Effect of the Fold Surface of the Lamellae on the Behavior of the Trapped Radicals in Irradiated Polyamide-1010

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ABSTRACT: Two types of macromolecular free radicals $—CH_2CONH\dot{C}HCH_2—$ (a) and $—CH_2\dot{C}{=}O$ (b) trapped in irradiated Polyamide-1010 (PA1010) and PA1010 filled with neodymium oxide (Nd_2O_3) were characterized by an ESR approach. It was found out that a was mainly trapped in the fold surface of the lamellae and b in the amorphous phase. This result suggested that trapped radicals mainly existed in the noncrystalline phases. The effect of the fold surface area of the lamellae on the behavior of the trapped radicals are discussed in this article. Whether for the specimens with similar crystallinities but different crystallite sizes or for those with the same concentration of neodymium oxide but different crystallinities, radical a exists dominantly in a specimen with a larger fold surface area of the lamellae. Under a certain circumstance, radical a can transform into radical b for a specimen with a larger fold surface area of the lamellae. It means that the fold surface area of the lamellae plays an important role in the transformation of radical a to b. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1335–1339, 1998
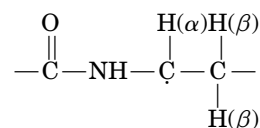
Key words: free radicals; ESR; polyamide-1010; fold surface area of the lamellae; radical transformation

INTRODUCTION

Polyamide-1010 (PA1010) is one of the most important engineering plastics specially produced commercially in China. Similarly, it is a typical semicrystalline with different microstructures under various thermal histories.[1] Attention to radiation effects on PA1010 has been paid.[2–9] There is divergence of views about where the free radicals are trapped, for irradiated crystalline polymers. It was thought in the early researches that the possibilities of producing radicals in the amorphous and crystalline phases on irradiated crystalline polymers[10,11] are the same. The free radi-

cals in the crystalline phase must transfer to the fold surface of the lamellae to take reactions, such as coupling, and transformation etc.[12]

A previous study[13] on irradiated amides (model compounds of polyamide) indicated that the site of the free radical is on the carbon adjacent to carbonyl group, regardless of their structures. Furthermore, the radical shows quartet line ESR spectrum with 1 : 3 : 3 : 1 in height. Graves[14] put forward that the observed quartet arise from the unpair spin coupling with the α-hydrogen and the two β-hydrogen atoms, as listed below.

$$\underset{\displaystyle \underset{H(\beta)}{|}}{—\overset{\displaystyle \overset{O}{\|}}{C}—NH—\overset{\displaystyle \overset{H(\alpha)}{|}}{C}—\overset{\displaystyle \overset{H(\beta)}{|}}{C}—}$$

Table I   Some Structural Properties of Specimens Chosen to Be Irradiated

Specimens	A	B	C	D	B′	C′	A″	B″	C″
$C_n(\%)^a$	0.0	0.5	1.0	1.5	0.5	1.0	0.0	0.5	1.0
$W_c(\%)^b$	47.5	46.8	49.7	50.8	10.8	10.8	0.0	0.0	0.0
$L_{100}(nm)^c$	19.7	18.7	17.6	16.0	6.8	5.7	0.0	0.0	0.0
$L_{010}(nm)^c$	8.6	8.1	8.0	7.7	3.7	3.4	0.0	0.0	0.0

[a] The concentration of neodymium oxide.
[b] Crystallinity measured by the Ruland method,[17] of specimen without irradiation.
[c] Crystallite sizes determined by the Scherrer Equation[18] of crystalline PA1010.

As far as irradiated polyamides are concerned, the trapped radicals were advocated as follows below:[15,16]

(a) $-CH_2CONH\dot{C}HCH_2-$
(b) $-CH_2\dot{C}=O$
(c) $-CH_2\dot{C}(OH)NHCH_2CH_2-$
(d) $-\dot{C}HCH=CHNHCH_2-$

Based on the above radical identification of irradiated polyamides, the two major kinds of free radicals, $-CH_2CONH\dot{C}HCH_2-$ (a) and $-CH_2\dot{C}=O$ (b) in irradiated PA1010 were proposed in this article, and the authors put forward that quartet line radical a exists mainly in the fold surface of the lamellae; radical b with singlet line spectrum, in the amorphous phase.

EXPERIMENTAL

Materials and Preparations of Specimens

PA1010 powder[4] (shanghai cellulose factory in China) and its mixtures with different concentrations of neodymium oxide (Nd_2O_3, the average size is 0.5 µm) were dried at 50°C under reduced pressure for 10 h, and then molded at 220°C into sheets of 0.3–0.5 mm in thickness. By the way, the mixtures were mechanically stirred in a stirrer at three to five circles per second. Specimens with 0.0% crystallinity were obtained by being quenched in ice water. Annealing at different temperatures causes specimens to possess various crystallinities. Of those, we chose the following specimens whose structural properties are listed in Table I, to be focused on.

ESR Measurements

For the ESR investigation, 1×8 mm bar-shaped films about 30 mg weight were placed in glass tubes, evacuated to the pressure of 0.1 Pa, and sealed. They were irradiated at room temperature by ^{60}Co γ-ray at a rate of 10 kGy/h. After irradiation, electrons trapped in the glass tubes were annealed out so that the ESR spectra of the radi-

cals trapped in irradiated PA1010 cannot be interfered. ESR determinations of the trapped radicals were taken on a JES-P10B ESR spectrometer, as detailed in the previous publication.[19]

RESULTS AND DISCUSSION

The Amount of the Fold Surface of the Lamellae

For specimens A, B, C, and D having similar crystallinities, the fold surface area of the lamellae depends on crystal sizes (L100 and L010). The smaller crystallite sizes, the larger the fold surface area of the lamellae.[4] On the other hand, for specimens B, B′ and B″, which possess the same concentration of neodymium oxide, the fold surface area of the lamellae is proportional to the crystallinity. The higher the crystallinity, the larger the surface area of the lamellae.[5]

The Radicals Trapped in Irradiated PA1010

According to Burrell's identification[13] and the principle of radiation chemistry of polymers,[20,21] PA1010 with flexible CH_2 groups in the main chain subjected to high-energy radiation undergoes the following reaction (as depicted in Scheme 1) to release H radicals so that radical a is brought about, while radical a can transform into radical b, called chain scission, resulting in radiation-induced crystallization.[6,7]
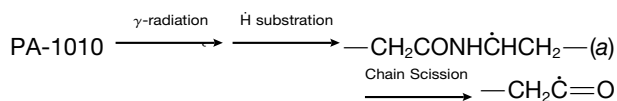
Scheme 1

Table II The Relative Intensities of Singlet and Quartet Line Spectra for Irradiated B, B′, and B″

Specimens	$W_c(\%)$	$I_{rs}{}^a$	$I_{rq}{}^b$
B	46.8	7.0	30.6
B′	10.8	9.3	7.8
B″	0.0	12.2	4.8

The relative intensities of singlet[a] and quartet[b] line spectra, respectively.

Dependence of the Amount of Free Radicals on the Fold Surface Area of the Lamellae

The amount of radicals can be determined by the relative intensities of ESR spectra instead of the integral area of peaks. The relative intensities (I_r) of singlet- and quartet-line radicals trapped in irradiated B, B′, and B″ with the same concentration of neodymium oxide, are listed in Table II. From Table II, we can easily see the fact that the amount of radical a increases when W_c is up. It can be apparently deduced that radical a is trapped in the crystalline phase. But the decay of the radicals reveals that radical a is mainly trapped in the fold surface of the lamellae not in the crystalline phase, and is discussed further in a later section of this article. The amount of radical b is proportional to the amorphous fraction, indicating that it is trapped in the amorphous phase.

Figure 1 illustrates the relationship of the relative intensities of singlet and quartet line spectra
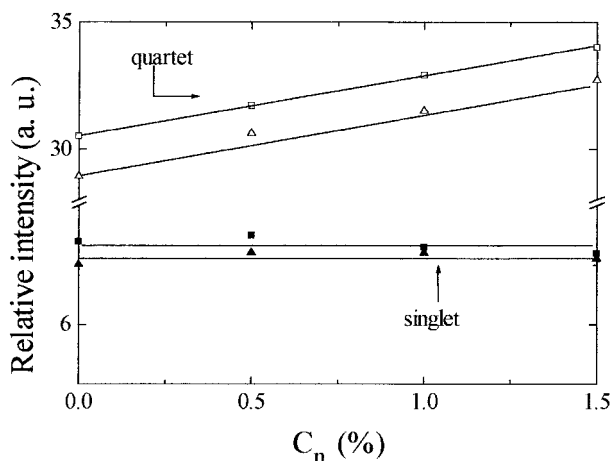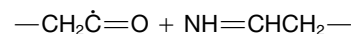

Figure 1 The relationship of the relative intensities of singlet and quartet line spectra as a function of the concentration of neodymium oxide (uptriangle, at a dose of 250 kGy; square, 500 kGy).

—$CH_2CONH\dot{C}HCH_2$— →

—$CH_2\dot{C}$=O + NH=$CHCH_2$—

Scheme 2

as a function of the concentration of neodymium oxide. The relative intensity of quartet line spectrum increases linearly with the concentration of neodymium oxide. The more the concentration of neodymium oxide, the smaller the crystallite sizes and the larger the fold surface area of the lamellae. Accordingly, radical a is preferentially trapped in the fold surface of the lamellae. Thus irradiated specimen with a larger fold surface area holds more amount of radical a. Specimens A, B, C, and D show similar amount of amorphous fraction, and for which the amount of radical b in these specimens shows no difference.

Transformation and Decay at Room Temperature

At room temperature, radicals a trapped in the fold surface of the lamellae cannot terminate easily because of the restriction imposed by the crystalline phase. They only have the ability to vibrate at their equilibrium sites, when the temperature is far below T_{g1} (about 50°C, glass transition temperature in the amorphous phase), while the following reaction called disproportionation scission or chain scission (Scheme 2) may occur in the course of disposal at the room temperature for a longer time.

The comparison of the relative intensities of the ESR spectra of irradiated B′ and C′ before and after decay times of 145 days are listed in Table III. The characteristic decaying coefficient (CDC), defined as $1 - I/I_0$, whereas, I_0 is the relative intensity of ESR spectrum before de-

Table III   Comparison of the Relative Intensities of ESR Spectra Before and After Decaying at Room Temperature

	I_{rq} (Arbitrary Unit)		I_{rs} (Arbitrary Unit)	
	B′	C′	B′	C′
Before decaying	7.8	8.4	9.3	9.3
After decaying	2.1	2.4	6.2	7.2
CDC (%)[a]	73.1	71.4	33.3	22.6

[a] Characteristic decaying coefficient, defined as $1 - I/I_0 \cdot I_0$ and I refer to ESR intensities before and after decaying.
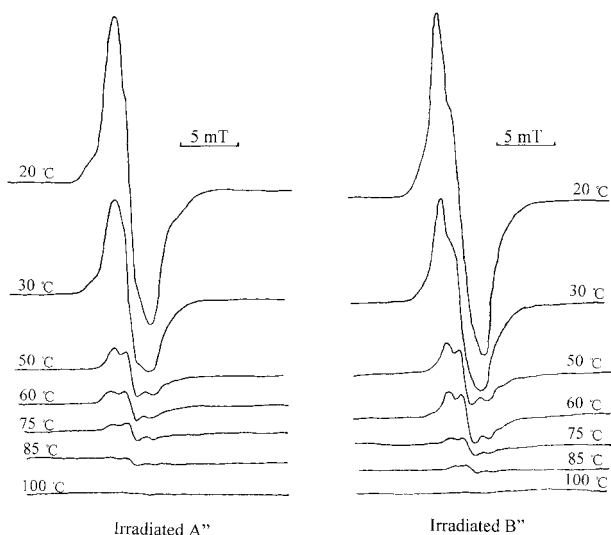
Figure 2 ESR spectra for irradiated specimens A″ and B″ (250 kGy) at different temperatures.

caying, and *I,* the relative intensity after decaying; may be a proper means to show the difference between the transformation of radical *a* to *b* in irradiated B′ and C′ with CDC of radical *b* in irradiated B′ greater than that in irradiated C′, while, CDCs of radical *a* for both of irradiated B′ and C′ keep almost the same. From the comparison of CDCs of radical *a* and *b* in irradiated B′ and C′, the conclusion can be drawn that the amount of the transformation of radical *a* to *b* for irradiated B′ is less than that for irradiated C′, due to a larger fold surface area of the lamellae in specimen C′, in which free radical *a* is dominantly trapped.

Transformation and Decay of Radicals Under the Condition of Heating

The transformation and decay of radicals depend on macromolecular motions and the relaxation of polymers. When irradiated specimens are heated, the transformation and decaying of the radicals are favored, and further, it is beneficial for chain scission to occur. As for irradiated amorphous specimens (A″ and B″), ESR spectra at different temperatures are shown in Figure 2, from which it is seen that the relative intensities of radical *a* and *b* decrease with increasing temperature. We can draw the conclusion that radicals *a* and *b* decay when the temperature increases. Specimens A″ and B″ are amorphous, and consequently, radicals *a* and *b* in irradiated A″ and B″ decay similarly. By the way, it is worth noting that radical

a in irradiated A″ and B″ is directly produced by subtraction of H radicals from the main chain and trapped in the amorphous phase.

As far as irradiated specimens with higher crystallinities (A and B) are concerned, the changes in relative intensities of ESR spectra with temperature are illustrated in Figure 3. The relative intensity of the quartet line ESR spectrum for both of irradiated A and B decreases with the temperature, while the tendencies of the relative intensities of singlet line spectra for irradiated A and B changing with temperature are of interest. Radical *b* decays by itself when the temperature rises, meanwhile, there is some amount of radical *b* transformed from *a*.

For the case the temperature is below T_{g1}, radical *b* decays slowly, because of the glassy domains restricting motions of macromolecular chains. At around T_{g1}, the motions of macromolecular chains
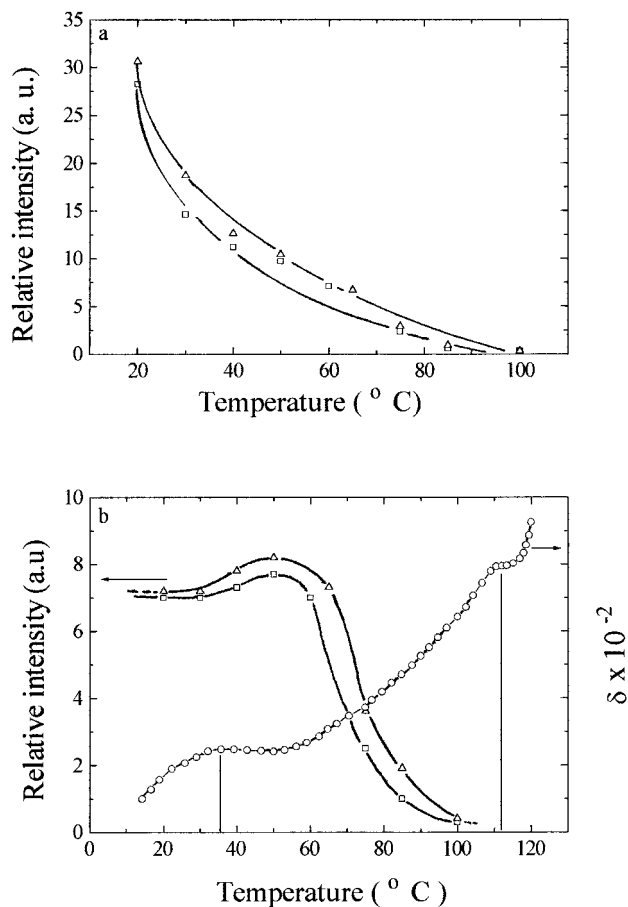

Figure 3 The dependence of the relative intensities of ESR spectra of irradiated specimens A and B on the temperatures [Figure 3(a) for quartet line ESR spectra; Fig. 3(b) for singlet line ESR spectra. □ for irradiated A; △ for irradiated B; ○ for tan δ vs. temperature].

in the amorphous phase increase with the result that radical b can transfer to couple with other radicals to produce crosslinks, as a result, the amount of radical b drops. Meanwhile, as the temperature rises, radical a transforms into b to compensate the decreasing amount of radical b, and totally the amount of radical b increases. There is a more amount of radical a in irradiated B than that in irradiated A. The transformation of a to b is much more for irradiated B than that for irradiated A. At the range of T_{g1} and T_{g2}, radicals a and b decay so that the amount of them drops. When the temperature gets T_{g2} (far from T_m, 205°C), there are no ESR signals, indicating radicals a and b both terminate. The radicals, if trapped in the crystalline phase, may not terminate at the temperature below T_m, because macromolecular radicals in the crystalline phase are too inactive to interact and a lot of detection of ESR spectra. There is no ESR spectrum, wherein it concluded that there are no radicals trapped in the crystalline phase.

CONCLUSION

The amount of quartet-line radical a ($-CH_2$-$CONH\dot{C}HCH_2-$) is proportional to the fold surface area of the lamellae, and the amount of singlet-line radical b ($-CH_2\dot{C}=O$) is proportional to the amorphous fraction, indicating that a is trapped in the fold surface of the lamellae, and b in the amorphous phase. Consequently, the radicals are trapped mainly in the noncrystalline phases. Irradiated specimen with a larger fold surface area of the lamellae shows a higher relative intensity of quartet-line ESR spectrum. Under certain conditions, the transformation of radical a to b becomes obvious and more in irradiated specimens with a larger amount of radical a. The fold surface area of the lamellae shows an important role in the transformation and decay of the trapped radicals.

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