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ESR study of poly(β-alanine) and its derivatives

Poli(β-alanin) ve türevlerinin ESR çalışması

Review Article

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ABSTRACT

Gamma radiation-induced radicals in poly(β-alanine), poly(α-methyl-β-alanine) and poly(β-methyl-β-alanine) have been investigated by Electron Spin Resonance Spectrometry technique. ESR spectra of polymers irradiated in nitrogen and air have been simulated by curve fitting software (Winsim2002). The type of radicals generated, their relative abundances, conversion into other radicalic species and their room temperature stability were evaluated. At least two types of radicals have been detected for each polymer. Most stable radicals have been obtained in the case of poly(α-methyl-β-alanine).

Key Words
ESR spectroscopy, radiolysis, curve fitting, dosimetry.

ÖZET

Poli(β-alanin), poli(α-metil-β-alanin) ve poli(β-metil-β-alanin)'in gama ışıması muamelesi ile oluşan radikalleri Elektron Spin Rezonans tekniği ile incelendi. Azot ve hava ortamlarında ışınlanan polimerlerin ESR spektrumları eğri simülasyon yazılımı (Winsim2002) kullanılarak simülasyonları yapıldı. Oluşan radikal türleri, bağıl miktarları, diğer radikalik türlere dönüşümleri ve oda sıcaklığındaki kararlılıkları incelendi. Her polimer için en az iki tür radikal belirlendi. En kararlı radikallerin poli(α-metil-β-alanin)'den elde edildiği tesbit edildi.

Anahtar Kelimeler
ESR spektroskopisi, radyoliz, eğri uydurma, dozimetri.

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INTRODUCTION

Electron spin resonance (ESR) spectroscopy is a standard technique in the characterization of radicalic species can be used to investigate their stabilities and decay kinetics. It has therefore been the main experimental technique in understanding the effect of ionizing radiation on polymers. Radiation-induced radicals, provided that they have long-term stability can be used in the establishment of radiation dose-radical concentration relations. The most successful example of such a case is alanine-ESR dosimetry. Alanine has now been accepted as standard and reference radiation dosimeter material by International Atomic Energy Agency (IAEA). However, its sensitivity is not high for low doses.

Polymeric materials are widely used in radiation technology as vital transformations occur when they exposed to ionizing radiation such as gamma rays, accelerated electrons and x-rays. Important properties of commercial polymers such as mechanical strength, thermal stability, chemical resistance, melt flow, processability, and surface property may be modified or improved by radiation-induced modifications like grafting, coating and crosslinking. Even, some polymers such as poly (ethylene), ethylene-propylene rubber, polystyrene [1] and poly (methyl methacrylate) [2] are used in dosimetry systems as binding materials of alanine and radiochromic film dosimetry system, respectively. In all these applications; interaction of ionizing radiation with polymers, determination of radicalic and ionic active species generated, their decay behavior and amount of the species, the changes taking place in the structure of the polymers are extremely important as the parameters identify their usage.

In some applications of radiation technology like radiotherapy, it is vital to adjust precise and accurate integral dose and dose rate. That is why there are many attempts [3-12] to develop more sensitive radiation dosimetry systems than conventional systems. Olsson et al [8] have reported that methyl-alanine exhibits at least 70% more precise radiation dosimetric properties than alanine which is accepted as standard and reference radiation dosimeter by International Atomic Energy Agency (IAEA).

Although there are plenty of studies on radiation chemistry of nylon6 [13-19], nylon66 [15-16] and Nylon1010 [17], to the best of our knowledge, there is no study on radiation chemistry of nylon3 (poly(β-alanine)) and its derivatives. Poly-β-alanine is a highly crystalline polymer with high thermal and chemical resistance. As it is well-known, the radiation-induced radicals in polymers are widely trapped in crystalline regions. Moreover, the repeating units of poly(β-alanine), poly(α-methyl-β-alanine) and poly(β-methyl-β-alanine) are similar to that of 2-methyl alanine that was reported as an excellent dosimetric material by Ollson et al [8]. Poly(β-alanine), poly(α-methyl-β-alanine) and poly(β-methyl-β-alanine) were synthesized and investigated within the scope of this study.

In the radiation-induced modification of polymers, it is also important to know the type of radiation-induced radicals as they will be initiation sites of modification. The radiation yields of the radicals are also determining parameter for degree of grafting. By the present study, the information collected on the type, stability and abundance of macroradicals generated on poly(β-alanine), poly(α-methyl-β-alanine) and poly(β-methyl-β-alanine) would also be helpful in further modification studies on these polymers.

Materials and Methods

Poly(β-alanine), poly(α-methyl-β-alanine) and poly(β-methyl-β-alanine) were synthesized through base-catalyzed hydrogen transfer polymerization of acrylamide, methacrylamide and crotonamide, respectively. Polymer samples were irradiated in air and nitrogen at room temperature by ^{137}Cs gamma source (Indiana University, Department of Biology, Bloomington, USA) at a dose rate of 700Gy h^{-1}. ESR measurements were performed by X-band Bruker ESR spectrometer (Indiana University, Department of Chemistry, Bloomington, USA) at room temperature using a microwave power of 0.2 mW, modulation amplitudes of 2.0, 4.0 and 6.0 G, and a modulation frequency of 100 kHz.

Simulations of experimental ESR spectra for each polymer were carried out using the Winsim2002 software designed for isotropic simulations. The procedure was applied to each experimental ESR spectrum to follow the change in the intensity (concentration of corresponding radical) of each component of the simulated ESR spectrum.

RESULTS

Types of Radicals

Simulation of experimental ESR spectra of poly(β-alanine), poly(α-methyl-β-alanine) and poly(β-methyl-β-alanine) irradiated in nitrogen were carried out by iterating various types of radicals and ESR line parameters such as line-width,

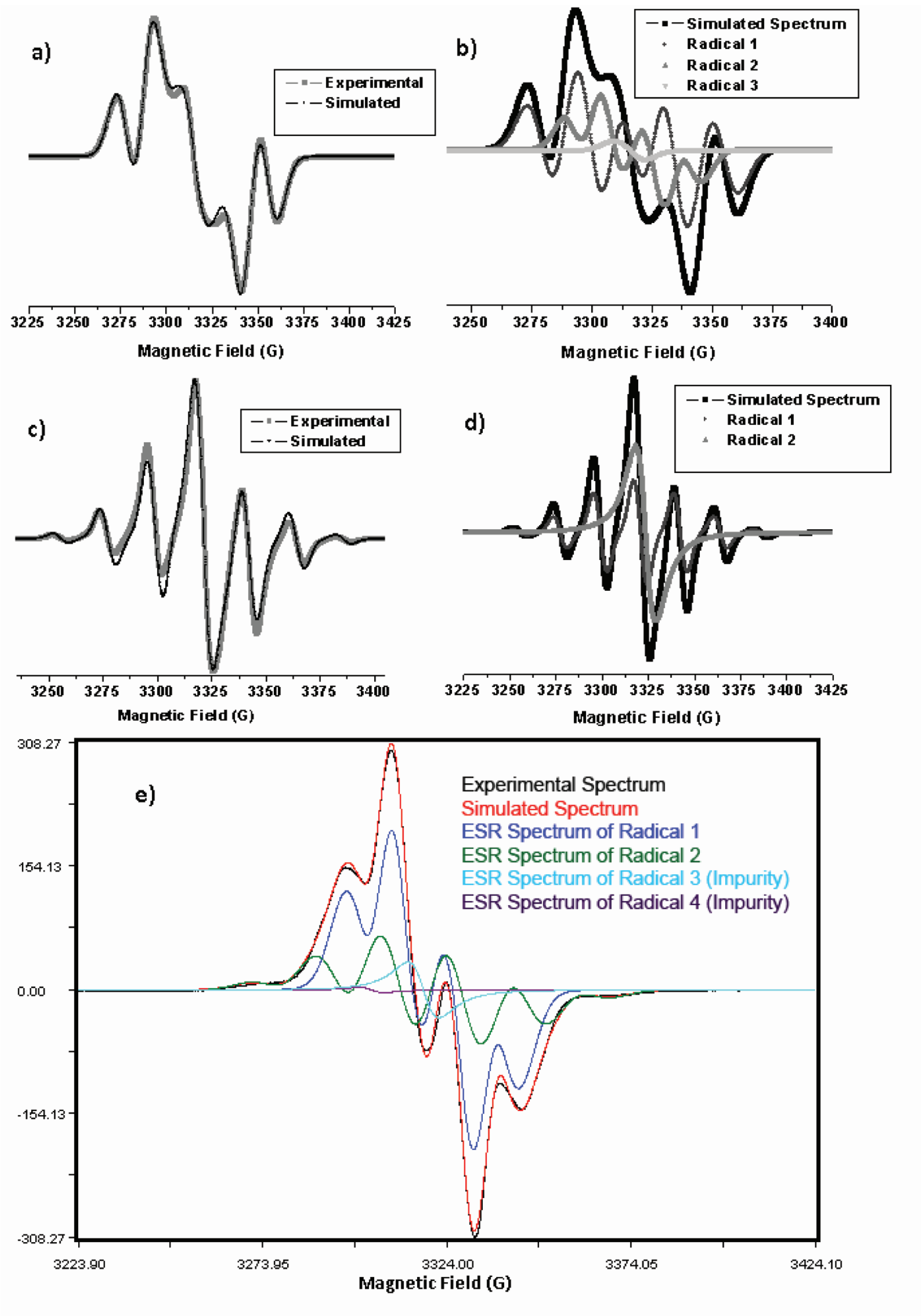


Figure 1. Experimental and simulated ESR spectra of radiation-induced radicals of poly(β-alanine) (a and b), poly(α-methyl-β-alanine) (c and d) and poly(β-methyl-β-alanine) (e)

Table 1. Parameters obtained from the simulation of experimental ESR spectra of poly(β-alanine), poly(α-methyl-β-alanine) and poly(β-methyl- β-alanine) irradiated in nitrogen

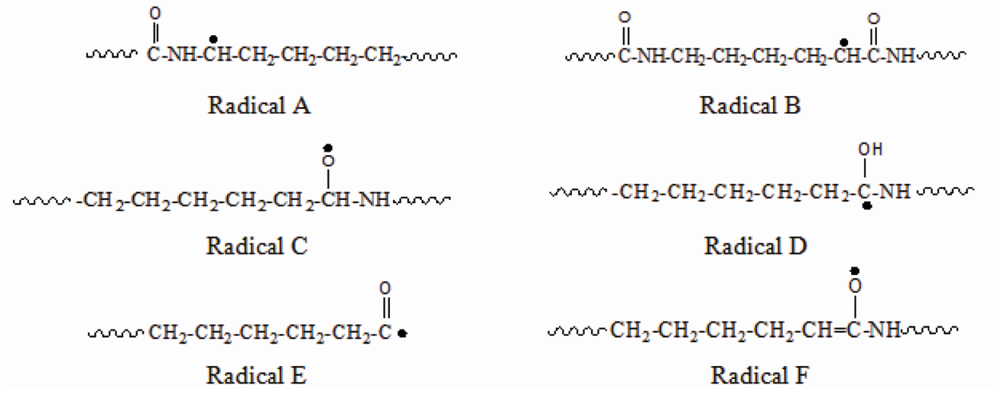
		1.Hfs (G)	2. Hfs (G)	Line-width (G)	g-value	ESR Lines	%
poly(β-alanine)	R_1	19.35	13.81	5.52	2.0032	Gaussian	32
	R_2	35.03	20.31	6.09	2.0031	Gaussian	49
	R_3	-	-	10.12	2.0042	Lorentzian	19
poly(α-methyl-β-alanine)	R_1	21.74	-	3.85	2.0032	Gaussian	40
	R_2	-	-	11.24	2.0017	Lorentzian	60
poly(β-methyl-β-alanine)	R_1	16.26	11.03	5.06	2.0030	Gaussian	66
	R_2	17.00	-	6.37	2.0033	Gaussian	22
	R_3	-	-	7.30	2.0045	Lorentzian	11
	R_4	-	-	5.71	2.0130	Lorentzian	1

hyperfine splitting constant, line-shape (Gaussian and Lorentzian) and g-value. Experimental and simulated ESR lines of each polymers irradiated in nitrogen were shown in Figure 1. After simulation workouts the best results were summarized in Table 1. The table gives simulated ESR line parameters for each polymer.

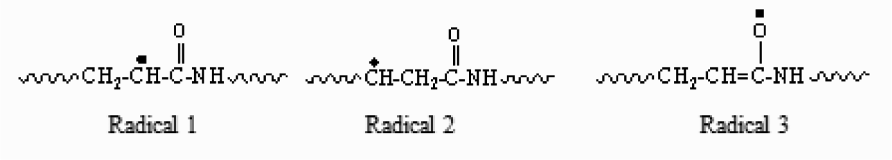
Radiation-induced radicals of Poly(β-alanine)

Graves and Ormerod [16] attributed the ESR spectrum of irradiated nylon6 (superimposition of a quartet and a singlet) to a free radical (Radical A) formed by hydrogen abstraction from CH_2 group next to the amide group and a free radical (Radical C) formed by addition of hydrogen atom to carbonyl group. Szocz et al [20] attributed the ESR spectrum of nylon6 (a quartet, a triplet and an unresolved spectrum) to Radical A, Radical D and an allylic radical. Kashiwagi [15] attributed the ESR spectrum of nylon6 (a doublet of triplet and a quintet) to Radical A and a biradical (H_2C^* $^*CH_2$) formed by scission of C-C bond. Shinora and Ballantine [14] attributed the ESR spectrum of irradiated nylon6 (a quintet and an unresolved spectrum) to Radical A and a resonating allylic radical. Takigami et al [21] attributed the spectrum (a six-line, a quartet and an unresolved spectrum) to Radical A, Radical D and a resonating allylic radical. Li and Zhang [17] attributed the ESR spectrum of irradiated nylon1010 (a quartet and a singlet) to Radical A and Radical E. Although Zimmerman [22] assigned the spectrum as a quartet (belonging to Radical B), Simon et al [13] assigned the spectrum (a quartet and a singlet) to Radical B and Radical F as shown in Scheme 1.

The long lived singlet ESR line was attributed to the radical similar to the Simon et al's [13] claim. Furthermore, our study showed that the



Scheme 1. Macroradicals proposed by the previous authors.



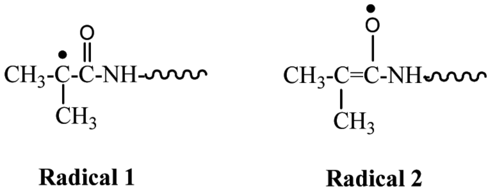
Scheme 2. Structures of radiation induced radicals proposed for poly(β-alanine)

experimental ESR spectrum of poly(β-alanine) irradiated in nitrogen is a combination of two types of six-line spectra superimposed belonging to two types of radiation induced primary radical and the singlet belonging to the radical discussed above.

The simulation calculation was carried out in order to determine the radical types responsible from the ESR spectrum of gamma irradiated N3 and their relative contributions. The experimental spectrum of of gamma irradiated N3 was found to explained best from simulation calculations based on a model of three different radical species. Radical 1 and Radical 2 are both giving rise to six-line ESR spectra and Radical 3 gives rise to an ESR singlet. The structures of the proposed radical species are given in Scheme 2. The spectroscopic parameters such as line-widths, hyperfine splittings, g-factors and relative amounts calculated from simulation calculations for the proposed radical species were given in Table 1. The experimental and calculated spectra by using the parameter values given in Table 1 for the proposed radical species were given in Figure 1a. The calculated ESR spectra for the proposed radical species were also given in the same graph (Figure 1b) to clarify their contributions to the experimental ESR spectrum. As it is seen from the Figure 1a, the agreement between the experimental and calculated spectra is fairly good and the calculated g-factors and hyperfine splitting constants for the proposed radical species are in good agreement with the values calculated for similar carbon- and oxygen-centered radicals.

Radiation-induced radicals of Poly(α-methyl-β-alanine)

Best result have been obtained for poly(α-methyl-β-alanine) when an equally spaced seven-line pattern and a broad singlet were assumed to be the components of the experimental ESR spectra. The seven-line spectrum was assigned to a radical (Radical 1) shown below with an unpaired electron coupling with 6 equivalent protons as the simulated ESR spectrum lines are equally spaced. The theoretical ratios of the hyperfine splitting components are 1:6:15:20:15:6:1. The singlet spectrum is most probably due to the unpaired electron on the oxygen atom (Radical2). A similar broad singlet observed in polyamides reported by some authors [13,14,20]. Simon et al [13] was assigned to the conjugating structures as in our present study.



Scheme 3. Structure of radiation induced radicals proposed for poly(α-methyl-β-alanine).

Radiation-induced radicals of Poly(β-methyl-β-alanine)

The ESR spectrum seems to be an unequally spaced six-line ESR spectrum. This may be due to the coupling of an unpaired electron with magnetically unequivalent protons. When simulation of the experimental ESR spectra of poly(β-methyl-βalanine) irradiated in nitrogen was carried out assuming that the spectrum consists of a four-line (actually six-line superimposed), an equally spaced six-line spectra belonging to the radiation-induced radicals and two different singlets belonging to paramagnetic impurities in poly(β-methyl-βalanine), fitting study gave the best results. (R1: 66%, R2: 22%, R3: 11%, R4: 1%).

According to the results obtained from the simulation study, the experimental spectra were attributed to paramagnetic impurity (impurities) in addition to the presence of the radicals in Scheme 4.

Scheme 4. Proposed structures of the radiation-induced radicals of poly(β-methyl-βalanine).

Stability of radiation-induced radicals

Poly(β-alanine)

ESR spectrum of a poly(β-alanine) sample irradiated to a radiation dose of 5 kGy in nitrogen was recorded as such and it was exposed to air to see the effect of oxygen on the decay of the primary free radicals of poly(β-alanine).

As shown in Figure 2a, the ESR spectrum recorded before the sample exposed to air has a multiple line ESR pattern. After exposing to air, the spectrum turned into a singlet, loosing intensity of side peaks. This shows that majority of the primary radicals decay in a short time comparing to the radical belonging to singlet line. It is clear that primary radicals are extremely vulnerable to oxygen attack.

As the γ-ray induced radicals in poly(β-alanine) are not stable enough in air to identify, additional irradiation process has been carried out in nitrogen and the sample has been stored in nitrogen to eliminate the effect of oxygen on the radicals sensitive to oxygen attack in air. The ESR spectra in Figure 1b were recorded as a function of time after γ-irradiation of poly(β-alanine) sample in nitrogen. Change in the shape of ESR lines at room temperature has been followed as a function of time. The spectrum turned into a singlet as in the case of storage in air.

Poly(α-methyl-b-alanine)

The change in the shape of ESR spectrum (Figure 3a) has been investigated to examine stability of the radicals in air. Although ESR spectrum recorded immediately after irradiation of poly(α-methyl-β-alanine) seems to be an equally spaced seven-line structure, it does not seem to belong to only one type of radical because of deformation in the ESR shape comparing to a perfect seven-line ESR spectrum. The intensity of the ESR spectrum recorded immediately after irradiation decreased slowly to about 20% of its initial value in 11 days without showing any change in its shape when the sample was stored at room temperature in air. The intensity of the spectrum continued to decrease slowly and remained as an almost singlet-line in 45 days. Therefore, it was estimated that at least two types of radicals existed in poly(α-methyl-β-alanine) irradiated in air.

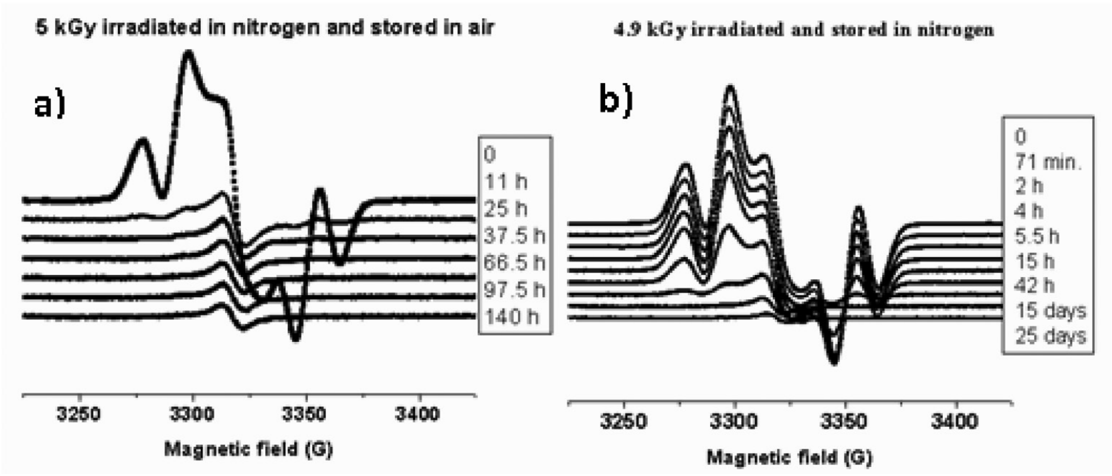


Figure 2. a) Change in the shape of ESR spectra of poly(β-alanine) irradiated in nitrogen and stored in air. **b)** Change in the shape of ESR spectra of poly(β-alanine) irradiated and stored in nitrogen at room temperature

The shape of the ESR spectrum and its change with time (Figure 3b) is very similar to the spectra obtained in air. The main difference is in the intensities of ESR lines. Although the samples used in both experiments have almost the same mass, the intensity of ESR lines of the sample irradiated in nitrogen is much greater than those obtained in air. This shows clearly the scavenging effect of oxygen on the enhanced decay of the primary radicals.

Poly(β-methyl-β-alanine)

A poly(β-methyl-β-alanine) sample was irradiated in nitrogen. As soon as the first ESR spectrum was recorded, it was exposed to air to see the effect of oxygen on the life time of the primary free radicals of poly(β-methyl-β-alanine).

As shown in Figure 4a, the significant amounts of the radicals decay in four hours by the scavenger effect of oxygen. In two days after exposing the radicals to air, the spectrum turned into the ESR spectrum recorded for pristine poly(β-methyl-β-alanine) and then the intensity and the shape of the ESR spectrum remained almost unchanged.

Additional irradiation process has been carried out in nitrogen and the sample was stored in nitrogen to eliminate the effect of oxygen on the radicals sensitive to oxygen attack in air. The ESR spectrum in Figure 4b was recorded immediately after γ-irradiation of poly(β-methyl-β-alanine) sample in nitrogen at room temperature. The change in the shape of ESR lines at room temperature was followed as a function of time. In five days the spectrum turned into the ESR spectrum recorded for pristine poly(β-methyl-β-alanine) and then the intensity and the shape of the ESR spectrum remained unchanged.

The ESR spectra of poly(β-methyl-β-alanine) recorded as a function of time were subtracted from the spectra recorded earlier to obtain the ESR spectra of radical (s) decayed during the elapsed time period. The subtracted spectra were magnified by multiplying with the numbers given at their left side to compare them better (Figure 5).

As can be seen from Figure 5, the ESR spectra of the radical (s) decayed in 1 hour seem to be due to a spectrum with four-line (actually it is a triplet of doublet). After the 1 hour period completed, the ESR spectra of radical (s) decayed in each period seem to be a five-line or six-line spectrum (see the shoulders at about 3275 and 3375 G). Therefore, there seems to be at least two types of ESR spectrum superimposed. One of them is four-line ESR spectrum belonging to the radical with low stability as the four-line spectrum was observed only at the first 1-hour period. The result was verified by ESR line simulation as mentioned above.

Decay mechanisms of radicals

Poly(β-alanine)

Figure 3 shows the time dependence of normalized

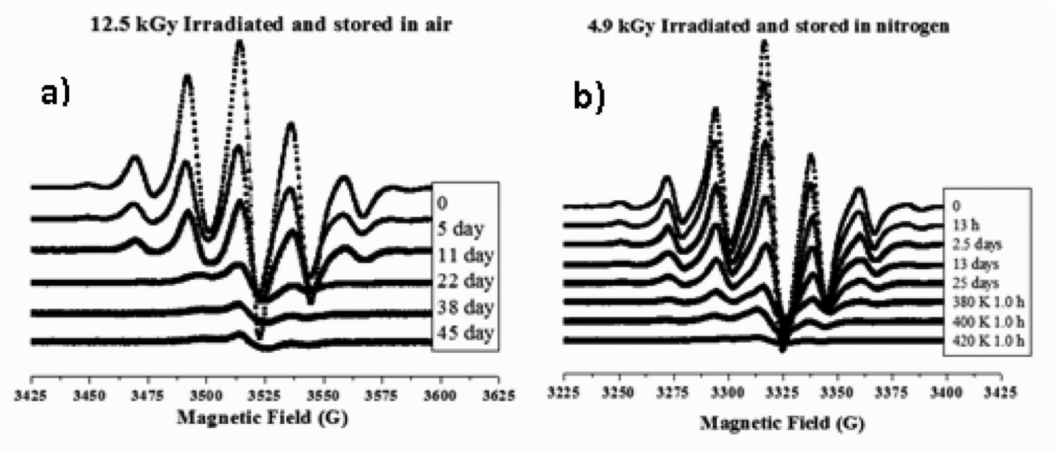


Figure 3. a) Change in the shape of experimental ESR spectrum of poly(α-methyl-β-alanine) irradiated and stored in air with time. **b)** Change in the shape of ESR spectrum of poly(α-methyl-β-alanine) irradiated in nitrogen with time

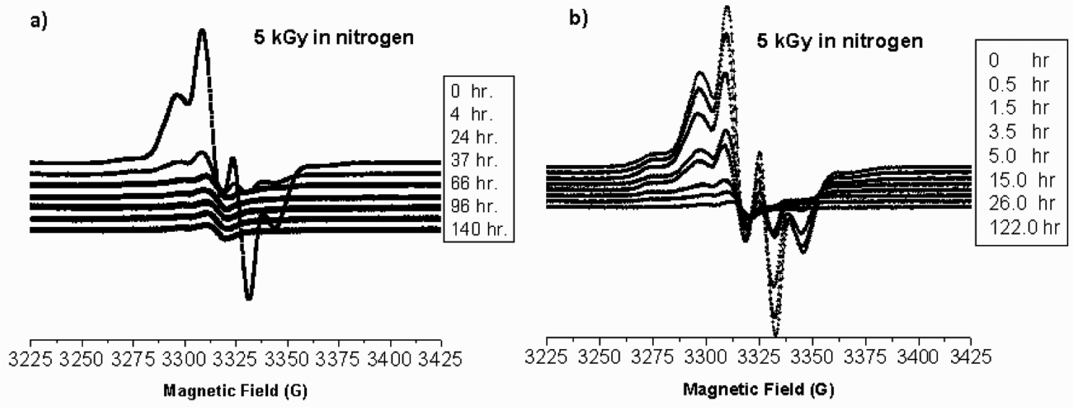


Figure 4. a) Change in the shape of ESR spectra of poly(β-methyl-β-alanine) irradiated in nitrogen and subjected to air once first spectrum was recorded. **b)** Change in the ESR pattern of γ-irradiated poly(β-methyl-β-alanine) sample at room temperature and in nitrogen

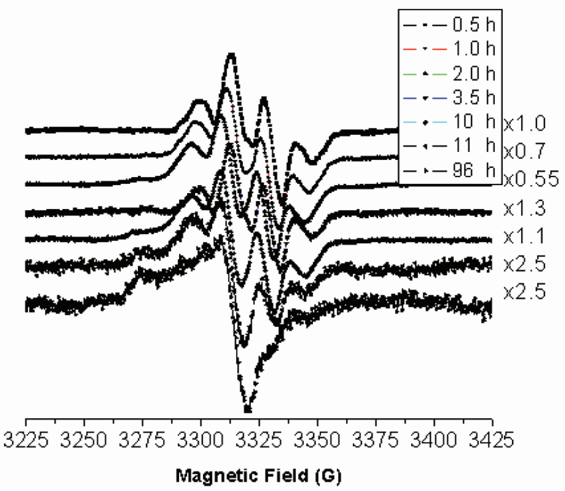


Figure 5. ESR spectra of the radicals decayed during storage in nitrogen at room temperature.

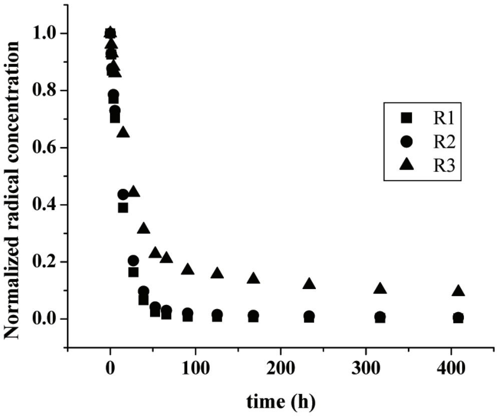
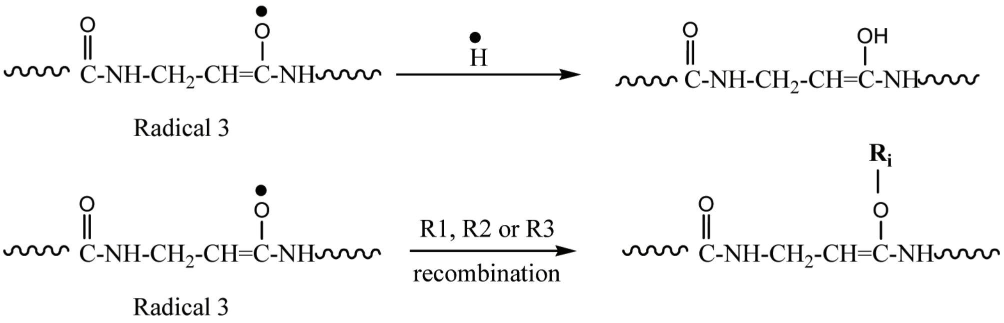


Figure 6. Change in the relative concentration of the radicals with time

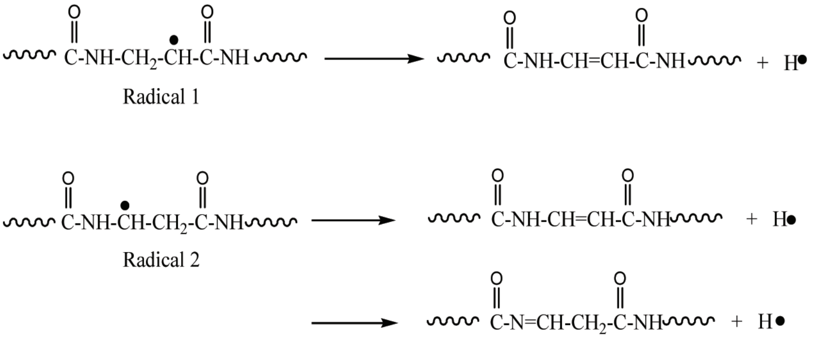
radical concentrations. At first glance, the R_3 seems to have higher stability than the others. It is very interesting to note that the R_3 began to decay slowly when the concentrations of R_1 and R_2 approached to zero (after about 50-hours storage) as shown in Figure 6. This behavior may be explained if the decay of R_3 undergoes through proton abstraction or recombination with radicalic species in the medium as shown in Scheme 5.

According to the decay reactions given in Scheme 5, decay rate of the R_3 depends on the concentration of hydrogen radicals nearby, the availability of hydrogen atoms that can be abstracted from neighboring chains and concentration of all other radicalic species. As the amount of hydrogen atoms around the R_3 will not change considerably, decrease in the decay rate of R_3 may be explained by the decrease in the concentrations of hydrogen radicals (H*) and other radicalic species with time. Generation of hydrogen radicals (H*) is possible by decay of R_1 and R_2 according to the reactions in Scheme 6.

After about 50-hour storage, as the concentrations of R_1 and R_2 reach to zero, the decay of the R_3 may be possible just by recombination of R_3 and abstraction of hydrogen atom from macromolecules. This is why the decay rate of R_3 decreases when the concentration of R_1 and R_2 reaches to zero. This approach also explains the decay mechanisms of R_1 and R_2 as shown in Scheme 6.



Scheme 5. Decay mechanisms of R_3. R_i denotes any of the R_1, R_2 and R_3.

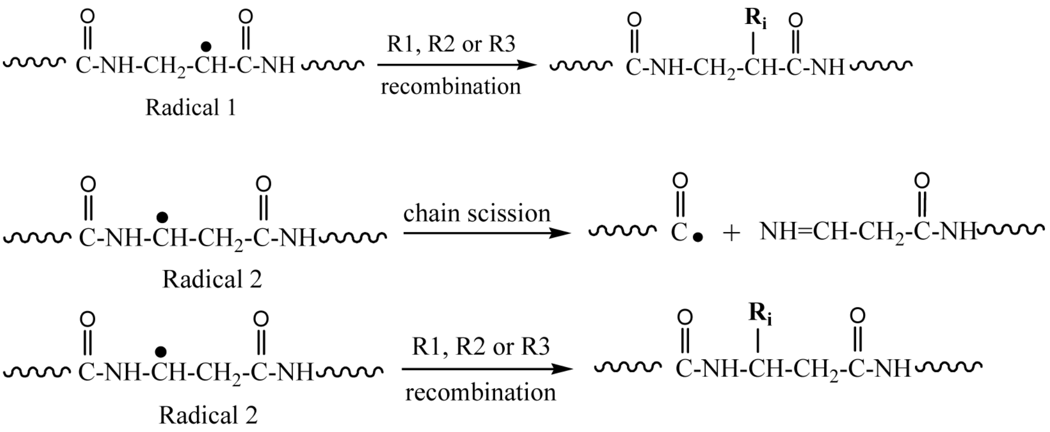


Scheme 6. Decay mechanisms of R_1 and R_2 through hydrogen radical removal.

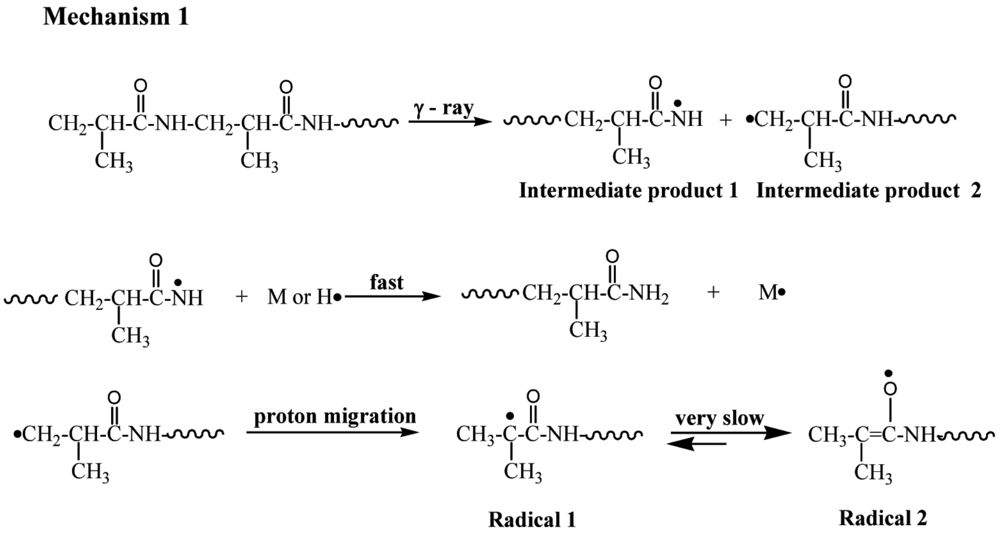
As it is well-known, when a polymeric material is exposed to ionizing radiation chain-scission and crosslinking reactions occurs simultaneously. Either one of the reactions dominates over the other or they experience competition. Relative viscosities of poly(β-alanine) samples irradiated and stored in nitrogen and air were followed to understand the situation in poly(β-alanine). However, relative viscosities of samples stored in air decreased abruptly. Relative viscosities of samples irradiated and stored in nitrogen have no significant change. Therefore, additional mechanisms (in Scheme 7) including chain-scission [17] and crosslinking may be suggested for the consumption of radicals in nitrogen.

Poly(α-methyl-β-alanine)

Two mechanisms have been proposed for the formation of Radical 1 and Radical 2. Both mechanisms require that chain-scission dominates over crosslinking during the radiolysis. Inherent viscosity of irradiated poly(α-methyl-β-alanine) exhibited decrement after being exposed to irradiation in conformity with this



Scheme 7. Decay mechanisms of R_1 and R_2 through recombination and chain-scission.



Scheme 8. A mechanism proposed for formation of Radical 1 and Radical 2.

proposal. The mechanism 1 is given in Scheme 8.

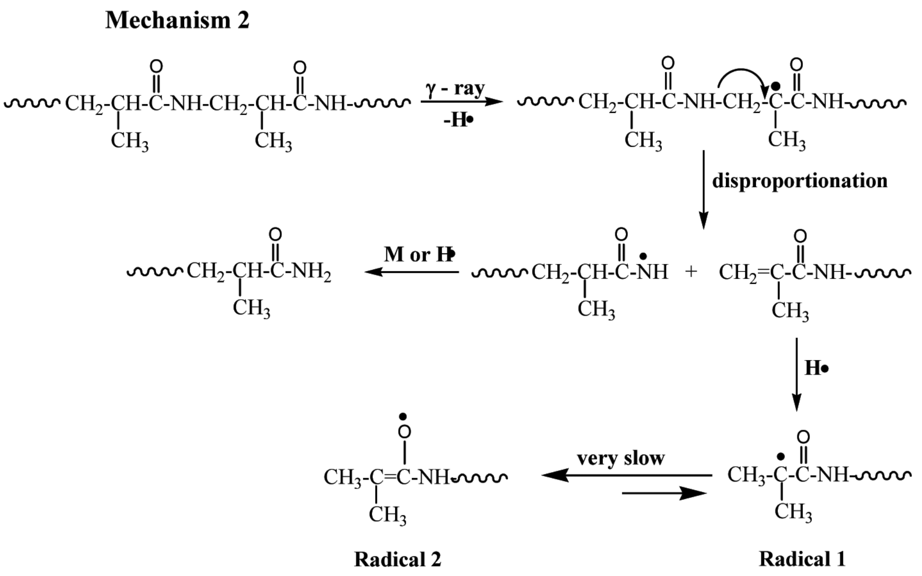
In the above proposed mechanism, it was assumed that chain scission between amide nitrogen and methylene carbon occurred during irradiation. As the unpaired electron on the NH group is very active species, the intermediate product abstracts a hydrogen atom (or catch a hydrogen radical generated by irradiation) from vicinal chains to form stable primary amide group. Formation of primary amide groups in polyamides have also been reported by Chang and La Verne [19]. As this reaction is very fast, no ESR signal was observed for the intermediate product. The intermediate product 2 has an unpaired electron on the primary alkyl group, which is also unstable, transforms to methyl group by proton migration from the next carbon atom resulting in a tertiary alkyl radical (Radical 1). As it is well-known, the unpaired electrons on the tertiary carbon atoms are more stable than the electrons on the primary and secondary carbon atoms [23]. It is assumed that the transformation of Radical 1 into Radical 2 is very slow as the seven-line and singlet spectra coexist for a considerable amount of time. Another reason for the relatively long-term existence of these two radicals is the resonance between the two radical structures as shown in last reaction mechanism given in Scheme.8.

In the mechanism 2 proposed (Scheme 9), once the proton on carbon atom next to the carbonyl group was removed during irradiation, chain scission takes place via disproportionation reaction (reason for the decrease of inherent viscosity of irradiated poly(α-methyl-β-alanine)). The nitrogen radical ended intermediate product by hydrogen atom abstraction. The other intermediate product of disproportionation reaction may react with hydrogen radical to form Radical 1.

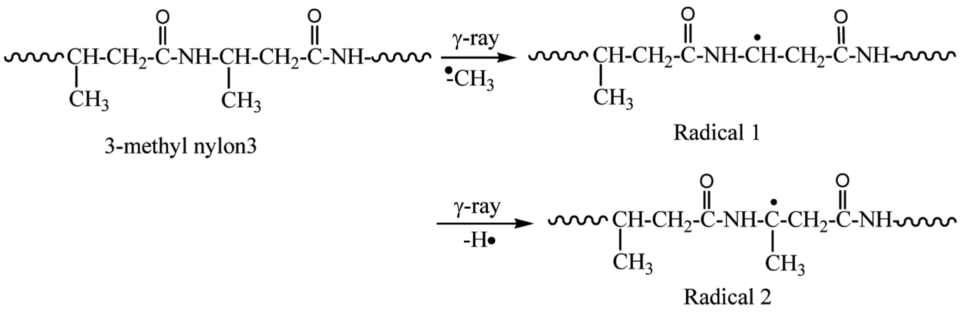
Poly(β-methyl-β-alanine)

The radiation-induced radicals of poly(β-methyl-β-alanine) are assumed to be developed by the removal of pentant methyl groups and hydrogen atoms from the carbon atom at the beta position of carbonyl group as shown in Scheme 10.

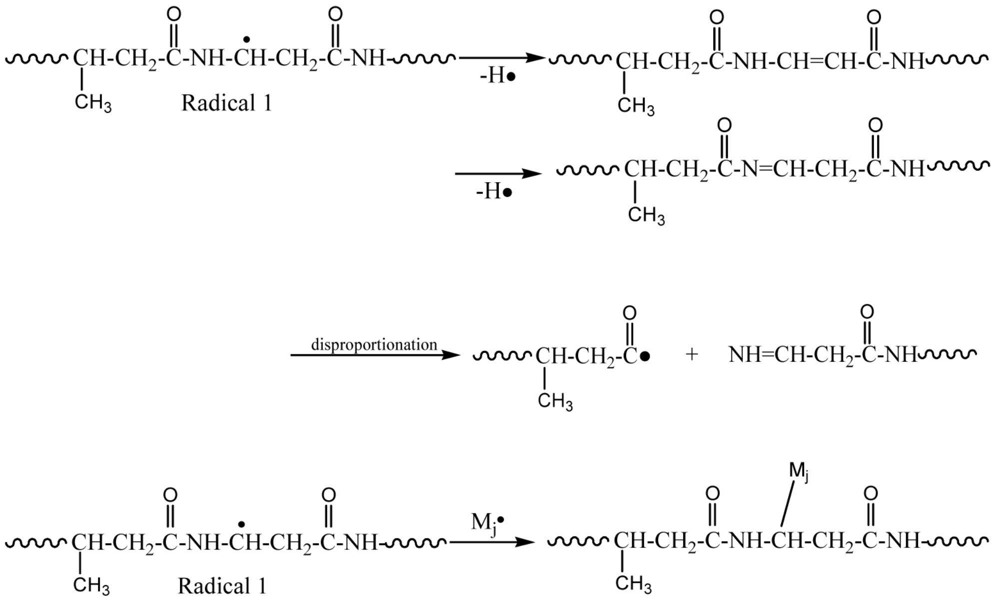
Inherent viscosities of pristine and irradiated polymers in air and nitrogen were determined. Inherent viscosity of samples irradiated in nitrogen and air increased slightly. This behavior shows that crosslinking predominates slightly over chain-scission in air and nitrogen. Considering these results, it may be deduced that the crosslinking reactions proposed below for both radicals are more likely to take place than the others as proposed in Scheme 11 and Scheme 12. The mechanisms and types of radicals proposed are in conformity with the results of viscosimetric analysis.



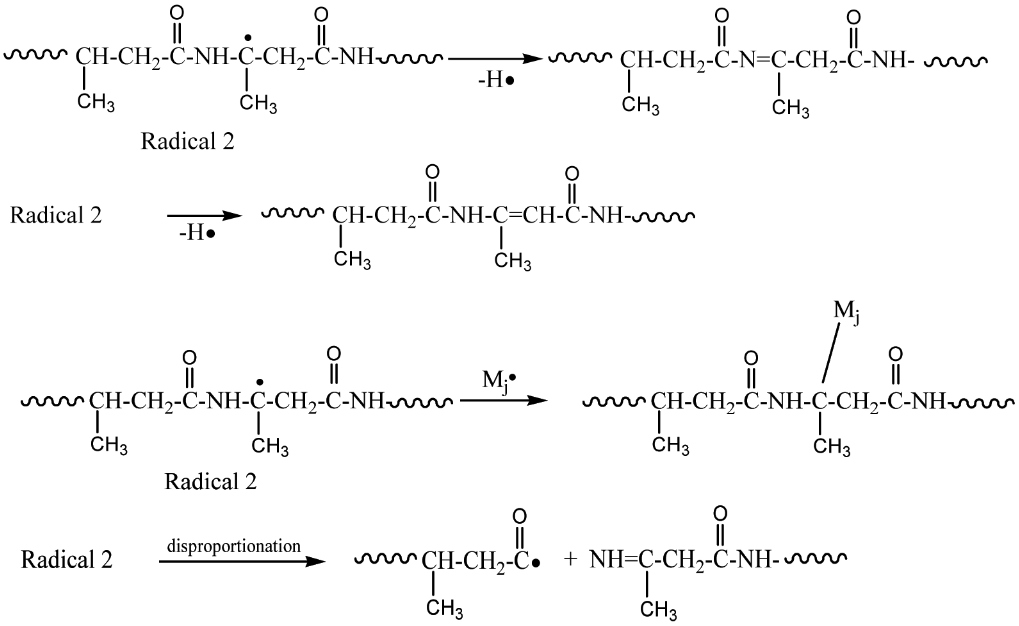
Scheme 9. The second mechanism proposed for formation of Radical 1 and Radical 2.



Scheme 10. Formation reactions of the radicals of poly(β-methyl-β-alanine)



Scheme 11. Possible decay mechanisms of Radical 1. M_j denotes any macromolecular radical (R1and R2)



Scheme 12. Probable decay mechanisms of Radical 2. M_j denotes any macromolecular radical

Discussion

Gamma radiation-induced radicals of poly(β-alane), poly(α-methyl-β-alanine) and poly(β-methyl-β-alanine) were characterized and their stabilities in air and nitrogen were evaluated. In summary, the radiation-induced primary radicals occur mainly by hydrogen abstractions from both methylene groups next to the carbonyl group and amide group. Although the polymers used in the study have similar structure and chemical properties, poly(α-methyl-β-alanine) yielded radicals with much longer lives in both air and nitrogen. Ionizing radiation-induced radicals of poly(α-methyl-β-alanine) have life-times of months. However, the long-term stability of the radicals are not enough for use as a radiation dosimeter material.

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