

# Arylidene Polymers. VI. Gamma Irradiation Effects on the Electrical Conductivity Behavior, IR Absorption Spectra, and DSC Measurements of Some New Synthesized Poly(arylidene-cycloalkanones)

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## SYNOPSIS

Gamma irradiation effects on the electrical conductivity behavior of some new synthesized poly(2,5-arylidene-cyclopentanone) **1**, poly(2,6-arylidene-cyclohexanone) **2**, and their copolymers **3**, have been investigated. Thermal studies over the temperature range 300–500 K showed that the conductivity behavior follows a two-term Arrhenius-type equation. The first term has a small activation energy and predominates at lower temperature (extrinsic region), and the second term with higher activation energy predominates at higher temperatures (intrinsic region). Change in the activation parameters with the change in the  $\gamma$ -ray dose and the nature of the polymers are discussed. The IR absorption spectra showed a decrease in the intensity of most bands of the  $\gamma$ -irradiated samples. A mechanism based on the formation of trapped free radicals and their recombination has been suggested. DSC measurements indicated that the crystallization and the melting temperature transitions decreased in size considerably with the increase in the  $\gamma$ -ray dose until they nearly disappeared at higher  $\gamma$ -ray dose.

## INTRODUCTION

Radiation effects in solids are broadly characterized as are those that are primarily crystallographic structural defects and those that are chemical in nature. The predominant type of damage will depend to a large measure on the material and on the source of radiation. Electrical properties of solids are among the most important properties sensitive to radiation damage. There are several electrical property measurements that can be made and are of value to the radiation chemist. However, of these, there are only two that are tractable: the conductivity and the photoconductivity. These measurements give a very good indication of the number of free charge carriers able to transfer energy to the surrounding molecules.<sup>1-3</sup>

In recent years there has been great interest in studying the electrical properties for polymeric sys-

tems due to the observation that their electrical conductivities can vary with the change in their chemical and crystal structure. The electrical properties of these compounds are also sensitive to a number of variables such as type of irradiation, impurities, and doping with foreign ions.<sup>4-8</sup>

In the present work,  $\gamma$ -irradiation effects on the electrical properties of new synthesized poly(arylidene-cycloalkanones) i.e., poly(2,5-arylidene-cyclopentanone) **1**, poly(2,6-arylidene-cyclohexanone) **2**, and their copolymers **3** have been investigated. To gain information on the type of charge carriers and the mechanism of their migrations in these types of polymers, the IR absorption spectra and DSC measurements of unirradiated and gamma-irradiated samples of the investigated polymers are evaluated and discussed.

## EXPERIMENTAL

The polymers investigated in the present study are poly(2,5-arylidene-cyclopentanone), poly(2,6-ary-

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lidencyclohexanone), and their copolymers. They were prepared and purified as reported in our previous work.<sup>9</sup> Polymer samples in the form of circular discs with a diameter of 13 mm and a thickness of 1.2 mm were used for electrical conductivity measurements. These discs were made by using an IR die at a constant pressure of 1000 psi. Two standard graphite electrodes were contacted to the surface of polymer samples and then mounted onto a designed temperature-controlled electric furnace provided with a standard copper/constantans thermocouple.

Conductivity has been measured over the temperature range of 300–500 K using a Keithley 610 C Electrometer. The IR spectra were recorded on a Pye Unicam SP3 100 Spectrophotometer by using the KBr pellet technique. Differential scanning calorimetry (DSC) was carried out in air with DuPont models 951 and 910 and DuPont 1090 thermal analyzer at a heating rate of 10°C/min. For  $\gamma$ -irradiation, the samples were kept in small glass containers and irradiated for different irradiation times using a CO-60 Gamma Cell having a dose rate of 1.1 Gys<sup>-1</sup> measured by a Frinckes dosimeter.<sup>10</sup>

## RESULTS AND DISCUSSION

The effects of  $\gamma$ -irradiation on the electrical conductivities and  $\sigma$  of the unirradiated and gamma-irradiated samples with different  $\gamma$ -ray doses at ambient (300 K) are listed in Table I. The results show that the electrical conductivity increases with increasing absorbed  $\gamma$ -ray dose for the three types of

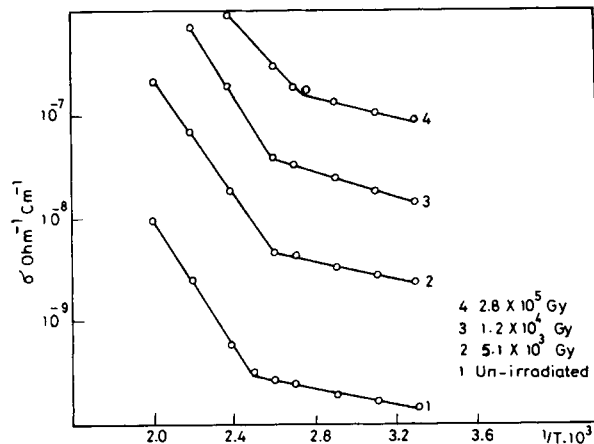


Figure 1 Arrhenius plots of poly(2,5 arylidenecyclopentanone) polymer.

arylidenecycloalkanone polymers. This behavior may be attributed to the formation of impurity centers, e.g., low molecular weight units, trapped in the crystals. These impurity centers act as donor levels, giving rise to the increase in the number of free charge carriers and, hence, in the conductivity. In some cases, a relation between the electrical conductivity of the unirradiated sample ( $\sigma$ ) and that for irradiated one ( $\sigma_i$ ) has been given by the equation

$$\text{Log } \frac{\sigma}{\sigma_i} = a \cdot D$$

where  $D$  is the  $\gamma$ -ray dose and  $a$  is a constant. The values of the constant are calculated according to

Table I Electrical Conductivities at Ambient, 300 K, and at 500 K of Some New Synthesized Poly(arylidenecycloalkanone) Polymers Irradiated to Different  $\gamma$ -Ray Doses

Type of Polymer	$\gamma$ -Ray Dose (Gy)	Electrical Conductivity ( $\sigma$ ) (ohm <sup>-1</sup> cm <sup>-1</sup> )	
		300 K	500 K
Poly(2,5 arylidene-cyclopentanone)	$2.8 \times 10^5$	$8.2 \times 10^{-8}$	$1.2 \times 10^{-4}$
	$1.2 \times 10^4$	$1.3 \times 10^{-8}$	$6.2 \times 10^{-5}$
	$5.1 \times 10^3$	$2.4 \times 10^{-9}$	$1.9 \times 10^{-6}$
	Unirradiated	$1.4 \times 10^{-10}$	$8.5 \times 10^{-8}$
Poly(2,6 arylidene-cyclohexanone)	$2.8 \times 10^5$	$7.5 \times 10^{-8}$	$2.4 \times 10^{-4}$
	$1.2 \times 10^4$	$3.2 \times 10^{-8}$	$8.5 \times 10^{-5}$
	$5.1 \times 10^3$	$5.4 \times 10^{-9}$	$3.2 \times 10^{-6}$
	Unirradiated	$3.4 \times 10^{-10}$	$9.2 \times 10^{-8}$
Copolymer	$2.8 \times 10^5$	$4.3 \times 10^{-7}$	$3.2 \times 10^{-3}$
	$1.2 \times 10^4$	$5.4 \times 10^{-8}$	$7.1 \times 10^{-4}$
	$5.1 \times 10^3$	$7.8 \times 10^{-9}$	$2.7 \times 10^{-5}$
	Unirradiated	$1.2 \times 10^{-9}$	$1.2 \times 10^{-7}$

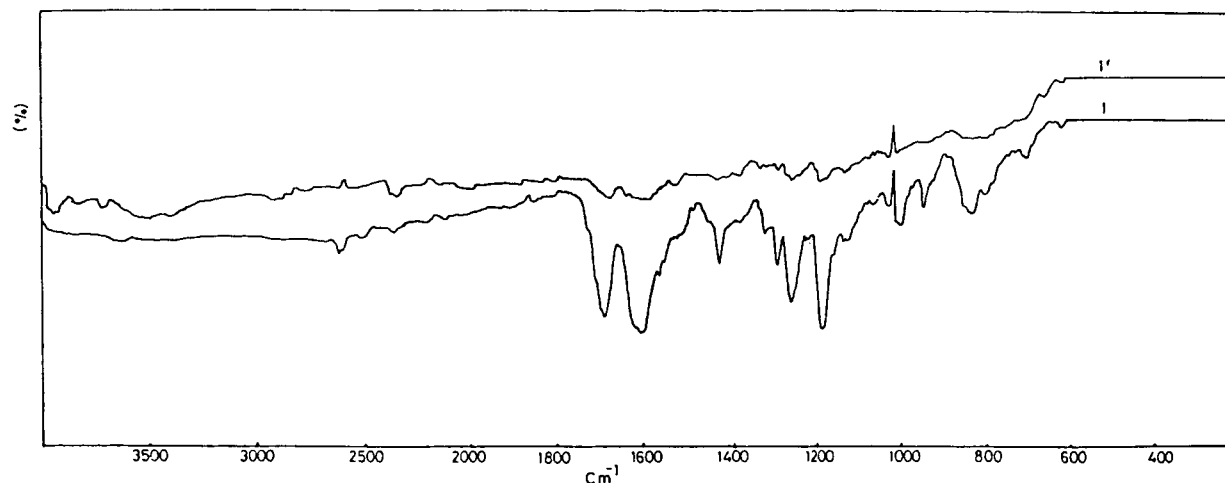
**Table II** Kinetic Data in the Temperature Range 300–500 K for Poly(arylidene-cycloalkanone) Polymers

Type of Polymer	$\gamma$ -Ray Dose	Activation Energy (eV)	
		Extrinsic Region	Intrinsic Region
<b>1</b> Poly(2,5 arylidene-cyclopentanone)	$5.1 \times 10^3$	0.85	1.91
	$1.2 \times 10^4$	0.86	1.95
	$2.8 \times 10^5$	0.91	1.98
	Unirradiated	0.81	1.85
<b>2</b> Poly(2,6 arylidene-cyclohexanone)	$5.1 \times 10^3$	0.81	1.91
	$1.2 \times 10^4$	0.77	1.92
	$2.8 \times 10^5$	0.75	1.95
	Unirradiated	0.75	1.94
<b>3</b> Copolymer	$5.1 \times 10^3$	0.93	1.97
	$1.2 \times 10^4$	0.91	1.91
	$2.8 \times 10^5$	0.88	1.87
	Unirradiated	0.85	1.82

this equation for the systems under investigation and indicate that these polymers are not convenient as  $\gamma$ -ray dosimeters.

The temperature dependence of the electrical conductivity  $\sigma$  of the unirradiated and preirradiated samples of poly(arylidene-cycloalkanone) polymers with different  $\gamma$ -ray doses have been studied in the temperature range 300–500 K. The results showed that the conductivity increases with increasing temperature for both the unirradiated and the gamma-irradiated samples (see Table I). The  $\ln \sigma$  vs.  $1/T$  plots in Figure 1 showed that the conductivity behavior follows a two-term Arrhenius-type equation. The first term has a small activation energy and

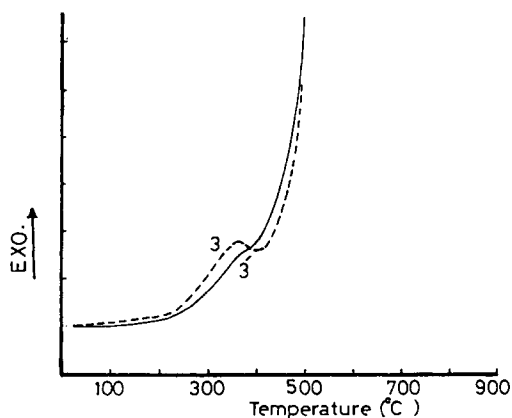
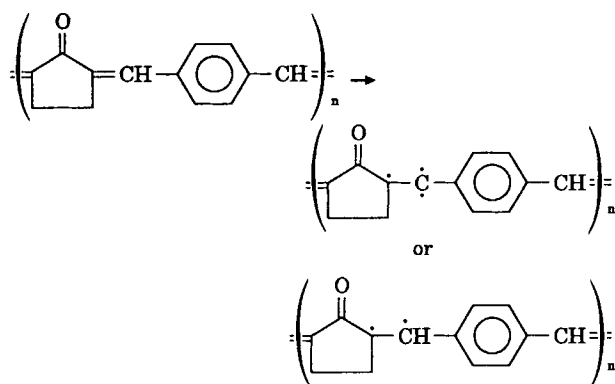
predominates at lower temperature (extrinsic region) below 400 K, and the second term with a higher activation energy predominates at higher temperature (intrinsic region) above 400 K. These results indicate that the samples contain two kinds of impurity centers with different activation energies. The first type anneals at a fast rate during thermal heating of samples and is due to thermal recombination of electrons characterized by a low activation energy ( $< 1$  eV). The second type of electronic impurities anneal at a slow rate, and the activation energies are associated with a lower impurity content and represent a higher probability of having electrons being excited from levels of the perfect lattice (pure



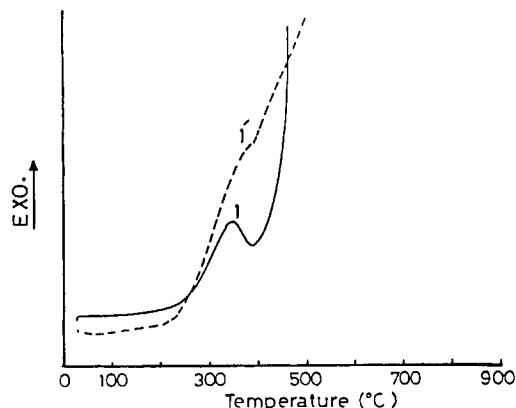
**Figure 2** IR absorption spectrum of unirradiated sample 1 and irradiated sample 1' with  $\gamma$ -ray dose  $2.8 \times 10^5$  Gy.

crystals).<sup>11</sup> However, in the present study, it is possible that the mechanism of migration of charge carriers change from electronic conduction at lower temperature to ionic conduction at higher temperature. The activation energy values calculated from the least-squares method for the unirradiated and irradiated samples are listed in Table II.

The infrared absorption spectra of the investigated sample before and after  $\gamma$ -irradiation showed the characteristic absorption bands expected in these types of polymers. Neither change in frequency of the absorption band nor the appearance of new bands have been noticed as a result of  $\gamma$ -irradiation, but a sharp decrease in the intensity of most bands took place. A typical IR spectrum of poly(2,5-arylidencyclopentanone) polymer before and after  $\gamma$ -irradiation with total  $\gamma$ -ray dose ( $2.8 \times 10^5$  Gy) is shown in Figure 2. The degradation of the C=C bonds of the investigated polymers leads to the formation of trapped free radicals as follows:



**Figure 3** DSC of unirradiated copolymer sample **3** (---) and irradiated copolymer **3'** (—) with  $\gamma$ -ray dose  $1.2 \times 10^4$  Gy.



**Figure 4** DSC of unirradiated polymer sample **1** (—) and irradiated sample **1'** (---) with  $\gamma$ -ray dose  $2.8 \times 10^5$  Gy.

The free radicals formed are enclosed in the Frank-Robinowitch "cage" and, consequently, are likely to react with each other.<sup>1</sup>

Differential scanning calorimetry (DSC) measurements were made on several of the irradiated samples, and the results are shown in Figures 3 and 4. Before irradiation, the polymer samples were amorphous and show the characteristic transitions observed in such samples as crystallization  $T_c$  and melting  $T_m$ . As the irradiation proceeded, the two temperature transitions decreased in size considerably until they were completely gone when the dose was up to  $2.8 \times 10^5$  Gy. Figure 3 showed that the decrease in size of both  $T_m$  and  $T_c$  was typically represented by copolymer **3**, and the near disappearance of  $T_c$  and  $T_m$  transitions is consistent with poly(2,5-arylidencyclopentanone) **1**. It should be also noted that irradiation by  $\gamma$ -ray doses is reported<sup>12,13</sup> to cause curing reactions involving the olefinic bonds. Our DSC and IR results are in agreement with those reported.<sup>12-15</sup>

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