101 pc) Shimadzu.

RESULTS AND DISCUSSION

Structural Characterization

The films were characterized spectroscopically using FTIR. The FTIR spectra of dye/PMMA films were essentially identical to that of the starting PMMA except for new bands associated with the dye doped in PMMA. Table 1 summarizes the peak position of the groups in the PMMA and dye/PMMA. It can be seen that the doped dye is not affected by the doping. This means that no interaction occurs between the polymer and dye, indicating that the PMMA is a good matrix for dyes and acts as an inert medium. The appearance of C−C1 peak indicates that the solvent is not completely evaporated.

Optical Properties

The study of the optical absorption spectra is one of the most productive method in developing and understanding the structure and energy gap of amorphous non-metallic materials. The absorption coefficients $\alpha\ (w)$ show an exponential dependence on photon energy $\hbar w$, and obey Urbach's relation [14].

$$\alpha(w) = \alpha_o \exp\ (\hbar w/E_u).$$

where α_o is a constant, w is the angular frequency of the incident photon, $\hbar$ is Plank's constant and E_u is the band tails width of the localized states in the band gap. In general it represents the degree of disorder in an amorphous semiconductor [15].

The optical absorption of the solvent cast Perylene/PMMA, Rh-6G/PMMA and K_1/PMMA samples of the same optical density have been studied. The values of the absorption coefficient (α) have been estimated. Figure 1 shows the dependence of Lnα on photon energy E for the samples.

In high absorption region, $\alpha(w)$ was discussed in terms of Davis and Mott [16].

$$\alpha(\mathrm{w}) = \mathrm{B}(\hbar\mathrm{w} - \mathrm{Eg})^{\mathrm{n}}/\hbar\mathrm{w}$$

where B is a constant, n is an index depending on the nature of the electronic transitions, and E_g is the optical band gap of the material. Figure 1 shows the dependence of $(\alpha E)^2$ on photon energy E that shows a linear behavior that can be considered as evidence of the direct transition (i.e., for $n = 1/2$) [17]. The optical gap was determined by extrapolating [18] the linear parts of the curves to $(\alpha E)^2 = 0$. From Figure 1 the value of E_g are 4.24, 4.17, and 3.95 ev for k1, perylene, and Rh-6G doped PMMA, respectively.

Table 2 summarizes the optical parameters (E_g and E_u) of three concentrations for Rh-6G and perylene doped PMMA. Table 2 shows that with increasing concentration of the doped dye, the value of E_g decreased and E_u increased. The increase in E_u with doping due to the effect of internal potential fluctuation associated with the structural disorder.

It is noticed that the dependence of E_g on the sample preparation does not match with E_u values because the sample having a narrower band gap is expected to have a wider band tail. The change in E_u is probably affected by potential fluctuations associated with the polymer structure but not the change in E_g because the initial and final states are practically the same potential.

Optical Constants

The variation with wavelength of the optical bulk absorption coefficient (α) of a medium is a unique parameter of the medium. As such, it provides the most valuable optical information available for material identification. The quantity α is related to the specular transmittance T through Lambert's law:

$$T = exp(-\alpha t)$$

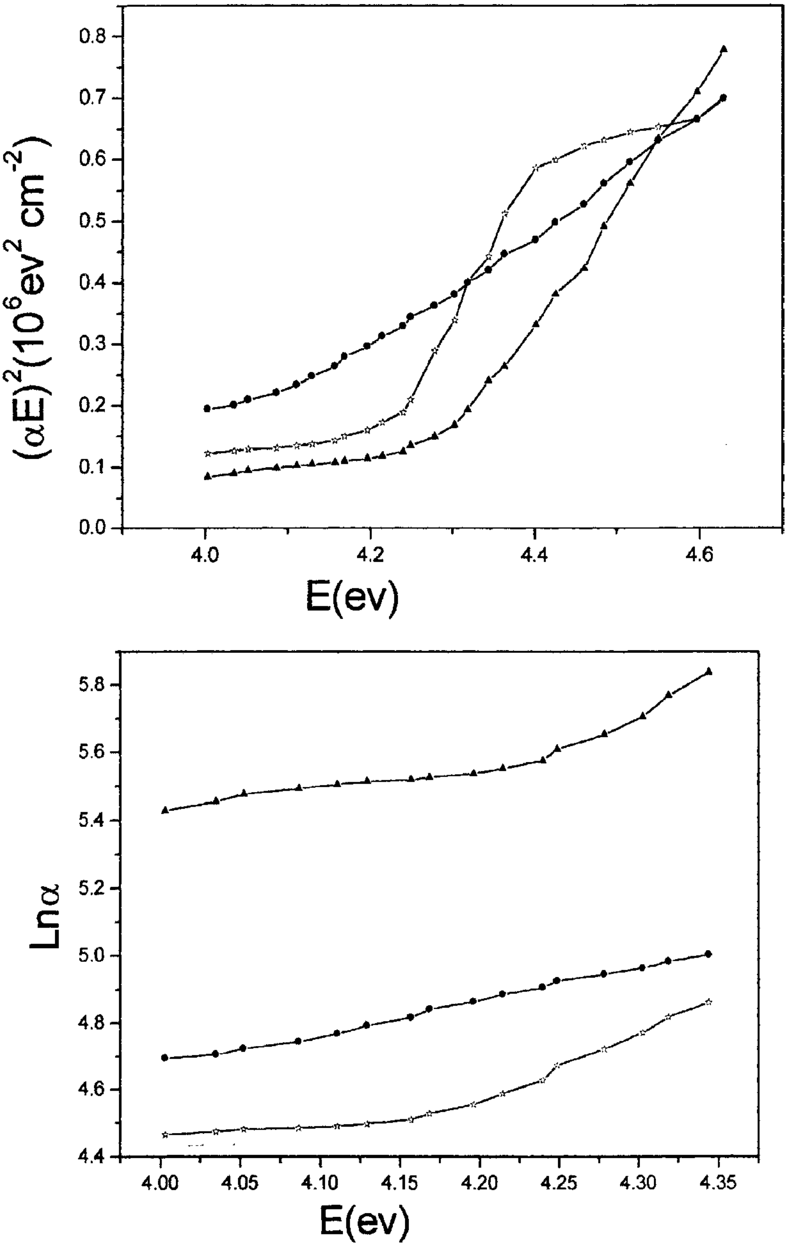

FIGURE 1 The dependence of $(\alpha E)^2$ and Lnα on photon energy E for (Δ) K1/PMMA, ($*$) perylene/PMMA and (o) Rh-6G/PMMA with the same optical density.

TABLE 2 The Optical Parameters (E_g and E_u) for Pure PMMA, Rh-6G/PMMA, and Perylene/PMMA of Three Concentrations

	PMMA		Perylene/PMMA		Rh-6G/PMMA	
Dye/PMMA Wt%	E_g	E_u	E_g	E_u	E_g	E_u
0	4.22	0.38	—	—	—	—
0.16	—	—	4.2	0.43	4.03	0.90
0.33	—	—	4.18	0.48	3.97	0.92
0.5	—	—	4.14	0.51	3.93	0.95

where t is the thickness of the medium. The absorption coefficient (α) is related to extinction coefficient (K) by the relation

$$\alpha = 4\pi K/\lambda$$

where λ is the wavelength in vacuum.

Reflectance (R) and transmition (T) data are basic to study the optical behavior of any material. So, the measured specular reflectance and transmittance are utilized to calculate the optical constants (the refractive index, n, and extinction coefficient, K).

The reflectance of an absorbing surface in air for normal incidence is given by [19].

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2}$$

The refractive index n(λ) and the absorption index k(λ) [attenuation coefficient] have been calculated from the combination of transmission and reflectance. Figures 2 and 3 show the spectral distributions of n and k for different concentrations of Rh-6G/PMMA ($S_0 \rightarrow S_1$ absorption peak of Rh-6G at 535 nm) and perylene/PMMA ($S_0 \rightarrow S_1$ absorption peak of perylene at 415 nm), respectively. These figures reveal the trend of higher index with dye concentration. This is consistent with the increase in density with increasing dye concentration, as well as increasing polarizability. This is indicated by the Lorentz–Lorenz equation

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3}\pi N\alpha$$

As indicated, the refractive index of materials depends on the linear polarizability (α) and the number density of molecules (N). Three

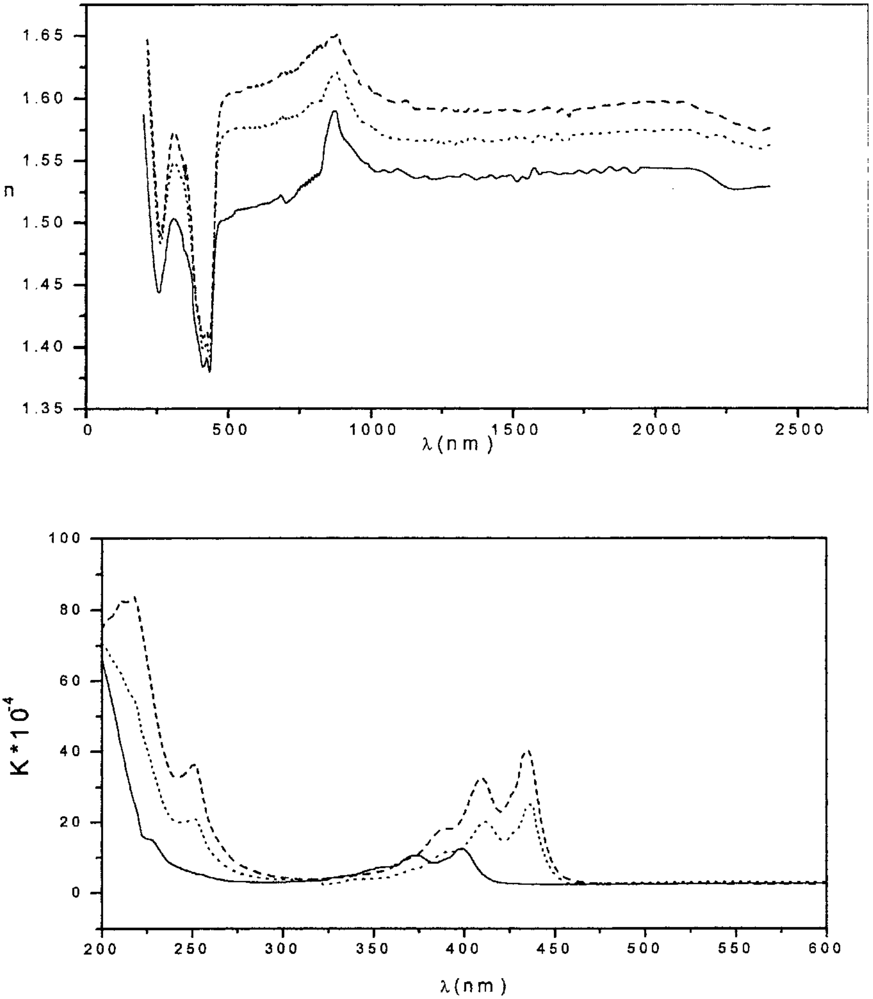

FIGURE 2 The refractive index n and absorption index k of perylene/PMMA (–) 0.16, (…) 0.33, and (–) 0.5 wt%.

samples, Rh-6G/PMMA, perylene/PMMA, and K_1/PMMA, were prepared by the casting method and had the same optical density. The refractive index and absorption index were calculated from specular reflection and transmition at the same range of wavelengths. Figure 4 shows that the refractive index of Rh-6G/PMMA is greater than perylene/PMMA, which is greater than K1/PMMA. It is noted that the refractive index increases as the band gap decreases.

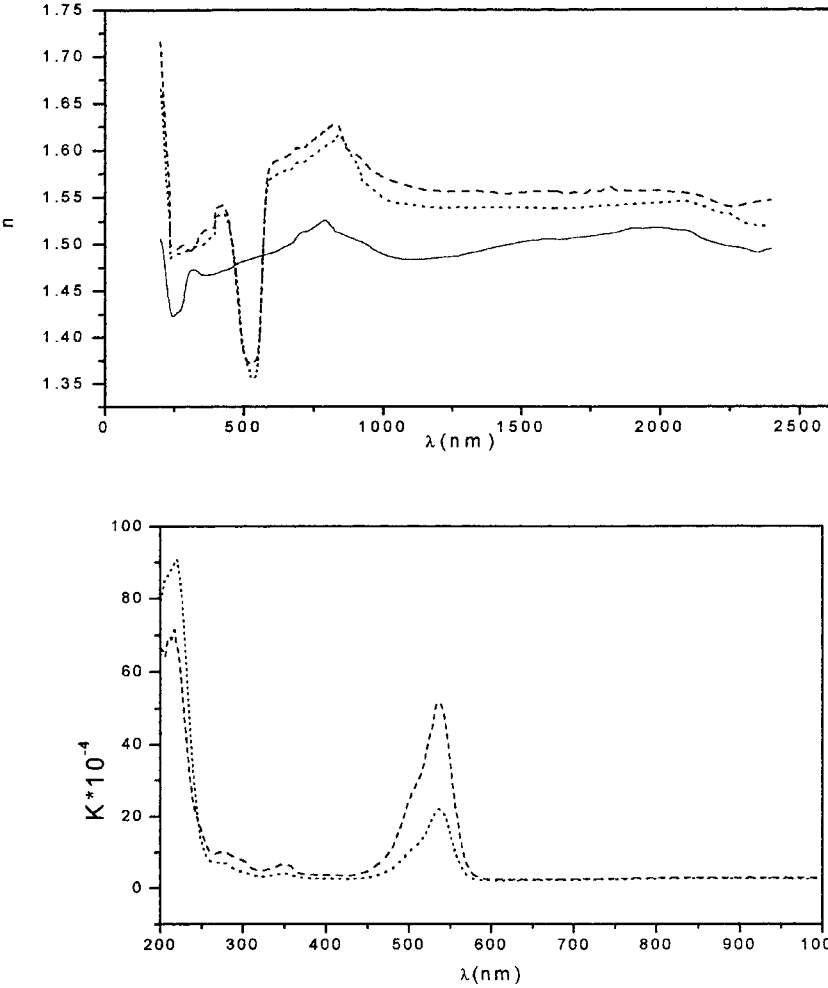

FIGURE 3 The refractive index (n) and absorption index (k) of Rh-6G/PPMA (– –) 0.5, (. . .) 0.16 wt%, and (–) PMMA.

From the prior discussion it can be inferred that the increase in concentration of the dye (Rh-6G and perylene) doped in PMMA matrix, leads to increasing the refractive index of the matrix material, which increases the loss of sunlight due to surface reflections, but it also increases the fraction of fluorescence light that is trapped by total internal reflection [20]. The refractive index of FSC can be controlled to obtain the optimum condition for high optical efficiency (η_{opt}).

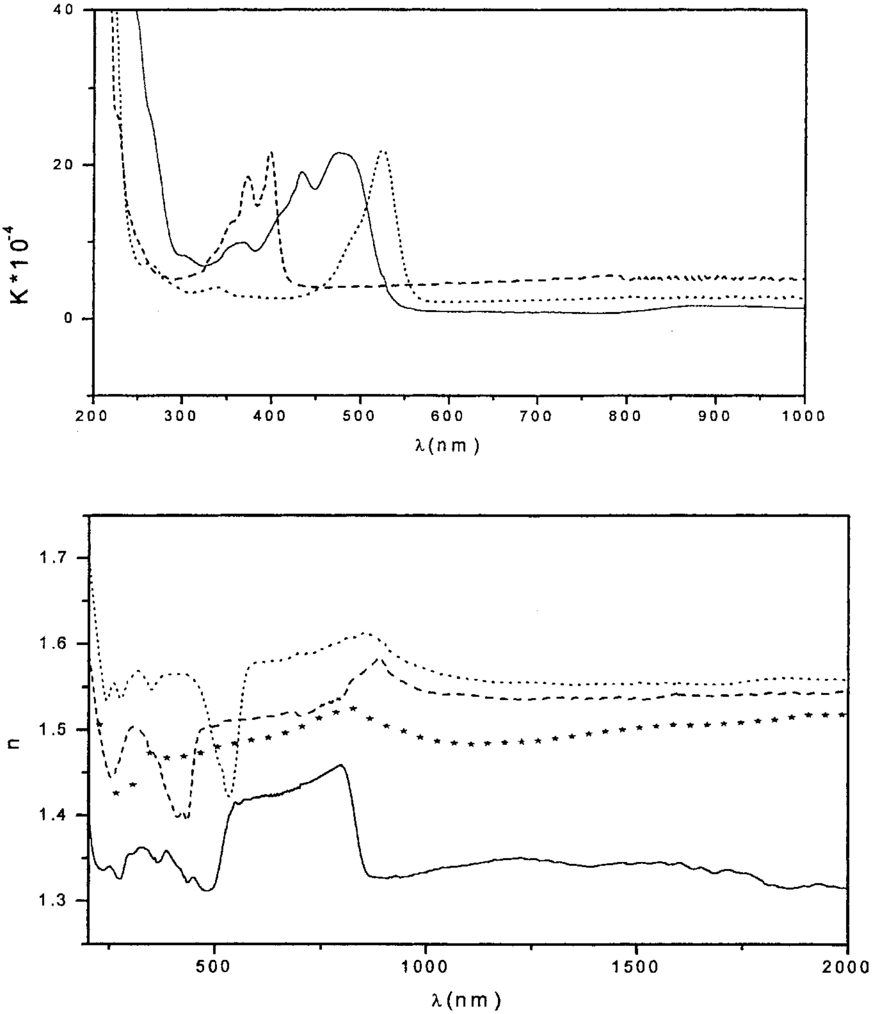

FIGURE 4 The refractive index (n) and absorption index (k) of (...) Rh-6G/PMMA, (——) perylene/PMMA, (–)K1/PMMA of the same optical density and (∗) pure PMMA.

CONCLUSION

Several films for fluorescent solar concentrators applications were prepared by doping different organic dyes in PMMA. The products were characterized spectroscopically using FTIR. The FTIR spectra of different dye/PMMA are identical to that of pure PMMA except for the new bands corresponding to each dye. The optical energy gap and the band tail width were calculated. The band gap reduced with the concentration of dye doped in PMMA.

A simple but effective method is used to determine the optical constants (refractive index n and absorption index K) for the films from combination of transmission and specular reflection in a wide range of wavelengths (200–2400 nm). The results of these measurements show that the value of the refractive index increases with dye concentration in PMMA. Three films of Rh-6G/PMMA, perylene/PMMA, and K1/PMMA were prepared with the same optical density n and k were calculated. The results show that the refractive index is higher for Rh-6G/PMMA than that for perylene/PMMA, which is higher than that of K1/PMMA. It is noted that the refractive index increases as the band gap decreases. From the prior discussion, the refractive index of FSC can be controlled to obtain the optimum condition for high optical efficiency (η_{opt}).

REFERENCES

[1] Goetzberger, A., Heidler, K., Wittwer, V., Zastrow, A., Baur, G., and Sah, E. (1979). 2nd Photovoltaic Solar Energy Conf., Berlin, pp. 515.

[2] Weber, W. H. and Lamb, J. L., *J. Appl. Opt.*, **15**, 2299 (1976).

[3] Swartz, B. A., Zewail, A. H., and Cole, T., *Opt. Lett.*, **31**, 4 (1977).

[4] Goetzberger, A. and Greubel, W., *Appl. Phys.*, **14**, 123 (1977).

[5] Zastrow, A. *SPIE*, 2255 (1994).

[6] Bistac, S. and Schultz, J., *J. Int. Adhesion and Adhesives* **17**, 197 (1997).

[7] Pakhamov, P. M., Kropotova, E. D., Zubkov, A. J., Levin, M., and Chegolya, A. S., *Vyskomolekularynye Soedineniya Serya A.* **34**, 139 (1992).

[8] Khanarian, G. *Opt. Eng.*, **40**(6) 1024 (June 2001).

[9] Leupacher, W. and Penzkofer, A., *Appl. Opt.*, **23**(10), 1554 (1984).

[10] Yutian, Lu. and Penzkofer, A., *Appl. Opt.*, **25**(2), 221 (1986).

[11] Siqueiros, J. M., Regalado, Luis, E., and Machorro, R., *Appl. Opt.*, **27**(20), 4260 (1988).

[12] Kondepudi, R. and Srinivasan, S., *Solar Energy Material* **20**, 257 (1990).

[13] Kondepudi, R. and Srinivasan, S., *Indian Pure Appl Phys.*, **30**, 389 (1992).

[14] Urbach, F., *Phys. Rev.*, **92**, 1324 (1953).

[15] Olloy, J. A., *Solid State Commun.*, **13**, 1437 (1973).

[16] Davis, E. A. and Mott, N. F., *Phil. Mag.*, **22**, 903 (1970).

[17] Joseph, C. M. and Menon, C. S., *Semiconductor Sci. Technol.*, **11**, 1668 (1996).

[18] Màrquez, E., Wagner, T., Leal, J. M., Oliva, A. M., Alcòn, R. P., and Garay, R. J. *J. Non-Cryst Solids* **62**, 274 (2000).

[19] Fox, M. (2001). *Optical Properties of Solids* (Oxford University Press Inc., New York), pp. 7–

[20] Batchelder, J. S., Zewail, A. H., and Cole, T., *Applied Optics* **18**, 3090 (1979).