

# High Energy Electron Irradiated Polystyrene: Free Volume and Thermal Properties Studied by PALS and DSC

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**Abstract** The variation in the microstructure in terms of free volume and the thermal properties, such as specific heat ( $C_p$ ), glass transition temperature ( $T_g$ ) of 8 MeV electron irradiated Polystyrene (PS) at different doses have been measured using Positron Annihilation Lifetime Spectroscopy (PALS) and Differential Scanning Calorimetry (DSC) respectively. PALS results showed that at irradiation dose 75 KGy the free volume of the polymer matrix decreases suggesting cross linking of the inter chain and structure appears to be stabilized. In the DSC measurements the specific heat at constant pressure suggests the scission of chains at 100 KGy which is well reflected in the increase of the free volume at this dosage. The observed changes in  $T_g$  are not prominent and do not really reflect the changes in free volume upon irradiation.

**Keywords:** positron annihilation lifetime, differential scanning calorimetry, polystyrene, free volume, specific heat

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## 1. Introduction

In polymer an electron beam irradiation induces effects such as chain scission and cross linking resulting to a change in the properties of polymers that may extend the range of applications of the materials. The effects of irradiation also change the crystallinity as well as microstructure. Usually the irradiation process degrades the polymer, thus, the irradiated polymers can be characterized using PALS, DSC, XRD, FTIR, SEM etc.

The positron annihilation lifetime spectroscopy (PALS) has been proved to be a very useful tool for studying the microstructure of polymeric materials in terms of free volumes as it has two prominent advantages, firstly the ability to detecting down to the atomic scale and secondly the high sensitivity to the microstructure change of 1 ppm [1,2,3,4,5]. Additionally PALS is an ideal non destructive method for the detail microstructure study of polymeric materials. The experimental determination of free volume plays an important role in polymer research as it greatly influences physical and thermal properties of a polymer [6,7]. The free volume cavities in the polymers are evolved in many irregular shapes of atomic and molecular dimension due to the chain architecture and get affected by irradiation, by aging and by addition of various fillers [8,9,10]. In positron experiments the positron from a radioactive source enters the polymeric matrix and after thermalization captures an electron from the surrounding

medium to annihilate as a free positron with an electron or form a bound state called positronium (Ps). The positronium is known to exist in two states, para-positronium (p-Ps) and ortho-positronium (o-Ps) with the statistical weight ratio 1:3 [11]. The lifetime of p-Ps is too short to be influenced by the free volume factors. But confined within a free volume in polymer, the long lived o-Ps has a finite probability of annihilating with an electron other than its bound partner (and of opposite spin), following a process called "pick-off" annihilation and the changes in o-Ps lifetime and intensity can be related to the size of free volume holes that confines the o-Ps and the content of free volume in the medium [12,13,14].

The body of information increases when PALS is engaged in combination with differential scanning calorimetry (DSC), which has been turned out as one of the most informative method for evaluation of the change in thermal properties due to irradiation [15,16]. V.A. Bershtein et al. reported that DSC has been vastly used in the study of irradiated polymers [17].

Thus, in the present research the variations in the specific heat of the polystyrene (PS) sample with temperature for different electron irradiation doses have been carried out using differential scanning calorimetry. The findings are combined with that of positron measurements in order to interpret the structural changes of the material due to irradiation. The presence of benzene ring PS structure, it is expected, exhibits high radiation resistivity. The effect of high-dose electron and gamma

irradiation on microstructure of PS was reported by E.E. Abdel-Hady et al [18]. The change of specific heat of PS as a function of high dose electron irradiation was investigated by F. Ziaie et al [19]. A study on the critical behavior of heat capacity and mass density of PS was made by S.Z. Mirzaev et al [20]. However, to the best of our knowledge, the effect of high energy electron irradiation with low doses on the microstructure of PS in terms of free volume characterization is absent in the literature. Thus, this paper presents the correlated observation about the changes in the free volume structure and thermal properties after high energy electron irradiation at low doses in PS.

## 2. Experimental

### 2.1. Samples

Polystyrene samples, made by the BASF AG Ludwigshafen, Germany, are used for irradiation with 8MeV electron beam at doses 50, 75 and 100 KGy respectively in the as received state. The reference sample is also investigated with both PALS & DSC. For DSC measurement the samples are cut into suitable sizes so that the weights of the samples remain in between 15 to 20 mg as specified for DSC. For PALS study the samples used are of size  $1 \times 1 \text{ cm}^2$  and thickness 2mm each.

### 2.2. Irradiation

The irradiation was done at room temperature ( $25^\circ\text{C}$ ) in air atmosphere. The energy of the electron beam was 8MeV at a beam current 20 mA with a pulse repetition rate of 50 Hz, and the pulse width was 2 $\mu\text{sec}$ . The distance from the output beam source to the sample was 30cm. The accelerator produced a stable beam of the same energy and the samples were irradiated at different doses by irradiating for different time durations. Care was taken that the sample temperature was not very much different from room temperature.

### 2.3. Positron Annihilation Lifetime Spectroscopy

Positron annihilation lifetime spectroscopy (PALS) measurements were carried out at room temperature ( $25^\circ\text{C}$ ) using a fast-fast coincidence system with  $\text{BaF}_2$  scintillators as detectors. Samples of  $1 \text{ cm}^2$  and 2 mm thick were used to acquire PALS spectrum. The time resolution of the spectrometer was 220 ps. The positron source  $^{22}\text{Na}$  on a kapton foil backing was sandwiched between two samples and was placed between the two detectors of the spectrometer. Typical spectrum accumulation time was around 2h resulting in more than  $10^6$  counts under each spectrum. The experimental procedure and other details of this experiment can be found in references [4,5]. The time resolution and source correction terms were obtained from the analysis of well annealed Al lifetime spectrum. All the spectra were analyzed into three lifetime components using the standard LT 9.0 program with proper source and background corrections.

### 2.4. Differential Scanning Calorimetry

The Differential Scanning Calorimetry measurements carried out by employing 2000F3 model of DSC with intra-cooler 70 versions that is capable of lowering the temperature up to  $-70^\circ\text{C}$ . The experiment was performed in  $\text{N}_2$  atmosphere with constant pressure of 0.3bar to prevent any oxidation of the samples. The temperature has been varied up to  $230^\circ\text{C}$  from ambient at a constant heating rate of  $10^\circ\text{C}/\text{min}$  throughout the experiment. Proteus analysis software is used to study the variation of specific heat ( $C_p$ ) and glass transition temperature ( $T_g$ ).

## 3. Results and Discussion

### 3.1. Analysis of Lifetime Spectra

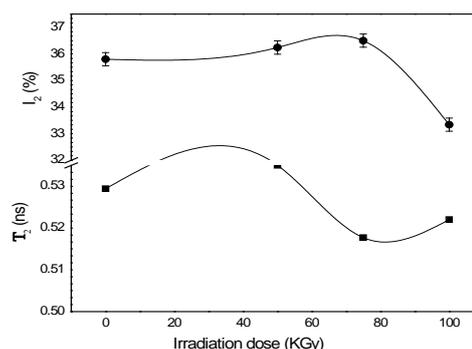
The three lifetime components as obtained for non irradiated and irradiated polystyrene (PS) samples have been attributed to different annihilation states following the conventional method for polymers [21]. The shortest lifetime component ( $\tau_1$ ) is due to the annihilation of p-Ps and free annihilation of positrons, the intermediate one ( $\tau_2$ ) is attributed to the positron annihilation at the crystalline defects or at the interface between crystalline and amorphous domains in the polymer but it excludes Ps annihilation. The longest lifetime component ( $\tau_3$ ) arises due to the annihilation of o-Ps from the free volume holes in the amorphous region of the polymer via pick-off annihilation. As the o-Ps annihilates from the free volume holes, it gives direct information about the size of the hole and the corresponding intensity ( $I_3$  %) of o-Ps gives a measure of the concentration of the free volume holes [22,23]. As the o-Ps annihilates from free volume holes, the radius of the hole ( $R_h$ ) can be calculated using a semi empirical model by Tao-Eldrup model [13,22].

$$\tau_{o-ps} = 0.5 \text{ ns} \left[ 1 - \frac{R_h}{R_h + \partial R} + \frac{1}{2\pi} \text{Sin} \left( \frac{2\pi R_h}{R_h + \partial R} \right) \right]^{-1}$$

Where  $\partial R = 1.66 \text{ \AA}$ , the penetration depth of the Ps wave function into the hole wall and the pre-factor 0.5 ns is the spin average of the Ps –annihilation lifetime [24,25,26]. Using spherical approximation, the hole size ( $V_h$ ) and the fraction of free volume ( $V_f$ ) can be calculate [19].

$$V_h = \frac{4}{3} \pi R_h^3. \quad V_f = A V_h I_{o-ps}$$

Where A is a constant,  $V_h$  is the mean free volume size and  $V_f$  is the free volume fraction [18].



**Figure 1.** Variation of the intermediate lifetime component ( $\tau_2$ ) and Intensity ( $I_2$ ) with irradiation dose (KGy)

The annihilation of p-Ps is unaffected by the material properties due to its very short lifetime and measures the correctness of the spectrum. Figure 1 shows the variation of the intermediate lifetime ( $\tau_2$ ) and intensity ( $I_2$ ) components with irradiation dose (KGy) attributed to the annihilation at the crystalline defects or at the interface between crystalline and amorphous domains in the polymer. Figure 2 shows the variations of the o-Ps lifetime component ( $\tau_3$ ) and Intensity ( $I_3$ ) with irradiation doses (KGy). The behavior of  $\tau_2$  and  $I_2$  in Figure 1 is very similar to that of  $\tau_3$  and  $I_3$  in Figure 2 but the variation in  $\tau_3$  and  $I_3$  is an evidence for the o-Ps being localized at the free volume holes [26]. The variation of the most important parameters o-Ps lifetime ( $\tau_3$ ) and intensity ( $I_3$ ) with irradiation dose (KGy) shows that  $\tau_3$  increases at 50 KGy dose and reaches its lowest value at 75 KGy and as the irradiation dose increases beyond 75 KGy, it again increases. The variation of  $I_3$  shows exactly the opposite behavior of  $\tau_3$  as expected. In Figure 3, the variations of the free volume fraction ( $V_f$ ) and the mean free volume ( $V_h$ ) have been plotted against irradiation dose (KGy).

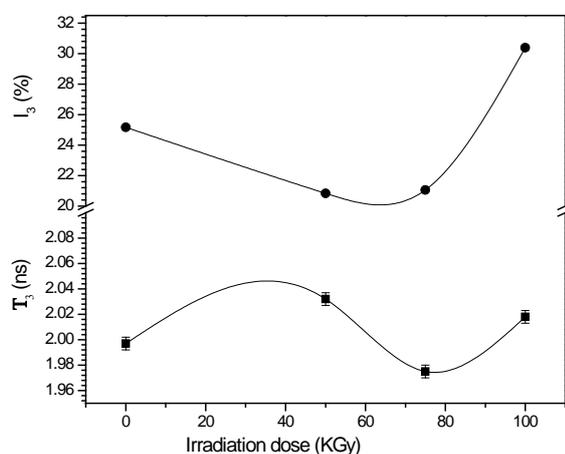


Figure 2. Variation of the o-Ps lifetime component ( $\tau_3$ ) and Intensity ( $I_3$ ) with irradiation dose (KGy)

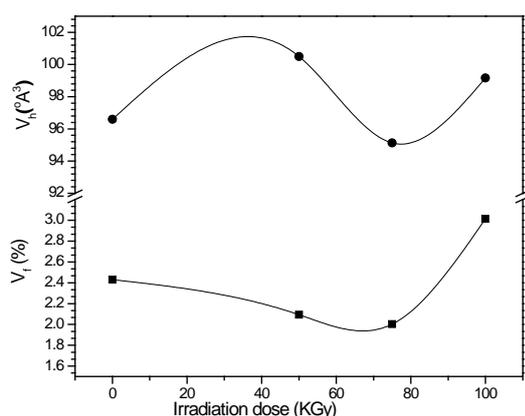


Figure 3. Variation of the free volume fraction ( $V_f$ ) and the mean free volume ( $V_h$ ) with irradiation dose (KGy)

The size of the free volume hole ( $V_h$ ) and the free volume fraction ( $V_f$ ) are calculated by using above three relations.  $V_h$  is directly related to  $\tau_3$  and shows the same pattern. But  $V_f$  is a function of both  $\tau_3$  and  $I_3$ . The value of  $V_f$  gives the fraction of free volume in percent (%) not the size. From Figure 3 it is observed that the variation of  $V_f$

follows the variation pattern of  $V_h$  and reaches its minimum value at the dose 75 KGy.

Irradiation with high energy electron beam promotes two simultaneous processes within the polymer. It produces free radicals and as a result forms new bonds or cross-linking which decrease o-Ps lifetime as well as free volume. The other process is scission or depolymerization which ruptures molecular chains as well as creates new unoccupied spaces (i.e. free volume in polymer) and increases o-Ps lifetime as well as the size of free volumes [10,19]. From Figure 2 and Figure 3 it is observed that the first process i.e. cross-linking becomes dominant at dose 75.

Figure 4 shows the variation of specific heat ( $C_p$ ) of PS with both KGy and causes decrease in o-Ps lifetime and amount of free volume. Both below and beyond 75 KGy, chain scission dominates over cross-linking and results in increase of o-Ps lifetime and amount of free volume. This behavior indicates that most stable structure is achieved at 75KGy e-beam dose.

### 3.2. DSC Results and Heat Capacity

DSC measures the change in thermal properties and due to microstructural changes of any sample as a function of temperature. The variation of specific heat ( $C_p$ ) of electron irradiated Polystyrene (including the reference one) with temperature both above and below the glass transition temperature ( $T_g$ ) are observed. The effect of irradiation dose on  $C_p$  is though prominent but on  $T_g$  it is not pronounced.

Since the DSC is at constant pressure, heat flow is equivalent to enthalpy changes

$$\left(\frac{dq}{dt}\right)_p = \frac{dH}{dt}$$

In DSC measurement the specific heat of the sample can be determined by comparing it to that of a known sample. In our experiment we have considered sapphire as the standard known sample. The heat that flows into the sample is directly proportional to the specific heat. The heat flow into the sample is given by,

$$\frac{dH}{dt} = m \times C_p \times \frac{dT}{dt}$$

Where  $dH/dt$  is the heat flow rate measured in calories/seconds,  $m$  is the mass of the sample measured in grams,  $C_p$  is the specific heat measured in Calories/gram/ $^{\circ}$ K,  $dT/dt$  is the rate of change of temperature in  $^{\circ}$ K/second.

This equation is used in order to derive the final equation which determines the specific heat of the sample given by,

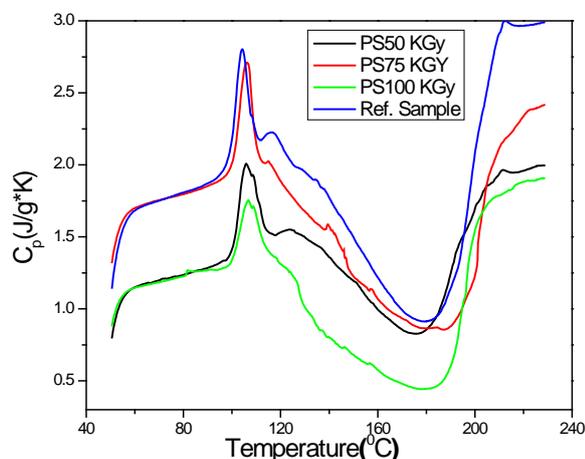
$$\frac{C_p}{C_p'} = \frac{m'y}{my'}$$

Where  $C_p'$  and  $m'$  are the specific heat and mass of the standard,  $y$  and  $y'$  are the ordinate deflections due to the sample and standard respectively measured in centimeters [28].

The heat capacity of a substance can be defined as the amount of heat required to change its temperature by unity. A more useful quantity is the specific heat capacity, which

is the heat capacity per unit molecular weight of the substance. Heat capacity is one of the most important thermal parameter because its macroscopic behavior can be linked with the microstructure of a substance and hence can be treated as an entity capable of illustrating the physical endeavor of atoms or molecules within a substance to maneuver themselves upon heating [29,30].

Figure 4 shows the variation of specific heat ( $C_p$ ) of PS with both temperature and irradiation dose. It is found that the glass transition of PS starts in the vicinity of 90-100°C with an endothermic enthalpic relaxation peak almost at the end of the glass transition process. It occurs immediately after the enthalpic relaxation, right after the glass transition process is complete. At a temperature around 115°C – 120°C, disordered PS chains start to order themselves in regular spherulitic structures. Spherulite is the basic higher order structure of crystalline polymers composed of lamellar structures filling in the inner part by the repetition or the re-orientation and branching on the growth in the radial direction.



**Figure 4.** Variation of specific heat ( $C_p$ ) of Polystyrene (PS) samples with temperature and irradiation doses (KGy)

The variations of  $C_p$  values have interesting features; it increases with temperature up to the glass transition temperature and then decreases up to a certain temperature (~180°C) and again increases with increase of temperature. It also shows a trend to give another peak at the temperature range 240-250°C due to melting on heating and crystallization on cooling. But PS has a rather bulky pendant phenyl group at regular intervals; steric hindrance makes it difficult to crystallize evenly and extensively. Thus its crystallization peak is not very sharp and is rather diffusively spread. High energy irradiation thus may be thought to set off two primary processes which may lead to structural changes in PS. They are chain scission and cross linking. In effect, these are competitive processes, one leading to a lowering of molecular weight and the other increasing it. Both have a direct bearing on the packing and the crystallization of the polymer. In all probability, the process of chain scission turns out to be a dominating phenomenon. The overall effect of this is a decrease in the chain lengths as well as the molecular weight upon exposure to radiation and it also decreases the value of  $C_p$ .

The variation of glass transition temperature ( $T_g$ ) with irradiation doses are shown in the Table 1. At 50 KGy dose  $T_g$  increases by 1.5°C with respect to the reference

sample. The  $T_g$  value at 75 KGy and 100 KGy are almost same and lesser than that of 50 KGy. The variation of  $T_g$  is negligible, thus it does not give any significant information on the microstructural changes in PS upon e-beam irradiation.

**Table 1.** Glass Transition Temperature ( $T_g$ ) at different Irradiation doses (KGy)

Irradiation dose (KGy)	$T_g$ (in °C)
Reference sample	99.1
50	100.7
75	99.6
100	99.9

## 4. Conclusion

From the PALS study it is found that at an irradiation dose 75 KGy, shrinking of inner and inter-chain free volume holes occur i.e. compact and stable structure is attained.

In the DSC measurements, the variation in size of free volume influences very little on the value of  $T_g$ , it increases as the free volume size increases. It is also found that the specific heat at constant pressure and the rate of heat absorption decreases with the increase of electron irradiation dose. As the irradiation dose increases, the scission process becomes dominant and causes decrease of molecular weight and increase the amount of free volume in the sample. Hence the segmental motion of the molecules increases and the  $C_p$  value becomes less.

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