

ESR STUDY OF FREE RADICALS IN IRRADIATED POLYAMIDE-1010

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ABSTRACT

Polyamide-1010 samples were irradiated in vacuum at room temperature by Cobalt-60 γ -rays. The free radicals formed in irradiation were studied by means of electron spin resonance (ESR) techniques. The ESR spectra consisted of a quartet and a superimposed singlet which were attributed to radical $-\dot{\text{C}}\text{O}-\text{NH}-\dot{\text{C}}\text{H}-\text{CH}_2-$ and $-\text{CH}_2-\dot{\text{C}}=\text{O}$, respectively. The effects of temperature and crystallinity on the radicals were discussed and the mechanism for the production and decay of the radicals was also proposed.

INTRODUCTION

The free radicals generated by gamma-radiation in various polyamides have been studied by several authors^[1]. The ESR spectra observed were ascribed to the radical $-\text{CO}-\text{NH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$ whose spectrum was predominant in the overall spectra at room temperature, but other components also appeared due to the production of various kinds of reactive intermediates by irradiation and the multiplicity of the polymer structure. The identification of these latter radicals is still not clear.

Polyamide-1010 (PA-1010) is one of the important polyamide engineering plastics produced commercially in China. In the previous papers^[2,3], the radiation effects on PA-1010 have been extensively studied. In this work, the trapped radical structures in irradiated PA-1010 were investigated using ESR techniques. The relation between the formation of free radicals and the multiplicity of the polymer structure was discussed. The experimental data were related to the previous studies on radiation chemistry of polymers.

EXPERIMENTAL

Samples and irradiation

Polyamide-1010, with $\overline{M}_n = 3.7 \times 10^4$, was obtained commercially. Their crystallinities are presented in Table 1^[2,3].

Table 1 Sample and Crystallinity*

Sample No.	A	B	C	D	E
$W_c(\%)$	5.6	8.8	17.6	38.2	43.2

* By WAXD.

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The samples were cut into strips with dimension of $0.5 \times 2 \times 15\text{mm}$. About 50mg weighed specimen was put into the ESR tube and sealed under vacuum (0.1Pa). The tube was then subjected to gamma irradiation at room temperature. The dose rate was 10kGy/hr.

ESR measurements

After irradiation, the tube end without specimen was treated by heating to eliminate the ESR signal produced by the glass tube. Subsequently, the irradiated specimen was carefully transferred into this pre-treated end for ESR measurement. The spectra were obtained on a JES-P10B ESR spectrometer.

DSC, WAXD and dielectric spectrum measurement

Thermograms of the irradiated specimen were determined on a Perkin-Elmer DSC-2C differential scanning calorimeter. Heating rate was $10^\circ\text{C}/\text{min}$. The crystallinity was obtained on a D/MAX-II BX diffractometer and the dielectric spectrum in a TRS-10C dielectric loss measuring set.

RESULTS

Figure 1 shows the temperature dependence of the ESR spectra of the PA-1010 specimen after irradiation to a dose of 48kGy, while Fig. 2 are the ESR spectra

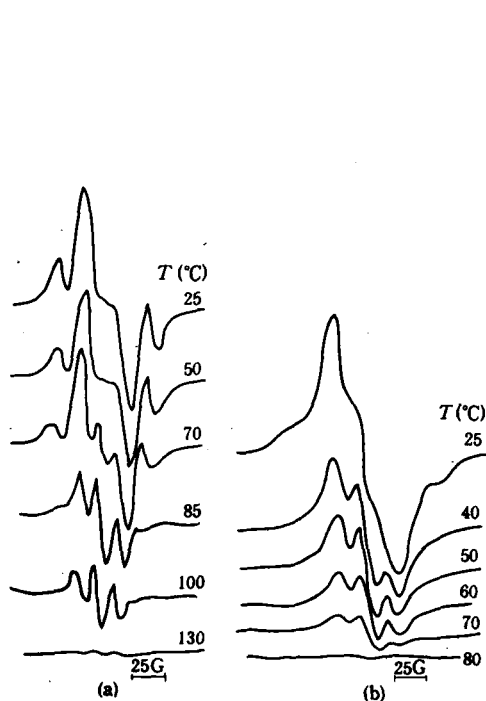


Fig. 1 The temperature dependence of ESR spectra of the irradiated PA-1010 specimen R: 480kGy

(a) specimen D with $W_c = 38.2\%$;

(b) specimen A with $W_c = 5.6\%$.

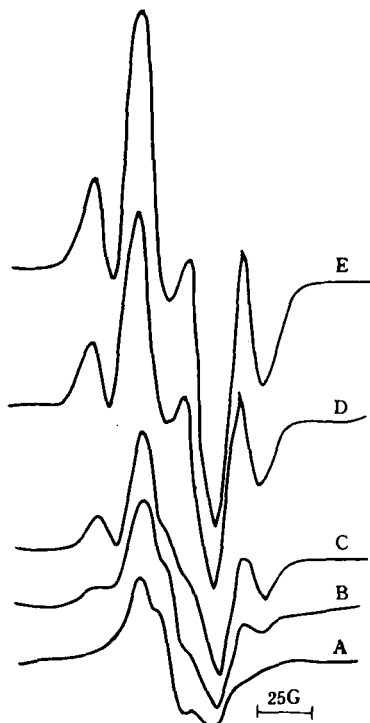


Fig. 2 The ESR spectra of the irradiated specimen with different crystallinities

W_c , %: A, 5.6; B, 8.8; C, 17.6; D, 38.2;

E, 43.2.

R: 480. kGy

of the irradiated specimen with different crystallinities. The typical spectra consist of a quartet with hyperfine splitting of about 21 gauss and a superimposed singlet, the relative proportions differing from specimen to specimen. The g value of singlet and that of quartet are 2.0029 and 2.0022, respectively. The radicals were quite stable at room temperature, for no significant decay was found upon depositing the tube in the dark for several days. On warming, the quartet and singlet behaved in different manners.

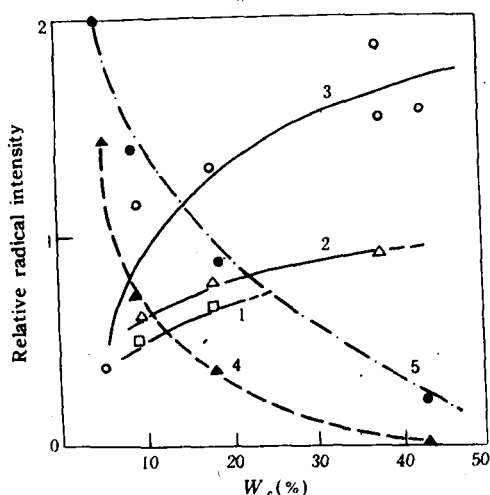


Fig. 3 The crystallinity dependence of relative radical concentration of the irradiated PA-1010

R, kGy: 1, 140; 2, 480; 3, 1287; 4, 480; 5, 1287.
1, 2 and 3 for quartet 4 and 5 for singlet.

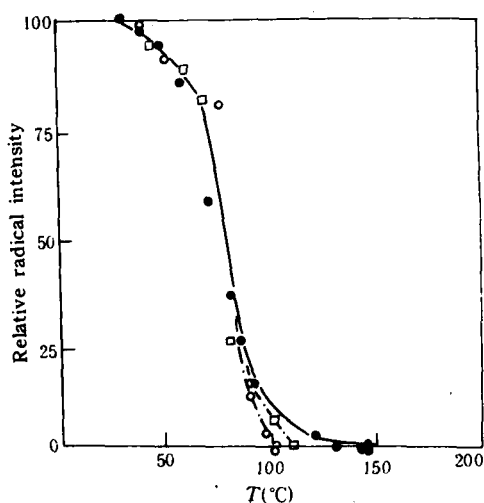


Fig. 4 The decay curve of the quartet on raising temperature

(○) B; (□) C; (●) E.
R: 480kGy.

The crystallinity dependence of the ESR spectrum intensity with unit specimen weight is shown in Fig. 3. It was seen that, after being subjected to the same dose level of irradiation, the spectrum intensity of the quartet increased with the increase of crystallinity, while that of the singlet decreased with the increment of the crystallinity. These results seem to indicate that the quartet exists in crystalline phase while the singlet exists in amorphous phase. However, this is in disagreement with our previous work^[2], in which we proposed that the post-crosslinking and scission mainly occurred in the amorphous region.

In Fig. 4, the relative peak intensity of the quartet, were plotted against temperature. It was found that the quartet decayed near 50 °C and disappeared completely within the temperature range from 100 to 120 °C. The temperature at which the quartet fully disappeared increased with the specimen crystallinity as well as the radiation dose. Unlike the quartet, the singlet intensities of the specimen with different crystallinities changed with the increasing temperature in different ways (Fig. 5). For the specimen with very low crystallinity, the relative intensity of the singlet decreased with the increasing temperature and disappeared within the temperature range from 100 to 120 °C. But it was found that for the specimen with higher crystallinity, the relative intensity of the singlet increased initially, with the increment of temperature reached the peak, and then decreased and disappeared at higher temperatures. Moreover, the higher the crystallinity, the more significant

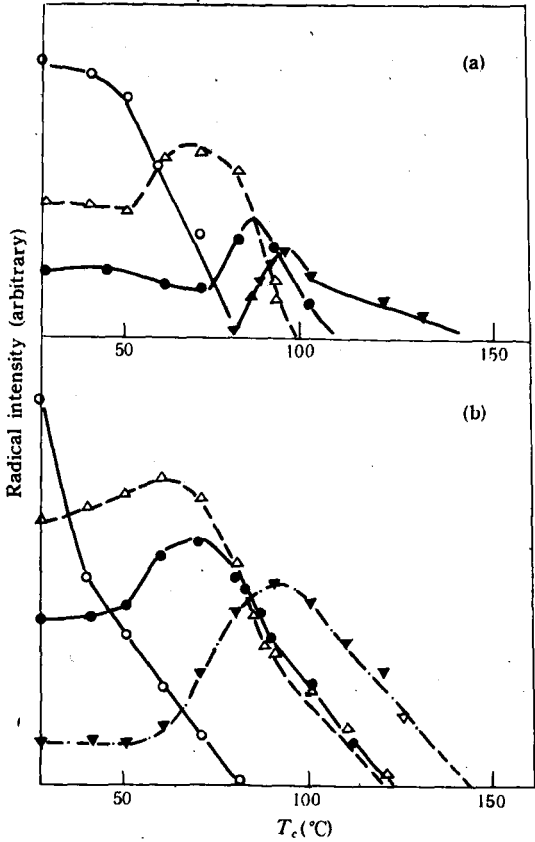


Fig. 5 The decay curve of the singlet on raising temperature
(○) specimen A; (△) specimen B; (●) specimen C;
(▲) specimen E.
(a) 480kGy; (b) 1287kGy.

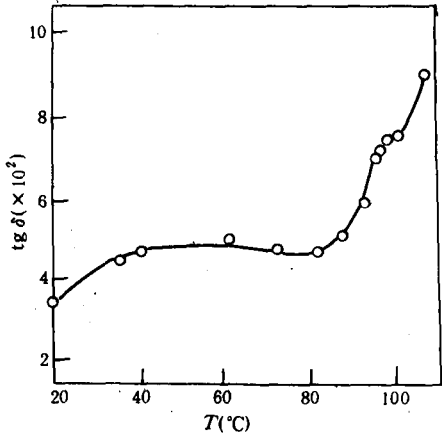
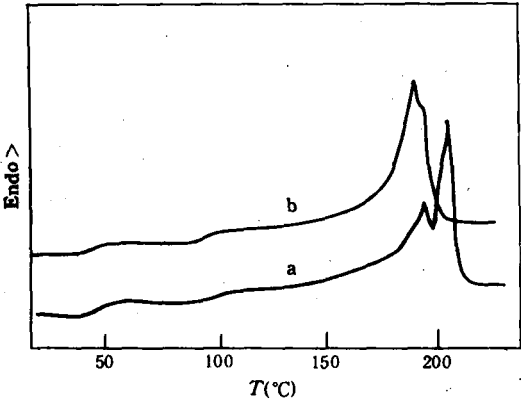


Fig. 6 The DSC of the irradiated specimen D.
a: 0 kGy; b: 1000 kGy

Fig. 7 The variation of $\text{tg } \delta$ with temperature of
the irradiated PA-1010 specimen

the initial increment.

The variation of the ESR peak intensity during the process of raising temperature is associated with the multiplicity of the polymer structure. In order to correlate these relations, the data of DSC, WAXD and dielectric spectrum of sample D (Table 1) were presented in Figs. 6, 7 and 8, respectively. It can be seen from Fig. 6 and Fig. 7 that there are two glass transition temperatures, one of which is within the temperature range from 45 to 55 °C and the other

is in the range of 95 to 100 °C.

It was also found that the peak melting temperatures of the irradiated specimen were within the temperature range from 199 to 205 °C and the crystallinities remained unchanged until the temperature was close to 200 °C, where the crystallinities began to decrease abruptly with the increasing temperature.

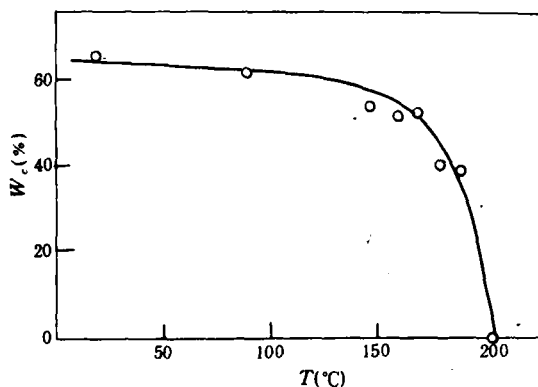


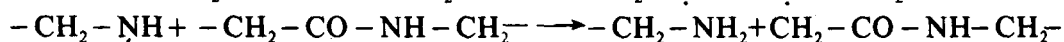
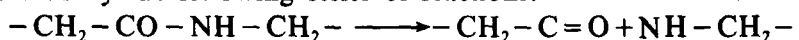
Fig. 8 The temperature dependence of the crystallinity of PA-1010

DISCUSSION

1. Identification of the radical components

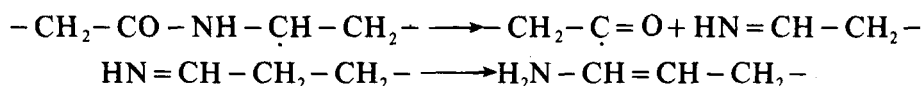
The free radical generated during the gamma irradiation has been generally ascribed to the radical $-\text{CO}-\text{NH}-\dot{\text{C}}\text{H}-\text{CH}_2-$ in many early literatures^[1]. It seems reasonable to associate the observed quartet with this radical since four lines would arise from the unpaired electron coupling with the α -hydrogen and the two β -hydrogens. The hyperfine splitting constants are: $a_{\alpha}^{\text{H}} = 22.5\text{G}$, $a_{\beta_1}^{\text{CH}_2} = 36.7\text{G}$ and $a_{\beta_2}^{\text{CH}_2} = 22.5\text{G}$, respectively^[3]. The only effect of the $-\text{NH}-$ group of a line broadening due to unresolved coupling with the nitrogen-14. Therefore, we also attribute the observed quartet to this radical.

The assignment of the singlet is more difficult. Graves and Ormerod^[4] suggested that the central singlet in the gamma-irradiated polyamides was due to the addition of a hydrogen atom to the carbonyl group to give rise to the radical $-\text{CH}(\text{Q})-\text{NH}-\text{CH}_2-$. However, this assignment is evidently in disagreement with our observations (Fig. 2 and Fig. 4). It also could not explain their own observations that the singlet was less intense in the drawn samples than in the undrawn ones. On the other hand, the singlet spectrum of the UV-irradiated nylon-6 was attributed to the radical $-\text{CH}_2-\dot{\text{C}}=\text{O}$ in an early literature^[5]. Besides, there was evidence that $-\text{NH}_2$ end groups were formed during the gamma irradiation of polyamides^[6]. Therefore, we suggest that the central singlet is due to the main chain fracture to give rise to the radical $-\text{CH}_2-\dot{\text{C}}=\text{O}$, which is possibly formed by the following series of reactions:



Thus, our experimental data as well as the observation of Graves et al. can be

well explained by the aforementioned discussion, which indicates that the singlet is due to a radical generated by main chain fracture. It is generally agreed that main chain fracture preferentially occurs in amorphous or interfacial region, rather in crystal region^[7]. It is thus naturally deduced that the radical $-\text{CH}_2-\dot{\text{C}}=\text{O}$ is mainly in the amorphous or interfacial region, because if main chain bond scission occurs in the crystal region to form two free radicals, the limited mobility of the resultant chain fragments must mitigate against permanent scission, thereby consuming the radicals by cage recombination^[8]. Therefore, it is reasonable that the intensity of the singlet decreases with the increasing crystallinity (as shown in Fig. 2). The observation that the singlet is less intense in the drawn samples than in the undrawn ones can be also explained by the fact that the drawn samples have higher crystallinities. The data in Fig. 4 can also be well explained. For a specimen with a comparatively high crystallinity, the formation of the radical species with quartet ESR spectra dominates during irradiation. Due to the accelerated molecular motion in the process of raising temperature, the quartet species will give rise to a chain fracture and an $-\text{NH}_2$ group, possibly by the reactions of the type shown:



Because of this conversion, the relative intensity of the singlet in a specimen with a higher crystallinity increases initially with the increasing temperature, reaches the peak, and decreases gradually at higher temperatures (Fig. 4). Moreover, the degree of this augment diminishes with the decreasing crystallinity. For a specimen with crystallinity being close to zero, no such increment is observed. From the discussion, we can conclude that the free radicals generated by gamma irradiation of PA-1010 mainly consist of two components, one of which is the radical $-\text{CH}_2-\text{CO}-\text{NH}-\dot{\text{C}}\text{H}-\text{CH}_2-$ and the other is the radical $-\text{CH}_2-\dot{\text{C}}=\text{O}$. The latter is formed by main chain fracture.

2. The location of the generated radicals

As discussed in the preceding section, the singlet is generated by main chain fracture and is mainly in the amorphous or interfacial region. Now where is the quartet mainly located? It is seen from Fig. 2 that the relative intensity of the quartet increases with the increasing crystallinity, which seems to indicate that the quartet is closely relevant to the crystalline phase. But we can find from Fig. 5 that the maximum decay rate of the quartet ranges from 50 to 100 °C. This is the same temperature range within which loss maxima or the alpha-transition temperature (60–90 °C) in dielectric spectrum (Fig. 7) and glass transitions from $T_g(1)$ (42–45 °C) to $T_g(u)$ (97–100 °C) in DSC thermogram (Fig. 6) can be observed, but it is much lower than the melting temperature (205–210 °C) of PA-1010 (Fig. 8). All these facts show that the behavior of the quartet species is closely relevant to the molecular motions in amorphous region, thereby indicating that, the quartet is mainly in the amorphous region. However, this is evidently in disagreement with the data shown in Fig. 2.

Polyamide-1010 is a typical semicrystalline polymer. It is now generally

believed that semicrystalline polymers are composed of three morphological phases, i. e. amorphous, interfacial and crystalline phase^[9]. In fact, it has been verified that PA-1010 actually consists of three phases^[10]. During the ionization irradiation, the reactive species is formed randomly. But the generated radicals in different phases have quite different fate and lifetime. In the amorphous region, the microradicals have a higher mobility, and hence the probability of these radicals being terminated by a coupling reaction will be higher, thereby resulting in the formation of intermolecular crosslinking. However, with the increase of crosslinks in amorphous region, the molecular motion in this region is gradually hindered, and the probability of radicals being trapped in this region will also increase. On the contrary, due to the very low molecular mobility, the generated radicals in crystalline region are mainly consumed by the cage recombination of H-atoms with their parent radicals. On the other hand, the interfacial region between crystalline and amorphous phase is a special region, where molecular chains are restrained by both amorphous and crystalline phases. The moderate molecular chain mobility enables the radicals generated in this region to escape the cage recombination. But the probability of radicals being terminated by a coupling reaction to form intermolecular crosslinks is considerably lower than that in the amorphous region. As a result, the lifetime of free radicals in the interfacial region is comparatively long and we thus incline to believe that the quartet is mainly in the interfacial region. The proportion of interface in the whole specimen increases with the increasing crystallinity, and thereby the relative intensity of the quartet is also directly proportional to the crystallinity (Fig. 2). However, the fate of the free radicals during the post-irradiation heat-treatment is not determined by crystalline phase. The heat-treatment leads to the competition between disproportion which gives rise to the radical $-\text{CH}_2-\dot{\text{C}}=\text{O}$ and migration which gives rise to crosslinks. The former is predominant in a specimen with high crystallinity (Fig. 4). In a word, the quartet irradiated species is mainly in the interfacial region and it is responsible for post-irradiation crosslinking.

CONCLUSIONS

1. The ESR spectrum of gamma-irradiated PA-1010 consists of two major components, one of which is a quartet due to removal of a hydrogen in the α -position of the amide group, and the other is a singlet due to main chain fracture.

2. The radical $-\text{CH}_2-\text{CO}-\text{NH}-\dot{\text{C}}\text{H}-\text{CH}_2-$ with a quartet spectrum is mainly in the interfacial region, while the radical $-\text{CH}_2-\dot{\text{C}}=\text{O}$ with a singlet ESR spectrum mainly in the amorphous as well as in the interfacial region. With the increase of temperature part of the radicals with a quartet spectrum convert into the radical with a singlet spectrum.

Keywords:

ESR; Radiation; Polyamide; Free radical

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