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Annihilation kinetics of color center in irradiated syndiotactic polystyrene at elevated temperatures

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Abstract

In situ absorbance of syndiotactic polystyrene (sPS) at elevated temperatures is investigated. The irradiation environments of air, vacuum and oxygen are considered. The decreasing loss in transmittance after irradiation follows the sequence: oxygen, air and vacuum. The UV cut-off and shoulder wavelengths of sPS irradiated in an air atmosphere are greater than those in vacuum. Two types of color centers are responsible for the reduction of transmittance in the irradiated specimen. They are annealable and permanent. A first order annihilation model is proposed to analyze the annealable color centers. The results show that the annealable color center of sPS irradiated in vacuum required to overcome less energy barrier to annihilate than that in air, but the permanent color centers in the former is less than those in the latter after annealing. No annealable color center is observed in sPS irradiated in an oxygen atmosphere. The EPR spectra and FTIR spectra were also studied to enhance the understanding of kinetics of color center.

Keywords: Color center; Syndiotactic polystyrene; Annealing

1. Introduction

It is well known that ionizing radiation produces color centers in glassy polymers, but not well understood. Two types of color centers are formed: annealable and permanent. Clough et al. [1] surveyed 17 different types of optical polymers, in which those materials form both types of color center in different magnitudes and ratios. Wallace et al. [2] investigated that annealable color centers in gamma ray irradiated polystyrene are due to the formation of cyclohexadienyl, benzyl and other radicals. Harmon et al. [3] found that the annealable color centers are minimized when permeability and flexibility of the polymer matrix are enhanced. The color centers were monitored using UV/VIS transmission spectra. Harmon et al. [4] compared the bathochromatic shift in the transmission spectra of the elastomers and glassy polymers. They found that glassy polymers exhibited a pronounced, initial bathochromatic shift upon irradiation which diminished considerably after ageing, but elastomers behaved the opposite trend. Whitaker and Johnson [5] investigated the effect of oxygen and thermal treatment prior to irradiation on the optical density of polystyrene in the ultraviolet range. Hamada et al. [6] studied the radiation damage of polystyrene doped with PPO and POPOP. They found that the PPO and POPOP restrict the transparency of the polymer block to the wavelength of fluorescence spectra and the recovery of transmittance follows an exponential function of time. Milinchuk et al. [7] proved benzyl macroradicals to be efficient quenchers of the excited scintillator molecules. The literatures above were emphasized on the phenomena description or optical absorbance mechanism with gamma ray doses below 100 kGy.

The bleaching of gamma ray-irradiated-induced optical absorption bands in polystyrene is commonly observed. Mechanisms of thermal bleaching and oxidation were proposed. Holm et al. [8] used a diffusion model to study oxygen diffusion in irradiated polystyrene. Trimmer et al. [9] proposed a simple self-diffusion model to analyze the oxygen induced bleaching of color centers. They measured the absorption profiles of irradiated PS at different annealing times. The oxygen kinetics reported by above literature was

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an indirect evidence of evolution of transmission recovery in irradiated PS.

Herod et al. [10] studied the recovery of color centers in irradiated poly(vinyltoluene) using in situ UV–vis spectrophotometry and EPR spectroscopy. Their result showed that the recovery of blue region (480 nm) is a two-step process and the long term recovery rate is characterized by a bimolecular reaction. They did not study the short term recovery. Evolution of transmission in irradiated hydroxyethyl methacrylate copolymer was analyzed by Lu et al. [11]. They found that the color centers were enhanced at elevated temperatures and their increment was followed a first-order kinetic process. Lu et al. [12] also studied the transmission loss in irradiated poly(methyl methacrylate) at elevated temperatures in which the color center is annihilated by a second order kinetic process. Chiang et al. [13] analyzed absorbance data of polystyrene irradiated in vacuum ($\Phi = 100$ kGy) to the annealing in air and vacuum obtained by Wallace et al. [2]. They proposed a first-order annihilation process and a second order annihilation process to the annealing in air and vacuum, respectively. This prompted us to study annealing of color center of sPS irradiated at high dose (≥ 200 kGy) in vacuum, air and oxygen atmosphere. The in situ absorbance measurement was undergone which is different from the periodical measurement by Wallace et al. [2]. UV–vis spectra of sPS irradiated in different environments were studied. Further, a kinetic model of color center was proposed to analyze the in situ absorbance data. FTIR spectra and EPR spectra of irradiated sPS at 70 °C were analyzed to correlate the color center. The results are summarized in the conclusion.

2. Experimental procedure

The syndiotactic polystyrene (sPS) pellets (Qustera QA 102 crystalline crystal) with molecular weight $M_w = 3.5 \times 10^5$ g mol^{-1} were obtained from Dow Chemical Company, Midland, Michigan. In addition to sPS, there are very small amount (0.1–0.5 ppm) of additives such as antioxidants, processing aids, etc., in the pellets. Their melting temperature, glass transition temperature and crystallization temperature are 270, 99 and 147 °C, respectively. The sPS pellets were molded in a Carver 3851 hot press with pressure of about 0.98 MPa ($=10$ kgw/cm^2) at 300 °C hold for 5 min. The samples were removed from the hot press and quenched to ice water (0 °C). The purpose of this step is to obtain a clear and amorphous sPS. Each sample was ground with 1200 grit emery paper and polished with 1, 0.3 and 0.05 μm aluminum slurries. The sample was put into an oven maintained at 90 °C for 24 h. This step is used to eliminate residual stresses. The final size of sample is $10 \times 10 \times 1$ mm^3.

Three types of samples were prepared in this study. They were put in air-filled, oxygen-filled and vacuo glass tubes, respectively. These three types of samples were irradiated via a 30 K Curie Co-60 gamma source at a dose rate of 9.86 kGy/h at room temperature at the Radioisotope Division of the National Tsing Hua University. The irradiation doses were 200, 300, 400 and 500 kGy.

After irradiation, the samples were taken out from glass tube and placed in a heating chamber maintained at constant temperature. The transmission spectra of both types of samples before and after annealing were recorded on a Hitachi U-3410 spectrometer with a scanning speed of 300 nm/min in the wavelength range from 250 to 800 nm at 25 °C.

The in situ transient transmittance as a function of time was studied. The sample in the heating chamber was placed between a Bentham M300EA monochromatic light source and a DH-Si photo-detector connected with a personal computer. The wavelength of incident light is 400 nm and data are recorded every 30 s.

The glass transition temperatures of irradiated sPS were measured using a Seiko SSC 5200 differential scanning calorimeter (DSC) (Chiba, Japan). The irradiated sPS was cut into small pieces about 5 mg and sealed in an aluminum pan then placed into DSC immediately. The sample was heated up from room temperature to 300 °C with a heating rate 10 °C/min. Argon was used as a flow gas in the DSC measurement.

The FT-IR transmission spectra of irradiated sPS at elevated temperature were measured using a Nicolet AVATAR 320 FT-IR spectrometer, Madison WI, USA, with the scan range of 4000–650 cm^{-1}. The total number of scans is 64 and resolution is 1 cm^{-1}. The specimen size is $10 \times 10 \times 1$ mm^3.

The EPR spectra of irradiated sPS samples were recorded with an EMX-10 electron paramagnetic resonance (EPR) spectrometer made by Bruker Instrument, Karlsruhe, Germany, with a dual cavity at 70 °C. The operation microwave frequency is 9 GHz, microwave power is 20.02 mW, and sweep width is 150 G. The specimen size is $10 \times 2.5 \times 1$ mm^3. Radical concentration was measured by comparison of the double integral spectra with a reference DPPH which contains a total spins of 2.0×10^{15}.

3. Results and discussion

Amorphous sPS is transparent before gamma ray irradiation and becomes yellow after irradiation. The yellow changes to dark brown when dose increases. This phenomenon is attributed to color center created by gamma ray irradiation. The concentration of color center depends on the dose, irradiation environment and annealing condition.

Fig. 1(a)–(c) shows the UV–vis spectra of sPS irradiated in vacuum, in air and in oxygen atmospheres, respectively. For a given wavelength the transmittance increases with decreasing dose regardless of irradiation environment. The shoulder wavelength shifts from 318 nm for non-irradiated

Table 1
The UV cut-off wavelengths (nm) of sPS irradiated in different atmospheres

Irradiation environment	Dose (kGy)			
	200	300	400	500
Oxygen	293	–	326	–
Air	329	341	353	364
Vacuum	329	333	340	345

sPS to 370 nm for sPS irradiated in vacuum and to 400 nm for sPS irradiated in an air atmosphere. However, no shoulder was observed in sPS irradiated in an oxygen atmosphere. It is also found that shoulder disappears after annealing regardless of irradiation environment. The difference in transmittance between two doses decreases with increasing wavelength. The UV cut-off wavelengths of irradiated sPS in different atmospheres are listed in Table 1. All of them shift to the long wavelength side. For a given dose, the UV cut-off wavelength increases according to the sequence: oxygen, vacuum and air. It can be seen from Fig. 1 that for a given dose the transmittance of sPS increases according to the sequence: vacuum, air and oxygen. Because the summation of absorbance and transmittance is constant and absorbance is proportional to the color center concentration, the color center concentration of sPS irradiated in air is greater than that in vacuum.

Wallace et al. [1] found that when the polystyrene samples of thickness = 10 mm (path length ≥ 10 mm) were irradiated with 100 kGy, a number of absorption bands corresponding to the benzyl and cyclohexadienyl radicals appeared in the UV–vis spectra; these absorption bands receded slowly and then disappeared during annealing. Huggenberger et al. [14] and Jordan et al. [15] studied the UV–vis absorption of the benzyl and cyclohexadienyl radicals in liquid solution or solid phase. They found the absorption bands for these radicals listed in Table 2. According to Fig. 1, no obvious absorption peaks of benzyl and cyclohexadienyl radicals were observed in the UV–vis spectra. This is because the sample thickness in this study is 1 mm which less than the path length 10 mm of above radicals.

The color centers of sPS can be annealed at elevated temperatures. The absorbances A of irradiated sPS at wavelength 400 nm as a function of annealing time for $\Phi = 200$, 300, 400 and 500 kGy are plotted in Fig. 2(a)–(d), respectively. The data of absorbance A are obtained from transmittance, I, with the assumption of reflectance being equal to zero, i.e. $A = 1 - I$. If the reflectance is not zero, the result will be negligibly affected in our analysis. The reflectance depends on the surface roughness and surface defects. Because the annealing temperature is low, the

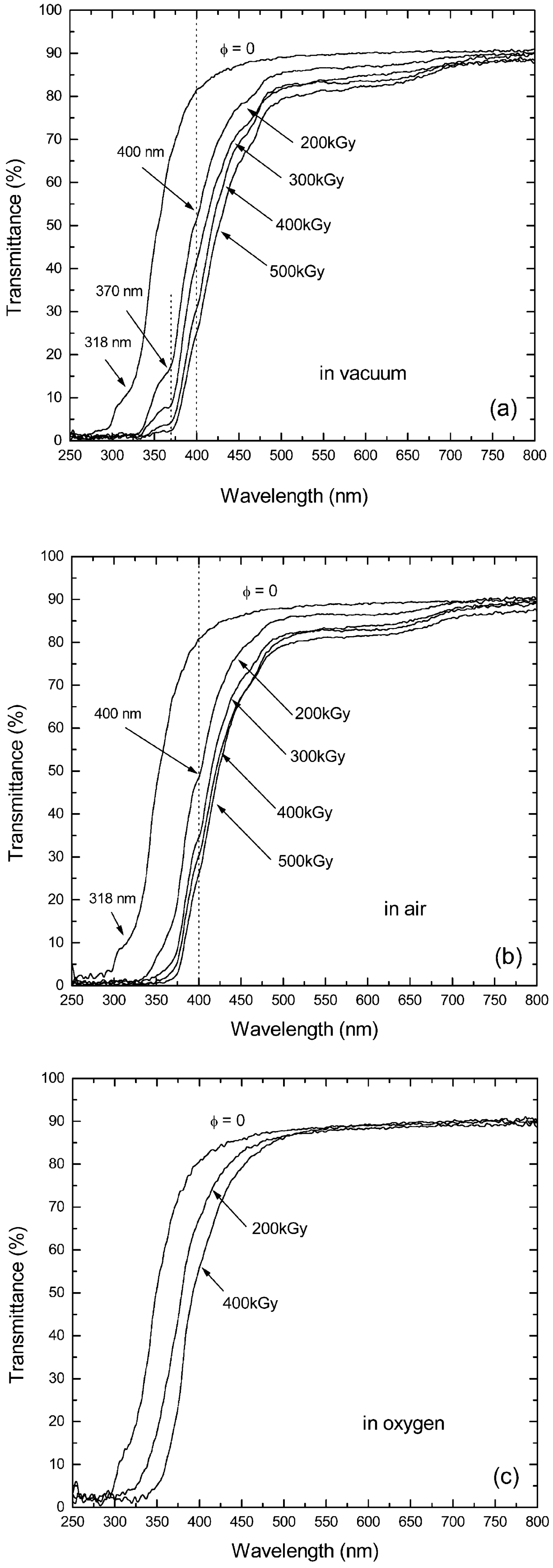


Fig. 1. UV/VIS spectra showing the transmissions (a) for a vacuum irradiated syndiotactic polystyrene, (b) for an air irradiated syndiotactic polystyrene, and (c) for an oxygen irradiated syndiotactic polystyrene.

Table 2
The Absorption bands of benzyl and cyclohexadienyl radicals

Radical	λ_{max} (nm)	ε_{max} (M^{-1} cm^{-1})
Benzyl [14]	258	31,400±3,200
	293	1400±200
	304	3500±400
	316	8800±700
	422	95±20
	436	120±20
	452	130±20
Cyclohexadienyl [15]	308	–
	314	–
	512	–
	554	–

surface condition does not change. Furthermore, reflectance is independent of color center. It can be seen from Fig. 2 that the absorbance of sPS irradiated in vacuum decreases with increasing time for all doses.

The absorbance data can be analyzed using a first order annihilation process proposed by Chiang et al. [13]. They assumed that the concentration n of color centers is followed the first order annihilation process during annealing,

$$\frac{dn}{dt} = -\alpha(n - n_\infty) \tag{1}$$

where α is the rate constant, n_∞ the concentration of color center at time infinity, and t, the annealing time. They also assumed that the absorbance is proportional to the concentration of color center,

$$A = \beta n \tag{2}$$

where β is a constant. If at the initial time $A = A_0$, the solution of Eq. (1) with Eq. (2) is

$$\frac{A}{A_\infty} = 1 - \left(1 - \frac{A_0}{A_\infty}\right)e^{-\alpha t} \tag{3}$$

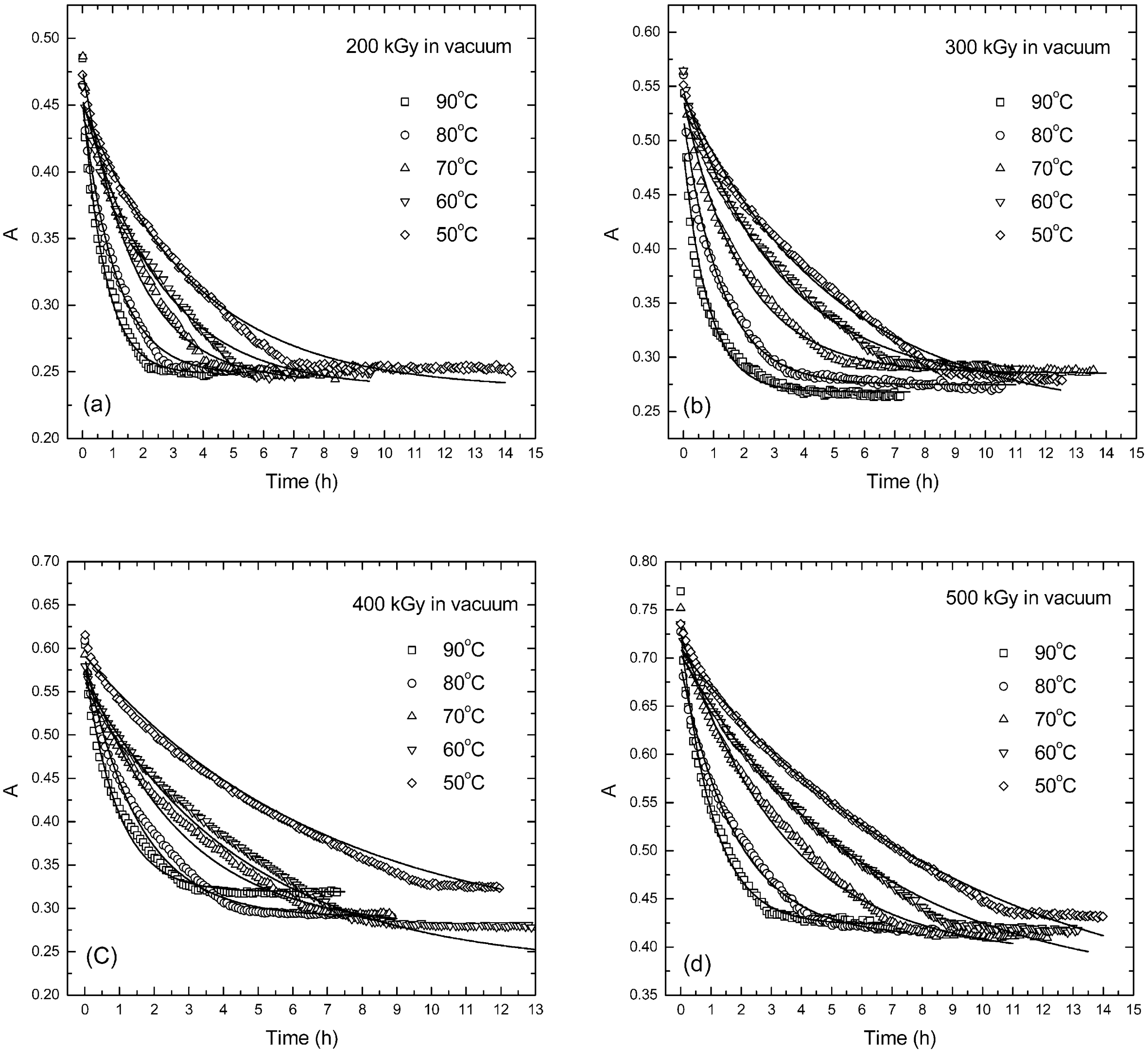


Fig. 2. Absorbances of vacuum irradiated sPS at $\lambda = 400$ nm as a function of annealing time for samples with various doses: (a) 200, (b) 300, (c) 400, and (d) 500 kGy.

where A_∞ ($=\beta n_\infty$) and A_0 ($=\beta n_0$) are the absorbance at $t=\infty$, 0. n_0 and n_∞ are the color center concentrations at $t=0$ and ∞. All solid lines in Fig. 2 were obtained from Eq. (3) with parameters A_0, A_∞ and α tabulated in Table 3. It is found that the experimental data are in good agreement with theoretical prediction. According to Table 3, A_∞ increases with increasing dose at a given temperature. Because A_∞ is proportional to n_∞, the color concentration at a long time is not zero. This implies that some color center cannot be annealed out at elevated temperature. These permanent color centers are associated with a permanent change in structure of the macromolecules and/or low molecular weight components present in the matrix at annealing temperatures [1]. The other type of color centers associated with a reactive species is annealable which is annihilated at elevated temperature. The annealable color center can be characterized by rate constant α. Fig. 3 replots the curve of α obtained from Table 3 vs. $1/T$ with different doses. For a given dose α increases with increasing temperature. The rate constant satisfies the Arrhenius equation as shown in Fig. 3 by solid lines. The activation energies of color center with different doses are listed in Table 4. The activation energy increases with increasing dose. Chiang et al. [13] also obtained the activation energy of color center as 56.6 kJ/mol for PS irradiated with 100 kGy in vacuum and being annealed in air. Their value is greater than that in this study. The reason may be due to different structures of macromolecular and low weight molecular components. The sPS exhibits high regularity of molecular structure which differs from the common PS with random stereochemistry. Clough et al. [1] indicated that the macromolecular structure, e.g. aromatic rings, double bonds, etc., and the low weight molecular component, such as stabilized additives, were influenced the radiation-induced color center formation of polymers.

The temperature dependence of absorbance A of sPS irradiated in an air atmosphere is shown in Fig. 4(a)–(d) for dose 200, 300, 400 and 500 kGy, respectively. The solid lines were obtained using Eq. (3) with parameters A_0, A_∞ and α listed in Table 5. The experimental data are in good agreement with a first order annihilation model. It is found that A_∞ increases with increasing dose at a given temperature. This implies that the concentration of permanent color center ($A_\infty=\beta n_\infty$) increases with increasing dose. Comparing Table 5 with Table 3, the concentration of permanent color center in sPS irradiated in air is greater than that in vacuum. The difference between A_0 and A_∞ of irradiated sPS is greater for the sPS irradiated in vacuum than for the sPS irradiated in air. That is, the concentration of annealable color center in sPS irradiated in vacuum is more than that in air. The annealable color center of sPS irradiated in air can be also characterized by the rate constant α. The rate constants α listed in Table 5 were replotted in Fig. 5. According to Fig. 5, α increases with increasing temperature and satisfies the Arrhenius equation. The activation energies of color center of sPS irradiated in air increases slightly and monotonically with increasing

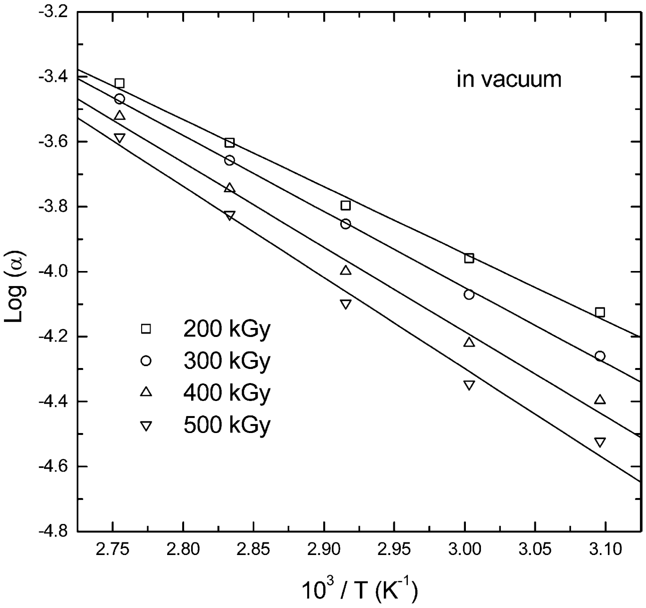


Fig. 3. Arrhenius plots of rate constant α of color center in vacuum irradiated sPS where the unit of α is s^{-1}.

Table 3
The values of A_0, A_∞ and α for sPS irradiated in vacuum annealed at different temperatures

Dose (kGy)		T (°C)				
		50	60	70	80	90
200	A_0	0.452	0.454	0.476	0.451	0.459
	A_∞	0.237	0.238	0.242	0.248	0.249
	α (10^{-4} s^{-1})	0.75	1.1	1.6	2.5	3.8
300	A_0	0.541	0.545	0.538	0.520	0.491
	A_∞	0.245	0.275	0.285	0.275	0.268
	α (10^{-4} s^{-1})	0.55	0.85	1.4	2.2	3.4
400	A_0	0.592	0.562	0.577	0.590	0.822
	A_∞	0.264	0.233	0.277	0.290	0.319
	α (10^{-4} s^{-1})	0.4	0.6	1.0	1.8	3.0
500	A_0	0.709	0.704	0.724	0.692	0.726
	A_∞	0.328	0.356	0.390	0.410	0.423
	α (10^{-4} s^{-1})	0.3	0.45	0.8	1.5	2.6

Table 4
Activation energies (kJ/mol) of color center in γ-irradiated sPS

Irradiation environment	Dose (kGy)			
	200	300	400	500
Air	50.72	54.67	56.81	58.76
Vacuum	39.57	44.77	49.87	53.70

dose. Comparing the irradiation environment of vacuum with air, the activation energy in the specimen irradiated in vacuum is smaller than that in air. This implies that the annealable color center of sPS irradiated in air is more difficult to annihilate than that in vacuum.

The absorbance of sPS irradiated in oxygen atmosphere with doses 200 and 400 kGy, was found to be independent of annealing time at temperatures 50–90 °C. That is, all color centers are permanent. If there exists color center to annihilate, the activation energy should be very high. It is known that air consists of approximate 20 vol% oxygen and 80 vol% nitrogen. Thus it is an indirect evidence to see that the activation energy of color center is greater for specimen irradiated in air than that in vacuum (Table 4).

The results of DSC measurement of sPS irradiated in air and in vacuum are shown in Fig. 6(a) and (b), respectively. Both glass transition temperatures of the sPS irradiated in air and in vacuum are decreased with increasing dose. The glass transition temperature increases with increasing molecular weight for the polymeric material. It is implied that the reduction of molecular weight of sPS is caused by the radiation-induced chain scission. Note that the glass transition temperature of sPS irradiated in vacuum is greater slightly than that in air. The activation energy of annealable color center increases with dose. It is also found that the permanent color centers increases with dose.

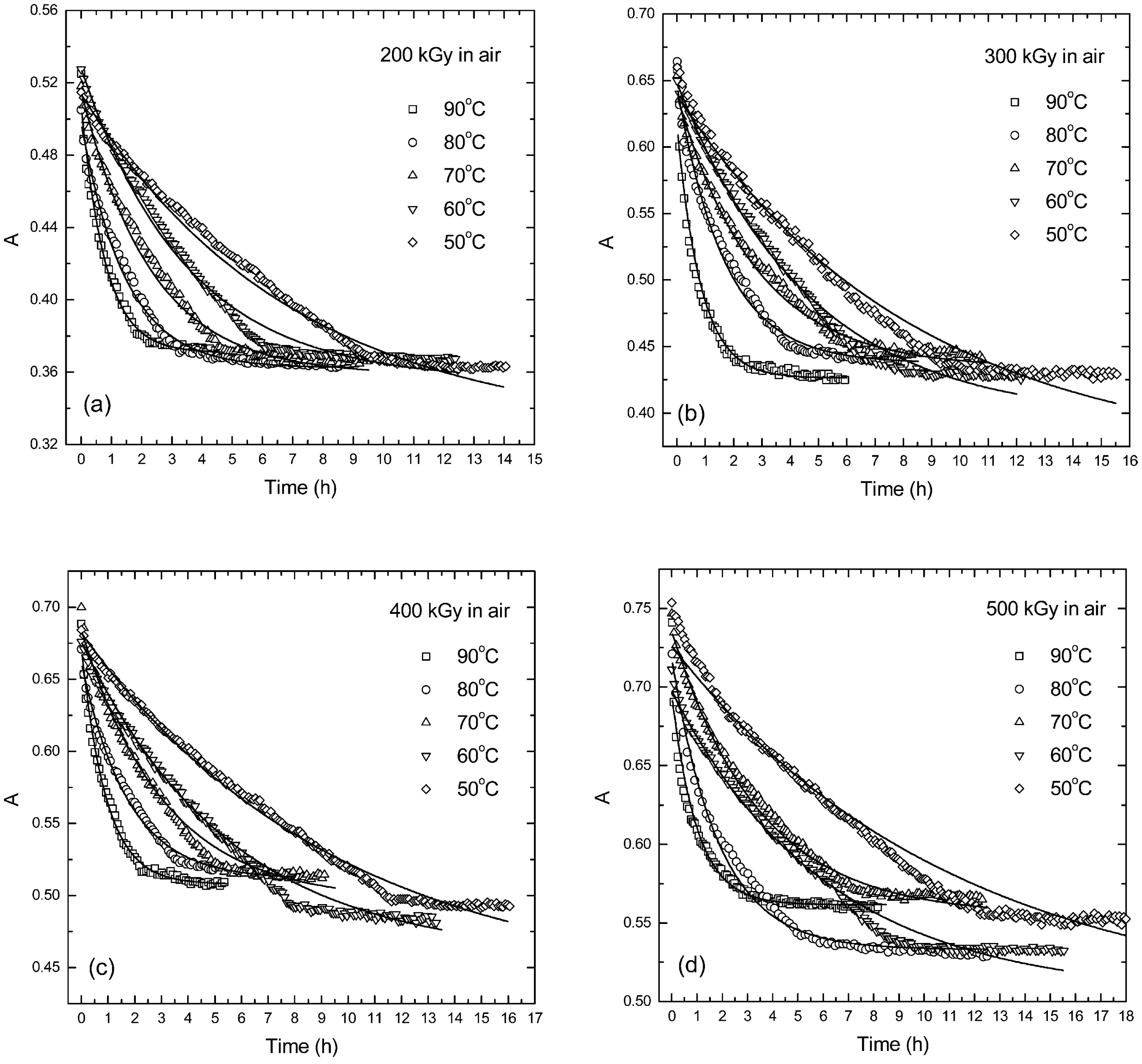


Fig. 4. Absorbances of air irradiated sPS at $\lambda = 400$ nm as a function of annealing time for samples with various: (a) 200, (b) 300, (c) 400, and (d) 500 kGy.

Table 5
The values of A_0, A_∞ and α for sPS irradiated in air annealed at different temperatures

Dose (kGy)		T (°C)				
		50	60	70	80	90
200	A_0	0.514	0.528	0.516	0.498	0.508
	A_∞	0.327	0.355	0.359	0.362	0.371
	α (10^{-4} s^{-1})	0.4	0.8	1.2	1.9	3.5
300	A_0	0.639	0.648	0.639	0.646	0.616
	A_∞	0.364	0.395	0.434	0.438	0.426
	α (10^{-4} s^{-1})	0.33	0.6	1.0	1.65	3.3
400	A_0	0.682	0.676	0.684	0.662	0.672
	A_∞	0.436	0.457	0.497	0.511	0.508
	α (10^{-4} s^{-1})	0.29	0.5	0.9	1.6	3.0
500	A_0	0.726	0.697	0.735	0.718	0.695
	A_∞	0.497	0.504	0.555	0.533	0.562
	α (10^{-4} s^{-1})	0.25	0.45	0.8	1.5	2.8

The polymer sPS has high melting temperature of 270 °C and glass transition temperature of 99 °C. The sPS pellets were molded by hot press at 300 °C which temperature is close to its thermal degradation temperature of 310 °C. Schut et al. [16] used the DGEBA monomers as a solvent for sPS to lower the melting point of sPS. Ravanetti et al. [17] studied the thermal degradation kinetics of sPS in which the activation energy was found to be 209 kJ/mol. Xue et al. [18] added dicumyl peroxide (DCP) to enhance the thermal decomposition of sPS even at lower temperature 140 °C.

The sPS in this study contains 0.5 ppm anti-oxidant as a stabilizer. There are no change in the UV–vis spectra of the sPS before and after annealing. The curves (a) and (b) in Fig. 7 show the FT-IR spectra of the non-irradiated sPS before and after 90 °C annealing in air, respectively. No new absorption peaks were formed or shifted in the FT-IR spectra of non-irradiated sPS after annealing. That is, the annealing does not cause the formation of peroxides. The curves (c) and (f) in Fig. 7 show the FT-IR spectra of sPS irradiated with 200 and 400 kGy in vacuum. The specimens did not oxidize during irradiation in vacuum. However, the specimens irradiated in an air or in pure oxygen atmospheres were oxidized during irradiation. The curve (d), (e), (g) and (h) in Fig. 7 show the FT-IR spectra of sPS irradiated with 200 and 400 kGy in air and pure oxygen atmospheres, respectively. The peak position 1730 cm^{-1} corresponds to the carbonyl group and the peaks 1600, 1493, 1453 cm^{-1} correspond to the phenyl group. When the specimen is irradiated with the higher dose in pure oxygen, the oxidation is more obviously. It is found that the transmittance of specimens irradiated in pure oxygen cannot recover during annealing at all. This implies that the annealable color centers do not form during gamma ray irradiation. The activation energies of color center recovery of specimens irradiated in air are greater than that in vacuum at the same dose. In summary, the oxidation of specimens during irradiation influences significantly the recovery of the transmittance.

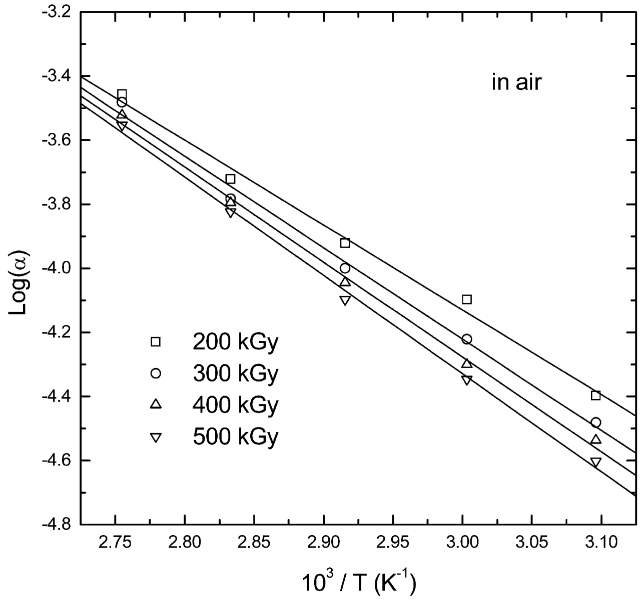


Fig. 5. Arrhenius plots of rate constant α of color center in air irradiated sPS where the unit of α is s^{-1}.

Parkinson and Keyser [19] found two different free radicals developed in irradiated polystyrene. The first one is the disubtituted benzyl radical (radical I) formed by loss of a hydrogen atom bound to the carbon atom α to the benzene ring as shown in Fig. 8(a). The second one is the cyclohexadienyl radical (radical II) formed by addition of a hydrogen atom to the benzene ring as shown in Fig. 8(b). Kaptan et al. [20] measured the diffusion coefficient of oxygen in irradiated PMMA and PVAc spherical particles using ESR. They found that the concentration of free radicals vary with the aging time and follows the Fick's law.

Solid lines in Fig. 9(a) and (b) show the EPR spectra of sPS irradiated with 200 kGy in vacuum and in air, respectively. These EPR spectra can be simulated by radicals I and II shown in Fig. 8 [19]. The solid and dashed lines in Fig. 9(c) correspond to radicals I and II, respectively. The physical data of both radicals are listed in Table 6. Using the data in Table 6, we simulate the EPR spectra in Fig. 9(a) and (b) and plot the curves in Fig. 9(a) and (b) by dashed lines. It is found in Fig. 9(a) that the

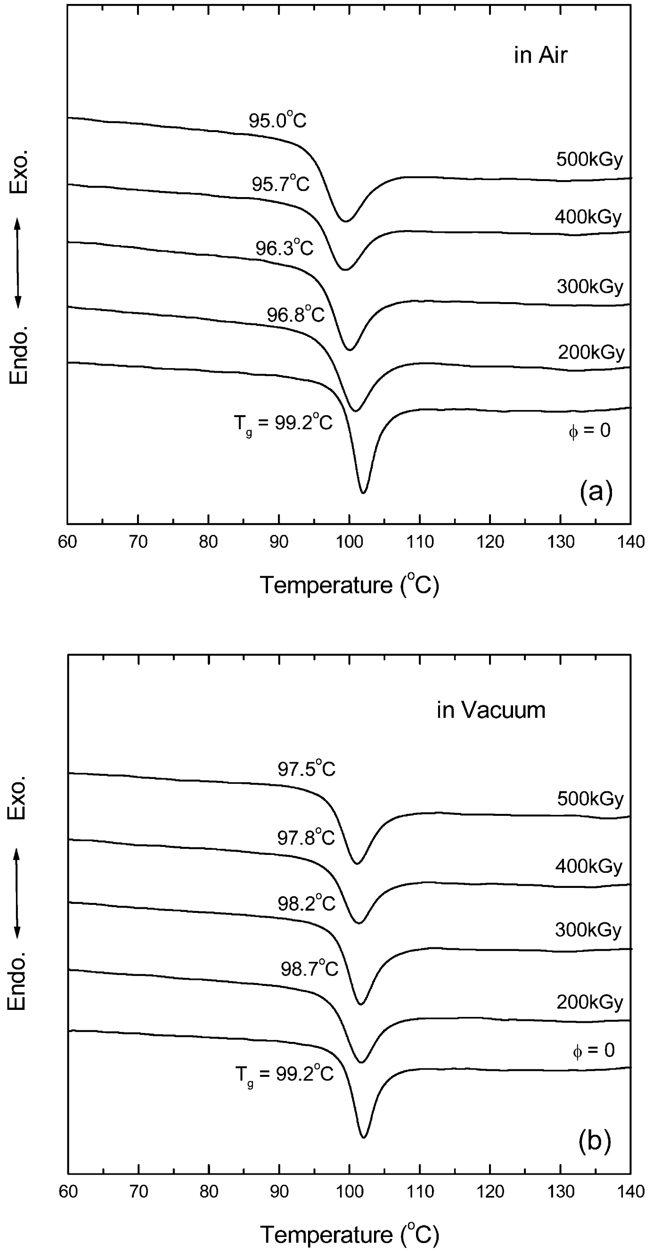


Fig. 6. The DSC curves of sPS irradiated (a) in air and (b) in vacuum.

simulation curve is almost overlapped with experimental data of sPS irradiated in vacuum. The simulation curve is also consistent with the experimental data of sPS irradiated in air, but not as good as the curve of sPS irradiated in vacuum. It may exist other radical arising from oxygen.

The EPR spectra of sPS irradiated with 200 kGy in vacuum and in air annealed at 70 °C were studied. These spectra can be simulated with two-type radicals shown in Fig. 9(c). After double integral and compare with DPPH concentration, we find the concentrations of both type radicals as a function of time shown in Fig. 10(a) and (b) for the sPS irradiated in vacuum and in air, respectively. The radicals of specimen irradiated in vacuum and air were analyzed using the second order and first order kinetic models, respectively. Assume that concentrations of both radicals follow the second order annihilation process for sPS irradiated in vacuum,

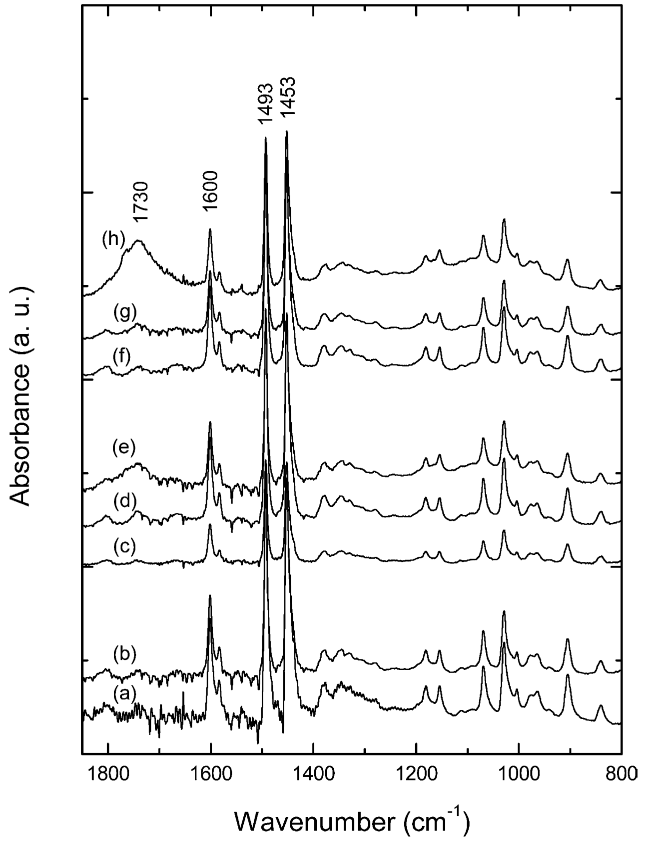


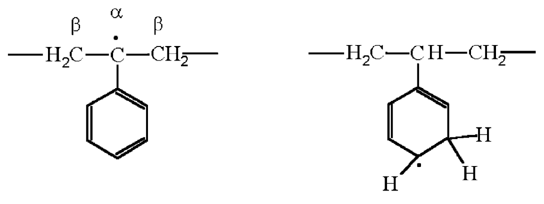
Fig. 7. FT-IR spectra of sPS irradiated by gamma ray in different atmospheres. (a) 0 kGy and before annealing; (b) 0 kGy and annealing at 90 °C for 24 h in air; (c) irradiated with 200 kGy in vacuum; (d) irradiated with 200 kGy in air; (e) irradiated with 200 kGy in oxygen; (f) irradiated with 400 kGy in vacuum; (g) irradiated with 400 kGy in air; and (h) irradiated with 400 kGy in oxygen.

$$\frac{dN}{dt} = -\beta_1 N^2 \tag{4}$$

where β_1 is the rate constant. Let the initial concentration be equal to N_0. Then the solution of Eq. (4) is

$$N = \frac{N_0}{(1 + N_0\beta_1 t)} \tag{5}$$

The solid lines in Fig. 10(a) are plotted based on Eq. (5).



(a) disubstituted benzyl radical (I) (b) cyclohexadienyl radical (II)

Fig. 8. Two types of free radicals in irradiated sPS: (a) disubstituted benzyl radical (I) and (b) cyclohexadienyl radical (II).

Table 6
The physical parameters of radicals I and II

Radical type	*g*-Factor	Peak to peak line width (G)	No. of equivalent protons	Hyperfine coupling constant (G)
Disubstituted benzyl	2.0008	5.64	4	10.869
Cyclo-hexadienyl	2.0046	14.03	2	3.424
			1	0.824
			1	0.820
			1	0.735
			1	0.604

The theoretical prediction is in good agreement with the experimental data. N_0 is 6.19×10^{15} and 32.66×10^{15} for radical I and radical II, respectively; while β_1 is 0.58×10^{-4} and $0.157 \times 10^{-4}\ \mathrm{s}^{-1}$ for radical I and radical II. Similarly, assume that concentrations of both radicals of sPS irradiated in air follow the first order annihilation process,

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -\beta_2 N \tag{6}$$

where β_2 is the rate constant. Let the initial concentration be equal to N_0. Then the solution of Eq. (6) is

$$N = N_0 \mathrm{e}^{-\beta_2 t} \tag{7}$$

The solid lines in Fig. 10(b) are plotted using Eq. (7). All experimental data are almost in the solid lines. The initial concentration is 19.0×10^{15} and 43.41×10^{15} for radical I and radical II, respectively; and the rate constant is 1.59×10^{-4} and $1.42 \times 10^{-4}\ \mathrm{s}^{-1}$ for radical I and radical II. It is found that the concentrations of radicals I and II in sPS irradiated in air are greater than those in vacuum, respectively. The rate constants of the former are also greater than those in the latter.

Compare annealing kinetics between color center and radical, we find that sPS irradiated in air has the same first order annihilation kinetics and almost the same rate constant for both color center and radical. This implies that the color center arises from the radical I and radical II in sPS irradiated in air. On the other hand, sPS irradiated in vacuum has the first order annihilation process for the color center and the second order annihilation process for the radical. The rate constant for color center ($1.6 \times 10^{-4}\ \mathrm{s}^{-1}$) is greater than that of radical I ($5.8 \times 10^{-5}\ \mathrm{s}^{-1}$). Thus the color center is not completely contributed by radicals I and II in sPS irradiated in vacuum. Other chemical changes may be involved in color center kinetics. It will be studied in the near future.

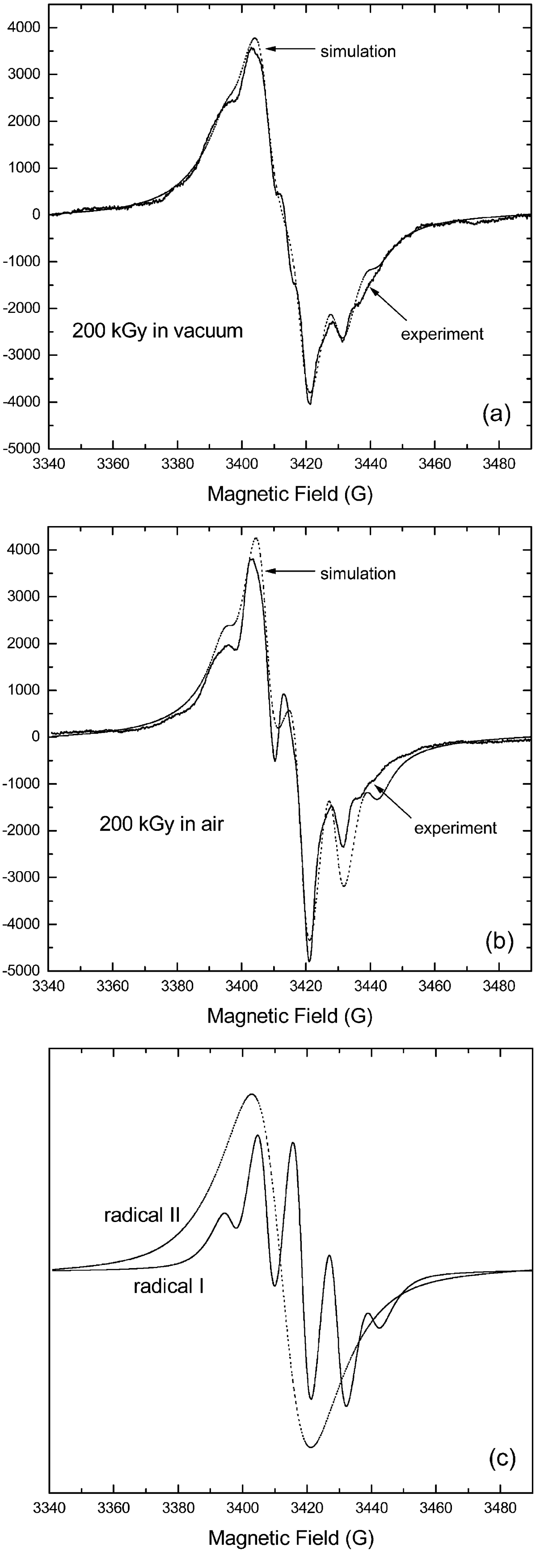


Fig. 9. (a) and (b) shows the EPR spectra of sPS irradiated with 200 kGy in vacuum and air, respectively. The solid and dashed lines in (c) are the EPR spectra corresponding to radicals I and II, respectively.

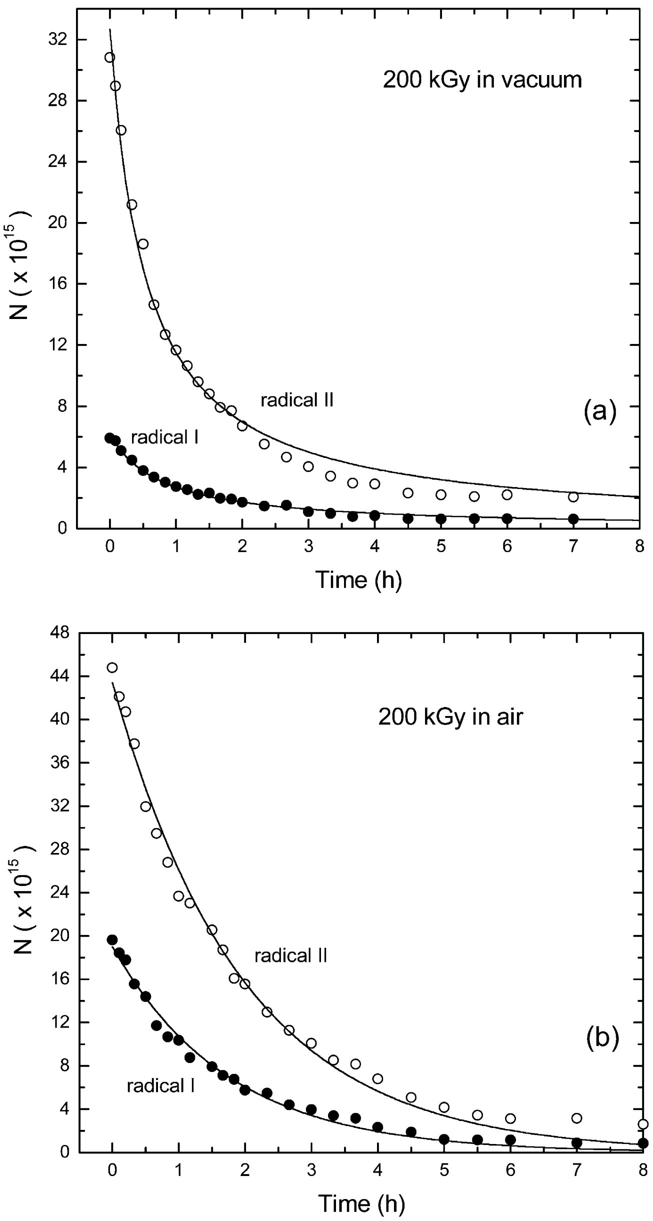


Fig. 10. The radicals I and II of gamma irradiated sPS with 200 kGy in different environments decay as a function of annealing time at 70 °C. (a) irradiated in vacuum; (b) irradiated in air. The solid lines are fitted (a) by Eq. (5) and (b) by Eq. (7), respectively.

4. Summary and conclusions

In situ absorbance in irradiated syndiotactic polystyrene (sPS) at elevated temperatures has been analyzed quantitatively. Three types of irradiation in vacuum, air, and oxygen atmospheres are considered. The loss in transmittance of irradiated sPS is attributed to color centers. UV–vis spectra show that the increasing loss in transmittance follows the sequence of irradiation environment: vacuum, air and oxygen. UV cut-off and shoulder wavelengths increase according to the sequence: oxygen, vacuum and air.

Two types of color centers are observed: one is annealable and the other is permanent. A first-order kinetic model of annealable color centers is proposed to simulate the in situ of absorbance of specimen irradiated in air and vacuum during thermal annealing. The activation energy is in the range 39–53 kJ/mol for specimen irradiated in vacuum and 50–58 kJ/mol for specimen irradiated in an air atmosphere. This implies that the annealable color centers is more difficult to annihilate in the specimen irradiated in air than that in vacuum. When specimen is irradiated in an oxygen atmosphere, no annealable color centers are observed. The permanent color centers are the greatest in the specimen irradiated in oxygen and the smallest in the specimen irradiated in vacuum. Compare the EPR spectra and UV–vis spectra, the annealable color center is contributed by disubstituted benzyl radical and cyclohexadienyl radical for sPS irradiated in air. In addition to both disubstituted benzyl and cyclohexadienyl radical, the chemical structure may also affect the annealable color center in sPS irradiated in vacuum.

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