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EPR kinetics in irradiated syndiotactic polystyrene at elevated temperatures

Chiao-Chi Lin [a], Li-June Ming [b,c,1], Chien-Chen Lee [a], Sanboh Lee [a,*]

[a] *Department of Materials Science and Engineering, National Tsing Hua University, 101, Section 2, Kuang Fu Road, Hsinchu 300, Taiwan*
[b] *Department of Chemistry, University of South Florida, Tampa, FL 33620-5250, USA*
[c] *Department of Chemistry, National Cheng Kung University, Tainan 701, Taiwan*

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ABSTRACT

Free radicals are formed upon irradiation of polymers. The annealing of γ-ray irradiated syndiotactic polystyrene (sPS) with doses 10, 23 and 36 kGy was studied with electron paramagnetic resonance (EPR) spectroscopy. The EPR spectra are possibly attributed to three types of radicals, (a) the benzyl radical Ra, (b) resonance structure of the phenyl radical Rb, and (c) carbon-superoxide-centered radical Rc with three-, four-, and single-line features, respectively. Radical Ra can be easily formed by the removal of the proton from the tertiary carbon; radical Rb is created from delocalization of the spin of the radical Ra onto the benzene ring; and radical Rc may be generated from the interaction of a carbon-centered radical with dioxygen from the air which forms a carbon-superoxide center. By comparing EPR spectra of the radicals with a DPPH standard, the spin numbers of the radicals can be calculated. The spin number of all radicals decreases exponentially with time in the temperature range of 60–90 °C regardless of dose of the irradiation. The annealing of Ra, Rb, and Rc follows first-order kinetics. The activation energies of the annihilation are determined to be 15.8–19.0, 16.0–19.5, and 23.2–26.6 kJ/mol for radicals Ra, Rb, and Rc, respectively. The kinetic study presented herein can serve as a criterion for γ-ray irradiation process in various applications, such as sterilization of polymer materials and devices.

1. Introduction

According to the stereoregularity arrangement, there are three kinds of polystyrenes, i.e., atactic polystyrene (aPS), isotactic polystyrene (iPS), and syndiotactic polystyrene (sPS). Ishihara et al. [1] were the first to synthesize sPS with high stereoregularity. This sPS has small specific heat, high melting point, good chemical resistance, and superior mechanical strength.

γ-ray irradiation produces scissions and/or cross-links of polymeric chains and changes their physical and chemical properties. Wall and Brown [2] studied a number of scissions generated in poly(methyl methacrylate) (PMMA) and polystyrene irradiated with γ-rays. Kanappe and Yamamoto [3] observed color changes of PMMA from transparent to yellow at low irradiation doses and to brown at high dose. The color changes were suggested to be resulted from the interactions among the trapped free radicals, ionic species and/or oxygen atoms. Clough and Wallace [4] observed anneable and permanent color centers in polymers. Wallace et al. [5] studied polystyrene irradiated with γ-rays in air and in vacuum. Chiang et al. [6] and Liu et al. [7] investigated the annihilation kinetics of color centers in irradiated polystyrene at elevated temperatures. Svorcik et al. [8] and Tsao [9] found that the structural changes in aPS and sPS were dominated by chain scission for doses below 300 kGy and by cross-link for doses above 300 kGy.

The use of electron paramagnetic resonance (EPR) spectroscopy for the studies of free radicals produced in irradiated polymers has been previously reported. Hama and Shinohara [10] compared the effects of γ-ray and ultraviolet irradiation on free radical generation of polycarbonate by means of EPR spectroscopy. David et al. [11] investigated the effect of benzophenone groups either presented as a low molecular weight additive or linked to the polymer backbone through benzoylation of polystyrene. The di-substituted benzyl radical and cyclohexadienyl radical were proposed in irradiated polystyrene [12–15]; however, herein the cyclohexadienyl radical is an energetically much less favorable configuration relative to the benzyl radical. Chipara et al. [16] investigated the isothermal free radical decay in γ-ray irradiated polystyrene. Their experimental data satisfy the combination of first and second-order recombination processes. Recently, we have studied the free radicals in irradiated poly(methyl methacrylate) with EPR spectroscopy [17]. Since irradiation is an important practice for sanitizing polymer-containing medical and pharmaceutical devices [18–21] and has become an important procedure in the food industries [22] (especially for keeping freshness and destruction of pathogens in meats, fish, and/or fruits) that also use large amount of polymer

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* Corresponding author. Tel./fax: +886 3 571 9677.
E-mail address: sblee@mx.nthu.edu.tw (S. Lee).
[1] Visiting Professor at National Cheng Kung University.

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materials, it prompts us to further investigate the effect of irradiation on sPS and annihilation kinetics of free radicals in the irradiated sPS at elevated temperatures by means of EPR spectroscopy. The previous assignment of the EPR spectrum of irradiated PS has also been reevaluated.

2. Experimental

The sPS pellets (Qustra QA 102 crystalline polymer) with molecular weight of 3.5 × 105 g/mol were obtained from Dow Chemical Company, Midland, Michigan. A very small amount of additives of antioxidants, processing aids, etc., were in the received pellets. The pellets have melting point, glass transition temperature, and onset crystallization temperature of 270, 99, and 147 °C, respectively. To form a sPS sheet, the sPS pellets were placed in a Carver 3912 hot press under compression of about 0.98 MPa, heated to 300 °C and held for 5 min. The sheet was removed from the hot press and immediately quenched to ice water. This quenching step is used to obtain an amorphous and transparent sPS sheet. The specimens were cut from the sheet to a volume of $1.5 \times 0.25 \times 0.1\ \text{cm}^3$, ground with 800 and 1200 grit carbimet papers, and then polished with 1 μm alumina slurries. These specimens were irradiated at room temperature by the Co^{60} γ-ray source located at the Radioisotope Division of National Tsing Hua University. The doses are 10, 23 and 36 kGy with a dose rate of 6.81 kGy/h.

The EPR spectra were recorded on an EMX-10 spectrometer (Bruker Instrument, Kahrsrule, Germany) with a dual cavity at 25 °C. The EPR data were measured immediately after the completion of γ-irradiation. The experiment was operated at microwave power of 20.02 mW, modulation amplitude of 3 G, time constant of 81.9 s, and scan range of 120 G. The irradiated specimens were annealed at 65, 70, 75, 80, 85, and 90 °C. In order to get the accurate spin number in the EPR spectrum of each specimen, the spectrum of the specimen was measured in one port and the EPR spectrum of a DPPH standard was also recorded under the same conditions in the other port of the dual cavity. The DPPH standard contains spins of 2.0×10^{15}, which was calibrated with Cu^{2+} and Mn^{2+} specimens of known concentrations.

The EPR spectra of the sPS specimens were deconvoluted into subspectra by the use of the computer simulation software WINEPR SimFornia and WinSim. A minimum of three spectral constituents seems necessary to reconstitute the experimental spectra. The integrated area of an EPR absorption line is proportional to the signal height H and to the square of the peak-to-peak width ΔH_{pp} of its first derivative spectrum. Comparing the total $H\Delta H_{\text{pp}}^2$ of a deconvoluted spectral component of sPS specimen with that of the DPPH, the number of spins for the corresponding component can be obtained.

3. Results and discussion

Upon γ-ray irradiation, free radicals are formed in sPS whose population increases with the irradiation dose as shown by their EPR spectra (Fig. 1). The g values of the EPR signals are centered at around 2 (or 3410 G herein), which are characteristics of organic-based free radicals. The signals can be deconvoluted to reveal at least three radicals Ra, Rb, and Rc in the sPS specimen irradiated with a low γ-ray dosage (Fig. 2; Table 1). Each spectrum can be deconvoluted into three components as shown in Fig. 2(a). The three-line, four-line and single-line deconvoluted spectra in Fig. 2(a) correspond to radicals Ra, Rb and Rc, respectively. Fig. 2(b) shows the simulated and experimental results for the sPS after being irradiated with a dose of 10 kGy, which are in good agreement with each other. The g-factor, number of equivalent protons, n, peak-to-peak linewidth of individual line, ΔH, and hyperfine coupling constants, A, used for the simulation are listed in Table 1. The chemical structures of the suspected radicals Ra, Rb, and Rc are shown in Fig. 3.

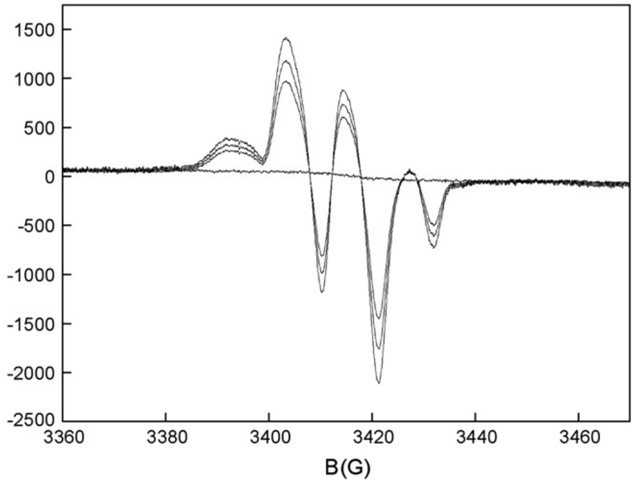


Fig. 1. X-band EPR spectra of irradiated sPS before annealing with irradiation doses of 0, 10, 23, and 36 kGy (from bottom to top traces at ∼3405 G).

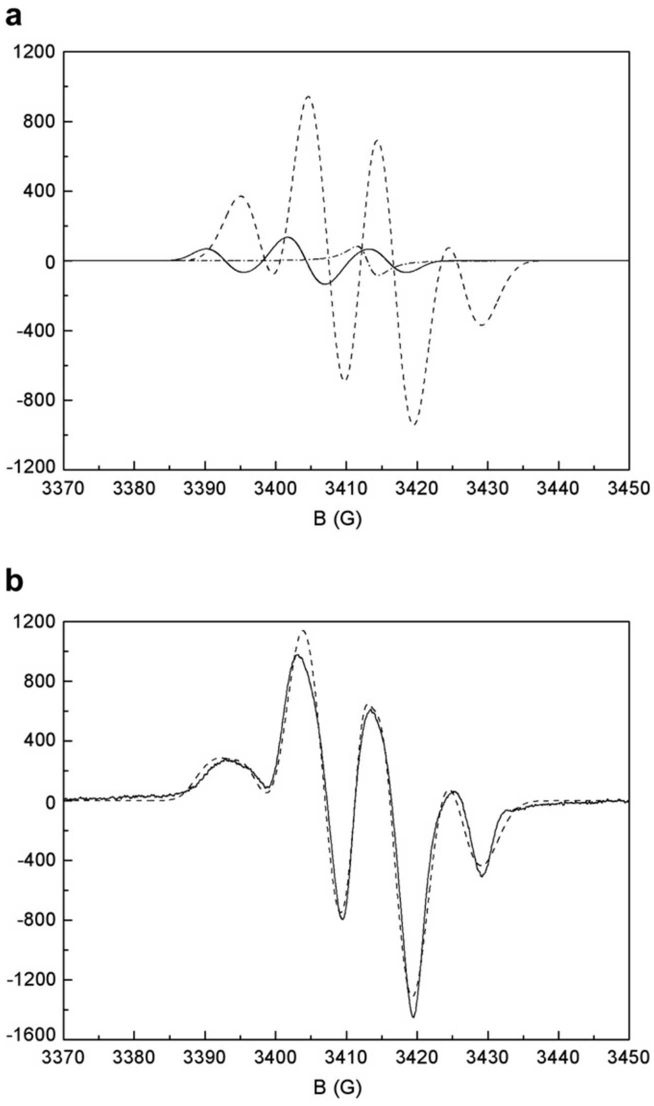
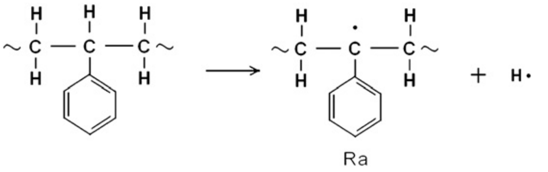


Fig. 2. (a) Deconvoluted X-band EPR spectra of radical Ra (solid trace), radical Rb (dashed trace), and radical Rc (dash-dotted trace). (b) Experimental (solid) and simulated (dashed) X-band EPR spectra of sPS irradiated with 10 kGy γ-rays where the three components in the simulation are shown in (a).

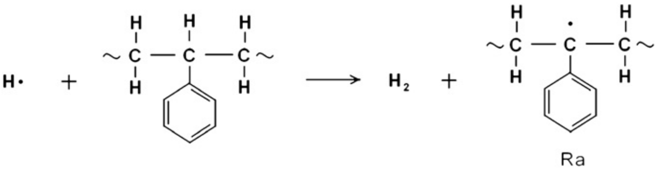
Table 1
Values of the *g*-factor, number of equivalent protons, *n*, peak-to-peak linewidth of individual line, ΔH, and hyperfine coupling constants, *A*, of radicals Ra, Rb, and Rc obtained from simulation

Radical	*g*-factor	*n*	ΔH [Gauss]	*A* [Gauss]
Ra	2.009	2, 2	2.0	12.5, 2.5
Rb	2.004	2, 1, 2	2.72	9.85, 10.6, 2.6
Rc	2.0034	0	2.8	–

Radical Ra is expected to be a di-substituted benzyl radical formed by the loss of a hydrogen atom from the tertiary carbon atom linked to the benzene ring. According to Verma and Peterlin [12], radical Ra is formed by a tertiary C–H bond rupture under the high energy radiation shown in Eq. (1a) or the hydrogen atom abstracts hydrogen from the aliphatic chain as shown in Eq. (1b).

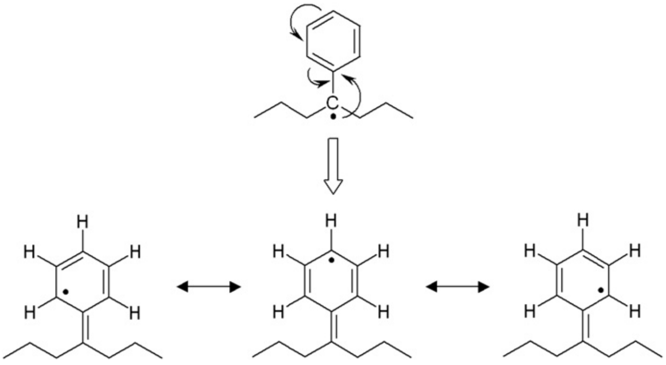


(1a)

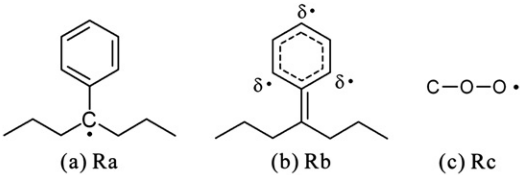


(1b)

A benzyl radical is expected to exhibit hyperfine coupling with the ring protons, especially with the *ortho* protons to afford a hyperfine coupling constant of ~5 G for a free rotating methylene substituent [23,24] wherein the radical-residing orbital is expected to be perpendicular to the benzene ring to show good overlap with the benzene π orbitals. Such hyperfine coupling is not revealed in the spectrum, which suggests that the mobility of the radical-residing methylene moiety in the polymer may be restricted with the radical orbital less parallel to the benzene ring π orbitals to exhibit smaller hyperfine coupling with the ring protons. Radical Rb is suspected to be a resonance structure of the phenyl radical formed by the delocalization of the spin from the tertiary carbon onto the benzene ring as shown in Eq. (2).


(2)

Such resonance structure can also result in stabilizing the original benzyl radical Ra, which is a well-established mechanism for radical-initiated halogenation reactions on the methyl group of toluene derivatives. The stabilization of radical Rb is also reflected by its higher intensity in the EPR spectrum (Fig. 2(a)). Radical Rc has to be a radical without any hyperfine interaction with adjacent proton(s), and is possibly attributed to a carbon-superoxide-centered radical generated from the interaction of a carbon-centered radical with dioxygen in the air which forms a carbon-superoxide center shown below.



(a) Ra (b) Rb (c) Rc

Fig. 3. The chemical structures of Ra, Rb, and Rc.

$$\mathrm{C}^{\bullet} + \mathrm{O}_2 \rightarrow \mathrm{C{-}O{-}O}^{\bullet} \tag{3}$$

The EPR spectra of sPS irradiated at room temperature with irradiation doses 10, 23, and 36 kGy and measured immediately after the γ-irradiation are very similar and their intensity increases with the dose (Fig. 1). According to the parameters shown in Table 1, the singlet cannot be hydrogen atom since a very large hyperfine coupling constant of ~500 G is expected between the proton and the unpaired electrons right on the atom. The extracted hydrogen atoms by irradiation may decay rapidly at room temperature through diffusion and recombination. A few different radicals may possibly be produced by chain scission during the γ-ray irradiation (Fig. 4). Bond scission at the polymer main chain will produce carbon-based benzyl and methylene radicals (Fig. 4(a) and (b)). The hyperfine coupling constants between the free radical and the geminal-proton(s) through the •C–H single bond should be around or greater than 15 G [23,24]. The experimental values (Table 1) are smaller than 15 G which may not be attributable to these two radicals. This implies that the irradiation dose of 36 kGy and/or the exposure time may not be high/long enough to do main chain scission in sPS. The phenyl radical shown in Fig. 4(c), if formed from side-chain cleavage, is expected to have a large hyperfine coupling constant of ~17 G for the *ortho* protons [25]. However, this large hyperfine coupling is not seen in this experiment. A phenyl cation radical can possibly be generated by γ-ray irradiation to afford hyperfine coupling constant in a wide range of ~5–12 G [26], but it may be excluded in the case herein based on the magnitude of the

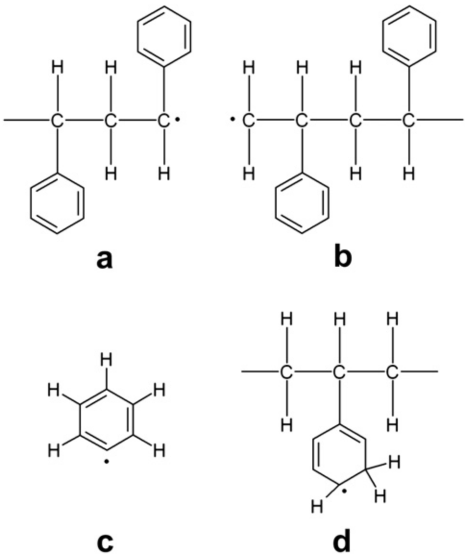


Fig. 4. Other possible radicals produced from γ-ray irradiation: radicals in (a) and (b) are generated from main-chain breakage, the phenyl radical (c) is produced from side-chain breakage, and the cyclohexadienyl radical (d) is generated by trapping of a hydrogen atom suggested in the literature.

hyperfine coupling constants. In addition, cyclohexadienyl radical shown in Fig. 4(d) was previously proposed in irradiated polystyrene [12–15]. However, this radical is chemically unsound since the breakdown of aromaticity to form that radical is not an energetically favorable process. Furthermore, this radical does not generate the quartet or triplet in EPR spectra. Therefore, cyclohexadienyl radical is ruled out in this experiment.

The thermal annealing of irradiated sPS was carried out at temperatures of 65, 70, 75, 80, 85 and 90 °C and the nature of the spectral change was observed. Fig. 5(a)–(c) shows the evolution of the EPR spectra for the samples irradiated with 10 kGy and annealed at various temperatures. As mentioned above, each spectrum was decomposed into three components, which were then integrated and compared with the DPPH standard to obtain the spin numbers of the radicals. The spin numbers of the radicals Ra, Rb, and Rc decrease with time as shown in Fig. 6(a)–(c), wherein N_0 is the initial spin number of radical in sPS irradiated with 10 kGy. The values at different temperatures are listed in Table 2. Moreover, the changes in intensity of the radicals with time at doses 23 and 36 kGy are very similar to those of 10 kGy. These changes were analyzed with standard patterns in chemical kinetics in terms of the reaction order [17,27]. The changes seem to follow an exponential decay. If it is indeed the case, the annealing process would follow first-order kinetics and thus the rate for the decrease of the spin number N of a radical can be described by the rate law in Eq. (4),

$$dN/dt = -\alpha N \tag{4}$$

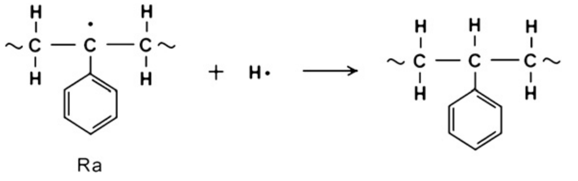
wherein α is the rate constant. The solution of Eq. (4) is shown in Eq. (5),

$$N = N_0 \exp(-\alpha t) \tag{5}$$

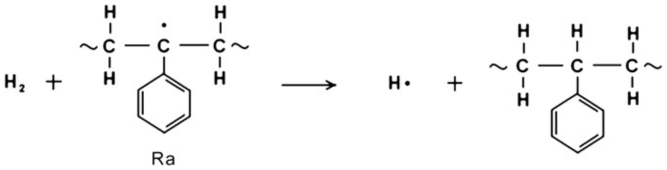
where N_0 is the initial spin number. The data for the annealing process can be well fitted to Eq. (5), which corroborate the validity of the kinetic model. The results from the fitting are shown in Fig. 6(a)–(c).

It is found that the theoretical predictions are in good agreement with the experimental data. The temperature dependence of the rate constant can be obtained from the fittings (Fig. 6), wherein the logarithm of the rate constant α decreases linearly with respect to $1/T$ for a given dosage and increases with temperature, satisfying the Arrhenius equation (the insets of Fig. 6). From which, the activation energies Q for the annealing processes of Ra, Rb, and Rc generated at different doses can be obtained (Table 3). At a given dose the activation energy for the annealing of Ra is close to that of Rb. As discussed above (cf. Fig. 3), radical Rb can be originated from radical Ra through spin delocalization. Thus, these two radicals may take a similar annealing pathway with similar activation energy.

The thermal annealing of the radicals is described by the following chemical reactions.



(6)



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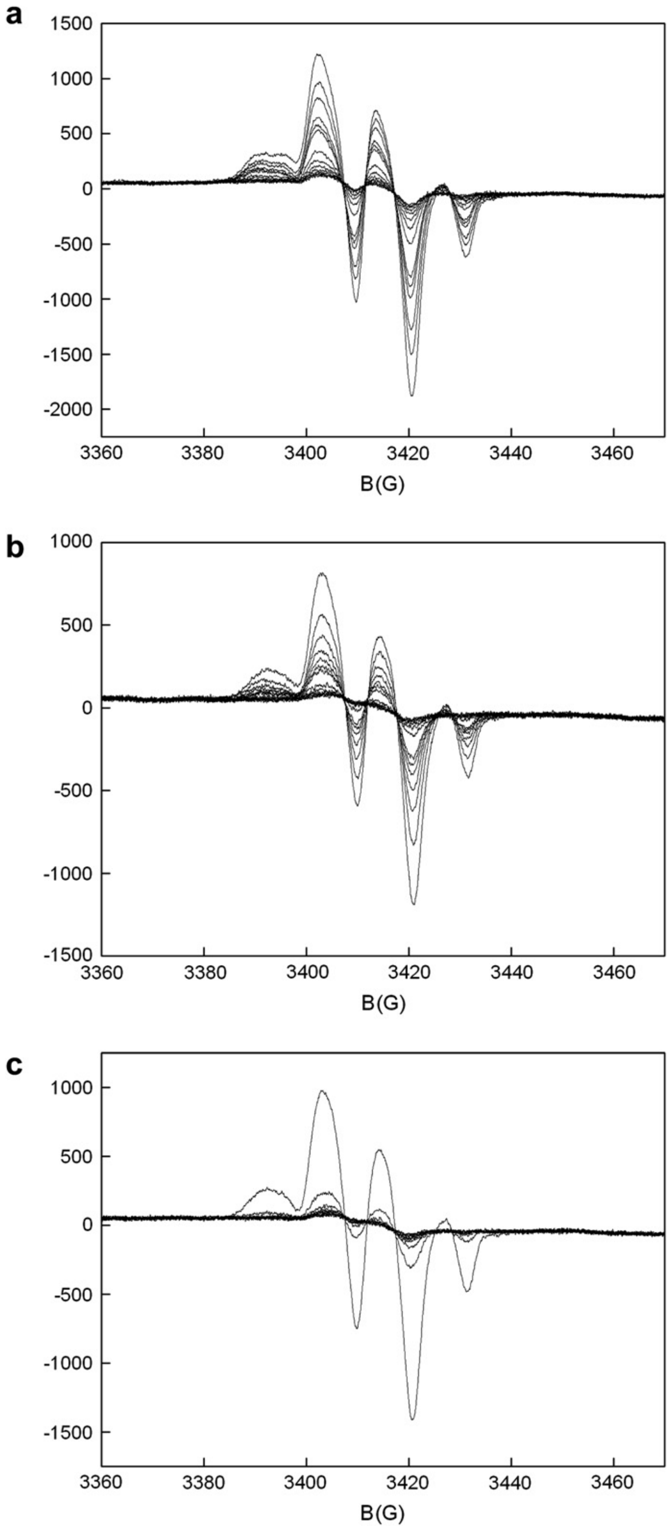
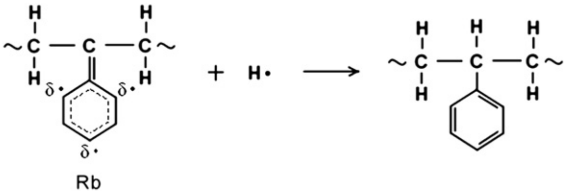


Fig. 5. Evolution of the EPR spectra of sPS irradiated with 10 kGy and annealed at (a) 65, (b) 80, and (c) 90 °C. The traces from top to bottom at ~3405 G in (a)–(c) represent increasing time from $t = 0$ min to $t = 5$ h.



(8)

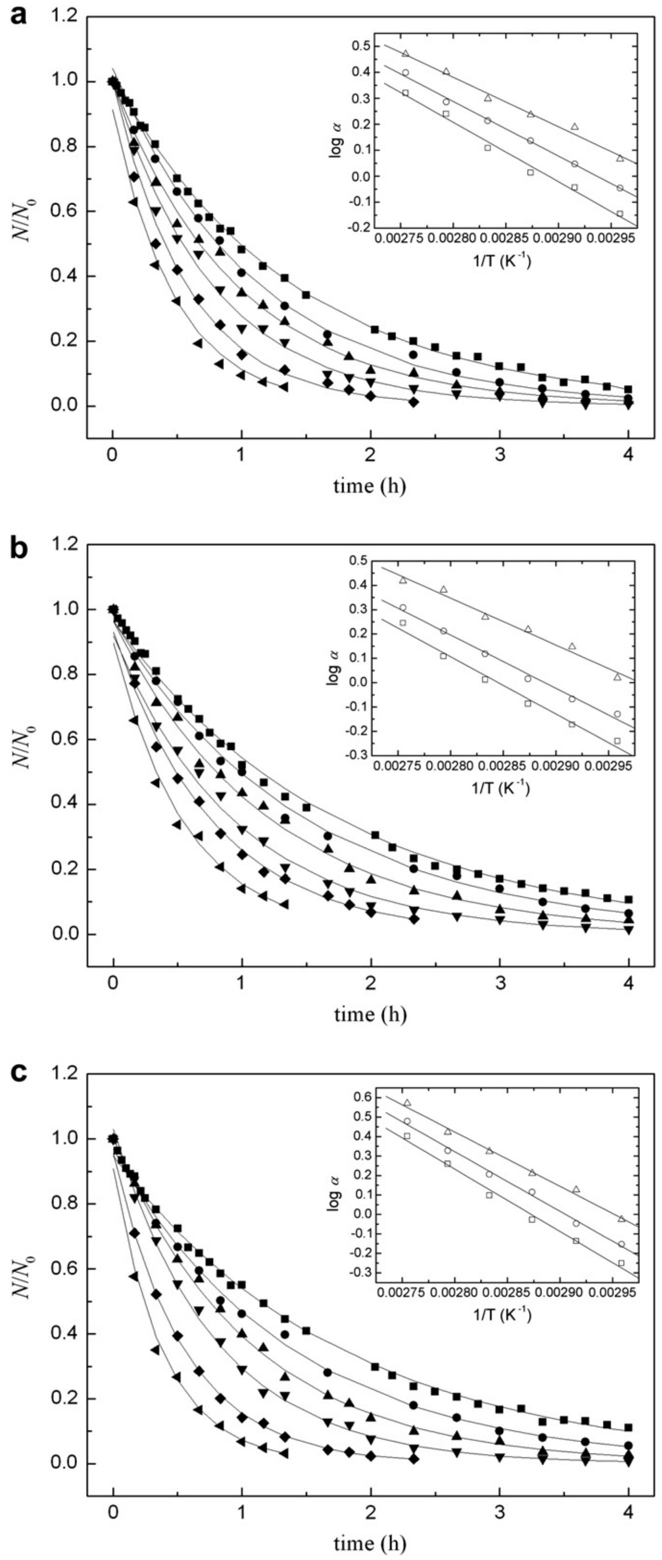
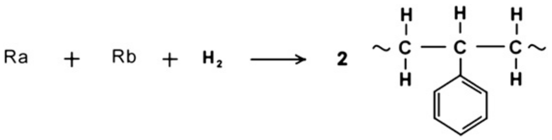


Fig. 6. Spin numbers of radicals (a) Ra, (b) Rb, and (c) Rc of sPS irradiated with 10 kGy and annealed at 65–90 °C (from top to bottom traces in every 5 °C). Insets are the corresponding Arrhenius plots where □, ○ and △ represent 10, 23 and 36 kGy, respectively.

 (9)

$$\mathrm{Ra} + \mathrm{Rb} + \mathrm{H_2} \longrightarrow 2\ \sim\mathrm{CH_2{-}CH(C_6H_5){-}CH_2}\sim \qquad (9)$$

Table 2
The experimental spin numbers N_0 ($\times 10^{14}$) of Ra, Rb, and Rc of irradiated sPS at different doses and temperatures

N_0 of Ra			
T (°C)	10 kGy	23 kGy	36 kGy
65	4.13 (4.20)	7.54 (8.36)	8.58 (8.76)
70	4.50 (4.70)	8.71 (9.07)	10.80 (10.95)
75	4.21 (4.22)	9.39 (9.30)	9.86 (9.73)
80	4.04 (4.05)	9.09 (8.35)	11.01 (10.87)
85	3.78 (3.79)	9.56 (8.64)	9.57 (8.98)
90	3.88 (3.55)	7.24 (5.71)	8.66 (7.13)
N_0 of Rb			
65	60.04 (57.99)	84.14 (87.56)	102.03 (101.12)
70	61.07 (59.01)	77.45 (81.42)	105.57 (112.56)
75	59.56 (57.30)	80.49 (80.34)	109.04 (104.05)
80	59.83 (54.94)	83.16 (81.85)	108.82 (100.39)
85	60.82 (56.64)	77.46 (74.32)	106.58 (103.98)
90	58.80 (52.79)	76.68 (67.83)	105.43 (96.26)
N_0 of Rc			
65	1.48 (1.40)	1.84 (1.86)	2.27 (2.29)
70	1.22 (1.18)	1.81 (1.87)	3.82 (3.87)
75	1.50 (1.51)	1.65 (1.62)	2.91 (2.85)
80	1.25 (1.29)	1.76 (1.74)	3.04 (2.86)
85	1.30 (1.24)	2.01 (1.99)	2.48 (2.34)
90	1. 19 (1.08)	1.91 (1.75)	2.68 (2.48)

Numbers in the parentheses refer to theoretical prediction

Table 3
The activation energies (kJ/mol) of radicals Ra, Rb, and Rc during their annealing process

	10 kGy	23 kGy	36 kGy
Ra	19.05	17.56	15.85
Rb	19.58	18.23	16.04
Rc	26.63	25.49	23.21

$$\mathrm{Rb} \rightarrow \mathrm{Ra} \qquad (10)$$

$$\mathrm{Ra} + \mathrm{Ra} \rightarrow \text{cross-links and/or disproportionation} \qquad (11)$$

$$\mathrm{Rb} + \mathrm{Rb} \rightarrow \text{cross-links and/or disproportionation} \qquad (12)$$

$$\mathrm{Ra} + \mathrm{Rb} \rightarrow \text{cross-links and/or } \beta\text{-proton extraction} \qquad (13)$$

$$\mathrm{C{-}O{-}O^{\bullet}} \rightarrow \mathrm{C^{\bullet}} + \mathrm{O_2} \qquad (14)$$

Although the reaction of Eq. (7) follows first-order kinetics for radical Ra, this reaction is not likely to occur in the present study. The reason is that the hydrogen molecule formed from combining hydrogen atoms may readily escape from the sPS specimen before reacting with the radical Ra. This reason is also applied to Eq. (9). Eq. (13) is more reasonable radical termination/annihilation process than Eqs. (11) and (12) since the chance of two Ra or two Rb radicals located side by side may be less likely than Ra and Rb being to each other. β-hydrogen extraction will yield double bond, similar to disproportionate reaction above. The formation of double bond can afford extended conjugation to yield colors in irradiated polymers. However, Eqs. (9) and (13) are the geminate recombination process in which both radicals Ra and Rb are annihilated in pair. The geminate recombination process is a kind of second-order annihilation kinetics for both radicals Ra and Rb. This second-order kinetics is different from the first-order kinetics we observed (Fig. 6), thus can be ruled out. The pathway in Eq. (10) would increase the concentration of Ra and decrease the concentration of Rb. This is contradictory to the results we observed, in which the concentrations of both Ra and Rb decrease at the same pace. Therefore, the pathway in Eq. (10) is not likely. The pathways in Eqs. (11) and (12) would afford second-order annihilation process for the radicals Ra and Rb, respectively. Again, this reaction is excluded in the present study because the radicals were observed to follow first-order kinetic process as shown in Fig. 6. The pathways followed Eqs. (6), (8) and (14) are the first-order annihilation reactions for the radicals. Based on the above arguments, the reaction ways shown by Eqs. (6) and (8) are possible to anneal out radicals Ra and Rb, respectively. Eq. (14) implies that the radical Rc is unstable at elevated temperatures. Since radical Ra has lower activation energy than radical Rb during the annihilation process, its decay would occur more preferably than that of radical Rb.

4. Conclusions

Irradiation has been a common practice for sanitizing polymer materials and devices in medicinal and pharmaceutical fields [18–21] and has also become an important procedure for keeping freshness in the food industry [22]. Since γ-ray irradiation can affect the molecular weight, structure, and physical properties of polymers, it is thus important to understand the relationship between sterility and irradiation time and dose as well as the kinetics of the annealing after the irradiation. The radical formation and temperature-dependent decay in irradiated sPS with various γ-ray doses have been investigated with EPR spectroscopy to reveal the possible presence of at least three radicals consistent with a tertiary benzyl radical, a phenyl radical, and a carbon-superoxide-centered radical. Radicals attributed to main chain scission and side-chain scission do not seem to form in sPS irradiated with doses of 10–36 kGy on the basis of EPR spectral analysis. By comparing with the spin density of the DPPH standard, the spin densities of the radicals annealed at 65–90 °C can be quantified, from which, the annealing process has been determined to follow first-order kinetics for all the radicals, and the rate constant and activation energy of the process are obtained. We expect that the EPR and kinetic analyses of irradiated sPS described herein can serve as prototypical studies for irradiated polymers in a variety of applications.

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