Arylidene polymers: 15. Optical band gap and structural relationship of new polyester films of dibenzylidenecyclohexanone

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(Received 26 June 1990; revised 27 September 1990; accepted 19 October 1990)

The optical properties of poly[oxyisophthaloyloxy-(2-methoxy-*p*-phenylene)methylidene-(2-oxo-1,3-cyclohexanediylidene)methylidyne-(3-methoxy-*p*-phenylene)] (I) and poly[oxysebacoyloxy-(2-methoxy-*p*-phenylene)methylidene-(2-oxo-1,3-cyclohexanediylidene)methylidene-(3-methoxy-*p*-phenylene)] (II) polymer films were studied. The transmission and absorption measurements were carried out in the energy range 1.9–3.2 eV at 300 K. The data on absorption coefficient *versus* photon energy were analysed and interpreted in terms of the Tauc model, $(\alpha\hbar\omega)^{1/2} = B^{1/2}(\hbar\omega - E_g^{opt})$. Analysis of experimental results shows that the absorption characteristics give a good fit to the Tauc model, and indicates that both polymers I and II have an indirect band gap. The values of the optical gap E_g^{opt} and the slope of the Tauc plots $B^{1/2}$ were determined. The study shows that the indirect allowed optical transitions are the predominant transitions in the optical absorption process. From the data a correlation between optical band gap and polymer structure was observed and discussed.

(Keywords: structure; optical properties; polyesters; films; dibenzylidenecyclohexanone)

INTRODUCTION

In continuation of our scientific programme for the synthesis of a new class of linear unsaturated arylidene polymers, the synthesis of arylidene polymers for semiconducting applications has been considered and investigated[1,2]. Other systems include polyesters with good mechanical properties[3] and interesting morphological structures[4], and polyhydrazides with liquid-crystalline rod-like anisotropic behaviour have been reported[5]. Studies and determination of the optical properties of the solid materials are of great interest.

The present work deals with the measurement and study of the optical properties of two newly synthesized cast thin films of high-performance polyesters, namely poly[oxyisophthaloyloxy-(2-methoxy-*p*-phenylene)-methylidyne-(2-oxo-1,3-cyclohexanediylidene)methylidyne-(3-methoxy-*p*-phenylene)] (I) and poly[oxysebacoyloxy-(2-methoxy-*p*-phenylene)methylidene-(2-oxo-1,3-cyclohexanediylidene)methylidene-(3-methoxy-*p*-phenylene)] (II).

A major target of this work was the determination of the optical band gap.Moreover, the effect of structural units in the polymer main chain upon the absorption process was also investigated.

EXPERIMENTAL

Sample preparation and casting of films

The polymer samples were prepared as reported in our recent work[4]. A methylene chloride solution (4% w/v) of each polymer was poured onto glass Petri dishes with diameter 3 or 4 inch (~7.5 or ~10 cm). The solvent was evaporated at room temperature in a dust-proof chamber. The films formed were dried at 40°C under reduced pressure (0.1 mmHg) to remove the entrapped solvent. Finally the compact dried transparent films with desired thickness and clarity were then carefully stripped from the glass Petri dishes.

Optical measurements

Two samples with high optical quality were used for absorbance and transmittance measurements. The thickness of the samples was measured using a travelling microscope and a micrometer with an accuracy of about 2%. The thickness of sample I was 14 μm and that of sample II was 10 μm. The optical measurements were carried out at room temperature (300 K) using a Perkin–Elmer Lamda 1 A spectrophotometer in the wavelength range λ = 190 to 900 nm. The method of least squares has been used for the determination of the optical parameters for our samples.

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0032-3861/92/010052-05

RESULTS AND DISCUSSION

Numerous work concerning the study of optical properties of both crystalline and amorphous materials has been carried out. It was found that the former is characterized by a sharp and well defined absorption edge due to long-range periodicity[6], whereas the latter possesses a broad absorption edge.

Tauc[7], Bardeen *et al.*[8] and Davis and Mott[9] independently derived an equation relating the absorption coefficient $\alpha(\omega)$ to the photon energy $\hbar\omega$ in the form:

$$\alpha(\omega) = \frac{B}{\hbar\omega}(\hbar\omega - E_g^{\mathrm{opt}})^m \qquad (1)$$

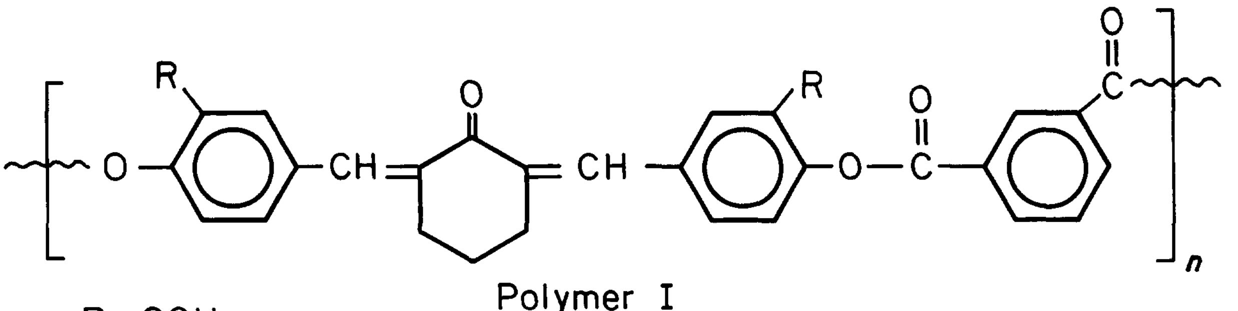
where B is a constant that reflects the degree of randomness of the structure of the amorphous solid, E_g^{opt} is the optical band gap and m is a number that characterizes the optical absorption process: $m = 1/2$ for a direct allowed transition, $m = 3/2$ for a direct forbidden transition, $m = 2$ for an indirect allowed transition, and $m = 3$ for an indirect forbidden transition.

In the present work the absorption coefficient α was calculated using the formula:

$$\alpha = (2.303/d)\log_{10}(1/T) \qquad (2)$$

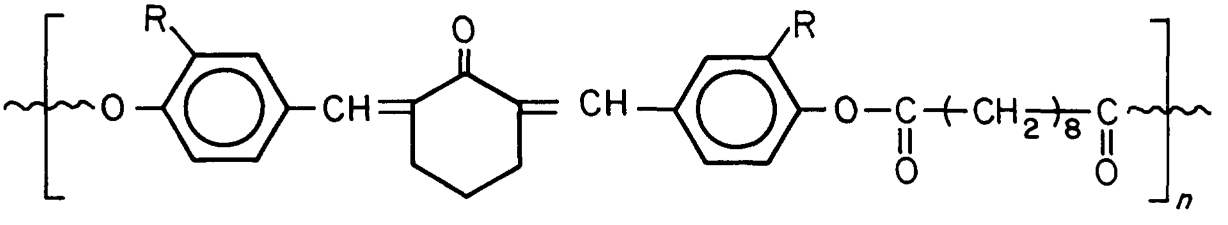
taking into account the background effects, where T is the transmittance and d is the thickness of the sample.

The absorption coefficient *versus* photon energy is shown in *Figure 1*. In the high-absorption region, both polymer films exhibit a sharp absorption edge. On the other hand, in the long-wavelength region, at $\alpha < 3 \times 10^2\ \mathrm{cm}^{-1}$, the absorption of polymer I varies slightly with photon energy. For polymer II at $\alpha < 10^3\ \mathrm{cm}^{-1}$, a remarkable increase in the absorption with $\hbar\omega$ is observed. Furthermore the broader structure of the optical absorption for polymer II in comparison with polymer I (*Figure 1*) can be interpreted by the relatively higher flexibility of polymer II, which contains an aliphatic flexible spacer within its main chain, whereas polymer I has an aromatic one. The structures of polymers I and II are shown below:



R=OCH$_3$

Polymer I



Polymer II

Analysis of optical absorption data using equation (1) was carried out to determine the predominant optical transition mechanism.

The plots of $(\alpha\hbar\omega)^2$ *versus* $\hbar\omega$ (*Figure 2*) show that the direct transition may occur at a photon energy above 2.7 eV. *Figure 3* shows $(\alpha\hbar\omega)^{2/3}$ as a function of $\hbar\omega$; the turning point at 2.7 eV indicates the onset of a direct transition. From the $(\alpha\hbar\omega)^{2/3}$ *versus* $\hbar\omega$ plot and the dependence of α on the photon energy, it can be seen that this transition is a forbidden one. The plots of $(\alpha\hbar\omega)^{1/2}$ *versus* $\hbar\omega$ (*Figure 4*) show two distinct linear

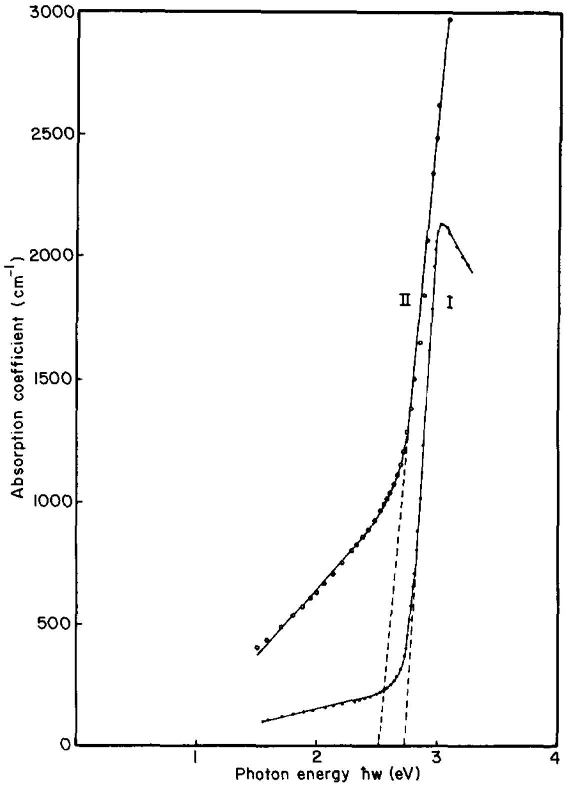


Figure 1 Optical absorption coefficient *versus* photon energy for the polymer films I and II at 300 K

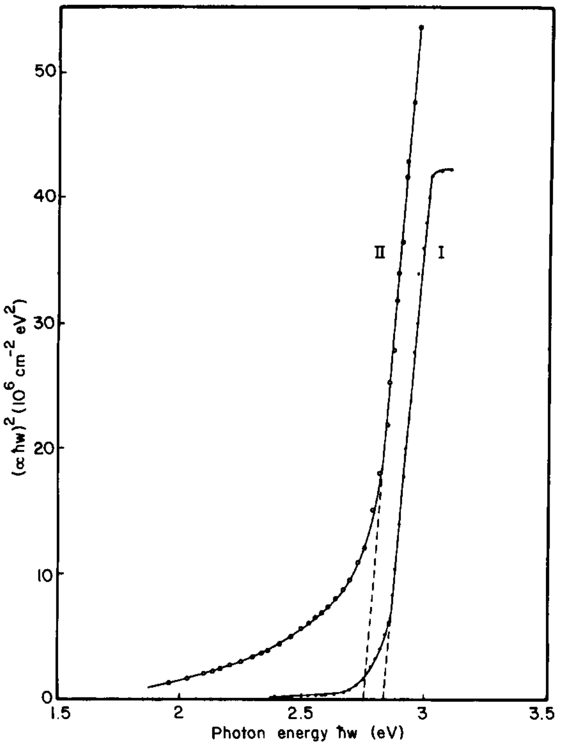


Figure 2 Plots of $(\alpha\hbar\omega)^2$ *versus* $\hbar\omega$ at 300 K for polymer films I and II

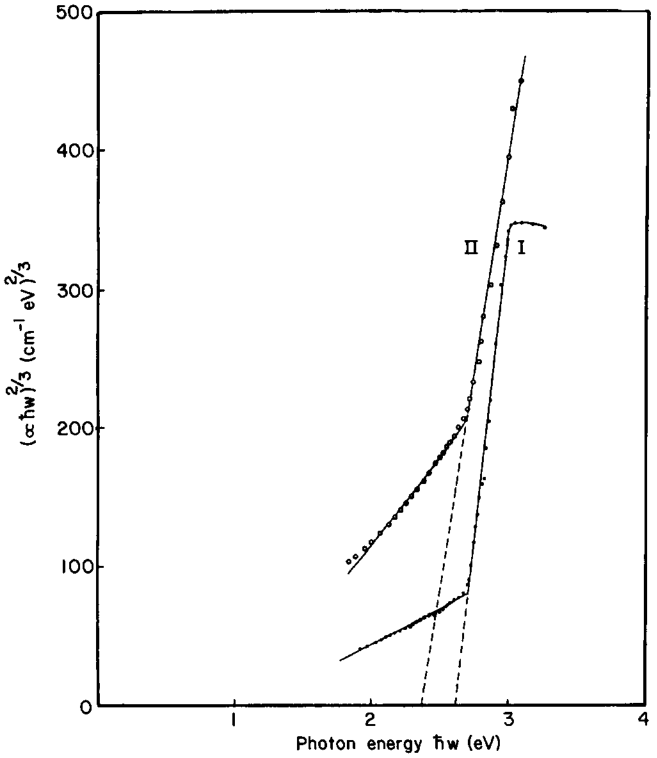


Figure 3 The dependence of $(\alpha\hbar\omega)^{2/3}$ on photon energy $\hbar\omega$ at 300 K for polymer films I and II

parts in the Tauc plot. These linear parts were fitted to the following linear quadratic equation derived by Tauc[7] and Davis and Mott[9]:

$$(\alpha\hbar\omega)^{1/2} = B^{1/2}(\hbar\omega - E_g^{\text{opt}}) \quad (3)$$

The slope $B^{1/2}$ and the intercept $B^{1/2}E_g^{\text{opt}}$ were calculated by applying the method of least squares[10] and are listed in *Table 1*. The obtained values of $B^{1/2}$ and E_g^{opt} coincide with the values determined by extrapolation of the graphical data in *Figure 2* to $(\alpha\hbar\omega)^{1/2} = 0$. This indicates that the indirect allowed transitions are predominant in the optical absorption processes.

The calculated values of phonon energies, 0.88 and 0.75 eV from *Figure 4* for films I and II respectively, are too high to be considered as lattice phonons. Therefore it may be suggested that the observed structure in $(\alpha\hbar\omega)^{1/2}$ plots is not due to emission or absorption of phonons. It can be attributed to the presence of two mechanisms of the transition:

(1) The first one occurs at photon energy $\hbar\omega$ below the turning energy E_0. It can be attributed to the exciton absorption associated with the conjugated unit in the polymer backbones.

(2) The second indirect transition occurs at photon energy $\hbar\omega$ above E_0. It can be attributed to the electronic transitions between deeper extended states lying in the valence band and conduction band.

It should be noted that the value of E_g^{opt} for polymer I is greater than that for polymer II. This may be due to the following factors. (i) The morphological studies by TEM (Philips Model 400 T) reported in our recent

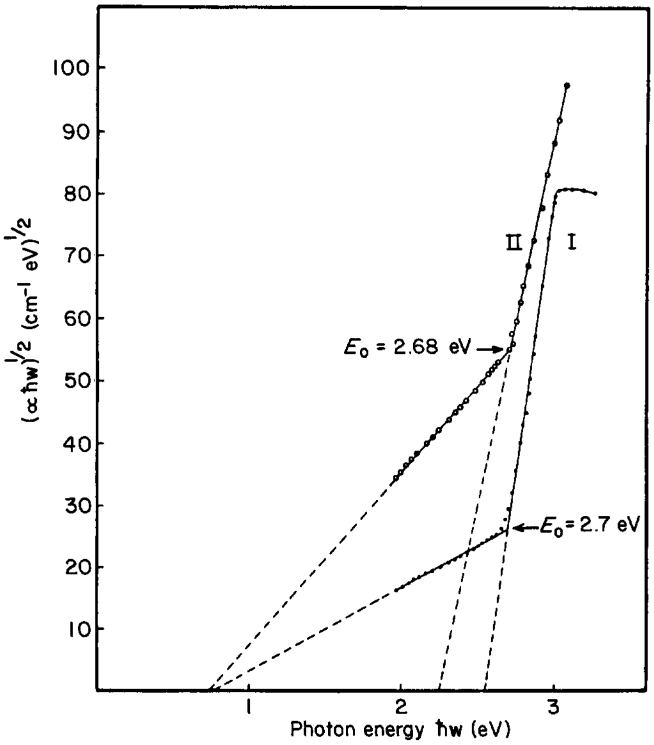


Figure 4 Variation of $(\alpha\hbar\omega)^{1/2}$ with $\hbar\omega$ to demonstrate that the index m in equation (1) is 2, for polymer films I and II at $T = 300$ K

Table 1 Optical absorption parameters for polymer films I and II at 300 K. Optical data were fitted to $(\alpha\hbar\omega)^{1/2} = B^{1/2}(\hbar\omega - E_g^{\text{opt}})$ to estimate values for $B^{1/2}$ and E_g^{opt} (± 0.02 eV) above and below E_0 for each sample

		$\hbar\omega$ below E_0		$\hbar\omega$ above E_0	
Polymer number	E_0 (eV)	$B^{1/2}$ ((cm^{-1} eV)$^{-1/2}$)	E_g^{opt} (eV)	$B^{1/2}$ ((cm^{-1} eV)$^{-1/2}$)	E_g^{opt} (eV)
I	2.70	13.73	0.79	176.89	2.55
II	2.68	28.05	0.75	118.38	2.25

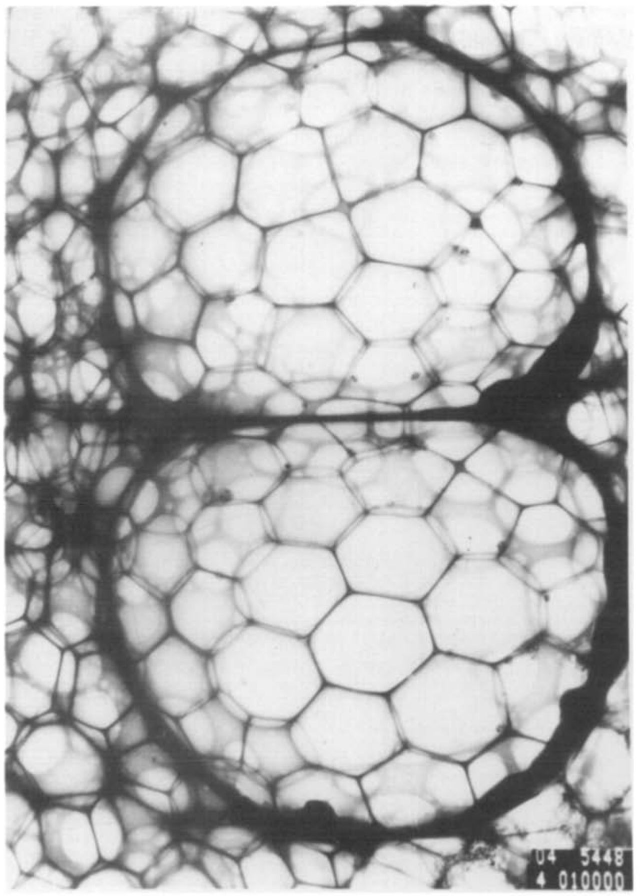


Figure 5 TEM image of polymer I (as reported in ref. 4)

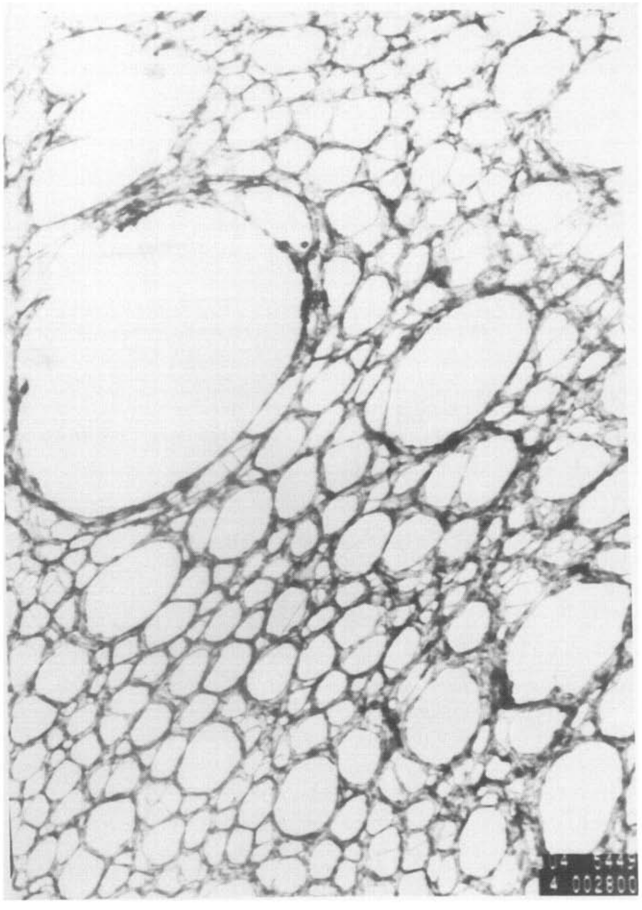


Figure 6 TEM image of polymer II (as reported in ref. 4)

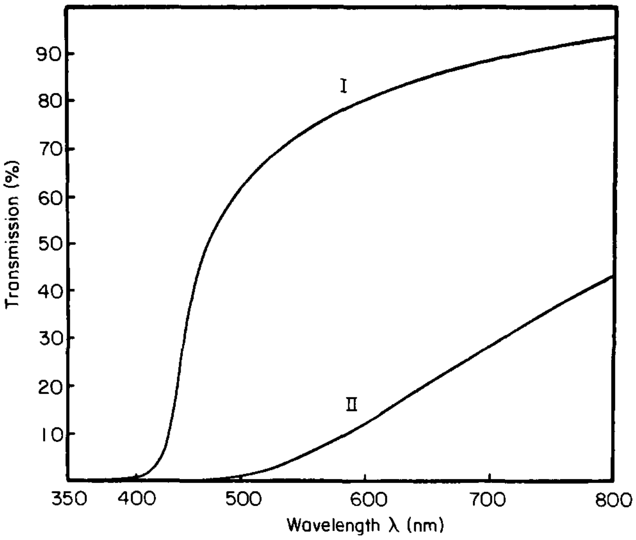


Figure 7 Transmission spectra of polymers I and II

publication[4] for polymer thin films of I and II showed that these polymers possess the structure of aggregated globules as shown in *Figures 5* and *6*. In the case of polymer I a crystal lattice of (penta- and hexagonal) inter-structure was found in its globules. (ii) The replacement of the rigid benzene moiety in polymer I by the long aliphatic sequence could result in a localized, excitonic, excited state on the conjugated segment of polymer II. This leads to the broadening of localized states and decreasing of the optical band gap.

It is important to indicate that the behaviour of the optical absorption process of polymers I and II is similar to that which occurs in polydiacetylene polymers, because both have conjugated segments in their backbones.

Moreover, the transition spectra of polymers I and II (*Figure 7*) indicate that the transmission (T%) tends to zero at 400 and 500 nm for polymers I and II respectively. These results show that both polymers can be used as u.v. shielding materials.

CONCLUSIONS

Two newly synthesized polyester polymeric films were prepared by the casting technique. Analysis of the measured data on absorption coefficient as a function of photon energy gives a good fit to the 'Tauc' model $(\alpha\hbar\omega)^{1/2} = B^{1/2}(\hbar\omega - E_g^{opt})$. This indicates that both polymers I and II possess an indirect optical band gap. The values of the slope $B^{1/2}$ and the band gap E_g^{opt} were calculated above and below an energy referred to as E_0. The excitons associated with the conjugated segments play an important role in the optical absorption process.

The results show that these low-cost polymers are promising as u.v. shielding materials.

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