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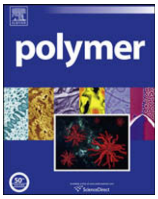

Melting and chemical behaviors of isothermally crystallized gamma-irradiated syndiotactic polystyrene

Chien-Kuo Liu [a], Tinh Nguyen [b], Tsong-Jen Yang [c], Sanboh Lee [a,*]

[a] *Department of Materials Science, National Tsing Hua University, Hsinchu, Taiwan*
[b] *Building and Fire Laboratory, National Institute of Standards and Technology, Gathersburg, MD 20899, USA*
[c] *Department of Materials Science, Feng Chia University, Taichuang, Taiwan*

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Melting and chemical behaviors of isothermally crystallized gamma-irradiated sPS have been investigated using differential scanning calorimetry, FTIR, and X-ray diffraction techniques. Amorphous sPS samples were subjected to gamma radiation in vacuum and in oxygen at different doses from 200 to 1000 kGy. Irradiated samples were heated to 310 °C, cooled to 220–260 °C range, held for 10 min, and re-melted. Three melting endothermic peaks observed for irradiated and non-irradiated samples isothermally crystallized at 220 °C were decomposed into individual Gaussian distributions, and enthalpies of the total melting endotherm and individual peaks were determined. Both α and β crystalline forms coexist in the crystallized irradiated sPS, regardless of the radiation treatment environment. Dose and irradiation environment have a great effect on the melting behaviors and chemical structures of the isothermally crystallized gamma-irradiated sPS. Crystallinity increases with increasing dose of irradiation in both vacuum and oxygen, with level of increase is greater in oxygen. The three melting peak temperatures decrease with increasing dose regardless of irradiation environments. Ketone and aldehyde oxidized products are formed in the isothermally crystallized gamma-irradiated sPS in oxygen through a combination of hydrogen abstraction or chain scission process and hydroxyl free radicals formation.

1. Introduction

Polystyrene is commonly used in the atactic form with no crystallinity. However, there is an increasing interest in the syndiotactic form because of its complex polymorphic behaviors [1,2] and other advantageous properties, including rapid crystallization rate, high melting point, good chemical resistance, and superior mechanical strength. The morphological behaviors of non-irradiated syndiotactic polystyrene (sPS) crystallized under a variety of conditions have been extensively studied [3–16]. sPS possesses a complex polymorphism containing four different crystalline forms: α, β, γ, and δ, depending upon the thermal history and crystallization conditions such as temperature, rate and environments (air or solution) of crystallization [1]. The α form is the hexagonal crystalline structure with lattice constants $a = 26.26$ Å and $c = 5.1$ Å [2,3], while the β form is the orthorhombic crystalline structure with lattice constants $a = 8.81$ Å, $b = 28.82$ Å and $c = 5.1$ Å [4]. Both α and β crystals obtained by cooling from the melt are the stable forms and have a planar zig-zag conformation of backbone chains [5]. β form tends to develop at long crystallization times and at high crystallization temperature, while α form is dominated for short crystallization times and at low crystallization temperature. In terms of structure, α- and β-forms are between disordered structures α′ and β′ and perfect-ordered structures α″ and β″ [2–4]. Melt crystallization experiments generally generate α and β modifications close to α″ and β′ forms, respectively [1,5]. Both γ and δ forms are originated from solvent-induced crystallization [4,6].

The effect of gamma irradiation on morphology and chemical structure of polymers is a subject of great interest [17–23]. Under gamma radiation, free radicals and/or small molecules are generated, leading to molecular structural changes and degradation in polymers. This high-energy radiation influences not only the crystalline structure but also the phase transformation from amorphous to crystalline state. In crystalline polymers, gamma radiation induces crosslinking and breaks up regularity in the crystalline regions. For amorphous polymers, this form of radiation causes both chain scission and crosslinking. As a result, gamma radiation can markedly modify the morphological and chemical structures of polymers, leading to substantial changes in their mechanical and optical properties. Both the irradiation environment and dose play an important role in the morphological changes of polymers. For example, gamma irradiation in vacuum has been shown to cause a decrease in the crystallinity and an increase in the crosslinking of ultrahigh molecular mass polyethylene (PE), and

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* Corresponding author. Tel./fax: +886 3 5719677.
E-mail address: sblee@mx.nthu.edu.tw (S. Lee).

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both changes depend strongly on the radiation dose [22]. Cross-linking has also been reported in PE [23] and PS [21] irradiated in non-oxygen environment.

Polystyrene is being used as a scintillator in high-energy radiation, and much research has focused on the effects of gamma radiation on its mechanical, optical, and transport properties [24–27]. The effects of irradiation environment and annealing conditions on the kinetics of color changes in gamma-irradiated sPS have been also examined [28–30]. The main objective of the present study is to study the isothermal crystallization behaviors of sPS that had been subjected to gamma radiation. Particular emphasis is on the effects of irradiation environment and radiation intensity (i.e., dose) on the melting, morphological, and chemical behaviors of isothermally crystallized gamma-irradiated sPS. Differential scanning calorimetry (DSC), FTIR spectroscopy, and X-ray diffraction techniques were used to characterize these properties. The melting endotherms of the isothermally crystallized non-irradiated and irradiated sPS samples were decomposed into individual Gaussian distributions to enable accurate identification and analysis of each melting peak and its corresponding crystal form.

2. Experimental section[1]

2.1. Materials and gamma ray irradiation

The syndiotactic polystyrene (sPS) pellets (Qustera QA 102 crystalline crystal) were obtained from Dow Chemical Company (Midland, Michigan). This material had a molecular mass of 3.5×10^5 g/mol, a melting point of 270 °C, a DSC glass transition temperature (T_g) of 99.6 °C, and contained a small amount of additives such as antioxidants, processing aids, etc. sPS pellets were cleaned thoroughly with deionized water, followed by conditioning in an oven at 80 °C for 6 h to completely remove the water. They were molded in a Carver 3851 hot press (Wabash, Indiana) at 300 °C and 0.98 MPa pressure with 5 min holding. After removing from the hot press, the samples were immediately quenched in ice water (0 °C). This procedure produced sPS samples having good transparency. Each sample was then ground with 1200 grit sand paper, followed by polishing using aluminum slurries of decreasing particle size of 1 μm, 0.3 μm, and finally 0.05 μm. All sPS samples were annealed in an oven at 90 °C for 1 day to remove residual stresses. The final sample size was approximately 20 mm × 10 mm × 1 mm. sPS samples prepared using this procedure were purely amorphous, as evidenced from X-ray diffraction analysis.

sPS samples were placed in the oxygen-filled and vacuum-filled glass tubes that had an inner radius of 12.4 mm and an outer radius of 15 mm. They were irradiated at room temperature (24 °C) at different doses from 200 kGy to 1000 kGy at a rate of 9.57 kGy per hour using a 29 K Curie Co-60 gamma source at the Radioisotope Division, the National Tsing Hua University.

2.2. Measurements of isothermal crystallization behaviors

Isothermal crystallization behaviors of non-irradiated and gamma-irradiated sPS materials were monitored using a Seiko SSC 5200 differential scanning calorimeter (Chiba, Japan). For this experiment, sPS samples were cut into small pieces of approximately 8 mg, sealed in an aluminum pan, and placed in a sample holder. The sample was first heated up from room temperature to the melt temperature at 310 °C at a heating rate of 10 °C/min, followed by a 5 min holding. Non-irradiated and gamma-irradiated sPS materials have completely melted at this stage. Samples were then cooled down to various crystallization temperatures (T_c) in the 220–260 °C range at a rate of 150 °C/min, followed by a 10 min holding for isothermal crystallization. They were heated up again to the same melt temperature with a heating rate of 10 °C/min. DSC thermograms during isothermal crystallization/melting experiments were recorded. All DSC experiments were carried out under an argon atmosphere. Data from preliminary experiments using different isothermal crystallization schedules showed that the above procedure gives reproducible endothermic peaks of the melting following the crystallization for sPS. This scheme has allowed us to analyze in detail the isothermal crystallization behaviors of gamma-irradiated sPS.

FTIR and X-ray diffraction analyses were also carried out to aid in the interpretation and understanding of the isothermal crystallization and chemical behaviors of gamma-irradiated sPS. FTIR spectra of both non-irradiated and irradiated sPS samples were recorded at a resolution of 1 cm^{-1} using a Nicolet AVATAR 320 FT-IR spectrometer in the attenuated total reflection (ATR) mode, an average of 64 scans, and purged dry air. X-ray diffraction patterns of non-irradiated and irradiated samples were measured using a Rigaku D/MAX-IIB diffractometer (Shibuya-Ku, Tokyo, Japan) equipped with Cu K_α radiation. The operation current and voltage were 20 mA and 30 kV, respectively. The scanning range was $2\theta = 5°–35°$ and scanning rate was 4°/min.

3. Results and discussion

3.1. Melting behaviors of isothermally crystallized gamma-irradiated sPS

Crystallization process in sPS is fast when it is cooled from its melting point (≈270 °C) or above to the crystallization temperatures (T_c = 220–260 °C used in this study). Even at a high cooling rate (e.g., 150 °C/min), sPS tends to crystallize before the crystallization temperature is reached. This behavior often complicates the analysis of sPS crystallization data. Therefore, in order to follow the melting behaviors of isothermally crystallized gamma-irradiated sPS in detail, this study employed a particular heating/cooling/holding/heating scheme for the crystallization experiment, as described in Section 2. Fig. 1 displays the heat flow characteristics

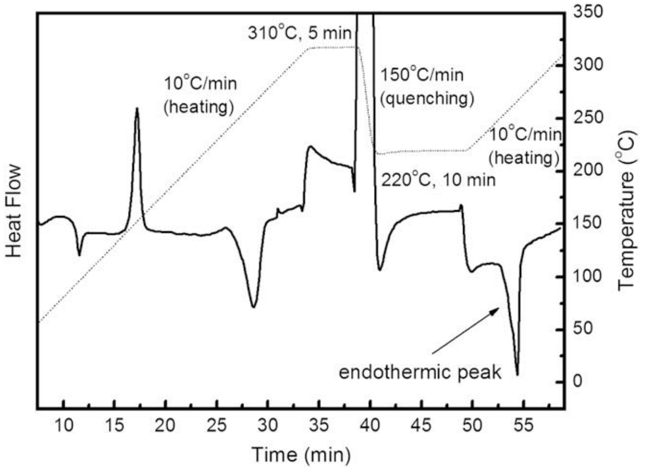

Fig. 1. Temperature changes (dashed lines) and heat flow (solid lines) during isothermal crystallization experiment for, as an example, a non-irradiated sPS sample.

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[1] Certain commercial product or equipment is described in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that it is necessarily the best available for the purpose.

corresponding to temperature changes at various steps during the isothermal crystallization/melting experiment for, as an example, a non-irradiated sPS sample. The dashed and solid lines represent the temperature profile and DSC thermogram (i.e., heat flow), respectively, during the isothermal crystallization experiment. Although the peak intensity and peak shape are different, DSC thermograms of the isothermally crystallized gamma-irradiated samples (not shown) exhibit similar features to those displayed in Fig. 1. It should be mentioned that all T_c values used in this study were above the onset crystallization point of sPS, which is at 147 °C. Further, Ho et al. [8] have shown previously that the melting enthalpy of sPS is essentially constant after 2 min of crystallization at 245 °C. Therefore, with a 10 min crystallization period used in this study for all T_c values, it is expected that the peak area of the endotherm formed during the re-melting following the isothermal crystallization represents the total enthalpy (i.e., the crystallinity or the amount of crystalline materials) of the sample.

As seen in the DSC curve, the heat flow during the isothermal crystallization/melting experiment is very complex, consisting of many exothermic and endothermic peaks corresponding to various phase transition processes occurring in the sample. In this study, the endothermic envelop (indicated by the arrow in Fig. 1) of the heating step immediately following the 10 min holding after cooling from 310 °C to 220 °C (i.e., after the isothermal crystallization) was selected for the analysis of isothermally crystallized irradiated sPS. This endothermic envelop, which comprises single or multiple peaks and extends from approximately 252–278 °C, represents the melting of all crystalline materials in the sample. We found that, by applying a proper deconvolution procedure, this endothermic envelop can provide reproducible data suitable for investigating isothermal crystallization behaviors of irradiated sPS.

Fig. 2 displays DSC thermograms in the 250–285 °C region for non-irradiated (a), vacuum-irradiated (b), and oxygen-irradiated sPS (c) samples that were isothermally crystallized at different T_c values. The irradiation in both environments was conducted at 200 kGy dose. As seen in these figures, the size and shape of the endothermic peaks for both non-irradiated and irradiated samples are highly dependent on their crystallization temperatures, consistent with previous reports for non-irradiated sPS [5,15,16].

In Fig. 2, either no or a barely visible peak is observed when $T_c = 260$ °C; this is because the extent of cooling is too small to induce phase transformation in the material. On the other hand, two peaks are noticed for $T_c = 250$ °C, and three peaks for $230\ ^\circ\text{C} \leq T_c \leq 245\ ^\circ\text{C}$. It should be mentioned that DSC thermogram of the amorphous sPS material before subjecting to crystallization/melting experiment is similar to that when $T_c = 260$ °C; that is, no or little evidence of crystallized material was present in the sample. The multiple-peak melting phenomenon has been explained is due to the presence of two or more crystalline structures (dual morphology mechanism) and reorganization/lamellae thickening (recrystallization-melting mechanism) [15].

The observation of multiple endothermic peaks during melting following the crystallization of non-irradiated sPs has been widely reported [5,15,16]. For example, Ho et al. [16] observed three melting peaks on the DSC thermograms of sPS crystallized at various temperatures from the melt temperature of 290 °C but only two peaks from the melt of 345 °C. For the case of three melting peaks, these authors have attributed the lowest (between 258 °C and 262 °C) and highest (at 272 °C) temperature peaks to melting of the α form and the re-organized lamellae crystals, respectively. These authors also suggested that the intermediate peak at 267 °C is due to a mixture α and β crystals, involving lamellar thickening of α, transformation of α to β phase, and possibility of β reorganization. Woo and Wu [15] have observed three endothermic peaks at 260.9 °C, 266.5 °C and 272.2 °C for sPS crystallized between 242 °C and 250 °C. Based on X-ray and DSC results at different T_c values for pure sPS and sPS blends with other miscible polymers, these authors have attributed the lowest and intermediate temperature peaks to the stable β and α forms, respectively, and the highest temperature peak probably to the less stable β′.

There are several pieces of data suggesting that the assignment by Woo and Wu [15] is credible and applicable to the sPS material used in our study. First, the temperature values for the three peaks of 260.3, 268.8, and 272.7 °C (from Table 1) of our non-irradiated samples are close to those reported in Reference [15]. Second, our enthalpy results (Table 3) indicate that the crystal form corresponding to the intermediate peak at 268.8 °C is the dominant material in the non-irradiated sPS. Both X-ray diffraction (Fig. 5a, 0 kGy) and FTIR (Fig. 6a, 0 kGy) data obtained in our study clearly show that α is a major component and β is a minor component of the non-irradiated sPS sample. These thermal and chemical data strongly indicate that the intermediate and lowest temperature peaks represent the α and β crystals, respectively, consistent with the assignment by Woo and Wu. Third, the plots of peak temperatures vs. T_c (not shown) for the data of Fig. 2a showed that the highest (272 °C) and immediate peak (268.8 °C) temperatures disappear at T_c of 240 °C and 250 °C, respectively; this is in good agreement with the results of Reference [15]. The disappearance of the highest peak at $T_c = 240$ °C suggests that the crystal associated with this peak is unstable and readily transformed to another crystal form, consistent with observation and assignment of Reference [15] to the β′ form. Fourth, although Ho et al. [16] have attributed the intermediate peak to a mixture of thickened α, α-transformed β, and possibly β reorganization, evidence from X-ray and DSC obtained by De Rosa et al. [5] indicated that the recrystallization involves only lamellar thickening of the same crystal form, with no phase transformation. This result suggests that, if the lowest peak temperature is associated with the α form (as suggested by Ho et al.), then the intermediate temperature peak should correspond to the α form, similar to that proposed by Woo and Wu. For these strong reasons, the assignment by Woo and Wu for the three endothermic peaks is adopted for studying the crystallization behaviors of gamma-irradiated sPS.

Many studies have also attempted to relate the multiple endothermic peaks to the specific crystal forms of sPS crystallized under different conditions [5,8,15,16]. However, there is a good deal of uncertainty about the assignment of an individual melting peak to a particular crystal structure. For example, Ho et al. [16] have suggested that the intermediate melting peak temperature is due to lamellar thickening and a transformation of α to β form, with reorganization of the β structure is another possible contributor. On the other hand, De Rosa et al. [5] have asserted that recrystallization occurred during the melting involves only the lamella thickening of the same crystal forms without any evidence of structural transformation. The difficulty of assigning the melting endothermic peaks to appropriate crystal forms in crystallized sPS likely stems from a number of complicated factors, such as the presence of different molecular structures, thicknesses, and sizes in a particular crystal form, the complex melting and crystallization processes of sPS, and the variation of α and β proportions between samples.

The effects of irradiation environments on the melting behaviors of isothermally crystallized gamma-irradiated sPS can be seen by comparing DSC thermograms at the same T_c in Fig. 2a–c. For example, the three peaks in the curves of T_c between 230 °C and 245 °C for the oxygen-irradiated and vacuum-irradiated samples are more clearly resolved than those of the curves for the non-irradiated material crystallized at the same temperatures. Another noticeable difference is the peak intensity ratios for vacuum-irradiated samples are quite different from those for the oxygen-irradiated counterparts. The effects of the conditions used to irradiate sPS on its isothermal crystallization behaviors are treated quantitatively in the following section.

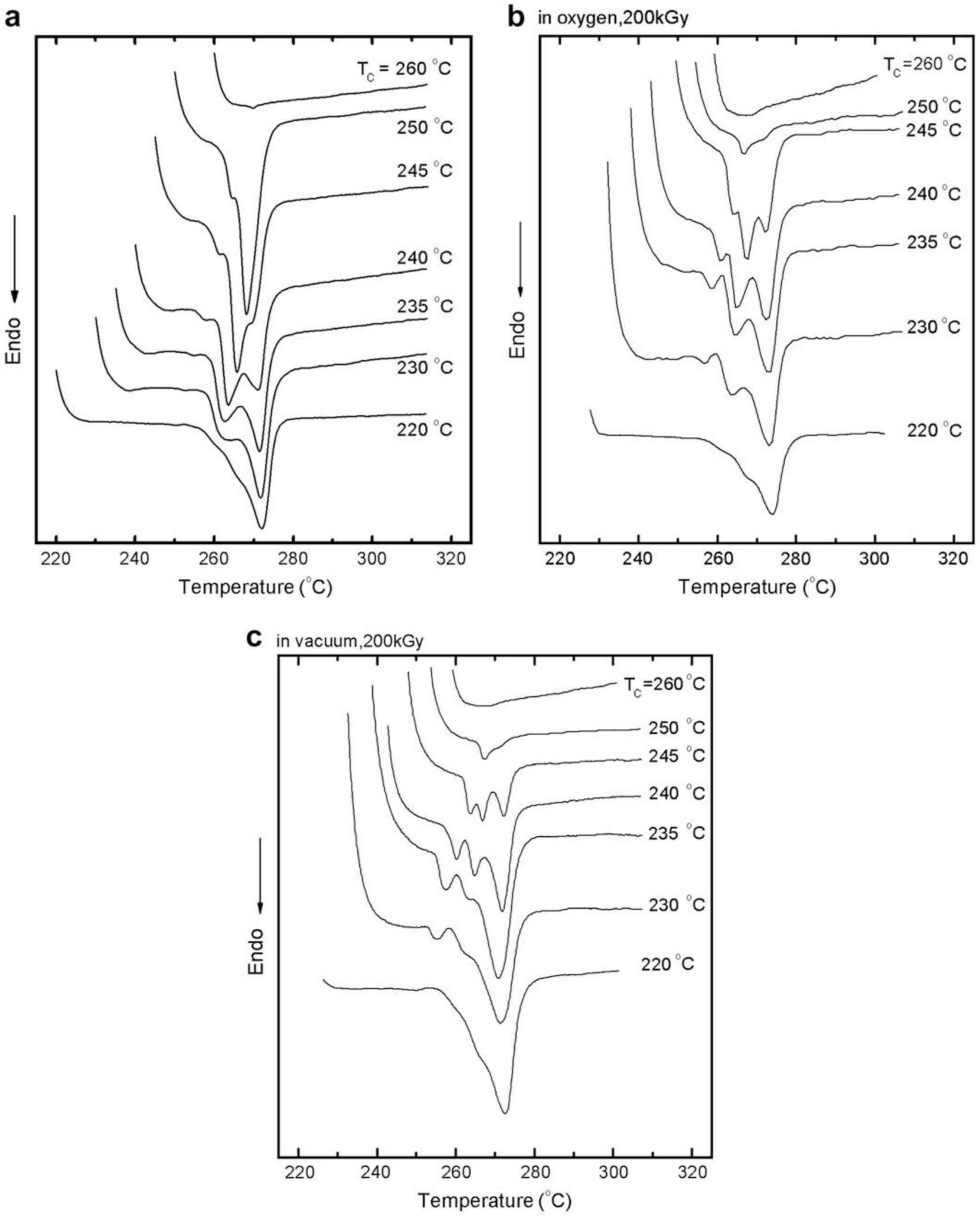

Fig. 2. DSC thermograms of various sPS samples isothermally crystallized at different temperatures: (a) non-irradiated, (b) gamma-irradiated in vacuum, and (c) gamma-irradiated in oxygen. All samples were exposed to 200 kGy dose.

Fig. 3a and b displays typical effects of gamma radiation dose on the characteristics of the 252–278 °C endothermic envelop for sPS samples irradiated in vacuum and in oxygen, respectively. These DSC thermograms were obtained for $T_c = 220$ °C. It should be mentioned that all analyses hereafter are from data measured at this T_c, which represents the largest difference between the melt temperature and the crystallization temperature range used in this study. As seen in Fig. 3, there are three overlapping

Table 1
Parameters A_i, γ_i, T_i and B in Eq. (1) to fit the endothermic melting peaks of isothermally crystallized gamma-irradiated sPS in vacuum.

In vacuum	0 kGy	200 kGy	400 kGy	600 kGy	1000 kGy
A_1 (J/g °C)	−362.2 ± 15.4	−183.1 ± 17.7	−208.8 ± 28.8	−192.4 ± 16.1	−145.4 ± 16.5
A_2 (J/g °C)	−1572 ± 19	−1579 ± 17	−1812 ± 19	−2171 ± 23	−2109 ± 18
A_3 (J/g °C)	−1688 ± 25	−1634 ± 25	−1725 ± 30	−1744 ± 33	−1414 ± 27
γ_1 (°C)	3.93 ± 1.32	3.00 ± 1.87	2.77 ± 1.96	2.98 ± 1.12	2.51 ± 1.09
γ_2 (°C)	7.31 ± 0.07	6.74 ± 0.06	6.28 ± 0.06	6.57 ± 0.05	6.61 ± 0.05
γ_3 (°C)	2.47 ± 0.03	2.56 ± 0.04	2.57 ± 0.04	2.56 ± 0.04	2.72 ± 0.04
T_1 (°C)	260.3 ± 0.5	258.2 ± 0.5	257.0 ± 0.5	256.0 ± 0.5	255.3 ± 0.3
T_2 (°C)	268.8 ± 0.1	267.0 ± 0.1	266.4 ± 0.1	266.0 ± 0.1	264.8 ± 0.1
T_3 (°C)	272.7 ± 0.1	271.3 ± 0.1	270.7 ± 0.1	270.4 ± 0.1	269.4 ± 0.1
B (J/g °C)	9.18 ± 0.14	−3.08 ± 0.18	0.20 ± 0.29	−4.58 ± 0.15	−2.66 ± 0.17

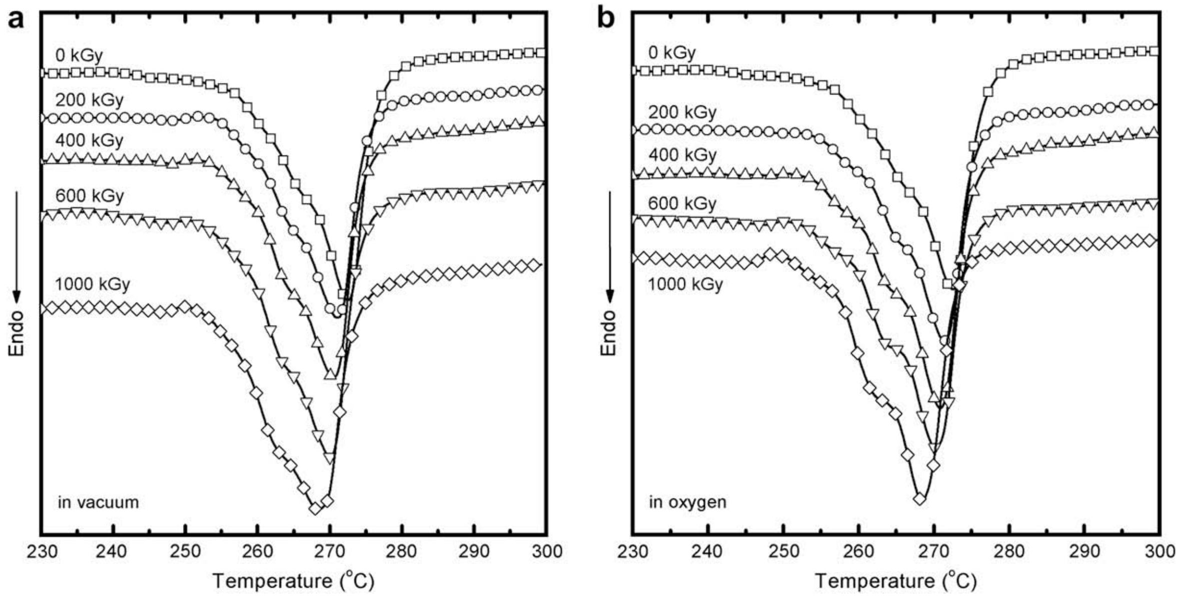

Fig. 3. Endothermic melting peaks of isothermally crystallized gamma-irradiated sPS for different radiation doses: (a) irradiated in vacuum, and (b) irradiated in oxygen. All samples were cooled from the melt temperature at 310 °C to $T_c = 220$ °C and held for 10 min.

endothermic peaks in the isothermally crystallized irradiated and non-irradiated sPS materials. In both irradiation environments, gamma radiation intensity has a strong effect on both the peak shape and peak temperature. For example, the minima of the highest peak temperatures gradually shift to lower temperatures with increasing dose. Further, in non-irradiated sPS (i.e., the 0 kGy curves), the two peaks corresponding to the low and intermediate temperatures appear as shoulders and barely visible. After irradiation in both vacuum and oxygen, however, these peaks not only become more pronounced but their minima also shift to lower temperatures as the radiation intensity increases (the extent of the temperature shift is readily seen in Tables 2 and 3).

Fig. 3 shows that the three peaks within the endothermic envelop are overlapping and so close to each other. In order to study in detail the effects of irradiation environment and dose on the melting behaviors of various phases in the crystallized gamma-irradiated samples, these three peaks must be resolved. This is illustrated in Fig. 4, as an example, for sPS irradiated in oxygen at 200 kGy followed by isothermally crystallized at 220 °C. These curves were obtained by Gaussian distribution simulation, assuming that the phase change around the peak minima is symmetrical. The solid line in Fig. 4 was acquired by superposition of the three Gaussian distributions (dotted line, dashed line, and chained line). The simulated curve is in good agreement with the experimental data, which are represented by the solid square symbols in Fig. 4. Similar results are obtained for non-irradiated and vacuum-irradiated samples.

The enthalpy difference of the melting endothermic envelop, which consists of three different Gaussian distributions, is calculated by

$$\frac{\Delta H}{\Delta T} = \sum_{i=1}^{3} A_i \exp\left[-\left(\frac{T - T_i}{\gamma_i}\right)^2\right] + B \tag{1}$$

where ΔH, A_i, T_i, and γ_i represent the enthalpy fraction corresponding to temperature change from T to $T + \Delta T$, amplitude (peak height), melting temperature, and the Gaussian radius, respectively; B is a constant. The subscript i represents 1, 2, or 3 corresponding to the three overlapping peaks, which are designated as P1–P3. Integrating Eq. (1) with respect to temperature, one can obtain the enthalpies of the melting endothermic envelop and of the individual P1–P3 for sPS material before and after irradiation. Tables 1 and 2 provide values of parameters A_i, γ_i, T_i, and B for sPS irradiated in vacuum and oxygen, respectively, at different radiation doses. Although no statistical analysis was performed, several noticeable effects of gamma radiation dose on these parameters are observed. All three melting peak temperatures (i.e., T_1–T_3) decrease slightly with increasing dose for both irradiation environments. This is likely due to a greater attack on the chain length and chain regularity at higher radiation intensity, resulting in changes in the microstructure. It is not clear whether the shifts in T_i induced by the radiation dose observed in Tables 1 and 2 are due to the effect of

Table 2
Parameters A_i, γ_i, T_i and B in Eq. (1) to fit the endothermic melting peaks of isothermally crystallized gamma-irradiated sPS in oxygen.

In oxygen	0 kGy	200 kGy	400 kGy	600 kGy	1000 kGy
A_1 (J/g °C)	−362.2 ± 15.4	−240.0 ± 2.7	−235.1 ± 7.1	−228.0 ± 5.6	−224.9 ± 4.7
A_2 (J/g °C)	−1572 ± 19	−1682 ± 8	−1765 ± 7	−1701 ± 4	−1809 ± 6
A_3 (J/g °C)	−1688 ± 25	−1782 ± 4	−2208 ± 4	−2245 ± 8	−2694 ± 1
γ_1 (°C)	3.93 ± 1.32	2.93 ± 0.15	2.55 ± 0.18	2.17 ± 0.21	2.46 ± 0.13
γ_2 (°C)	7.31 ± 0.07	6.25 ± 0.07	6.33 ± 0.11	5.8 ± 0.09	5.01 ± 0.10
γ_3 (°C)	2.47 ± 0.03	2.52 ± 0.03	2.69 ± 0.04	2.86 ± 0.04	3.17 ± 0.04
T_1 (°C)	260.3 ± 0.5	258.12 ± 0.13	257.11 ± 0.16	256.20 ± 0.17	254.29 ± 0.14
T_2 (°C)	268.8 ± 0.1	267.4 ± 0.1	266.2 ± 0.1	265.4 ± 0.1	262.9 ± 0.1
T_3 (°C)	272.7 ± 0.1	271.6 ± 0.1	271.0 ± 0.1	270.7 ± 0.1	268.9 ± 0.1
B (J/g °C)	9.18 ± 0.14	0.02 ± 0.97	2.47 ± 0.71	−9.01 ± 0.14	−42.34 ± 0.81

Table 3
Total melting enthalpy (*H*), T_g, and relative proportions[a,b] of the three individual peaks as a function of radiation dose for isothermally crystallized gamma-irradiated sPS in vacuum and oxygen.

	0 kGy	200 kGy	400 kGy	600 kGy	1000 kGy
In vacuum					
H (J/g)	18.54 ± 1.28	18.99 ± 2.33	19.03 ± 3.15	19.27 ± 2.18	19.63 ± 2.76
Proportion of P1 (%)	8	4	3	3	2
Proportion of P2 (%)	67	70	71	74	77
Proportion of P3 (%)	25	26	26	23	21
T_g	99.6	97.6	96.2	95.8	94.6
In oxygen					
H (J/g)	18.54 ± 1.28	19.70 ± 0.36	19.96 ± 0.72	20.50 ± 0.62	22.57 ± 0.55
Proportion of P1 (%)	8	4.5	3	3	3
Proportion of P2 (%)	67	67	63	59	51
Proportion of P3 (%)	25	28.5	34	38	46
T_g	99.6	95.9	95.1	94.6	93.7

[a] Ratio between the melting enthalpy of individual P_i and the total melting enthalpy (*H*).
[b] The uncertainties for P1–P3 at different doses in vacuum and oxygen are similar to those of the *H*.

gamma irradiation on a particular crystal form, e.g., thinning of its lamellae or alteration of chain packing.

Among the Gaussian radii, γ_1 appears to decrease and γ_3 increases slightly with increasing dose in both environments, but γ_2 seems to be unaffected by dose change under vacuum and noticeably decreases at very high doses (>600 kGy) in oxygen. Under vacuum, the heights of P1 and P3 (i.e., A_1 and A_3) decrease the most at the highest level of radiation, while that of P2 (A_2) appears to increase when radiation dose is >400 kGy. In oxygen, a rise of radiation dose increases the height of P3, but has little effect on the heights of the other two peaks.

Integrating Eq. (1) using values of the parameters given in Tables 1 and 2, the total melting enthalpies (*H*) of sPS irradiated in vacuum and in oxygen at various radiation doses were obtained and are given in Table 3, which also includes changes in T_g with irradiation conditions. Adopting the assignment by Woo and Wu, i.e., P1–P3 are associated with β, α, and β′, respectively [15], and assuming that the area under a Gaussian distribution represents one particular crystal form, the majority of the crystals present in the non-irradiated sPS crystallized under the conditions used in this experiment (melt temperature of 310 °C, T_c of 220 °C, and crystallization time of 10 min) is in the α form (67%), with lesser amounts are in the β′ (25%) and β (8%) forms. Table 3 also provides changes in the enthalpies of P1–P3 (expressed as percentages of *H*) as a function of radiation dose in both vacuum and oxygen. Since the melting enthalpy represents the amount of crystalline material in a polymer, these data can provide some useful information on the effects of gamma radiation intensity and irradiation environment on the morphology of isothermally crystallized irradiated sPS.

In both vacuum and oxygen environments, the total melting enthalpy rises with increasing dose, but the rate of increase is greater in oxygen than in vacuum. This result suggests that irradiation in oxygen is more effective than irradiation in vacuum for increasing the level of crystallinity in sPS. Table 3 also shows that T_g decreases with increasing irradiation dose, and that the decrease rate of T_g with dose is greater in oxygen than in vacuum. This T_g behavior suggests that gamma irradiation causes chain scission in sPS, and this degradative effect is more severe in an oxidative environment than in a non-oxidative environment. This result is consistent with previous report on gamma irradiation of normal PS, showing that both chain scission and crosslinking occur in the oxygen environment with the chain scission enhanced at the expense of crosslinking [20]. Apparently, some macromolecule free radicals that normally undergo crosslinking react with oxygen to form peroxides, which then cause oxidative degradation of the main chains. Extensive chain scission was also observed for poly(tetra fluoroethylene-co-perfluoro(methylvinylether)) (TFE/PMVE) gamma-irradiated in oxygen (31). These authors also found that there is a relationship between chain scission and sample crystallinity, the lower molecular mass of the polymer chains the faster the rate of crystallization is. In vacuum, both normal PS [21] and TFE/PMVE [31] polymers undergo only crosslinking during gamma irradiation.

The exact mechanism by which gamma irradiation increases the crystallinity in sPS is not certain. One explanation is gamma radiation attacks mostly the amorphous regions and leaves the crystalline regions essentially intact, as experimentally observed for TFE/PMVE copolymer [31]. In sPS amorphous regions, high-energy gamma radiation causes bond cleavages, which generates shorter polymer chains and small molecules (see degradation mechanism in Fig. 8). Some of these small molecules evaporate and escape the sample, resulting in an increase of the crystalline fraction in the sample. Since enthalpy is proportional to the sample mass, the higher crystalline fraction sample will have a higher melting enthalpy. This explanation is also consistent with the observation that the increase of crystallinity is greater in oxygen than in vacuum. This is because, in addition to enhancing the chain scissions to produce a greater amount of shorter polymer chains, as indicated above, oxygen also combines with small molecule free radicals to form volatile products, such as water (see Schemes 1 and 2 of Fig. 8). The effects of gamma radiation on the morphology and crystallinity of sPS are the subject of great interest. However, the

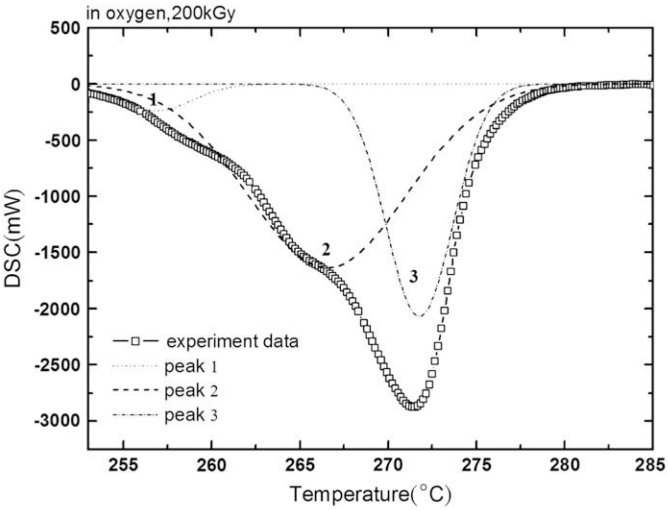

Fig. 4. Gaussian distributions of three endothermic peaks for, as an example, isothermally crystallized gamma-irradiated sPS in oxygen. The sample was cooled from melt temperature at 310 °C to T_c = 220 °C and held for 10 min.

Table 4
The crystalline forms of sPS cooled from melt temperature and the corresponding diffraction angle 2*θ* and diffraction plane (*hkl*).

Crystalline form	2*θ* (diffraction plane)					
α	6.7° (110)	11.6° (300)	13.2° (220)	15.6° (400)	17.8° (410)	20.2° (211)
α″	6.7° (110)	11.7° (300)	14.0° (310)	15.6° (400)	20.3° (211)	
β	6.2° (020)	10.4° (110)	12.3° (040)	13.6° (130)	18.6° (060)	20.2° (111)
β′	6.2° (020)	12.3° (040)	18.6° (060)	20.2° (111)	21.3° (041)	

data generated in this study are not sufficient, and more study is needed, to address this issue.

For Peak 1 (assigned to the β form), gamma irradiation under both vacuum and oxygen reduces slightly the enthalpy of this melting process, although the radiation dose between 200 kGy and 1000 kGy appears to have little influence on the enthalpy. This result suggests that the amount of β was reduced by the gamma radiation treatment, but the level of effect appears to be independent of the irradiation environment or dose. The effect of radiation intensity on the enthalpies of P2 and P3 is different for different environments. The enthalpy of P2 (assigned to the α form) increases substantially with increasing dose under vacuum but decreases markedly under oxygen. On the other hand, the enthalpy of P3 (assigned to the β′) decreases with increasing dose in vacuum, but increases more substantially when the irradiation was performed in oxygen. The latter result implies that gamma irradiation in oxygen at high dose is favorable to form β′ crystals. In summary, both the radiation intensity and irradiation environments have a strong influence on the amounts and distributions of crystalline materials in isothermally crystallized gamma-irradiated sPS. In vacuum, gamma irradiation causes an increase and a decrease of the α and β amounts, respectively, with increasing dose, and radiation intensity has a small effect on the β′ form amount. In oxygen, gamma irradiation reduces the quantities of both α and β, but markedly increases the β′ quantity, with increasing dose.

3.2. *Chemical and morphological behaviors of isothermally crystallized gamma-irradiated sPS*

The DSC results above indicate that the enthalpies and peak temperatures of P1–P3 of crystallized irradiated sPS vary greatly with gamma radiation intensity and irradiation environment. That is, the amount and distribution of different crystal forms in sPS undergo considerable changes after irradiation with gamma ray. To better understand the nature of crystalline structures corresponding to P1–P3, X-ray diffraction patterns and FTIR spectra of isothermally crystallized samples of non-irradiated and gamma-irradiated sPS samples in vacuum and oxygen at different doses were obtained. Table 4 provides the diffraction peak values and planes together with their crystal forms for non-irradiated sPS isothermally crystallized at 220 °C from 310 °C melt temperature. The α peaks at 6.8° and 11.6° and β peaks at 6.2° and 12.3° have been commonly used to study the crystal structures of non-irradiated sPS crystallized under different conditions [1,5,16].

Fig. 5a and b displays the X-ray diffraction patterns of isothermally crystallized samples of sPS that were irradiated in vacuum and oxygen, respectively, for different radiation doses. Using the assignments given in Table 4, the peaks corresponding to the α and β forms are indicated in Fig. 5. The results show that, under the crystallization conditions used for this experiment, a mixture of α and β forms exists in both non-irradiated and irradiated sPS samples regardless of the environment of irradiation and radiation dose. Fig. 5 also shows that the α peak intensity of non-irradiated sPS is much greater than that of the β peak. These results and those of Table 3 on the enthalpy are in agreement with literature reports that crystallization from the 300 °C to 340 °C melt temperature range generally produces a mixture of α and β crystal forms, and that crystallization at temperature below 230 °C favors the formation of the α form [5,15, 16]. A quantitative agreement between the α X-ray diffraction and the P2 enthalpy data obtained in this study strongly supports the assignment by Woo and Wu that the intermediate peak at 268.8 °C is due to the α form crystal.

In oxygen environment (Fig. 5b), radiation dose has a strong influence on the intensities of both α and β peaks. For example, the intensities of the α peaks at 6.7°, 11.6°, and 15.6° decrease, and those associated with the β peak at 12.3° appear to increase, with increasing dose. The intensity ratios between the α peak at 6.7° and the β peak at 6.2° and between the α″ peak at 14° and the β peak at

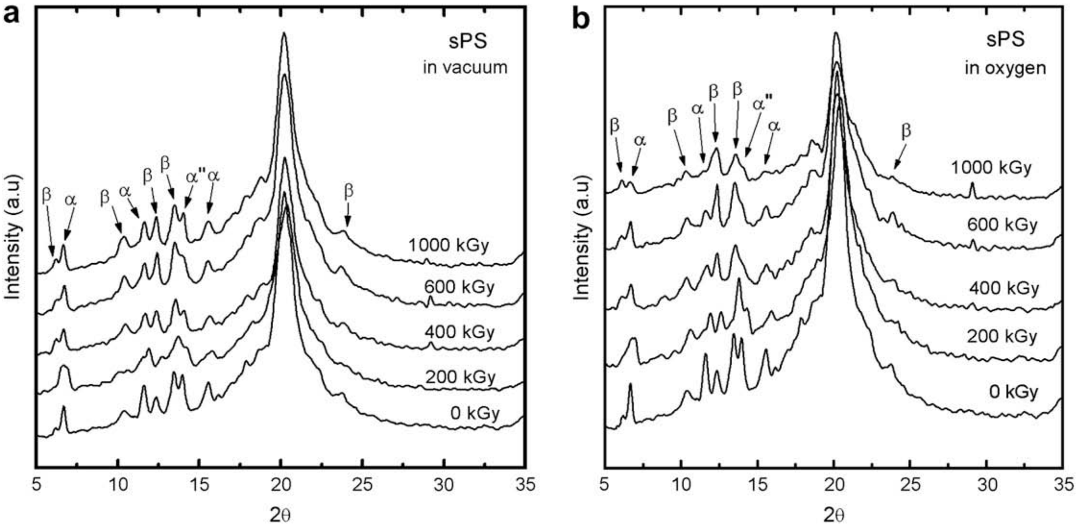

Fig. 5. X-ray diffraction patterns of isothermally crystallized gamma-irradiated sPS for different radiation doses: (a) irradiated in vacuum, and (b) irradiated in oxygen. All samples were cooled from melt temperature at 310 °C to $T_c = 220$ °C and held for 10 min.

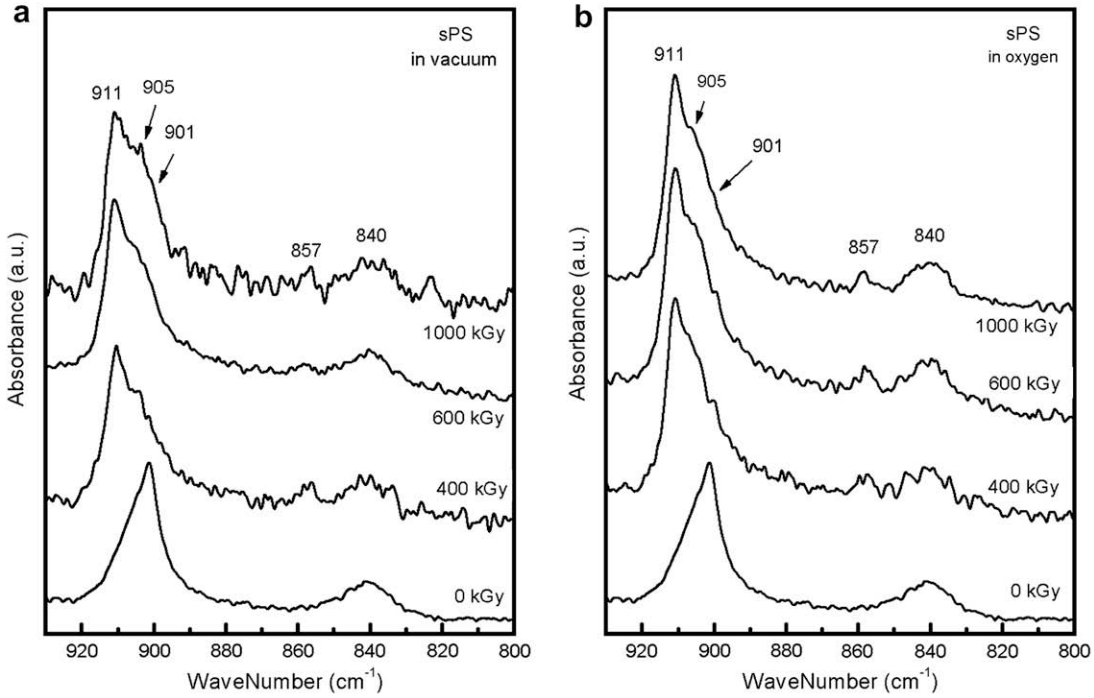

Fig. 6. FTIR-ATR spectra in the 800–930 cm^{-1} region of isothermally crystallized gamma-irradiated sPS for different radiation doses: (a) irradiated in vacuum, and (b) irradiated in oxygen. All samples were cooled from melt temperature at 310 °C to $T_c = 220$ °C and held for 10 min.

13.6° also decrease with increasing dose for irradiation in oxygen. However, the effect of radiation dose on the intensity of the β peaks at 6.2°, 10.4° and 13.6° under oxygen is not noticeable. In vacuum (Fig. 5a), the intensity change of both α and β peaks with dose does not show any particular trend. For example, the intensities of the α peaks at 6.7° and 11.6° and β peaks at 10.4° and 12.3° decrease with doses at 200 and 400 kGy, but appear to rise at 600 kGy and 1000 kGy.

Fig. 6a and b displays the FTIR-ATR spectra in the 950–800 cm^{-1} region of isothermally crystallized samples of sPS gamma-irradiated in vacuum (a) and in oxygen (b) for different radiation doses. The FTIR spectrum of sPS containing amorphous material and a mixture of crystallized forms is complex, because the intensity of a particular functional group is the sum of three distinguishable components (amorphous material, α crystal, and β crystal). Isothermally crystallized non-irradiated sPS shows two broad absorption bands peaking near 840 cm^{-1} and 901 cm^{-1} (Fig. 6, 0 kGy) and two shoulders near 905 cm^{-1} and 911 cm^{-1}. The 840 cm^{-1} and 905 cm^{-1} bands have been assigned to the amorphous region, and the bands at 901 cm^{-1} and 911 cm^{-1} have been attributed to the α and β crystalline regions, respectively [32,8]. Based on these assignments and on the line shape of the absorption band peaking at 901 cm^{-1} shown in Fig. 6, it can be concluded that α is the dominant crystal in the isothermally crystallized non-irradiated sPS, with β form occupying a lesser amount. This result is in good agreement with the enthalpy data given in Table 3 and the X-ray results shown in Fig. 5 (0 kGy curve). This result further supports the assignment of the P2 peak to the α form.

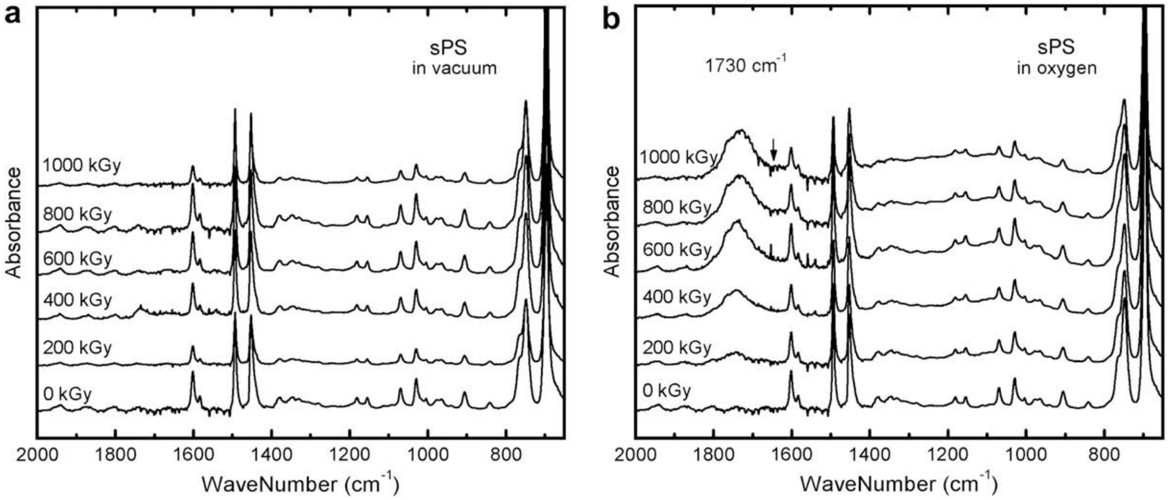

Fig. 7. FTIR-ATR spectra in the 650–2000 cm^{-1} regions of isothermally crystallized gamma-irradiated sPS for different radiation doses: (a) irradiated in vacuum, and (b) irradiated in oxygen. All samples were cooled from melt temperature at 310 °C to $T_c = 220$ °C and held for 10 min.

FTIR-ATR spectra of the isothermally crystallized gamma-irradiated sPS show a new band peaking appears near 857 cm^{-1} and the peak at 901 cm^{-1} becomes less pronounced, regardless of the irradiation environment and radiation intensity (Fig. 6). The 857 cm^{-1} band has also been attributed to the β crystalline regions [32]. On the other hand, the shoulder at 911 cm^{-1} has become a distinct peak after gamma radiation treatment in both vacuum and oxygen. One reason for the pronounced appearance of the 911 cm^{-1} peak after irradiation may be due to a change in the packing/orientation of the polymer chains due to gamma radiation treatment. This explanation is supported by the observation of Musto et al. [32] that the bands in the 900–911 cm^{-1} region of sPS are quite sensitive to its chain packing; that is, the band at 905 cm^{-1} present in the amorphous material is shifted to 911 cm^{-1} in the orthorhombic β form and to 902 cm^{-1} in the hexagonal α form. Another reason may be this crystal form of the isothermally crystallized gamma-irradiated sPS is more abundant near the sample surface, which is detected by FTIR-ATR spectroscopy. It is noted that, with a KBr prism (used in this study), the FTIR-ATR technique can provide chemical information at a depth less than 2.5 μm from the surface in the 900–911 cm^{-1} region. Based on the enthalpy data and its change with dose in both vacuum and oxygen (Table 3), the 911 cm^{-1} band is probably associated with the chemical structure of the β′ crystals. Further study is needed to verify the above postulations.

In addition, the line shape and symmetry of the bands in the 900–920 cm^{-1} region have changed drastically after irradiation in both environments; for example, the broadness on the left of the 901 cm^{-1} peak has shifted to the right of the 911 cm^{-1} peak. However, it is clearly seen from Fig. 6a and b that a substantial amount of the α and amorphous materials is still present in the isothermally crystallized gamma-irradiated samples. By deconvoluting the FTIR spectra

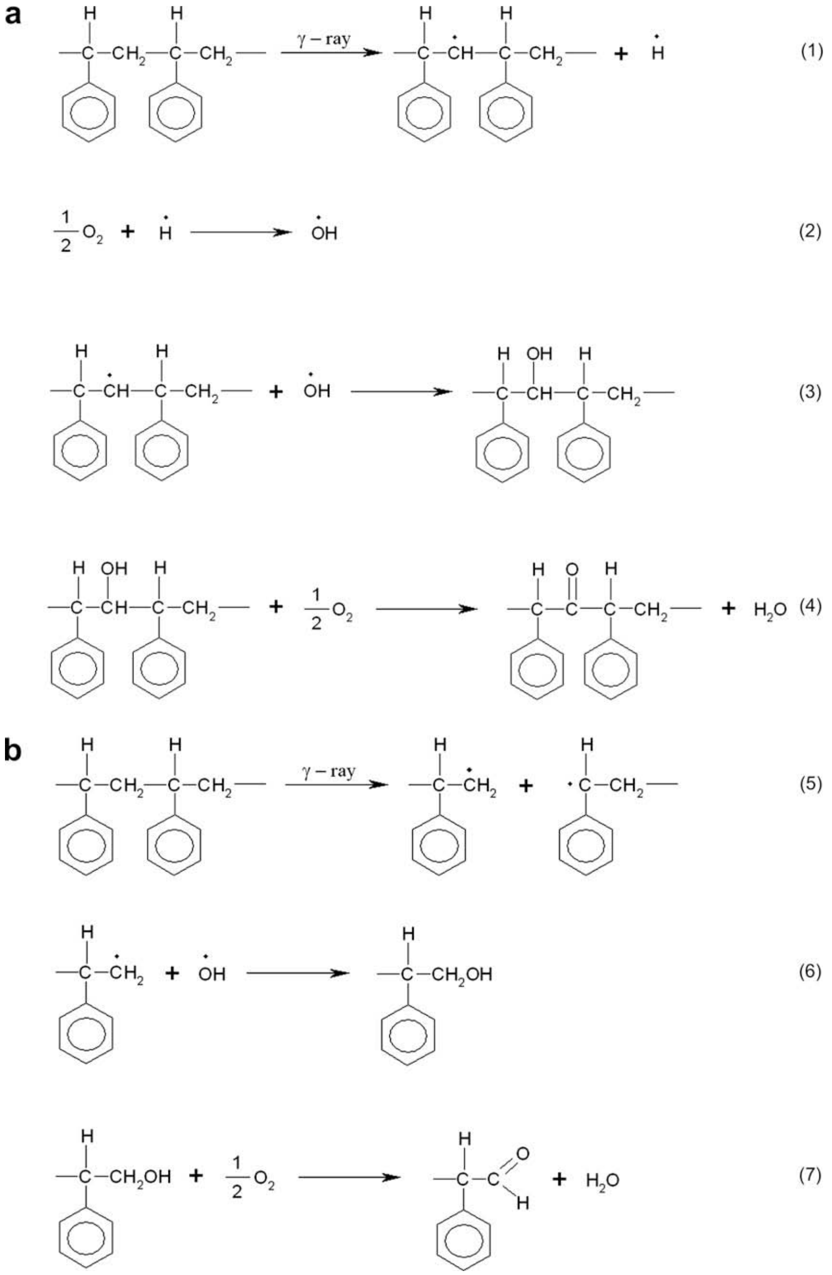

Fig. 8. Plausible reaction pathways for ketone and aldehyde formation in isothermally crystallized gamma-irradiated sPS under oxygen: (a) Scheme 1, ketone formation, and (b) Scheme 2, aldehyde formation.

measured on the same gamma-irradiated sPS samples used in this study, Ting [33] was able to show that the amount of the α and β forms increases and decreases, respectively, with time of crystallization at 250 °C. Further, FTIR results of this study are in good agreement with DSC data.

A close examination of Fig. 6a and b reveals that there are numerous visible peaks and shoulders in the region between 901 cm^{-1} and 911 cm^{-1} in the spectra of the crystallized irradiated material. This result indicates that the crystal structures in the gamma-irradiated sPS crystallized at 220 °C for 10 min are complex, containing a variety of α and β materials. From the enthalpy results given in Table 3 and FTIR spectra shown in Fig. 6, we can state that the amounts of β and α crystals formed in sPS can be substantially changed by varying the gamma irradiation conditions used to treat this material prior to the crystallization. Previously, the control of β or α levels in sPS may be achieved by controlling the crystallization conditions and the crystalline form of the starting materials [5,16].

The effect of irradiation environment on chemical changes of isothermally crystallized gamma-irradiated sPS can be seen in the 700–2000 cm^{-1} region of the FTIR spectra shown in Fig. 7a and b. The only noticeable difference between irradiation in vacuum and in oxygen is the presence of a broad absorption band peaking near 1730 cm^{-1}, which is due to the formation of carbonyl groups ($C{=}O$), for the latter environment, similar to that reported for normal PS [34]. Using the styrene aromatic band at 1500 cm^{-1} as a reference, it can be seen that the intensity of the 1730 cm^{-1} band increases with increasing dose. The formation of carbonyl products in the crystallized oxygen-irradiated sPS probably follows our proposed Schemes 1 and 2 presented in Fig. 8. Scheme 1 (Reactions 1–4), in which secondary alcohols are the intermediate products, involves abstraction of a hydrogen atom from the methylene (CH_2) group to form free radicals in the polymer chains and hydroxyl free radicals. These reaction pathways generate ketones in the irradiated polymer, which are observed as the band peaking near 1730 cm^{-1}, and water molecules released in the air during irradiation. No attempt was made to detect the released water. Scheme 2 (Reactions 5–7) involves a chain scission of the CH_2–C bonds of the polymer structure to generate macromolecule free radicals, which combine with the hydroxyl free radicals generated in the Reaction 2 of Scheme 1 to produce secondary alcohol products. In the presence of oxygen, primary alcohols undergo oxidization to form aldehydes as the products in the irradiated sPS polymer. In the absence of oxygen, macromolecule free radicals generated in Reactions 1 and 5 would undergo crosslinking to form large molecules. The chemical processes occurred during irradiation in vacuum and air of normal PS under UV radiation have been reviewed briefly by Rabek [35].

4. Summary and conclusions

Melting and chemical behaviors of isothermally crystallized gamma-irradiated sPS have been investigated using differential scanning calorimetry, FTIR, and X-ray diffraction techniques. Amorphous sPS samples were subjected to gamma radiation in vacuum and in oxygen at different doses from 200 to 1000 kGy. Irradiated samples were heated to 310 °C, cooled to 220–260 °C range, held for 10 min, and re-melted. Three melting endothermic peaks observed for irradiated and non-irradiated sPS samples isothermally crystallized at 220 °C were deconvoluted using Gaussian simulation, and peak temperatures and enthalpies of the individual peaks were determined. Isothermally crystallized non-irradiated sPS is dominated with α crystals, with β′ and β forms present at lesser amounts. Gamma irradiation of sPS has a great effect on its isothermal crystallization/melt and chemical behaviors. Irradiation in oxygen produces an increase in the crystallinity of sPS, probably due to a large amount of lower molecular polymer chains generated by this irradiation process. All three melting peak temperatures decrease with increasing radiation dose regardless of irradiation environments, and the amounts of β′ crystals increase substantially with radiation dose for sPS irradiated in oxygen. The amount of α crystal increases and amounts of β and β′ crystals decrease with increasing dose for samples irradiated in vacuum. Ketone and aldehyde products are formed in the isothermally crystallized oxygen-irradiated sPS through a combination of hydrogen abstraction or chain scission process and hydroxyl free radicals formation. Thermal analytical and spectroscopic data indicate that the amounts of β and α crystals in sPS can be substantially changed by varying the gamma irradiation conditions used to treat the material prior to the crystallization.

Acknowledgements

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