

Effect of Low Gamma-Irradiation Doses on Cellulose Triacetate Polymer Films: I. Dispersion Properties

M. S. Abd El Keriem

Physics department, Faculty of Science, Ain Shams University, Abbasia, Cairo, Egypt

Abstract In the work, optical behavior of cellulose triacetate films and related parameters are investigated under the effect of low dose gamma irradiation. The irradiation by a 10 kGy got success to reduce the refractive index of the cellulose triacetate polymeric film to reach 10.3% of its original value. At this irradiation dose the material dispersion is decreased by 65% associated with a reduction of 64% in the ratio between carrier density to the effective mass of carrier. The average oscillator strength and the average interband oscillator wavelength are suffered also drop of 36% and 15.3% in their initial values, respectively. An increase of about 18.6% in the band gap energy is achieved also with a dose of 10 kGy. The chemical bond approach and electronic polarizability are used to analysis and explain the results.

Keywords Gamma irradiation, Cellulose triacetate, Dispersion

1. Introduction

Conjugated polymers with alternating C=C and C-C bonds along the polymer backbone are important for space development and the design of fusion reactors [1, 2]. They have also a variety of advanced optical, optoelectronics and photonics applications [3]. Since the advances in electrical telecommunication and information processing are approaching their physical limits, therefore, to achieve processing rates greater than 50 GHz polymeric-based optical technologies are definitely required [4].

Polymers are increasingly recognized as significant photonic and bio-photonic materials due to their molecular structure tailoring abilities [5]. Beside their ability to produce nano-objects as building blocks for nanotechnologies [6], surface functionalization, pre- and post-doping of the bulk-phase and producing inorganic-organic hybrid structures expand the function of polymers for photonics industry.

Cellulose triacetate (CTA) as a polymeric material has important scientific and technological applications [7]. On the other hand, gamma irradiation can lead to a significant alteration in the structure and physical characteristics of the polymers. Accordingly, the optical properties of CTA have been studied under different preparation processes and treatments [8-12]. In this work the effect of low gamma irradiation on the dispersion and on dispersion related parameters of CTA films using the Fresnel

spectro-interferometric-based technique [13] is carried out.

2. Experimental

2.1. Film Samples

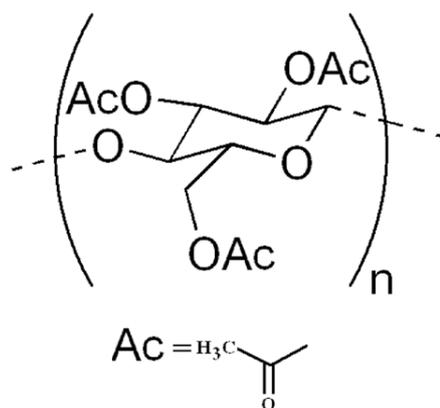


Figure 1. CTA chemical formula

Cellulose triacetate with the chemical formula $[C_6H_7O_2(OOCCH_3)_3]_n$ is made from cellulose [14] by heterogeneous acetylation of the corresponding respective cello-oligosaccharide and purified by recrystallization twice from ethylacetate-hexane. All the six OH groups in the cellobiose units of cellulose are substituted by six $COOCH_3$ groups, see Fig. 1. It is usually an amorphous polymer and rigid as supposed from the molecular structure. Developed Fortepan photographic film plates (Forte Photochemical Co. Ltd., Vác, Hungary) with dimensions of 6.3 cm \times 8.8 cm and thickness of $180 \pm 1 \mu\text{m}$ are studied. Table 1 records the different irradiation doses and the reference number of each sample used throughout the text and plots. The CTA film

* Corresponding author:

magdy36721@yahoo.com (M. S. Abd El Keriem)

Published online at <http://journal.sapub.org/materials>

Copyright © 2015 Scientific & Academic Publishing. All Rights Reserved

samples are irradiated by different gamma doses up to 25 kGy. A Cobalt source providing radiation flux of 275.6 rad/min is used.

2.2. Spectrometric Measurements

Computer aided two-beam spectrophotometer (shimadzu-3101PC UV-VIS NIR) is used to record the reflectance, R , and the transmittance, T , data of plane-parallel polymeric film samples. A resolution limit of 0.2 nm and a sampling interval of 2 nm are utilized for the different measuring points. The accuracy of measuring $R(\lambda)$, and $T(\lambda)$ is 0.003 with the incident beam making an angle of $5.0^\circ \pm 0.1^\circ$ to the normal to external slab faces. The measurements are carried out at room temperature for the entire spectral range 0.2-2.5 μm .

3. Results and Discussion

3.1. Structure Properties

Table 1. Gamma irradiation doses, Cauchy constants, high-frequency dielectric constant, ratio of carrier density to its effective mass, average oscillator strength, the average interband oscillator wavelength and band gap energy

S	Dose (kGy)	a	b (nm ²)	ϵ_∞	$N_c/m^* \times 10^{45}$	$S_0 \times 10^{13}$ (m ⁻²)	λ_0 (nm)	E_g (eV)
1	0	1.3853	27860	1.947	4.55	8.47	142.7	7.9
2	5	1.4172	24488	2.038	4.76	7.25	146.8	7.6
3	10	1.2940	8034	1.680	1.64	5.43	120.9	9.7
4	15	1.3988	24265	1.983	4.52	8.72	158.4	7.8
5	20	1.2813	9898	1.650	1.71	4.64	129.7	9.8

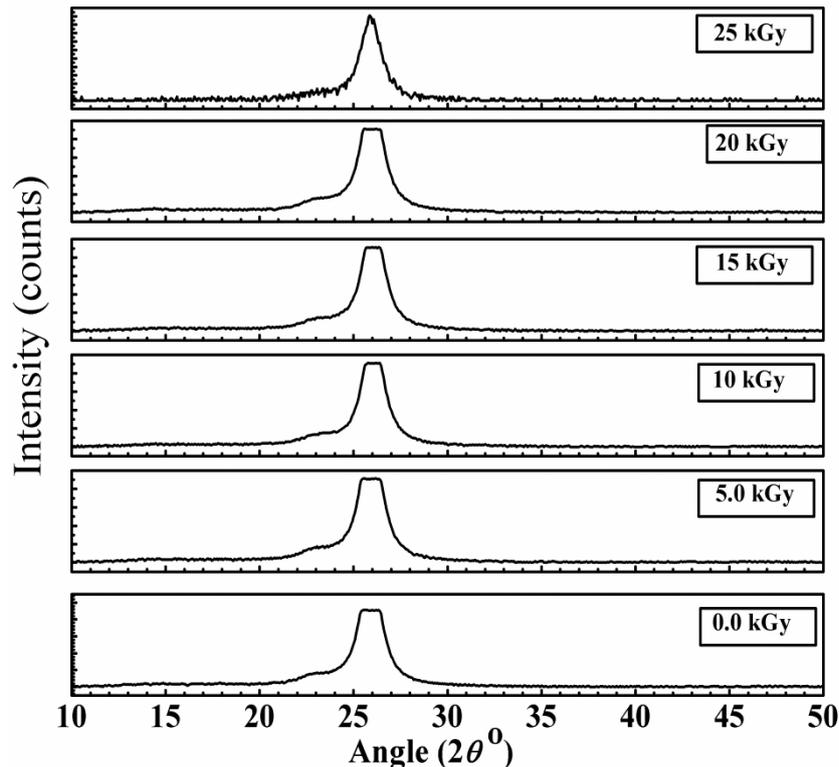


Figure 2. X-ray curves of irradiated and nonirradiated CTA films

Figure 2 shows the x-ray curves for irradiated and nonirradiated cellulose triacetate films. All curves of polymeric films illustrate a single maximum approximately located at 26° correspond to the Van der Waals halo [15, 16]. This means that CTA films have mainly amorphous characteristics.

3.2. Determination of Refractive Index

Refractive index, n , is one of the fundamental physical parameter of the matter explaining its response to electromagnetic waves. It is closely related to the electronic polarizability of ions and the local field distribution inside the material network. The evaluation of the refractive index is important task to employ the materials for their proper applications. Furthermore, the refractive index is the key parameter for the optical device design [17]. Controlling the index of refraction, n , of polymers plays an imperative role in their advanced nonlinear optical and electro-optical applications as well as in nano-photonics and bio-photonics technologies.

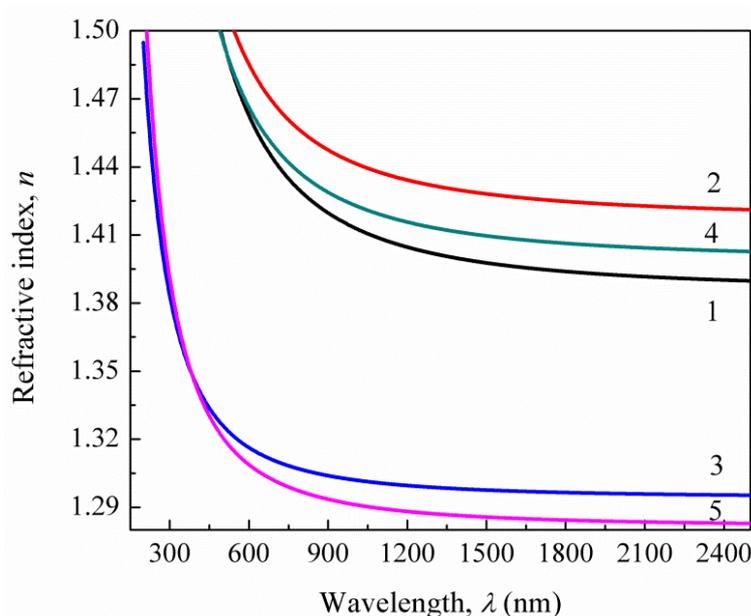


Figure 3. Refractive indices versus wavelength

Fig. 3 illustrates the fitted refractive indices with Cauchy formula versus wavelength. The Cauchy formula has taken the form; $n = a + b/\lambda^2$, where a and b are Cauchy constants of the studied material, see Table 1. It can be seen that there is obvious change in refractive index in split of the low used gamma irradiation doses. The obtained result is a sign of the effectiveness of the irradiation process on CTA. As seen in the figure, there is alternation in the index versus irradiation dose. Samples 1, 2 and 4 show a disparate increase in CTA index of refraction. A sharp decrease in the index of refraction is offered along with increasing the irradiation dose, as it seen with samples 3 and 5.

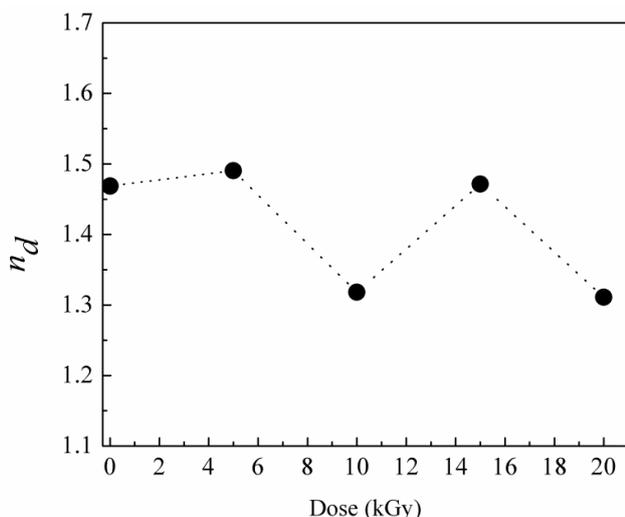


Figure 4. Variation of refractive indices versus irradiation dose

According to the dose, an irregular variation in the chemical structure of carbonyl group in the CTA network may occur. Thus, irradiation may provide vibrational–electronic transition of the non-bonded electron of the carbonyl C=O: lone pair of electrons from the n state

to the π^* unoccupied valence state orbital of the C=O bond (transition: $n \rightarrow \pi^*$) [18]. Existence of these types of lone pair electrons is responsible to supply the network with delocalized electrons. The $n \rightarrow \pi^*$ transition can be seen through the high polarizability of the polymer that increases drastically the refractive index of the polymer. Fig. 4 illustrates more quantitatively the index variation of CTA (provided by n_d) with gamma irradiation doses at the standard wavelength $\lambda_d = 587.56$ nm. The alternating behavior is illustrated with a great emphasis on the index reduction as seen with sample 3.

3.3. Material Dispersion Behavior

The variation of n with respect to wavelength characterizes the dispersion properties of the material. The dispersion measurements are very significant for photonic materials, especially if the incident wavelength of the pump beam is around the band gap of the material. A positive Abbe number, V_d , specifies any transparent medium so that a material with a high V_d (i.e., low dispersion material) produces less chromatic aberration than one with a low V_d , where the reciprocal of the V_d is called dispersive power. Abbe number V_d is given by:

$$V_d = \frac{n_d - 1}{n_F - n_C} \quad (1)$$

where n_d , n_F and n_C are refractive indices at wavelengths $\lambda_d = 587.56$ nm, $\lambda_F = 480.0$ nm and $\lambda_C = 643.8$ nm. Considering the reciprocal of V_d is a measure for dispersion power, the dispersion of the irradiated polymer confers also an alternating decrease with the dose as shown in Fig. 5. Abbe number of the irradiated CTA films (sample 3) is similar to fluorinated materials that are using for energy conversion [19]. It can be seen also that the dispersion of sample 3 is

deeply decreased in comparison with the nonirradiated sample (for example sample 1). Sample 3 indicates that irradiation dose ~ 10 kGy reduced effectively the CTA dispersion power down to 65% of the nonirradiated sample.

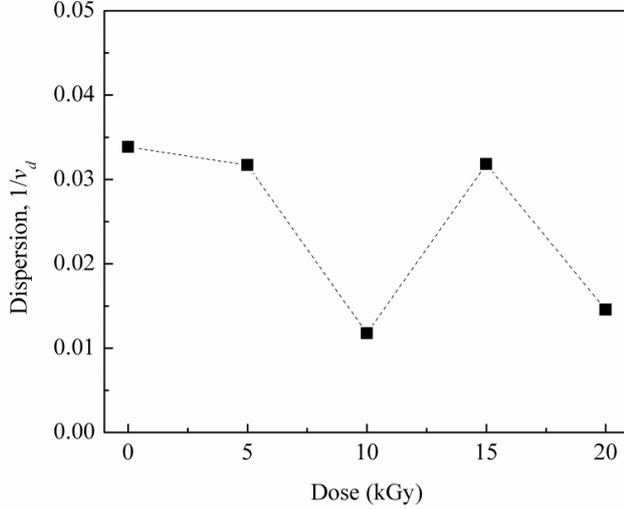


Figure 5. Variation of material dispersion versus irradiation dose

Such large reduction in the material dispersion offers a possibility for using CTA as polymer optical fiber (POF) in fiber optic communication systems and in high power laser delivering systems for two reasons; first the reduction in the dispersion value will decrease the chromatic pulse broadening leading to increase the capacity of propagated information and then a very high data rate too. Therefore, controlling the materials dispersion to reach the value of waveguide dispersion (which has an opposite sign) will give a zero total dispersion at the proper operating wavelength [20].

Second reason, according to Böling et al. [21], the nonlinear refractive index (Kerr nonlinearity) of an optical material having a refractive index less than 1.7 is proportional to $1/v_d^{5/4}$. Thus, the obtained reduction in material dispersion with such relative low value of irradiation dose gives the investigated polymer a possible resistance for damage due to Kerr nonlinearity (i.e., self focusing) which in turn expands the operational limits of polymers to be used in the industrial delivering high power laser system [22].

3.4. Free Carrier Density

To study the effect of gamma irradiation on the electronic polarizability of CTA films, and hence to understand the variation of determined refractive indices, the ratio of carrier density N_c to the effective mass m^* of the carrier should be calculated. Consider the case of greater value of n than absorption index, the ratio of carrier density to the effective mass of the carrier (N_c/m^*) is given by [23-25]:

$$n^2 = \epsilon_\infty - \left(\frac{e^2}{\pi c^2}\right) \left(\frac{N_c}{m^*}\right) \lambda^2 \quad (2)$$

where e is the electronic charge, c is the speed of light, and ϵ_∞

is the high-frequency dielectric constant. Plotting n^2 as a function λ^2 , the intersection at $\lambda^2 = 0$ for the linear part of the curve at higher wavelength gives the high-frequency dielectric constant ϵ_∞ while the slope gives the N_c/m^* ratio as shown in Fig. 6, where sample 1 has taken as an example. Table 1 lists the obtained values of the two evaluated parameters of the different samples. It can be seen that, the density of states per effective mass of carrier has an oscillating manner and as it increases the refractive index increases and the high-frequency dielectric constant as well. Such relative decrease in the carrier density seen with sample 3 confirms and explains the recorded decrease in its refractive index and dispersion.

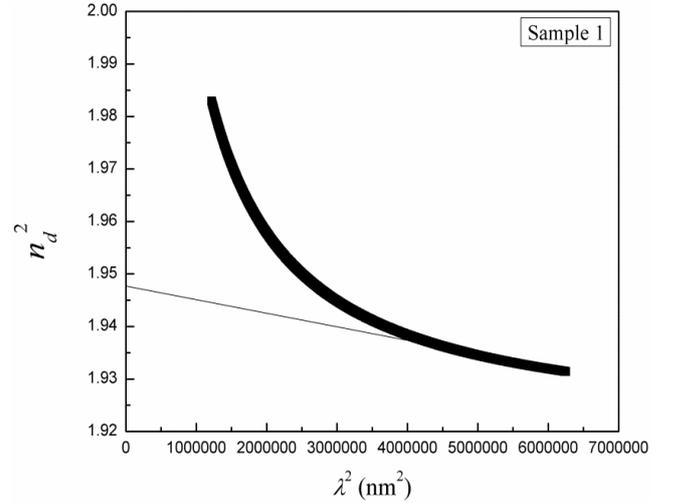


Figure 6. Plotting n^2 as a function λ^2 to determine the ratio of carrier density to its effective mass

3.5. Oscillator Model and Network Interband Characteristics

To understand the nature of the obtained optical properties of the gamma-irradiated CTA polymer films, the dispersion properties will be explained using the single-oscillator model [26]. Several Sellmeier dispersion expressions are proposed depending on the number of considered oscillators one of them is given in the form of [27]:

$$n^2(\lambda) - 1 = A + \frac{B\lambda^2}{\lambda^2 - C} \quad (3)$$

where B and C are fitting parameters and λ is the wavelength of the incident light. Typically, one oscillator dominates and combines the other oscillators into a constant A . This fits the dispersion of the refractive index using the long wavelength approximation of the single-term Sellmeier relation. The fitting retains the physical significance of the oscillator parameters. The general single-term relation of the Sellmeier equation is given by [28]:

$$n^2(\lambda) - 1 = \sum_j \frac{A_j \lambda^2}{\lambda^2 - \lambda_j^2} \quad (4)$$

The wavelengths λ_j with the corresponding constants A_j represent the wavelengths of maximum absorption at resonant absorption bands. According to DiDomenico and

Wemple for single-oscillator model [26], the refractive indices used in the present work are fitted using a one-term Sellmeier equation with wavelengths λ far distant from the immediate region of the absorption band at λ_0 . Accordingly the refractive index is given by [26]:

$$n^2(\lambda) - 1 = \frac{S_0 \lambda_0^2}{\left[1 - \left(\frac{\lambda_0}{\lambda}\right)^2\right]^2} \quad (5)$$

where S_0 is the average oscillator strength and λ_0 is known as the average interband oscillator wavelength. As shown in Fig. 7, plotting of $(n^2(\lambda) - 1)^{-1}$ against λ^{-2} gives a straight line where the values of $1/S_0$ and $1/\lambda_0^2 S_0$ can be calculated from the slope and the intercept, respectively, and they are listed in Table 1. The blue shift seen in the values of the average interband oscillator wavelength λ_0 for samples 3 and 5 indicates the increase in the network energy of polymer. The blue shift means a decrease in the available negative sites needed to increase the electronic polarizability of the investigated samples [29]. Thus the obtained chromatic dispersion results are compatible with the calculated values of the average interband oscillator wavelengths. Also the recorded trend of the average oscillator strength with the observed decrease of its values in samples 3 and 5 indicate that the band gap energies are increased which is associated with a decrease in the index value [30].

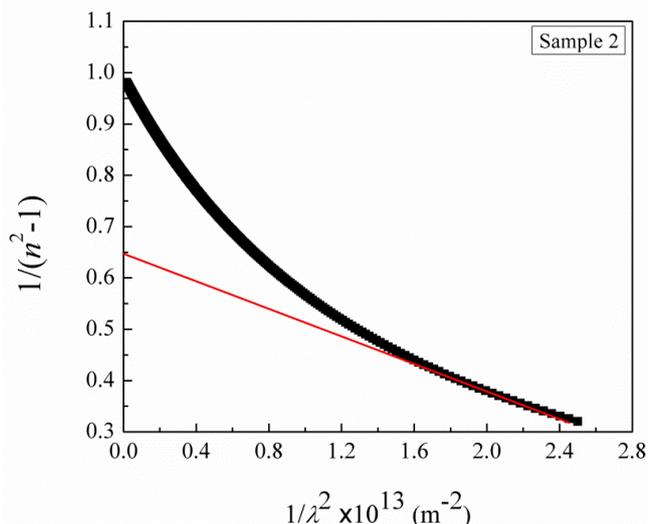


Figure 7. Plotting of $(n^2(\lambda) - 1)^{-1}$ as a function of λ^{-2} to calculate both of average oscillator strength and the average interband oscillator wavelength

The material band gap energy E_g has been calculated from the refractive index by using a relation proposed by Dimitrov et al. [31]:

$$\frac{(n^2-1)}{(n^2+2)} = 1 - \sqrt{\frac{E_g}{G}} \quad (6)$$

where G is a constant. Table 1 contains the calculated values of band gap energy. And as it can be seen, sample 3 for instance has relatively the lower refractive index which is accomplished by the obtained large $E_g = 9.7$ eV. This verifies also the reversible relation between refractive index and the energy of electronic transition through the pseudo gap [30].

The reverse relation between electronic polarizability and band gap energy means that sample 3 which has the lowest index and hence the lowest polarizability should have the largest band gap energy.

The C=O double bonds have π -electrons which have the large electron mobility. Therefore it is easy for C=O π electrons to demonstrate deformation of their electronic clouds by applying an electromagnetic field. Accordingly, irradiation dose for sample 3 was enough to decompose some of the C=O double bonds which have delocalized electrons with large electronic polarizability (1.020 \AA^3) into C-O bonds with their tightly bound electrons that have lower polarizability (0.584 \AA^3) [32]. Thus this transformation or decomposition of C=O bonds into C-O bonds which are associated with low electronic polarizability reflects itself in the recorded enlarging of band gap energy.

4. Conclusions

A small dose of gamma irradiation of 10 kGy was enough to reduce potentially the refractive index and the material dispersion of cellulose triacetate polymeric film. An obvious reduction is determined in the values of the ratio of carrier density to the effective mass of the carrier, the average oscillator strength and the average interband oscillator wavelength. The band gap energy is raised up by 18.65% of its original value. These results confirm the sensitivity of cellulose triacetate and its optical properties for small gamma-irradiation doses. The used gamma irradiation doses are not sufficient to induce noticeable degradation or crosslink in the CTA backbone. Instead of that, it was enough to introduce, according to the dose, alternating remarkable changes in the chemical structure of the carbonyl groups converting some of them from having C=O bond into C-O bond or vice versa. This is adequate to the record fluctuation in physical properties of the polymer. The findings are key structural feature make cellulose triacetate polymer a promising candidate for applications in optoelectronics devices through the ability to manipulate delocalized π -electrons which are belong to carbonyl group by gamma irradiation processing.

REFERENCES

- [1] P. N. Prasad, J. E. Mark, and T. J. Fai, Ed. of "Polymers and Other Advanced Materials, Emerging Technologies and Business Opportunities," V. N. Krishnamurthy, "Polymers in space environments," (1995) 221-226.
- [2] H. Yamaoka, "Polymer materials for fusion reactors," Recent Trends in Rad. Poly. Chem. Adv. Poly. Sci. 105 (1993) 117-144.
- [3] W. Barford, "Electronic and Optical Properties of Conjugated Polymers," Oxford Univ. Press, 2013.
- [4] L. R. Dalton, A. W. Harper, B. Wu, R. Ghosn, J.

- Laquindanum, Z. Liang, A. Hubbel, C. Xu, "Polymeric electro-optic modulators: materials synthesis and processing," *Adv. Mater.* 7 (1995) 519-540.
- [5] P. N. Prasad, "Polymer science and technology for new generation photonics and biophotonics," *Curr. Opin. Solid State Mater. Sci.* 8 (2004) 11-19.
- [6] C. Park, J. Yoon, and E. L. Thomas, "Enabling nanotechnology with self assembled block copolymer patterns," *Polymer* 44 (2003) 6725-6760.
- [7] N. Grassie, J. C. W. Chien, (ed) *Proc. Conf. on Technique and Mechanism of Polymer Degradation and Stabilization*, Elsevier, Karking, England; *Polym. Degr. Stab.* 25 (1989) 102.
- [8] S. A. El-Fiki, M. S. Abd El-Wahab, M. El-Sherief, S. A. Nooh, M. A. El Fiki, "Investigation of the effect of gamma rays on optical properties of polymers," *Radiat. Phys. Chem.* 47 (1996) 761-764.
- [9] M. A. Khashan, A. Y. Nassif, S. A. El-Fiki, "Dispersion of the optical constants of cellulose triacetate irradiated by gamma rays in a wide spectral range 0.2-3 μm ," *Opt. Commun.* 208 (2002) 359-369.
- [10] F. El-Diasty, M. A. Soliman, A. T. Elgendy, A. Ashour, "Birefringence dispersion in uniaxial material irradiated by gamma rays: cellulose triacetate films," *J. Optics A: Pure & Appl. Opt.* 9 (2007) 247-252.
- [11] F. El-Diasty, A. M. Bakry, "Spectroscopic and sub-bandgap optical properties of gamma-irradiated cellulose triacetate polymer," *J. Phys. D: Appl. Phys.* 42 (2009) 145413-145417.
- [12] K. Songsurang, H. Shimada, S. Nobukawa, M. Yamaguchi, "Control of three-dimensional refractive indices of uniaxially-stretched cellulose triacetate with low-molecular-weight compounds," *Euro. Poly. J.* 59 (2014) 105-112.
- [13] M. A. Khashan, A. M. El-Naggar, "A new method of finding the optical constants of a solid from the reflectance and transmittance spectrograms of its slab," *Opt. Commun.* 174 (2000) 445-53.
- [14] M. A. Peterson, K. B. Lipkowitz, "Structure and dynamics of cellulose triacetate," *J. Mol. Strut.: THEOCHEM* 395-396 (1997) 411-423.
- [15] N. S. Murthy, S. T. Correal, and H. Minor, "Structure of the amorphous phase in crystallisable polymers: Poly (Ethyleneterephtalate)," *Macromolecules* 24 (1991) 1185-1189.
- [16] G. Vancso, D. Snetvy, and I. Tomka, "Structural changes during polystyrene orientation: A study of optical birefringence and wide angle X-ray scattering," *J. Appl. Polym. Sci.*, 42 (1991) 1351-1359.
- [17] M. Abdel-Baki, F. El-Diasty, "Glasses for photonic technologies," *Inter. J. Opt. Appl.* 3 (2013) 125-137.
- [18] D. C. Harris, M. D. Bertolucci, "Symmetry and Spectroscopy," (New York: Dover, 1978).
- [19] Tsuyoshi Nakajima, Henri Groult, "Fluorinated Materials for Energy Conversion," Elsevier Ltd. 2005.
- [20] K. Jürgensen, "Dispersion-optimized optical single-mode glass fiber waveguides," *Appl. Opt.* 14 (1975) 163-168.
- [21] N. L. Böling, A. J. Glass, A. Owyong, "Empirical relationships for predicting nonlinear refractive index changes in optical solids," *IEEE J. Quantum Electron.* 14 (1978) 601-608 (1978).
- [22] S. W. Allison, G. T. Gillies, D. W. Magnuson, and T. S. Pagano, "Pulsed laser damage to optical fibers", *Appl. Opt.* 32 (1993) 291-297.
- [23] E. Kh. Shokr, M. M. Wakkad, "Optical properties of Bi₂Te₂Se thin films," *J. Mater. Sci.* 27 (1992) 1197-1201.
- [24] W. G. Spitzer, H. Y. Fan, "Determination of optical constants and carrier effective Mass of Semiconductors," *Phys. Rev.* 106 (1957) 882-889.
- [25] M. M. Waakkad, "Effect of heat treatment on some of the optical parameters of Bi_{1.5}Sb_{0.5}Te₃ thin films," *J. Phys. Chem. Solids* 51 (1990) 1171-1176.
- [26] M. DiDomenico, S. H. Wemple, "Oxygen-octahedra ferroelectrics I. Theory of electro-optical and nonlinear optical effects," *J. Appl. Phys.* 40 (1969) 720-734.
- [27] R. W. Ditchburn, "Light," (New York: Dover, 1991).
- [28] G. Ghosh, "Sellmeier coefficients and dispersion of thermo-optic coefficients for some optical glasses," *Appl. Opt.* 36 (1997) 1540-1546.
- [29] F. A. Moustafa, M. Abdel-Baki, A. M. Fayad, F. El-Diasty, "Role of mixed valence effect and orbital hybridization on molar volume of heavy metal glass for ionic conduction pathways augmentation," *Am. J. Mater. Sci.* 4 (2014) 119-126.
- [30] M. Abdel-Baki, F. A. Abdel Wahab, A. Radi, F. El-Diasty, "Factors affecting optical dispersion in borate glass systems," *J. Phys. Chem. Solids* 68 (2007) 1457-1470.
- [31] V. Dimitrov, T. Komatsu, "Classification of simple oxide: A polarizability approach," *J. Solid State Chem.* 163 (2002) 100-112.
- [32] W. C. Oliver, G. M. Pharr, "An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments," *J. Mater. Res.* 7 (1992) 1564-1583.