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Gamma-irradiation effects on the structural and electrical properties of poly(2,6-dimethyl-1,4-phenylene oxide)

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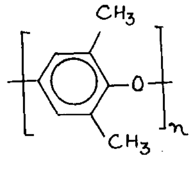
Post-irradiation studies on poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) have been carried out to elucidate the effects of γ-radiation on the electrical conduction mechanism. Irradiation was performed in air at room temperature by use of a ^{60}Co γ source at different dosages. The electrical conductivity of PPO was studied in a metal/polymer/metal sandwich configuration in the temperature range of 298–353 K and the applied voltage range of 100–2000 V. No change in the conduction mechanism was observed when compared to unirradiated PPO. However, the magnitude of the current gradually decreased from 3.6×10^{-12} A for unirradiated PPO to 6.5×10^{-13} A for the sample irradiated with the maximum dose (0.60 MGy). The irradiated PPO has been characterized for its chemical structural changes using wide-angle X-ray diffraction, differential thermal analysis, high-performance liquid chromatography and Fourier-transform infra-red (*FT*i.r.) spectroscopy techniques. A degradation mechanism is postulated based on *FT*i.r. results. The dose-dependent changes in electrical conduction have been discussed on the basis of decrease in average molecular weight and changes in the chemical structure of PPO.

(Keywords: poly(dimethyl phenylene oxide); gamma-irradiation effects; electrical properties)

INTRODUCTION

Ionizing-radiation-induced changes in high-performance polymers are of continuing interest because of the utility of these materials in the field of nuclear energy and aerospace technology, where potential exposure to high-energy radiation such as electrons, protons and gamma-radiation exists[1–3]. In this context high-performance engineering polymers with aromatic rings in the main chain are comparatively more resistant to radiation damage[2]. However, under long-term exposure to ionizing radiation, these polymers also degrade. Depending on the radiation environment conditions, particularly the temperature and the radiation dose, they typically undergo chain scission, sometimes with simultaneous crosslinking, leading to progressive reduction in molecular weight and eventual degradation to non-polymeric materials[2–9]. These characteristic chemical structural changes lead to extensive modifications in their mechanical and electrical properties. Thus, the radiation-induced degradation mechanism and its effect on these properties in such polymers is a subject of prime importance and concern.



PPO

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with the repeat unit shown is a high-performance engineering plastic ($T_g = 483$ K) with strength, clarity, heat resistance and dimensional stability. In spite of being an engineering polymer, little information has so far been reported on radiation-induced degradation in PPO. The reported resultant degradation of PPO is manifested by the deterioration of mechanical properties, particularly decrease in tensile strength and elongation[9,10]. On the other hand, the mechanisms of the thermal oxidation and u.v. photo-oxidation of PPO have been reported extensively. The oxidation of PPO results in the evolution of carbon dioxide and traces of hydrogen, with the introduction of considerable crosslinking[2,11,12].

Electrical conduction in pristine and doped PPO films has been reported by the present authors[13,14] in an attempt to understand the charge transport mechanism. However, to our knowledge no studies on the effects of γ-radiation on the electrical conduction behaviour of PPO have been reported.

In the present paper we report on the investigation of electrical conduction in γ-irradiated PPO. The main objective is to study the electrical conduction mechanism in irradiated PPO and to relate this to concurrent changes in molecular structure. The post-irradiated PPO samples have been characterized for structural changes by wide-angle X-ray diffraction (WAXD),

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high-performance liquid chromatography (h.p.l.c.) and Fourier-transform infra-red (*FT*i.r.) spectroscopy.

EXPERIMENTAL

Materials and sample preparation

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) of molecular weight 100 000 obtained from Aldrich, USA, was used in this study. Thin films of thickness 70 ± 2 nm were prepared using spectral-grade chloroform as solvent. Evaporation of the solvent was accomplished by exposing the solutions to the atmosphere for 24 h. Further, films were subjected to vacuum drying for 12 h to remove any remaining traces of solvent. The film was then cut into pieces of appropriate size for irradiation.

Irradiation

Irradiation was performed using a ^{60}Co γ source (gamma cell type 900) installed at Bhabha Atomic Research Centre (BARC), Bombay. The dose rate was 3.2 kGy h^{-1}. The films kept on open tubes were irradiated in air at room temperature. Except for the *FT*i.r. spectral measurements, these irradiated specimens were used for electrical conduction measurements and other characterization experiments. A separate thin film (30 ± 2 nm) was cast and irradiated for infra-red spectral studies.

Characterization

Wide-angle X-ray diffraction. X-ray diffraction of the samples was measured on a Philips model PW-1710 diffractometer using Ni-filtered Cu Kα radiation. The specimens were films and were mounted gently on the film holder. All the diffractograms were recorded under identical instrumental conditions of power level, amplifier gain and collimated slit widths, and were scanned from an angle of $2\theta = 5°$ to $2\theta = 35°$ at constant speed of 1° min^{-1}.

Differential thermal analysis. Differential thermal measurements were performed using a Stanton Redcroft model STA-780 differential thermal analyser. Samples (15 mg) cut from the irradiated samples were analysed for their glass transition temperature by heating from 20 to 230°C at a heating rate of 2°C min^{-1} under a nitrogen atmosphere. The glass transition temperature was located at the mid-point of the step change in the thermogram.

Molecular-weight determination. A high-performance liquid chromatograph (h.p.l.c.) unit from Waters Associates, USA, was employed for the determination of the molecular weight ($\bar{M}_n$) of irradiated samples. Chloroform and polystyrene (ranging from 50 000 to 200 000 in molecular weight) were used as solvent and standard, respectively, in these experiments.

Fourier-transform infra-red spectral measurements. The *FT*i.r. spectra were recorded on an IFS-88 Bruker *FT*i.r. spectrometer equipped with a DTGS (deuterated triglycine sulfate) detector and Ge/KBr beam splitter. Spectra were recorded in absorbance mode with a resolution of 2 cm^{-1}. The samples were cut for irradiation from a specially prepared master PPO film of 30 ± 2 nm uniform thickness showing nearly 80% transmission at 2.5 nm. A minimum of 100 scans were signal-averaged, keeping identical instrumental parameters for each spectrum.

Electrical conductivity measurements. For electrical conductivity measurements, metal electrodes were deposited (at 10^{-3} Torr vacuum) with suitable masks on the polymer films, so as to form a metal/polymer/metal sandwich structure (of 1 cm^2 cross-section) by thermal evaporation of spectroscopically pure aluminium (99.999% pure, Merck). Further contacts were made by bonding copper leads to the metal films by means of an air-drying silver paint. The actual temperature, with ±1 K variation, of the sample was measured with a calibrated copper–constantan thermocouple attached to a digital temperature indicator (Naina model NT 503). The d.c. voltages across the sample were fed from a highly regulated power supply (ECIL, India). The steady-state values of the current in the circuit were measured by means of a Keithley electrometer (model 610 C).

RESULTS AND DISCUSSION

The X-ray diffraction patterns of γ-irradiated films are identical to that of an unirradiated film, and show none of the reflections due to crystalline PPO[14]. The absence of characteristic crystalline peaks at 8°, 13° and 22° (ref. 15) indicates no irradiation-induced crystallization. Furthermore, except for the 0.15 MGy dose, the area under the diffraction peak profiles decreases rapidly with increase in the dose (*Figure 1*). This indicates the loss of scattering unit groups in post-irradiated PPO.

Figure 2 presents a plot of the glass transition temperature (T_g) of the irradiated samples as a function of radiation dose. It is observed that the T_g of PPO decreases from 484 K to 465 K at maximum dose (0.60 MGy). However, initially, at 0.15 MGy the PPO shows an increase in T_g (491 K). This low-dose behaviour could be understood in terms of branching and then crosslinking (equation (3)). However, the very small

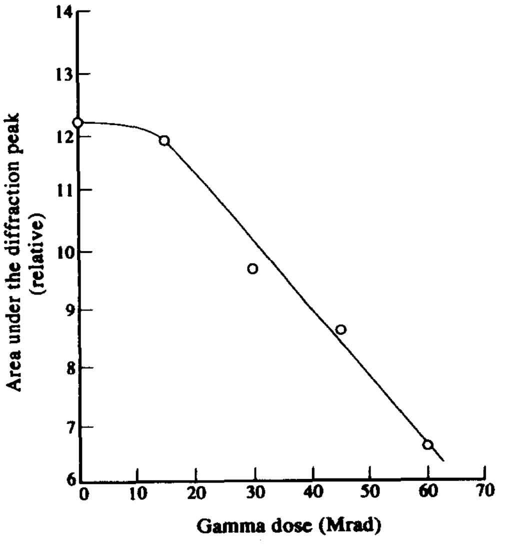


Figure 1 Variation of area under the X-ray diffraction peak profile as a function of radiation dose

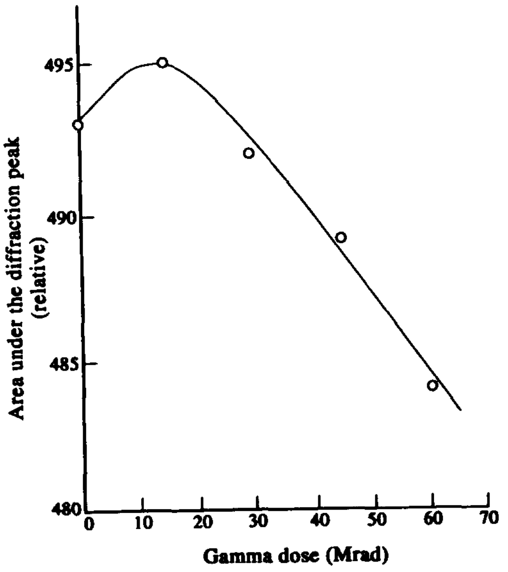


Figure 2 Variation of T_g as a function of radiation dose

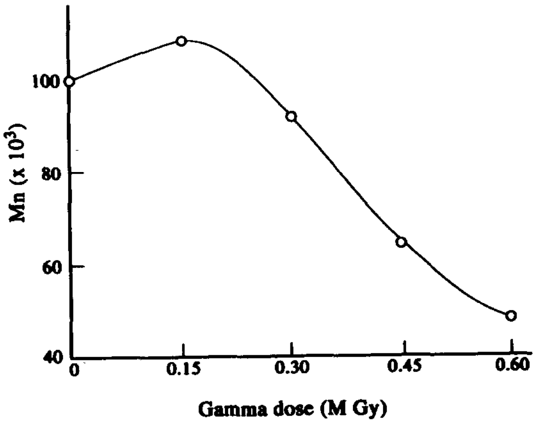


Figure 3 Degradation in molecular weight ($\bar{M}_n$) as a function of radiation dose

decrease in the area under the WAXD peak profile for 0.15 MGy dose also indicates the possibility of initiation of chain scission (equation (1)). The further decrease in T_g with increasing dose (0.15 MGy) implies random chain scission (equation (1)); as a result, average molecular weight decreases and free volume increases[16]. The progressive decrease in molecular weight with increasing radiation dose (*Figure 3*) illustrates considerable degradation through main-chain cleavage (equation (1)) in irradiated PPO.

*FT*i.r. spectroscopy is an excellent method for detection of probable molecular sites affected by irradiation in polymers. Degradation products are generally shown by the appearance of new absorption bands, whereas the formation of gaseous products evolved should always be reflected in changes in intensity of certain bands[17].

In irradiated PPO, the absorption bands at 2960, 2921 and 2842 cm^{-1} (C–H stretch in CH$_3$), 1306 cm^{-1} (C–CH$_3$ stretch) and 1188 cm^{-1} (–C–O–C– stretch) have been found to be reduced in intensity (*Figure 4a*). In addition, two new radiation-induced absorption bands have emerged at 3642 and 1702 cm^{-1} (*Figure 4b*).

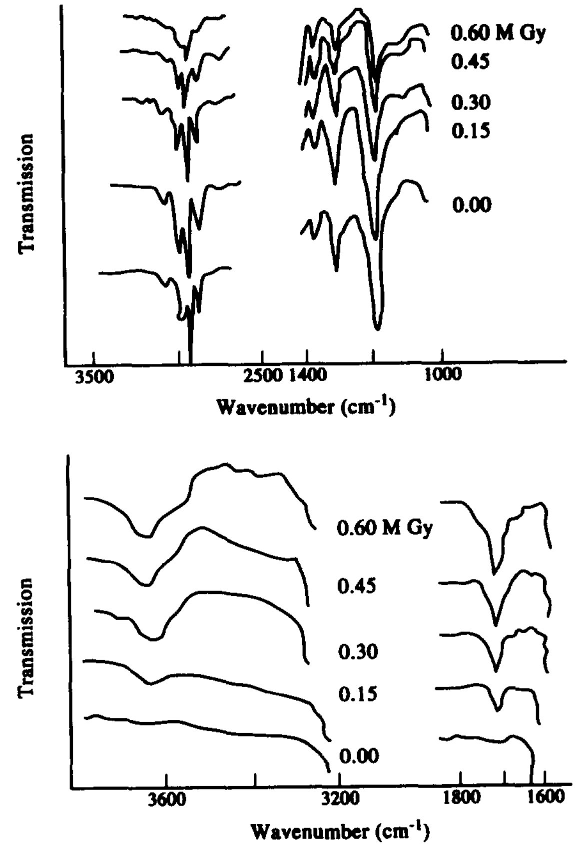


Figure 4 *FT*i.r. spectra of irradiated PO in (a) the 3200–2800 cm^{-1} (C–CH stretch in CH$_3$) and 1300–1000 cm^{-1} (C–CH$_3$ stretch and –C–O–C– stretch) regions, and (b) the 3680–3200 cm^{-1} (O–H stretch) and 1850–1600 cm^{-1} (C=O stretch) regions

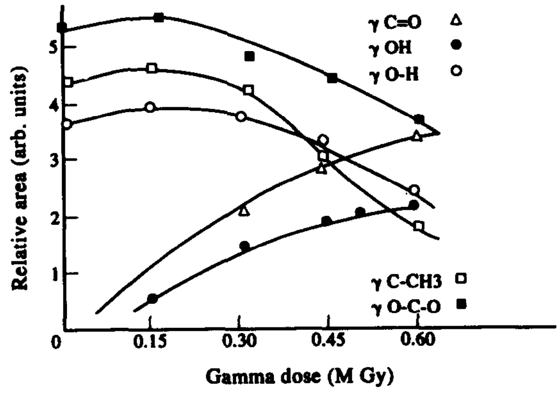


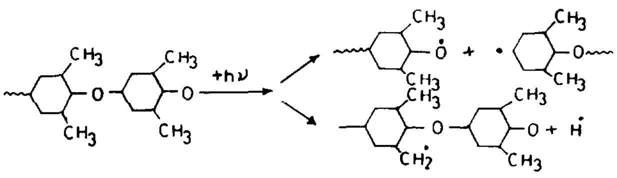
Figure 5 Variation of area under the i.r. absorption bands as a function of radiation dose

The area under the band profile at 3680–3265 cm^{-1} is a function of radiation dose (*Figure 5*), and appears even at low dose. This indicates the production of stable phenoxy end-groups (equation (5)). In this broad band profile the indication of the presence of free (3642 cm^{-1}) and bonded (3562 cm^{-1}) hydroxyl stretching suggests monomeric and dimeric materials (equation (5)). Similarly the gradual appearance of a band at 1702 cm^{-1} (*Figure 5*) indicates carbonyl-containing degradation products; this band also turns into a broad band profile with increasing irradiation dose. This gradual increasing broadness in the 1702 cm^{-1} band may be due to different types of carbonyl-containing degradation products (equation (7)), particularly for high-dose irradiation.

The area under the 3642 and 1702 cm^{-1} band profiles increases with increasing irradiation dose (*Figure 5*).

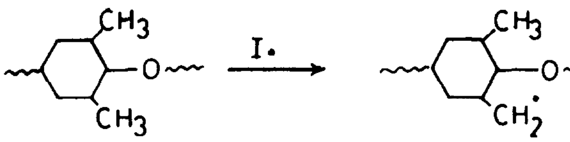
The absorption bands at 2960, 2921 and 2842 cm^{-1} involving methyl group vibrations exhibit gradual decrease in band profile areas in irradiated PPO (*Figure 4a*). This can be attributed to abstraction of hydrogen from methyl groups (equation (5)). Similarly the reduction in the 1188 cm^{-1} band profile area, which corresponds to –C–O–C– motions in PPO, and, as mentioned earlier, the emergence of the hydroxyl stretch band, suggest the gradual rupture of the –C–O–C– linkage. This subsequently leads to chain scission and ultimately leads to formation of alcohol and aldehyde degradation products (equation (7)).

On the basis of *FT*i.r. analysis, supported by WAXD and d.t.a. observations, the radiation-induced chemical structural changes in post-irradiated PPO films are postulated as follows. Photolysis of PPO occurs with scission of the main chain:



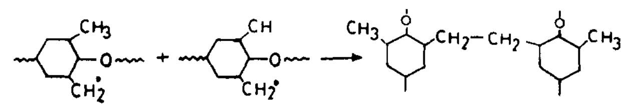
(1)

The photo-reaction propagates via initiator radicals:



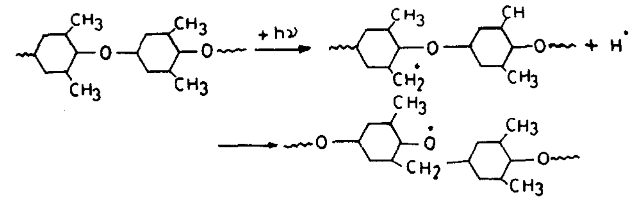
(2)

These polymeric radicals further continue the chain scission process in the material or cause crosslinking:



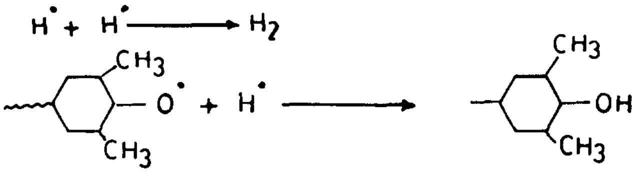
(3)

In the absence of crosslinking, photo-reaction results in the formation of stable benzyl radicals with abstraction of hydrogen:



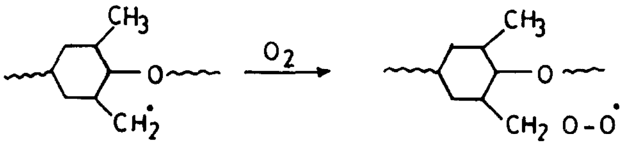
(4)

Hydrogen radicals react with one another or also with polymer radicals, resulting in the formation of photoproducts:



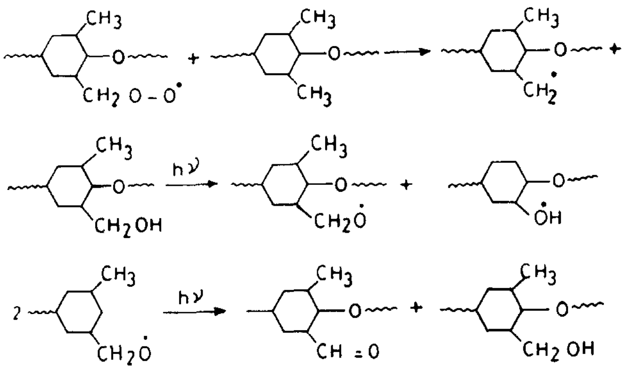
(5)

Then the formed polymer radicals undergo photooxidation:



(6)

resulting in aldehydic and alcoholic degradation products:



(7)

The electrical conduction mechanism of pristine PPO films has been discussed in detail previously[13], but is summarized here for convenience. In PPO, there are two distinct regions of conduction: region I at low fields suggests ohmic conduction; and region II is attributed to non-ohmic conduction. It is observed that with increasing temperature there is a decrease in the non-ohmicity of the *I*–*V* characteristics. It has also been argued that the high-field non-ohmic conduction is governed by space-charge-limited currents.

The *I*–*V* characteristics of γ-irradiated PPO films having thickness 70 ± 2 nm obtained at a fixed temperature (298 K) but for different doses of γ-radiation are shown on a log–log plot in *Figure 6*. Curves 1 to 5 in *Figure 6* correspond to γ-radiation doses of 0, 0.15, 0.30, 0.45 and 0.60 MGy, respectively. From a comparison of curve 1 with curves 2 to 5 it is observed that the general feature of the *I*–*V* characteristics of pure as well as γ-irradiated PPO films are the same but the magnitude of the current depends on dosage. The *I*–*V* curves show two distinct regions corresponding to two different types of

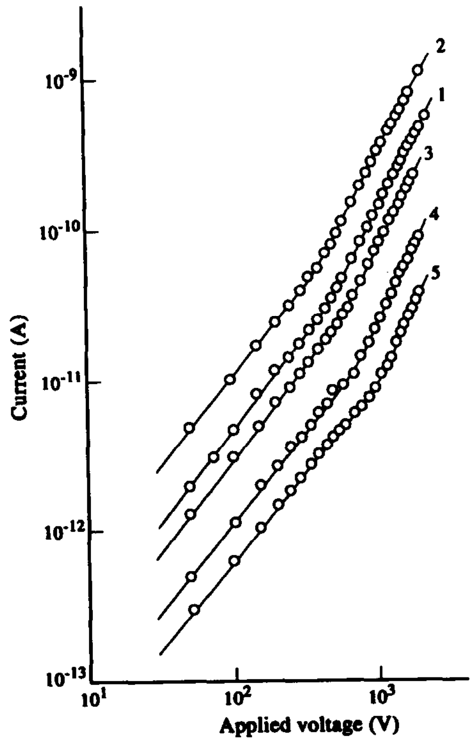


Figure 6 I–V characteristics of gamma-irradiated PPO films at 298 K: curves 1 to 5 correspond to gamma dose of 0, 0.15, 0.30, 0.45 and 0.60 MGy respectively

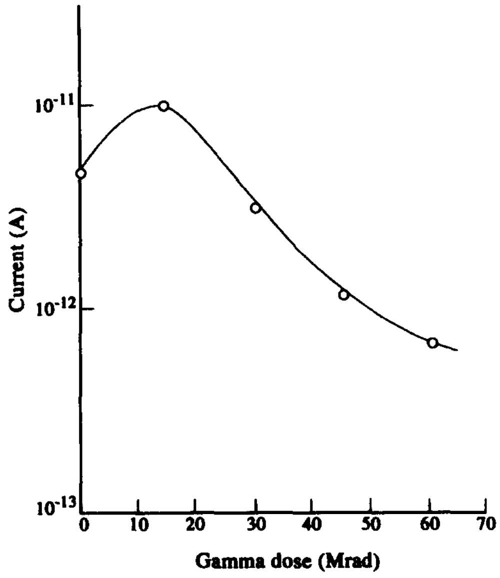


Figure 7 Variation of current (I), for a bias of 100 V, as a function of radiation dose

conduction, that is, ohmic and non-ohmic conduction similar to unirradiated PPO. The transition voltage, V_{trans}, which separates these two regions, is found to increase with increasing radiation dose except in the case of the low dose of 0.15 MGy. It decreases for 0.15 MGy radiation dose. For a bias of 100 V, the variation in the current with radiation dose is shown in *Figure 7*. It is observed that the current magnitude increases from 3.6×10^{-12} A to 1.0×10^{-11} A initially for 0.15 MGy radiation dose; however, finally it decreases to 6.5×10^{-13} A with subsequent increase in irradiation dose.

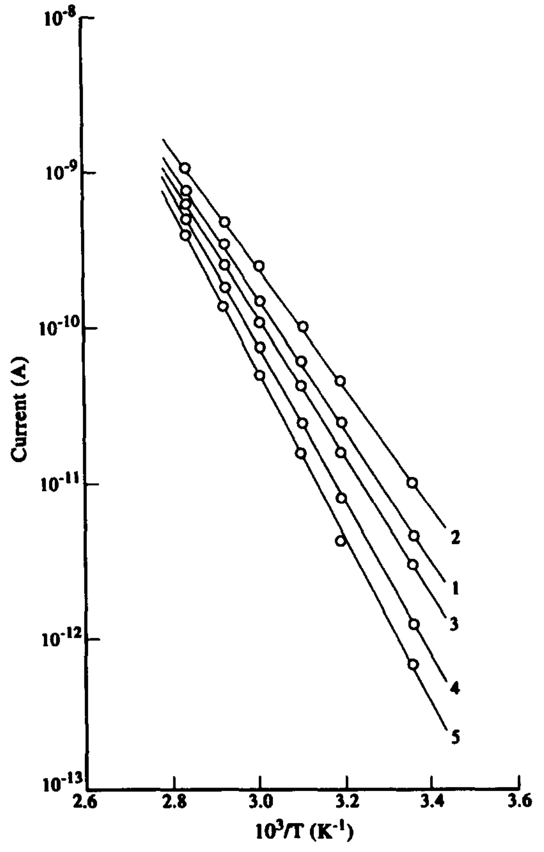


Figure 8 Log I vs. $1/T$ plots of gamma-irradiated PPO films at fixed bias (100 V): curves 1 to 5 correspond to 0, 0.15, 0.30, 0.45 and 0.60 MGy respectively

In order to understand the effect of γ-irradiation on the activation energy of the charge carriers responsible for conduction in PPO films, a plot of log I *versus* $1/T$ for a fixed bias of 100 V is presented in *Figure 8*. The values of activation energies evaluated from the slopes of these linear plots are plotted against the corresponding doses in *Figure 9*. It can be seen from *Figure 9* that initially activation energy decreases from 0.81 eV to 0.77 eV for 0.15 MGy and then gradually increases up to 1.07 eV for the maximum radiation dose of 0.60 MGy.

PPO has enhanced conjugation between neighbouring phenyl groups through the ether bond and thereby extended electron delocalization along the polymer chain. The random molecular-weight degradation due to cleavage of the methyl groups (equations (1) and (2)) and then main-chain ether bond scission (equation (4)) results in the formation of a semi-isolated polynuclear system distributed throughout the material. The evolution of hydrogen as a gaseous product (equation (5)) may result in voids in irradiated material. Such radiation-induced isotropic structural changes in PPO generate short-distance isolated structural ordering and non-planarity. This disturbs the original effective π-orbital overlap within the PPO, which ultimately decreases the overall resultant conjugation length in irradiated PPO. Such disorder in irradiated PPO results in hindrance to charge mobility along the segments of conjugated unirradiated PPO. This subsequently results in hindered intra-chain transport carrier hopping. Thus, the

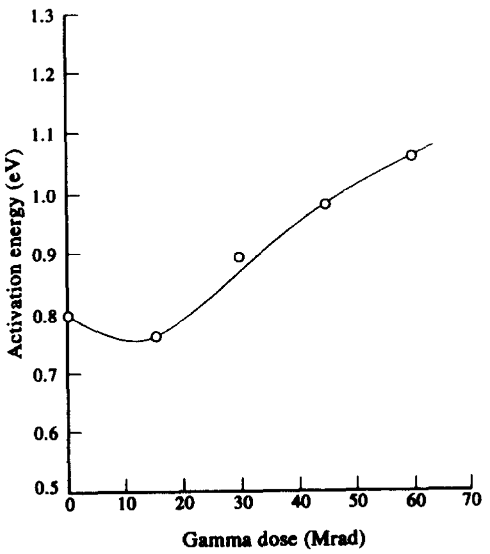


Figure 9 Variation of activation energy as a function of radiation dose

enhanced activation energy of conduction with increasing radiation dose is due to increased temporal fluctuations in the charge hopping distance. Such post-irradiation structural changes in PPO control the electrical conduction in irradiated PPO, which decreases with increase in radiation dose.

However, the initial rise in conductivity and fall in activation energy at low radiation dose level (0.15 MGy) may be due to the formation of low crosslinked regions (equation (3)). These are caused by recombination of macroradicals formed as a result of the action of radiation on PPO chains and ultimately increase the molecular weight. However, with increasing radiation dose, finally the reaction of oxygen (equation (6)) with these macroradicals results in rupture of the polymer chain into smaller fragments and thereby decrease in the molecular weight.

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