DETERMINATION OF FREE RADICALS CONCENTRATION IN γ-IRRADIATED POLYMETHYLMETHACRYLATE USING POSITRON ANNIHILATION LIFETIME SPECTROSCOPY

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Abstract

Low dose γ-irradiation effects on Polymethylmethacrylate (PMMA) polymer are studied by means of positron annihilation lifetime spectroscopy. An empirical formula is suggested to relate the ortho-positronium (o-Ps) lifetime, τ_3 with the molecular weight of the polymer, M_n, and the concentration of the free radicals, $[X]$, generated in PMMA polymer due to irradiation in air. It is shown that free radicals concentration increase with the absorbed dose, and it is measurable from the results of τ_3. The results showed that the positron lifetime parameters illustrate a significant behavior as the dose increase. In addition, a unique behaviors of the free positron annihilation parameters, τ_2 and I_2, are reported. τ_2 is found to increase as the dose increased and the formation of (free radicals-positron) compound is thought to explain this result. The value of I_2 is found to reach a nearly constant (saturated) value at a threshold dose, which is shown to support the lifetime results.

تحديد تركيز الجذور الحرة في البولي مثيل ميثا أكريليت المشعع بأشعة كاما باستخدام مطيافية فناء البوزترون

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الخلاصة

دُرسَ تأثير جرع واطئة من أشعة كاما على بوليمير البولي مثيل ميثا أكريليت (PMMA) باستخدام مطيافية فناء البوزترون. اُقتُرِحَتْ معادلة تجريبية لربط العمر الزمني (τ3) لفناء ذرة البوزترونيوم في الحالة المتعامدة (o-Ps) مع معدل الوزن الجزيئي للبوليمير (M_n) ومع تركيز الجذور الحرة [X] المتولدة في الـ(PMMA) نتيجة لتشعيعه في الهواء. شوهدت زيادة لتركيز الجذور الحرة مع زيادة الجرعة وكانت هذه الزيادة ممكنة القياس من نتائج (τ3). بينت النتائج أيضاً ان معلمات فناء البوزترون تتصرف مميزا مع زيادة الجرعة الممتصة. بالإضافة إلى ذلك، قُدِمتُ نتائج متميزة بمعلمات فناء البوزترون الحر (τ2 و I_2) فقد وجد أن (τ2) تزداد مع زيادة الجرعة الممتصة والتي يعتقد بأن السبب وراءها هو تكوين المركب (الجذر الحر – بوزترون). أما قيمة (I_2) فقد وجدت بأنها تصل إلى قيمة عظمى (مشبعة) عند جرعة عتبة معينة، وهي نتيجة تدعم نتائج البحث الخاصة بالعمر الزمني للفناء.

I. Introduction

The technique of positron annihilation lifetime spectroscopy (PALS) includes the measurements of positron annihilation lifetime from its different physical states. The usefulness of PALS arises from the information content. The positron annihilation lifetime is sensitive to many physical features, such as the electron

density at annihilation site, mobility of the polymer chains, the concentration of active chemical species...etc. The positron, when it passes through a material, annihilates with one of the atomic electrons. The annihilation process terminates by the emission of two γ-photons, usually, each of energy 0.511 MeV emitted in two collinear directions. The period between the positron entrance to the material and its annihilation specifies, to a good approximation, the positron lifetime. The positron may form a bound system with the electron before annihilation takes place, called the *Positronium Atom, Ps*. This system is formed in materials containing "*Free Volume*" [1], it is a nanostructure site of material where the electron density is low. There are, at least, three physical systems that the positron may form in molecular materials. Those are the para-Ps (p-Ps) with lifetime component τ_1 ~100-200 ps, the free positron with τ_2~300-500 ps and ortho-Ps (o-Ps) with τ_3~2000-5000 ps. Each component is also described by its relative intensity, *I*.

When the o-Ps is formed in molecular materials such as polymers, it will annihilate mostly via pick-off annihilation by a lifetime that correlate experimentally with the free volume V_h such as[2]:

$$\tau_3 = 0.5\left[1 - \frac{R_h}{R_h + dR} + \frac{1}{2\pi}\sin\left(\frac{2\pi R_h}{R_h + dR}\right)\right]^{-1} \ (ns) \quad (1),$$

where R_h is the free volume hole radius and *dR* is the electron layer thickness, its value was found to be 0.1665 nanometer (nm) for solid and 0.1830 nm for liquid molecular materials [3]. Formula (1) is generally accepted to represent the free volume radius, specially for polymers [4]. V_h is then given as $V_h = (4\pi \Box R_h^3)/3$ in a spherical geometry approximation. Another quantity can be measured from τ_3 and I_3, that is the free volume hole fraction, F_h, given as[2]:

$$F_h = C I_3 V_h \qquad (2),$$

where *C* is an empirical constant of a value between 1 and 2 nm⁻³, when V_h is given in nm³ and I_3 in percentage.

The effects of different irradiation types on the PMMA polymer have been studied extensively [5-8]. The damage of ionization radiation on PMMA polymer chain is mainly due to breaking of the side chain (or chain scission).

Polymethylmethacrylate, (PMMA), is an amorphous polymer that usually suffers from degradation in the side chain (scission) by irradiation. An important result of scission is the reduction of molecular weight M_n [7]. The number of molecules per unit mass is proportional to the reciprocal of M_n and each scission produces new molecule. Therefore, if the reciprocal of the polymer molecular weight is plotted against the absorbed dose, there must be a linear relation (represented by a straight line) of a positive slop proportional to the radiation energy absorbed per unit scission in the polymer chain. It was found that 60-65 eV deposited energy (of ⁶⁰Co γ-rays) caused scission in PMMA [8] at room temperature.

The chemical structure of PMMA polymer is– $[CH_2C(CH_3)[C(O)OCH_3]]_{-n}$. When PMMA is irradiated in air, the free radical – $[CH_2C(CH_3)[C(O)OCH_3]]$– is observed [8] which is generated due to the interaction of atmospheric oxygen with the free radicals. This interaction is also sample thickness-dependent. For PMMA specimens of about 1 cm thickness, oxygen presence will not affect scission sufficiently. At very high absorbed doses, oxygen diffusion to the samples interior is negligible regardless the specimen's thickness.

Another important feature of PMMA polymer is its post-irradiation effects. The presence of free radicals and trapped electrons in some polymer molecular sites will introduce further changes that continue in time. It was found that the molecular weight of PMMA is reduced further by such effect. However, post-irradiation effects of this polymer are negligible at low dose. This is a temperature-dependent effect.

The linear energy transfer (LET) of the ionization radiation is important in determining the nature of the physical effect of radiation on PMMA. Many studies reported a reduction in scission yield values as LET increases [5-7]. In vacuum, scission yield is constant for LET range from 1.8 to 16.0 MeV cm² g⁻¹, i.e. from γ- rays (of ⁶⁰Co) to 30 MeV protons. LET effects on polymers are considered to be due to the high density of ionization and excitation in the localized sites referred to as a track. As the LET increases, the recombination probability increases between two successive spurs in the track, which causes an increment in cross-linking and a reduction in scission rates. In the case of low LET radiation, the spurs in the track are isolated from each other. Increasing LET will reduce the average distance between the

intermediate spurs leading to a significant cross-linking probability. The LET value at which the scission begins to overlap is called the "Threshold LET (*TLET*)", below which the apparent effect of radiation is scission, and above it the LET effect appear as a reduction in scission and an increment in the cross-linking probabilities can be represented as the ratio of the energy required to form a spur to the radius of the spurs. For PMMA, the TLET was found to be about 300 MeV cm^2 g^{-1} for irradiation under vacuum [6, 7].

The effects of γ-rays on PMMA were also studied using PALS technique. The first attempt made to do that was by Al-Bayati et al. [9]. Irradiation was performed in air at room temperature to a total γ-dose of 889 kGy using ^{60}Co-gamma rays. Their study showed that τ_2 results were nearly dose-independent [9], with an initial value 359 ps (of the unirradiated samples); whereas the initial value of τ_3 was 1993 ps. It was found that an increment in τ_3 occurred as dose increased up to 14.1 kGy, reaching a maximum value, and then τ_3 decreased as γ-dose increased. Their explanation was that the increment in τ_3 was due to the degradation in the mean and side chain of PMMA polymer, which causes increment in the free volume, while the accumulation of the free radicals causes the reduction in τ_3 due to the different interactions between free radicals and Ps atom [9]. Other studies included PMMA polymer structure but without irradiations [10]. Rubiolo et al. [11] made an experimental investigation of γ-irradiated PMMA using PAL. The yield behavior of this polymer and its dependence on the strain rate in compression tests was also performed with maximum γ-dose 200 kGy in vacuum at room temperature. The initial value of lifetime was 1900 ps. They also found a sudden increment in τ_3 at γ-dose of 50 kGy, which was explained due to the sudden rupture of the PMMA side chain. Also observed a reduction in the o-Ps intensity I_3 that was explained due to the reduction in the free volume, resulting from reduction in the lateral groups [11].

In the present paper, PALS technique is used to experimentally study γ-ray irradiation effects on PMMA polymer. The free radicals concentration generated in PMMA polymer due to irradiation in air will be shown detectable from the lifetime of the o-Ps component, τ_3.

II. Experimental Method

Samples properties: PMMA samples were prepared in laboratory from commercial grains. Each sample was a disk-shaped of radius 32.0 mm and thickness 1.5 mm. The density of PMMA is 1.230 g cm^{-3}, its effective atomic number Z_{eff} is 5.852, its effective atomic weight A_{eff} is 9.00 and the ionization potential of the PMMA molecule lion is 64.370 eV.

Samples irradiation: Irradiation was performed in air at room temperature using ^{60}Co γ-Cell. The dose rate was 0.425 kGy/hr. The total γ-energy emitted from ^{60}Co is 2.5 MeV. The maximum γ-dose was 28.05 kGy, given in steps of order of 0.10 kGy. Low γ-dose steps were chosen to allow only small changes to occur in the measurable positron lifetime parameters.

Apparatus: A conventional fast-slow coincidence lifetime spectrometer was used in the present research. The system's time resolution was characterized by a full width at half maximum (FWHM) of 400±20 ps, using 45% energy window of ^{22}Na. The positron source was supplied as ^{22}NaCl salt, kept between two Al foils each of thickness ~1.5 μm. The positron source was of activity 2.14 μCi (79.18 kBq). Independent analyses of the positron source spectrum (no samples attached) showed that there are three lifetime components. Those were assigned due to free positron annihilation in Al foils and NaCl salt (τ_1=212 ps, I_1=11.961 %), beside, in NaCl alone, the p-Ps annihilation τ_2= 42 ps and I_2=38.205%), and o-Ps annihilation τ_3=2133.5 ps, I_3=49.834%). These components were subtracted from the measured spectra - the source correction.

Data analysis: The analysis of PALS spectra were performed using PFPOSFIT program [12]. Except for τ_1, no other fixed values were assumed in the analysis. The value: of τ_1 was fixed at its average value which is 182 ps, as found from analyzing the five spectra corresponding to the doses 0-0.425 kGy free of concentrations. The analysis were made again using PFPOSFIT including the above correction.

III. Results and Discussions

The results of PMMA lifetime spectra for γ-doses are given in Figures (1-a) to (3-b), respectively for: τ_2, I_2, τ_3, I_3, the free volume hole size, V_h, and the corresponding free volume hole fraction, F_h. The initial values of τ_3 and τ_2 for the un-irradiated samples are in an agreement with those found in the literature [9,

10, 11, 13]. The free volume radius was calculated using formula (1) and free volume hole fraction was calculated from formula (2) using the average value of the constant $C=1.5nm^{-3}$.

The general behavior of τ_3 indicates that chain scission occurs in PMMA as γdose increases. Chain scission causes increasing of the free volume hole size. An important reason of that is the reduction of the number-average molecular weight of the polymer, M_n where each chain scission produces a new free molecule in the polymer chain. Since reducing M_n increases the available free volume size, the o-Ps pick-off annihilation rate will decrease and thus τ_3 value will increase. This should be the only reason of increasing τ_3 as γ-dose increases up to at least 0.637 kGy because at such low doses the participation of the free radicals' concentration in the o-Ps lifetime quenching is negligible due to their low concentration. It is important to mention that the effect of post-irradiation on PMMA at such low doses is not important [8]; therefore, it is totally ignored in this research.

LET of positrons from ^{22}Na (E_β^+~0.54 MeV) in PMMA is about 2.033 MeV/m, the maximum range of such positrons in PMMA is 1.205 mm. In addition, the total absorption of γ-rays with energy E_γ ~2.5 MeV is about 1.962 MeV /m. From that we notice that TLET which is reported for PMMA [7] (its value is 300 MeV $cm^2 gm^{-1}$; equivalent to 3.69 MeV/m) is larger than the energy absorption for both γ-rays and positrons. Thus, neither positrons of ^{22}Na nor γ-rays of ^{60}Co will induce cross-linking this material. This confirms that only scission occurred in PMMA due to irradiation. The range of the positrons in PMMA is less than the thickness of the samples used (1.5 mm); therefore, the only practical correction needed in the current experiment is due to positron annihilation in the ^{22}NaCl and Al foils.
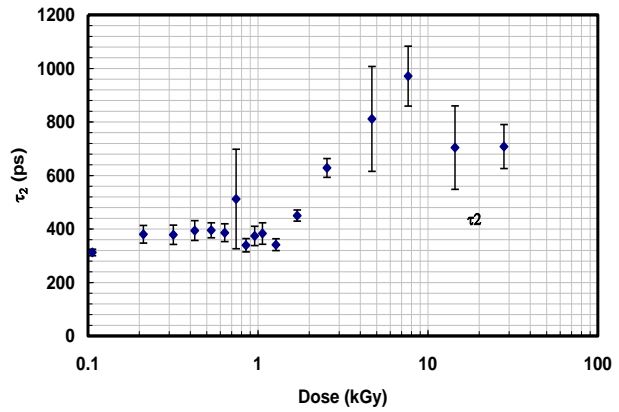

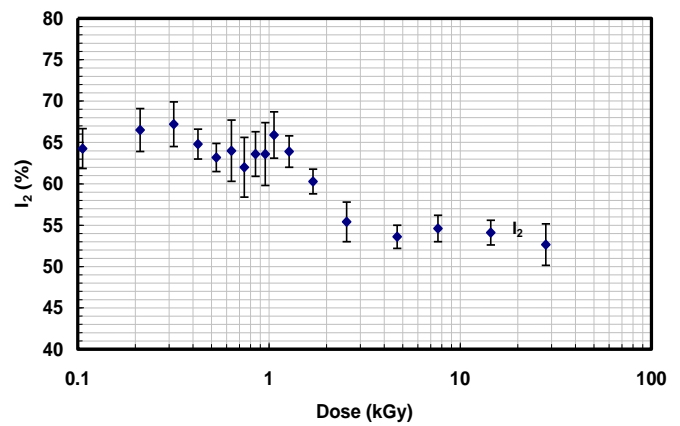**Figure 1-a: The effect of γ-ray irradiation on τ_2 for PMMA samples.**

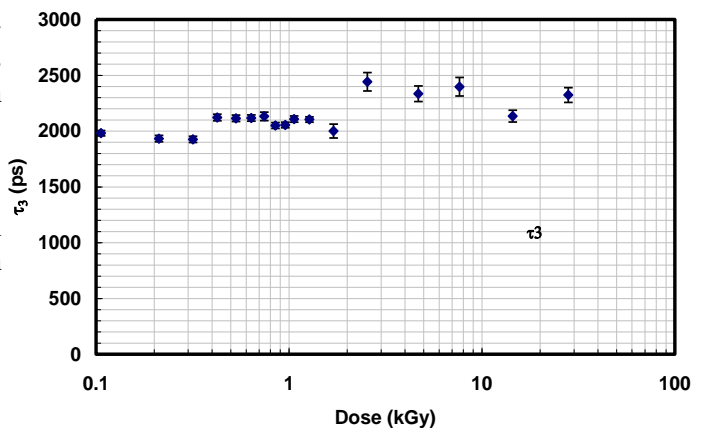**Figure 1-b: The effect of γ-ray irradiation on I_2 for PMMA samples.**

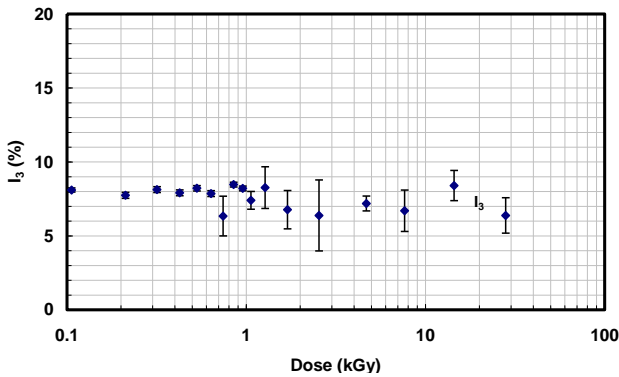**Figure 2-a: The effect of γ-ray irradiation on τ_3 for PMMA samples.**

Figure 2-b: The effect of γ-ray irradiation on I_3 for PMMA samples.
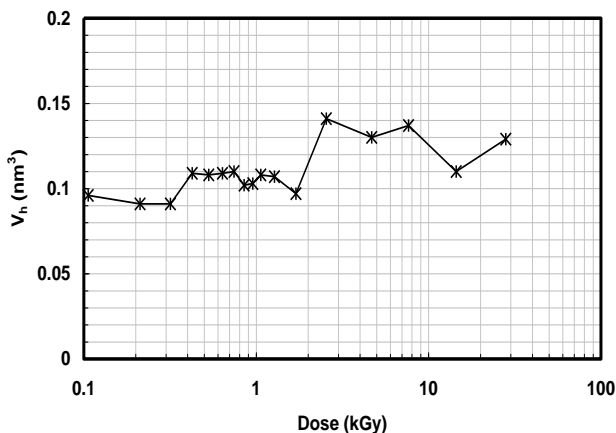

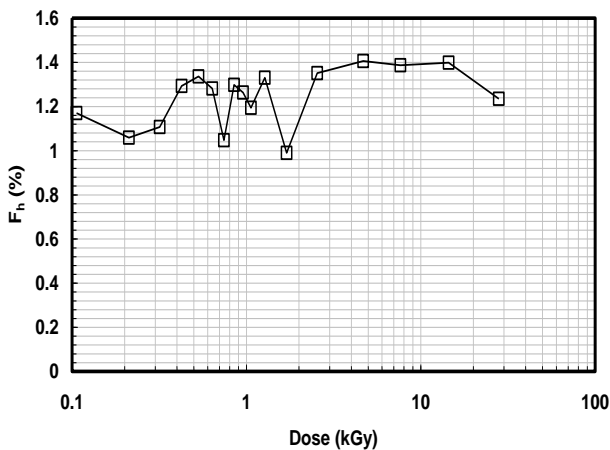**Figure 3-a: The effect of γ-ray irradiation on V_h for PMMA samples.**

Figure 3-b: The effect of γ-ray irradiation on F_h for PMMA samples.

The consistency of τ_3 values for γ-dose interval from 0.850 kGy to 1.700 kGy reflects the high formation rate of the free radicals in such a way that the effect of o-Ps lifetime quenching in this interval is equivalent to the increment of $\tau_3$due to reduction in M_n of PMMA. Above γ-dose

1.700 kGy, the increment in τ_3 may be due to either:

1- M_n of PMMA starts to decrease with a higher rate, or

2- The formation rate of free radicals begins to be slower. It is most probable because it is known that the change in M_n of PMMA polymer is a slow dose-independent process [8].

It will be shown that the free-radicals formation rate becomes slower as the dose increases. The contribution of free radicals can be estimated from values of τ_3 and M_n. To do that, we take the values of M_n found in reference [7] and [11]. Using those values and fitting them to:

$$Y = \frac{1}{M_n} = A \times D(\mathrm{Gy}) + B \tag{3},$$

where $D(\mathrm{Gy})$ is the absorbed dose (in Grays), A and B are empirical constants, then the following empirical formulae are found:

$$\frac{1}{M_n} = 1.844 \times 10^{-10} D(\mathrm{Gy}) + 9.738 \times 10^{-7} \tag{4},$$

$$\frac{1}{M_n} = 1.550 \times 10^{-10} D(\mathrm{Gy}) + 3.803 \times 10^{-7} \tag{5},$$

for the values reported in reference [7] and [11] respectively. In both references, irradiation was performed under vacuum and the results could be applied for irradiating PMMA with both γ-rays from ^{60}Co and 2 MeV electrons. Comparing with the general formula (3), the constants A and B in formulae (4) and (5) are of the same order; therefore, one can roughly assume that any of these formulae can be applied to any commercial PMMA sample. Although irradiation is performed in air in the present research, formulae (4) and (5) can still be applied at low γ-doses. Let us assume that such application is safe for doses from zero up to ~500 Gy, where the effects of the free radicals interactions with atmospheric oxygen is expected to be negligible. For comparison, we chose the dose interval from 0 to 0.425 kGy. Then the values of M_n are given in Table (1) as calculated from both formulae (4) and (5).

It can be shown that the relation between M_n and τ_3 is given by[14]

$$\tau_3 = \frac{1}{\lambda_o + \Omega M_n} \tag{6},$$

where λ_o and Ω are empirical constants. This rather direct relation reflects that τ_3 decreases as M_n increases, a rational behavior between the two physical quantities. When the molecular weight increases, the packing parameter of the polymer lattice increases, this will make higher electron density, corresponding to an increment in the occupation volume. As a result, V_h decreases and τ_3 decreases. Then using values from Table (1), it can be found that:

$$\tau_3 = \frac{1}{5.78 \times 10^{-5} + 4.547 \times 10^{-10} M_n} \quad \text{from(4)} \quad \text{(6-a)}$$

$$\tau_3 = \frac{1}{2.938 \times 10^{-4} + 8.827 \times 10^{-11} M_n} \quad \text{from(5)} \quad \text{(6-b)}$$

where τ_3 is given in ps.

Table 1: The approximate values of M_n for γ-irradiated PMMA polymer, as calculated from eqs.(4 and 5).

Dose (kGy)	M_n x 10^6 (eq.4)	M_n x 10^6 (eq.5)
0	1.026	2.629
0.106	1.006	2.520
0.212	0.986	2.421
0.318	0.967	2.327
0.425	10.948	2.241

Furthermore, it was suggested [15] that, if there was some chemical reaction taking place between the o-Ps and active chemical specie of concentration [X], then the following relation holds:

$$\lambda_o \propto \lambda_{o3} + k[X] \qquad (7)$$

where λ_{o3} is the annihilation rate of the o-Ps, λ_o reflects the o-Ps pick-off annihilation rate at [X] =0, k is the reaction speed and the term $k[X]$ is chemical effect rate. Equation (7) may be extended to include this and it can now be written as follows,

$$\tau_3 = \frac{1}{\lambda_3} = \frac{1}{\lambda_o + \Omega M_n + k[X]} + \Delta \qquad (8),$$

where Δ is a term corresponding to any additional effect(s), such as due to changes in crystallinity and density. For now let this term be ignored.

At very low doses, the term of the chemical effect rate is negligible and formula (6) holds. For higher doses where the effect of that term is important, one can extrapolate the relation between M_n and the absorbed dose and then the

participation of $k[X]$ can be found directly from formula (8). For γ-doses, the calculated values of the chemical effect rate are listed in Table (2). The values of $(k[X])^{-1}$ are plotted against the absorbed γ-dose in Figure (4). Both curves indicate the increment in $k[X]$ values as γ-dose increases. If the value of k is constant, then the changes in the chemical rate effect reflect the increment in the free radicals' concentration [X]. This causes an increment in τ_3 because the probability of (o-Ps–Compound) formation increases. When this is formed the potential that affects the o-Ps pick-off annihilation rate will increase leading to increase the pick-off annihilation rate and to reduce τ_3. Therefore, the term $k[X]$ will contribute less in reducing τ_3 comparing to the effect of reducing M_n. The formation of other systems, such as the Ps$^-$ (the Positronium negative ion, or e$^-$e$^+$e$^-$ atom) is of high probability only when the free radicals concentration is high.
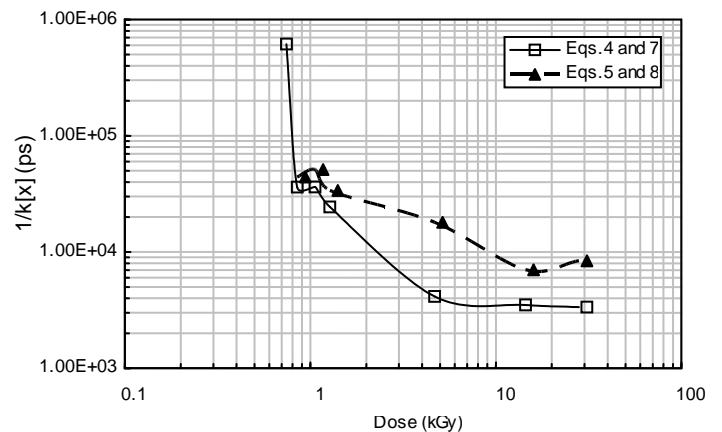
Figure 4: The effect of γ-ray irradiation on the free radicals' concentration [X] for PMMA samples.

Furthermore, the effect of $k[X]$ could be observed from the inhibition of the o-Ps, which is correlated with the reduction in I_3 given in Figure(1-b). Beside their effects on the lifetime, the free radicals may also attract the free electrons generated due to the primary radiation effects, or they may attract the positron itself according to the nature of the free radicals. Also there is a possibility to change the intensity due to interaction of free radicals with o-Ps, an interaction that may cause ionization or oxidation. All such interactions inhibit Ps formation. Consequently, the value of I_3 will be reduced depending on the concentration.

Therefore, decreasing I_3 in Figure (1-b) reflects the free radicals' concentration increment. It was suggested [16] that I_3 follows the form (for irradiated polymers)

$$I_3 = \bar{I}_3 + I_{o3} \exp[-\phi D] \qquad (9),$$

where $I_3, \bar{I}_3, I_{o3}$ are respectively: the measured o-Ps intensity, the intensity as $D \rightarrow \infty$, the value of $I_3 - \bar{I}_3$ at $D=0$, with D being the absorbed dose and ϕ a proportionality constant. However, the preferred formula may be given as:

$$I_3 = I_{o3} \exp[-\phi D] \qquad (10),$$

which means that as the dose becomes very high, the formation probability of the o-Ps will be unlikely, a result that is expected due to the high inhibition of free radicals generated in polymers due to irradiation.
Fitting I_3 values to the empirical formula (10), the following is found:

$$I_3 = 7.761 \exp\left[-4.28 \times 10^{-6} D(\text{Gy})\right] \qquad (11),$$

The behavior of τ_2 shows a rise at a total γ-dose of 7.65 kGy. Since irradiating a polymer in air form peroxy radicals, therefore it is expected for a fraction of the free positrons to form a bound system with the peroxy radicals. The positrons may be bounded into another system. The changes in free positron lifetime due to (e^+–Free radical) bound system formation is not observed clearly before. In the present results, that effect may be apparent because of the small amount of doses given to the polymer samples each time, which allows small changes to occur in the polymer's properties.

Table 2: Contribution of the term $1/k[X]$ in the measured lifetime τ_3.

Dose (kGy)	τ_3 (ps)	$1/k[X]$ (from eq.4 and eq.7)	$1/k[X]$ (from eq.5 and eq.8)
0.743	2132	614632	--
0.850	2050	36052	44148
1.062	2108	36184	51191
1.275	2104	24387	33811
4.678	2335	4140	19768
14.45	2134	3500	7036
28.05	2323	3384	8402

The carbonyl group produced from the decomposition of peroxy radical is a favorable site for the formation of (e^+–Carbonyl) system. The lifetime of positron annihilation from that system is changed due to the high electro-negativity of the oxygen atom that may act as a typical trap for the free positrons. The initial free radical concentration is low and the efficiency such trapping at the initial dose is also small. As absorbed dose increases, that efficiency increases as a function of the free radicals' concentration, thus leading to decrease the annihilation rate of the free positrons and to increase their lifetime. The values listed in Table (2) approximately reflect this behavior. This will also cause a slower annihilation rate for the free positrons and thus a longer lifetime. This behavior appears to continue to a certain dose, which is ~7.65 kGy in this case. We call such a dose as the "*Threshold Dose, TD*". Above that dose, the free positron lifetime decreases. The reduction of τ_2 value above TD is explained on the bases of free radicals' presence. When the concentration of the free radicals is high, they will be distributed rather closer to each other; thus, the free positron lifetime will sense the competition between the closer free radicals to attract it. Such closer potentials appear as an increment in the electron density and the annihilation rate increase, leading to the reduction of τ_2. Furthermore, the effects of the free radicals could be seen from the behavior of I_2, given in Figure (2-b). I_2 decrease after irradiation from 67.5% to 60.2% at a total γ-dose of 1.7 kGy. After that, I_2 remains unchanged. It is observed that the first constant value occurs at about the same dose range where τ_2 increases rapidly, that dose is ~2.55 kGy for this polymer. This indicates the reduction in the probability of the free positron annihilation event from the -as named- free state. The extracted fraction of the positrons is added to the p-Ps intensity, I_1.
It could also be observed from the small changes in I_3 This is due to the large value of τ_2, where the existence of the free positron in such an un-stable format (such as the terminal spur or the free radicals) provides a better chance for the Ps atom formation. Ps atom is suffering from a high transition rate from the o-Ps state to the p-Ps state due to spin conversion in such environment. The p-Ps conversion to the o-Ps is not likely due to its short lifetime.

IV. Conclusions

The effects of low γ-irradiation doses on PMMA were studied by means of PALS and it was shown that the free radicals concentration are measurable to some extent by means of this technique. An attempt was made to correlate these effects with the o-Ps lifetime component and the molecular weight of the polymer, as affected due to irradiation. These effects were shown to be calculated from simple empirical formula. Furthermore, some significance was observed in the free positron annihilation component, where the concept of the threshold dose was introduced in order to explain competition between scission and cross-linking in this type of polymer. Some comparisons were made with earlier work and an expectation was made that some important effects might only be seen when using small doses of ionizing radiation on polymers.

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