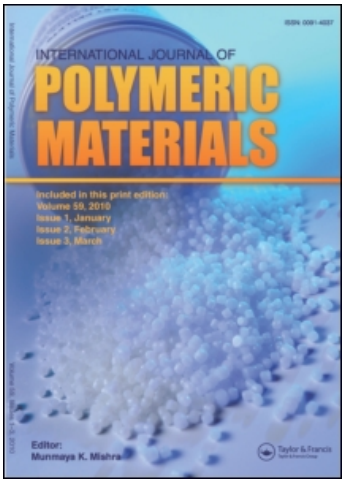

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Effect of γ-Irradiation on the Electrical Properties of Poly(Methyl Methacrylate) Doped with Some Transition Metal Complexes

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The electrical resistivity (ρ) of pure and doped poly(methyl methacrylate), PMMA, with dithizone (HDZ) and its metal complexes, $Zn(HDZ)_2$, $Cd(HDZ)_2$ and $Hg(HDZ)_2$ has been investigated before and after γ-irradiation. The results show a phase transition at nearly 323°K. The activation energy of the conduction process has been calculated below and above the transition temperature. Further information concerning the electrical behaviour is obtained by considering the type and mechanism of the conduction process. This has been achieved by studying the effect of temperature and γ-irradiation on the mobility and the number of charge carriers which take part in the conduction process.

Keywords: γ-irradiation; electrical properties; poly(methyl methacrylate)

INTRODUCTION

The increasing interest in the field of polymer science lead to the use of electrically conductive polymers as a materials for electromagnetic shielding [1], antistatic electricity [2], preparation of conducting discs for information storage [3], and thermoelectric switching.

In recent years there has been a great interest for studying the electrical properties of some polymers doped with inorganic transition

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metal complexes due to the observation of variety of its electrical conductivity with the change in valency of the transition metal ions, and type of its chemical and crystal structure. Although there are many studies on the effect of γ-irradiation on the polymer structure, very little has been reported on poly(methyl methacrylate) doped with metal dithizonates [2].

The present study was carried out to investigate the effect of γ-irradiation on the electrical resistivity of PMMA doped with dithzone and its complexes with the isoelectronic cations nd [10], where $n = 3, 4, 5$ for Zn, Cd and Hg. Also to get idea about the structural changes due to γ-irradiation and conduction mechanism.

EXPERIMENTAL

The three metal complexes of HDZ were prepared by the method described in literature [3]. PMMA solution was prepared by dissolving 0.2 gm PMMA in 20 ml chloroform. Solutions of HDZ and its metal complexes 2×10^{-3} mol/L in chloroform were prepared and mixed with the PMMA solution in the ratio 1 : 1. The mixture were stirred well for 1 hour. Thin films were prepared by casting the solutions on a glass plated and lifted for about 24 h. Discs of 1.5–2.0 mm thickness and diameter 15 mm were obtained. The front faces of the discs were coated with silver paste to achieve good contact.

The cell used for electrical measurements was reported before [4], and the resistance was measured using a 600 B keithly type electrometer. The temperature was measured by a copper-constantant thermocouple placed close to the sample.

The samples were irradiated by a Co-60 source of chamber 4000 A represented at the National Centre for Irradiation Research and Technology. The dose rate is about 0.67 Mrad/h.

RESULTS AND DISCUSSION

The electrical resistivity (ρ) of the investigated samples were measured at 303°K and given in Table I. From this table it is interesting to note

TABLE I Electrical resistivity (ρ) of pure and doped PMMA with dithizone and its metal complexes at room temperature and at different doses

	$\rho\ \Omega.cm$ *at* $303°K$					
Samples \ *Dose in K.Gy*	*Non-irradiated*	50	100	150	200	300
PMMA-HDZ	1.93×10^{12}	1.01×10^{14}	1.05×10^{14}	1.05×10^{13}	1.05×10^{12}	0.65×10^{12}
PMMA-Zn$(HDZ)_2$	4.54×10^{14}	1.02×10^{14}	6.46×10^{13}	0.99×10^{13}	0.91×10^{12}	3.45×10^{12}
PMMA-Cd$(HDZ)_2$	1.75×10^{12}	1.72×10^{14}	6.59×10^{13}	0.98×10^{13}	0.58×10^{13}	0.70×10^{12}
PMMA-Hg$(HDZ)_2$	3.25×10^{12}	1.29×10^{14}	0.74×10^{13}	0.72×10^{13}	1.11×10^{12}	0.65×10^{12}
Pure PMMA	1.52×10^{13}	2.62×10^{12}	3.27×10^{12}	1.90×10^{12}	1.10×10^{12}	3.20×10^{12}

that the investigated samples posses electrical resistivity in the order of $10^{12}-10^{14}$ Ω.cm which lie in the range of insulators [5].

The data revealed that the treatment of PMMA with $Zn(HDZ)_2$ increases its electrical resistivity by about 10 times, whereas PMMA doped with HDZ, $Cd(HDZ)_2$ and $Hg(HDZ)_2$ showed a marked decrease in their electrical resistivity.

The electrical resistivity of the pure and doped PMMA irradiated with different doses namely 50, 100, 150, 200 and 300 K.Gy at room temperature are given in Table I and Figure 1. It is clear from this table that γ-radiation produces a decrease in the value of (ρ) for pure PMMA samples with the increase of radiation dose. On the other hand, the values of ρ for PMMA doped with HDZ and its metal complexes increases with increasing radiation dose up to 50 K.Gy and then decreases again with the increase of radiation dose. Thus gamma radiation produces two effects upon the electrical resistivity of doped PMMA. The first effect is the increase of ρ with increasing radiation dose up to 50 K.Gy. This can be explained according to Varley [6] who pointed out that, gamma rays produces atomic displacement. The

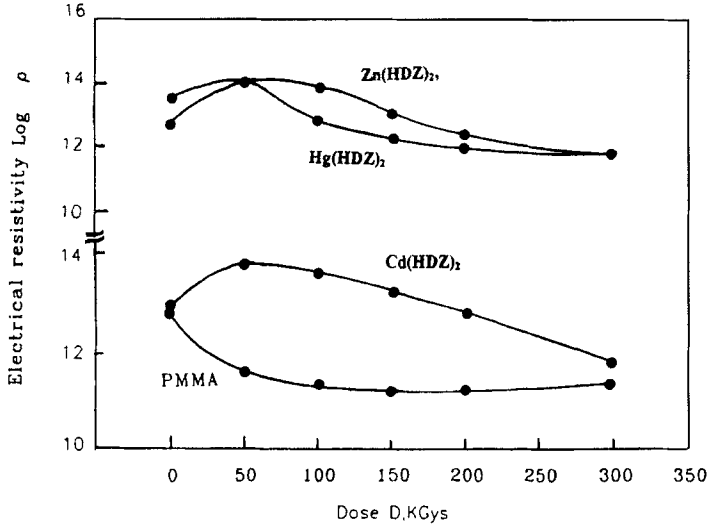

FIGURE 1 Relations between electrical resistivity log ρ and Dose D at room temperature.

primary effects are the production of electrons and positive vacancy in interstitial positions as well as negative vacancies due to the leaving of the positive ions from its normal lattice sites. The negative vacancies introduce impurity levels in the crystal lattice, which serve as a recombination centers for electrons and cause a decrease in the concentration of the free electrons. These trapped electrons lead to an increased scattering of the free electrons, which causes a considerable decrease in their mobility and subsequently increases the electrical resistivity.

The second and important effect appears after extended exposure higher than 50 K.Gy where a decreases in the values of ρ is observed. This decrease in ρ for the pure and doped PMMA is associated with the lattice damage.

Wertheim [7], noted that γ-rays can produce a compton electron, which has sufficient energy to displace an atom. This damage is uniform and extends to greater depth in the material.

Smith [8] observed that the lattice damage introduced by γ-radiation dose not, generally alter lattice parameters, bonding length, effective mass or over-all band structure, but damage is accompanied by vacancies and interstitial atoms which leads to additional energy levels. According to the above views, we can attribute the decrease in ρ to the formation of small size molecules which are generated by the degradation of the main chain of PMMA [9].

The principal problem for organic semiconductor is the charge transfer mechanism between different energy states. There are two types of conduction, the ionic and electronic conduction. The distinction between the two types represent a complex problem requiring more investigation about the electrical behaviour.

The experimental measurements made on all the investigated samples indicates that, there is no electrical polarization at the electrodes (*i.e.*, after releasing the potential there is no reversible e.m.f). This observation suggesting that the conduction is mainly electronic.

The effect of temperature on the electrical resistivity of un irradiated and irradiated samples are shown in Figures 2–6. The inspection of these figures show that, the relation consists of one linear part, others of two linear regions connected with a boundary at a characteristic temperature T_t. The phase transition was observed in

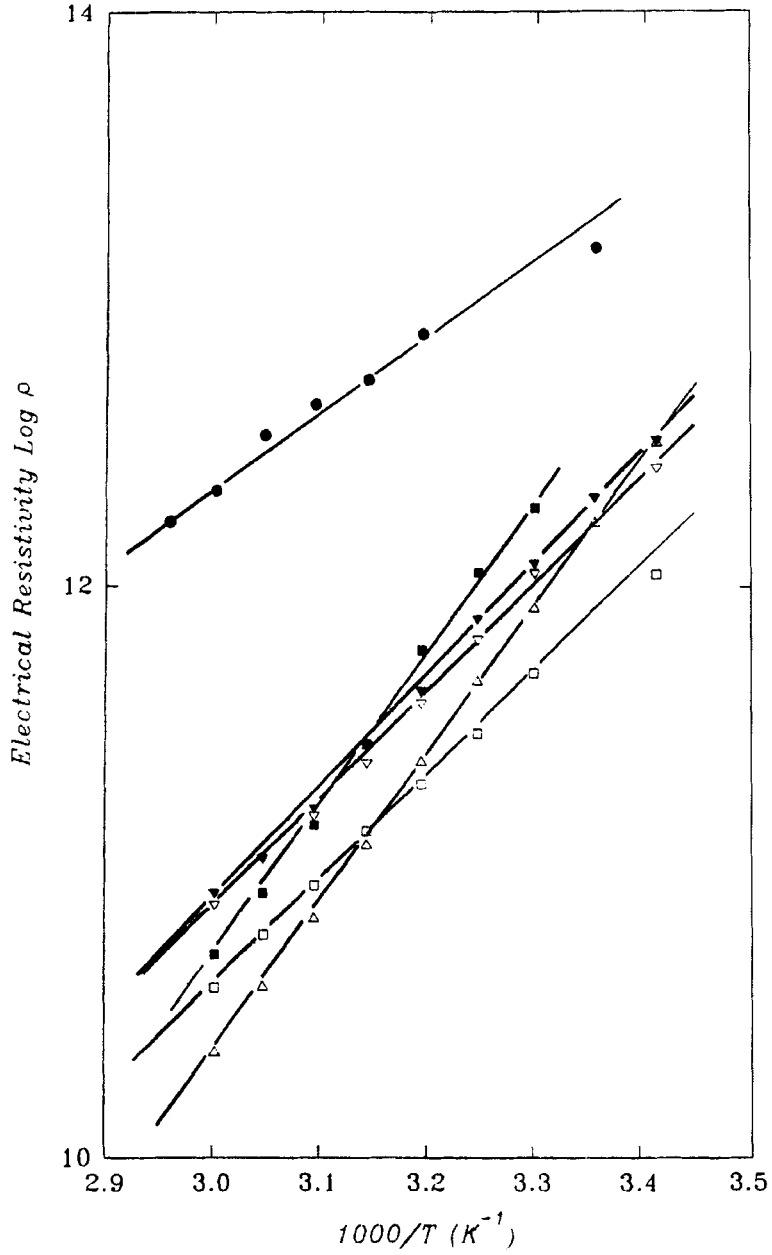

FIGURE 2 Relations between electrical resistivity log ρ and $1000/T$ for the studied PMMA at different doses [0 (•), 50 (▽), 100 (▼), 150 (■), 200(□), 300(Δ) KGy].

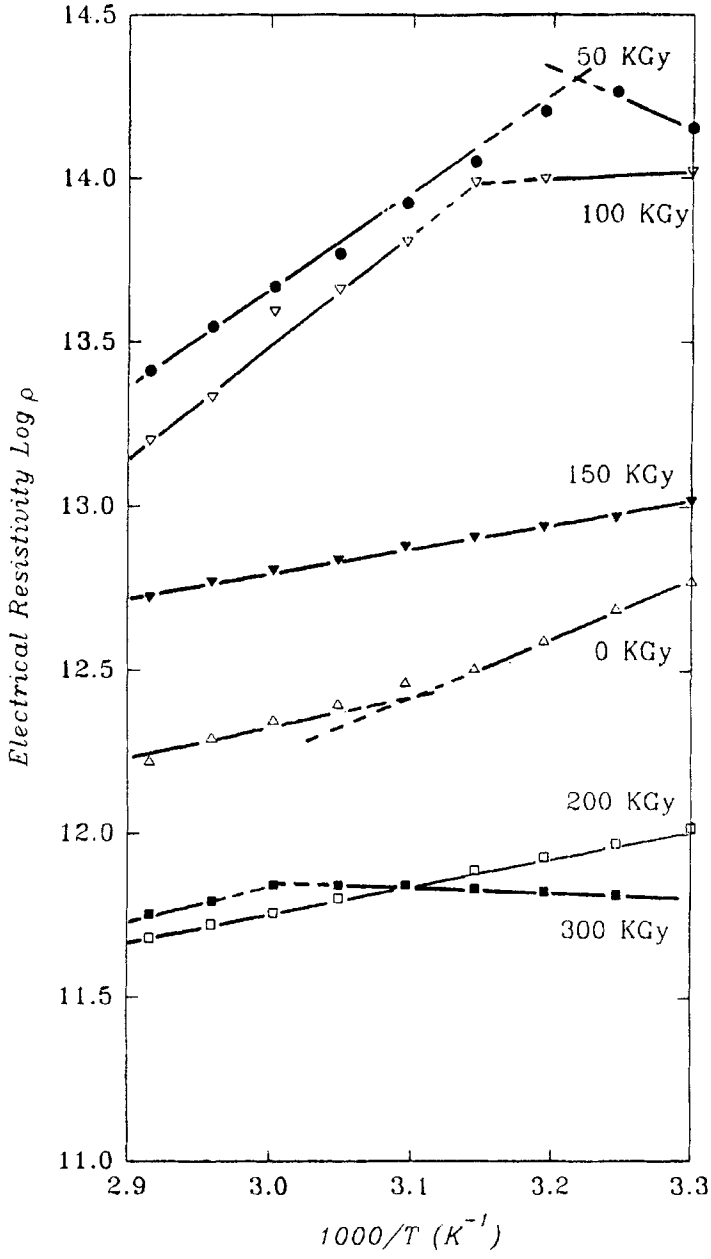

FIGURE 3 Relations between electrical resistivity log ρ and $1000/T$ for PMMA doped with HDZ at different doses.

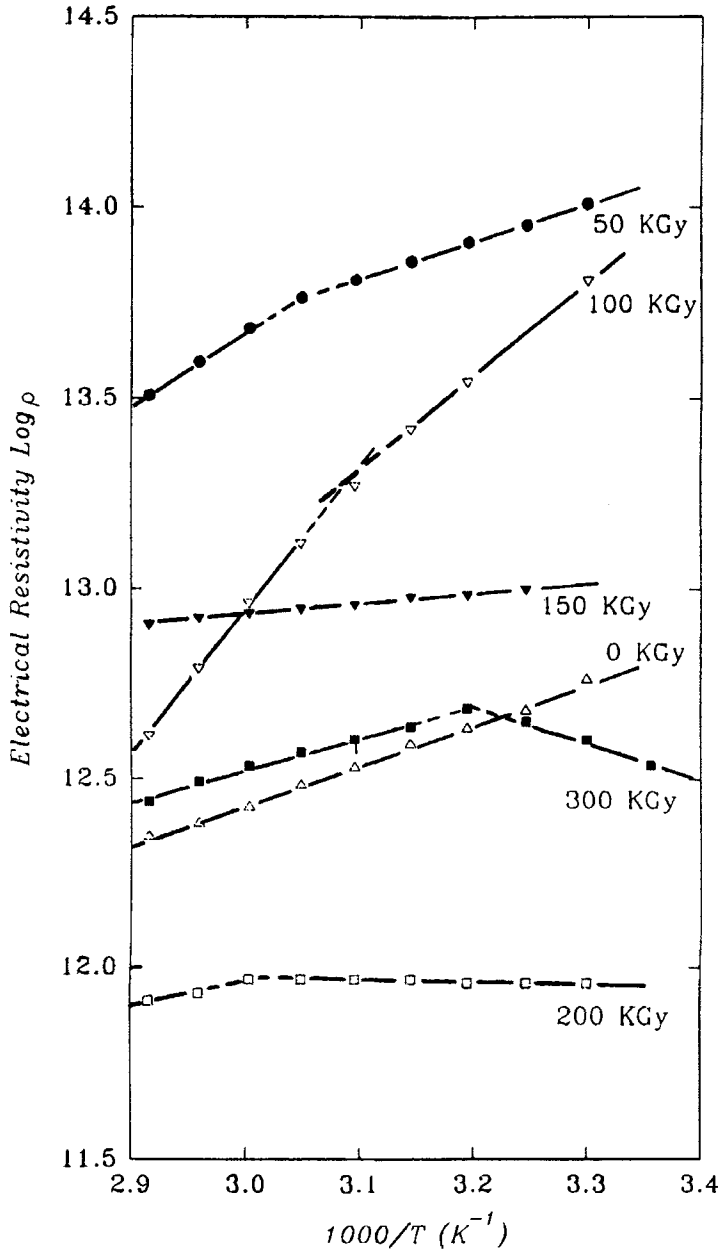

FIGURE 4 Relations between electrical resistivity log ρ and $1000/T$ for PMMA doped with $Zn(HDZ)_2$ at different doses.

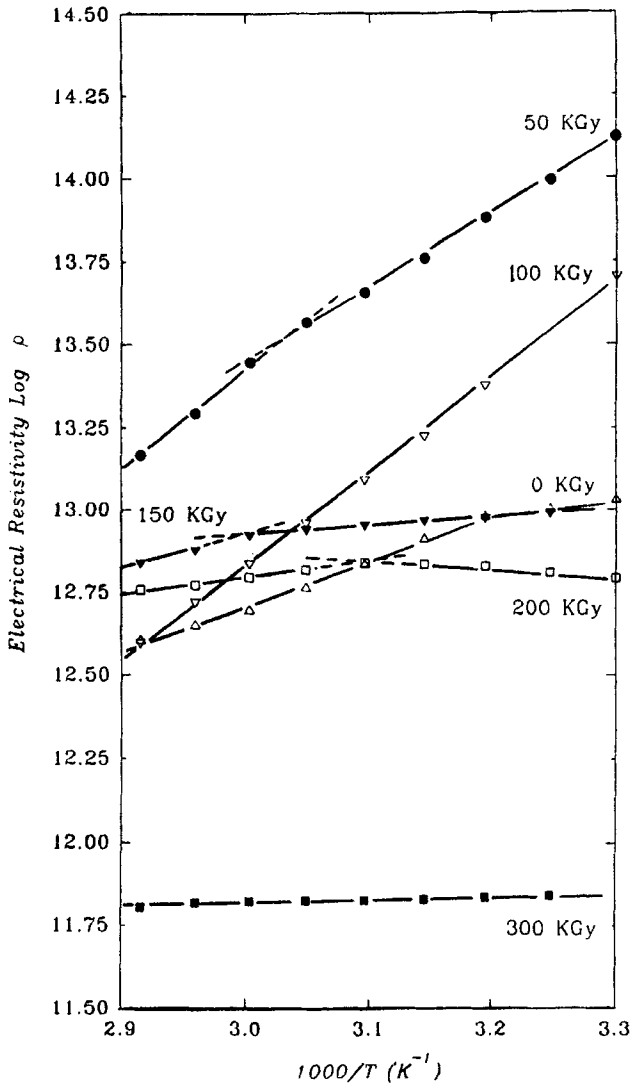

FIGURE 5 Relations between electrical resistivity log ρ and $1000/T$ for PMMA doped with $Cd(HDZ)_2$ at different doses.

doped PMMA samples, while the pure PMMA samples has no transition temperature. The transition temperature (T_t) depends on the radiation dose. This phase transition may be due to the volume

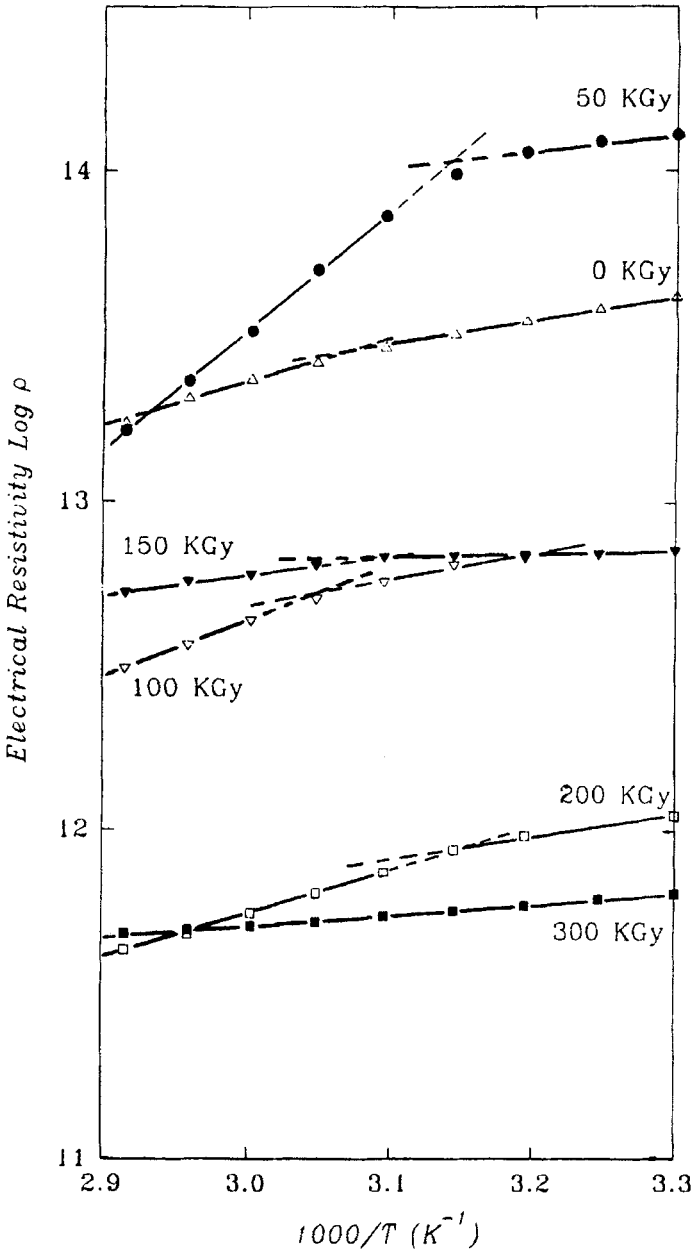

FIGURE 6 Relations between electrical resistivity log ρ and $1000/T$ for PMMA doped with $Hg(HDZ)_2$ at different doses.

TABLE II Activation energy (E) for pure and doped PMMA irradiated at different doses of γ-radiation

Samples	*E, eV*											
	Non-irradiated		50 *K. Gy*		100 *K. Gy*		150 *K. Gy*		200 *K. Gy*		300 *K. Gy*	
	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2	E_1	E_2
PMMA-HDZ	0.276	–	0.416	0.562	0.043	0.689	0.153	–	0.176	–	0.037	0.211
PMMA-Zn$(HDZ)_2$	0.215	–	0.192	0.397	0.499	0.752	0.056	–	0.007	0.122	0.210	0.165
PMMA-Cd$(HDZ)_2$	0.104	0.294	0.454	0.262	0.571	–	0.051	0.180	0.055	0.090	0.020	–
PMMA-Hg$(HDZ)_2$	0.153	0.297	0.101	0.714	0.157	0.332	0.023	0.129	0.135	0.259	0.065	–
Pure PMMA	0.478		0.743		0.770		0.739		1.049		1.033	

E_1 = Activation energy for the low temperature range.
E_2 = Activation energy for the high temperature range.

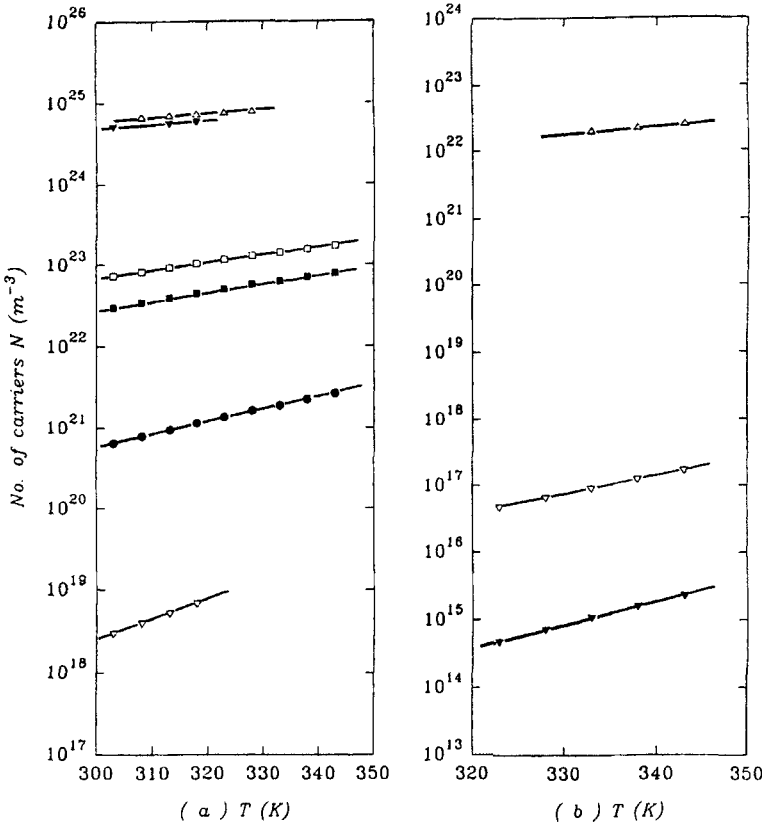

FIGURE 7 Relations between number of carriers N and T for PMMA + HDZ at different doses [0 (•), 50 (▽), 100 (▼), 150 (□), 200 (■), 300 (△) KGy for transition (a) E_1, and (b) E_2.

change. This change in lattice would be expected to cause a change in the singlet-triplet separation energy.

The activation energy (E_a) were calculated and given in Table II. From this table it is clear to observe that, the activation energy in the low temperature range (E_1) is less than that in the high temperature range (E_2).

For more detailed study, the effect of temperature on the mobility (μ) and the number of current carriers (N) which take part in the conduction process was also studied. The number of charge carriers

can be obtained by calculating the Fermi distribution function $F(E)$ and the density of state function $Z(E)$ [10, 11].

The product of the two functions gives the actual number of carriers per cubic meter (N). The mobility of the charge carriers μ ($cm^2\ v^{-1}\ s^{-1}$) was calculated using the single model relation [12].

$$\sigma = N e \mu$$

Where σ is the electrical conductivity and e is the electronic charge.

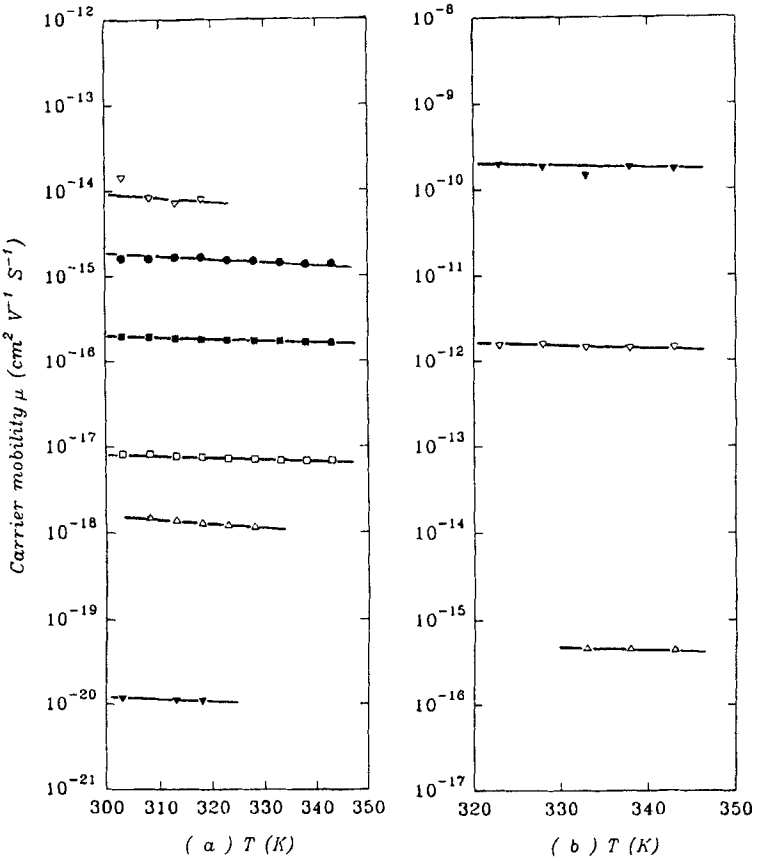

FIGURE 8 Relations between carriers mobility μ and T for PMMA + HDZ at different doses [0 (•), 50 (▽), 100 (▼), 150 (□), 200 (■), 300 (Δ) KGy for transition (a) E_1, and (b) E_2.

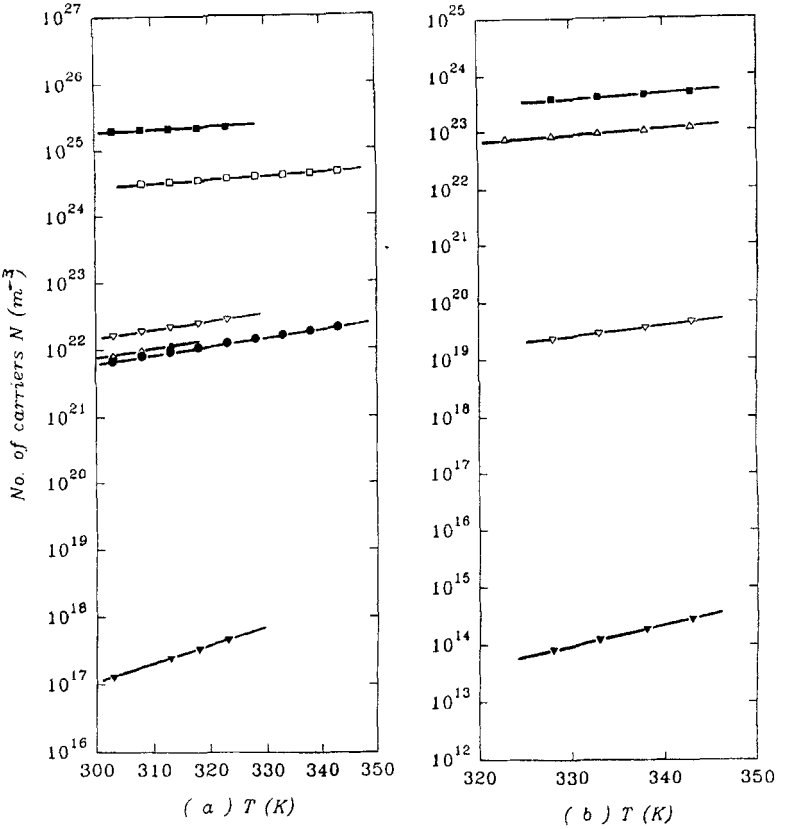

FIGURE 9 Relations between number of carriers N and T for PMMA + $Zn(HDZ)_2$ at different doses [0 (•), 50 (▽), 100 (▼), 150 (□), 200 (■), 300 (Δ) KGy for transition (a) E_1, and (b) E_2.

The density of the free charge carriers (N) in the conduction band and its drift mobility (μ) was calculated at different temperatures and different doses as shown in Figures 7–10. From these figures it is obvious that the mobility (μ) of the carriers decreases by increasing temperature. While the density of the carriers increased with temperature.

This indicated that the activation process in the investigated samples is due to the electron transfer from the valence band to the conduction band by the thermal activation.

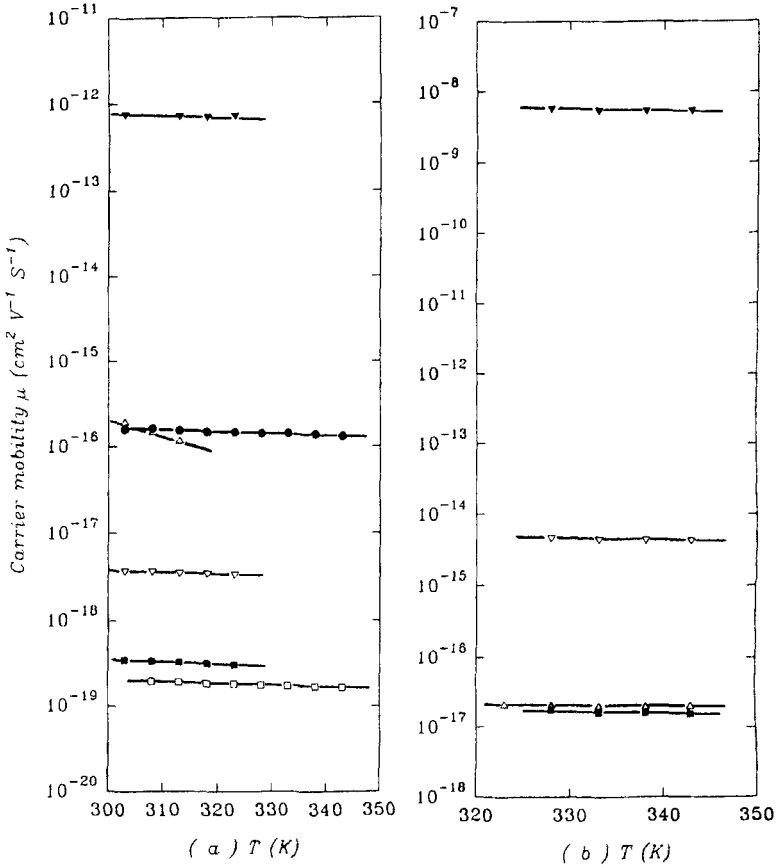

FIGURE 10 Relations between carriers mobility μ and T for PMMA + $Zn(HDZ)_2$ at different doses [0 (•), 50 (▽), 100 (▼), 150 (□), 200 (■), 300 (Δ) KGy for transition (a) E_1, and (b) E_2.

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