



TEMPERATURE DEPENDENT ESR SPECTRA OF IRRADIATED NYLON HOMOPOLYMER

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ABSTRACT

Temperature dependent free radical decay behavior in irradiated nylon homopolymer has been investigated by electron spin resonance (ESR) and Fourier transform infrared (FTIR) techniques. The ESR spectrum observed for nylon irradiated to 1 M rad radiation dose has shown a complex shape and eight hyperfine lines. The spectrum is analysed by computer simulations and resolved to be superposition of component spectra arising due to macroradicals of the $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2-$ (**I**) and radicals of the type $\sim\text{CH}_2-\dot{\text{C}}=\text{O}$ (**II**). The magnetic parameters corresponding to the free radicals were evaluated by theoretical methods. ESR spectra of irradiated nylon were also recorded in the temperature range 300-400 K. The hyperfine structure observed at room temperature (RT) gradually diminished and the ESR signal completely vanished around 405 K. Reasons for this temperature dependent free radical decay has been explained. Fourier Transform Infrared (FTIR) spectra of unirradiated and irradiated nylons were recorded to ascertain chemical changes induced by radiation.

Key words: Electron spin Resonance (ESR), Fourier transform infrared (FTIR), Nylon polymer, Magnetic parameter, Free radicals, Gamma irradiation.

INTRODUCTION

Degradation of nylon has been studied by various authors¹⁻⁷. Thermal degradation of nylon homopolymer is reported to occur through evolution of volatile products, which are formed by the cleavage of C-N bond. The volatile products include carbon monoxide and ammonia and HCN^{1,2}. Photodegradation of nylon is reported to cause a reduction in

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molecular and mechanical properties^{3,4}. Radiative degradation of nylon including degradation with gamma rays and X-rays have also been studied by different experimental techniques⁵⁻⁷. These studies indicate a reduction in mechanical strength and crystallinity of the polymer. As a result of irradiation, the viscosity of the polymer is reported to increase probably due to cross links⁵. The ESR studies indicate the presence of carbon centered radicals⁶. The ESR spectra of irradiated nylon has shown a complex shape and free radicals formed during irradiation disappeared on thermal treatment⁷. The radical decay is found to depend on the crystallinity of the polymer. These studies indicate the presence of macroradicals $\sim\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2\sim$ and radicals of the type $\sim\text{CH}_2-\dot{\text{C}}=\text{O}$. Formation of peroxy radicals is also reported in irradiated nylon⁸.

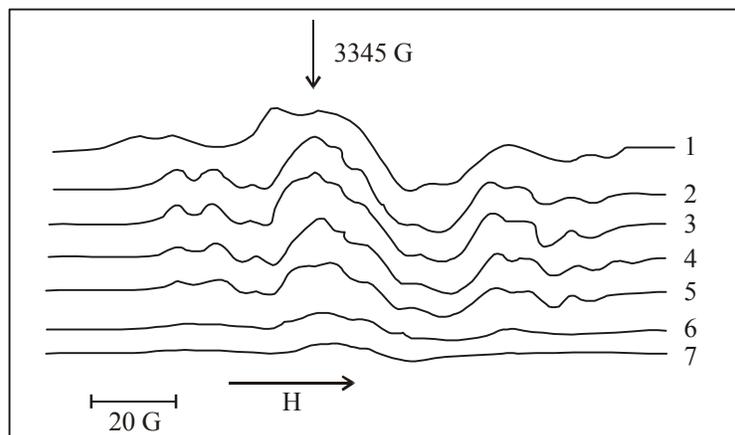
Though degradation studies of nylon are available, these studies confine to certain doses only. Radiation effects in nylon at lower doses ($\sim 1\text{M}$ rad radiation dose) is attempted by very few authors. Further reasons for temperature dependent free radical decay has not been explained clearly. Therefore, the authors have made an attempt in this regard. The nylon homopolymer is irradiated with gamma rays to a dose of 1M rad. The ESR spectra are recorded under different conditions. To analyse the ESR spectra, computer simulations are employed. The data obtained from ESR studies is compared with the results obtained from Fourier transform infrared spectroscopy.

EXPERIMENTAL

Nylon-6 homopolymer in the form of powder has been gifted by Dr. S. Veerabhadraiah, Polymer Blends Laboratory, Dressden, Germany. The polymer is irradiated with cobalt 60 gamma source with a dose rate of 15 KGy/hr and irradiations are performed in air at room temperature. The dose of irradiation has been controlled by time duration. ESR spectra of irradiated samples have been recorded on Varian E-Line spectrometer operating at X-band frequencies and 100 KHz modulation. Fourier transform infrared spectra of unirradiated nylon samples have been recorded on Perkin-Elmer spectrometer by making the pellets of nylon along with potassium bromide (KBr).

RESULTS AND DISCUSSION

Unirradiated nylon has not shown any ESR spectrum, indicating the absence of any types of free radicals. ESR spectrum observed for nylon irradiated to 1M rad radiation dose is shown as Curve 1 in Fig. 1. The spectral parameters are as listed in Table 1. The spectra of the irradiated nylon have also been recorded at different temperatures (310 K , 330 K , 350 K , 370 K , 390 K and 400 K) and these are shown as curves 2, 3, 4, 5, 6 & 7, respectively.

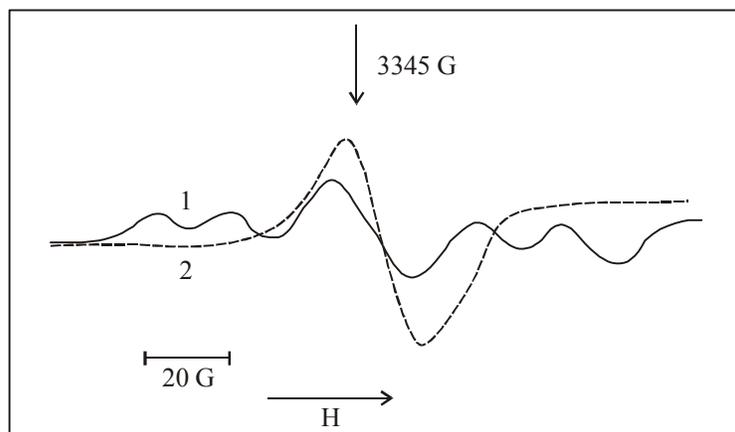


Curve-1: 300 K, Curve-2: 310 K, Curve-3: 330 K, Curve-4: 350 K,
Curve-5: 370 K, Curve-6: 390 K, Curve-7: 400 K.

Fig. 1: ESR Spectra of irradiated nylon at different temperatures.

It can be observed from the Table 1 that hyperfine pattern gradually smeared out and the signal vanished around 400 K.

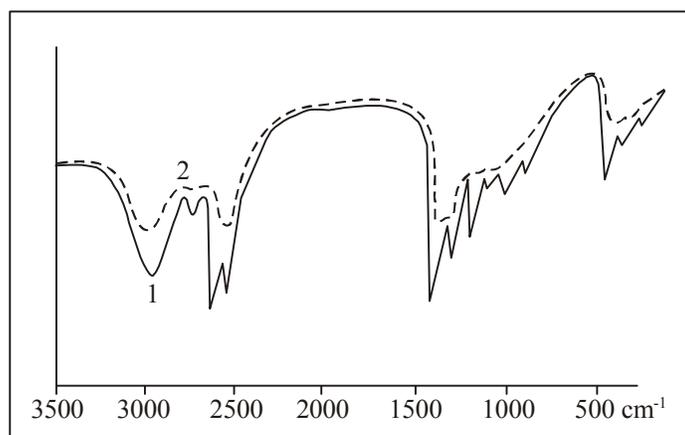
The ESR spectrum observed at room temperature (RT) has been simulated with the component spectra shown in Fig. 2. Curve 1 in Fig. 2 is the component spectrum arising due to macro radicals; while Curve 2 is the component singlet. The magnetic parameters associated with the component spectra are as listed in Table 1.



Curve-1: Component multiplet, Curve-2: Component Singlet.

Fig. 2: Component ESR spectra at 300 K.

Fourier transform infrared spectra of unirradiated nylon is shown as Curve 1, (Fig. 3); while Curve 2 is the spectrum of irradiated nylon.



Curve-1: Unirradiator, Curve-2: Irradiated

Fig. 3: FTIR spectra of nylon homopolymer

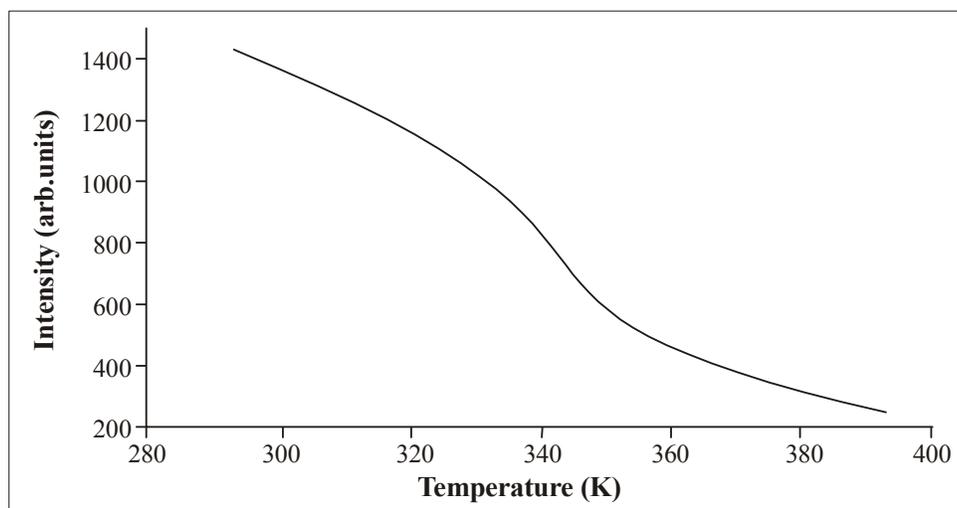


Fig. 4: Variation of ESR intensity with temperature

Computer simulations

ESR spectrum of irradiated nylon has shown a complicated behavior. Neither the intensity distribution, nor the hyperfine spacing are compatible with the expected values. The main reason for this incompatibility is considered to be due to two reasons -

- (i) Presence of more than one resonance at the same time and
- (ii) Interplay of hyperfine interaction of the existing free radical species. These two reasons are considered to contribute to the complexity of ESR line shape.

The ESR spectra of irradiated nylon have been simulated to be superposition of component spectra arising due to various types of free radical species produced on irradiation of the polymer. Various possibilities of chain cleavages on irradiation of nylon and formation of corresponding free radicals has been discussed by Reddy⁹.

Based on various types of chain cleavages, formation of different types of free radicals is expected. All such free radicals will give their own component spectra and the resultant spectrum will be a broadened spectrum as has been observed in the present investigation. Simulation of the component spectrum has been carried out by suitable magnetic parameters like relative intensity ($Y_{\max i}$), line width (a_i) centre of spectrum (X_{ai}) hyperfine splitting constants (A_i, B_i) and values of n_i & m_i i.e. the number of hyperfine lines resulting from the adjacent nuclei. The component spectra was simulated using the expressions of Lorentzian and Gaussian line shape functions involving magnetic parameters. The component spectra simulated by this method are superposed and compared with the experimentally observed spectrum in aspects like line intensity for each line position. The method of simulating ESR spectra has been successfully applied to various polymers¹⁰ and copolymers¹¹.

ESR spectrum of nylon irradiated to 1 M rad radiation dose and spectrum recorded at room temperature has been simulated employing Lorentzian line shape function. The spectrum compose component spectra are shown in Fig. 2. Curve 1 is component multiplet and Curve 2 is component singlet. The multiplet is simulated with the values of $n_i = 2$, $m_i = 5$, $A_i = 23.0$ G and $B_i = 12.0$ G. These values infer that the free radical responsible for component 1 will have an interacting α – proton and four beta protons, having a structure of $\sim\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2\sim$ (**I**). Since radical (**I**) has shown different number of hyperfine lines ranging from two to ten, depending on the extent of hyperfine interaction, it is designated as component multiplet¹². The presence of macroradicals in irradiated nylon has also been reported by various authors previously^{1,8}. Component 2 could be simulated with the values of $n_i = m_i = 1$ and $A_i = B_i = 0$ indicating that the free radical giving component singlet does not have any protons in neither alpha nor beta position. Component 2 is assigned to the free radicals of the type $\sim\text{CH}_2-\dot{\text{C}} = \text{O}$ (**II**). Formation of radical, **I** and **II** occurs through the cleavage of C-N bond initially and during subsequent reactions^{1,3}. Magnetic parameters employed to simulate the component spectra are as listed in Table 1.

Table 1: Magnetic parameters of irradiated nylon homopolymer at room temperature

Components	Relative intensity $Y_{\max i}$	Line width (a_i) G	Centre of spectrum (X_{oi}) G	Hf splittings G		n_i	m_i
				A_i	B_i		
Multiplet	15.0	9.0	3345	23.0	12.0	2	5
Singlet	20.0	5.0	3346	0	0	1	1

Regarding the ESR spectra recorded at higher temperatures, the spectral parameters indicate that although the values of spread, hyperfine spacings have changed, a decrease in the value of intensities have been observed. Therefore, almost similar type of radicals, are present at other temperatures also. The spectra recorded at higher temperatures could also be simulated with almost same set of magnetic parameters i.e., $n_i = 2$ $m_i = 5$ indicating the presence of component multiplet and singlet. However, a change in values of A_i , B_i , $Y_{\max i}$, a_i are observed. Change in the values of magnetic parameters indicate -

- (i) Reduction/increase in concentration of free radicals and
- (ii) A change in the hyperfine interaction of component multiplet.

It is proposed that both the factors contribute to the anisotropy of the spectra at higher temperatures. Such types of variations in line shape has also been observed previously¹³.

Fourier transform infrared absorption spectra of unirradiated and irradiated nylon have been recorded to ascertain chemical changes induced by irradiation. The absorption bands and their interpretation is listed in Table 2.

Table 2: FTIR absorption bands of nylon homopolymer

S. No	Central wave number (cm^{-1})	Intensity	Functional group
1	3458	v. strong	Amide/ NH_2
2	2933	m	Methyl/methylene
3	1663	m	$\text{C} = \text{O}$
4	1040	w	CH/CH_2

Unirradiated nylon possesses absorption bands around 3350, 2930, 2910, 1650, 1550, 1450, 950 cm^{-1} region. These groups are assigned to N-H, CH_3 , C-N, C=N, C=O, CH_3 , CH/CH₂ groups present in the polymer. On irradiation, the 3350 and 1660 cm^{-1} bands have shown a reduction in their intensity. Therefore, it is proposed that these groups might have been effected by irradiation of the polymer. As these groups are assigned to C-N, C=O groups, cleavage of these groups on irradiation of nylon is proposed.

Intensity of the ESR spectra observed at different temperatures have been calculated using double integration methods as given in Table 3. The values of ESR intensity against temperature is plotted as shown in Fig. 4. The curve is almost linear indicating the complicated decay of free radicals with temperature. The free radical decay with temperature indicate that the free radical, formed on irradiation of nylon might have recombined with temperature. Such types of free radical decay has also been reported previously for several polymers^{10,15}.

Table 3: Spectral areas of nylon homopolymer

S. No	Temperature (K)	Intensity in arbitrary units
1	300	1426
2	310	1250
3	330	974
4	350	540
5	370	356
6	390	245

REFERENCES

1. A. L. Bhuiyan, *Polymer*, **25**, 1699 (1984).
2. H. K. Reimschuessel, *J. Polym, Sci. A*, **12**, 65 (1977).
3. N. S. Allen and J. K. Mc Keller, *J. Polym Sci A*, **13**, 241 (1978).
4. R. F. Moore, *Polymer*, **4**, 493 (1958).
5. F. Szocs, *Angew Macro Mol. Chem.*, **263**, 31 (1988).
6. B. Li and L. Zhong, *Rad. Phys Chem.*, **49**, 395 (1997).

7. G. A. George and M. S. O. Shen, *Polym Degrad. Stab.*, **28**, 289 (1990).
8. M. Igarshi, *J. Polym. Sci.*, **A1**, 2405 (1983).
9. N. Ramana Reddy, Identification of Free Radical in Some Polymers and Copolymers, Ph. D. Thesis, Kakatiya University, Warangal (2008).
10. B. Sanjeeva Rao, S. Indira, V. Sridhar, G. Punnaiah and T. Venkatappa Rao *Rad. Effects and Defects in Solids*, **161**, 31 (2006).
11. B. Sanjeeva Rao, S. Indira, V. Sridhar, G. Punnaiah, *Rad. Effects and Defects in Solids*, **160**, 145 (2005)
12. B. Sanjeeva Rao and M. Ramakrishna Murthy, *J. Polymn Sci. B*, **27**, 1187 (1989).
13. B. Sanjeeva Rao, Y. Sudershana Reddy, N. Subbarami Reddy and M. F. Hasan, *J. Polym. Sci. B*, **32**, 1787 (1994).
14. J. F. Rebek, *Experimental Methods in Polymer Research*, John-Wiley, (1980) p. 141.
15. O. Bartos and M. Klimova, *Colloid Polym. Sci.*, **273**, 766 (1995).

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