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H. M. Zidan^a; E. M. Abdelrazek^b

^a Department of Physics, Faculty of Science at Damietta, Mansoura University, New Damietta, Egypt ^b

Department of Physics, Faculty of Science, Mansoura University, Mansoura, Egypt

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Structural and Optical Properties of PMMA Films Filled with Different Contents of Iodine

H. M. Zidan

Department of Physics, Faculty of Science at Damietta, Mansoura University, New Damietta, Egypt

E. M. Abdelrazek

Department of Physics, Faculty of Science, Mansoura University, Mansoura, Egypt

Films of Poly (methyl methacrylate) filled with different contents of iodine were prepared using the casting technique. The results, obtained by DSC, indicate that, increasing the iodine content leads to a decrease in both T_g and T_D of the PMMA films. The UV/VIS spectral analysis for the present system suggests that the addition of iodine leads to formation of charge transfer complex with two different modes. The infrared analysis revealed the formation of new species between the polymer and iodine. Also, the assigned conjugated double bonds suggest the presence of polarons and/or bipolarons in the polymer matrix. The optical parameters λ_o , S_o and n_∞ were determined from the reflection and transmission spectra in the spectral range of 400–1600 nm. It has been observed that the refractive index of PMMA changes non-monotonically with increasing of the iodine filling level.

Keywords: PMMA, filler, DSC, UV/VIS, IR, optical constants

INTRODUCTION

The introduction of dopant ions into a polymer often imparts new or improved properties to the polymer. Films of pure and doped polymers are quite important for various engineering and technological purpose [1–2]. The doping of polymers cause changes in the structure and, therefore, in the chemical and physical properties [3]. The changes in the physical properties of polymers due to doping depend on the

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Address correspondence to H. M. Zidan, Department of Physics, Faculty of Science at Damietta, Mansoura University, P.O. Box 34517, New Damietta, Egypt. E-mail: hmzidan@yahoo.com

chemical nature of the doping substances and the way in which they interact with the host matrix [4].

After doping a polymer, a complex may be formed with the dopant molecule. The formation of complex is reflected in the IR spectrum of the doped polymer. It has been reported that iodine doping of nylon-6 changes its structure from monoclinic (α) to hexagonal (γ) [5]. It is well known that when PVA films are soaked in comparatively low concentrated iodine-KI solutions. The PVA forms a complex with iodine of an amorphous phase [6–7]. Moreover, at high concentrations of iodine, it penetrates into PVA crystals to form co-crystals with PVA whose structure was proposed on the basis of X-ray diffraction [8]. Iodine has been used as a dopant in many other polymers like polyaniline and polyacetylene.

PMMA has received great attention due to its optical properties and its possible use in nonlinear optics. PMMA is known for its medical applications, particularly for hard tissue repair and regeneration [9]. PMMA beads have been developed to deliver aminoglycoside antibiotics locally for the treatment of bone infections [10].

In a previous work [11], the optical properties and the structural modifications were studied when metal chlorides (CrCl_3 and CoCl_2) have been used in different concentrations as a dopant for PMMA. In this article, iodine has been used as an additive for PMMA. The optical and structural properties of iodine-filled PMMA with different contents are investigated using DSC and spectroscopic methods.

EXPERIMENTAL PROCEDURE

Sample Preparation

The PMMA and iodine used in this work were supplied by Aldrich Chemical CO., USA. PMMA films filled with different amounts of iodine were prepared by the casting method as follows. PMMA was dissolved in benzene for two days at room temperature. Iodine crystals were added to the polymeric solution. The mixture was left to reach a suitable viscosity and then casted in glass dishes and kept in a dry atmosphere at room temperature for two weeks to ensure the removal of solvent traces. The thickness of the obtained films was in the range of 0.05 to 0.1 mm. PMMA films filled with mass fractions 0, 1, 3, 5, 7, 10, 15, 20, and 25% of iodine were prepared.

Physical Measurements

UV/VIS absorption spectra of the studied samples were carried out in the 200–900 nm wavelength range using a Perkin-Elmer UV/VIS

spectrophotometer. The spectrophotometric method was used to determine the optical constants of the studied samples. The transmittance $T(\lambda)$ and the reflectance $R(\lambda)$ of PMMA films filled with iodine were measured using a double beam spectrophotometer JASCO model V-570-UV-VIS-NIR. The transmittance and reflectance spectrum were measured at wavelength range of 190–2500 nm. A deuterium discharge tube (190–350 nm) is used in the ultraviolet region and a tungsten iodine lamp (340–2500 nm) is used in the VIS/NIR region as a light source. An infrared spectrophotometer (Perkin Elmer 833) was used for measuring the IR spectra in the wave number range 400–4000 cm^{-1} . The differential scanning calorimetry (DSC) thermograms were performed using DSC-50 Shimadzu Differential Scanning Calorimeter. A heating cycle was carried out from room temperature up to 680 K using a programmed heating rate of 5°C/min.

RESULTS AND DISCUSSION

Thermal Analysis

The thermal behavior of PMMA films filled with different levels of iodine was studied with the traces of the DSC thermograms from 300–680 K (Figure 1). The thermograms show that the pure PMMA displayed two transitions. The first transition, at about 369 K, was assigned to the glass-transition temperature (T_g) of the relaxation process resulting from micro-Brownian motion of the main chain backbone. This value seems to be consistent with the results reported in the literature [12]. The second transition, at about 653 K, was assigned to the thermal degradation temperature (T_D) of pure PMMA. Figure 1 reveals also that the thermal behavior of PMMA films filled with different levels of iodine was similar to that of the pure PMMA films. The values of the transition temperatures (T_g and T_D) for PMMA films filled with different amounts of iodine, as obtained from the DSC thermograms, are reported in Table 1.

The magnitude of T_D of pure PMMA films is greater than that of the filled films. Apparently, the addition of iodine of PMMA films reduced their thermal stability. Also, the position of T_g for PMMA films filled with different filling levels of iodine samples is slightly shifted toward temperatures lower than those of the unfilled films. This indicates that the segmental mobility of pure PMMA increases upon the addition of iodine and that the PMMA segments become less rigid. This indicates that the iodine filler acts as plasticizer. Increasing the iodine content resulted in a decrease in both T_g and T_D of the PMMA

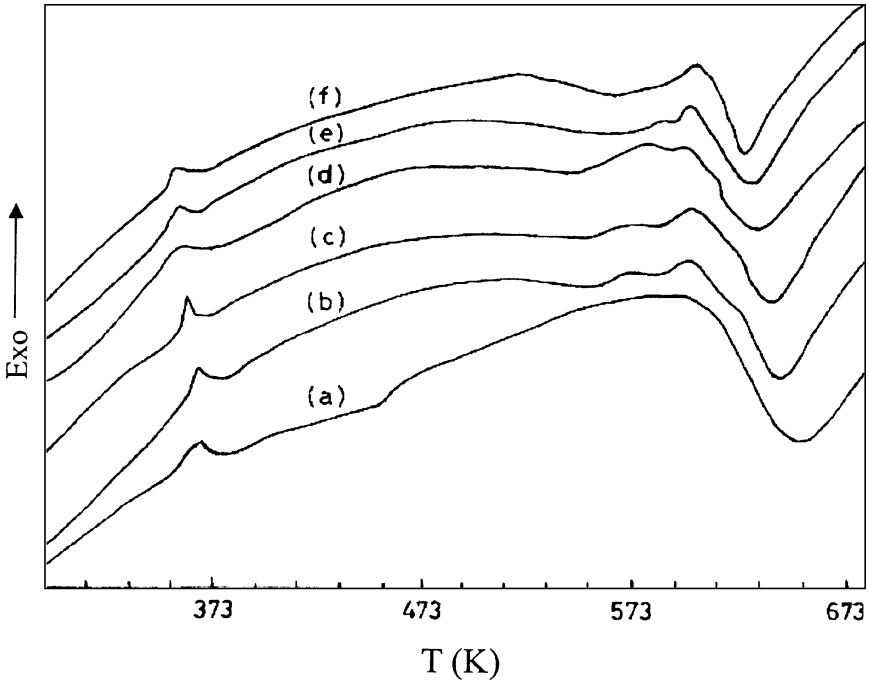


FIGURE 1 DSC thermograms for PMMA films filled with different W values of iodine: (a) 0; (b) 5 wt%; (c) 10 wt%; (d) 15 wt%; (e) 20 wt%; and (f) 25 wt%.

films; therefore, the iodine molecules greatly affected the PMMA structure. A similar result were reported for other polymers such as PVA films [4] filled with CrF_3 or MnCl_2 and PVAc films [13] filled with MgCl_2 or MgBr_2 .

TABLE 1 Transition Temperature of the DSC Thermograms for PMMA Films Filled with Different Levels of Iodine

W (wt %)	T_g (K)	T_D (K)
0	369	653
5	367	645
10	363	641
15	361	633
20	358	627
25	356	623

UV/VIS Optical Absorption

The absorption spectra in the UV/VIS region (200–900 nm) for iodine dissolved in benzene and films of PMMA filled with different levels of iodine are shown in Figures 2 and 3. The observed spectrum of iodine has an absorption bands at 293 and 500 nm in addition to the band at 256 nm, which may be due to the benzene solvent (Figure 2). The spectra recorded for the PMMA films filled with different contents of iodine show a new broad band at 395 nm (Figure 3). It is noticed that the position of the iodine band at 293 nm is slightly shifted in the case of filled films. Moreover, its intensity increases with increasing the filling level, providing an evidence for the incorporation of iodine into the PMMA matrix. On the other hand, it is remarkable that the intensity of the new band at 395 nm increases with increasing iodine content. This band splits upon increasing the iodine filling level. It may be reasonable to suggest that this new band is attributed to the formation

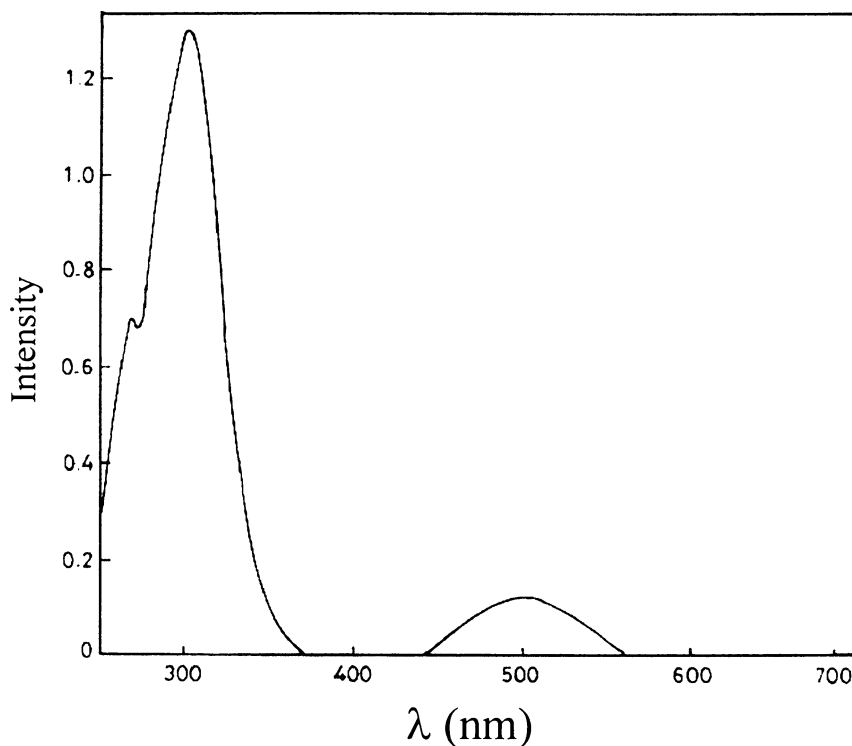


FIGURE 2 The UV/VIS absorption spectrum for iodine dissolved in benzene.

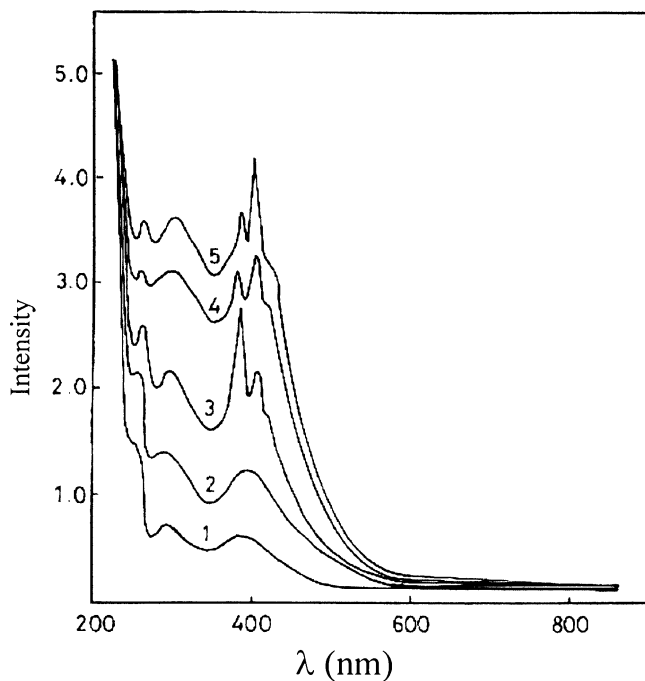


FIGURE 3 The UV/VIS absorption spectra for PMMA films filled with different values of iodine: (1) 3 wt%; (2) 7 wt%; (3) 10 wt%; (4) 15 wt%; (5) 20 wt%.

of a charge transfer complex between the polymer and the iodine. The splitting at a narrow range of wavelength may be attributed to transitions occurring with the same energy. It is noticed that at low iodine filling level the intensity of the band (due to splitting) at shorter wavelength is higher than that at longer wavelength. Upon increasing the iodine content, the intensity of the band at longer wavelength is enhanced at the expense of the other one. It may be reasonable to suggest that the formation of the charge transfer complex occurred with two modes. The first one may be due to polymer (donor) to iodine (acceptor) charge transfer with certain species that are predominant at low iodine filling level. The second is predominant at high iodine filling level with the formation of other species.

It is worthwhile to mention that the UV-VIS reflection spectra of poly-Schiff bases, poly (p-aniline) and poly (m-aniline), doped by iodine showed new absorption band at 400–550 nm [14]. This band was attributed to charge transfer between the poly-Schiff base and iodine. Similar results showed that when PVA was soaked in iodine-KI

solution, the PVA formed a complex with iodine in the amorphous [7] as well as in the crystal [15] phase of PVA.

Reflection and Transmission Spectra

The optical properties obtained from the measurements of reflection and transmission were studied. Figure 4 represents the spectral distribution of both transmittance $T(\lambda)$ and reflectance $R(\lambda)$ for the PMMA film filled with 3 wt% iodine in the 400–1600 nm wavelength range. The spectral distribution of $T(\lambda)$ and $R(\lambda)$ for PMMA films filled with $W = 5, 7, 10,$ and 15 wt% of iodine were found to be similar to that shown in Figure 4, hence they are not presented here. It is clear from this figure that at longer wavelength, $\lambda > 900$ nm, the investigated film becomes transparent with no light scattered or absorbed, that is $T + R \sim 1$. However the inequality $T + R < 1$ at short wavelength $\lambda < 900$ nm is due to the existence of absorption. The sample shows anomalous dispersion in the visible range, where the absorption of the sample is maximum ($\cong 0.87$) at $\lambda \cong 460$ nm and decreases rapidly as the wavelength increases and reaches its minimum value ($\cong 0.008$) at $\lambda \cong 750$ nm.

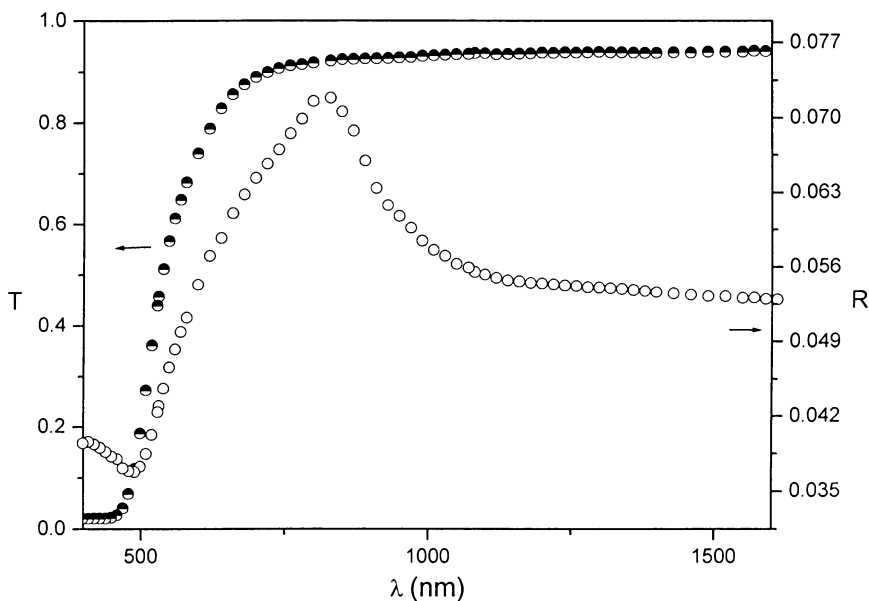


FIGURE 4 The spectral distribution of $T(\lambda)$ and $R(\lambda)$ for PMMA film filled with 3 wt% iodine.

The refractive index (n) of PMMA films filled with different contents of iodine was computed from the measured value of $T(\lambda)$ and $R(\lambda)$ according to the following equations:

$$T(\lambda) = (1 - R) \exp(-4\pi kd/\lambda) \quad (1)$$

$$R(\lambda) = [(n - 1)^2 + k^2]/[(n + 1)^2 + k^2] \quad (2)$$

where k is the absorption index and d is the film thickness.

Figure 5 shows the dispersion curve of the refractive index $n(\lambda)$ in the wavelength range 400–1600 nm for PMMA film filled with 3 wt% iodine. The observed spectrum shows a peak at $\lambda < 900$ nm indicating an anomalous dispersion in this region. This peak is due to a rapid increase in the absorption mechanism in the fundamental absorption edge, or due to the presence of absorbing color centers induced as a result of the presence of iodine ions in the polymer matrix. This behavior obeys a multi-oscillator model. The change of refractive index in the visible region has a great importance in the field of nonlinear optics and photonic applications such as optical switches and

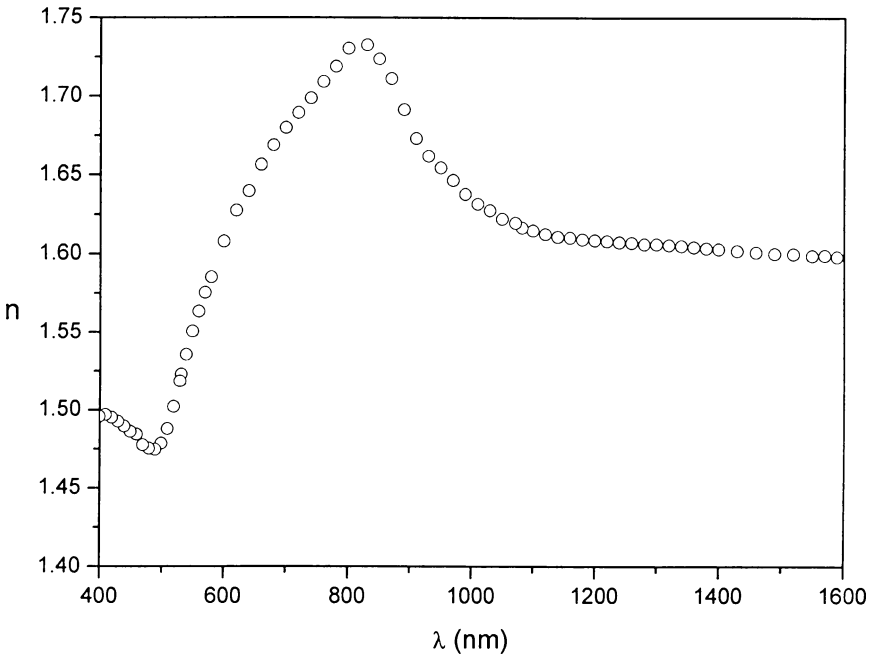


FIGURE 5 The dispersion curve of refractive index $n(\lambda)$ for PMMA films filled with 3 wt% iodine.

integrated optics. On the other hand, at $\lambda > 900$ nm the refractive index decreases with increasing λ and reaches a nearly constant long wavelength value suggesting a normal dispersion.

Plotting $(n^2 - 1)^{-1}$ versus λ^{-2} yields a straight line characterizing the material (Figure 6). This indicates that the dispersion of the refractive index follows a single oscillator model, according to Sellmeier's relation [16],

$$[n^2(\lambda) - 1]^{-1} = [1 - (\lambda_0/\lambda)^2] / (S_0\lambda_0^2), \quad (3)$$

where λ_0 is an average oscillator position and S_0 is the average oscillator strength. From the slope of the resulting straight line ($1/S_0$) and the infinite wavelength intercept ($1/S_0\lambda_0^2$), the Sellmeier's parameters were computed. Also, the data of fitted straight line was found to obey the simple classical dispersion relation for a single oscillator centered at wavelength λ_0 according to the following relation [17],

$$(n_\infty^2 - 1)/(n^2 - 1) = 1 - (\lambda_0/\lambda)^2, \quad (4)$$

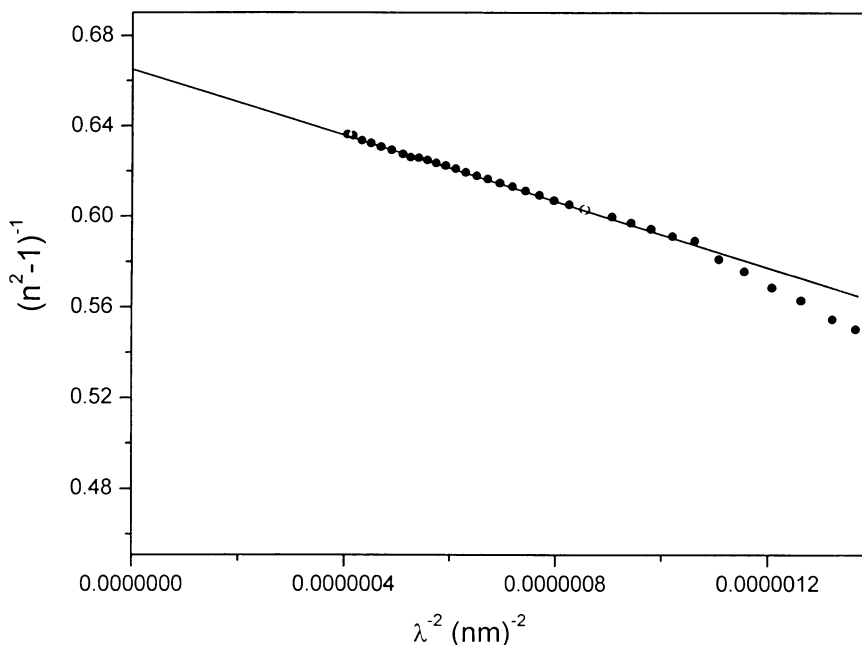


FIGURE 6 Plot of $(1/n^2 - 1)$ versus λ^{-2} for PMMA film with 3 wt% iodine.

TABLE 2 The Dependence of Sellmeier's Parameters (λ_0 , S_0), and the Infinite Wavelength Refractive Index, n_∞ on the Iodine Filling Level W

W (wt %)	λ_0 (nm)	S_0 ($10^{13}/\text{m}^2$)	n_∞
3	327	1.41	1.5836
5	320	1.35	1.5435
7	337	1.46	1.6304
10	333	1.73	1.7083
15	317	1.52	1.5898

where n_∞ is the infinite wavelength refractive index, and was found to be related to the oscillator strength S_0 by the relation,

$$n_\infty^2 = 1 + S_0\lambda_0^2, \quad (5)$$

The optical parameters λ_0 , S_0 , and n_∞ were computed for the PMMA films filled with different levels of iodine and given in Table 2. From this table, it is observed that the optical parameters change non-monotonically with increasing iodine filling level. It may be said that the structural changes take place after filling with iodine as a result of complex formation of iodine with the carbonyl group of PMMA with different models depending on the filling level. Thus it may be concluded that the structural changes in PMMA after filling are responsible for changing the refractive index of PMMA.

IR Spectroscopy

To provide further information regarding the filling effect of iodine on the structural modification of PMMA, their IR spectra were measured. Figure 7 depicts the IR transmission spectra ($400\text{--}4000$) cm^{-1} for pure PMMA and iodine filled PMMA films with different contents. It appears from Figure 7 that there is no appreciable difference in the absorption bands of pure PMMA film when compared with that previously reported [18–19]. For pure PMMA film as with most organic compounds, the absorption bands at 2949 and 2997 cm^{-1} , may arise from the $\nu(\text{C-H})$ vibrations. The methyl groups can be confirmed by the appearance of the stretching absorption band at 1446 cm^{-1} . Moreover, the absorption band observed at 1020 cm^{-1} is attributed to C-O-C stretching of the ester group. A very distinctive absorption band observed at 1727 cm^{-1} is due to the $\nu(\text{C=O})$ of the ester side group, whereas the weak bands at 1638 and 1823 cm^{-1} are assigned to the $\nu(\text{C=C})$. It is remarkable that the present double bond segments

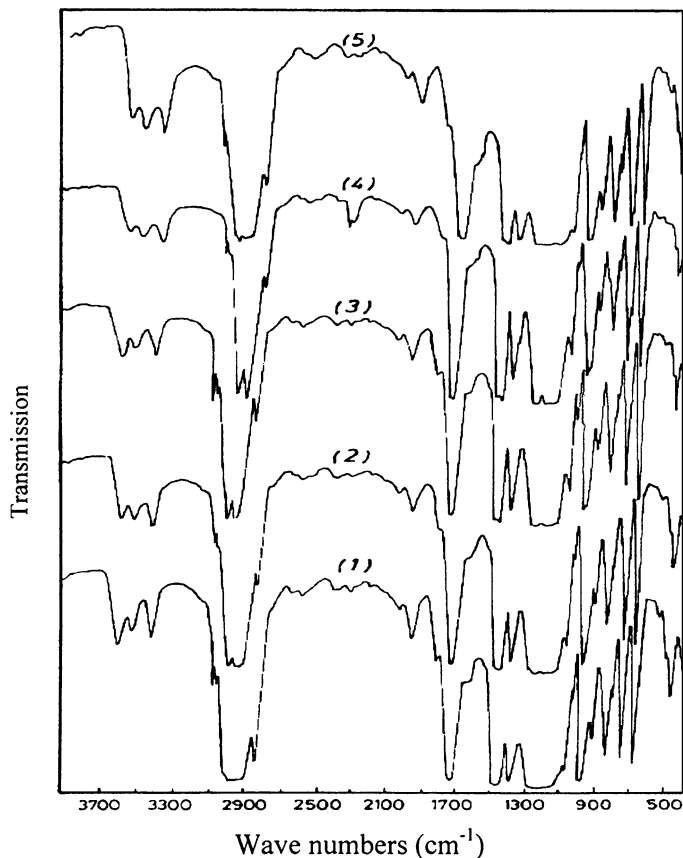


FIGURE 7 Transmission spectra for PMMA films filled with different values of iodine: (1) 0; (2) 5 wt%; (3) 10 wt%; (4) 15 wt%; and (5) 25 wt%.

are considered as suitable sites for polarons and/or bipolarons [20]. The appearance of the absorption band at 1067 cm^{-1} is an indication of either an atactic or syndiotactic nature of PMMA [18]. For PMMA films filled with different mass fractions (W) of iodine, the changes in various bands are not appreciable except for a remarkable change in the 1727 cm^{-1} band.

The changes in the 1727 cm^{-1} band point toward the possibility of iodine molecule associated with the C=O group in the side chain of PMMA molecule and may be taken as a good evidence for some structural modification [21]. The IR characterizing peaks of pure PMMA and iodine filled PMMA films were assigned and listed in Table 3.

TABLE 3 Assignment of the IR Characterizing Peaks for Pure PMMA Film and Its Films Filled with Different Levels of Iodine

Frequency (cm ⁻¹)		
PMMA	Filled samples	Assignment
683	683–684	$\nu(\text{C}-\text{O})$
844	842–843	$\nu(\text{C}-\text{C})$
1067	1064–1068	Indicative of either atactic or syndiotactic nature of PMMA
1020	1019–1022	$\nu(\text{C}-\text{O}-\text{C})$
1142	1140–1146	$\nu(\text{CO}-\text{O}-\text{C})$
1387	1384–1387	$\nu(\text{CH}_2)$
1446	1444–1448	$\nu(\text{CH}_3)$
1478	1474–1480	$\delta(\text{OCH}_3)$
1638	1638–1640	$\nu(\text{C}=\text{C})$
1727	1724–1730	$\nu(\text{C}=\text{O})$
1823	1820–1825	$\nu(\text{C}=\text{C})$
2949	2945–2954	$\nu(\text{CH}_2)$
2997	2995–3000	$\nu(\text{CH}_3)$

Note: ν = stretching, δ = bending.

The results are consistent with the UV/VIS study in the present work (section 3.2).

CONCLUSIONS

From the present work the following implications can be concluded. (1) the values of T_g and T_D decrease as the iodine content increases and this indicates that the iodine molecules acts as a plasticizer for PMMA films; (2) the observed IR absorption bands at 1638 and 1823 cm⁻¹ imply the presence of conjugated polyenes, suitable forms for polarons and/or bipolarons; (3) the UV/VIS spectra revealed that the PMMA films filled with iodine show a new broad band at 395 nm, which is attributed to the formation of charge transfer complex. The splitting of this band suggests that the formation of charge transfer complex occurs with two different modes depending on the iodine content; (4) analysis of the refractive index (n) showed an anomalous dispersion in the wavelength region $\lambda < 900$ nm as well as normal dispersion in the region $\lambda > 900$ nm. The values of the optical parameter λ_0 , S_0 , and n_∞ can be calculated for PMMA films containing different values of iodine. The optical parameters change non-monotonically with increasing iodine filling level. The structural changes in PMMA after

filling with iodine are responsible for changing the optical parameters of PMMA.

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