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Study on polystyrene via positron annihilation lifetime and Doppler broadened techniques

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Abstract

Positron annihilation lifetime and Doppler broadened annihilation radiation have been measured for six different samples of polystyrene at room temperature in vacuum. The polymerization of styrene was carried out as a free-radical emulsion polymerization in the presence of redox pair initiation system, potassium persulphate/sodium bisulphite as an initiator system and dodecyl benzene sodium sulphate as an emulsifier. The effect of the initiator amount on the viscosity-average molecular weight was also studied. It was found that the viscosity-average molecular weight of the polymer samples decreases with increasing the initiator amount. The *ortho*-positronium (*o*-Ps) lifetime decreases with increasing the viscosity-average molecular weight up to 8.56×10^4 and increases dramatically after that. The intensity of the *o*-Ps increases with increasing the viscosity-average molecular weight up to 10.43×10^4 and decreases slightly after that. A correlation between the *S*- and *W*-parameters, which reflect the electron momentum, and the *o*-Ps intensity reflecting the electron densities in the free volume sites is obtained. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Various methods including electro-chromic, photochromic, fluorescent probes, nuclear magnetic resonance, small-angle X-ray scattering, density measurement, and positron annihilation spectroscopy have been applied for the measurement of free volume in polymers and each of these methods carries its advantages and limitations [1–5]. Among these methods, the positron annihilation techniques have recently emerged as a unique nano-probe capable of measuring the free volume hole sizes in polymers [6]. Many reviews describing the basic process as well as the application of the positron annihilation spectroscopy in studying the free volume in polymer materials are found in the literatures [5–10].

Upon entering polymer material, a positron is very quickly (within 1 ps) thermalized, and later it may diffuse through the material as a free positron or form a bound state, called positronium (Ps) atom, which is preferentially formed and trapped in the free volume holes (which are the regions of low electron density). Two different states of Ps, spin-antiparallel *para*-positronium (*p*-Ps) has an intrinsic lifetime within 125 ps, decaying into two photons, with formation probability 25%. The second spin-parallel, *ortho*-positronium (*o*-Ps) annihilates into three photons with theoretical lifetime of 140 ns in vacuum [11] and formation probability 75%.

Polystyrene finds use as moulded objects such as combs, toys, novelties, brush handles, kitchen utensils, refrigerator parts, and many industrial parts. Moulded polystyrene's clarity and high refractive index are properties, which allow its use as plastic optical pieces. The low dielectric constant and ease of polymerization make it suited for imbedding electrical parts by polymerization in the mould [12,13]. Although several studies have been published on the application of positron annihilation lifetime (PAL) technique to polystyrene above room temperature [10,14–16], the samples were not well characterized. The summary of relaxation of molecular motion of polystyrene with elevation of temperature is reported in literature [17]. The *o*-Ps has been taken as an effective probe to estimate the free volume size and content present in amorphous region of polymers, since the lifetime and the intensity of the *o*-Ps are proved to be correlated well with the average size and content of the free volume, respectively [18].

In this study, the relation between the initiator amount and the viscosity-average molecular weight of the polystyrene

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has been studied. Also, the PAL and Doppler broadened annihilation radiation (DBAR) parameters of the polystyrene have been measured as a function of the viscosity-average molecular weight. For a better understanding of the structure of a material under investigation, it has become a standard practice to combine the PAL with the DBAR parameters. An attempt is done to establish a correlation between the viscosity-average molecular weight and the positron annihilation parameters through polymer structural properties and free volume parameters.

2. Experimental and data analysis

The styrene monomer (inhibited with 5–10 ppm 4-*tert*-butylcatechol) was supplied from Sigma Chemical, USA and purified by vacuum distillation while dodecyl benzene sodium sulphate was supplied from Aldrich Chemical and used as an emulsifier. Free-radical emulsion polymerizations of styrene monomer [19] were carried out in a 250 ml three-necked flask fitted with a mechanical stirrer and condenser. Various amounts of redox pair initiation system, formed from potassium persulphate/sodium bisulphite (PPS/SBS) were used. The following ingredients were added: water, the redox pair initiator, the emulsifier (0.0065 mol/l) and finally styrene (0.7 mol/l). The polymerization reactions were carried out at 40°C using different amounts of the redox pair initiator amount (0.020/0.010, 0.030/0.015, 0.040/0.020, 0.060/0.030, 0.080/0.040, and 0.014/0.070 mol/l). The purification and precipitation of the polymer were made by the method described by Grassie [20], where the polymer was dried in a vacuum oven at 50°C for 3 days. It was purified by dissolving it in benzene and precipitated by adding ethyl alcohol, after that the polymer was filtered and dried.

The polymer obtained was dissolved in benzene and the viscosity was measured using PROOKFIELD digital viscometers (model DV-II +). The viscosity-average molecular weight was determined by measuring the intrinsic viscosity $[\eta]$. The viscosity-average molecular weight can be calculated using the equation of Mark–Houwink–Sakurada [21–23]:

$$[\eta] = KM^{\alpha}, \qquad (1)$$

where α and K are constants dependent on polymers, solvents, and temperature. In the present work, α and K are 0.74 and 0.94×10^{-4} dl/g, respectively, for polystyrene as the polymer and benzene as the solvent at temperature of 25°C [24].

The positron source was prepared by depositing about 20 μCi of aqueous ^{22}NaCl on a thin kapton foil (7 μm thick). After drying, ^{22}NaCl spots, it was covered with another similar foil glued together by epoxy glue and evacuated for a long time (more than 24 h). The source absorption by the kapton foil was about 10% and contributed to the short lifetime components. This absorption was not separated in the analysis of the lifetime spectra. The PAL measurements were performed using a conventional fast–fast coincidence system. To calculate the time resolution of the system, the PAL spectrum of the kapton sample has been measured. The kapton seems to be the only polymer with no positron yield, i.e. has no long-lived component. The time resolution was calculated using RESOLUTION program [25,26] and it was 240 ps (full width at half maximum, FWHM). The samples were subjected to the same compression at room temperature of thickness 2 mm to avoid any visible bubble. The sample/positron source/sample sandwich was put in a glass tube in order to perform the PAL measurements in vacuum at room temperature (about 25°C).

The PAL spectrum from a polymer is normally characterized by three lifetimes: τ_1, τ_2, and τ_3, and their intensities I_1, I_2, and I_3 (which indicate the number fractions of annihilation events for each mode). In the present work, the lifetime spectra were analysed to finite term lifetimes using the PATFIT program [25,26] without source correction. Three lifetime components were found to give the best variance ratio and most reasonable standard deviations. The mechanism involved in the annihilation of the *o*-Ps state is by pick-off with surrounding electrons. The intensity, I_3, corresponding to the *o*-Ps state describes the probability of the formation of the *o*-Ps, and it may indicate the number of free volume holes in the polymer material. The *o*-Ps lifetime is expected to depend on the free volume hole sizes in polymer materials because the annihilation rate, λ_3 ($\lambda_3 = 1/\tau_3$) of *o*-Ps is proportional to the overlap of the positron and pick-off electron wave functions.

Several studies [7–11] showed the increase of the *o*-Ps lifetime with temperature, and this behaviour has been interpreted in terms of an increase of the free volume hole size with increasing the temperature. A semi-empirical approach based on a quantum mechanical model developed by Tao [27] for molecular liquids allows us to relate the *o*-Ps lifetime τ_3 to the radius, R of a spherical cavity as hole [28] as:

$$\tau_3 = 0.5\left\{1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right\}^{-1} \text{(ns)}, \qquad (2)$$

where $R_0 = R + \Delta R$ and $\Delta R = 0.1656$ nm is the thickness of the homogenous electron layer in which the positron annihilates [29]. Also, the average of the *o*-Ps hole size ($V_{\mathrm{Ps,h}} = (4/3)\pi R^3$), which is probed by the *o*-Ps lifetime, τ_3 could be calculated.

Measurement of the DBAR was performed simultaneously with the PAL measurement. The DBAR spectrometer was based on a high purity germanium detector with an energy resolution of 1.35 keV (FWHM) for 622 keV ^{137}Cs γ-line. Each DBAR spectrum was analysed using DOPPLERFIT program [30] from which *S*- and *W*-parameters are extracted. The *S*-parameter is defined as the ratio of the number of counts in a fixed central window with channels wide (511 ± 0.767 keV) to the number of counts in a spectrum with channels wide (511 ± 3.833 keV). On the other hand, the *W*-parameter is defined as the ratio of the sum of

Table 1
The intrinsic viscosities for polystyrene obtained at different initiator amounts

Initiator amount, PPS/SBS (mol/l)	Intrinsic viscosity $[\eta]$ (dl/g)
0.020/0.010	0.862
0.030/0.015	0.486
0.040/0.020	0.420
0.060/0.030	0.382
0.080/0.040	0.362
0.140/0.070	0.376

the two wing areas [(511 ± 2.555 keV) − (511 ± 1.278 keV)] to the total area (511 ± 3.833 keV).

3. Results and discussion

In the present study, the values of the measured intrinsic viscosities for the samples of polystyrene under investigation are listed in Table 1. The viscosity-average molecular weights have been calculated using Eq. (1) and are presented in Fig. 1 as a function of the initiator amount. The viscosity-average molecular weight decreased with increasing the initiator amount. This is entirely reasonable because the probability of termination increases with increasing the number of growing chains or increasing the number of nucleation centres, which decreases the viscosity-average molecular weight. This is in agreement with the data obtained by Odian [31], and Mohamed and Abd-Elsadek [32]. They expected that as the initiator amount increases the rate of the polymerization increases and the chain length will become shorter. On the other hand, it was observed that the hardness of the polymer decreased as the initiator amount increased. This is due to the fact that when the initiator amount is increased the number of sites at which the reaction occurs increases and as a result the viscosity-average molecular weight decreases.

All the lifetime spectra were resolved into three components as discussed before. The short-lived component ($\tau_1 = 0.12$–0.17 ns, $I_1 = 31$–41%) and the intermediate component ($\tau_2 = 0.41$–0.46 ns, $I_2 = 38$–54%) are attributed mainly to the *p*-Ps and direct annihilation of positrons, respectively. But a detailed analysis is difficult because of the possible formation of positron and positronium compounds that may overlap both components. The long-lived component ($\tau_3 = 1.97$–2.06 ns, $I_3 = 13$–19%) is due to the pick-off annihilation of the *o*-Ps in the free volume holes.

The *o*-Ps lifetime, τ_3, and its intensity, I_3, are shown in Fig. 2 as a function of the viscosity-average molecular weight. The *o*-Ps lifetime decreases with increasing the viscosity-average molecular weight up to 8.56×10^4, after that it shows a dramatic increase with increasing the viscosity-average molecular weight. On the other hand, the intensity I_3 shows a sharp increase with increasing the viscosity-average molecular weight and then decreases slightly. The rate of polymerization at a given temperature

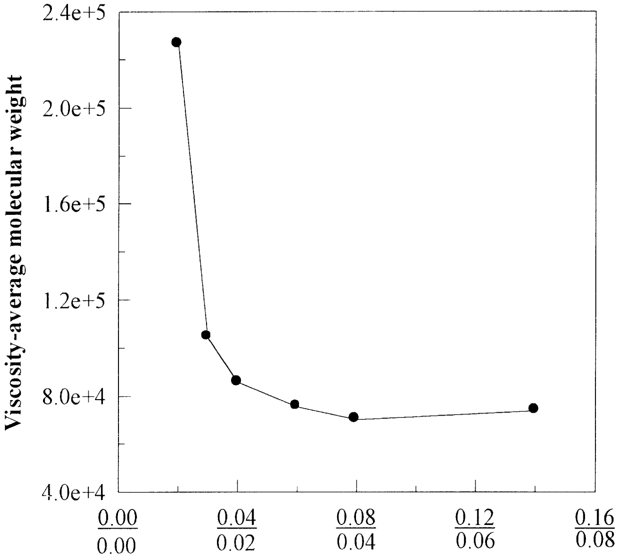

Fig. 1. The viscosity-average molecular weight of polystyrene as a function of the initiator amount (PPS/SBS). The statistical error on each data points is about the size of the circle.

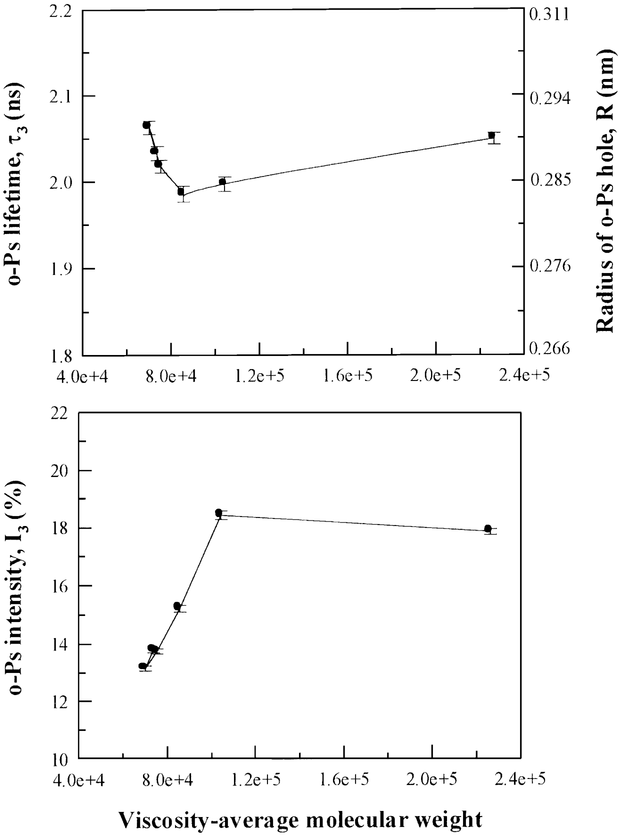

Fig. 2. The *o*-Ps lifetime and its intensity as a function of the viscosity-average molecular weight for polystyrene. The scale at the right ordinate is the radius of the hole in which the *o*-Ps is trapped.

varies with the square root of the initiator concentration and with the first power of the monomer concentration [33]. Also, the chain length inversely depends on the radical concentration [31]. So, the formation of the short chains gives a chance to form free volume between them. This is in accordance with the present data where the *o*-Ps intensity increases with increasing the viscosity-average molecular weight as a result of increasing the average length of polymer chains. Thus, the present polymer occupies a size, which is directly proportional to the viscosity-average molecular weight.

In the dramatic region (the viscosity-average molecular weight larger than 8.56×10^4), the *o*-Ps appears to feel the same environment of the vacancy. Probably the vacancy structure is not much different in the polymers created from low initiator amount and with high viscosity-average molecular weight. Furthermore, the *o*-Ps may not be sensitive to the differences in small vacancy sizes because it tends to get into larger vacancies. The *o*-Ps prefers larger vacancies where its zero-point energy becomes lower [11]. This means that the *o*-Ps feels the same environment of vacancy in the amorphous region.

The parameters which extracted from the DBAR (*S*- and *W*-parameters) are shown in Fig. 3 as a function of the viscosity-average molecular weight. The *S*-parameter shows a similar behaviour as the *o*-Ps intensity with respect to the viscosity-average molecular weight showing that the formation probability of the *p*-Ps and *o*-Ps are parallel. The *S*- and *W*-parameters are corresponding to low and high momentum positron annihilation, respectively [8]. As expected from theoretical considerations, there is a strong correlation between the *S*-parameter and *o*-Ps intensity. This correlation is explained by considering the contribution to the overall annihilation peak shape of combined free positron and the *o*-Ps annihilations (high momentum, high Doppler shifts) to the *p*-Ps annihilations (low momentum, low Doppler shifts). In simple terms, the greater the *p*-Ps yield and hence the *o*-Ps yield (since they are formed in the ratio 1:3) the larger will be the value of the corresponding *S*-parameter.

Fig. 4 shows a correlation between the *S*- and *W*-parameters with the *o*-Ps intensity, I_3. It is clear that the *S*-parameter shows an increase with increasing the *o*-Ps intensity. Using the value of the *o*-Ps intensity (I_3), one can calculate the Ps yield, $P = (4/3)I_3$. Behaviour of the Ps yield against the *S*- and *W*-parameters is also shown in Fig. 4. It is obvious that I_3 and P show exactly the same trend of variation against *S*- and *W*-parameters. It is interesting to note that both *S*- and *W*-parameters show a linear variation with I_3 and Ps yield. Therefore, I_3 and hence the Ps yield are less for the high

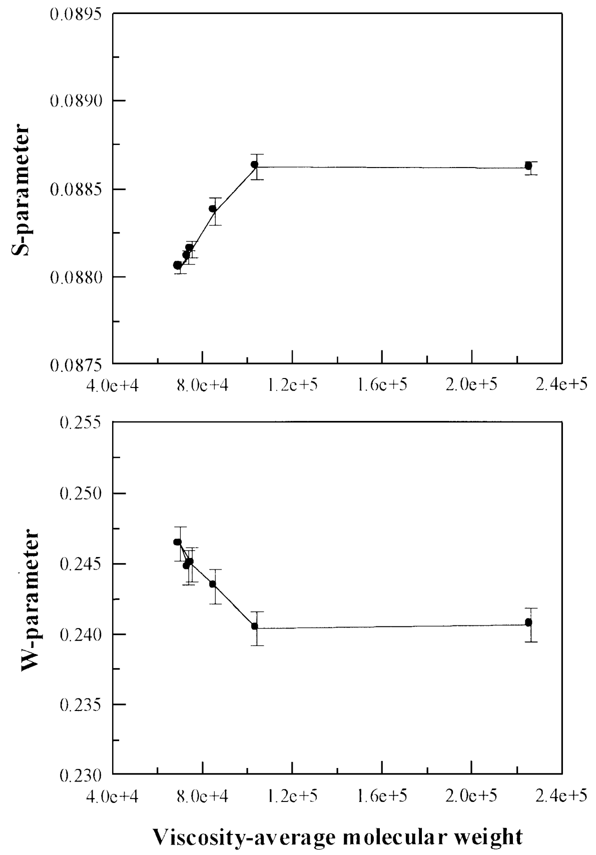

Fig. 3. The *S*- and *W*-parameters as a function of the viscosity-average molecular weight for polystyrene.

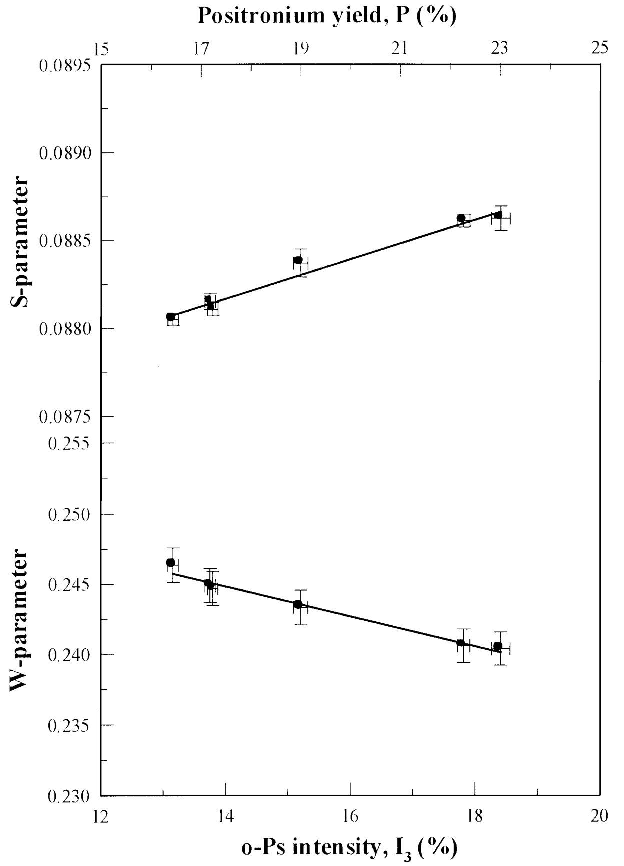

Fig. 4. The *S*- and *W*-parameters as a function of the *o*-Ps intensity, I_3, and the positronium yield, *P*, for polystyrene.

momentum component (i.e. high value of *W*-parameter). The momentum associated with a positron of the *o*-Ps is substantially greater than that of a free thermalized positron. Since, the *o*-Ps annihilates via a pick-off process in the free volume sites of the amorphous regions, the free volume cell size (Eq. (1)) has a greater effect on the *o*-Ps lifetime.

4. Conclusion

The PAL and the DBAR techniques have been used to elucidate the correlation between the density and momentum of the electrons participating in the annihilation process in a polymer matrix. The results indicate that with increasing the *o*-Ps intensity, the low momentum component of the annihilation line increases. DBAR measurement can be used in conjunction with the PAL measurement for a better interpretation of the positron annihilation results in polymers. As the initiator amount increases, the viscosity-average molecular weight decreases because the number of sites at which the reaction occurs increases.

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