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ESR study of gamma irradiated Nylon3

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ABSTRACT

Nylon3 (poly-β-alanine) gamma irradiated in nitrogen was investigated by Electron Spin Resonance Spectroscopy to elucidate the type of radicals generated, their relative abundance, conversion into other radicalic species and their room temperature stability. Two types of radiation induced primary radicals have been detected. One of them (R_1) occurs by hydrogen abstraction from methylene group next to the carbonyl group, while the other (R_2) by hydrogen abstraction from methylene group next to amide group. R_1 is observed to be converted into an alkoxy radical (R_3). Decay kinetics of the radicals in nitrogen was also examined and decay mechanisms have been proposed for each radical.

1. Introduction

Polymeric materials are widely used in Radiation Technology as vital transformations occur when they are exposed to ionizing radiations. 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, crosslinking and degradation etc. Even, some polymers such as polyethylene and poly (methyl methacrylate) are used in radiation 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 (Dias et al., 1999; Hassan and Sharaf, 2005; Lund et al., 2002; Maghraby and Tarek, 2006 Ollson et al., 2000, 2002; Gancheva et al., 2006; Catiker et al., 2008, 2010) to develop more sensitive radiation dosimetry systems than conventional systems. Ollson et al. (2002) 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).

There are many studies on the radiation induced modification (especially grafting and crosslinking) of polyamides in particular nylon6 and nylon66 (Dole, 1973). In the radiation-induced modification of polymers, it is also important to determine 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 the control of grafting. The information to be collected on the type, stability and abundance of macroradicals generated on nylon3 would be helpful in further modification studies on this polymer.

Nature, stability and transformation of radiation-induced primary radicals of polymers are important to determine their use in radiation chemistry. Although there are plenty of studies on radiation chemistry of nylon6 (Simon et al., 1977; Shinohara and Ballantine, 1962; Kashiwagi, 1963; Graves and Ormerod, 1963; Szöcs et al., 1973; Takigami et al., 1981; Zimmerman, 1959; Li and Zhang, 1997; Gupta and Pandey, 1988; Chang and LaVarne, 2002) nylon66 (Kashiwagi, 1963; Graves and Ormerod, 1963) and Nylon1010 (Li and Zhang, 1997), to the best of our knowledge, there is no study on radiation chemistry of nylon3. Nylon3, described also as 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 similarity of repeating unit of poly-β-alanine to alanine prompted us to expect that the polymer may exhibit an ESR/radiation dosimeter material behavior. Nylon3 was synthesized and its radiation response was investigated within the scope of this study.

2. Experimental

2.1. Synthesis

Nylon3 was synthesized through base-catalyzed hydrogen transfer polymerization of acrylamide. Water-insoluble fraction (crystallinity, 37% obtained from XRD Spectra and

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Molecular weight, 2000–2500 g mol^{-1} determined via MALDI-TOF) of the crude polymer was used in the study.

2.2. Irradiation and ESR measurements

Polymer samples were irradiated in nitrogen at room temperature by ^{137}Cs gamma source at a dose rate of 700 Gy h^{-1}. ESR measurements were performed by X-band Bruker ESR spectrometer 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. All the spectra were recorded as first derivative of the absorption intensity. 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.

2.3. Viscosity measurements

Inherent viscosities of 0.1 g/dL of pristine and irradiated samples in 85% formic acid were determined using an Ubbelohde type capillary viscometer at 25.0 °C.

3. Results and discussion

3.1. Stability of radiation-induced radicals

3.1.1. Irradiation in nitrogen and storage in air

ESR spectrum of a nylon3 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 N3.

As shown in Fig. 1a, 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 compared to the radical belonging to singlet line. It is clear that primary radicals are extremely vulnerable to oxygen attack.

3.1.2. Irradiation and storage in nitrogen

As the γ-ray induced radicals of N3 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 Fig. 1b were recorded as a function of time after γ-irradiation of N3 sample in nitrogen. The similar spectra have been reported for nylon6 irradiated in vacuum by Simon et al. (1977), Shinohara and Ballantine (1962), Kashiwagi (1963), Graves and Ormerod (1963), Szöcs et al. (1973), and Takigami et al. (1981).

Graves and Ormerod (1963) attributed the spectrum (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. Szöcs et al. (1973) attributed the spectrum (a quartet, a triplet and an unresolved spectrum) to Radical A, Radical D and an allylic radical. Kashiwagi (1963) attributed the spectrum (a doublet of triplet and a quintet) to Radical A and a biradical ($H_2C^* \, {}^*CH_2$) formed by scission of C–C bond. Shinohara and Ballantine (1962) attributed the spectrum (a quintet and an unresolved spectrum) to Radical A and a resonating allylic radical. Takigami et al. (1981) 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 (1997) attributed the spectrum (a quartet and a singlet) to Radical A and Radical E. Although Zimmerman (1959) assigned the spectrum as a quartet (belonging to Radical B), Simon et al. (1977) assigned the spectrum (a quartet and a singlet) to Radical B and Radical F as shown in Scheme 1.

As will be discussed later in detail, the long lived singlet ESR line was attributed to the radical similar to the Simon et al.'s (1977) claim. Furthermore, our study showed that the experimental ESR spectrum of N3 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.

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.

3.2. Type of radiation-induced radicals

When simulation of the experimental ESR spectra (in Fig. 2a and b) was carried out assuming that the spectrum consisted of two different six-line spectra and a singlet spectrum, fitting study gave best results for the following composition: (R_1:49%, R_2:32%, and R_3:19%). Parameters of the best fit were given in Table 1. According to the results of the simulation study, the experimental spectrum was attributed to the presence of radicals in Scheme 2.

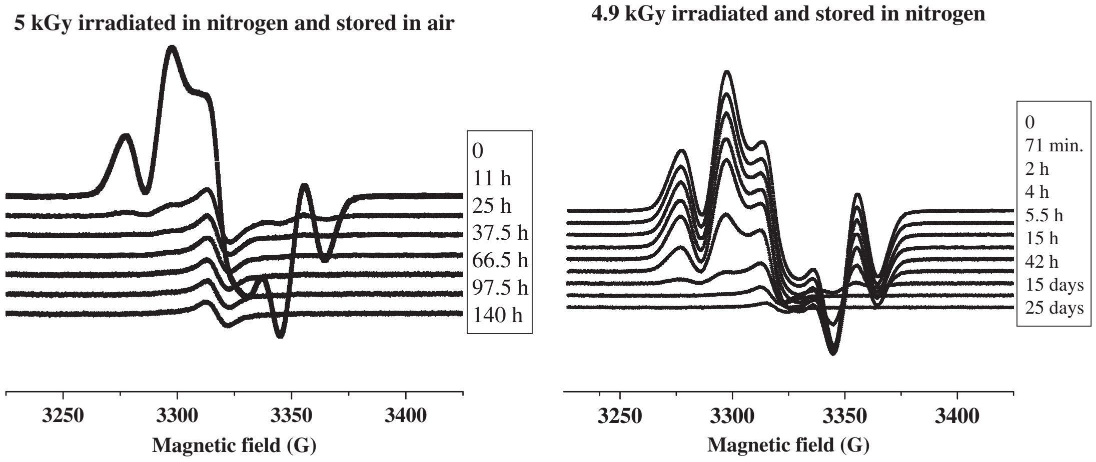

Fig. 1. (a) Change in the shape of ESR spectra of N3 irradiated in nitrogen and stored in air and (b) change in the shape of ESR spectra of N3 irradiated and stored in nitrogen at room temperature.