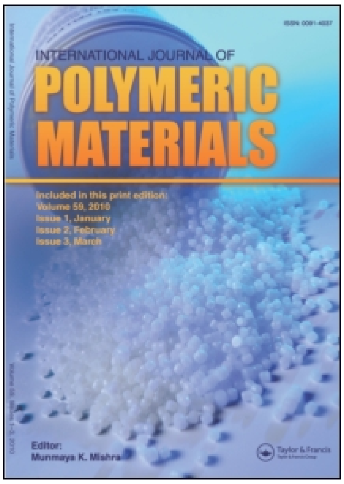

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Electrical Properties of Gamma-Irradiated ST/MMA Copolymers

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To cite this Article Nasr, G. M. , Mansour, A. F. , Ahmed, R. M. and Bassyouni, A. H.(2007) 'Electrical Properties of Gamma-Irradiated ST/MMA Copolymers', International Journal of Polymeric Materials, 56: 4, 371 — 386

To link to this Article: DOI: 10.1080/00914030600873501

URL: http://dx.doi.org/10.1080/00914030600873501

International Journal of Polymeric Materials, 56:371–386, 2007
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ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/00914030600873501

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Copolymer films with various concentrations of Styrene (ST) and Methylmethacrylate (MMA) were prepared by thermal polymerization method. The films were exposed to different doses of gamma radiation up to 10 Mrad. The effects of γ-radiation on the electrical properties were investigated for dosimetry applications.

Keywords: conduction mechanism, copolymer, dosimeter, gamma radiation, PMMA, PS

INTRODUCTION

The vigorous development of polymer science and the extensive utilization of polymeric materials in all fields of technology has led, in recent years, to an increased interest in various problems of the physics and chemistry of polymers [1]. It is known that one of the main objectives of polymer physics is the elucidation of the relationship between the chemical and physical structure and the physical properties of the polymers.

Polymethylmethacrylate (PMMA) and polystyrene (PS) are used extensively in situations requiring high-performance plastic materials because of their unique combination of superior mechanical, electrical,

Received 5 June 2006; in final form 13 June 2006.

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optical, chemical, and thermal properties [2–4]. These polymeric materials have great significance because of their good durability and ability to withstand different environmental conditions, and they have a wide range of applications, especially in industrial and consumer end-products.

Gamma irradiation of polymers has recently received a great deal of attention for two reasons: its increasing use as a sterilizer of medical articles made of semi crystalline polymers, and as a clean method of oxidation, which also helps to understand the oxidation process. It is well-known that the exposure of solid materials to γ-rays induces structural defects known as color centers. The presence of such color centers in a thick film matrix gives rise to changes in both the optical and the electrical properties of the material, which can be utilized to asses the radiation dose absorbed [5–8].

The aim of this work is to report the changes in the electrical properties of PMMA, PS, and their copolymers with different monomer concentrations under the influence of γ-irradiation and to study its suitability for dosimetry applications.

EXPERIMENTAL

Materials

Styrene (ST) and methylmethacrylate (MMA) were purchased from Aldrich to be used in this study. Pure-grade benzoyl peroxide (BP) supplied by BDH (England) was used as an initiator.

Preparation of the Samples

Films of pure ST, MMA, and copolymer with different concentrations were prepared by thermal polymerization method. The polymerization was performed with BP as an initiator (1 wt%) and the mixture was poured into a glass mold. The mold was then immersed in water bath at 80°C for 4 h then at 60°C for 72 h, followed by a final drying at 80°C for 4 h. The concentrations of the prepared (ST/MMA) copolymer are 100/0, 10/90, 30/70, 50/50, 70/30, 90/10, 0/100 by volume.

Gamma Irradiation

A ^{60}Co gamma source model GB150 type B manufactured by the Atomic Energy Agency of Canada and located at the National Center for Radiation Research and Technology, A.E.A. was used for irradiating the samples at a dose rate of 9.23 kGy/h, and a constant temperature 30°C.

Differential Scanning Calorimeter (DSC)

The DSC thermograms were obtained using a Shimadzu DSC 50 differential scanning calorimeter, for films before and after irradiated by gamma radiation at 10 Mrad. A heating rate of 5°C/min was utilized under nitrogen atmosphere. The recorded glass transition temperature was taken as the temperature grew from room temperature to 200°C.

Electrical Measurements

The samples were prepared in the form of rectangular discs of 1–1.4 mm thickness for the electrical measurements. The two parallel surfaces of each disc were coated with colloidal silver paste and checked for good conduction. The ammeter–voltmeter method was used for measuring the d.c. electrical conductivity (σ_{dc}). The samples were heated in a non inductive furnace and the data were collected in a temperature range of 303 to 413 K (using voltmeter type U722A, Poland). The temperature of the samples was measured using T-type thermocouple with its junction in contact with the samples.

RESULTS AND DISCUSSION

Effect of γ-Rays on the Conduction Mechanism of PS, PMMA, and their Copolymers

The electrical properties of polymeric materials depend not only on the chemical composition but also on the structural features associated with the type and degree of molecular order [9]. The current–voltage (I-V) characteristics are very important electrical properties of polymers and polymer composites [10]. For most polymers, the current does not vary linearly with applied voltage except at low fields [11–13].

Figures, 1a–d show the I-V characteristics of PS, PMMA, and their copolymers at room temperature and different γ-doses 1, 5, and 10 Mrad, respectively. For all samples except for pure PMMA at γ doses 1, 5, 10 Mrad, in the whole measuring voltage range show Ohmic conduction. Meanwhile, samples pure PMMA at γ doses 1, 5, 10 Mrad show an Ohmic conduction at low voltages and as the voltages increases, there are apparent deviations from Ohm's law. The current values are above the straight line that stands for the extrapolated Ohmic behavior. Additionally, the transforming voltages (V_s) from Ohmic to non-Ohmic region increases with γ-irradiation dose.

The deviation from Ohm's law can be discussed by different conduction mechanisms that may possibly take place in solid polymers. At

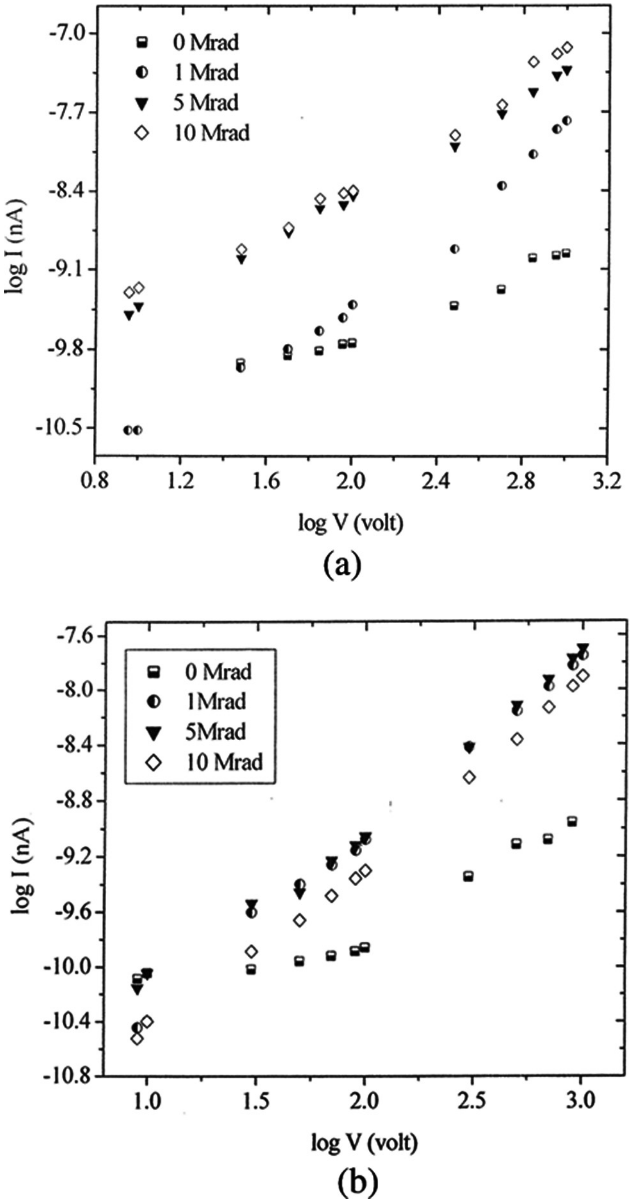


FIGURE 1 (a) The variation of log I–log V for pure PMMA irradiate with different γ-ray doses. (b) The variation of log I–log V for ST/MMA, 10/90 copolymer irradiated with different γ-ray doses. (c) The variation of log I–log V for ST/MMA, 50/50 copolymer irradiated with different γ-ray doses. (d) The variation of log I–log V for pure PS irradiated with different γ-ray doses.

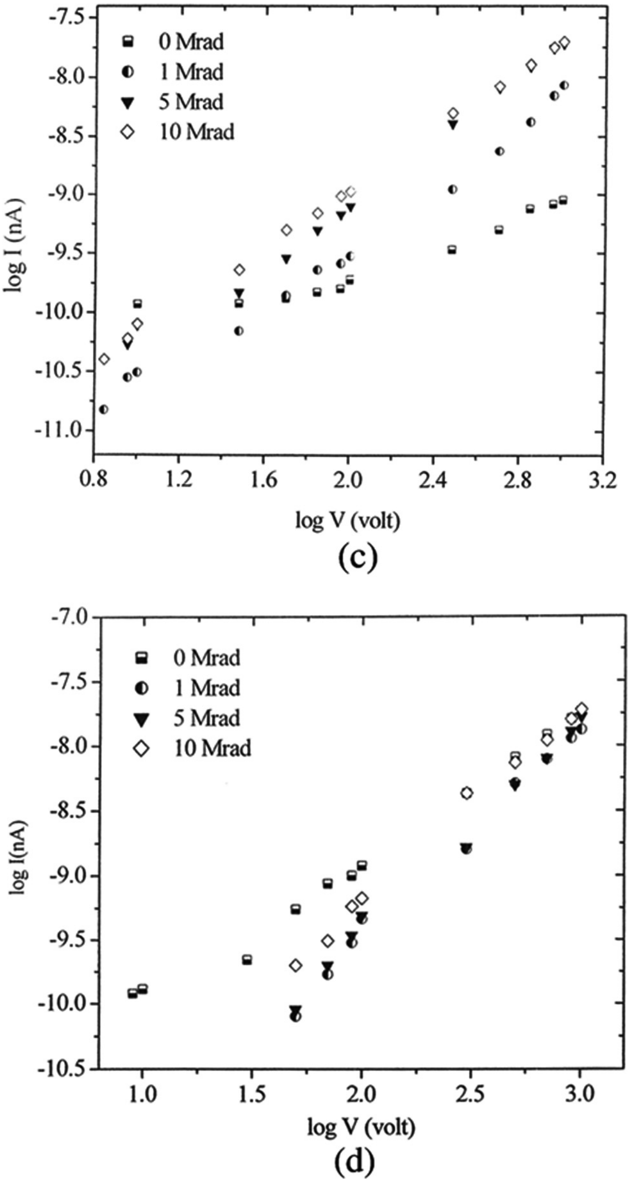


FIGURE 1 Continued.

first sight, it seems that space charge conduction is a dominant one and can explain the deviation from Ohm's law.

When ions are hopping by a thermally activated process, current density (J) is expressed as Eq. 1:

$$J = 2\,n\,\alpha\,\upsilon\,\exp(-U/kT)\,\sinh(eE\alpha/2kT) \tag{1}$$

where e, n, α, υ, U, k, and T are the charge of electron, carrier density, hopping distance, attempt to escape frequency, activation energy, Boltzmann's constant, and absolute temperature. This expression was proposed first by Mott and Gurney [14] and modified as Eq. 2 at high electric field [15].

$$J = n\,\alpha\,\upsilon\,\exp(-U/kT)\,\exp(eE\alpha/2kT) \tag{2}$$

In Eq. 2, exp(−U/kT) is independent of the electric field and can be treated as a constant with respect to electric field. It is also an intercept in a log(J) versus (E) plot.

Using Eq. 1, the hopping distance α can be estimated from a curve fitting between the current density and sinh term. The hopping distance estimated by this method are 1.058 nm for PS, 52 nm for PMMA and 39.98, 22.76, 9, 8.2, and 2.2 nm for 10/90, 30/70, 50/50, 70/30, 90/10 ST/MMA copolymer, respectively, and varies with γ doses as in Table 1. These values show that hopping distance decreases with the increase of the concentration of ST in the ST/MMA copolymer,

TABLE 1 The Hopping Distance (α) for all Samples Irradiated with Different γ-Ray Doses

Concentration of (ST/MMA)	The doses of γ-ray (Mrad)	α (μm)
(0/100)	1	4.10
	5	4.00
	10	1.82
(10/90)	1	9.58
	5	9.52
	10	5.20
(50/50)	1	10.0
	5	8.00
	10	3.80
(100/0)	1	7.20
	5	5.98
	10	4.40

which can be attributed to the relative increase of chain motion with increased ST concentration in the ST/MMA copolymer.

The current density as a function of electric field can be calculated by Eq. 1 using these hoping distances for all irradiated samples. Figures 2a–d show the measured data and the theoretical curve estimated by particular hoping distance.

Both Schottky and Poole–Frenkel mechanisms were also estimated as follows: The Schottky mechanism is an electrode limited conduction process and can be expressed by the following equations [16]:

$$J = A\,T^2 \exp\left(\frac{-\varphi}{Kt}\right)\exp\left(\frac{\beta_s E^{1/2}}{kT}\right) \tag{3}$$

$$\beta_S = \left(\frac{e^3}{4\,\pi\,\varepsilon\,\varepsilon_0}\right)^{1/2} \tag{4}$$

where J, φ, β_s, ε, and ε_0 are the current density, barrier height between the electrode and sample, Schottky coefficient, relative permittivity and permittivity in vacuum. The Poole–Frenkel mechanism can be expressed by the following equations [16]:

$$\sigma = \sigma_0 \exp\left(\frac{\beta_{PF}\,E^{1/2}}{kT}\right) \tag{5}$$

$$\beta_{PF} = \left(\frac{e^3}{\pi\,\varepsilon\,\varepsilon_0}\right)^{1/2} \tag{6}$$

where σ and β_{PF} are the conductivity and Poole–Frenkel coefficient. Both β_S and β_{PF} coefficients were calculated using Eq. 4 and 6 and compared with those calculated experimentally from Figures 2a–d as shown in Tables 2a & b. It could be observed that the predominant conduction mechanism for most samples is Poole–Frenkel conduction mechanism even at different γ-ray doses.

To examine whether or not the conduction process changes. In [J/sinh(eEα/2kT)] was plotted as a function of (1000/T) in Figures 3a & b. A nonlinearity is observed in these figures for all ST/MMA copolymers, which implies that the conduction mechanism changes at this temperature range, which is quiet reasonable since the range of test temperature is around the T_g of both PS and PMMA. The activation energy was calculated from the slopes of the activated parts in Figures 3a & b and was found to vary from 0.15 to 0.59 eV according to the ST concentration in the ST/MMA copolymer as shown in Table 3, column A.

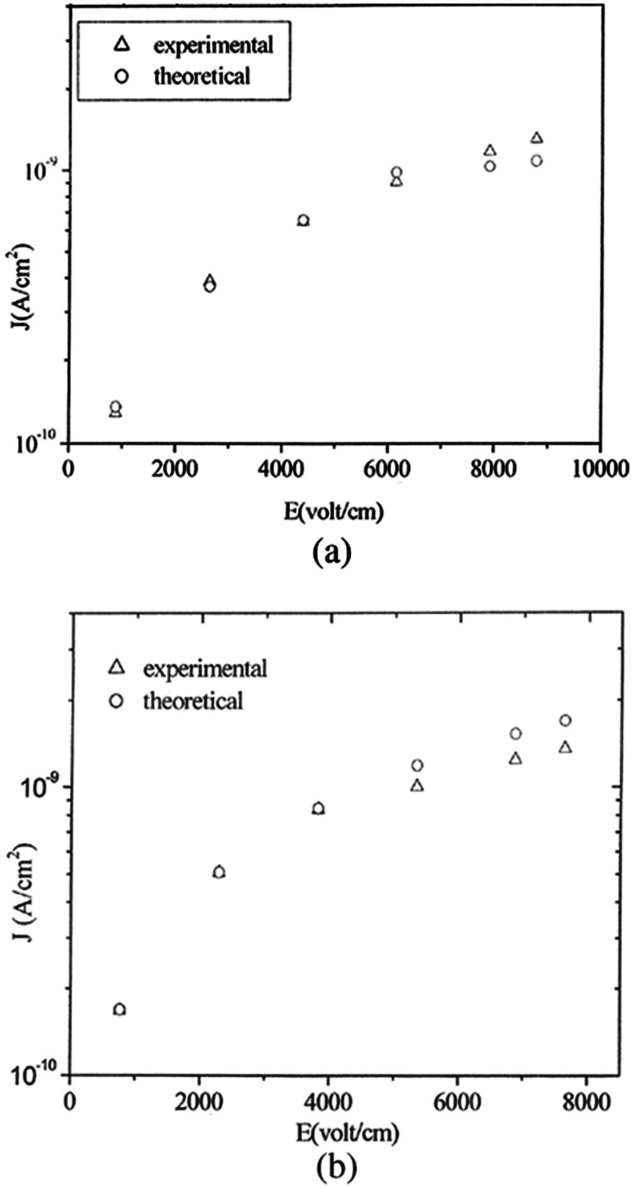


FIGURE 2 (a) The variation of J (A/cm^2) versus E (volt/cm) characteristics for pure PMMA. (b) The variation of J (A/cm^2) versus E (volt/cm) characteristics for ST/MMA, 10/90 copolymer. (c) The variation of J (A/cm^2) versus E (volt/cm) characteristics for ST/MMA, 50/50 copolymer. (d) The variation of J (A/cm^2) versus E (volt/cm) characteristics for pure PS.

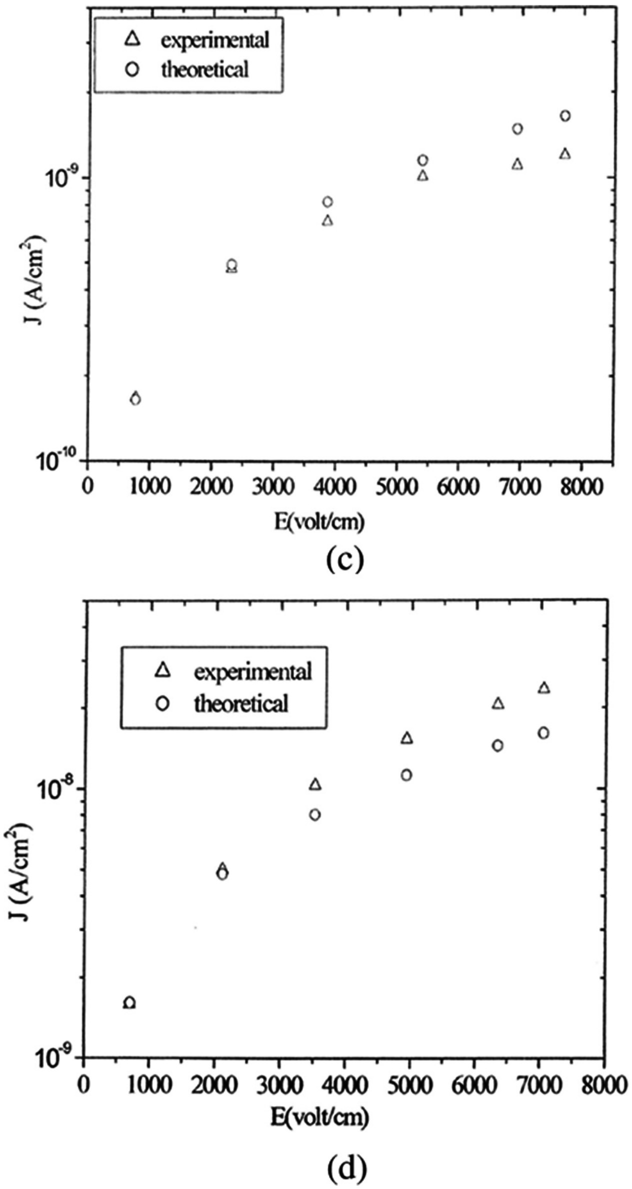


FIGURE 2 Continued.

In Figure 4, a linear relationship is shown between $(\Delta\sigma/\sigma_0) = [(\sigma - \sigma_0)/\sigma_0]$ where σ_0 is the conductivity of un-irradiated samples, whereas σ is its value at different γ ray dose (D) are shown for different

TABLE 2A The Dielectric Constant ε, and Both the Theoretical and Experimental β Values for Different Concentration of Copolymer ST/MMA

Concentration of (ST/MMA)	ε	β_{exp} [10^{-4} eV cm$^{1/2}$ volt$^{-1/2}$]	β_{S} [10^{-4} eV cm$^{1/2}$ volt$^{-1/2}$]	β_{PF} [10^{-4} eV cm$^{1/2}$ volt$^{-1/2}$]
(0/100)	7.52	3.03	1.40	2.80
(10/90)	6.23	3.14	1.53	3.07
(30/70)	5.55	3.52	1.69	3.39
(50/50)	8.65	2.82	1.31	2.62
(70/30)	6.78	2.99	1.48	2.96
(90/10)	6.96	3.08	1.47	2.94
(100/0)	10.4	2.61	1.20	2.40

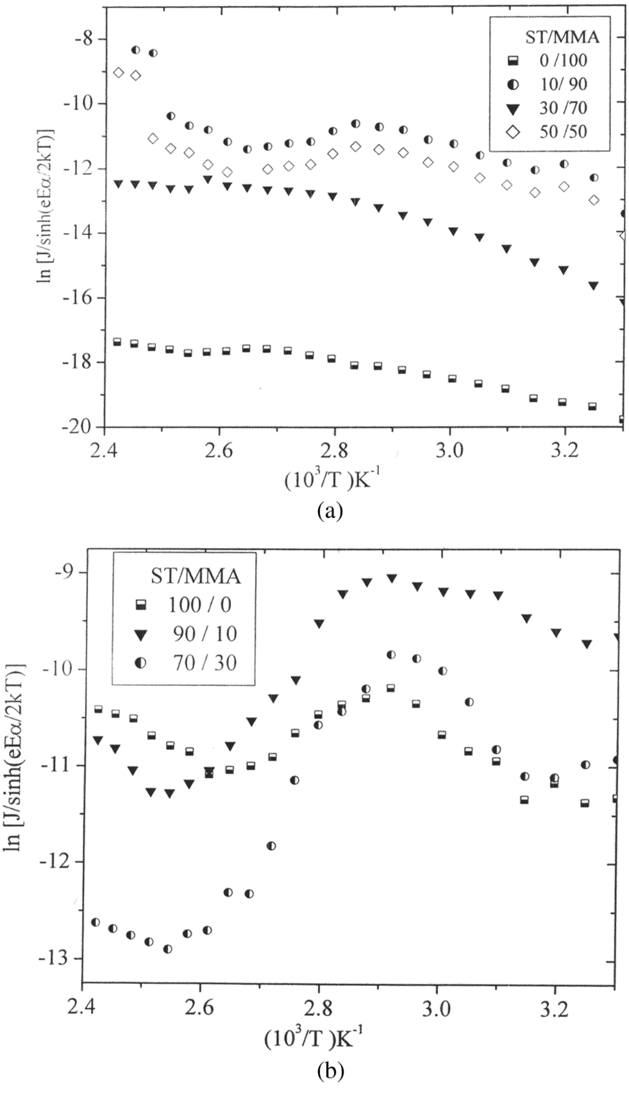
monomer concentrations in the ST/MMA copolymer. The linear changes in ($\Delta\sigma/\sigma_0$) with γ ray doses suggests the suitability of PS and PMMA and their copolymers for high doses dosimeters.

Effect of Temperature on the d.c. Conductivity

Figures 5a & b show the variation of conductivity (σ) of PS, PMMA, and their copolymers as a function of (10^3/T). The effect of the temperature on polymer is complex. The conductivity of pure PMMA and ST/MMA copolymer (10/90, 30/70) increases with an increase

TABLE 2B The Dielectric Constant ε, and Both the Theoretical and Experimental β Values for Different Concentrations of Copolymer ST/MMA Irradiated by Different Doses of γ-ray.

Concentration of (ST/MMA)	The doses of γ-ray (Mrad)	ε	β_{exp} [10^{-4} eV cm$^{1/2}$ volt$^{-1/2}$]	β_{S} [10^{-4} eV cm$^{1/2}$ volt$^{-1/2}$]	β_{PF} [10^{-4} eV cm$^{1/2}$ volt$^{-1/2}$]
(0/100)	1	6.32	3.50	1.55	3.10
	5	5.78	3.51	1.60	3.21
	10	6.75	3.37	1.48	2.96
(10/90)	1	6.93	3.02	1.50	3.00
	5	5.24	3.66	1.70	3.40
	10	6.06	3.32	1.56	3.12
(50/50)	1	6.66	3.39	1.49	2.98
	5	6.96	2.97	1.39	2.78
	10	7.72	2.82	1.40	2.80
(100/0)	1	6.53	3.24	1.49	3.00
	5	5.74	3.74	1.65	3.30
	10	6.4	3.39	1.51	3.03



(a)

(b)

FIGURE 3 (a) The variation of ln [J/sinh(eEα/2kT)] versus (10^3/T) K^{-1} characteristics for ST/MMA 0/100, 10/90, 30/70, and 50/50 copolymer. (b) The variation of ln [J/sinh(eEα/2kT)] versus (10^3/T) K^{-1} characteristics for ST/MMA70/30, 90/10, and 100/0 copolymer.

of temperature, but the rate of increase is different in different temperature regions. The rate of increase is fast at low temperature (below 100°C) but slow at high temperature (above 100°C). The

TABLE 3 The Calculated Values of U (eV) for ST/MMA Copolymer with Different Monomer Concentrations

		(A) Calculated from $J = 2\,n\,\alpha\,\upsilon\,\exp\,(-U/kT)\,\sinh(eE\alpha/2kT)$		(B) Calculated from $\sigma = \sigma_0\,\exp(-U/kT)$	
Concentration of (ST/MMA)	T_p (K)	Before T_p (K)	After T_p (K)	Before T_p (K)	After T_p (K)
(0/100)	377.36	0.335	0.261	0.312	0.275
(10/90)	363.63	0.203	0.310	0.190	0.280
(30/70)	374.50	0.550	0.133	0.560	0.137
(50/50)	353.00	0.439	0.675	0.420	0.645
(70/30)	341.29	0.590	0.189	0.570	0.160
(90/10)	342.90	0.158	0.515	0.150	0.480
(100/0)	343.00	0.292	0.274	0.290	0.268

activation energies are evaluated from slopes of the curves in accordance with the Arrhenius relation [18] and are presented in Table 3, column B and are comparable to those calculated from Figures 3a & b.

The activation energies are found to be ST/MMA monomer concentration dependent. Hence, it appears that there may be two types of

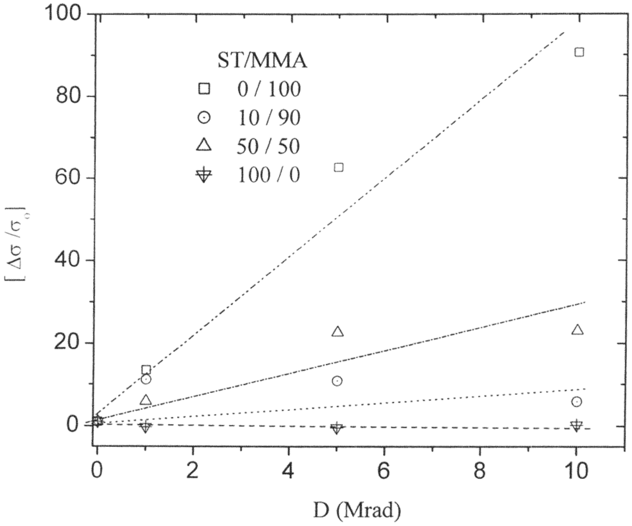


FIGURE 4 The variation of ($\Delta\sigma$) versus (D) characteristics for ST/MMA copolymer with different monomer concentrations.

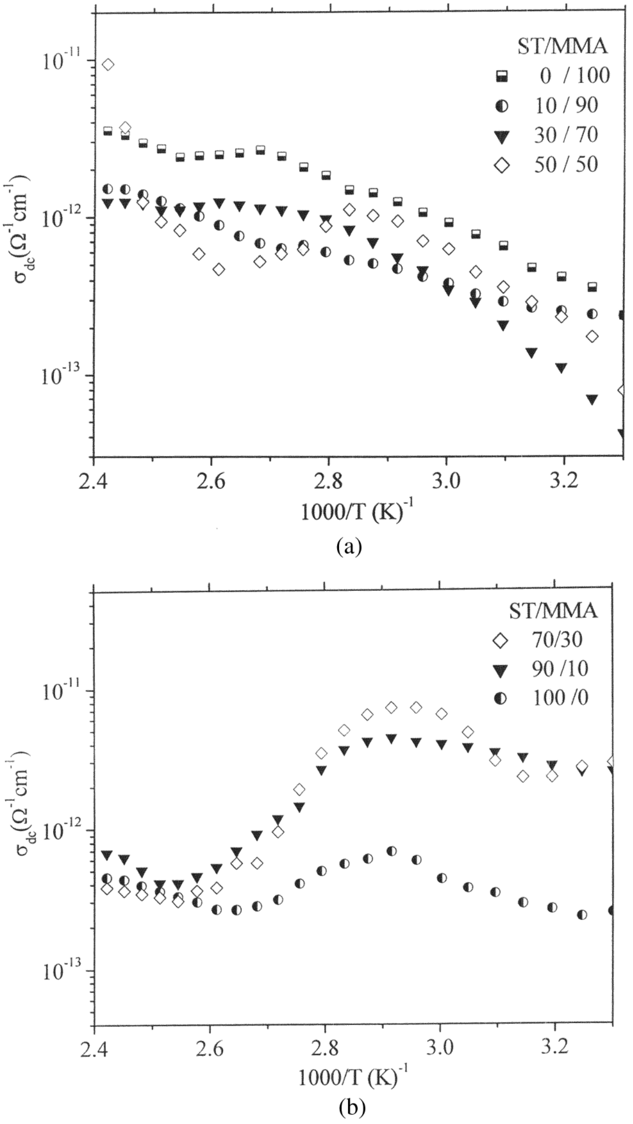


FIGURE 5 (a) The variation of (σ) versus (1000/T) characteristics for ST/MMA 0/100, 10/90, 30/70, and 50/50 copolymer. (b) The variation of (σ) versus (1000/T) characteristics for ST/MMA 70/30, 90/10, and 100/0 copolymer.

conduction mechanisms operating in different temperature regions, which may be a common phenomenon in most disordered systems [19].

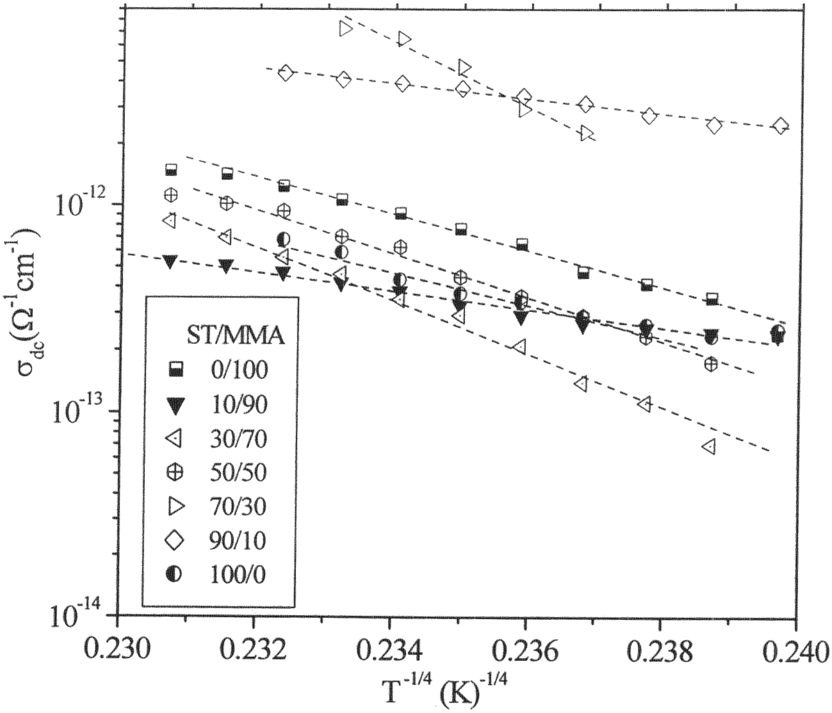


FIGURE 6 The variation of (σ) versus (1000/$T^{-1/4}$) characteristics for ST/MMA with different monomer concentrations.

Many workers [20–22] reported a similar type of behavior in many polymeric system. Copolymers with monomer concentration ST/MMA MMA 30/70, 50/50, 70/30, 90/10, and 100/0 show an anomalous behavior in their (σ)-(1000/T) dependence, where a maximum and/or

TABLE 4 The Values of T_g (K) for ST/MMA Copolymer with Different Concentrations Before and After Irradiated for 10 Mrad of γ-Ray

Concentration of (ST/MMA)	Doses of γ-ray (Mrad)	T_g (K)
(0/100)	0	384.49
	10	389.97
(50/50)	0	358.30
	10	371.84
(100/0)	0	353.34
	10	372.75

minimum appear in their conductivities. The attenuation of conductivity with temperature (in the temperature range 60–120°C could be explained as due to the fact that in this range of temperature the electron–phonon coupling becomes more pronounced, which restricts the charge carrier mobility resulting in a detected reduction in the d.c. electric conductivity. At both low temperatures ($<$60°C) and above 120°C for these samples and ($>$100°C) for the first ones, normal conduction may take place due to hopping between the localized states. The hopping conduction mechanism may be characterized by low activation energies and the dependence of log σ on ($T^{-1/4}$) as proposed by Mott and Davis [23].

For three-dimensional hopping the charge carriers can jump in any direction. In the present studies, the activation energies were found to be low in the mentioned temperature region. Also, log σ versus $T^{-1/4}$ shows a linear relationship, as seen from Figure 6 suggesting the hopping mechanism. The hopping process between the localized states with potential barriers lowered by the applied electric field according to Poole–Frenkle conduction mechanism may be the dominant mechanism at the activated conductivity part for each samples. It is possible to estimate the minimum or maximum temperature for the hopping mechanism to take place. Incidentally, it approximately coincides with the glass transition temperature (T_g) of the PS, PMMA, and their copolymers as detected from the DSC measurement tabulated in Table 4.

CONCLUSION

It may be concluded that the Poole–Frenkle conduction mechanism, namely field assisted thermal ionization of traps, may give rise to conduction at temperature up to 140°C. The hopping distances decreased from 39.98 nm at 90 MMA to 3.3 nm at 90 ST in the ST/MMA copolymer, which was attributed to the increase of chain motion with increase of ST monomer in the copolymer. Meanwhile, an anomalous behavior in the σ-(1000/T) dependence the samples is detected as maximum and/or minimum conductivity values in the studied temperature range. The investigated samples are proposed to be used as high dosimeters.

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