



ELSEVIER

Polymer Testing 18 (1999) 611–619

**POLYMER  
TESTING**

Material Properties

## The optical properties of polymethylmethacrylate polymer dispersed liquid crystals<sup>1</sup>

S.K.J. Al-Ani<sup>a</sup>, Y. Al-Ramadin<sup>a</sup>, M.S. Ahmad<sup>a,\*</sup>, A.M. Zihlif<sup>a</sup>, M. Volpe<sup>b</sup>, M. Malineonico<sup>b</sup>, E. Martuscelli<sup>b</sup>, G. Ragosta<sup>b</sup>

<sup>a</sup>Physics Department, University of Jordan, Amman, Jordan

<sup>b</sup>Institute of Research and Technology of Plastic Materials C.N.R. Arco Felice, Naples, Italy

Received 22 May 1998; accepted 14 July 1998

### Abstract

The effect of the addition of polymer liquid crystals as dispersed molecules to polymethylmethacrylate (PMMA) on the optical properties in the UV-visible and near infrared regions is investigated. From transmission, absorption and reflection spectra the absorption coefficient  $\alpha(\omega)$  and refractive index ( $n$ ) at angular frequency of radiation ( $\omega$ ) have been calculated at room temperature. The values of the optical band gap ( $E_{opt}$ ) have been obtained from the direct allowed transitions in  $k$ -space. The width of the tails of localized states in the band gap ( $\Delta E$ ) was evaluated from Urbach edges. Both the parameters ( $E_{opt}$ ) and ( $\Delta E$ ) vary with the mixing ratio of dispersed liquid crystals. © 1999 Elsevier Science Ltd. All rights reserved.

### 1. Introduction

Recently, a great effort has been made to study the physical characteristics of liquid crystalline polymers (LCP). Some recent reports on LCP are polymethylmethacrylate [1], polyamide [2,3], polyethylene terephthalate [4,5], polycarbonate [6,7], polystyrene [8,9], polyetherimide [10,11] and polysulfone [12]. These polymeric materials have great significance because of their good durability and ability to withstand different environmental conditions, and they have a wide range of applications, especially in industrial and consumer end-products. Because of this, numerous

\* Corresponding author.

<sup>1</sup> This work was supported by the Academic Deanship of Scientific Research of the University of Jordan.

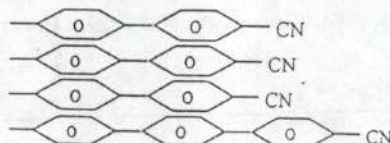
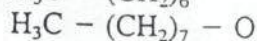
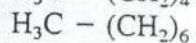
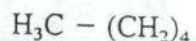
reports have been published on the mechanical, thermal and electrical properties of LCP systems. The most interesting system is a mixture of LCP with isotropic polymers. The interest lies in the utilization of its optical and electrical properties, such as the width of the optical band of the energy gap and the width of the energy tails in the forbidden band gap [13–15].

The present work is concerned with the optical properties of a LCP polymethylmethacrylate system. The present measurements include the transmission, absorption and reflection of electromagnetic wave in the wavelength range 300 up to 2000 nm.

## 2. Experimental

### 2.1. Materials

The samples used in this study are PMMA/liquid crystals E7, which are in the form of a polymer dispersed liquid crystal (PDLC) system. The synthesis of this system was carried out as follows: 10 g of methylmethacrylate (MMA) (used without further purification) and 0.02 g of dibenzoylperoxide (0.2% wt/wt) are prepolymerized at 90°C until the consistency of a low viscosity liquor is obtained. At this point, 4 g of liquid crystals E7 are added, which immediately dissolve in the prepolymer. After a few minutes at 90°C, the liquor is poured into a preheated mold, made up of two mirror-grade glass plates separated by teflon spacers, wrapped with adhesive tape and held together by a spring. The mold is placed in a controlled oven where curing occurs (at 70°C for 24 h plus 2 h at 100°C). At the end of the polymerization, all the samples were transparent independent of the content of E7. The indicative difference is the flexibility of the product, which increases with the amount of E7. The E7 is a liquid crystalline nematic mixture supplied by EM Chemical Co. It is an eutectic mixture of four cyanobiphenyls:



### 2.2. Optical measurements

Specimens of about 1 mm thickness were cut from the prepared PDLC sheets of various LCP concentration (10, 20, 40% by weight). The optical absorbance ( $A$ ), transmittance ( $T$ ) and reflectance ( $R$ ) were taken in at the wavelength range ( $\lambda = 300\text{--}2000$  nm) using Perkin-Elmer  $\lambda$ -9 double beam UV-visible-near infrared spectrophotometer. All measurements were performed at room temperature. The absorption coefficient ( $\alpha$ ) at angular frequency ( $\omega$ ) of radiation was calculated using the formula:

$$\alpha(\omega) = 2.303 \frac{A}{x} \quad (1)$$

where  $x$  is the sample thickness and  $A$  is the optical absorbance. Also,  $\alpha(\omega)$  is related to the optical transmission ( $T$ ) and reflection ( $R$ ) as follows:



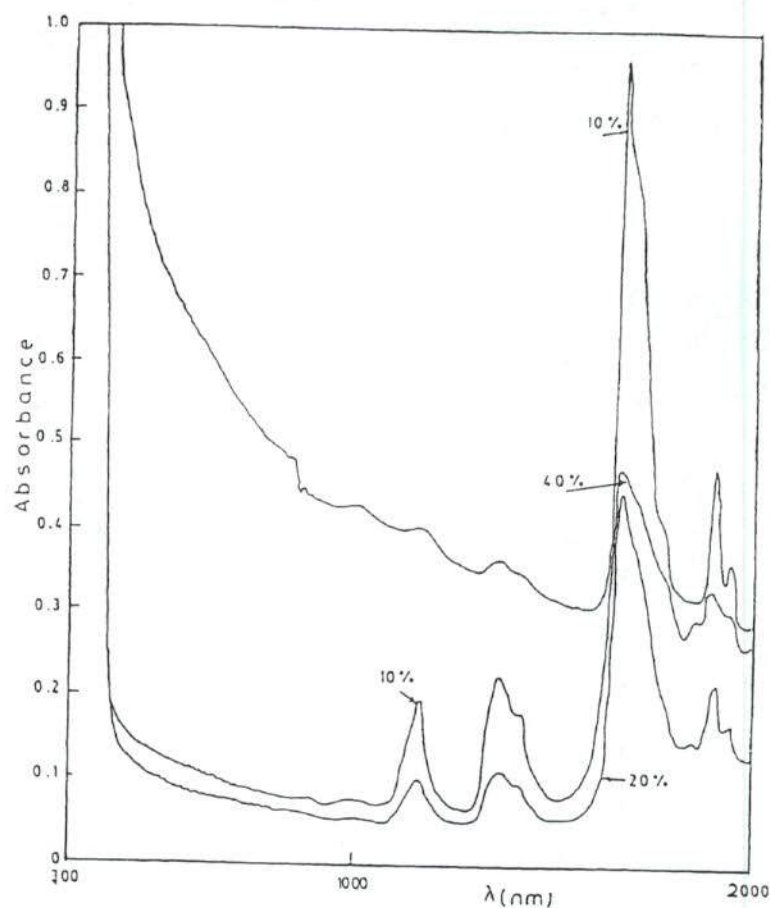


Fig. 1. The optical absorbance spectra of pure PMMA and (10, 20 and 40%) of DLCP system.

$$\alpha(\omega) = \frac{1}{x} \log \left\{ \frac{(1-R)^2}{2T} + \frac{(1-R)^2}{\sqrt{(2T)^2 + R^2}} \right\} \quad (2)$$

and the refractive index was obtained from

$$n = \left\{ \left[ \frac{4R}{(R-1)^2} - k^2 \right]^{1/2} - \frac{R+1}{R-1} \right\} \quad (3)$$

where  $k$  is the extinction coefficient which is related to the absorption coefficient and the wavelength as:

$$k = \frac{\alpha \lambda}{4\pi} \quad (4)$$

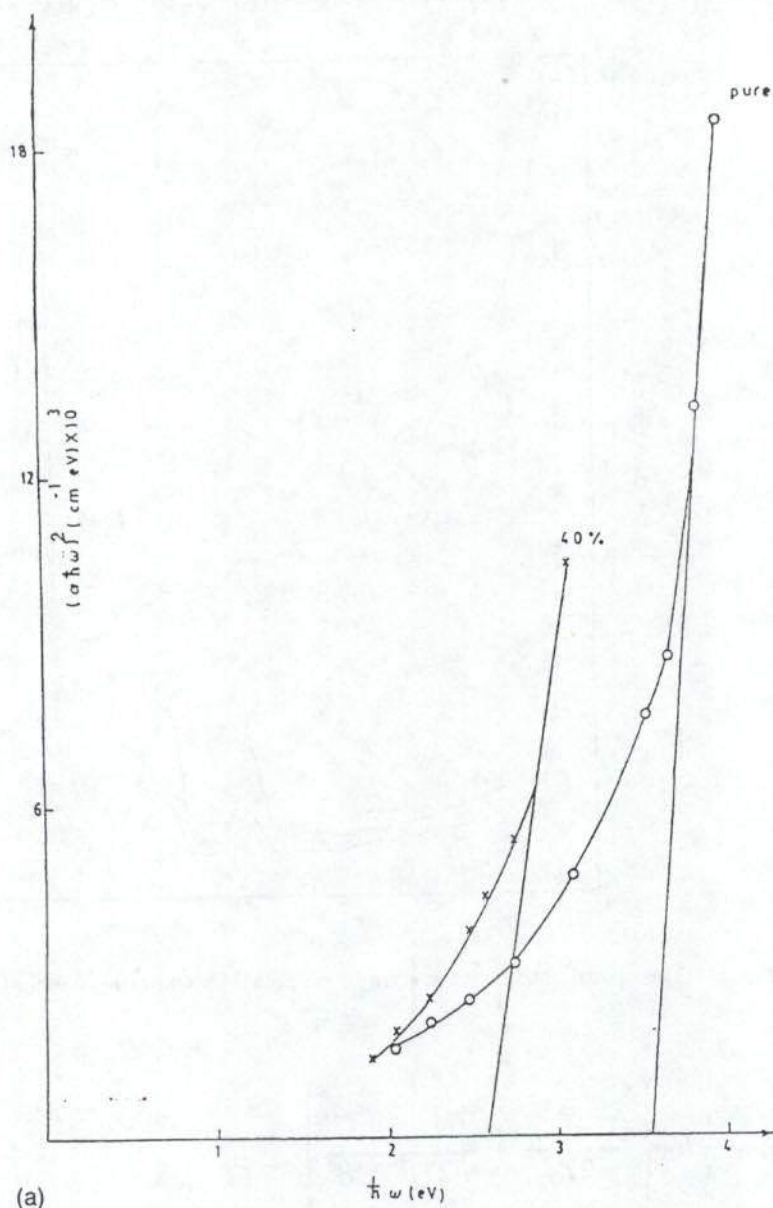


Fig. 2. The function  $(\alpha\hbar\omega)^2$  vs.  $\hbar\omega$  for the data in Fig. 1.

### 3. Results and discussion

Fig. 1 represents the absorbance spectra for pure PMMA, 10, 20 and 40 wt.% specimens of DLCP. At high absorption levels the optical energy gap  $E_{opt}$  of the system can be calculated using a relation given elsewhere [13-16]:

$$\alpha(\omega)\hbar\omega = B(\hbar\omega - E_{opt})^r \quad (5a)$$

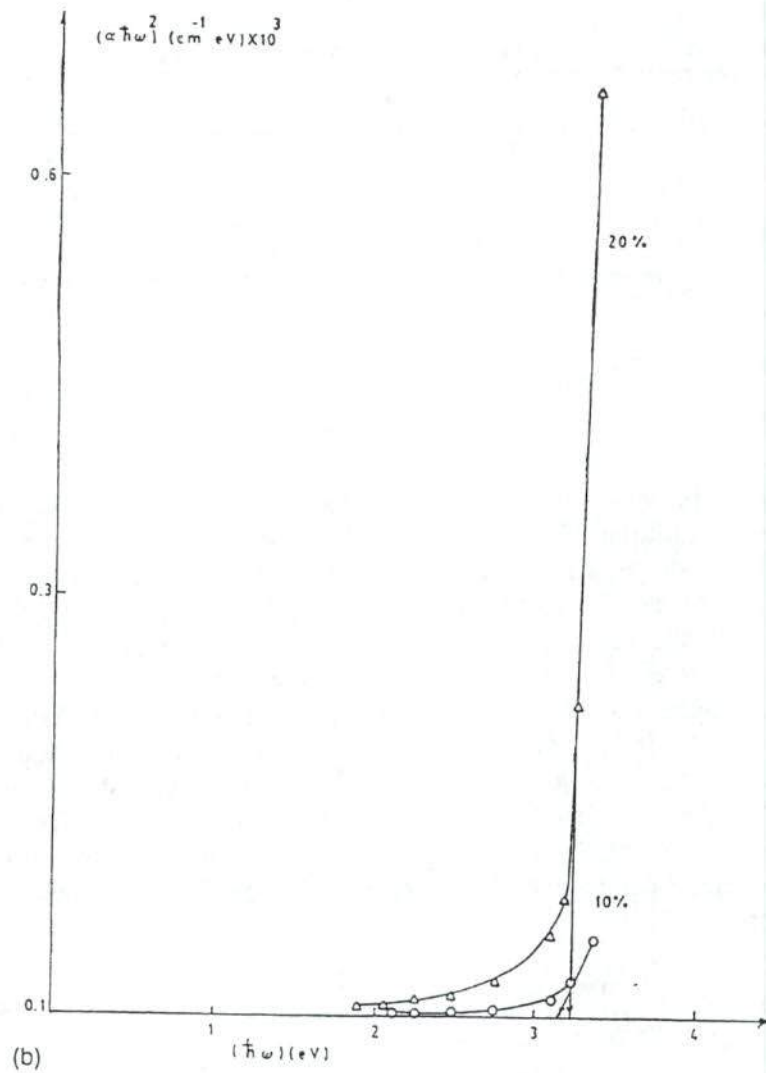


Fig. 2. Continued

$$n(\omega)\hbar\omega = B(\hbar\omega - E_{\text{opt}})^r \quad (5b)$$

where  $\hbar\omega$  is the incident photon energy,  $B$  is a constant and  $r$  is an exponent which can take values of 1, 2, 3,  $\frac{1}{2}$ ,  $\frac{3}{2}$ , depending on the nature of the electronic transitions responsible for the optical absorption. The best value of ( $r$ ) can be determined from the slope of the linear part of  $(\alpha\hbar\omega)^{1/r}$  versus  $\hbar\omega$ . When  $r$  equals  $\frac{1}{2}$ , 2, and  $\frac{3}{2}$  indicates allowed direct, allowed indirect and forbidden direct transition, respectively [17,18].

Fig. 2 shows the variation of  $(\alpha\hbar\omega)^{1/r}$  versus  $(\hbar\omega)$  in accordance with the equations. The values



Table 1

The optical parameters of polymethylmethacrylate dispersed liquid crystals

LCP (wt%)	$E_{\text{opt}}$ (eV) <sup>a</sup>	$E_{\text{opt}}$ (eV) <sup>b</sup>	$E_{\text{opt}}$ (eV) <sup>c</sup>	$\Delta E$ (eV)	$B$ (cm <sup>-1</sup> eV <sup>1/2</sup> )
0	3.55	—	—	0.7	155
10	3.15	3.08	3.1	0.2	50
20	3.20	3.08	3.38	0.2	65
40	2.58	2.10	2.15	1.5	98

<sup>a</sup>Using Eq. (1).<sup>b</sup>Using Eq. (2).<sup>c</sup>Using Eq. (2) and  $n = 2.02$ .

of energy gaps presented in Table 1 are determined by extrapolating the linear portion of these lines to zero absorption. The best straight line may be obtained when  $r = \frac{1}{2}$  for all examined specimens. This suggests that the transition energy for electrons may account for direct allowed transitions in  $k$ -space. Similar results were reported recently on some amorphous composites [17-21]. Non-direct transitions were observed in studying the optical properties of an epoxy glass microball composite [15] for ( $r = 2$ ), while direct transition ( $r = 1$ ) was assumed in the case of glass-fiber polyester composite [21] and PEO/salts polymer membranes [22].

The constant ( $B$ ) in Eq. (5a) and (5b) was determined from the slope of the linear part of Fig. 2. The unit may be given as cm<sup>-1</sup> eV<sup>(1 -  $r$ )</sup> [16]. The values of ( $B$ ) and ( $E_{\text{opt}}$ ) were obtained by using Eqs. (1) and (2) for  $n = 2.02$  and are listed in Table 1. Those values show a relative decrease of behavior while increasing the LCP content. Previous work on many system shows that an exponential dependence of the absorption coefficient on the photon energy ( $\hbar\omega$ ) follows the Urbach rule [23]

$$\alpha(\omega) = \alpha_0 \exp\left(\frac{\hbar\omega}{\Delta E}\right)$$

where  $\alpha_0$  is a constant and ( $\Delta E$ ) is the energy width of the tail of the localized state in the normally forbidden band gap.

Fig. 3 presents the Urbach [23] plot of ( $\ln\alpha$ ) versus ( $\hbar\omega$ ). The values of ( $\Delta E$ ) may be estimated from the slope of the linear portions of these curves. The obtained values of ( $\Delta E$ ) for different LCP concentrations are listed in Table 1. The high value of ( $\Delta E$ ) at large LCP content may be attributed to a certain structure occurring in the polymeric system.

Fig. 4 displays the observed reflectance spectra of the four examined samples in the wavelength range 300 to 2000 nm. The reflectance was used to estimate the refractive index ( $n$ ) by using Eq. (3). The calculated values of ( $n$ ) were plotted as a function of the wavelength as shown in Fig. 5. The plot shows that calculated ( $n$ ) decreases while increasing the content of the dispersed liquid crystals in the PMMA polymer. This is expected since the refractive index of E7 is smaller than that of the pure PMMA. However, the calculated values for ( $n$ ) are higher than those obtained by direct optical measurements in the visible region [24], since the formula used in the present work is too empirical.

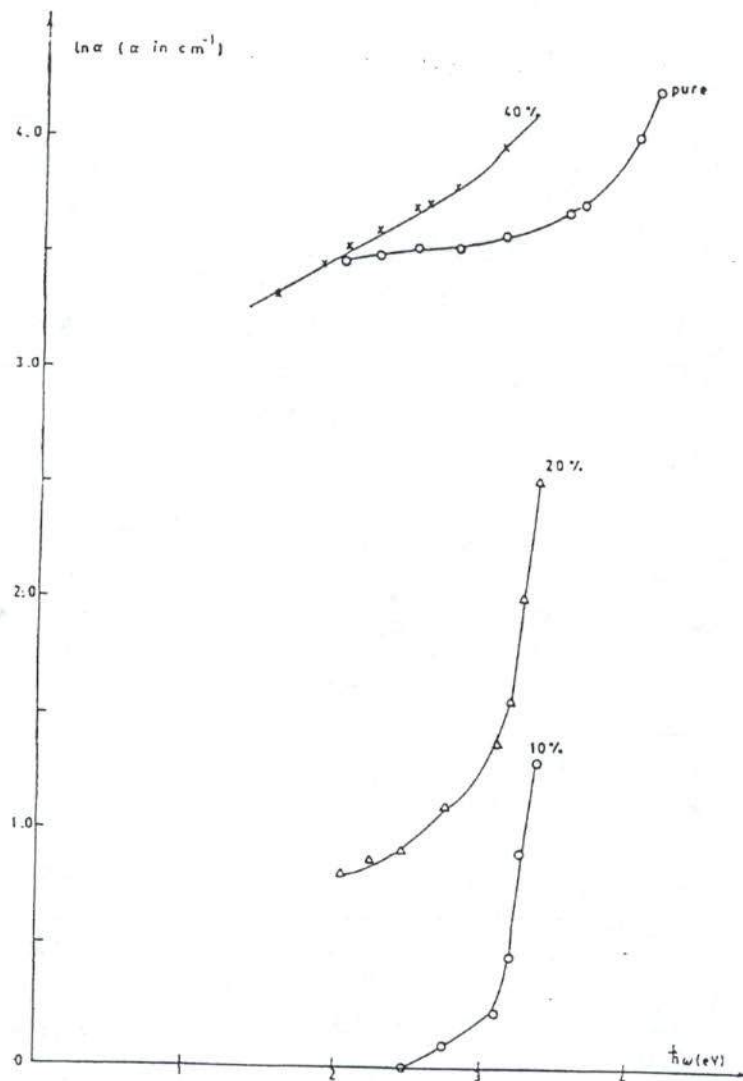


Fig. 3. Urbach plot for the data in Fig. 1.

#### 4. Conclusion

The present work deals with the optical properties of polymer liquid crystals dispersed in polymethylmethacrylate matrix. The results indicate that the refractive index and tail width of the localized states in the band gap vary unsystematically with the filler concentration. However, the determined optical parameters are in good agreement with previously reported results on similar polymer composites.



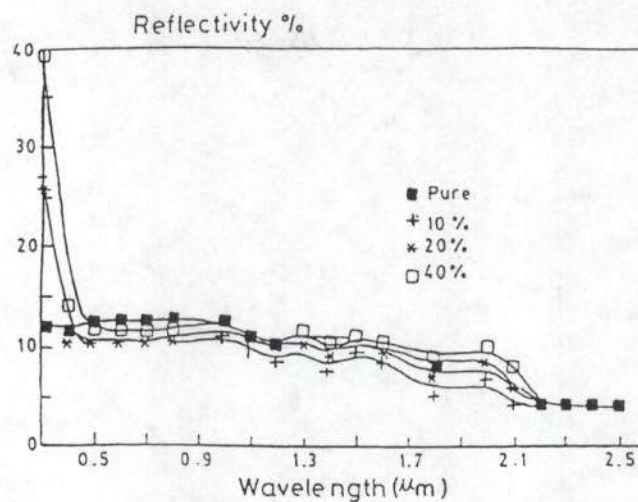


Fig. 4. The reflectance spectra of four samples of LCP in the DLPC system.

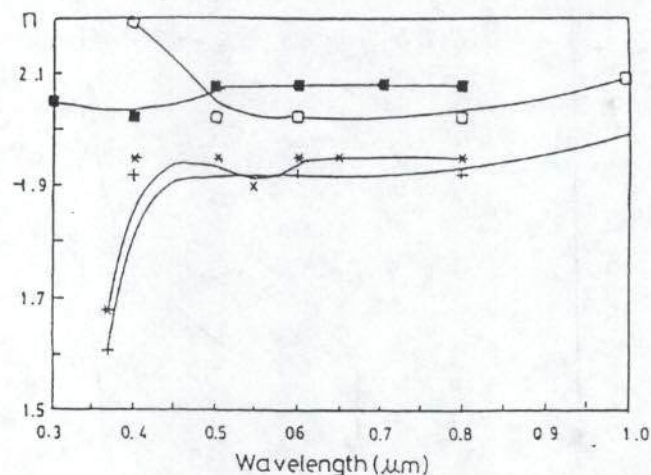


Fig. 5. The values of the refractive index as a function of wavelength for the data in Fig. 4.

### Acknowledgements

Professor A.M. Zihlif is very grateful to the International Center for Theoretical Physics (ICTP) for cooperation and support.

### References

- [1] Miyamoto A, Kikuchi H, Kabayashi S, Morimura Y, Kajiyama T. *Macromolecules* 1991;24:391.
- [2] Siegmann A, Dagan S, Kering S. *Polymer* 1985;26:1325.
- [3] Shin BY, Chung IJ. *Polym Engng Sci* 1990;30:22.
- [4] Seppala J, Heino M, Kapanen CJ. *Appl Polym Sci* 1992;44:105.



- [5] Dutta A, Chen HH, Baird DG. *Polymer* 1993;34:532.
- [6] Dutta D, Weiss RA, Kristal K. *Polymer* 1992;13:394.
- [7] Berry D, Kening S, Siegmans A. *Polym Engng Sci* 1991;31:459.
- [8] Bassett BR, Yee AF. *Polym Compos* 1990;11:10.
- [9] Ogata N, Tanaka T, Oghara T, Koshids K, Kondov Y, Hayashi K. *Polym Sci* 1993;484:383.
- [10] Sun T, Baird D, Hurg H, Done D, Wilkes GL. *J Compos Mater* 1991;25:788.
- [11] Carfagna G, Amendola F, Nicolais L, Acierno D, Francescangel O, Yang B, Rustichelli F. *J Appl Polym Sci* 1991;43:839.
- [12] Kulichikhin VG, Vasiteva OV, Litinov I, Antipor FM, Parsamyan IL, Plate NAJ. *Appl Polym Sci* 1991;42:363.
- [13] Ramadin Y, Jawad SA, Ahmad MS, Zihlif A, Volpe M, Malinconico M, Matuscelli E, Ragosta G. *J Dispersion Sci Tech*, submitted for publication.
- [14] Al-Ani SKJ. *Int J Electron* 1993;75:1153.
- [15] Ramadin Y, Al-Haj Abdallah M, Ahmad M, Zihlif A. *Opt Mater* 1996;5:69.
- [16] Mott NF, Davis EA. *Electronic processes in non-crystalline materials*, 2nd ed. Oxford: Clarendon Press, 1979.
- [17] Tauc J. *Amorphous and liquid semiconductors*. London, New York: Plenum, 1974.
- [18] Osman WH. *J Mater Sci Mater Electron* 1997;8:57-61.
- [19] Sharman GD, Sangodkar SG, Roy MS. *J Mater Sci Mater Electron* 1997;8:47-55.
- [20] Al-Houty L, Kassem ME, Abdel Kader HI. *J Mater Sci Mater Electron* 1995;6:17-20.
- [21] Al-Ani SKJ, Yosife RH, Zangana ThA. Submitted to the Second Jordanian International Conference for Mechanical Engineering JIMC 97, 1-5 June 1997, Amman, Jordan.
- [22] Zangana ThA, Zihlif A. *Optical Materials*, submitted for publication.
- [23] Urbach F. *Phys Rev* 1953;92:1324.
- [24] Bernini U, Garbonara G, Malinconico M, Mormile P, Russo P, Volpe MG. *Appl Optics* 1992;27:5794.

