

ELECTRON SPIN RESONANCE SPECTROSCOPIC INVESTIGATION
OF GAMMA IRRADIATED NYLON3 AND ITS DERIVATIVES

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DECEMBER 2007

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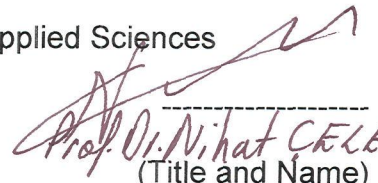
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EFKAN ÇATIKER

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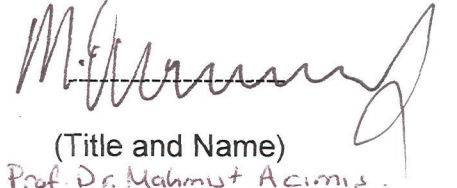
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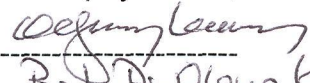

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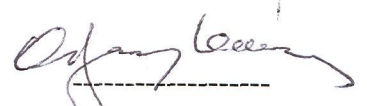
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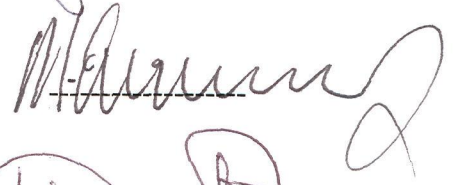
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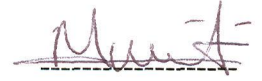
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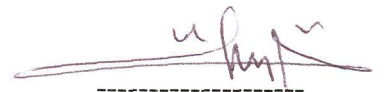
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ABSTRACT

ELECTRON SPIN RESONANCE SPECTROSCOPIC INVESTIGATION OF GAMMA IRRADIATED NYLON3 AND ITS DERIVATIVES

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The structural similarity between nylon3 (poly- β -alanine) and alanine, a well known radiation dosimeter material, prompted us to conduct studying the effect of ionizing radiation on nylon3 and its derivatives. It was expected that nylon3 and its derivatives may have stable radiation-induced radicals and hence exhibit dosimetric properties.

In the first part of the thesis, nylon3 (N3), 2-methyl nylon3 (2mN3) and 3-methyl nylon3 (3mN3) were prepared through base-catalyzed hydrogen transfer polymerization of corresponding monomers. Full characterization of the polymers was conducted by FTIR, NMR (^1H -NMR and ^{13}C -NMR), DSC, TGA, elemental analysis, viscosimetric analysis, and some end-group analyses. The

radiation induces changes on the structure of the polymers were followed by FTIR, ^1H -NMR and viscosimetry.

In the second part of the thesis, the polymers were irradiated by ^{137}Cs gamma rays in both air and nitrogen medium at room temperature. The ESR spectra of the polymers irradiated in both medium were recorded to determine the radiation induced radicals of the polymers. The changes in the ESR spectra of the samples with time were recorded in order to determine the stabilities and decay behavior of the radicals. The experimental ESR spectra of the polymers were simulated to obtain theoretical ESR spectra and its components (types of radicals). The change in the concentrations of the radicals in both medium was compared to elucidate the effect of oxygen on the decay rate of the radicals. The most important findings related to the type and decay of radicals found in nylon3 and its derivatives are the following:

Nylon3 has two types of radiation induced primary radicals; a radical (Radical 1) generated by removal of hydrogen from the carbon atom next to the amide group and a radical (Radical 2) generated by removal of hydrogen from carbon atom next to the carbonyl group. The Radical 1 transforms to a relatively long lived radical (Radical 3) with unpaired electron on the oxygen atom.

2-methyl nylon3 has only one type of radiation induced primary radical (Radical 2) formed by abstraction of hydrogen from the carbon atom next to the carbonyl group. This primary radical transforms to another radical (Radical 1) through disproportionation reaction and then the secondary radical transforms to a

relatively long lived radical (Radical 3) with unpaired electron on the oxygen atom.

3-methyl nylon3 has two types of radiation induced primary radicals; a radical (Radical 1) generated by removal of hydrogen from the carbon atom next to the amide group and a radical (Radical 2) generated by removal of methyl group from the carbon atom next to the amide group.

Relative abundances of the radicals generated by irradiation of nylon3 in nitrogen were determined as R1: 32%, R2: 49% and R3: 19% by simulation of the ESR spectrum recorded immediately after irradiation. Relative abundances of the radicals generated by irradiation of 2-methyl nylon3 in nitrogen were determined as R1: 13%, R2: 76% and R3: 11% by simulation of the ESR spectrum recorded immediately after irradiation. Relative abundances of the radicals generated by irradiation of 3-methyl nylon3 in nitrogen were determined as R1: 74.7% and R2: 25.3% by simulation of the ESR spectrum recorded immediately after irradiation.

Kinetic study of the decay of radicals of nylon3 and 3-methyl nylon3 showed that radicals follow apparently a first-order decay. Decay behavior of the radicals of 2-methyl nylon3 however did not reveal a clear order.

Radiation chemical yields of the radicals of polymers were found to follow the following order: 2-methyl nylon3 > 3-methyl nylon3 $\approx$ nylon3.

Keywords: Nylon3, 2-methyl nylon3, 3-methyl nylon3, Hydrogen Transfer
Polymerization, ESR Spectroscopy, Radiolysis, Simulation of ESR Spectra,
Decay Kinetics

ÖZET

GAMA IŞINLARIYLA IŞINLANMIŞ NAYLON3 VE TÜREVLERİNİN ELEKTRON SPİN REZONANS SPEKTROSKOPİSİ İLE İNCELENMESİ

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İyi bir radyasyon dozimetri materyali olarak bilinen alaninin naylon3'e olan yapısal benzerliği, bizi naylon3 ve türevlerine iyonlaştırıcı radyasyonun etkisi üzerine çalışmaya teşvik etti. Naylon3 ve türevlerinin kararlı radyasyon bazlı radikallere sahip olabileceği ve böylece dozimetrik özellik gösterebileceği beklendi.

Tezin ilk kısmında, naylon3, 2-metil naylon3 ve 3-metil naylon3 uygun monomerlerin baz katalizli hidrojen transfer polimerizasyonu ile hazırlandı. Polimerlerin tüm karakterizasyonları FTIR, NMR (^1H -NMR and ^{13}C -NMR), DSC, TGA, elementel analiz, vizkozimetrik analiz, ve bazı uç grup analizleri ile yapıldı.

Radyasyon etkisi ile gerçekleşen değişiklikler FTIR, ^1H -NMR ve vizkozimetri ile takip edildi.

Tezin ikinci kısmında, Polimerler ^{137}Cs gama ışınlarıyla hem hava hem azot atmosferinde oda sıcaklığında ışınladı. Her iki ortamda ışınlanan polimerlerin ESR spektrumları, radyasyon etkisi ile oluşan radikalleri belirlemek için kaydedildi. Örneklerin ESR spektrumlarında zamanla meydana gelen değişimler radikallerin kararlılıkları ve sönüm davranışlarını belirlemek için incelendi. Polimerlerin deneysel ESR spektrumlarının simulasyonu teorik ESR spektrumunu ve bileşenlerini elde etmek için yapıldı. Her iki ortamda radikal konsantrasyonundaki değişim karşılaştırılarak radikallerin sönüm kinetiğine oksijenin etkisi incelendi. Nylon3 ve türevlerinde bulunan radikal türleri ve sönümleri ile ilgili en önemli bulgular şöyledir:

Nylon3 radyasyon bazlı iki tür birincil radikale sahiptir; Amit grubuna komşu karbon atomundan hidrojen uzaklaşmasıyla oluşan radikal (Radikal 1) ve karbonil grubuna komşu karbon atomundan hidrojen uzaklaşmasıyla oluşan radikal (Radikal 2). Radikal 1 zamanla, oksijen atomu üzerinde eşleşmemiş elektronu bulunan uzun ömürlü başka bir radikale (Radikal 3) dönüşmektedir. 2-metil nylon3 radyasyon etkisiyle karbonil grubuna komşu karbon atomundan hidrojen kopması ile oluşan tek tür birincil radikale (Radikal 2) sahiptir. Bu radikal zamanla disproporsinasyon tepkimesi ile ikincil radikale (Radikal 1) ve o

da oksijen atomu üzerinde çiftleşmemiş elektronu bulunan uzun ömürlü radikale (Radikal 3) dönüşmektedir.

3-metil naylon3 radyasyon etkisi ile oluşan iki tür radikale sahiptir; Amit grubuna komşu karbondan hidrojen uzaklaşması ile oluşan bir radikal (Radikal 1) ve amit grubuna komşu karbondan metil grubu uzaklaşması ile oluşan diğer birincil radikal.

Azot ortamında ışınlanan naylon3'ün radikallerinin bağıl bulunurlukları, azot ortamında ışınlamadan hemen sonra kaydedilen ESR spektrumlarının simülasyonu ile R1:%32, R2:%49 ve R3:%19 olarak bulunmuştur. Azot ortamında ışınlanan 2-metil naylon3'ün radikallerinin bağıl bulunurlukları, azot ortamında ışınlamadan hemen sonra kaydedilen ESR spektrumunun simülasyonu ile R1:%13, R2:%76 ve R3:%11 olarak bulunmuştur. Azot ortamında ışınlanan 3-metil naylon3'ün radikallerinin bağıl bulunurlukları, azot ortamında ışınlamadan hemen sonra kaydedilen ESR spektrumunun simülasyonu ile R1:%74.7 ve R2:%25.3 olarak bulunmuştur.

Naylon3 ve 3-metil naylon3 radikallerinin sönüm kinetiği çalışması açıkça gösterdi ki, radikaller birinci derece sönümü takip etmekte. Buna rağmen, 2-metil naylon3 ün radikallerinin sönüm davranışı açık bir reaksiyon derecesi vermedi.

Polimerlerin radikallerinin kimyasal verimlerinin řu řekilde sıralandıęı tesbit edildi: 2-metil naylon3>3-metil naylon3≈ naylon3

Anahtar Kelimeler: Naylon3, 2-metil naylon3, 3-metil naylon3, Hidrojen Transfer Polimerizasyonu, ESR Spektroskopisi, Radyoliz, ESR Spektrumlarının Simölasyonu, Sönüm Kinetięi.

To My Parents

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ABBREVIATIONS

N3	Nylon3
2mN3	2-methyl Nylon3
3mN3	3-methyl Nylon3
INT	Iodine Number Test
DP	Degree of Polymerization
DB	Double Bond
Hsc	Hyperfine Splitting Constant
ESR	Electron Spin Resonance
$\Delta H_{1/2}$	Line-Width
FTIR	Fourier Transform Infrared Spectroscopy
DSC	Differential Scanning Calorimetry
TGA	Thermogravimetric Analysis
NMR	Nuclear Magnetic Resonance
R1	Radical1
R2	Radical2
R3	Radical3
R4	Radical4

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1. INTRODUCTION

Polymeric materials are widely used in Radiation Technology as vital transformations occur when they are 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, crosslinking and degradation etc. Even, some polymers such as poly (ethylene) and poly (methyl methacrylate) are used in dosimetry systems 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 to develop more sensitive radiation dosimetry systems than conventional systems. Olsson et al [1] 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).

Nylon3, described also 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. The repeating units of poly (2-methyl- β -alanine) and poly (3-methyl- β -alanine) are also very similar to that of 2-methyl alanine that was reported as an excellent dosimetric material by Ollson et al [1]. In addition to nylon3, some of its derivatives mentioned above were synthesized and investigated within the scope of this study.

There are many studies on the radiation induced modification (especially grafting and crosslinking) of polyamides in particular nylon 6 and nylon 66 [Dole, 2]. 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 degree of grafting.

Characterization of radiation-induced active species (free radicals) is widely carried out by Electron Spin Resonance (ESR) Spectroscopy. The technique gives not only information about the type of the radicals but also their concentrations, interactions between themselves, and their decay behavior.

The aim of this study was to synthesize Nylon3 (N3), 2-methyl nylon3 (2mN3) and 3-methyl nylon3 (3mN3) due to similarity of their repeating units with

corresponding alanine and its derivatives and to fully characterize them. Furthermore polymers gamma irradiated in air and/or nitrogen were 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. Experimentally determined radical types were further compared with the simulated ones.

2. RADIATION CHEMISTRY OF POLYMERS

2.1. Some Important Concepts

2.1.1 Radiation Sources

Ionizing radiations are generated in nature by radioactive elements which spontaneously emit α - and β -particles and γ -rays. Manmade machines produce more powerful radiation sources, such as x-rays, accelerated electrons and heavy particle beams. Two types of natural radiation sources are widely applied:

- (i) γ -rays emitted by an artificial radioactive element: cobalt-60, and
- (ii) electron beams generated by accelerators operating in a range of energies: 0.3-10 MeV and up to 20 MeV [3]

These energies are not high enough to initiate nuclear reactions such as nuclear fusion and fission. Therefore, the irradiated materials have no radioactivity.

2.1.2. Radiation Dose Units

Radiation dose is the amount of radiation energy absorbed per unit mass of material. It is measured in joules per kg. The unit is the gray denoted as Gy:

$$1\text{Gy} = 1\text{J kg}^{-1}$$

The doses used in commercial applications range from 0.1 kGy to 100 kGy. Up to the 1980s the accepted unit was the *rad*:

$$1\text{ rad} = 100\text{ erg g}^{-1} = 1/100\text{ Gy}$$

The unit, found in the earlier literature, is rather small. In polymer processing, doses are generally expressed in terms of megarads:

$$1 \text{ Mrad} = 10 \text{ kGy}$$

2.1.3. Absorption of Radiation Energy

Gamma-rays generated by artificial cobalt-60 isotope have quantum energies of about 1.2 MeV. They transfer their energy to the molecules of the medium largely by Compton scattering, ejecting electrons of high velocity. The ejected electrons interact with the electrons of the irradiated material, leading to ionization and excitation. As the penetrating power of γ -rays is very high, they are used in radiation technology for crosslinking of thick materials. Sterilization of food and biomedical devices also involves γ -ray facilities. As the dose rates available are limited to ca. $1\text{--}10 \text{ kGy h}^{-1}$, irradiation by γ -rays generated by cobalt-60 requires fairly long exposure times [Chapiro, 3].

Accelerated electrons transfer their energy to irradiated material by electrostatic interaction with the electrons of the irradiated material, generating more electrons, which in turn produce more ionization and excitation. Electron beams (EB) are produced at very high dose rates with the powerful accelerators. Dose rates of $1\text{--}10 \text{ kGy s}^{-1}$ are widely used. As the penetrating power of electrons is small, electron beam radiation is applicable for the processing of thin materials such as polymer films, pipes, insulated wires, etc.

Since energy deposition only involves electrostatic interaction of fast moving electrons with the electrons of the medium, it does not depend on the chemical structure of the irradiated material. This means that all molecules absorb radiation energy, and suffer damages from ionizing radiation. The feature of ionizing radiation contrasts with the behavior of ultraviolet and visible light which only transfer their energy to substances containing specific functional groups.

2.1.4. Radiation-Chemical Yields (G-Yields)

The yields of radiation induced processes are expressed in terms of the number of molecular events arising per 100 eV absorbed in the medium. They are referred to as “*G-values or G-yields.*” In polymers, $G(H_2)$ is the number of hydrogen molecules evolved per 100 eV, $G(S)$ is the number of chain-scissions generated per 100 eV, $G(X)$ is the number of crosslinks generated per 100 eV, etc.

2.2. Basic Radiation Induced Processes

2.2.1. Ionization–Excitation

Irradiated materials are electrically charged due to abstraction of electrons from the molecules of irradiated material. As the polymeric materials are generally organic based, binding energies of electrons are ca. 10-15 eV. Ionizing radiation has much more energy than binding energies of electrons in polymeric materials. That is why ionization is inevitable when a polymeric material is subjected to ionizing radiation. The energy required for the formation of one ion

pair in gases is 25–35 eV. It means that only a fraction of the deposited energy is used in ionization, the remainder causes electronic excitation. Since the energy levels reached with ionizing radiation are too high, the excited molecules break down, generating free radicals. When solid polymers are irradiated, ions and free radicals may remain trapped for a long time.



AB denotes a macromolecule, AB^+ a macromolecular ion, e^- an electron, AB^* excited macromolecule, A^* and B^* are free radicals. The ions and free radicals are responsible for the changes observed in macromolecules subjected to ionizing radiations. Most of changes occurring in polymeric materials are explained by free radical reactions.

2.2.2. Charge Recombination

The electrons abstracted from the irradiated molecules are subjected to the strong electric field of positive charges formed through ionization. Therefore, charge recombination is highly probable, either during irradiation or after the end of irradiation. 10–15 eV energy is recovered for each charge recombination and the energy causes the molecule to be an excited molecule. As mentioned above, the excited molecules break down to form pairs of free radicals. Charge recombination event may be outlined by the reaction.



2.3. Radiation Effects on Polymers

2.3.1. Trapped Species

Polymers in solid state have entangled macromolecules interacting with their neighbors. Physical state of a polymer defines flexibility of the polymer chains (polymer segments).

In vitreous state, all macromolecules are almost frozen and segmental motion is highly restricted. The same is valid for macromolecules in crystalline regions. In viscoelastic state, macromolecules vibrate freely and can also migrate. Therefore, ions and free radicals formed in irradiated polymers only disappear if mutual interaction occurs either between the free radicals or ions with an electron. Otherwise, they will remain trapped if their mobility is hindered.

The low mobility of trapped ions is responsible for radiation induced conductivity, which may be detected if the irradiated sample is placed in an electric field. After irradiation, the conductivity does not decrease immediately. Instead, it decreases exponentially with time. Trapped ion recombination is also responsible for the thermoluminescence observed in irradiated polymers. Trapped radicals induce post irradiation damage, such as oxidative degradation, by reaction with oxygen (air).

The slow decay of trapped positive charges and trapped radicals is due to recombination with mobile electrons or mobile radicals. This effect causes an

additional radiation induced process to take place. Such after-effects are widely observed in vitreous or partially crystalline polymers, during storage at room temperature after irradiation. They may be avoided by a post-irradiation heat treatment which liberates the trapped species.

2.3.2. Influence of Oxygen

The oxygen molecule, a biradical, contains two unpaired electrons which readily react with a free radical, $R^{\bullet}$, resulting in the formation of a peroxy-radical $RO_2^{\bullet}$.



Such peroxy-radicals are very reactive and abstract hydrogen atoms, $H^{\bullet}$, from neighboring RH molecules:



A new radical, $R^{\bullet}$, is generated in this process which starts new chain reactions which are responsible for oxidation of polymeric material. RO_2H is unstable hydro peroxide which slowly breaks down at room temperature, producing more radicals and more oxidative damage.

2.3.3. Gas Evolution

Gases are generated in all irradiated polymers. Hydrogen is the major product in the radiation induced gases evolved. Its formation results from a two-step process. At first a carbon–hydrogen bond is broken by radiation:



Here RH is a hydrogen-containing polymer, R^{*} a polymeric radical and H^{*} a hydrogen atom. This step is followed by hydrogen atom abstraction:



For example, the radiation chemical yield of hydrogen evolution is G(H₂) = 4.1 for polyethylene [3].

Short side-branches are selectively ruptured under irradiation. For example, methane is a major product in the radiolysis of polypropylene and polyisobutylene. Carbon monoxide and carbon dioxide arise among the gases evolved from polymers containing carbonyl and carboxyl groups such as polyacrylates and polymethacrylates, respectively. Halogenated polymers generate acidic gases; HCl from poly(vinyl chloride) and HF from fluorinated polymers.

2.3.4. Crosslinking versus Main-chain Scission

Crosslinking is a reaction by which two polymeric radicals R^{*} combine to form an intermolecular chemical bond or shortly called crosslink.



Crosslinking occurs in solid polymers with high yields. This shows that the mobility of radical sites is high in the solid medium, presumably by transfer of hydrogen atoms from one site to another ("*hydrogen hopping*"). As considered the reactions (6), (7) and (8), it is obvious that the formation of one crosslink provides the evolution of one hydrogen molecule. The yield of crosslinking is

enhanced in the presence of polyunsaturated compounds, such as polyfunctional vinyl monomers. Main-chain scission involves the break of a chemical bond in the main polymeric chain. In linear polymers, the resulting two polymeric radicals are trapped in a close vicinity and readily recombine, restoring the original structure. However, if the polymer contains side branches (methyl groups) in its monomeric unit, particularly if two branches are attached to the same carbon atom (tetra substituted carbon), the two polymeric radicals interact with by transfer of a hydrogen atom and formation of a double bond (called as disproportionation). The scission then becomes permanent.

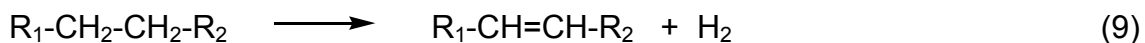
Different polymers have different responses to ionizing radiation. A parameter called “G value” is usually used to quantify the chemical yield resulting from the radiation. Materials with $G(S)/G(X)$ ratios smaller than 4.00 are favored for crosslinking. Materials with $G(S)/G(X)$ ratios greater than 4.00 tend to undergo degradation more [Sen, 4]. Materials whose $G(X)$ and $G(S)$ values are both low are more resistant towards ionizing radiation. The different responses to ionizing radiation for different polymers are essentially related to the chemical structures of the polymers. For example, polymers with more hydrogen atoms on the side (e.g., polyethylene) tend to crosslinking with radiation. Polymers with a methyl group (e.g., polypropylene) or di-substitutions (e.g., polymethacrylate) would more likely undergo degradation with radiation. Aromatic polymers with benzene rings either in the main chain or on the side (e.g., polystyrene and polycarbonate) are usually radiation resistant.

Crosslinking and chain-scission are two competing processes that always co-exist under radiation. The overall effect depends on which of the two is predominant at a certain time. It should also be kept in mind that for a given polymer $G(X)$ and $G(S)$ both change with radiation conditions such as the absorbed dose, the temperature and irradiation medium, etc. Both $G(X)$ and $G(S)$ would increase with the increase of the dose. However, $G(S)$ for a polymer generally increases more than $G(X)$ does with increasing dose. Therefore, when $G(X)$ of a polymer is much greater than $G(S)$, its molecular weight would continuously increase due to continuous crosslinking. When $G(X)$ is greater, but not much greater than $G(S)$, $G(S)$ will eventually catch up with $G(X)$, and the MW will show a turning point, with the overall reaction changing from crosslinking to degradation. For some polymers, elevated temperature may increase the mobility of the polymer chains and make it more favorable to crosslinking. As mentioned above, oxygen in the air usually assists the degradation more through a peroxide radical mechanism, so an oxygen-free atmosphere would usually be more favorable for crosslinking.

2.3.5. Unsaturation

As mentioned above, double bonds are formed in the interaction of branched free radicals. Moreover, if one compares the radiation chemical yields in polyethylene for hydrogen evolution, $G(H_2)=4$ and for crosslinking, $G(X)=2$, it appears that crosslinking only accounts for one-half of the hydrogen produced. Additional hydrogen is generated in the formation of intra-chain double bonds.

This may be summarized in reaction (9):



Double bonds arise with much higher yields in chlorinated polymers, such as PVC, where HCl is evolved. In polymers which initially contain double bonds, such as natural rubber or polybutadiene, a decrease in unsaturation is observed under irradiation. This is due to the reaction of free radicals with the double bonds, which enhances the yield of crosslinking.

2.4. Radiation Processing of Polyamides

Polyamides are used extensively as high performance plastic materials because of their unique combination of superior mechanical, electrical, chemical and thermal properties. Polyamides play an important role in textile, electrical as well as in electronic industries.

There are many studies [5-11] on radiation processing and radiolysis of polyamides in the literature. Polyamide radiolysis has been studied by a number of researchers since Charlesby [5] who first reported crosslinking of nylon 66. Deeley et al. [6], from a study of irradiated nylon 66 concluded that the degree of crosslinking is not proportional with radiation dose, suggesting main-chain scission also plays an important role in the reaction. Majury and Pinner [7] investigated the irradiation of polycaprolactam with both gamma rays and 2MeV electrons. Lyons and Glover [8] studied the dependence of radiation crosslinking and chain-scission on the molecular structure of the repeat unit in

certain polyamides. Also the radiation effects on nylon1010 have been investigated [Li and Zhang 9, 10].

A major activity associated with irradiation of polyamides has been in the area of grafting. A large variety of materials [Dole, 2] (CCl_4 , hexamethylenediamine, maleic acid, acrylamide, methacrylamide, acrylic acid, and itaconic acid etc.) were grafted to nylon6 and nylon66 to improve properties like moisture absorption, flame retardancy, crease resistance etc. Irradiation of polyamides results in the creation of grafting centers, peroxides or free radicals, depending on the conditions of irradiation. The grafting can occur throughout the bulk material or in superficial layers of a desirable thickness. The influence of experimental conditions upon the properties of the resulting modified materials present a particular focus of interest.

3. PRINCIPLES OF ELECTRON SPIN RESONANCE (ESR) SPECTROSCOPY

3.1. Introduction

Electron Spin Resonance (ESR), sometimes called Electron Paramagnetic Resonance (EPR), spectroscopy studies molecules and ions containing unpaired electrons. The technique detects paramagnetic substances by their resonant absorption of microwave radiation in an external magnetic field. It has found applications in a wide range of different fields spanning from chemistry and biology to medicine. ESR studies provide structural or environmental information, electron distribution, and geometry of paramagnetic molecules.

In ESR spectrometer, the sample material is immersed in a strong static magnetic field and exposed to an orthogonal low-amplitude high-frequency field. ESR spectrometer usually requires microwave-frequency radiation (~9.5 GHz). Energy is absorbed by the sample when the frequency of the radiation is appropriate to the energy difference between two states of the electrons in the sample, but only if the transition is suitable by the selection rules.

3.2. Electron Spin in External Magnetic Field

The electrons in atoms and molecules usually exist as pairs. When one of them has a spin magnetic quantum number,

$$m_s = -1/2$$

the spin magnetic quantum number of other electron must be, $m_s = +1/2$.

While the paired electrons do not give an ESR signal, an unpaired electron gives an ESR signal. An electron is characterized by its mass, charge, intrinsic angular momentum, and its magnetic moment.

Mass of electron, $m = 9.109558 \times 10^{-31} \text{ kg}$.

Charge of electron, $e = 1.602 \times 10^{-19} \text{ C}$.

Intrinsic angular momentum of electron (or spin vector), $\vec{S}$ is given as

$$|\vec{S}| = \hbar \sqrt{s(s+1)} = \hbar \sqrt{3}/2$$

where s is spin angular momentum quantum number and equal to $1/2$.

Projection of the spin angular moment vector on the z axis is denoted as S_z and given by

$$S_z = m_s \hbar$$

m_s is the magnetic spin quantum number. It has the values

$m_s = s, s-1, s-2, \dots, -s$, in this case; $m_s = \pm 1/2$. Hence,

$$S_z = \pm 1/2 \hbar$$

Magnetic moment vector of the unpaired electron is given by the equation

$$\vec{\mu}_{e,z} = -(g_e \beta_e / \hbar) \vec{S}_z \quad (3.1)$$

$$\mu_{e,z} = -(g_e \beta_e / \hbar) m_s \hbar$$

$$\mu_{e,z} = -g_e \beta_e m_s$$

$$\mu_{e,z} = -g_e \beta_e (\pm \frac{1}{2})$$

where g_e is the Lande g-factor (2.002319). β_e , Bohr magneton and equal to,

$$\beta_e = \frac{eh}{2mc} = 9.274096 \pm \times 10^{-24} \text{ J T}^{-1} \quad (3.2)$$

where c is the velocity of light in m s^{-1} .

The minus sign in Eq.3.1 shows that $\vec{\mu}_{e,z}$ is in opposite direction to the spin vector.

When an electron is in a magnetic field $\vec{H}$, its magnetic moment vector, $\vec{\mu}_{e,z}$ has two possible orientations as shown in Figure 3.1. They correspond to parallel and antiparallel orientations of spin vector ($\vec{S}$) to the applied magnetic field $\vec{H}$. The angle (Θ) between the magnetic moment vector (μ_e) of an electron and the direction of the magnetic field (H) can only have two possible values: $35^\circ 15'$ and $144^\circ 45'$. The orientation in which the magnetic moment is antiparallel to the field has the orientation of maximum energy.

Energy of an electron in the external magnetic field $\vec{H}$ is given by the equation:

$$E = -\mu_e \cdot \vec{H} \quad (3.3)$$

where $\vec{H}$ is the external magnetic field in tesla (T).

Considering that $\mu_e = -g_e\beta_e m_s$, the energy of an electron in the external magnetic field is given as;

$$E = g_e\beta_e \vec{S}_z \cdot \mathbf{H} \quad (3.4)$$

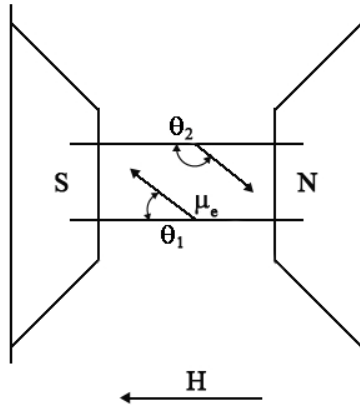


Fig.3.1. The two orientations of the electron magnetic moment (μ_e) in an external magnetic field ($\mathbf{H}$)

The spin quantum number (s) of one electron is $1/2$. Magnetic spin quantum number (m_s) in a magnetic field can have one of the two possible values $+1/2$ and $-1/2$. It means that the energy of an electron in an external magnetic field ($\mathbf{H}$) is either

$$E_1 = + \frac{1}{2} g_e\beta_e H \quad (3.5)$$

or

$$E_2 = - \frac{1}{2} g_e\beta_e H \quad (3.6)$$

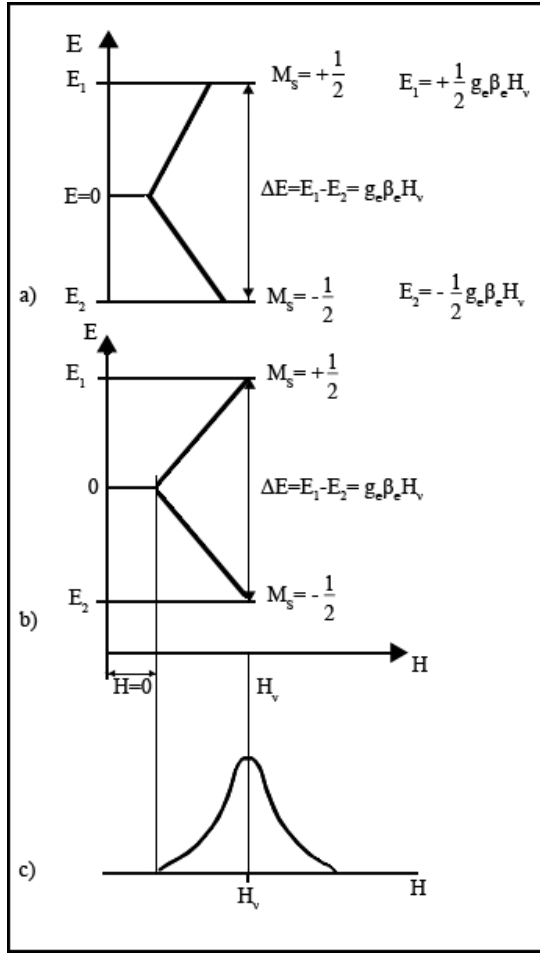


Fig.3.2. Energy levels diagrams showing Zeeman splitting for a free electron. **a.** In constant external field and variable frequency, **b.** In variable external magnetic field and constant frequency, H_v is the magnetic field at which the resonance conditions occur, **c.** Absorption line.

The difference between the two energy levels of the electron is given by:

$$\Delta E = E_1 - E_2 = g_e \beta_e H \quad (3.7)$$

The measurement of the energy difference is the basis of the EPR experiments. Application of an oscillating radio frequency field perpendicular to external magnetic field (H), whose quanta ($h\nu$) have an energy equal to $g_e \beta_e H$ (erg), induce transition between the two levels of the electron:

$$\Delta E = E_1 - E_2 = g_e \beta_e H = h\nu \quad (3.8)$$

ν is the frequency of the radiowaves (Hz). Microwaves have wavelengths from a millimeter to a meter. In conventional spectroscopy, frequency is varied or swept and the frequencies at which absorption occurs correspond to the energy differences of the states. In ESR spectrometers, external magnetic field is varied in a certain range. A commonly used X-band spectrometer operates at about 3 cm wavelength corresponding to a frequency of about 9500 MHz, which requires a magnetic field (H) about 340 mT. The shorter wavelength of the Q-band spectrometer have a frequency of about 35000 MHz, and the magnetic field (H) of 1250 mT. the Q-band spectrometer is commonly used for studies at very low temperatures.

Electromagnetic waves with the frequency (ν) has the amount of energy to provide transition between the two energy levels of the electrons (ΔE), which is called resonance or absorption.

$$\nu = \frac{g_e \beta_e H}{h} \quad (3.9)$$

3.3. Spin Relaxation

The ESR emission or absorption can only be detected if there is a population difference between the two energy levels. The transition between the two energy levels

$$E_1 (M_s = +1/2) \quad \text{and} \quad E_2 (M_s = -1/2)$$

can occur by either emission or absorption.

The microwaves of the oscillating magnetic field ($h\nu$) induce two types of transition:

- a) From the upper state (E_1) to the lower state (E_2) (emission)
- b) From the lower state (E_2) to the upper state (E_1) (absorption)

When the unpaired electron population is equally divided between the upper $N(E_1)$ population and the lower $N(E_2)$ population, the emission microwave quanta is higher than the absorption of these quanta, and no observable signal is obtained. When the population of the unpaired electrons is higher in the state (E_2) than in the state (E_1) a radio frequency absorption is observed. The ratio of the two populations in thermal equilibrium is given by the well-known Boltzmann equation:

$$\frac{N(E_2)}{N(E_1)} = e^{\frac{E_1 - E_2}{kT}} = e^{\frac{\Delta E}{kT}} = e^{\frac{g_e \beta_e H}{kT}} \quad (3.10)$$

where k is the Boltzmann constant $1.38065 \times 10^{-23} \text{ JK}^{-1}$.

The intensity of ESR signal recorded increases with increasing ratio $N(E_2)/N(E_1)$, because the absorption more and more predominates over the emission. The signal intensity is also increased when the signal is recorded at low temperatures.

The population difference, Δn is expressed by the equation:

$$\Delta n = \frac{N(E_1) - N(E_2)}{2kT} = \frac{Ng_e\beta_e H}{2kT} \quad (3.11)$$

where N is the total number of the unpaired electrons in both levels: $N = N(E_1) + N(E_2)$. The signal intensity is directly proportional to the quantity Δn , which varies inversely to the absolute temperature. For that reason the intensity of the absorption signal at liquid nitrogen temperature (77 K) is approximately four times higher than at room temperature (300 K).

The probability of the transition between the energy levels is proportional to the microwave energy density. With increasing incident microwave energy, the ESR signal intensity increases to a maximum. Further increase of power causes a decrease and broadening of the signal up to a moment when the signal completely disappears. This is called as saturation, where the population $N_1(E_1)$ is equal to $N_2(E_2)$. The return of the system to equilibrium is called relaxation.

3.4. The Shape of the ESR Resonance Lines

The magnetic interaction between the electron spins and the external magnetic field produces typical energy absorption spectra as shown in Figure 3.3a.

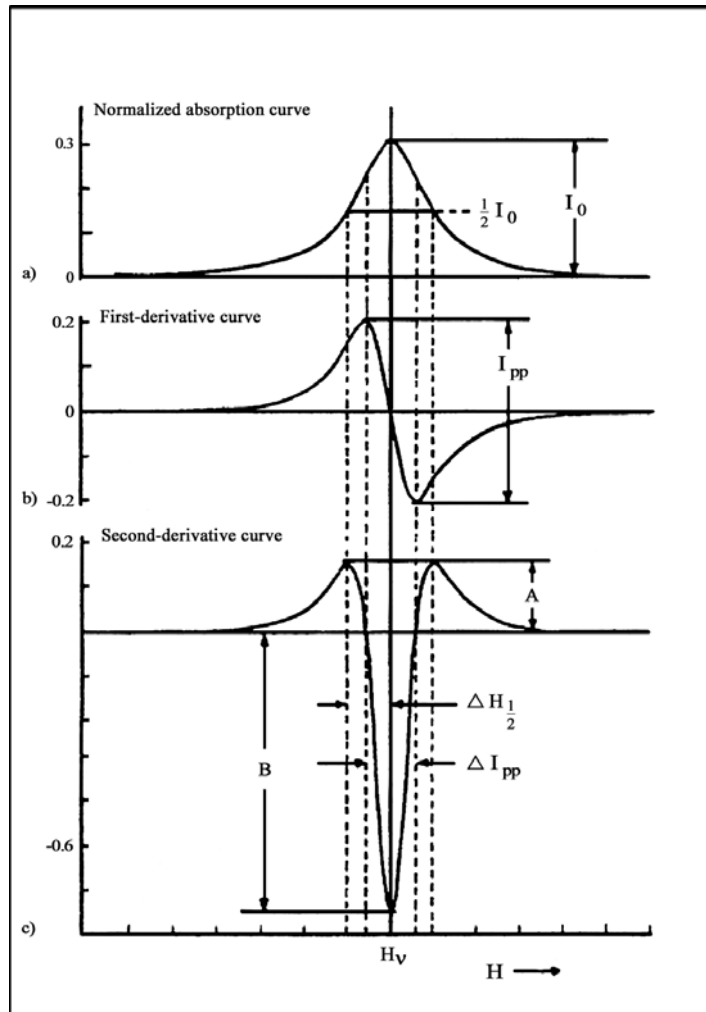


Fig.3.3. Lorentzian line shape: **a.** Absorption spectrum, **b.** First-derivative spectrum, **c.** Second-derivative spectrum

ESR spectrometers gives first derivative of the energy absorption curves as shown in Figure .3.3b.

The absorption curve is obtained by varying of the magnetic field and measuring the absorbed energy. It is often of considerable interest to obtain the second derivative of the energy absorption spectra as shown in Fig.3.3c. The

shape of the second derivative recordings is very sensitive to the nature of the absorption line.

3.5. Line Shape

There are two important types of ESR line shape: Lorentzian line shape and Gaussian line shape. The main difference between the two types of line shape is that the outer wings of the Lorentzian line are much longer and drop more slowly than those of the Gaussian as shown in Figure.3.4. and Figure.3.5. Properties of Lorentzian and Gaussian lines are given in Table.3.1.

In several cases the shape of an absorption line is a mixture of two types. The mathematical description of the exact shape of an absorption line is very complicated. There are two simple methods to identify the Lorentzian and Gaussian lines; ratio of slopes of the derivative curves as given in Figure. 3.4. and normalization plot as shown in Figure 3.5

Table.3.1. Properties of Lorentzian and Gaussian lines [12]

	Lorentzian Shape	Gaussian Shape
Peak-to-peak width	$H_{pp} = \frac{2}{\sqrt{3}} \Delta H_{1/2}$	$H_{pp} = \left(\frac{2}{\ln 2} \right)^{\frac{1}{2}} \Delta H_{1/2}$
Peak amplitude	$I_0 = \frac{1}{\pi \Delta H_{1/2}}$	$I_0 = \left(\frac{\ln 2}{\pi} \right)^{1/2} \frac{1}{\Delta H_{1/2}}$
Equation for absorption line	$I = I_0 \frac{(\Delta H_{1/2})^2}{(\Delta H_{1/2})^2 + (H - H_r)^2}$	$I = I_0 \exp \left[\frac{(-\ln 2)(H - H_r)^2}{(\Delta H_{1/2})^2} \right]$
Peak-to-peak amplitude	$I_{pp} = \frac{3\sqrt{3}}{4\pi (\Delta H_{1/2})^2}$	$I_{pp} = \left(\frac{2}{\ln 2} \right)^{1/2} \Delta H_{1/2}$
Equation for first derivative absorption line	$I' = -I_0 \frac{2(\Delta H_{1/2})^2 (H - H_r)}{[(\Delta H_{1/2})^2 + (H - H_r)^2]^2}$	$I' = -I_0 \frac{2(\ln 2)(H - H_r)}{(\Delta H_{1/2})^2} \exp \left[\frac{(-\ln 2)(H - H_r)^2}{(\Delta H_{1/2})^2} \right]$
Peak amplitude of positive lobe	$A = I_0 \left(\frac{1}{2(\Delta H_{1/2})^2} \right)$	$A = I_0 \left(\frac{4e^{-3/2} \ln 2}{(\Delta H_{1/2})^2} \right)$
Peak amplitude of negative lobe	$A = -I_0 \left(\frac{2}{(\Delta H_{1/2})^2} \right)$	$A = -I_0 \left(\frac{2 \ln 2}{(\Delta H_{1/2})^2} \right)$

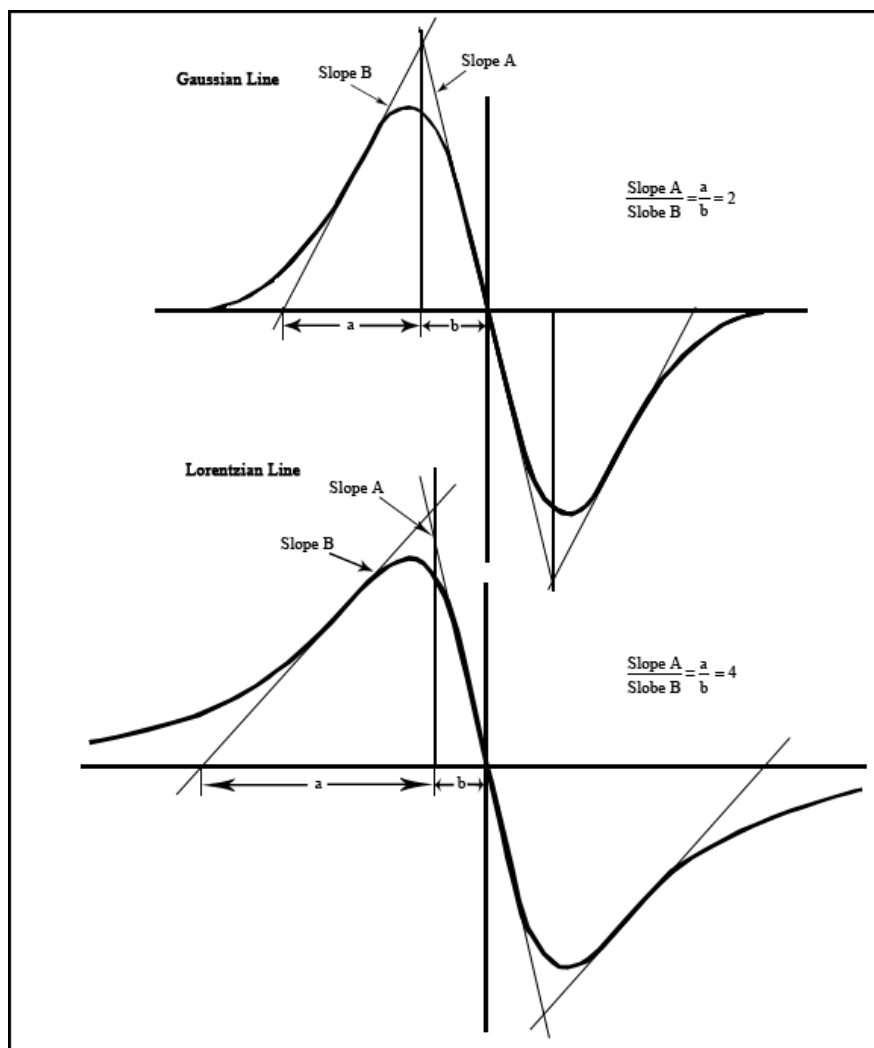


Fig.3.4. The slope ratio method

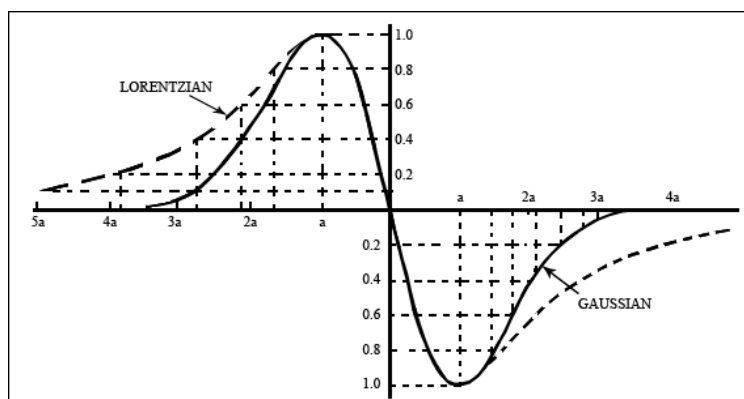


Fig.3.5. Normalization technique

3.6. Line Width

ESR lines measured under specified conditions have a finite “width”. There are two usual ways of expressing line width:

- a. “the half width at half-height ($\Delta H_{1/2}$) of the absorption line as shown in Figure.3.3. and Table 3.1).
- b. ”peak-to-peak width” (ΔH_{pp}) is the full width between the extremes of the first derivative curve as shown in Figure.3.3 and Table 3.1.

The width is influenced not only by interaction between the electron spin and the external magnetic field applied, but also by interaction of the electron spin with the environment inside the sample. This fact allows to obtain information about the spin environment from the line width. Typical environment effects are, for example, electron spin exchange between molecules and crystal lattice vibration.

When sufficient amount of microwave power is added to the sample the lifetime of the spin state decreases and a broadening of the absorption line shown in Fig.3.6 is produced. This process is known as saturation broadening. In the recording of a spectrum a wide line is much more difficult to detect than a narrow line of the same intensity.

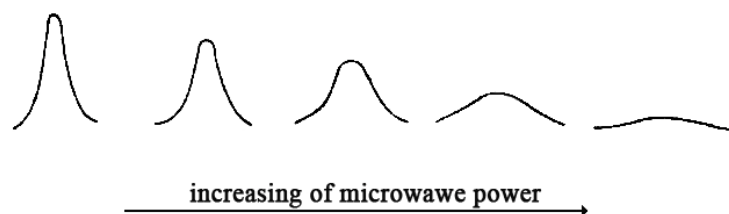


Fig.3.6. The saturation and power broadening of a homogeneous line

The width of the lines is dependent on the symmetry of the radicals examined. The reduction in the symmetry of the radicals leads to weakening of the spin-orbital coupling and to an increase in the spin-lattice relaxation time and consequently to narrowing of the lines.

3.7. Intensity

The intensity (I) of the absorption line as a function of the outer magnetic field (H) for Lorentzian and Gaussian line shape is given by the equations:

$$I = \frac{I_0}{T_2^2(H - H_r)^2 + 1} \quad \text{Lorentzian shape} \quad (3.12)$$

$$I = I_0 e^{-b(H-H_r)^2 T_2^2} \quad \text{Gaussian shape} \quad (3.13)$$

where I_0 is the intensity of the absorption line at its center, H_r is the field of the resonance at the line center, T_2 is the spin-spin relaxation time, b is a constant.

The double integration of the ESR signal represents the total energy absorbed by the sample at resonance conditions. This quantity is expressed by the total

area under the resonance curve and it can be used for the determination of the concentration of free radicals in the sample as the number of unpaired spins per a certain mass or per a certain volume.

3.8. g-value

Various ESR spectrometers use different frequencies, and various types of samples require different frequencies for the experiment. For that reason the position of ESR lines can not be indicated by the frequencies. The line positions are instead denoted in terms of “g-value”, which is expressed as a function of microwave frequency (ν) and external magnetic field (H_ν) at resonance.

$$g_e = \frac{h\nu}{\beta_e H_\nu} \quad (3.14)$$

If numerical values of the constants ($h: 6.626196 \times 10^{-34}$ J s, $\beta_e: 9.274096 \times 10^{-24}$ J T⁻¹ in Eq.(3.14) placed on the equation, the equation may be simplified as

$$g_e = 0.0714484 \frac{\nu}{H_\nu}$$

The value of g_e can then be calculated using frequency, ν (in GHz) and resonance magnetic field, H_ν (in tesla).

As mentioned before the g_e value of a free electron is 2.002322, whereas the g -values for free radicals in atoms, molecules and crystals depend on their structure.

The application of double cavity in the ESR apparatus simplifies the measurement of g -values. Standard compounds with precisely known g -values are used as reference. These standard compounds are inserted into the double cavity and their spectra are recorded by a dual-channel recorder. The separation of the centers of the two spectra represents the magnetic field difference at the two positions of the sample. One of the standard samples is replaced by a sample to be examined, and the field difference (ΔH) (corrected for the standard sample field difference) between the centers of the ESR spectra is measured. The g -value of the unknown sample (g_u) can be calculated from the equation:

$$g_u = g_s - \frac{\Delta H}{H} g_s = g_s \left(1 - \frac{\Delta H}{H} \right) \quad (3.15)$$

where g_s is the g -value of the known standard sample and H is the external magnetic field.

For free radicals in solution the g -value is shifted and measured as an average value. The deviation of the g -value of an organic radical from that of a free electron gives significant information. The g -value depends on the type of free

radical. e.g. the g-value for a peroxy radical RO_2^* is higher than that for an alkyl radical R^* (Ranby and Rabek, 12).

3.9. Interaction between the Electron and the Nuclear Spins

Magnetic moment of an electron can be represented as a classical bar magnet. A bar magnet will align itself to the external magnetic field (Zeeman interaction). The energy of a bar magnet can be influenced by interaction with a neighboring bar magnet (nuclear spin). In this latter case, the magnitude of the interaction depends on the distance of separation and the relative alignment of the two magnets. The magnetic interaction between the electron and the nuclear spins in the same molecule gives an ESR spectrum with a number of lines instead of one singlet line. This type of interaction is called “hyperfine coupling or nuclear hyperfine interaction” and produces ESR spectra with “hyperfine splitting”.

By analyzing the number of lines, their separation and their relative intensities it is usually possible to determine the type and the number of nuclear spins which interact with the electron, i.e., the structure of the free radical. The line separation depends on the interaction between the electron spin and each nuclear spin, and on the magnetic moments of the involved nuclei. From the number of resonance lines in ESR spectrum and their relative intensities, it is possible to identify the number of equivalent nuclei in the molecule and to determine the structure.

“spin angular momentum vector of a nucleus” (I) and its magnetic moment vector (μ_N) is given by the equation:

$$\mu_N = \frac{g_N \beta_N I}{\hbar} \quad (3.16)$$

where g_N is “the nuclear g-factor” which is characteristic for each type of nucleus, the g_N for proton is $g_N = 5.585564$ and β_N is “the nuclear magneton” and given by equation:

$$\beta_N = \frac{e\hbar}{2m_p c} = 5.050951 \times 10^{-27} \text{ JT}^{-1} \quad (3.17)$$

where m_p is the mass of proton, 1.672614×10^{-27} kg and c is the velocity of light, $2.997925 \times 10^8 \text{ m s}^{-1}$.

The spin angular momentum (I) in the external magnetic field have the restricted orientations: $I, I-1, I-2, \dots, -I$.

In this way, the nuclei have a limited number of spin quantum numbers $M_I = 2I + 1$, i.e. they split magnetic level of an electron into $2I + 1$ sublevels.

Magnetic moment of the electron (μ_e) is about thousand times larger than the magnetic moment of the nuclei (μ_N). The applied external magnetic field (H) is normally many times larger than the local magnetic field, at the electron cite produced by the nuclei. In a strong external field, the magnetic interaction is influenced by the interaction between the electron and the nucleus, so called

“contact interaction”. This interaction is determined by the “isotropic hyperfine coupling constant” (A) (measured in Hertz)

3.9.1. Hyperfine structure spectrum due to a single proton

In an external magnetic field, the magnetic moment of a proton has two possible orientations $\pm 1/2$, which affect the magnetic energy levels of an electron (E_1 and E_2) and split each of them into two sublevels (E_I , E_{II} , E_{III} and E_{IV}). This process is called “*Zeeman hyperfine splitting*” for proton as shown in Figure.3.7a and 3.7b.

First-order splitting of the lines occurs when the hyperfine coupling constant energy (hA) is very much smaller than the electron energy ($g_e\beta_e H$). The transition between four sublevels gives the “*hyperfine spectrum*”, but there are certain selection rules which determine the possible transitions between various levels. The allowed transitions (as shown in Fig3.7.a) are

1. Between energetic levels E_I and E_{IV} and levels E_{II} and E_{III} , because they require the absorption or emission of energy and change in angular momentum by the electron only.
2. Between energetic levels E_I and E_{II} and levels E_{III} and E_{IV} , because they require the absorption or emission of energy and change in angular momentum by the nucleus only.

Transition between energetic levels E_I and E_{III} and levels E_{II} and E_{IV} are not allowed because they require a simultaneous absorption or emission of energy by both the electron and the nucleus. As a conclusion, the selection rules give the allowed transitions for $\Delta M_s = \pm 1$ and $\Delta M_I = 0$, the forbidden transitions for $\Delta M_s = \pm 1$ and $\Delta M_I = \pm 1$

At a constant external magnetic field, the transition from level E_{IV} to level E_I occurs at a higher frequency than the transition from level E_{III} to level E_{II} . The difference between the two frequencies is called "*the hyperfine frequency*" ($\Delta\nu$) and is equal to A .

At a constant frequency (shown in Fig.3.7b), the transition level E_I to E_{IV} occurs at a lower magnetic field than the transition from level E_{II} to E_{III} .

In the commercial spectrometers, the microwave frequency is maintained constant but the magnetic field is varied. In this case the energy ($\Delta E = h\nu$) of the transition between energy levels $E_I - E_{IV}$ and $E_{II} - E_{III}$ must be equal:

$$h\nu_{I-IV} = h\nu_{II-III} = h\nu \quad (3.18)$$

In a constant magnetic field the transition in energy differs by the isotropic hyperfine coupling constant (A):

$$g\beta H_{I-IV} - hA/2 = g\beta H_{II-III} + hA/2 \quad (3.19)$$

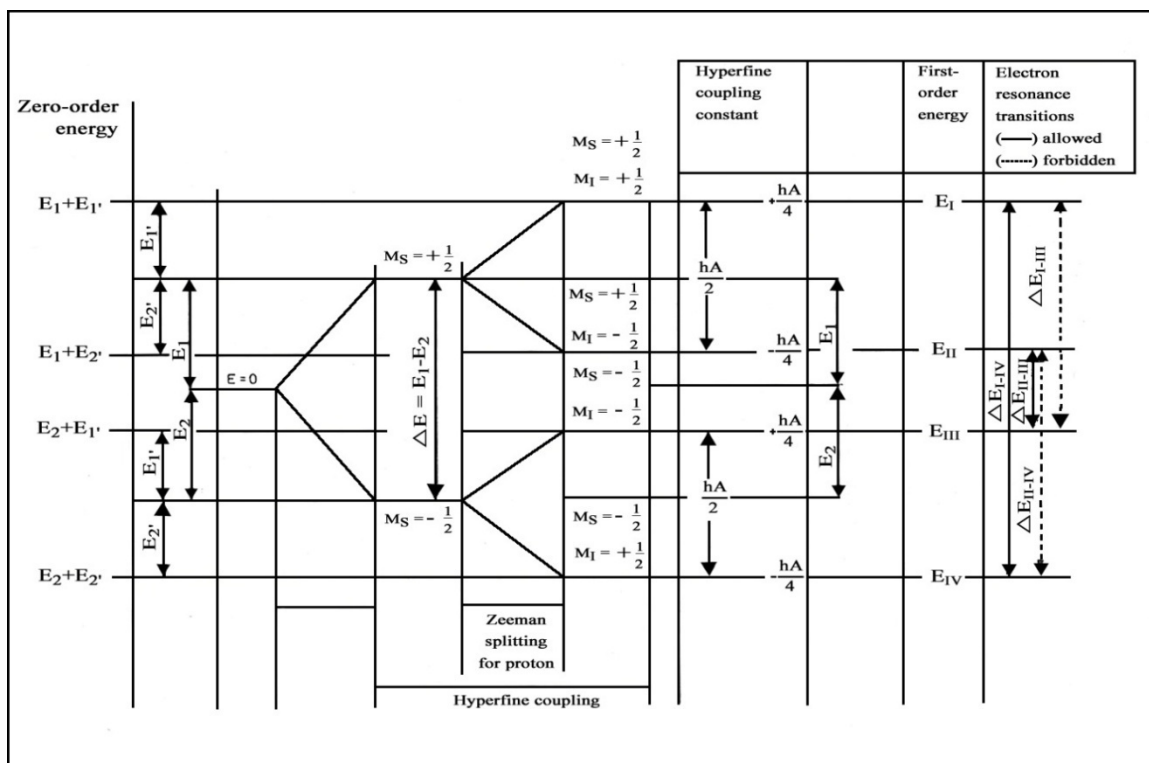


Fig.3.7a. Energy levels of the proton in a constant magnetic field and variable frequency

Electron Zeeman splitting energy

Zero-order energy

$$E_{1'} = +1/2 g_e \beta_e H$$

$$E_1 + E_{1'} = +1/2 g_e \beta_e H + 1/2 g_N \beta_N H$$

$$E_{2'} = -1/2 g_e \beta_e H$$

$$E_1 + E_{2'} = +1/2 g_e \beta_e H - 1/2 g_N \beta_N H$$

Nucleus Zeeman splitting energy

$$E_{1'} = +1/2 g_N \beta_N H$$

$$E_2 + E_{1'} = -1/2 g_e \beta_e H + 1/2 g_N \beta_N H$$

$$E_{2'} = -1/2 g_N \beta_N H$$

$$E_2 + E_{2'} = -1/2 g_e \beta_e H - 1/2 g_N \beta_N H$$

First-order energy (which consider contact interaction between the electron and the nucleus, which is determined by hyperfine coupling constant):

$$E_I = E_1 + hA/4$$

$$E_{II} = E_1 - \hbar A/4$$

The energies for the allowed transition are:

$$E_{III} = E_2 + \hbar A/4$$

$$\Delta E_{I-IV} = E_I - E_{IV} = g_e \beta_e H + \hbar A/2$$

$$E_{IV} = E_2 - \hbar A/4$$

$$\Delta E_{II-III} = E_{II} - E_{III} = g_e \beta_e H - \hbar A/2$$

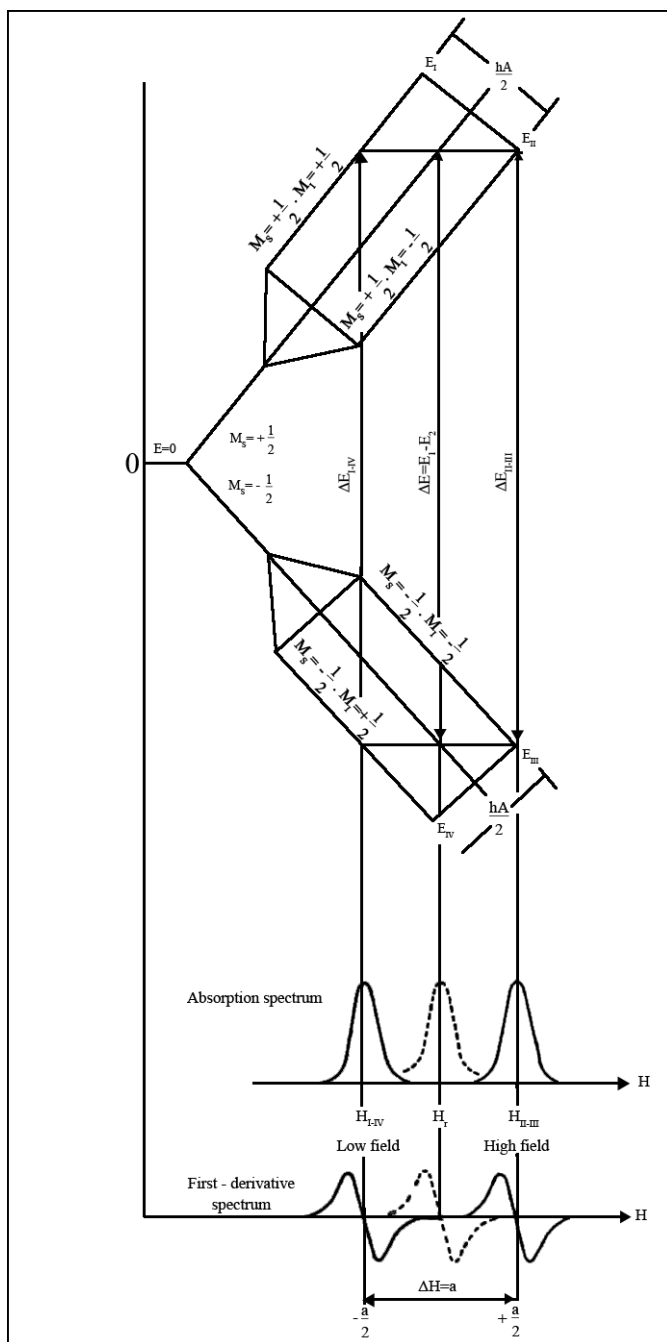


Fig.3.7b. Energy levels of the proton in variable external magnetic field and constant frequency.

Electron spin resonance transitions will occur at the resonant field:

$$H_{I-IV} = \frac{h \nu}{g_e \beta_e} - \frac{a}{2} \quad (3.20)$$

$$H_{II-III} = \frac{h \nu}{g_e \beta_e} + \frac{a}{2} \quad (3.21)$$

Where a is the hyperfine splitting constant (T)

$$H_{I-IV} - H_{II-III} = \frac{hA}{g\beta} \quad (3.22)$$

$$\Delta H = \frac{hA}{g\beta} = a \quad (3.23)$$

The value $\Delta H=a$ is called “hyperfine splitting constant” and expresses in tesla (T) the separation between the two hyperfine lines of the spectrum as shown in Figure. 3.7b.

In the case when there is no nuclear interaction ($A=0$) (mentioned above), the transition for the electron ($s=1/2$) occurs at one resonance field (H_v) as shown in Figure. 3.2.

$$H_v = \frac{h \nu_0}{g_e \beta_e} \quad (3.24)$$

When the magnetic moment of an unpaired electron ($s=1/2$) is affected by the magnetic field of a nucleus with $I = \frac{1}{2}$ (the proton), the transition occurs at two resonance fields as shown in Fig.3.7b.

$$\text{For } M_I = +1/2, H_{I-IV} = \frac{h\nu_0}{g_e\beta_e} - \frac{a}{2} \quad (3.25)$$

$$\text{For } M_I = -1/2, H_{II-III} = \frac{h\nu_0}{g_e\beta_e} + \frac{a}{2} \quad (3.26)$$

For the system with $s=1/2$ and $I=1$ (the deuterium), the transition occurs at three resonance fields showed by the dashed lines in Fig.3.7b.

$$\text{For } M_I = +1, H_{I-VI} = \frac{h\nu}{g_e\beta_e} - a \quad (3.27)$$

$$\text{For } M_I = 0, H_{II-V} = \frac{h\nu}{g_e\beta_e} \quad (3.28)$$

$$\text{For } M_I = -1, H_{III-IV} = \frac{h\nu}{g_e\beta_e} + a \quad (3.29)$$

In general, for a system where a single nucleus interacts with one unpaired electron, $2I + 1$ lines of equal intensity are obtained. They are separated by the constant hyperfine splitting (a). Using the hyperfine splitting constant (a), we can express the hyperfine coupling frequency ($\Delta\nu$) as:

$$\Delta\nu = \frac{g_e\beta_e a}{h} \quad (3.30)$$

For $g=2$

$$\Delta\nu = 2.8 a \text{ (Hz)}$$

The interaction of the unpaired electron with n equivalent protons results in ($n + 1$) lines whose relative intensities are proportional to the coefficients of the binominal expansion of $(1+x)^n$ as shown in Figure.3.8.

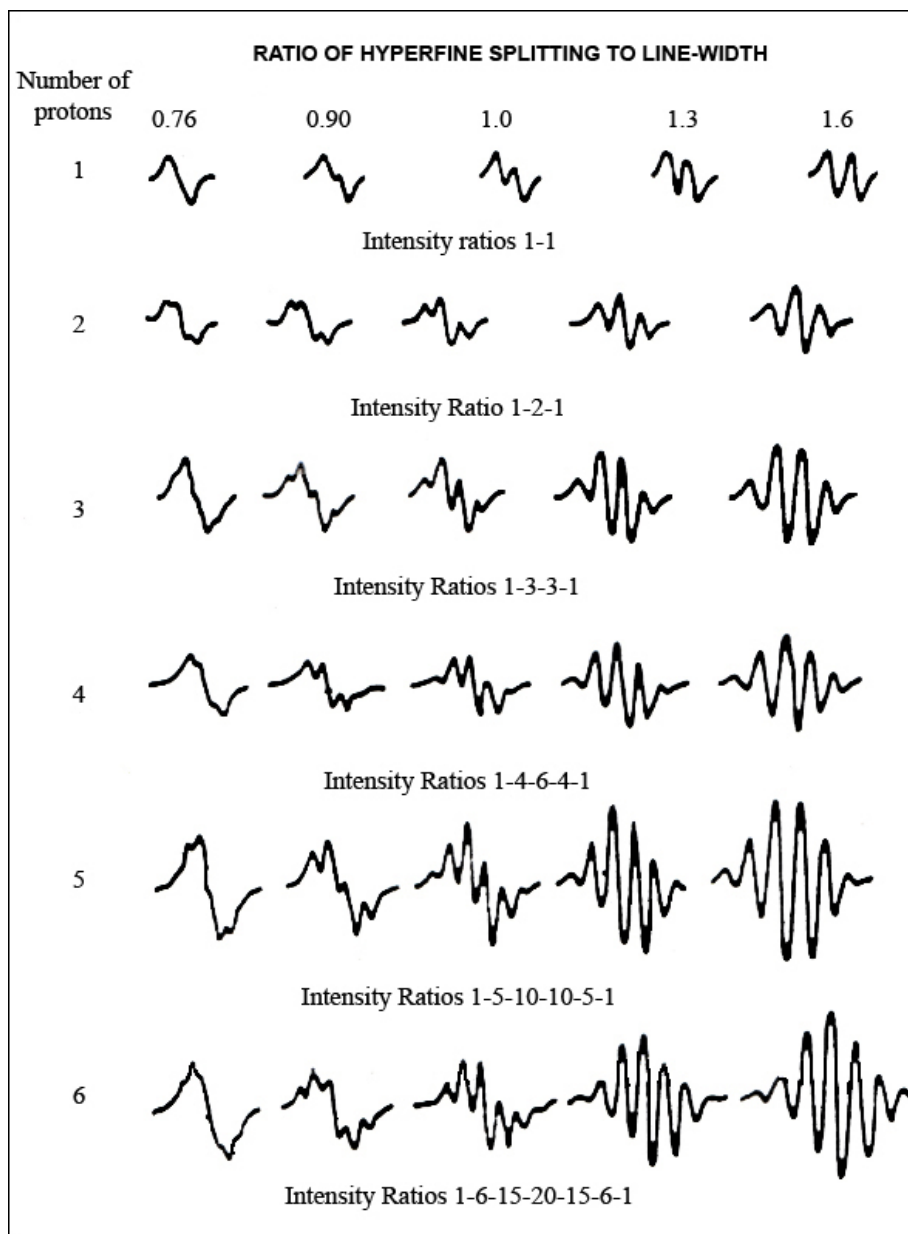


Fig.3.9. Theoretical hyperfine structure curves for a Gaussian derivative curves [Ranby and Rabek, 12]

3.10. Simulation of ESR Spectra

Computer simulation studies on experimental ESR spectra are common today to have information about ESR line parameters of a single or superimposed ESR lines. The accuracy of such determinations is considerably improved by optimizing these parameters by means of automated simulation programs resorting to the nonlinear least squares fit of experimental spectra. The principles of the simplex method of Nelder and Mead [13] and of the method of Levenberg-Marquardt [14, 15], are generally used for that purpose.

Some computer simulation softwares such as Winsim, Simfonia, Winepr, Origin etc. are widely used to fit experimental spectra to theoretically calculated ones. The softwares run by changing simultaneously ESR line parameters like hyperfine splitting constants, line-widths, g-values, peak intensities, and shape of lines (Gaussian and Lorentzian) to find out the best combination of them fitting to the experimental ESR spectrum.

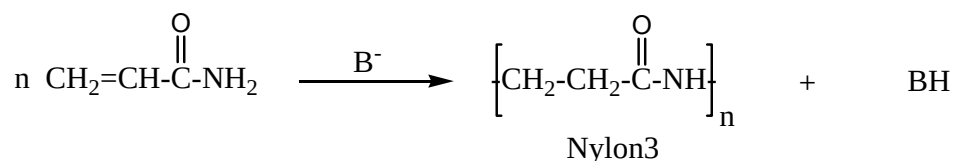
4. EXPERIMENTAL PART

4.1. Synthesis of Polymers

Materials: Acrylamide (Sigma, 99%), methacrylamide (Fluka $\geq 98\%$), crotonyl chloride (Fluka $\geq 90\%$), potassium chloride (Carlo Erba 99%) and lithium chloride (Merck 98%) obtained commercially were dried at 40 °C in vacuum before use. Sodium tert-butoxide (Aldrich 97%), xylene (99.9%) and toluene (99.9%) obtained commercially were used without any purification. 1-4 dioxane was redistilled in the presence of sodium before use. O-dichlorobenzene was redistilled in the presence of CaCl_2 before use.

4.1.1. Synthesis of Nylon3

Nylon3 (sometimes described as poly- β -alanine or polyamide3) was obtained by several scientist [27-34] using hydrogen transfer polymerization of acrylamide in the presence of an anionic catalyst according to the reaction below.



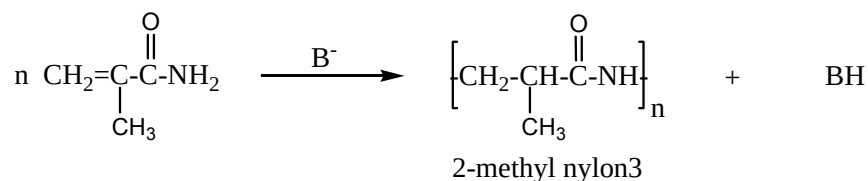
Initiation step of polymerization through hydrogen transfer polymerization was discussed in the literature [31-32]. Furthermore, alternative methods [35-36] have been used to prepare N3.

In our study, N3 was prepared by hydrogen transfer polymerization of acrylamide using sodium tert-butoxide as a basic catalyst. The polymerization was carried out in a three-necked flask with stirring under argon atmosphere at a temperature of 100 °C for 6 hours. O-dichlorobenzene, xylene, 1-4 dioxane were used as solvent. Potassium chloride was added into the reaction medium to increase the degree of polymerization by increasing the solubility of propagating chains. Hydroquinone was added to reaction medium to prevent possible thermally initiated vinyl polymerization of acrylamide. Monomer, catalyst, KCl and hydroquinone concentration was adjusted as in Masamoto's synthesis [28]. N3 crystals started to occur on the wall of the reaction vessel after a few minutes. Reaction mixture was filtered, dried in vacuum to remove solvent completely and washed by cold water to remove KCl, catalyst, monomer and possible oligomers. After filtering the white crystals, they were dried in vacuum for 48 hours. To obtain water-insoluble polymer fraction, dried polymer to which excess water was added was boiled for 30 min. After filtering the insoluble part, it was dried under vacuum for a day. The yield of base-catalyzed hydrogen transfer polymerization of acrylamide was at least 90%. As the crude polymer was extracted with hot water, water-soluble part (low molecular weight, including more acrylamide unit and branched fraction) was removed from water-insoluble fraction. Almost % 40 of the crude polymer was water-insoluble when o-dichlorobenzene was used as solvent. Yield of water-insoluble fraction was a bit lower (%35-37) than that of o-dichlorobenzene case

when xylene was used as solvent. Water-insoluble fraction was %8-9 when 1-4 dioxane was used.

4.1.2. Synthesis of 2-methyl Nylon3

2-methyl nylon3 (or Poly (α -methyl- β -alanine)) was also prepared by using hydrogen transfer polymerization of methacrylamide in the presence of an anionic catalyst (Breslow [27] Otsu et al [37], H. Wexler [38]).



In our study, reaction was performed at the conditions similar to that of the synthesis of N3. Methacrylamide was used as the monomer. Crude polymer was washed by cold water to remove catalyst, monomer, solvent and possible oligomers. The polymer was dissolved in formic acid. The solution was dropped slowly into excess acetone to precipitate out pure 2-methyl nylon 3. After filtering the white crystals, it was dried at 40 °C in vacuum for 48 hours. To obtain water-soluble fraction, dried polymer to which excess water was added was boiled for 30 min. Insoluble fraction was filtered and dried in vacuum for 48 hours. Yield of the polymerization was about 90% based on the methacrylamide used.

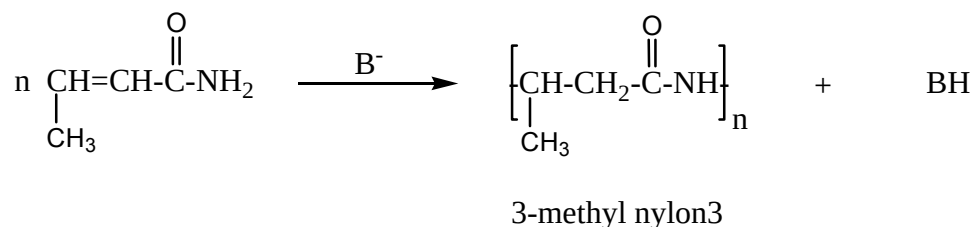
4.1.3. Synthesis of 3-methyl Nylon3

3mN3 was first prepared by Breslow [27] by hydrogen transfer polymerization of crotonamide, in the presence of anionic catalyst. It has been also reported that anionic polymerization of 3-butenamide [Raggazani et al 39] and vinyl acetamide [Nakayama et al 40] gives 2-methyl nylon 3 through isomerization of allyl group and proton transfer from amide group.

In our study, crotonamide was first prepared by the reaction of crotonoyl chloride and ammonia. It was recrystallized in acetone and its melting point was determined as 159°C (159.5°C in literature).



In the synthesis of 3mN3, reaction was performed in toluene under nitrogen atmosphere at 100 °C. Crude polymer was washed by water to remove catalyst, monomer, solvent and possible oligomers. After filtering the crystals, it was dried at 110 °C for 24 hours. The yield and degree of polymerization were lower than those of N3 and 2mN3.



4.2. Characterization of Polymers

4.2.1. FTIR Spectroscopy

FTIR spectra of polymers in KBr pellets were recorded on a Shimadzu FTIR Spectrometer in the range of 400-4000 cm^{-1} wavelength.

4.2.2. NMR Spectroscopy

^1H -NMR and ^{13}C -NMR spectra of pristine N3 were recorded using Bruker 400 MHz in 10 M LiCl solution. ^1H -NMR and ^{13}C -NMR spectra of pristine 2mN3 and 3mN3, and irradiated polymers were recorded in 85% (w/w) formic acid (HCOOH).

4.2.3. Elemental Analysis

Thermo 1112 elemental analyzer was used to find elemental composition of polymers.

4.2.4. Differential Scanning Calorimetry

DSC thermograms of polymers were recorded in the range of 20-400 $^{\circ}\text{C}$ under N_2 atmosphere using TA Instruments Q10 series DSC.

4.2.5. Thermogravimetry

TGA thermograms of polymers were recorded in dynamic nitrogen atmosphere at a heating rate of 20 $^{\circ}\text{C}/\text{min}$ using Perkin Elmer Pyris 1 model TGA.

4.2.6. Viscosimetry

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

4.2.7. Determination of Number-average Molecular Weight of Polymers by End-group Analyses

End-group analysis of polymers was carried out by three methods; the first is determination of double bonds at the end-group by iodine number test [Yasuda, 41], the second is using the ratio of intensities of methyl protons in the ^1H -NMR spectrum (for 2mN3 and 3mN3), the third is conversion of primary amide group (NH_2) to ammonia by extraction of the polymers with potassium hydroxide and titration of ammonia evolved [Yamamoto et al, 42].

4.3. ESR Spectroscopy and Irradiation of Polymers

4.3.1. Irradiation of Polymers

All the polymer samples were ground finely before adding vials. Samples for irradiation in air were prepared in glass vials in Figure.4.1. Samples for irradiation in nitrogen were prepared in dry box so that oxygen and moisture can remove from the polymer samples in vials. After the irradiation was completed, the irradiated polymers are poured into the ESR tubes in dry box.



Fig.4.1. Samples in glass vials.

Polymer samples were irradiated by ^{137}Cs γ -rays at three different dose rates (700 Gy/h, 220 Gy/h and 95 Gy/h) at room temperature. The samples were exposed to integral doses of 750 Gy to 100 kGy. As soon as the vials were removed from the irradiator, polymers were poured into the ESR tubes. The irradiated samples were kept at room temperature and in dark.

4.3.2. ESR Spectroscopy

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. Temperature dependence of radicals was followed using temperature dependence accessories of the instrument. All the spectra were recorded as first derivative of the absorption intensity.

4.3.3. Simulation of ESR Spectra

Simulations of experimental ESR spectra for each polymer were carried out using the winsim2002 software designed for isotropic simulations by the Downhill and Levenberg-Marquardt [13,14] simplex. ESR line parameters for each species superimposed in the experimental spectrum (number and type of nuclei coupling with corresponding unpaired electron, line-width, hyperfine splitting constants, g-shift, and line shape parameter between 0-100) were entered to the related part of the software, and then optimization of simulation was performed with Downhill simplex selecting the maximum iteration option. 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. Simulation of experimental ESR spectra of N3 irradiated in nitrogen was also carried out using Origin 6.1. Origin runs by applying a range of values (ESR line parameters) determined by user to a fitting function derived by user for the ESR spectrum.

5. RESULTS AND DISCUSSION

5.1. CHARACTERIZATION OF POLYMERS

5.1.1. Characterization of Pristine and Irradiated Nylon3

5.1.1.1. FTIR Spectroscopy of Nylon3

The FTIR spectrum of N3 showed characteristic secondary amide absorption bands: 3298 (NH stretching), 3080 (overtone of NH in plane bending), 1643 (amide I, carbonyl stretching), 1544 (amide II, N-H bending), 1286-1230 (amide III, coupled N-H bending and C-N stretching), 974 (amide IV, in-plane C=O bending) [Stuart, 43]. As shown, there is no observable difference between the FTIR spectra of pristine and irradiated samples. This shows that the radiation induced changes in the structure are under the detection limit of FTIR spectroscopy.

Table.5.1. FTIR data of N3

Wave number (cm ⁻¹)	Type of vibration [Stuart, 43]
3298	NH (symmetric stretching vib.)
3080	-NH....C=O
1643	Amide I
1544	Amide II
1286	Amide III
1230	Amide III
974	Amide IV

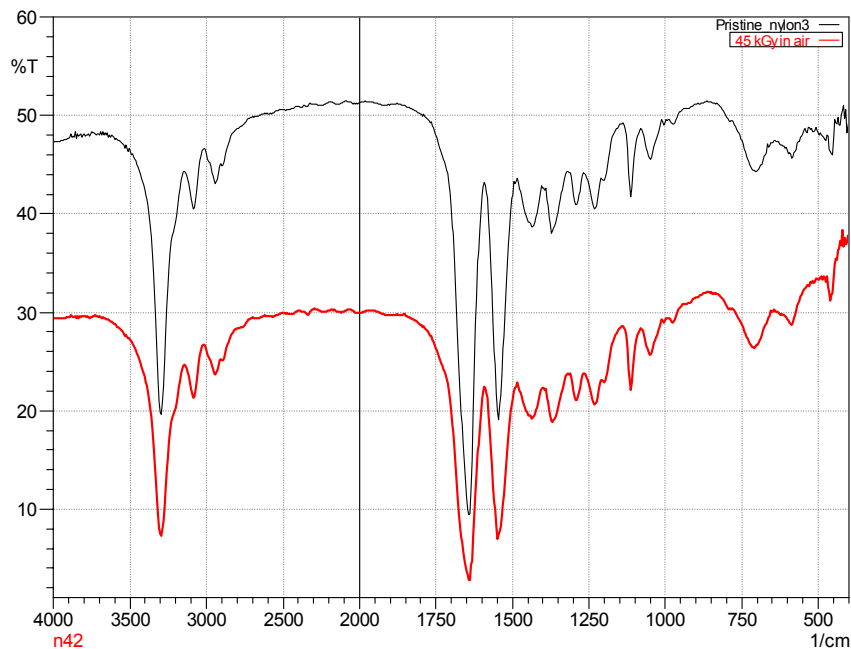


Fig.5.1. FTIR spectra of pristine N3 and N3 irradiated in air

5.1.1.2. NMR Spectroscopy of Nylon3

^1H -NMR spectrum of pristine N3 was obtained in 10 M LiCl- D_2O solution. Two triplets were observed at 2.68 and 3.62 ppm having almost equal intensity. These signals belong to methylene hydrogens $\text{CH}_2\text{-CO}$ (at 2.68 ppm) and $\text{CH}_2\text{-NH}$ (at 3.62 ppm). As an exchange has been expected to occur between D_2O and amide proton, amide proton was not observed on the spectrum. Instead, a signal, belonging to HOD [Glickson and Applequist, 44], has been shown at about 4.80 ppm. The small peaks 2.88 and 3.82 ppm were attributed to the olefinic protons at the end-group.

^1H -NMR spectrum of N3 irradiated in air was obtained in formic acid. The broad peaks between 8-9 ppm belong to formic acid protons. As shown, relative intensity of methylene protons ($\text{CH}_2\text{-N}$) at 3.74 ppm decreased after irradiation. The result shows that proton abstraction from carbon atom next to the NH group is favored than the others during irradiation or decay.

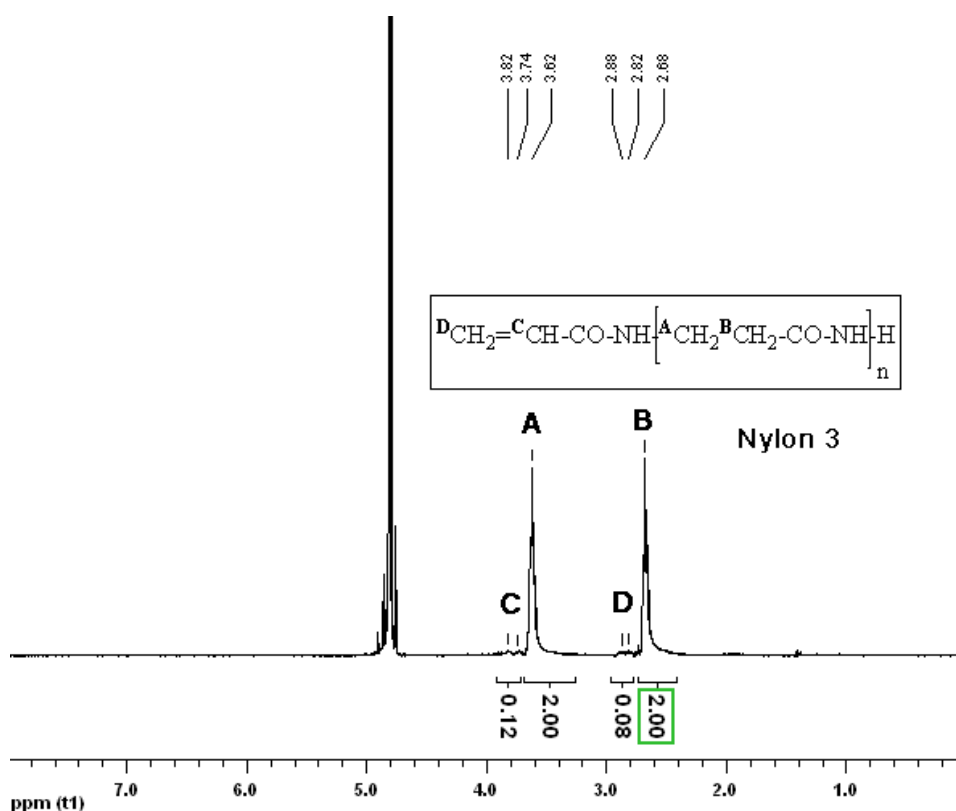


Fig.5.2. ^1H -NMR spectrum of pristine N3 in 10 M LiCl- D_2O solution

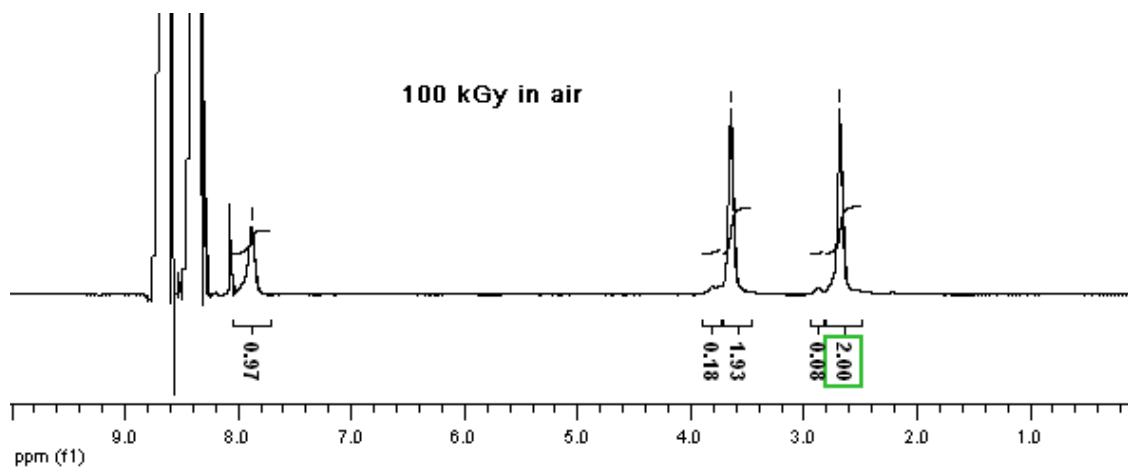


Fig.5.3. ^1H -NMR spectrum of N3 irradiated in air (in 85% formic acid)

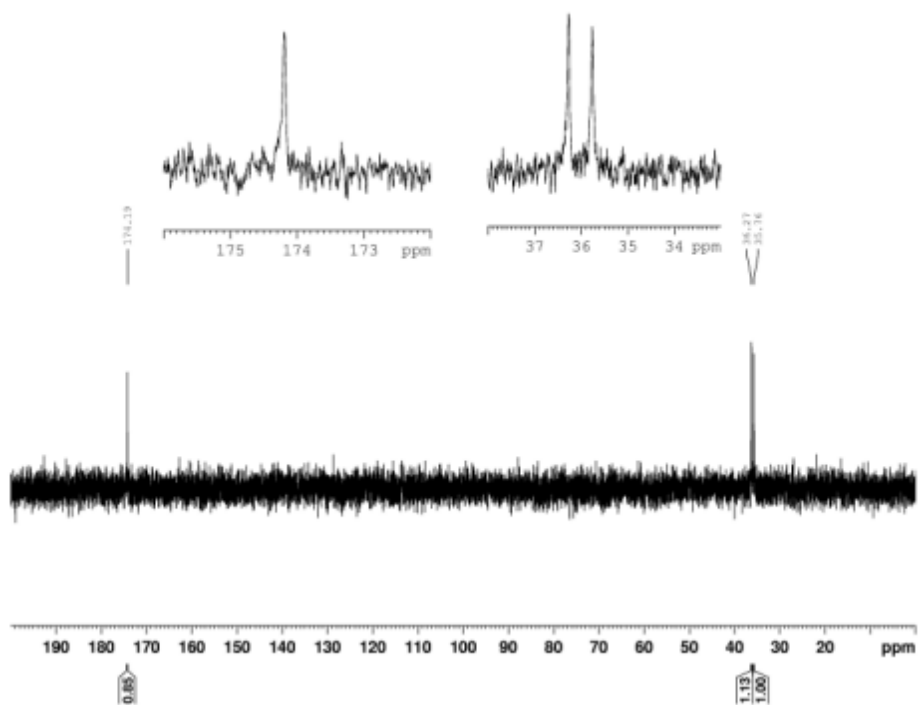


Fig.5.4. ^{13}C -NMR spectrum of N3 in 10 M LiCl- D_2O solution

^{13}C -NMR spectrum of N3 was obtained in 10 M LiCl- D_2O solution. Three signals were observed in the spectrum. The signals belong to methylene

carbon adjacent to carbonyl group (at 35.76 ppm), methylene carbon adjacent to amide group (at 36.27 ppm) and carbonyl carbon (at 174.19 ppm).

5.1.1.3. Elemental Analysis of Nylon3

For N3, $(C_3H_5NO)_n$, compositions of constituent elements were analytically calculated as C: 50.69%, H: 7.09%, N: 19.71%.

For N3, the compositions of elements were determined as: C: 45.69%, H: 6.72%, N: 15.97%.

The percentages of carbon, nitrogen and hydrogen experimentally determined are lower than those of analytically calculated. The deviations between the theoretical and the experimental results were attributed to the moisture (about 4%, it has been determined by TGA, will be discussed later) in the sample. The moisture in the samples was not able to be removed even they were dried in vacuum at 40 °C for days due to the high water-uptake property of N3. This property results from the high density of amide groups in N3.

5.1.1.4. Differential Scanning Calorimetry of N3

The DSC thermogram of N3 was recorded in the range of 20-400 °C. Glass transition temperature (T_g) of the polymer has been observed at about 124 °C (reported as 111 °C by Wexler [38], 73-121.2 °C by Berger [34]). The exotherm centered at about 225 °C is attributed to cold crystallization [Camino and

Guaita, 45]. The polymer started to melt at about 250 °C with an endotherm centered at 342.6 °C (reported as 340-350 °C by Berger [34] and 350-355 °C Wexler [38]). Before the melting process was completed, the polymer started to decompose.

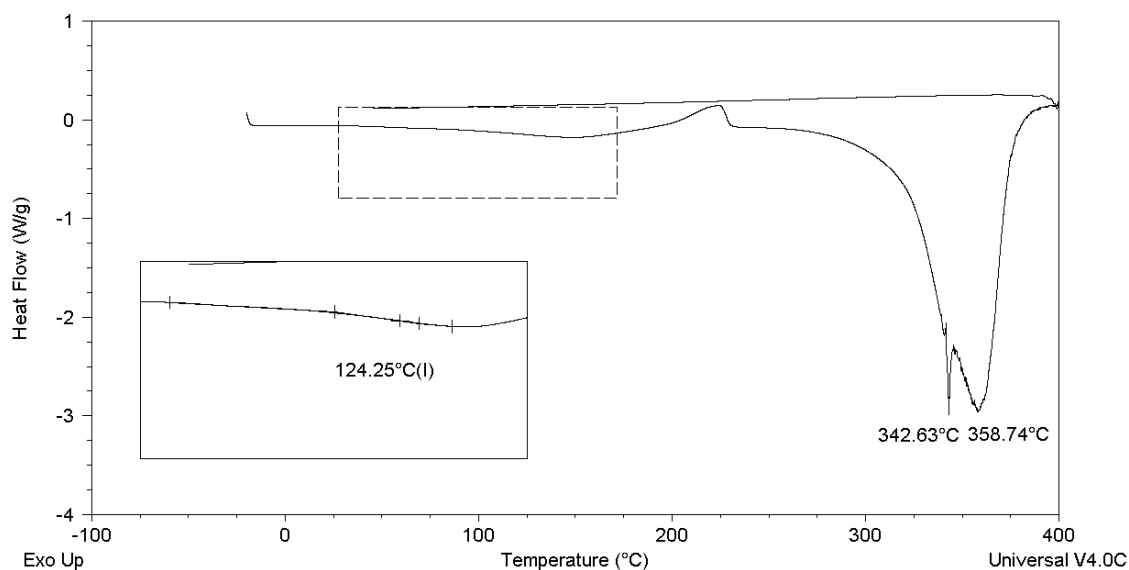


Fig.5.5. DSC thermogram of N3

5.1.1.5. Thermogravimetric Analysis of Nylon3

TGA thermogram of N3 was recorded in dynamic nitrogen atmosphere at a heating rate of 20°C/min. The decrease in the mass (about 4 %) between 25-100 °C was attributed to moisture in the sample. Onset of decomposition has been recorded at about 355 °C. About 86% of the sample decomposed until 390 °C. About 10% of the sample remained as ash.

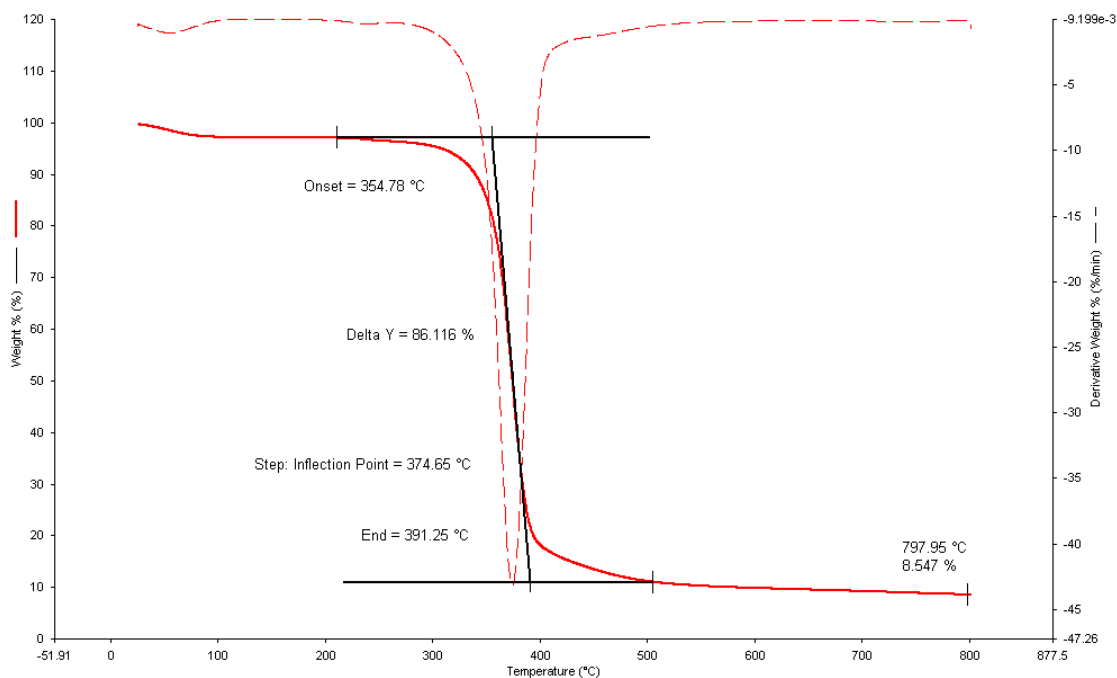


Fig.5.6. TGA thermogram of N3

5.1.1.6. Viscosimetric Analysis of Pristine and Irradiated Nylon3

Inherent viscosity of 0.1 g/dL of pristine and irradiated N3 in 85% formic acid was determined using an Ubbelohde type of viscometer at 25.0 °C. Inherent viscosities of pristine and irradiated samples of N3, 2mN3 and 3mN3 were given in Table.5.2.

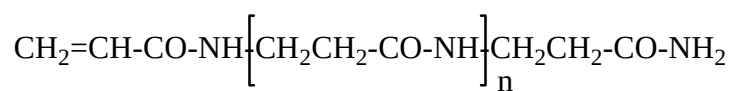
Table.5.2. Inherent viscosities of pristine and irradiated polymers in air and nitrogen

η_{inh}	pristine	50 kGy (in air)	100 kGy (in air)	4.9 kGy (N ₂)
N3	0.173	0.171	0.131	0.174
2mN3	0.242	0.196	0.165	0.211
3mN3	0.069	0.081	0.081	0.075

As shown, however inherent viscosity of N3 shows decrease with irradiation in air, it remains almost unchanged in nitrogen. That may be attributed to oxidative degradation through peroxydation taking place in air. Furthermore, as the inherent viscosities of pristine and the sample irradiated in nitrogen are almost equal, it may be explained by competition between the crosslinking and chain-scission reactions in nitrogen. Unfortunately, polymers in nitrogen could be irradiated with integral doses of 4.9 kGy due to the experimental difficulties.

5.1.1.7. Determination of Number-average Molecular Weight of Nylon3 by End-group (Double Bond and Primary Amide) Analyses

After ^1H -NMR spectrum of synthesized N3 was evaluated, the molecular structure of synthesized N3 has been estimated as;



Nylon 3

End-group analysis of polymer samples was carried out by two methods; the first is determination of double bonds analytically (iodine number test), the second is determination of NH_3 evolved by hydrolysis of primary amide group (NH_2). The end-group analysis of N3 could not be performed using ^1H -NMR data as the peaks belonging to protons at the end-group overlapped with those of repeating units. Results were given in Table.5.3.

Table.5.3. Results of end-group analyses for each polymer. DB, DP and INT denote double bond, degree of polymerization and iodine number test, respectively.

	NH ₂ % by Hydrolysis	DB % by INT	DB % by NMR	DP by Hydrolysis	DP by INT	DP by NMR
Nylon 3	5.21	4.83	N/A	19.2	20.7	N/A
2mN3	3.52	3.32	3.33	28.4	30.1	29
3mN3	10.4	10.45	11.1	9.6	9.6	9.0

The results of the two methods are quite consistent with each other. Average degree of polymerization, DP is about 20 for N3.

5.1.2. Characterization of Pristine and Irradiated 2-methyl Nylon3

5.1.2.1. FTIR Spectroscopy of 2-methyl Nylon3

The FTIR spectrum of 2-methyl nylon 3 shows characteristic secondary amide absorption bands: 3297 (NH stretching), 3087 (overtone of NH in plane bending), 1644 (amide I, carbonyl stretching), 1545 (amide II, N-H bending), 1256-1213 (amide III, coupled N-H bending and C-N stretching), 946 (amide IV, in-plane C=O bending) [Stuart, 43]. Clear difference between the FTIR spectra of N3 and 2mN3 is that the CH stretching bands at 2976 cm^{-1} in 2mN3 is more complicated than in N3 due to the additional methyl group in the 2mN3. Since there is no observable difference between the FTIR spectra of pristine and irradiated 2mN3 as in the case of N3, the FTIR spectrum of irradiated sample was not indicated together with that of pristine.

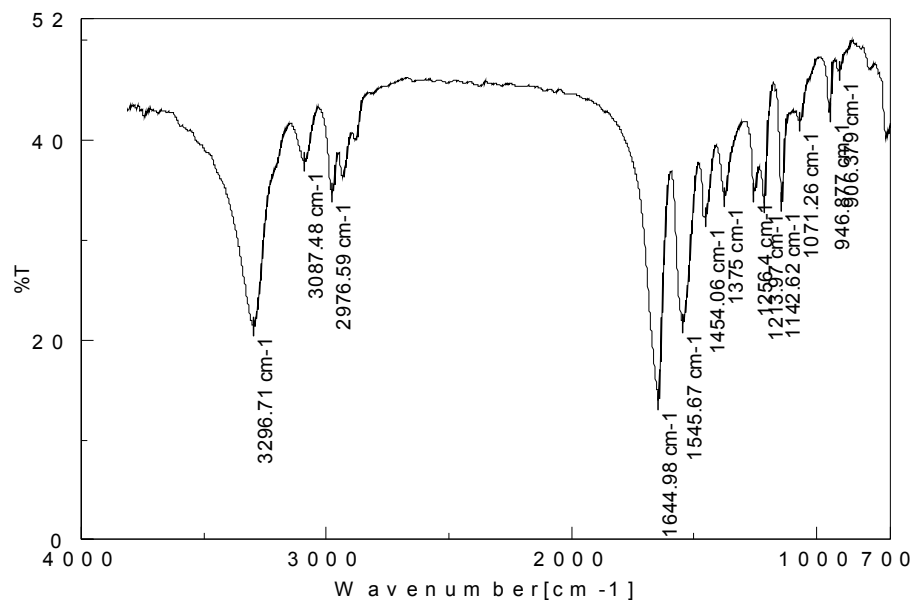


Fig.5.7. FTIR spectrum of 2mN3

Table.5.4. FTIR data of 2mN3

Wave number (cm^{-1})	Type of vibration [Stuart, 43]
3297	NH (symmetric stretching vib.)
3086	-NH....C=O
1644	Amide I
1545	Amide II
1256	Amide III
1213	Amide III
946	Amide IV

5.1.2.2. NMR Spectroscopy of 2-methyl Nylon3

The peaks at 1.10, 2.73 and 3.39 ppm having the relative intensity of 3:1:2 belong to methyl, methyn and methylene protons, respectively. The peak at 7.67 ppm belongs to NH proton. The peaks at 1.88, 5.45 and 5.76 ppm were attributed to the methyl and methylene protons at chain ends, respectively.

Therefore, the ratio of the intensities of methyl protons may give information about the degree of polymerization. Through a simple calculation, degree of polymerization and percentage of primary amide group have been found as 29 and 3.33 %, respectively.

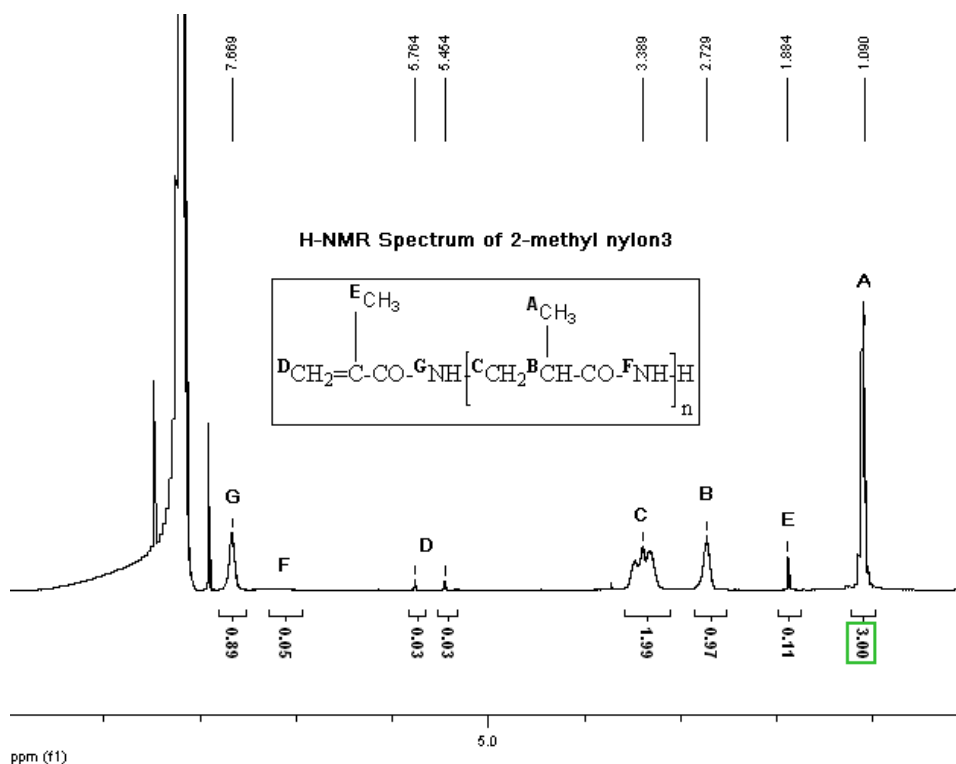


Fig.5.8. ¹H-NMR spectrum of pristine 2mN3 in 85% formic acid

¹H-NMR spectrum of 2mN3 irradiated in air was recorded to see the radiation-induced changes in the structure of the polymer. As shown, the relative intensities of CH, CH₂, and NH protons decreased after irradiation. Decrease in the relative intensity of NH protons is attributed to breaking the bond between NH and CH₂ groups and conversion of NH group to NH₂ group by hydrogen radical abstraction. The new peaks at 7.0-7.4 ppm shows the NH₂ groups generated. The decrease in the intensities of CH and CH₂ protons will be

explained later (by radical formation and decay reactions) in the section of ESR investigation of 2mN3

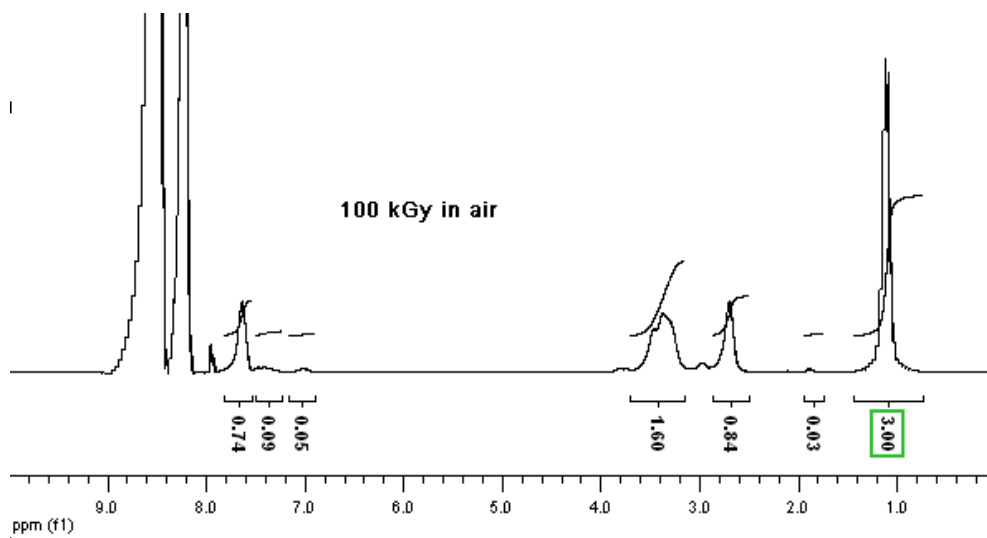


Fig.5.9. ^1H -NMR spectrum of 2mN3 irradiated in air (in 85% formic acid)

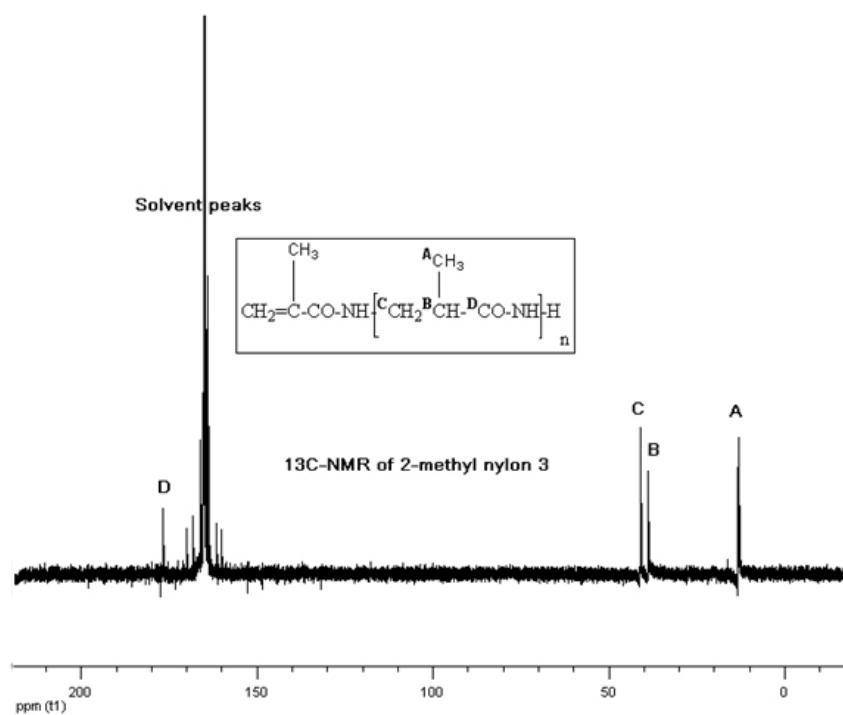


Fig.5.10. ^{13}C -NMR spectrum of 2mN3 in 85% formic acid

Four signals observed at the ^{13}C -NMR spectrum (at about 13, 39, 41, 177 ppm) belong to methyl, methyn, methylene and carbonyl carbons, respectively.

5.1.2.3. Elemental Analysis of 2-methyl Nylon3

For 2mN3, $(\text{C}_4\text{H}_{10}\text{NO})_n$, compositions of elements were analytically calculated as C:56.45%, H:8.29%, N:17.62%.

For 2-methyl nylon 3, the compositions of elements were determined as: C:54.85%, H:8.58%, N:15.41%.

However the percentages of carbon and nitrogen found are lower than those of analytically calculated, the percent of hydrogen found is higher than that of analytically calculated. The deviations between the theoretical and the experimental results were attributed to the moisture (about 2%, it has been determined by TGA, will be discussed later) in the sample. As discussed above, it is very difficult to remove the moisture in polymers with high density of amide groups.

5.1.2.4. Differential Scanning Calorimetry of 2-methyl Nylon3

The DSC thermogram of 2mN3 was recorded in the range of 20-400 °C. Glass transition temperature (T_g) of the polymer has been observed at about 87 °C (reported as 96 °C by Wexler [38]). The endotherm centered at about 299 °C is attributed to melting (reported as 300-305 °C by Wexler [38]). The polymer

started to decompose as soon as melting completed and gave two endotherms at about 364 and 374 °C during decomposition.

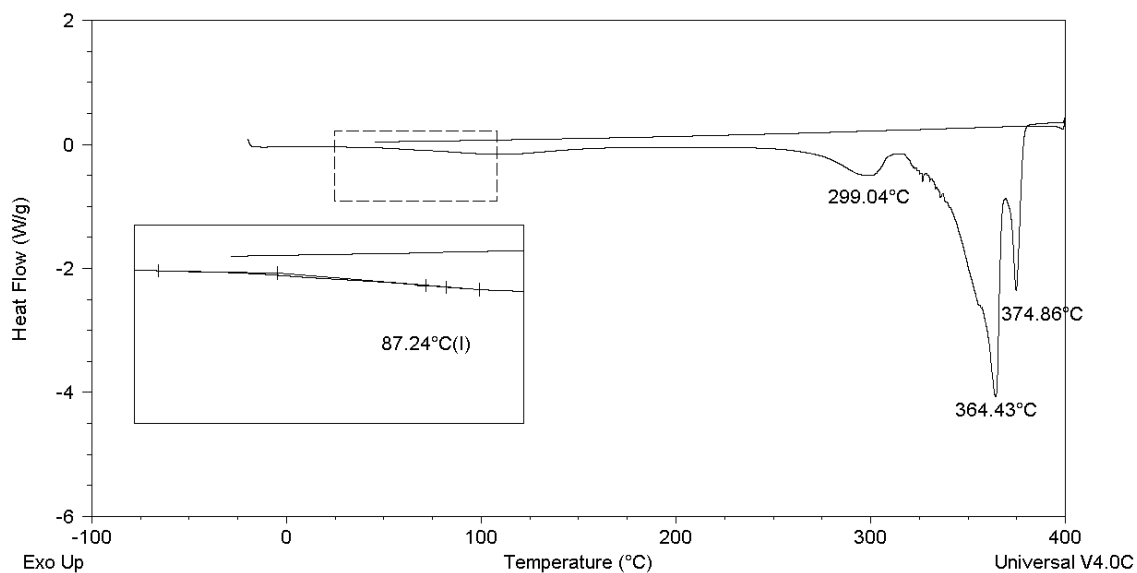


Fig.5.11. DSC thermogram of 2mN3

5.1.2.5. Thermogravimetric Analysis of 2-methyl Nylon3

TGA thermogram of 2mN3 was recorded in dynamic nitrogen atmosphere at a heating rate of 20 °C/min. The decrease in the mass (about 2 %) between 25-160 °C was attributed to moisture in the sample. Onset of decomposition has been recorded to be at about 350 °C. About 54% of the sample decomposed until 393 °C. About 40 % of the sample remained as ash.

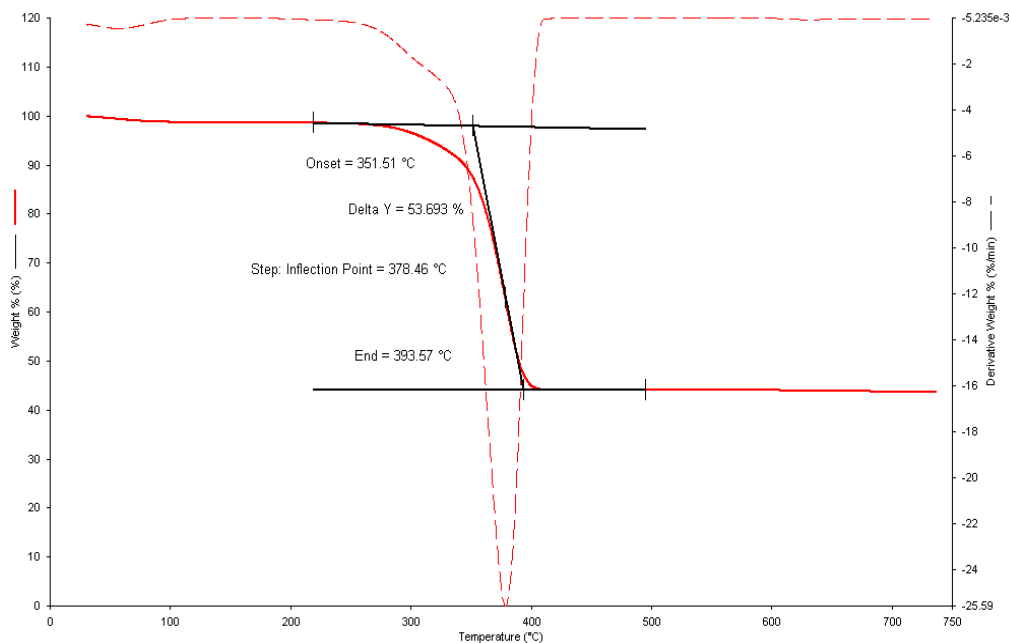


Fig.5.12. TGA thermogram of 2-methyl nylon 3

5.1.2.6. Viscosimetric Analysis of 2-methyl Nylon3

Inherent viscosity of 0.1 g/dL of pristine and irradiated 2mN3 in 85% formic acid was determined using an Ubbelohde type of viscometer at 25.0 °C. Inherent viscosities of pristine and irradiated samples of 2mN3 were given in Table.5.2

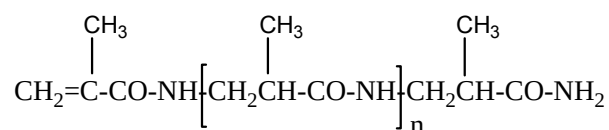
Table.5.2. Inherent viscosities of pristine and polymers irradiated in air and nitrogen

η_{inh}	pristine	50 kGy (in air)	100 kGy (in air)	4.9 kGy (N ₂)
N3	0.173	0.171	0.131	0.174
2mN3	0.242	0.196	0.165	0.211
3mN3	0.069	0.081	0.081	0.075

As shown, inherent viscosity of 2mN3 shows decrease with irradiation in both air and nitrogen. This shows clearly that chain-scission dominates over crosslinking in both air and nitrogen.

5.1.2.7. Determination of Number-average Molecular Weight of 2-methyl Nylon3 by End-group (¹H-NMR, Primary Amide and Double Bond) Analyses

After ¹H-NMR spectrum of synthesized 2mN3 was evaluated, the molecular structure of synthesized 2-methyl nylon 3 has been estimated as;



2-methyl nylon 3

End-group analysis of 2mN3 was carried out by three methods; the first is determination of double bonds by iodine number test, the second (discussed above) is using the ratio of intensities of methyl protons in the ¹H-NMR spectrum, the third is determination of primary amide group (NH₂) analytically. All the results were consistent with the each other and given in Table.5.3.

Table.5.3. Results of end-group analyses for each polymer. DB, DP and INT denote double bond, degree of polymerization and iodine number test, respectively

	NH ₂ % by Hydrolysis	DB % by INT	DB % by NMR	DP by Hydrolysis	DP by INT	DP by NMR
Nylon 3	5.21	4.83	N/A	19.2	20.7	N/A
2mN3	3.52	3.32	3.33	28.4	30.1	29
3mN3	10.4	10.45	11.1	9.6	9.6	9.0

Average degree of polymerization of 2mN3 was found to be about 30.

5.1.3. Characterization of Pristine and Irradiated 3-methyl Nylon3

5.1.3.1. FTIR Spectroscopy of 3-methyl Nylon3

The FTIR spectrum of 2mN3 in Figure.5.13 shows characteristic secondary amide absorption bands: 3289 (N-H stretching), 3077 (overtone of N-H in plane bending), 1642 (amide I, carbonyl stretching), 1546 (amide II, N-H bending), 1225-1193 (amide III, coupled N-H bending and C-N stretching), 910 (amide IV, in-plane C=O bending) [Stuart, 43]. FTIR spectrum of 3mN3 is almost same as in 2mN3 as the only difference is positions of methyl group in the repeating units. As it was expected, the positions of corresponding bands have small differences.

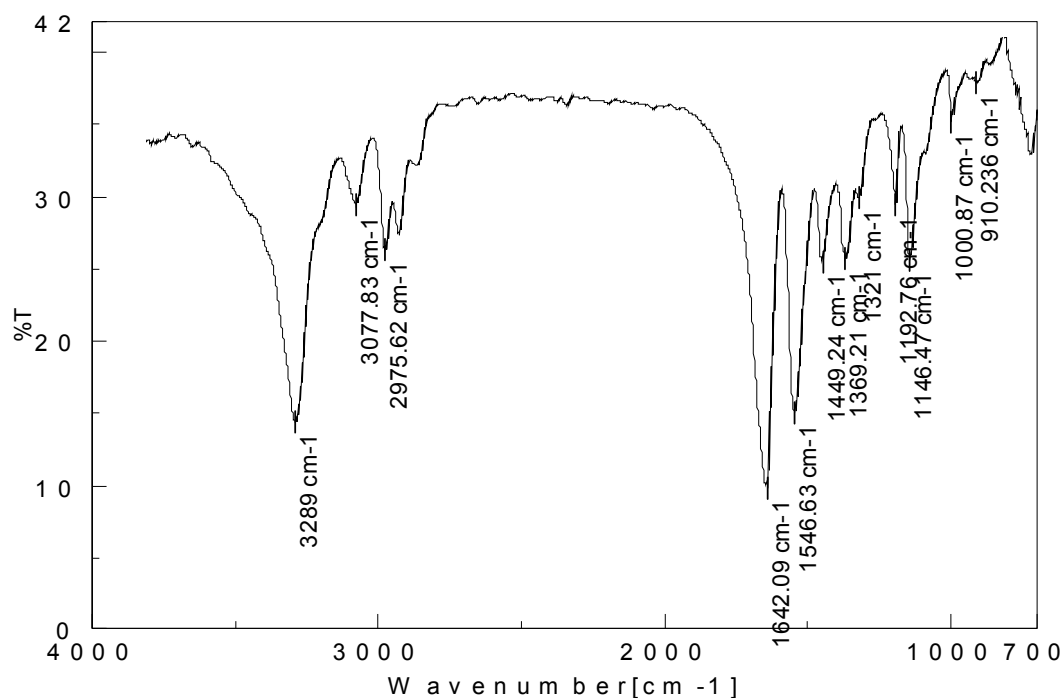


Fig.5.13. FTIR spectrum of 3mN3

Table.5.5. FTIR data of 3mN3

Wave number (cm ⁻¹)	Type of vibration [Stuart, 43]
3289	NH (symmetric stretching vib.)
3077	-NH....C=O
1642	Amide I
1546	Amide II
1225	Amide III
1193	Amide III
910	Amide IV

5.1.3.2. NMR Spectroscopy of 3-methyl Nylon3

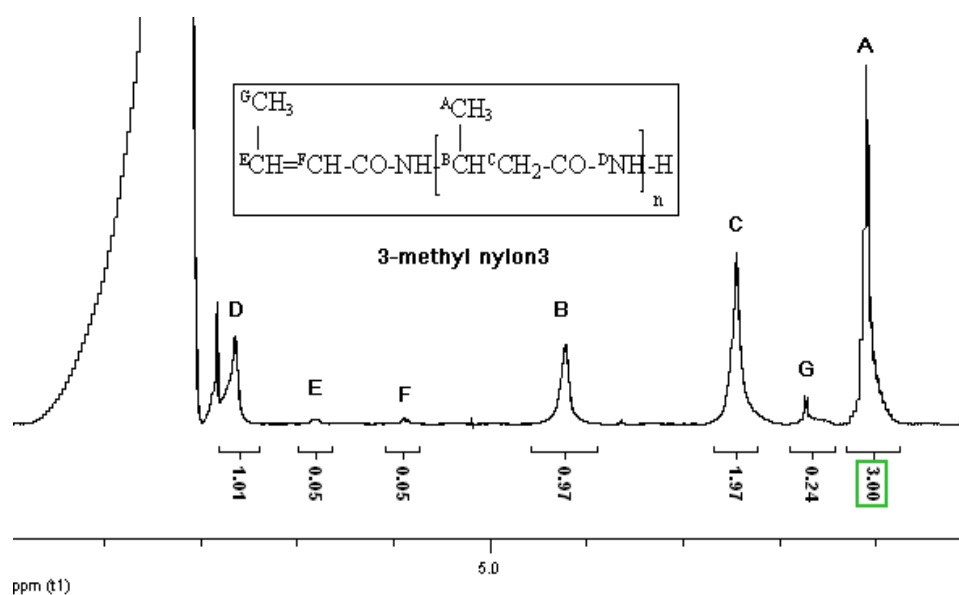


Fig.5.14. ¹H-NMR Spectrum of pristine 3mN3 in 85% formic acid

The peaks at 1.10, 2.45, and 4.22 ppm having the relative intensity of 3:2:1 belong to methyl, methylene and methyn protons, respectively. The peak superimposed at 7.64 ppm belongs to amide proton (NH). The peaks at 1.73, 5.89 and 6.81 ppm were attributed to the methyl and olefinic CH protons at the

end-group of the chains, respectively. Therefore, the ratio of the intensities of methyl protons may give information about the degree of polymerization. Through a simple calculation, degree of polymerization and percent of primary amide group has been found as 11, and 9.1%, respectively.

^1H -NMR spectrum of 3mN3 irradiated in air was recorded to see the radiation-induced changes in the structure of the polymer. As shown easily, there is an explicit change in the relative intensity of only NH proton. As will be discussed later in the section of ESR investigation of 3mN3, this is due to decrease in the amounts of all the NH, CH, CH_2 and CH_3 protons (via radical formation and decay reactions).

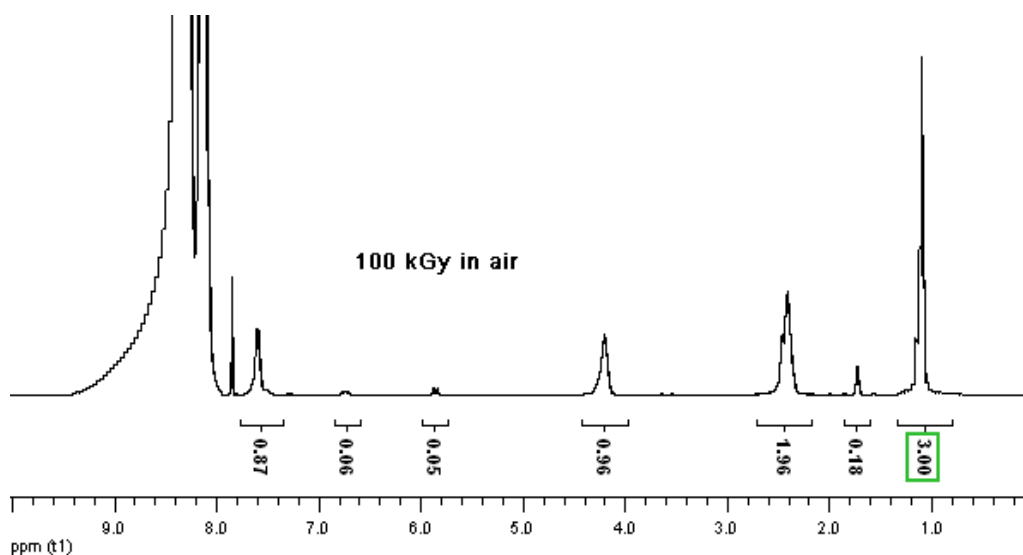


Fig.5.15. ^1H -NMR spectrum of 3mN3 irradiated in air (in 85% formic acid)

^{13}C -NMR spectrum of 3mN3 gave four peaks. The peaks at 13.7, 38.2, 41.0 and 177 ppm were attributed to the carbon atoms of methyl, methylene, methyn and carbonyl groups, respectively.

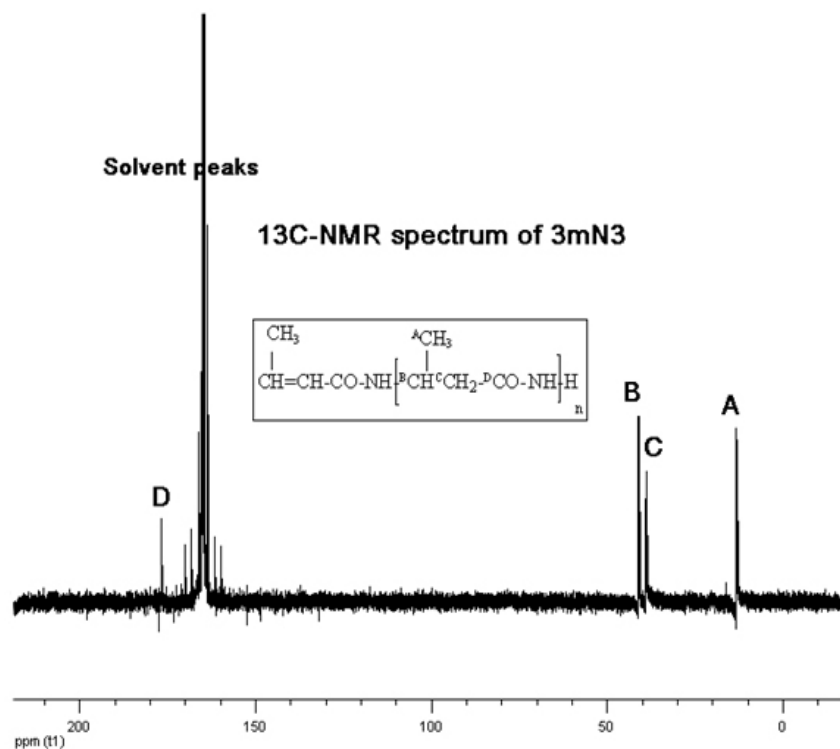


Fig.5.16. ^{13}C -NMR spectrum of 3mN3 in 85% formic acid

5.1.3.3. Elemental Analysis of 3-methyl Nylon3

Theoretical results: C:56.42 %, H:8.29 %, N:16.45 %

Experimental results: C:53.93 %, H:8.05%, N:15.73%

The percentages of carbon, nitrogen and hydrogen found were lower than in analytically calculated. The deviations between the theoretical and the experimental results were attributed to the moisture (about 3-4%, it has been determined by TGA, will be discussed later) in the sample.

5.1.3.4. Differential Scanning Calorimetry of 3-methyl Nylon3

The DSC thermogram of the 3mN3 was recorded in the range of 20-400 °C. Glass transition temperature (T_g) of the polymer has been observed at about 94 °C. The polymer started to melt at about 250 °C with an endotherm centered at about 328 °C. Before the melting process completed, the polymer started to decompose with an endotherm centered at about 349 °C.

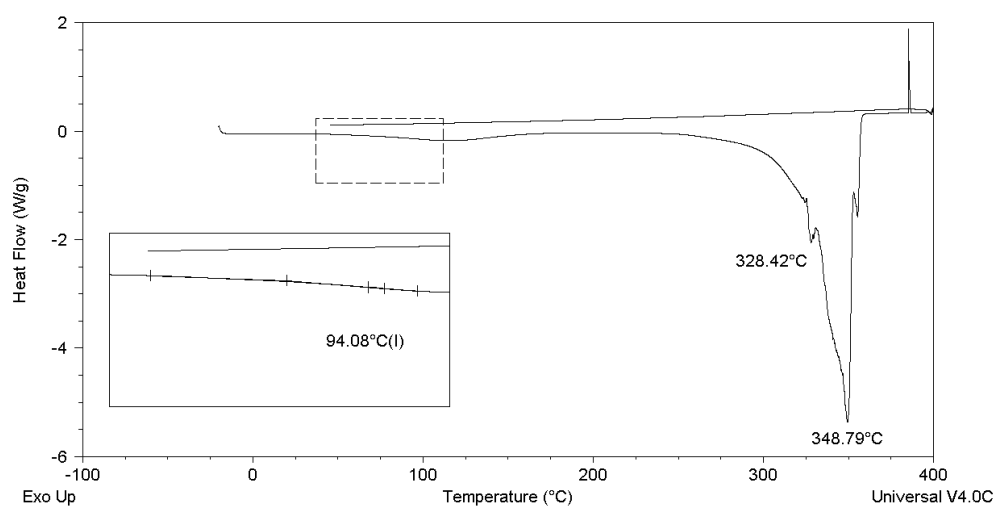


Fig.5.17. DSC thermogram of 3mN3.

5.1.3.5. Thermogravimetric Analysis of 3-methyl Nylon3

TGA thermogram of 3mN3 was recorded in dynamic nitrogen atmosphere at a heating rate of 20 °C/min. The decrease in the mass (about 4 %) between 25-100 °C was attributed to moisture in sample. Onset of decomposition has been recorded as 307 °C. About 90% of the sample decomposed until 357 °C. About 5% of the sample remained as ash.

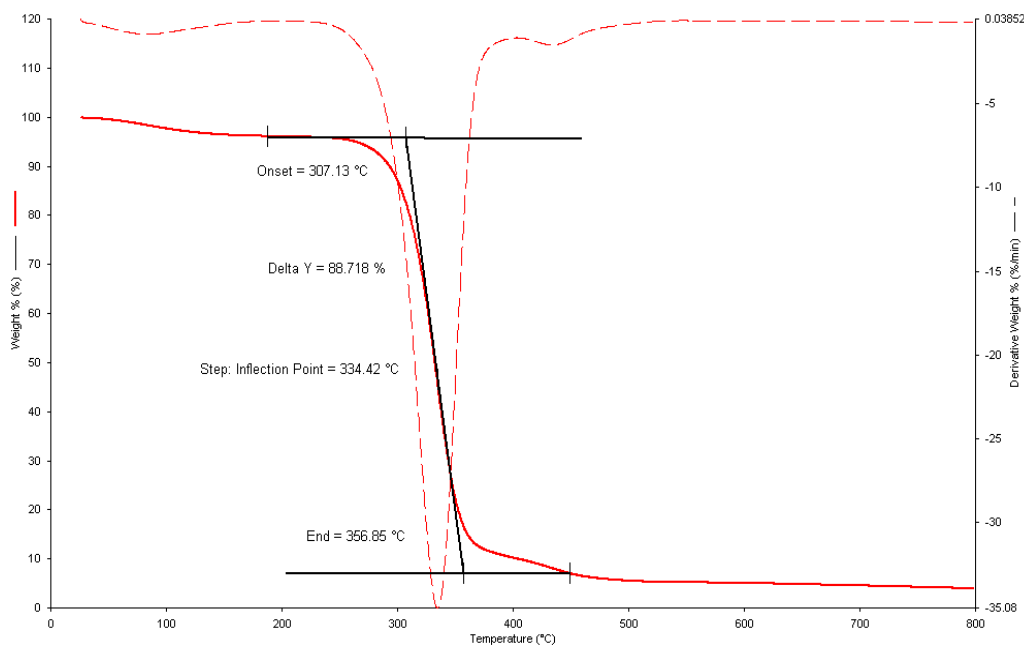


Fig.5.18. TGA thermogram of 3mN3

5.1.3.6. Viscosimetric Analysis of 3-methyl Nylon3

Inherent viscosity of 0.1 g/dL of pristine and irradiated 3mN3 in 85% formic acid was determined using an Ubbelohde type of viscometer at 25.0 °C. Inherent viscosities of pristine and irradiated 3mN3 were given in Table.5.2

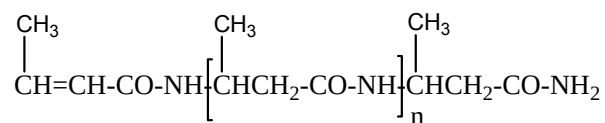
Table.5.2. Inherent viscosities of pristine and polymers irradiated in air and nitrogen

η_{inh}	pristine	50 kGy (in air)	100 kGy (in air)	4.9 kGy (N ₂)
N3	0.173	0.171	0.131	0.174
2mN3	0.242	0.196	0.165	0.211
3mN3	0.069	0.081	0.081	0.075

Inherent viscosity of 3mN3 shows increase with irradiation in both air and nitrogen. This shows clearly that crosslinking dominates over chain-scission in both air and nitrogen.

5.1.3.7. Determination of Number-average Molecular Weight of 3mN3 by End-group (¹H-NMR, Primary Amide and Double Bond) Analyses

After ¹H-NMR spectrum of synthesized 3mN3 was evaluated, the molecular structure of 3mN3 synthesized has been estimated as;



3-methyl nylon 3

End-group analysis of polymer samples was carried out by three methods; the first is determination of DB's by INT, the second is determination of primary amide group (NH₂) analytically. Furthermore, the ratio between the intensity of CH₃ protons to that of CH₃ protons at chain ends gave us the average repeating units. The results were very consistent with each other and given in Table.5.3.

Table.5.3. Results of end-group analyses for each polymer. DB, DP and INT denote double bond, degree of polymerization and iodine number test, respectively

	NH ₂ % by Hydrolysis	DB % by INT	DB % by NMR	DP by Hydrolysis	DP by INT	DP by NMR
Nylon 3	5.21	4.83	N/A	19.2	20.7	N/A
2mN3	3.52	3.32	3.33	28.4	30.1	29
3mN3	10.4	10.45	11.1	9.6	9.6	9

Average degree of polymerization of 3mN3 was found to be about 10. The results of the end-group analyses are also consistent with the results of viscosimetric measurements outlined above for each polymer.

6. ESR INVESTIGATION OF IRRADIATED POLYMERS

6.1. ESR INVESTIGATION OF NYLON3 IRRADIATED AND STORED IN AIR

The ESR spectrum shown in figure.6.1 has been recorded immediately after γ -irradiation of N3 in air atmosphere at room temperature. The weak long-lived singlet has been observed even after the polymer exposed to high integral doses.

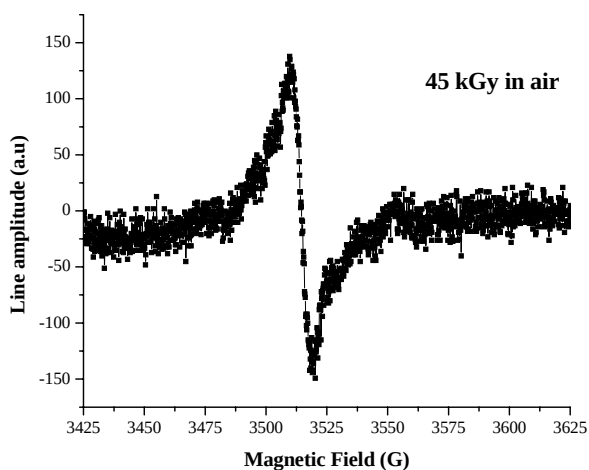


Fig.6.1. ESR spectrum recorded immediately after irradiation of N3 in air

It has been assumed that the primary radicals react with oxygen molecule to form peroxy radicals and then decays quickly through abstraction and (or) combination of hydrogen radicals (H^*) in the medium during relatively long irradiation period through the peroxydation chain reactions shown in Figure.6.2

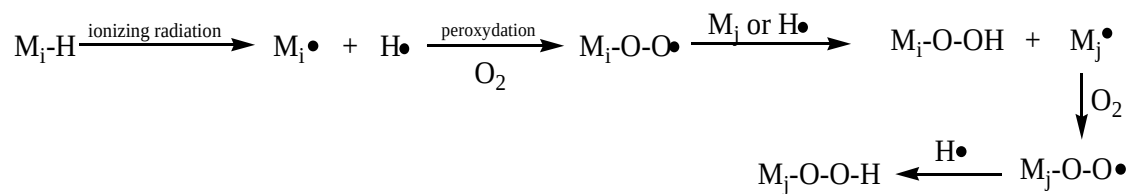


Fig.6.2. Formation and decay reactions of primary radicals of N3 through peroxydation M_i-H and M_j denote any main chains of N3. $M_i\bullet$ denotes primary macromolecular radicals generated by irradiation of N3. $M_j\bullet$ denotes secondary short lived macromolecular radicals.

As will be discussed later, the long-lived radical having the ESR spectrum shown in Figure.6.3 was assigned to the radical;

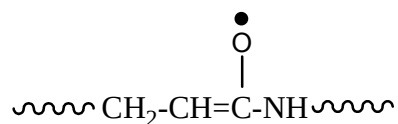


Fig.6.3. The structure proposed for the long lived radical

6.2. ESR INVESTIGATION OF NYLON3 IRRADIATED IN NITROGEN AND STORED IN AIR

A nylon3 sample has been irradiated at a radiation dose of 5 kGy 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 N3.

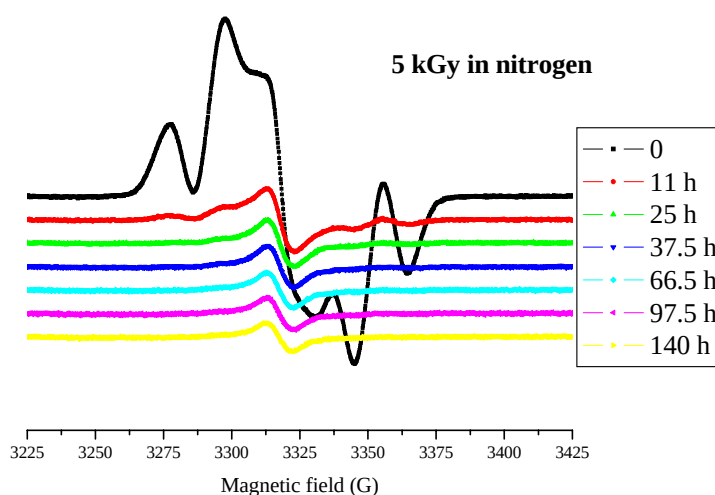


Fig.6.4. Change in the shape of ESR lines of N3 irradiated in nitrogen and stored in air.

As shown in figure.6.4, 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 in one day, losing intensity of side peaks. This shows that majority of the primary radical decayed in a short time comparing to the radical belonging to singlet line. It may be discussed that primary radicals were extremely vulnerable to oxygen attack and the ESR spectrum of samples irradiated in air atmosphere could not give information about the primary radicals generated during long irradiation period.

6.3. ESR INVESTIGATION OF NYLON3 IRRADIATED AND STORED IN NITROGEN

6.3.1. ESR Shape

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 spectrum in figure.6.5 was recorded immediately after γ -irradiation of N3 sample in nitrogen medium. The similar spectra have been reported for nylon6 irradiated in vacuum by Graves and Ormerod [16], Kashiwagi [18], Szocs et al [19], Shinohara and Ballantine [20], Simon et al [21] and Takigami et al [23].

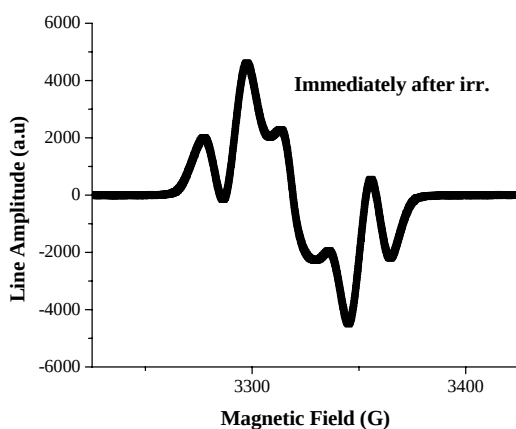


Fig.6.5. ESR spectrum recorded immediately after irradiation of N3 in nitrogen.

Several authors [16, 19-21] attributed the spectrum of γ - irradiated nylon6 to the combination of a four-line and a singlet. Some authors [18, 23] assumed it to be a six-line spectrum but, their suggestions about the type of radical were almost

same; a free radical (R1) forming by hydrogen abstraction from CH₂ group next to the amide group and a free radical (R2) forming by hydrogen abstraction from CH₂ group next to the carbonyl group as shown below.

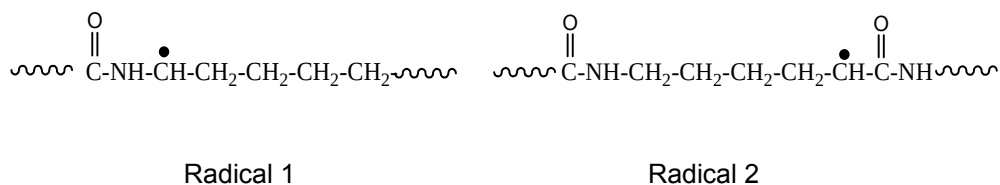


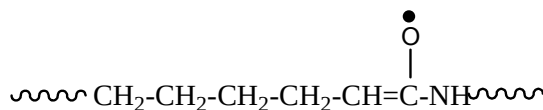
Fig.6.6. Structures of γ -ray induced primary radicals proposed for polyamides in the literature.

Difference between various author's points of view is whether the vicinal protons are magnetically equivalent or not. If the three protons are assumed to be magnetically equivalent, the free electron couples with the protons equally and gives a four-line spectrum with an intensity of 1:3:3:1 according to the rule (number of lines is equal to $2nI + 1$, n is the number of equivalent nucleus coupling with the free electron and I is the spin quantum number of the nucleus, in this case $I=1/2$). Thus, the peak at the center may be attributed to a singlet. As a result, the spectrum consists of a four-line and a superimposed singlet belonging to different radical.

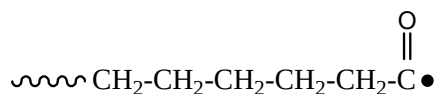
If the protons are not magnetically equivalent, the free electron couples with the proton at alpha position and then with the two protons at beta position. As a result, six-line spectrum is obtained according to the rule (number of line= $(2n_A I + 1) \times (2n_B I + 1)$, $n_A=1$, $n_B=2$, and $I = 1/2$)

Authors claiming that the spectrum has a four-line and a singlet, attribute the singlet to the structures given below.

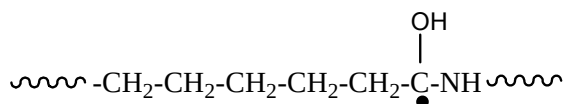
P. Simon et al [21]



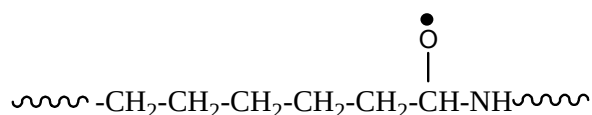
Li and Zhang [22]



F.Scosz et al [19]



Graves and Ormerod [16]



The radical proposed by Li and Zhang [22] for long lived ESR singlet is not as much stable as to detect after the long irradiation period. Moreover, it is expected that the radical should have a triplet like ESR spectrum as the carbon atom next to the carbonyl group has two hydrogen atoms.

However the radical proposed by Scosz et al [19] for long lived ESR singlet may be expected to be stable as the free electron is on the tertiary carbon atom, the radical should have an ESR spectrum with three lines due to the coupling of the free electron with two hydrogen atoms of carbon atom at the beta position.

The structure proposed by Graves and Ormerod [16] should have a doublet ESR spectrum due to the hydrogen atom on the carbon atom at the beta position.

As will be discussed later in detail, the long lived singlet ESR line was attributed to the radical as in the Simon et al's [21] claim. Furthermore, our study showed that the experimental ESR spectrum of N3 irradiated in nitrogen is a combination of two types of six-line superimposed belonging to two types of radiation induced primary radical and the singlet belonging to the radical discussed above.

6.3.2. Change in the Shape of ESR Spectra

In our study, 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.

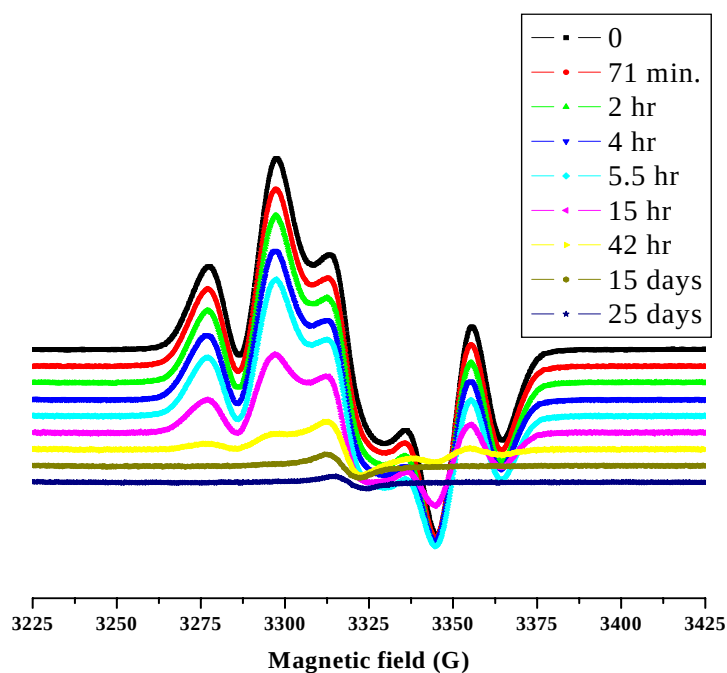


Fig.6.7. Change in the shape of ESR spectra of γ -irradiated N3 sample in nitrogen at room temperature

The ESR spectra of N3 recorded as a function of time were subtracted from the spectra recorded earlier to obtain the ESR spectra of radical (s) decayed in the period. As easily shown in figure.6.8, decayed radical (s) has almost same ESR pattern at each period except 4th day-10th day. It means that either only one type of radical decays or several types of radical co-exist and are decaying during the four days.

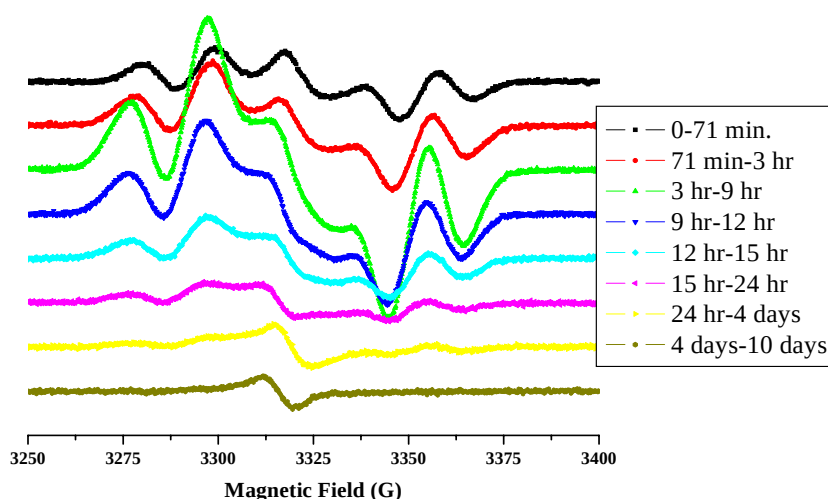


Fig.6.8. ESR spectra of the radicals decayed during storage in nitrogen at room temperature.

6.3.3. Simulation Study

When simulation of the experimental ESR spectra was carried out assuming that the spectrum consists of two different six-line spectra and a singlet spectrum, fitting study gave best results. (R1:49%, R2:32%, R3:19%) Parameters of the best fit were given in Table. 6.1. According to the results of

the simulation study, the experimental spectrum was attributed to the presence of radicals;

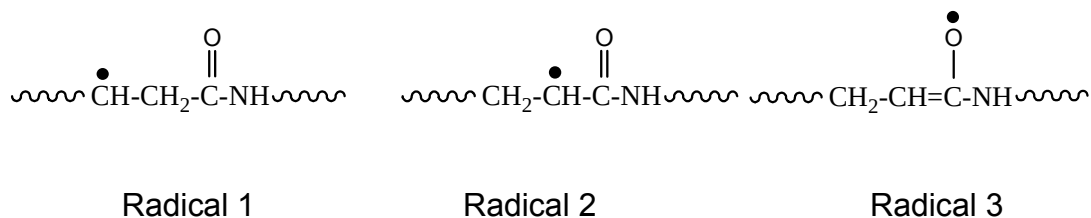


Fig.6.9. Structures of radiation induced radicals proposed for N3

Radical 1 has a hydrogen atom at alpha position to unpaired electron and two hydrogen atoms at beta position as in Radical 2. Coupling of the unpaired electron with a hydrogen atom at alpha position and then two hydrogens at beta position results in a six-line ESR shape as discussed above. As the chemical environments of unpaired electrons in two cases are different, the ESR lines of the two radicals have different parameters, too. It is very difficult to make a decision of which six-line spectrum belongs to which radical at this stage. As it will be seen later however, ESR study of 3mN3 will help to solve this dilemma.

Table.6.1. Parameters obtained from the simulation of experimental ESR spectra of N3 irradiated in nitrogen

	First Hyperfine Splitting Constant, (G)	Second Hyperfine Splitting Constant, (G)	Line Width, $\Delta H_{1/2}$ (G)	g-value	Type of ESR Lines	Abundance of radicals, %
Radical 1	19.35±0.13	13.81±0.13	5.52±0.9	2.0032±0.0003	Gaussian	32
Radical 2	35.03±0.10	20.31±0.10	6.09±0.5	2.0031±0.0002	Gaussian	49
Radical 3	-	-	10.12±0.14	2.0042±0.0004	Lorentzian	19

Figure.6.10 shows experimental and simulated ESR spectra.

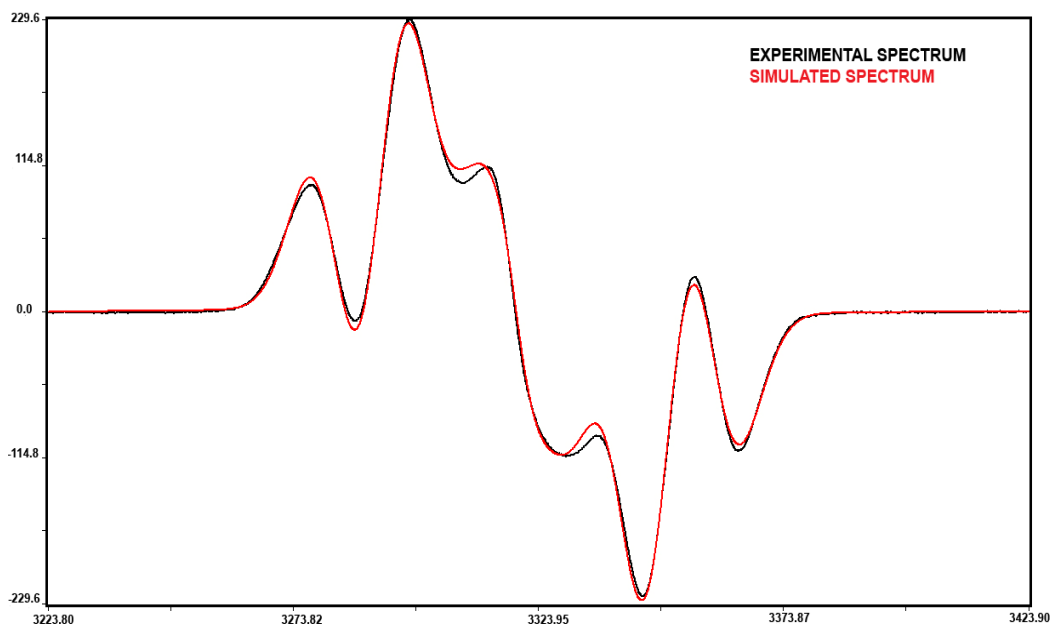


Fig.6.10. Simulated (red line) and experimental (black line) ESR spectra of N3 irradiated in nitrogen.

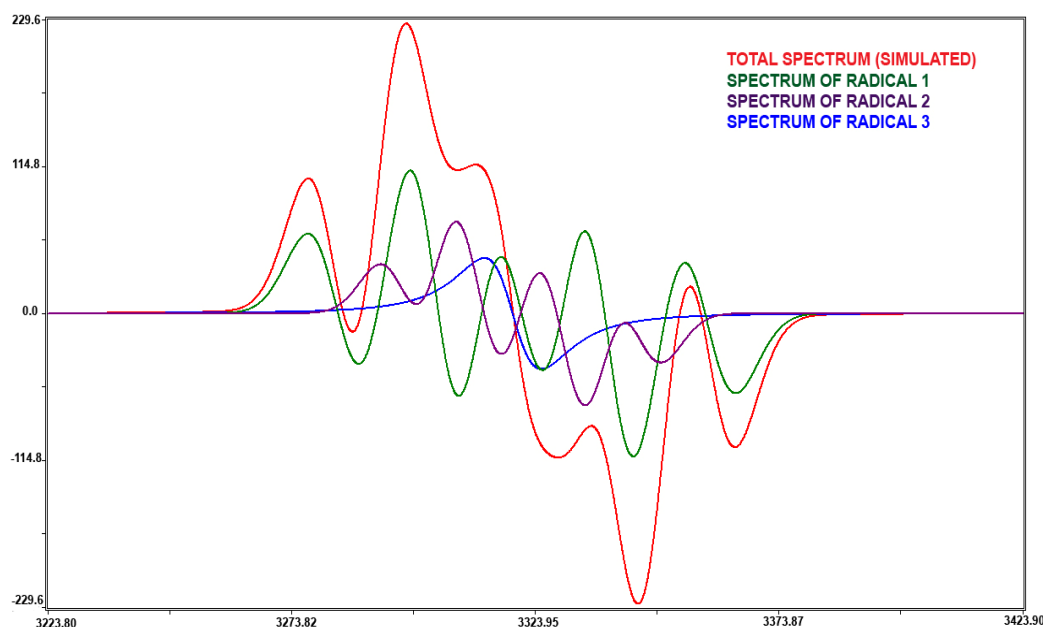


Figure.6.11. Simulated ESR spectrum of N3 irradiated in nitrogen and components of the simulated ESR spectrum

6.3.4. Radical Formation and Decay Mechanism

The mechanism given in Figure.6.12 may be proposed for the formation of the radicals responsible from the experimental ESR spectrum.

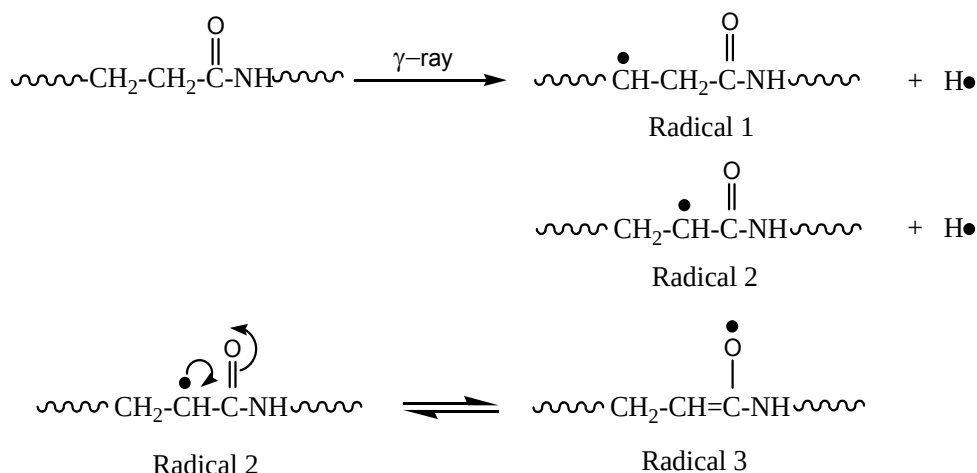


Fig.6.12. Formation mechanisms of the radicals proposed

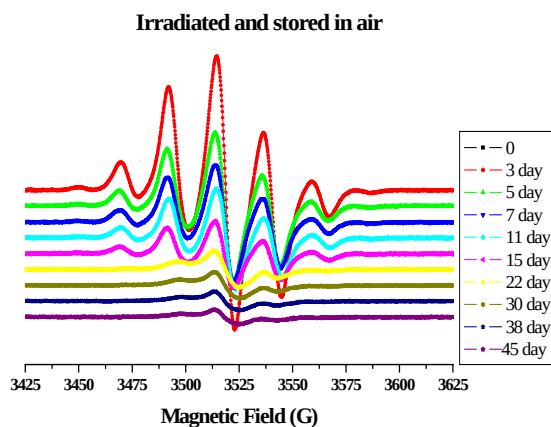


Fig.6.13. Change in the relative concentration of the radicals with time

Figure.6.13 shows the time dependence of normalized radical concentrations. At first glance, the R3 seems to have higher stability than the others. It is very

striking that the R3 began to decay slower than expected when the concentrations of R1 and R2 approached to zero (after about 50-hours storage). This behavior may be explained if the decay of R3 undergoes through the reactions below.

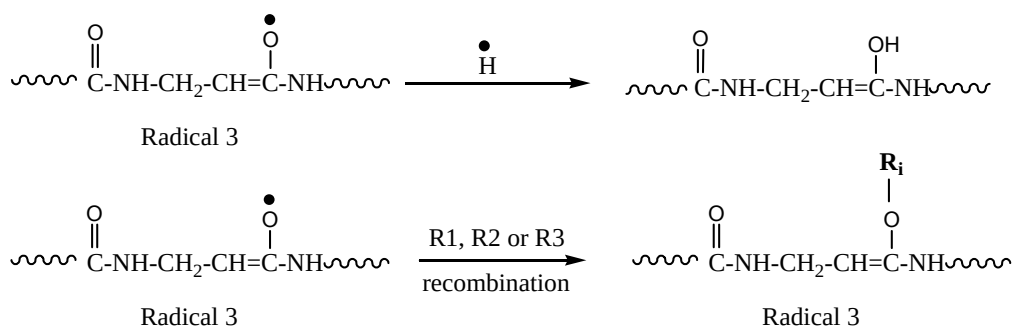


Fig.6.14. Decay mechanisms of Radical 3. R1, R2, and R3 denote Radical 1, Radical 2 and Radical 3, respectively. R_i denotes any of the R1, R2 and R3.

As the concentration of R3 is relatively low (19 % of total radical concentration), the probability of recombination is also very low. According to the decay reactions in Figure.6.14, decay rate of the R3 depends on the concentration of hydrogen radicals (H^{*}), the amount of hydrogen atoms around the R3 and concentration of all other radicalic species. As the amount of hydrogen atoms around the R3 will not change considerably, decrease in the decay rate of R3 may be explained by the decrease in the concentrations of hydrogen radicals (H^{*}) and other species with time. Generation of hydrogen radicals (H^{*}) is possible by decay of R1 and R2 according to the reactions;

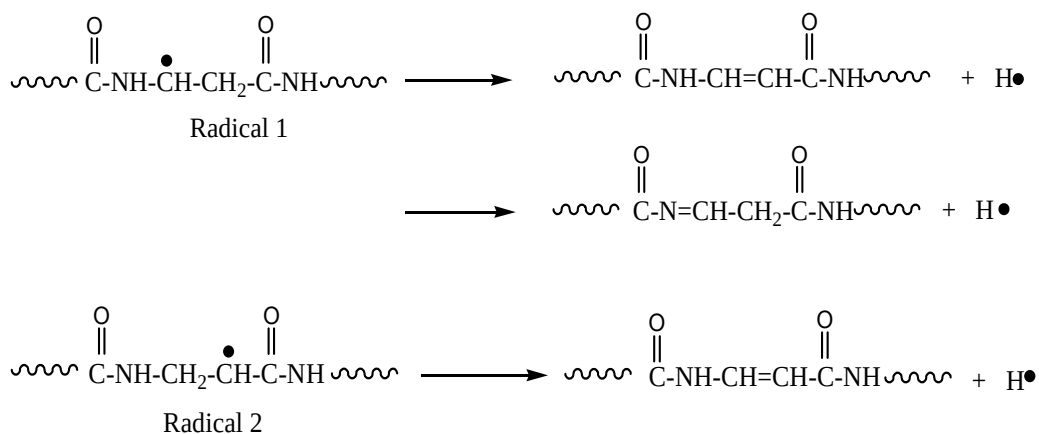
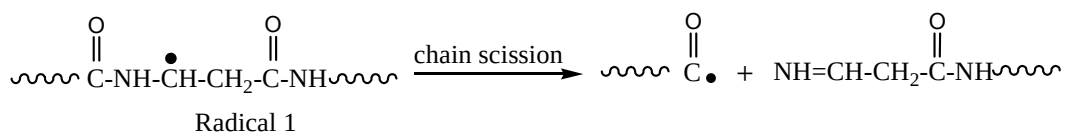


Fig.6.15. Decay mechanisms of R1 and R2 through hydrogen radical removal.

After about 50-hour storage, as the concentration of R1 and R2 reaches to zero, the decay of the R3 may be possible just by recombination of R3 and abstraction of hydrogen atom from macromolecules. This is why the decay rate of R3 decreases when the concentration of R1 and R2 reaches to zero. This approach explains also the decay mechanisms of R1 and R2 as shown in the reactions above.

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 experiences competition. Therefore, additional mechanisms (in Figure. 6.16) including chain-scission and crosslinking may be suggested for the consumption of radicals;



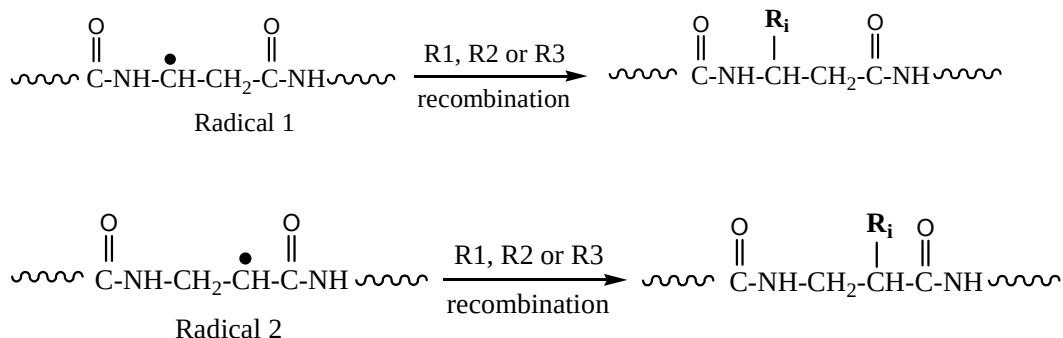


Fig.6.16. Decay Mechanisms of R1 and R2 through recombination and disproportionation.

As discussed above in the characterization of N3, inherent viscosities of pristine and irradiated polymers in air and nitrogen were determined. Inherent viscosity of a sample irradiated in nitrogen remained almost constant. This behavior may be deduced to competition of crosslinking and chain-scission reactions. However, inherent viscosity of N3 irradiated in air decreased with integral doses exposed. This shows that chain scission predominates over crosslinking in irradiation in air. The behavior may show that the primary radicals prefer peroxydation reaction instead of recombination in air.

As remembered in the characterization of pristine and N3 irradiated in air, relative intensity of methylene hydrogens decreased after irradiation. Considering the result as well, the decay mechanisms of each radical may be outlined as;

Decay Mechanisms of Radical 1:

The decay reactions in Figure.6.17 take place simultaneously during decay of the R1 in nitrogen. The reactions A and B were discussed before to explain the decrease in the decay rate of R3. The radiation induced unsaturation of

irradiated polyamides has been reported by Zimmerman [24] and Gupta and Pandey [25], too. The reaction C and D explain the competition between crosslinking and chain-scission reaction in nitrogen. Moreover, the reactions B, C and D result in decrease in the relative amount of aliphatic hydrogen next to the NH group as discussed in ^1H -NMR spectrum of irradiated N3. As the pristine N3 has double bonds at the end-groups, FT-Raman study of pristine and irradiated polymers did not give information about the radiation-induced unsaturation. In addition to reactions given below, peroxydation chain reaction take places in air as discussed before.

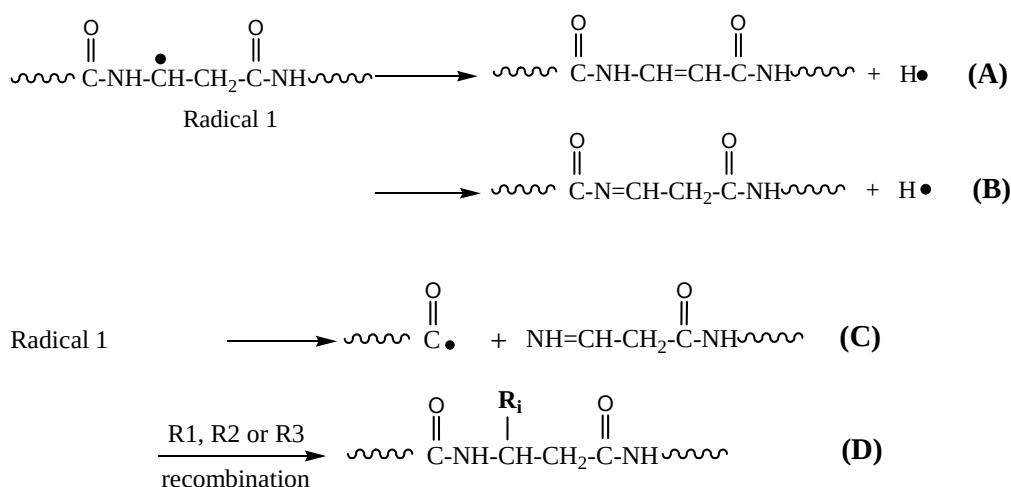


Fig.6.17. Probable decay mechanisms of Radical 1. R_i denotes any of the R1, R2 and R3.

Decay Mechanisms of Radical 2:

The same explanations including double bond formation and crosslinking may be done for the reaction E and G. The reaction F was discussed in the section of formation mechanism of R3.

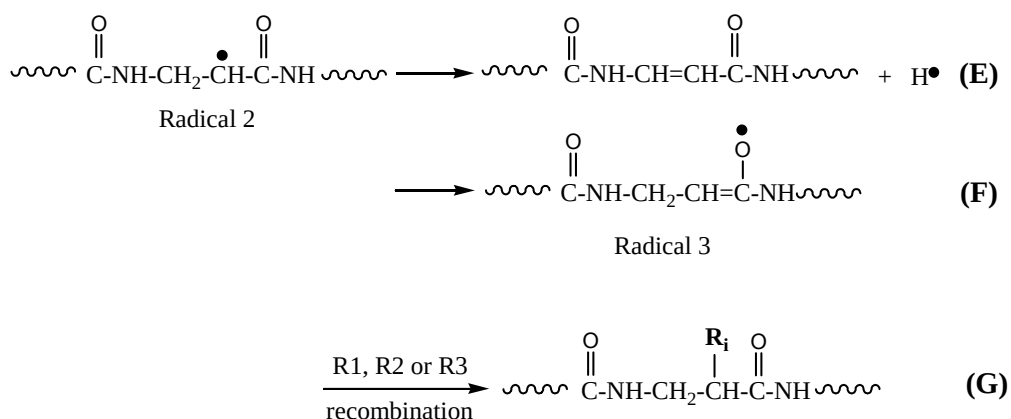


Fig.6.18. Probable decay mechanisms of Radical 2. R_i denotes any of the R1, R2 and R3.

Decay Mechanisms of Radical 3:

As discussed before, the reactions undergo relatively faster until R1 and R2 have consumed. As the probability of recombination of R3 is low, the decay of the R3 undergoes mainly by reaction H when the amount of other species reached to zero.

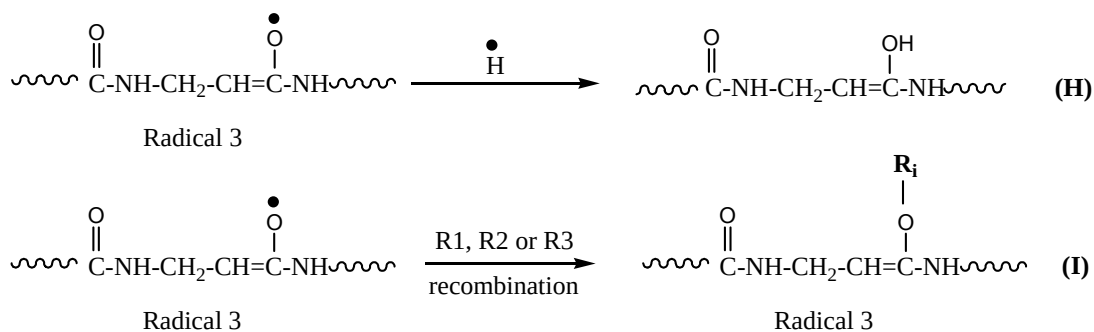


Fig.6.19. Probable decay mechanisms of R3. R_i denotes any of the R1, R2 and R3.

6.3.5. Decay Kinetics of the Radicals

Decay kinetics of radicals can be investigated with respect to first or second order kinetics by conventional analysis. The plot of $\ln$ (concentration) versus time in Figure.6.20 may be investigated in two stages. The first is the first stage of the storage (until 50th hours). At this stage, the plot shows linear behavior with a good correlation coefficient of 0.999 for the three radicals. The initial stage of decay kinetics apparently follows a first order decay. However, at the second stage, the plots showed deviations from linearity and the radicals continued to decay relatively slower. This may be explained by the semi-crystalline structure of the polymer. As the segmental motions in amorphous region are much more than those in crystalline regions at room temperature, the radicals in amorphous regions are responsible from the relatively fast decay at the first stage of storage. After the amount of radicals in amorphous regions reached to zero (at the end of the first stage), the slow decay behavior was observed for the radicals in crystalline regions.

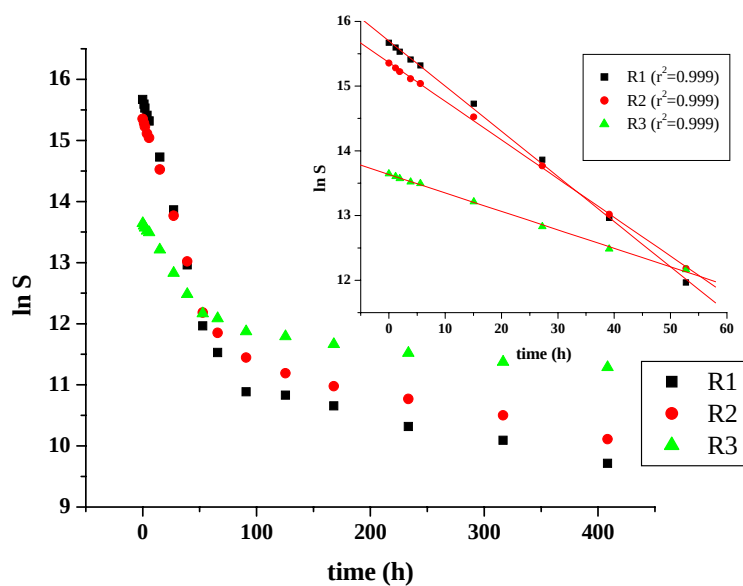


Fig.6.20. Plot of $\ln$ (radical concentration) versus time

To complete our understanding of the decay behavior of the radicals better, reciprocal of concentrations of each radical was plotted versus storage time. Figure.6.21 shows that the plots are not linear except R3 in the second stage.

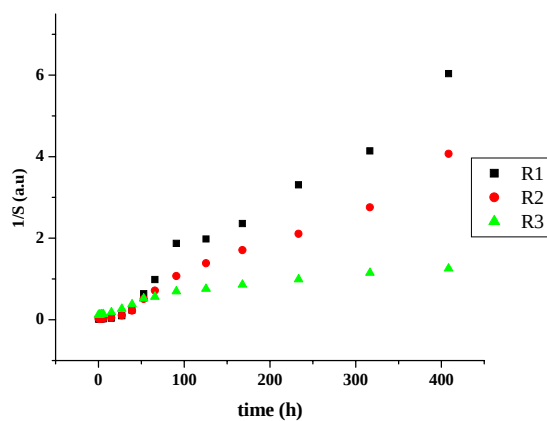


Fig.6.21. Plot of reciprocal of concentrations of each radical in nitrogen versus time

6.4. Comparison of Decay of the Radicals in Air and Nitrogen

As shown in Figure.6.22, decay rate of each radical is higher in air than in nitrogen. This explains the scavenging effect of oxygen on the decay mechanism of the radicals through relatively fast peroxydation reaction

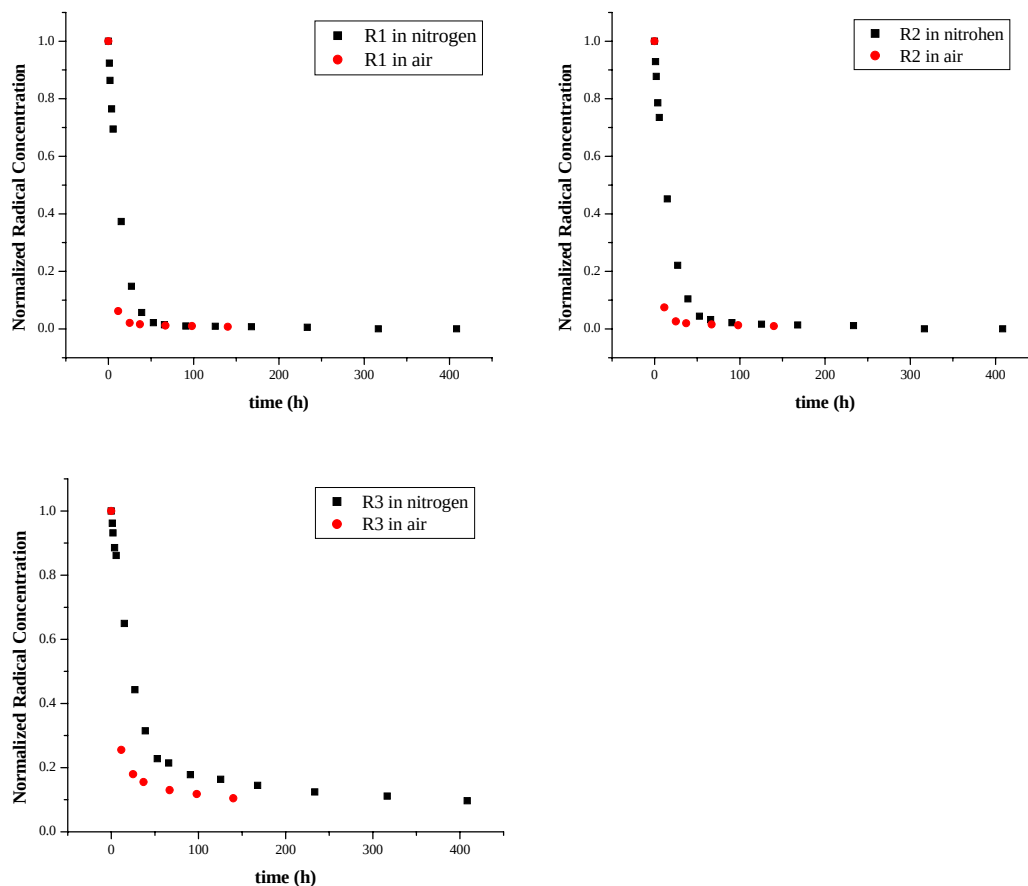


Fig.6.22. a) The plot of normalized concentration of Radical 1 in air and nitrogen versus time **b)** The plot of normalized concentration of Radical 2 in air and nitrogen versus time **c)** The plot of normalized concentration of Radical 3 in air and nitrogen versus time

6.5. ESR INVESTIGATION OF 2-METHYL NYLON3 IRRADIATED AND STORED IN AIR

6.5.1. ESR Shape

The spectrum shown in Figure.6.23 was recorded immediately after γ -irradiation of 2mN3 sample in air. Although the ESR spectrum of the irradiated 2mN3 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.

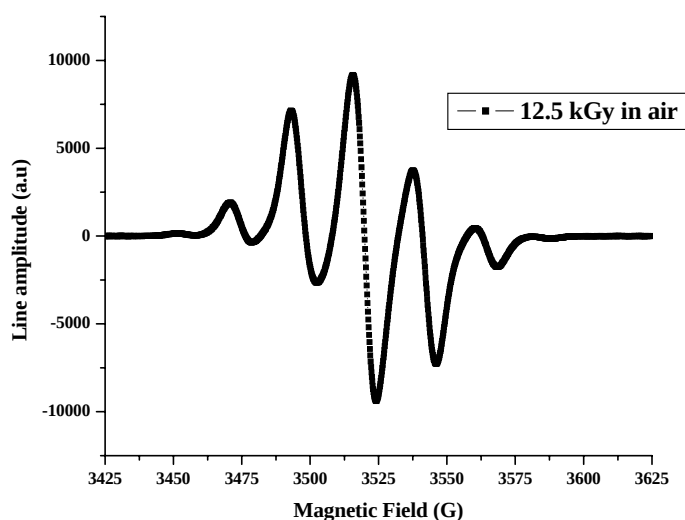


Fig.6.23. ESR spectrum recorded immediately after irradiation of 2mN3 in air

As will be discussed later, the spectrum has been resolved to be the combination of three types of ESR spectrum belonging to three types of radical.

6.5.2. Change in the Shape of ESR Spectrum

The change in the shape of ESR spectrum has been investigated to estimate the types of the radicals contributing to the spectrum. The intensity of the ESR spectrum recorded immediately after irradiation decreased slowly to about 25 % of its initial value in 15 days without showing any change in its shape when the sample was stored at room temperature. The spectrum was observed to be converted to almost a three-line ESR line spectrum with lower intensity as the intensity of the wing peaks reached to the noise level.

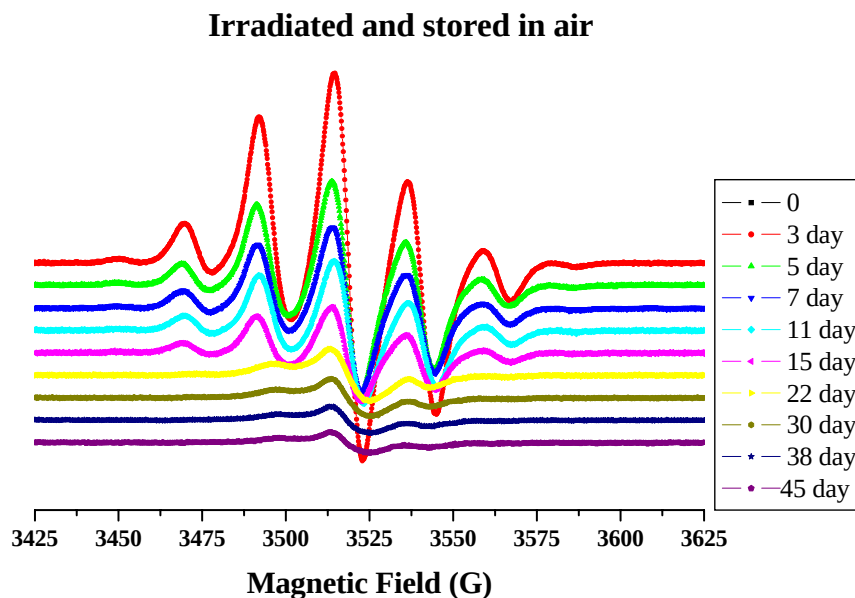
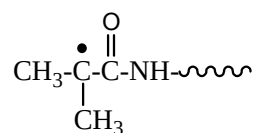


Fig.6.24. Change in the shape of experimental ESR spectrum of 2mN3 irradiated and stored in air with time

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 radical existed in 2mN3 irradiated in air.

6.5.3. Simulation Study

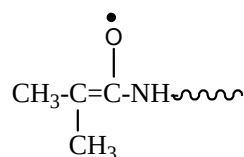
The simulation study did not give plausible results however, when two types of radicals (seven-line and singlet) were assumed to contribute to the experimental spectrum, simulation workouts of the experimental ESR spectrum showed an additional multiplet ESR spectrum in each case. The seven-line spectrum was assigned to a radical (R1 shown in Figure.6.25) 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.



Radical 1

Fig.6.25. Structure of the Radical 1

The singlet spectrum is most probably due to the unpaired electron on the oxygen atom (R3).



Radical 3

Fig.6.26. Structure of the R3

The probable radicalic structures were considered for the multiplet ESR lines obtained from simulation study.

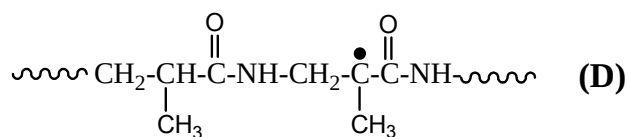
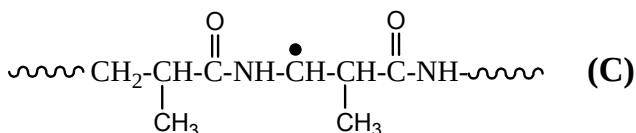
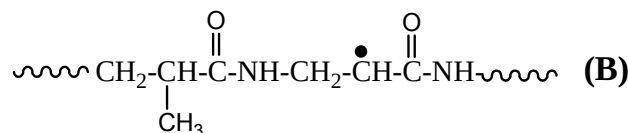
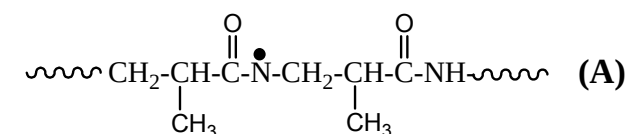


Fig.6.27. Probable radicalic structures responsible from the multiplet ESR spectrum obtained from simulation study

The radical A has an unpaired electron on nitrogen atom with nuclear spin of 1. Expected ESR spectrum for the radical should be equally spaced triplet or triplet of triplet (nine-line) if the two hydrogen atoms on the next carbon atom couples with unpaired electron, too.

The radical B, was discussed in the N3 section, should have a six-line ESR spectrum with intensity ratio of 1:2:1:1:2:1 as it is a triplet of doublet. Moreover, the radical B corresponds to the Radical 2 in N3 which has a life time of three-four days. However, the multiplet ESR spectrum has a life time of at least a month as will be seen later.

The Radical C should have a four-line ESR spectrum with equal intensity as it is a doublet of doublet. Here, the hydrogen atom on the nitrogen may be expected to couple with the unpaired electron. Some authors (Graves and Ormerod [16], Kashiwagi [18]), have reported that the effect of nitrogen atom is just line broadening due to a small splitting. Burrell [17] and Kashiwagi [18] reported that the hydrogen atom on the nitrogen do not include in the coupling of unpaired electron on the carbon atom at alpha position as the N-H bond does not overlap with the p-orbital of the radical. As a result, the Radical C should have an ESR spectrum with four-line.

The simulation study of a radical shown in Figure.6.28 with similar structure to the Radical D has been reported by Kuzuya et al [46] and Sakai and Iwasaki [47]. As both radicals (radical D and the radical reported by the authors) have CH_2 , CH_3 and carbonyl groups at alpha position of the tertiary carbon atom with unpaired electron, the radicals may be expected to have similar ESR spectrum. When the simulation of experimental ESR spectrum of 2mN3 was carried out using the parameters reported for the radical shown in Figure.6.28. Simulation yielded results with good correlation coefficients for each experimental ESR spectrum of 2mN3. The results were outlined in Table.6.2. Therefore, the

multiplet spectrum (actually superposition of sixteen lines) was assigned to the radical D (it will be mentioned as Radical 2).

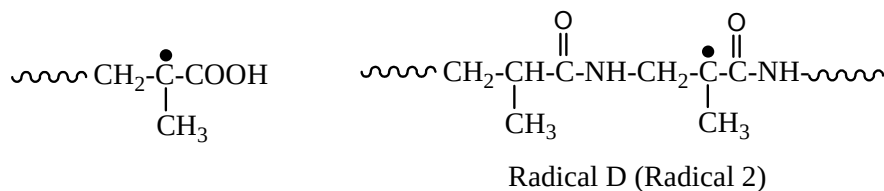


Fig.6.28. Structure of radical proposed by Kuzuya et al [46] and Sakai and Iwasaki [47] for the simulated multiplet ESR spectrum and structure of radical proposed for the simulated multiplet ESR spectrum

Table.6.2. The ESR parameters obtained from simulation of experimental ESR Spectra of 2mN3 irradiated in air. R1, R2 and R3 denote Radical 1, Radical 2 and Radical 3, respectively. Hsc, hyperfine splitting constants; $\Delta H_{1/2}$, line-width; A, abundance of the radicals

	1.Hsc (G)	2.Hsc (G)	3.Hsc (G)	$\Delta H_{1/2}$ (G)	g-value	Type of line	No of line	A, %
R 1	21.65 ± 0.05	-	-	3.40 ± 0.15	2.0030 ± 0.0001	Gaussian	Seven-line	20
R 2	21.05 ± 0.10	14.80 ± 0.10	8.95 ± 0.10	4.30 ± 0.20	2.0035 ± 0.0002	Gaussian	Multiplet	77
R3	-	-	-	4.62 ± 0.20	2.0029 ± 0.0001	Gaussian	Singlet	3

The experimental and simulated ESR spectra were given in Figure.6.29. The correlation coefficient of the simulation shown in Figure.6.29 was observed as 0.996. The simulated ESR spectrum and its components were given Figure.6.30.

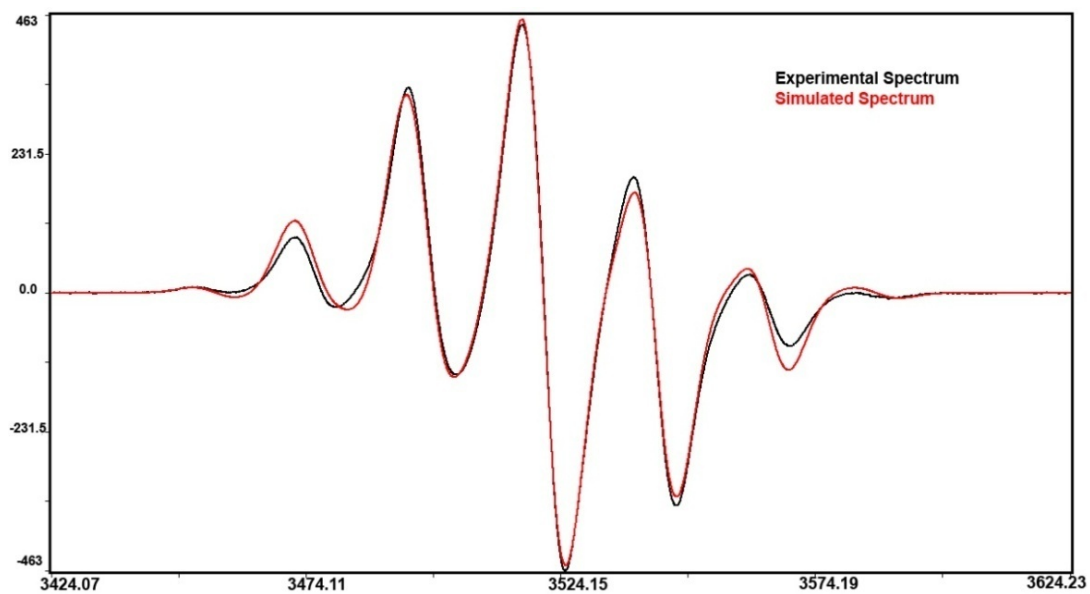


Fig.6.29. Experimental (black line) and simulated (red line) ESR spectra of 2mN3

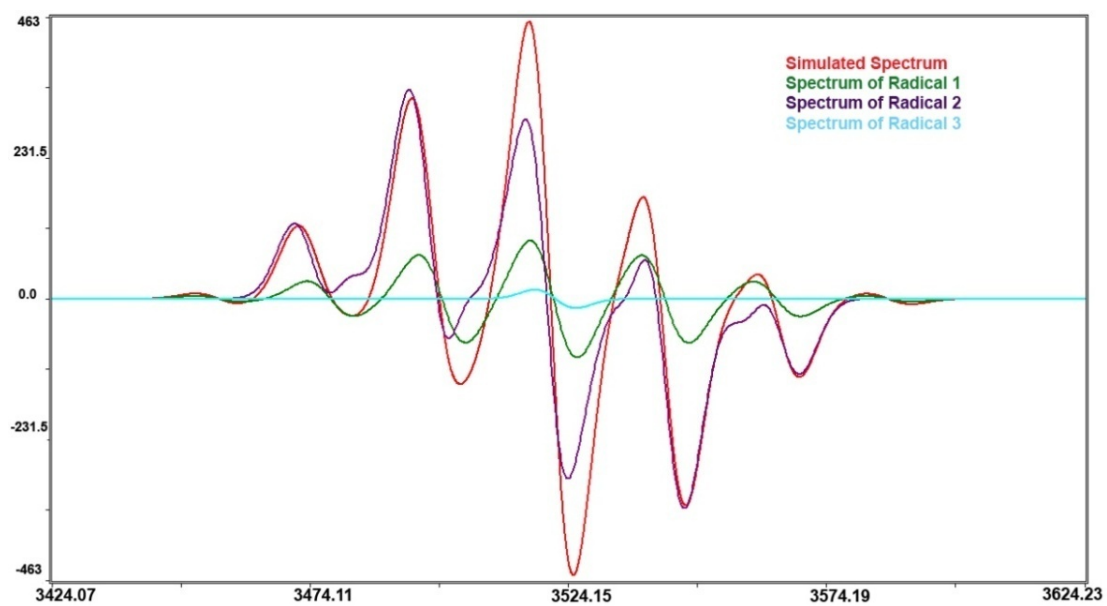


Fig.6.30. Simulated ESR spectrum (red line) and components of the simulated ESR spectrum

6.5.4. Radical Formation

Two mechanisms have been proposed for the formation of the radical 1. Both mechanisms require that chain-scission dominates over crosslinking during the radiolysis. As discussed before, inherent viscosity of irradiated 2-methyl nylon 3 decreased after being exposed to irradiation in conformity with this proposal. Moreover, the ^1H -NMR spectrum of 2mN3 irradiated in air showed results (decrease in relative intensities of CH, CH_2 , and NH protons and new peaks at 6-7 ppm attributed to NH_2 protons) consistent with the proposed mechanisms.

Mechanism 1

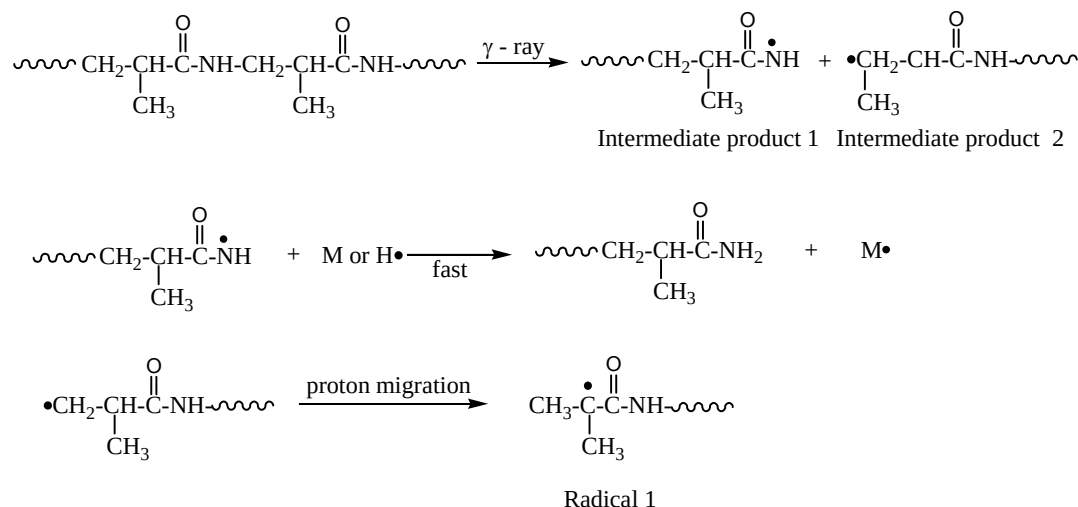


Fig.6.31. A mechanism proposed for formation of radical 1.

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 not stable enough, 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 been reported by Chang and La Verne [23]. As this reaction is too fast, any ESR signal was not 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 [Bruice, 48].

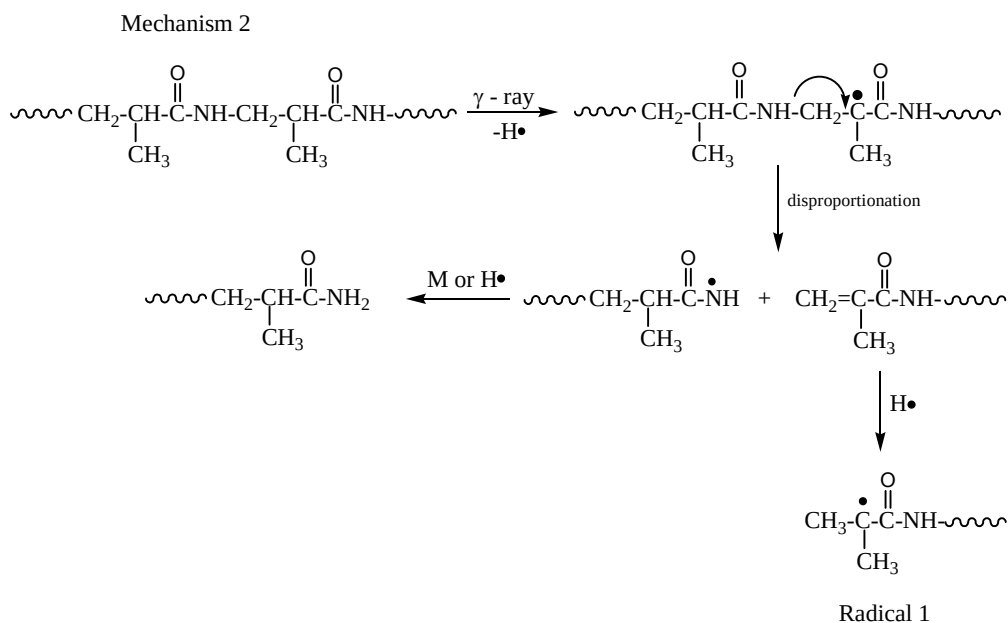


Fig.6.32. The second mechanism proposed for formation of Radical 1.

In the mechanism 2 proposed, once the proton on carbon atom next to the carbonyl group was removed during irradiation, chains scission takes place via disproportionation reaction (reason for decrease of inherent viscosity of irradiated 2mN3). The product decays by hydrogen atom abstraction. The other product of disproportionation may react with a hydrogen radical ($\text{H}\cdot$) to form

Radical 1. The second mechanism is more favorable as it also explains the formation of Radical 2 proposed in the simulated multiplet ESR spectrum. As remembered, 2mN3 have olefinic groups at chain ends. The olefinic groups have the same structure with the disproportionation product in Figure.6.32. Therefore, the Radical 1 may generate catching the hydrogen radicals ($H^{\bullet}$) as shown in Figure.6.33 during irradiation as well.

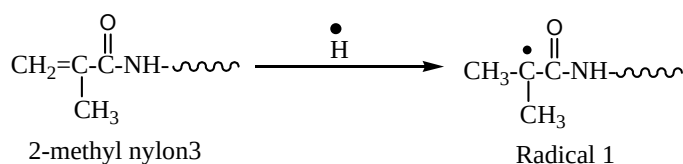


Fig.6.33. Generation of Radical 1 through abstraction of hydrogen radical ($H^{\bullet}$) by the olefinic methylene at the end of chain

As the radical 3 has a singlet ESR spectrum, the unpaired electron should be on an oxygen atom which has no nuclear spin. Furthermore, the atom next to the oxygen atom should have no hydrogen atom to couple with the unpaired electron on the oxygen atom. Radical 3 may develop by the transformation of radical 1 as shown in the reaction below;

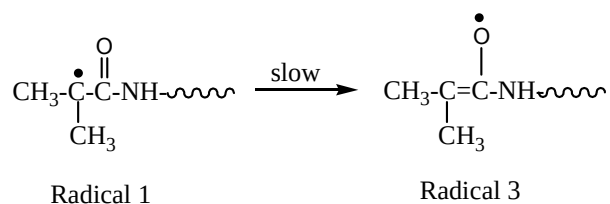


Fig.6.34. Formation reaction of radical 3

It is assumed that the above transformation is very slow as the seven-line and singlet spectra remain until all the radical decays.

Decay of each radical may take place through several reactions simultaneously. As the sample was stored in air, most of the radicals probably decay by peroxydation reactions discussed in the previous section (ESR investigation of N3). As stated above, ^1H -NMR spectrum of 2mN3 irradiated in air shows new NH_2 peaks at 6-7 ppm. This shows that the remaining radicals decay through disproportionation given above. The decrease in the inherent viscosity of irradiated 2mN3 verifies the disproportionation reaction.

6.5.5. Decay Kinetics of the Radicals

Time dependence of normalized radical concentrations was plotted and shown in Figure.6.35 As can be easily seen the concentrations of each radical are decreasing very fast in the first stage of the storage (until about 100 hours). After about 100 hours, the concentrations of each radical start to decrease slowly. This behavior may be explained if the semi-crystalline structure of 2mN3 is considered. The radicals at the amorphous regions decay faster as the chain segments are more flexible in the amorphous regions than those in crystalline regions at room temperature. This flexibility in amorphous region increases not only the recombination probability of radicals but also the probability of abstraction of hydrogen. Furthermore; as the sample was stored in air, diffusion of oxygen molecules, is easier into the amorphous regions than into the crystalline regions causing further decay reactions.

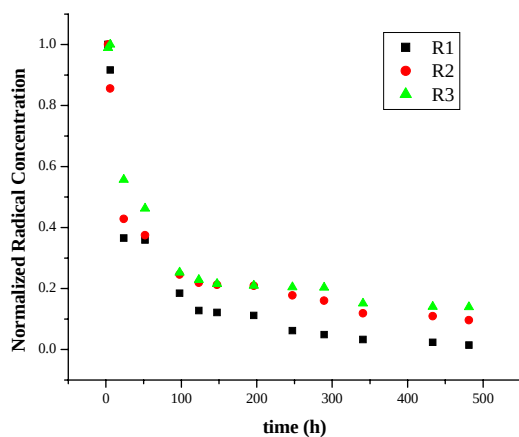


Fig.6.35. Plots of normalized radical concentration versus storage time.

To complete our understanding of the decay behavior of the radicals better, $\ln(\text{radical concentration})$ versus time and inverse of the radical concentrations versus time were plotted for each radical as shown in Figure.6.36.

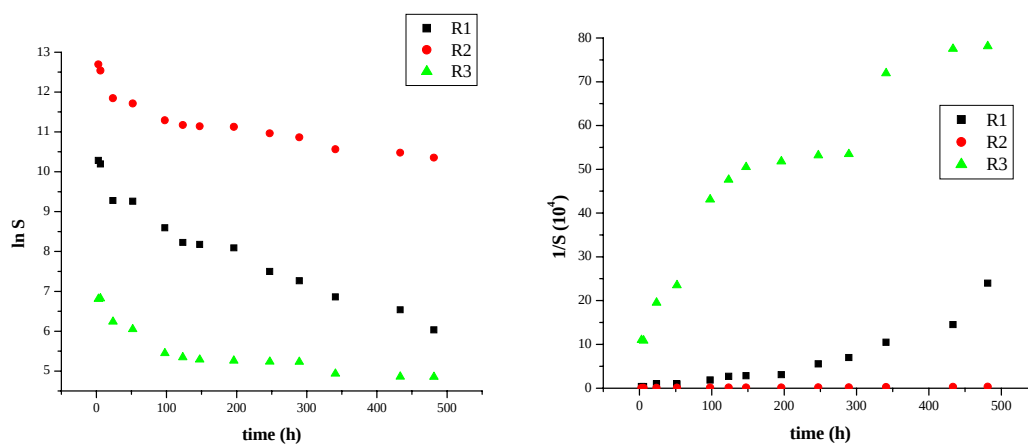


Fig.6.36. a) Plot of $\ln$ (radical concentration) versus time **b)** Plot of inverse of radical concentration versus time. S denotes radical concentration.

As the plots in above figures do not yield straight lines, it is difficult to propose whether the decays follow first or second order reactions.

6.6. ESR INVESTIGATION OF 2-METHYL NYLON3 IRRADIATED AND STORED IN NITROGEN

6.6.1. ESR Shape

The spectrum shown in Figure.6.37 was recorded immediately after γ -irradiation of 2mN3 in nitrogen at room temperature. The shape of the ESR spectrum is similar to the case in air. The main difference is in the intensities of ESR lines. However the samples have almost the same mass, the intensity of ESR lines of the sample irradiated in nitrogen is much greater than the case in air. Even, the integral dose subjected to the sample in nitrogen is lower than the case in air. This shows clearly the effect of oxygen on decay of the primary radicals.

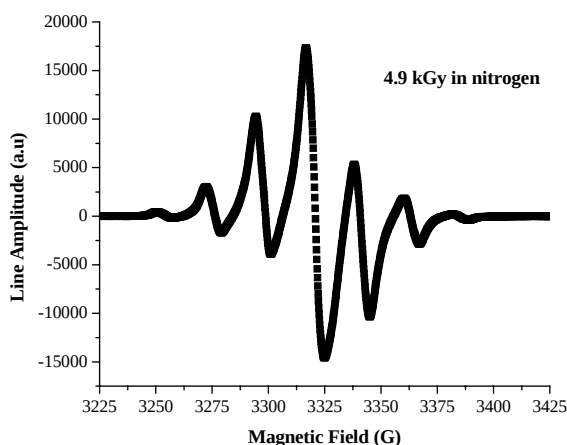


Fig.6.37. ESR spectrum recorded immediately after irradiation of 2mN3 in nitrogen.

As will be discussed later, once the simulation study was carried out the ESR spectrum shown in Figure.6.37 was assigned to the three types of radicals as in the case in air.

6.6.2. Change in the Shape of ESR Spectra

The changes in the ESR spectra of 2mN3 irradiated in nitrogen were followed with time to have information about the components of the experimental ESR spectrum. Although the change in the shape has been followed for almost a month, no significant changes in the shape of the spectra were observed except in intensities as shown in Figure.6.38.

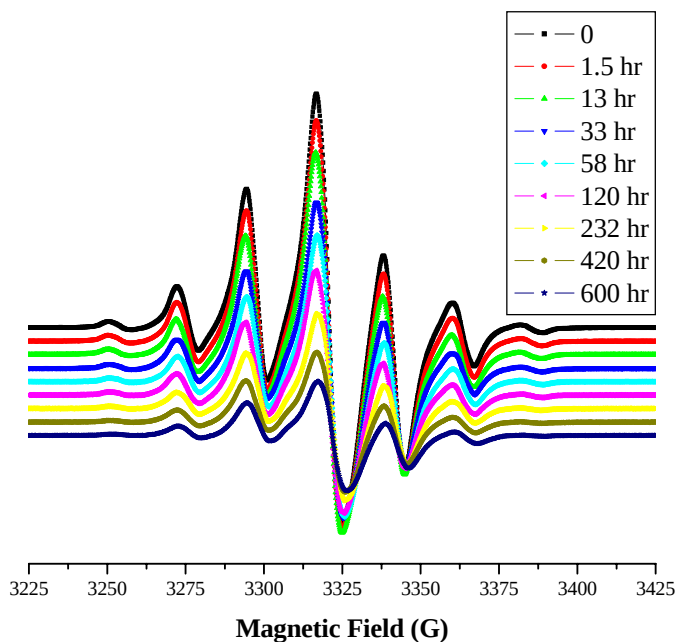


Fig.6.38. Change in the shape of ESR spectrum of 2mN3 irradiated in nitrogen with time.

Temperature dependence of the ESR lines was investigated by heating the sample irradiated in nitrogen. The change in the shape of ESR lines was shown in Figure.6.39.

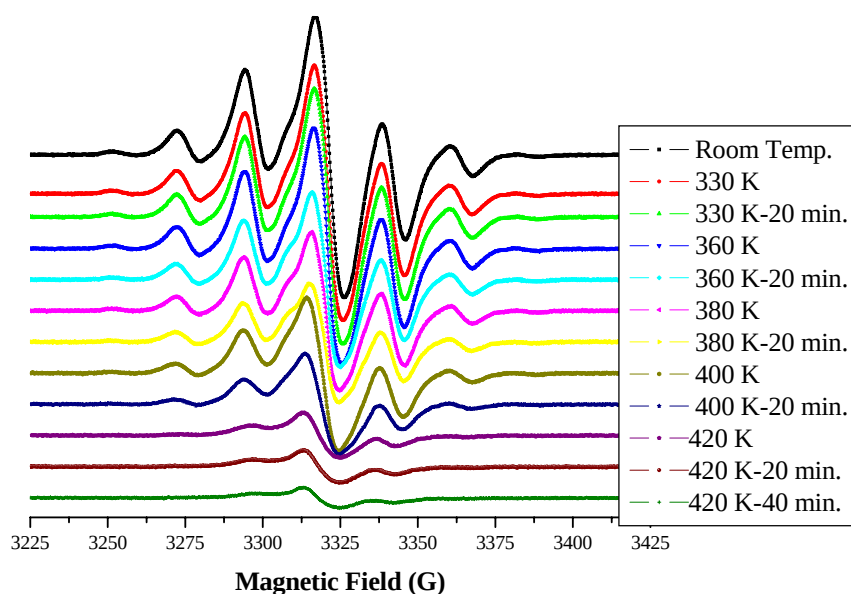


Fig.6.39. Change in the shape of ESR spectrum of 2mN3 irradiated in nitrogen with heat treatment

The shape of the ESR spectra did not change although the temperature of the sample reached above the glass transition temperature of the polymer (determined before as about $T_g=360$ K) and stored at a temperature (380K and 400K) above the T_g for about an hour). This behavior explains the trapping of some of the radicals in crystalline regions where the segmental motions are still restricted at the stated temperatures. ESR spectra began to seem as a five-line and three-line at 420 K as the intensity of the wing peaks decreased to the noise levels.

6.6.3. Simulation Study

Simulation of the experimental ESR spectra was conducted by assuming that three types of ESR spectra (seven-line, multiplet, and singlet) superimposed in the experimental spectra as in the case of the experimental ESR spectrum of 2-methyl nylon 3 irradiated in air due to the perfect similarity of both ESR spectra. Results of the simulation study were given in Table.6.3

Table.6.3. ESR parameters obtained from simulation of ESR spectra of 2mN3 irradiated in nitrogen

	1.Hsc (G)	2.Hsc (G)	3.Hsc (G)	Line-width (G)	g-value	Type of line	No of line	A, %
R1	21.6 ±0.10	-	-	4.30±0.28	2.0032±0.0002	Gaussian	Seven-line	13
R2	22.10±0.10	15.70±0.20	8.41±0.05	4.35±0.12	2.0034±0.0003	Gaussian	Multiplet	76
R3	-	-	-	4.05±0.15	2.0016±0.0002	Gaussian	Singlet	11

The main difference between the results of the simulation study of the ESR spectra of 2mN3 irradiated in nitrogen and air is the g-values of the singlet components. As the g-value is a parameter related to chemical structure of the radical, the singlet component of each experimental spectrum may possibly belong to different kinds of radicals.

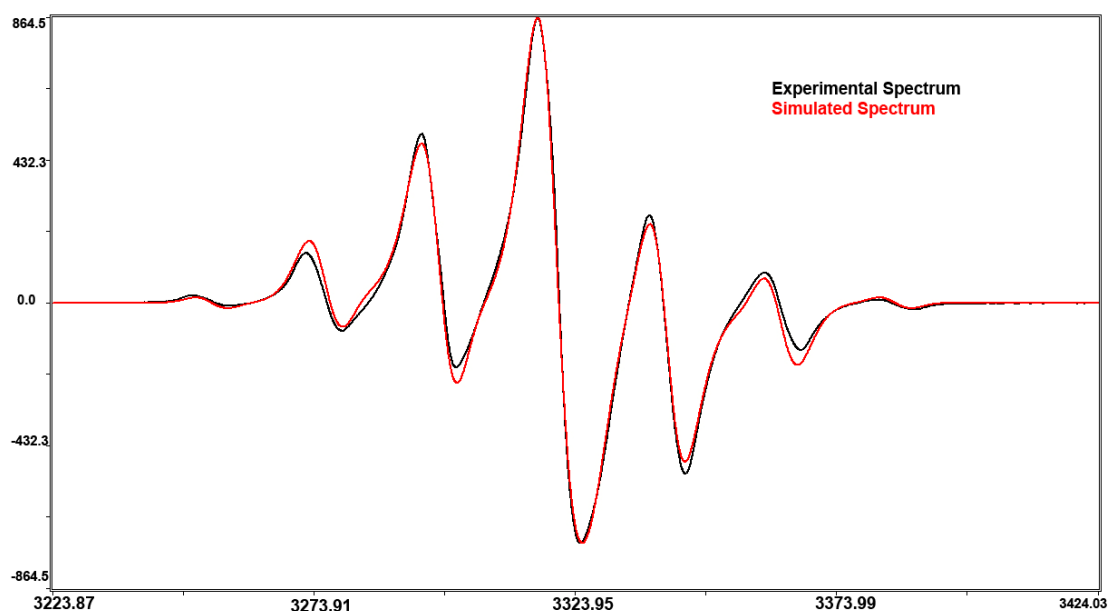


Fig.6.40. Experimental and simulated ESR spectrum of 2mN3 irradiated in nitrogen

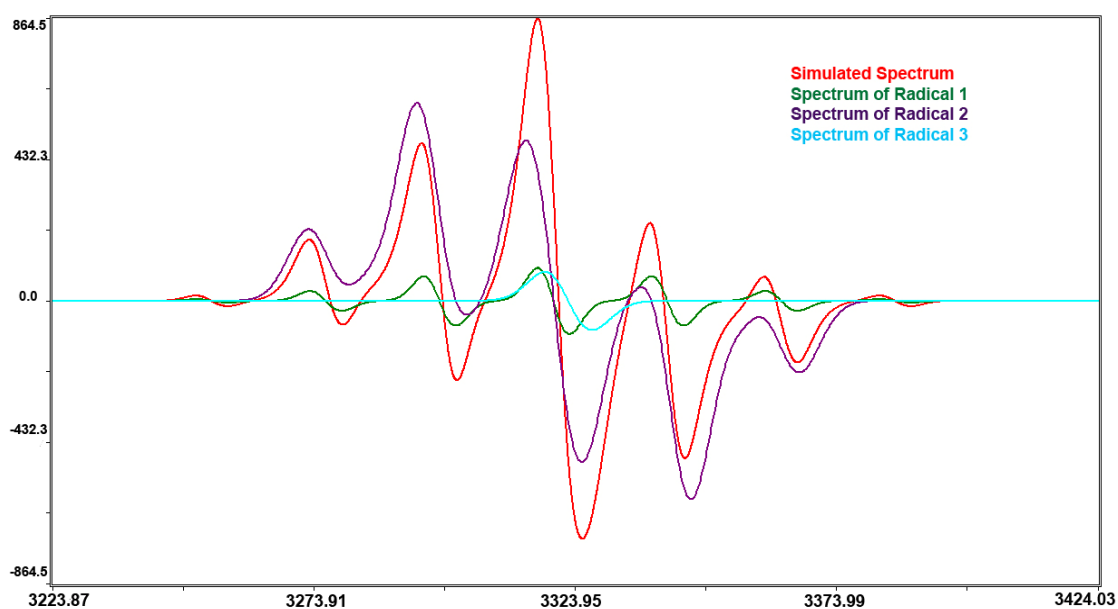


Fig.6.41. Simulated ESR spectrum of 2mN3 irradiated in nitrogen and components of the simulated ESR spectrum

The seven-line spectrum was assigned to a radical (Radical 1) with an unpaired electron coupling with six magnetically equivalent protons as the lines are

equally spaced. The theoretical ratios of the hyperfine splitting components are 1:6:15:20:15:6:1.

The multiplet ESR spectrum (actually sixteen line superimposed) was attributed to a radical (Radical 2) forming by hydrogen abstraction from the carbon atom adjacent to the carbonyl group.

The singlet spectrum is highly possible when the free electron is on the oxygen atom (Radical 3).

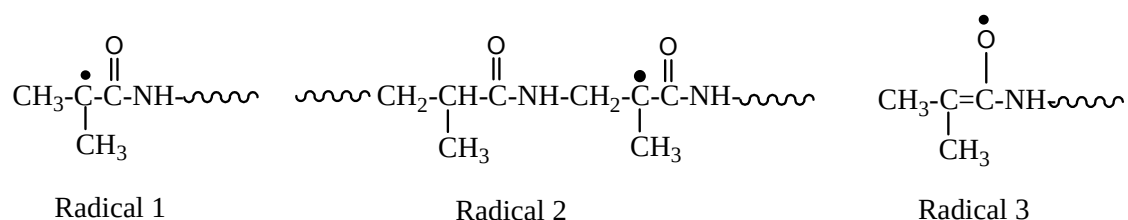


Fig.6.42. The structure of the radicals attributed to the simulated ESR spectrum

6.6.4. Radical Formation and Decay Mechanism

The formation and decay mechanisms of the three radicals were discussed in the previous section (2mN3 irradiated in air). The same mechanisms may be proposed in the case in nitrogen except the peroxydation reactions.

6.6.5. Decay Kinetics of the Radicals

Figure.6.43 shows the time dependence of normalized concentrations of each radical. It seems that the concentrations of each radical decrease abruptly in

one day and then the decay rates of the each radical decrease. This behavior was explained in the previous section considering the semi-crystalline structure of the polymer.

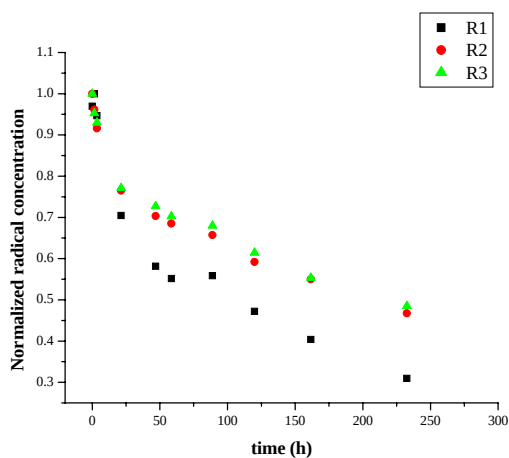


Fig.6.43. Change in the normalized radical concentrations of 2mN3 with storage time

Decay kinetics of each radical can be investigated with respect to first or second order kinetics by conventional analysis. Figure.6.44 shows the plots of $\ln(\text{radical concentration})$ versus time and inverse of radical concentration versus time for each radical. Both plots are not linear for the three types of radical possibly due to the decays of the radicals undergoing more than one type of reaction.

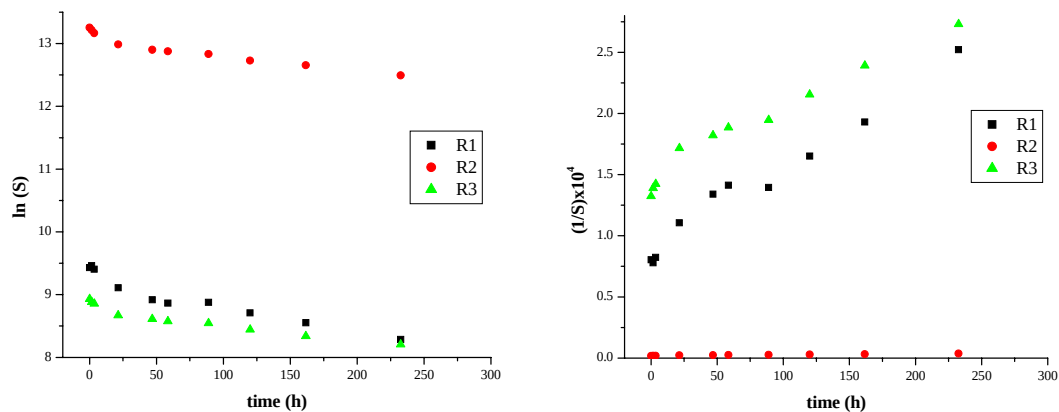


Fig.6.44. a) Plots of $\ln(\text{radical concentration})$ versus storage time. b) Plots of inverse of radical concentration versus storage time. S denotes radical concentration in arbitrary units.

6.7. Comparison of Decay of the Radicals in Air and Nitrogen

As shown in Figure.6.45, decay rate of each radical is higher in air than in nitrogen. This explains the scavenging effect of oxygen on the decay mechanism of the radicals through relatively fast peroxydation reaction.

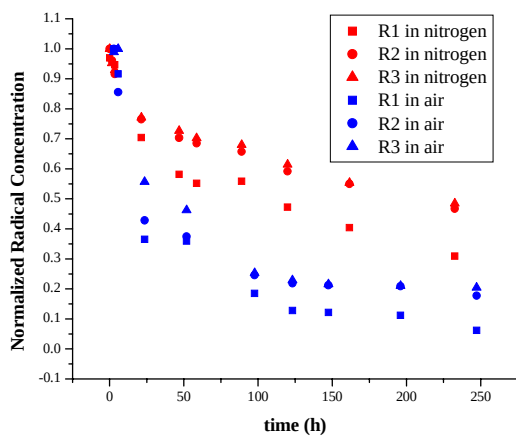


Fig.6.45. Change in normalized concentrations of the radicals in air and nitrogen

6.8. ESR INVESTIGATION OF 3-METHYL NYLON3 IRRADIATED AND STORED IN AIR

The ESR spectrum shown in Figure.6.46 has been recorded immediately after gamma irradiation of 3mN3 in air atmosphere at room temperature. Considering the low intensity and asymmetric character of the ESR spectrum, it was estimated that most of the primary radicals of 3mN3 decayed through relatively fast peroxydation reactions as discussed in the ESR study of N3 irradiated in air.

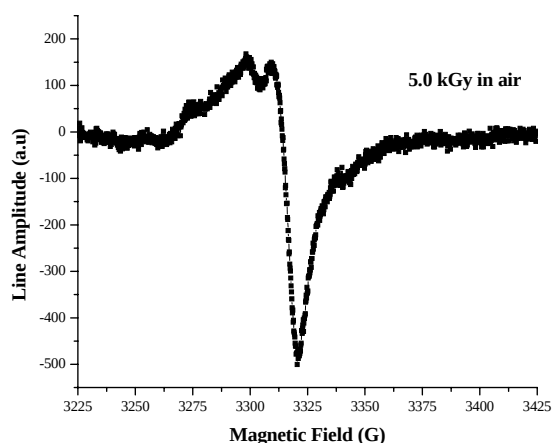


Fig.6.46. ESR spectrum recorded immediately after gamma irradiation of 3mN3 in air

To understand the structure of the ESR spectrum, the change in its shape was followed as a function of time. Moreover, the ESR spectrum of pristine 3mN3 was recorded to see if the asymmetry in the ESR spectrum might be due to the paramagnetic impurities coming from the pristine polymer. Figure.6.47 shows the change in the shape of ESR spectrum of 3mN3 irradiated and stored in air in addition to ESR spectrum of pristine polymer.

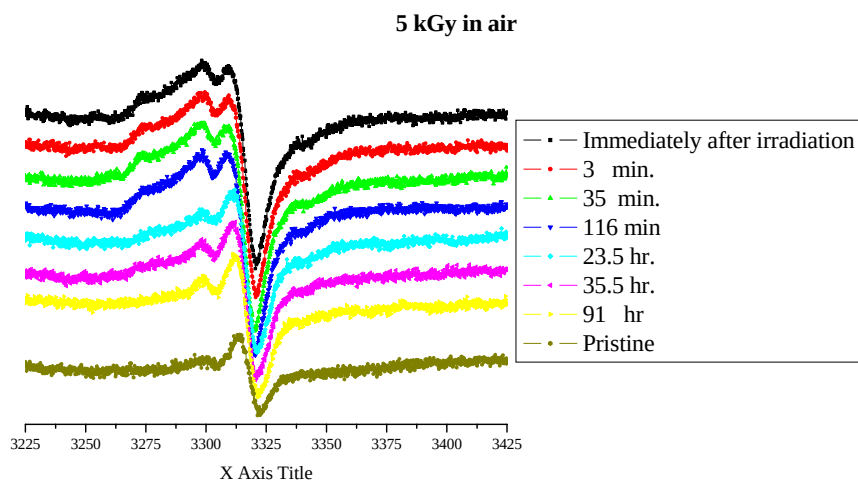


Fig.6.47. The change in the shape of ESR spectra of 3mN3 irradiated and stored in air and ESR spectrum of pristine 3mN3.

As can be easily shown, the asymmetry in the ESR spectra of 3mN3 is partly due to the paramagnetic impurity (or impurities) in 3mN3. The decrease in the intensity of wing peaks shows decay of the radiation-induced radical(s). The radiation-induced radicals will be characterized by simulation study in the next sections.

6.9. ESR INVESTIGATION OF 3-METHYL NYLON3 IRRADIATED IN NITROGEN AND STORED IN AIR

A 3mN3 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 3mN3.

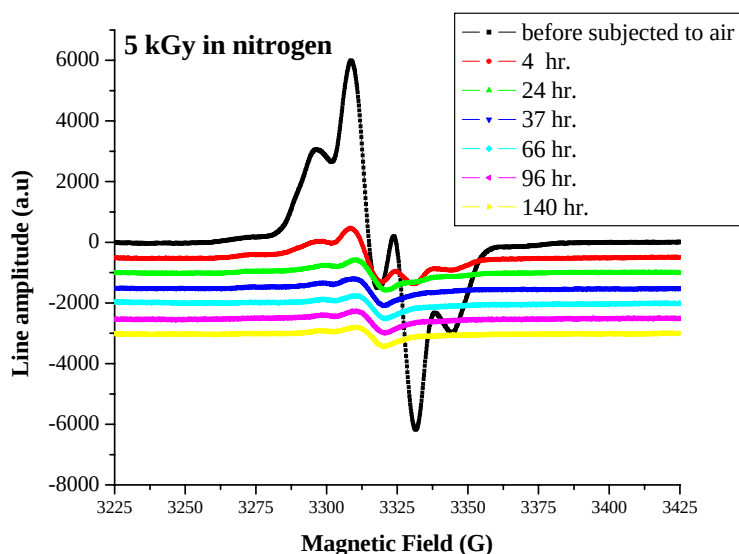


Fig.6.48. Change in the shape of ESR spectra of 3mN3 irradiated in nitrogen and subjected to air once first spectrum was recorded.

As shown in Figure.6.48, 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 3mN3 and then the intensity and the shape of the ESR spectrum remained almost unchanged.

It may be stated that primary radicals were extremely vulnerable to oxygen attack and the ESR spectrum of samples irradiated in air atmosphere could not give information about the nature of primary radicals generated during long irradiation period.

As will be discussed later in detail, the experimental ESR spectrum recorded earlier for samples irradiated in nitrogen was attributed to the radicals;

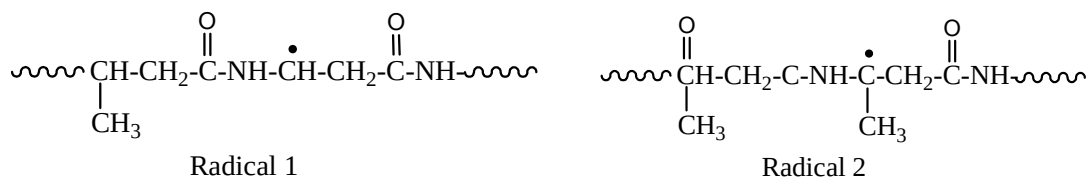


Fig.6.49. The structure of the radicals proposed for 3mN3 irradiated in nitrogen.

6.10. ESR INVESTIGATION OF 3-METHYL NYLON3 IRRADIATED AND STORED IN NITROGEN

6.10.1. ESR Shape

As the γ -ray induced radicals of 3mN3 are not stable enough in air to identify, 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.6.50 was recorded immediately after γ -irradiation of 3mN3 sample in nitrogen at room temperature.

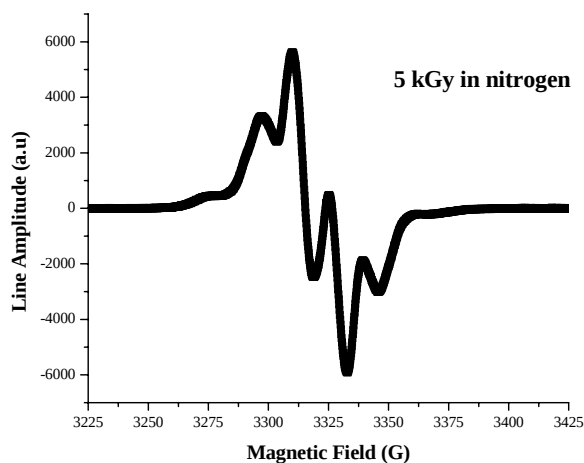


Fig.6.50. ESR spectrum recorded immediately after irradiation of 3mN3 in nitrogen

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 as in the case of N3. As will be discussed in detail later, the spectrum is proposed to be the combination of at least three types of ESR spectra belonging to two types of radiation-induced free radicals and the paramagnetic impurity (impurities) in the polymer sample.

6.10.2. Change in the Shape of ESR Spectra

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 3mN3 and then the intensity and the shape of the ESR spectrum remained unchanged.

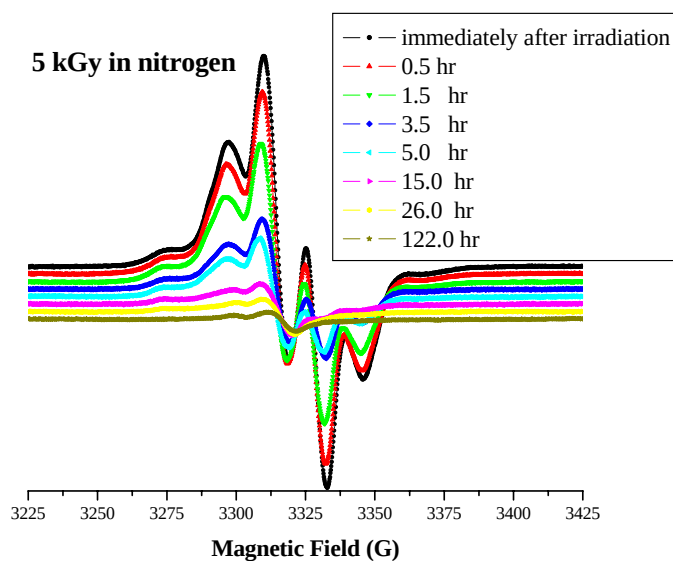


Fig.6.51. Change in the ESR pattern of γ -irradiated 3mN3 sample at room temperature and in nitrogen

The ESR spectra of 3mN3 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.

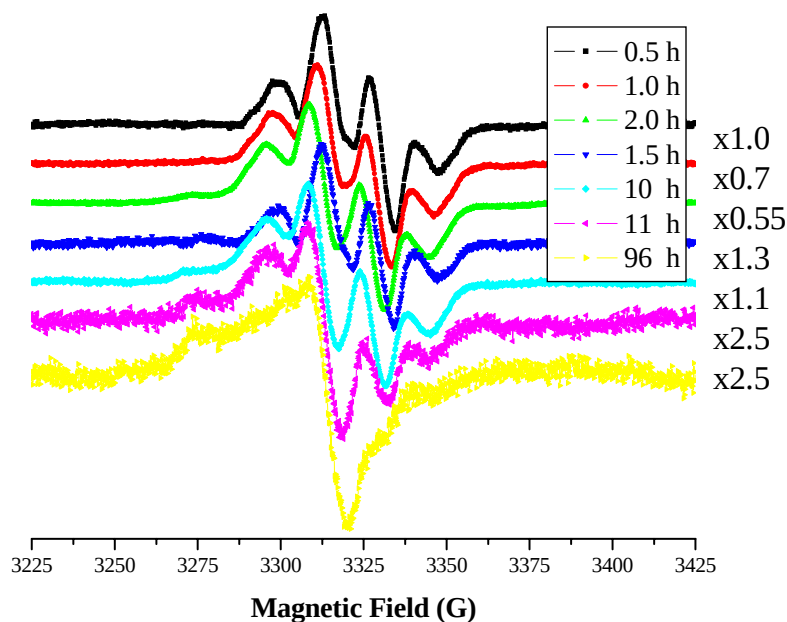


Fig.6.52. ESR spectra of the radicals decayed during storage in nitrogen at room temperature.

. As can be seen from Figure.6.52, the ESR spectra of the radical (s) decayed in 1.5 hours seem to be due to a spectrum with four-line (actually it is a triplet of doublet). After the 1.5 hours period completed, the ESR spectra of radical (s) decayed in each period seem to be a five-line or six-line spectrum. 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 1.5-hour period. The structure of the radical was shown as Radical 1 in the Figure.6.49.

6.10.3. Simulation Study

At first, simulation of the experimental ESR spectrum of pristine 3mN3 was carried out assuming that the experimental spectrum is a combination of two singlets with different g-values. However, identification of the species responsible from the two singlets could not be done.

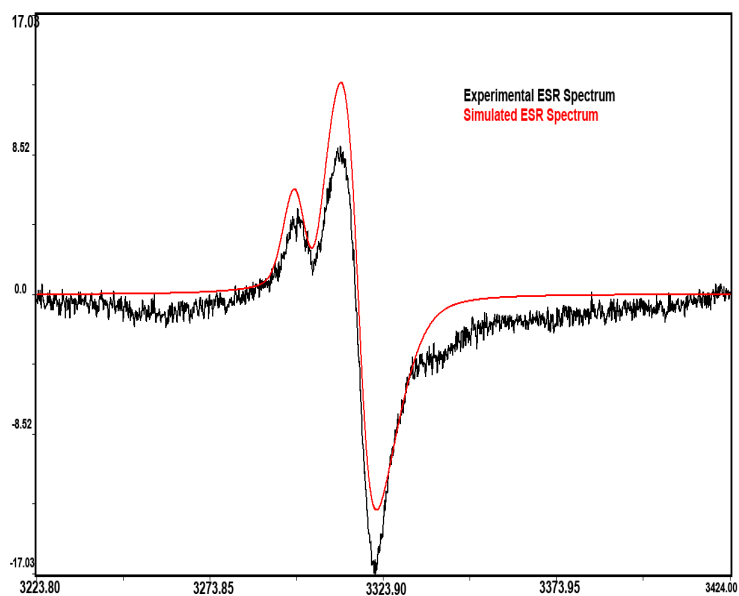


Fig.6.53. Experimental and simulated ESR spectra of pristine 3mN3

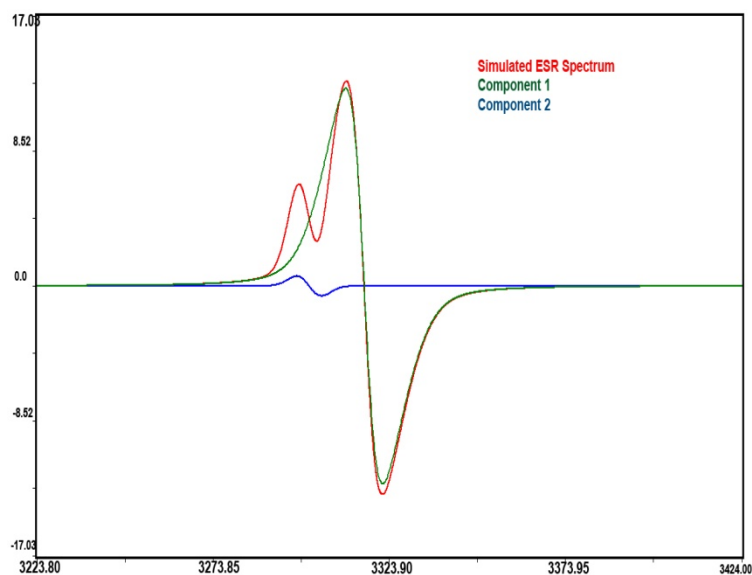


Fig.6.54. Simulated ESR spectrum of pristine 3mN3 and its components

When simulation of the experimental ESR spectra of 3mN3 irradiated in nitrogen was carried out assuming that the spectrum consists of a four-line (actually six-line superimposed) and an equally spaced six-line spectra belonging to the radiation-induced radicals and two different singlets belonging to paramagnetic impurities in 3mN3, fitting study gave the best results. (R1: 65.5%, R2: 22.2%, R3: 11%, R4: 1.3%)

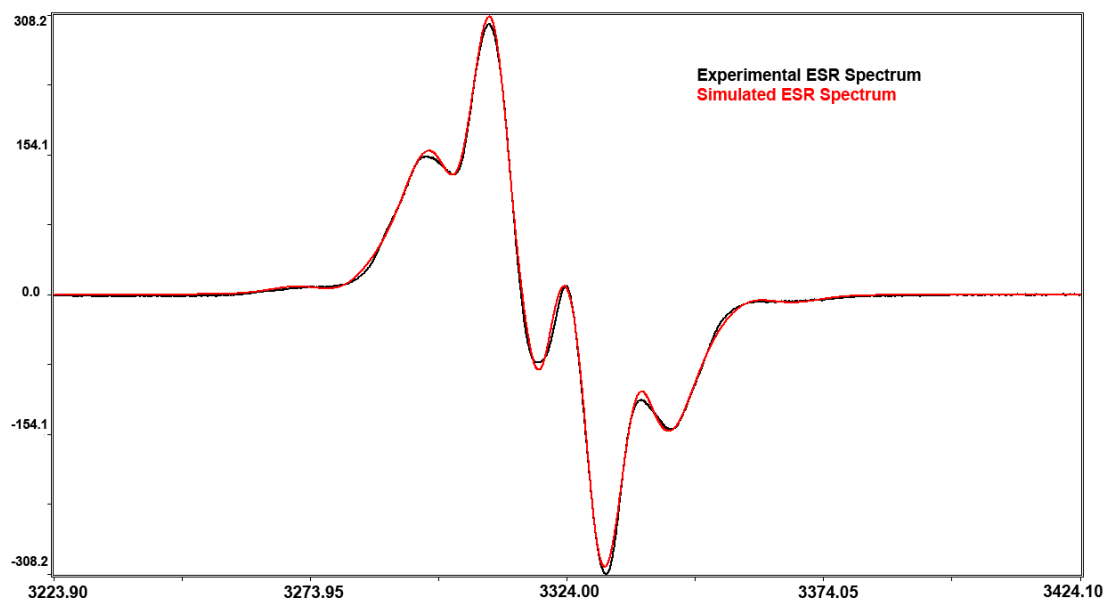


Fig.6.55. Experimental and simulated ESR spectra of 3mN3 irradiated in nitrogen

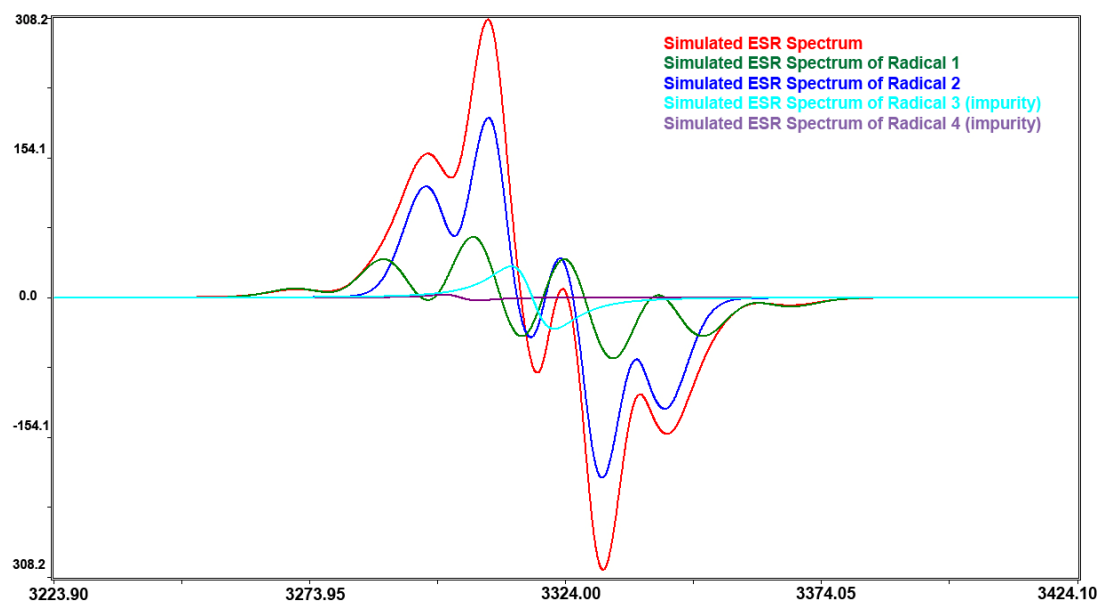


Fig.6.56. Simulated ESR spectrum of 3mN3 irradiated in nitrogen (red line) and the components of the simulated ESR spectrum of 3mN3 irradiated in nitrogen.

Parameters of the best fit were given in Table. 6.4

Table.6.4. ESR parameters obtained from simulation of ESR spectra of 3mN3 irradiated in nitrogen

	First Hyperfine splitting constant (G)	Second Hyperfine splitting constant (G)	Line width, $\Delta H_{1/2}$ (G)	g-value	Type of line	Percent %
Radical 1	16.26 $\pm$ 0.15	11.03 $\pm$ 0.10	5.06 $\pm$ 0.10	2.0030 $\pm$ 0.0002	Gaussian	65.5
Radical 2	17.00 $\pm$ 0.15	-	6.37 $\pm$ 0.15	2.0033 $\pm$ 0.0003	Gaussian	22.2
Radical 3	-	-	7.30 $\pm$ 0.10	2.0045 $\pm$ 0.0001	Lorentzian	11.0
Radical 4	-	-	5.71 $\pm$ 0.10	2.0130 $\pm$ 0.0001	Lorentzian	1.3

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 following radicals;

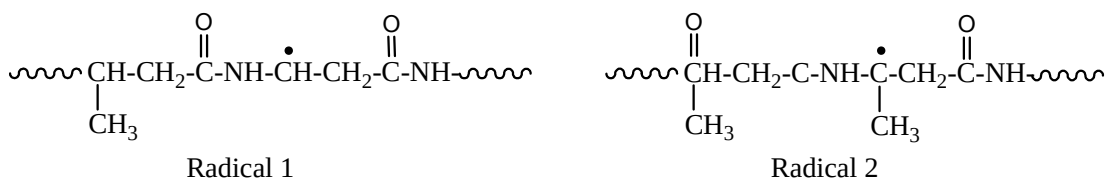


Fig.6.57. Proposed structures of the radiation-induced radicals of 3mN3.

As can be remembered, the Radical 1 had been proposed for a component (Radical 2) in the experimental ESR spectrum of N3 irradiated in nitrogen, too. As the ESR line parameters (first H_{sc} =16.26 G, second H_{sc} =11.03 G, $\Delta H_{1/2}$ =5.06 G, g-value=2.0030) of Radical 1 in 3mN3 are very close to those of Radical 2 (first H_{sc} =19.35 G, second H_{sc} =13.81 G, $\Delta H_{1/2}$ =5.52 G, g-value=2.0032) in N3, now we are able to assign specific radical type to one of the six-line spectra. The six-line spectrum corresponding to following parameters: first H_{sc} =19.35 G, second H_{sc} =13.81 G, $\Delta H_{1/2}$ =5.52 G, g-value=2.0032) belongs to the R2 of N3.

6.10.4. Radical Formation and Decay Mechanism

The radiation-induced radicals of 3mN3 are assumed to be developed by the removal of methyl and hydrogen groups from the carbon atom at the beta position of carbonyl group.

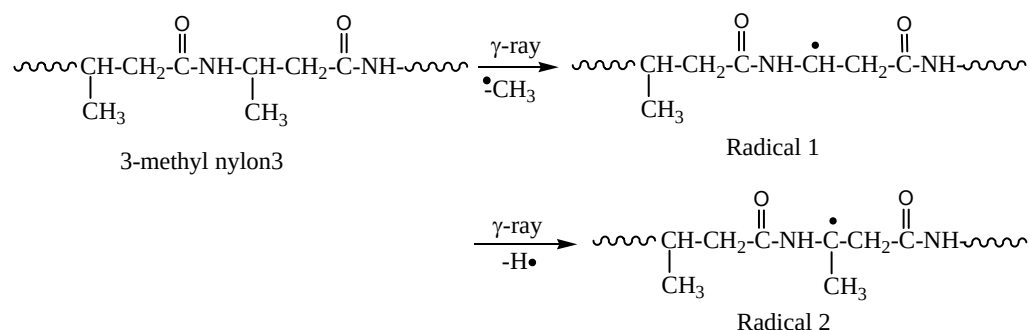


Fig.6.58. Formation reactions of the radicals of 3mN3

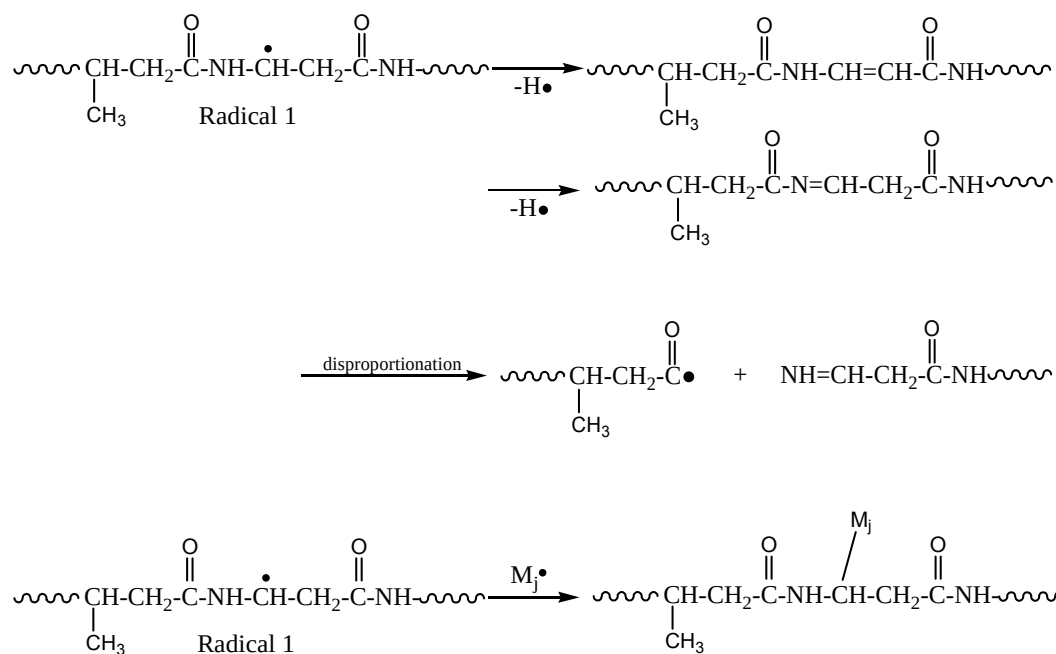


Fig.6.59. Possible decay mechanisms of Radical 1. M_j denotes any macromolecular radical (R1 and R2)

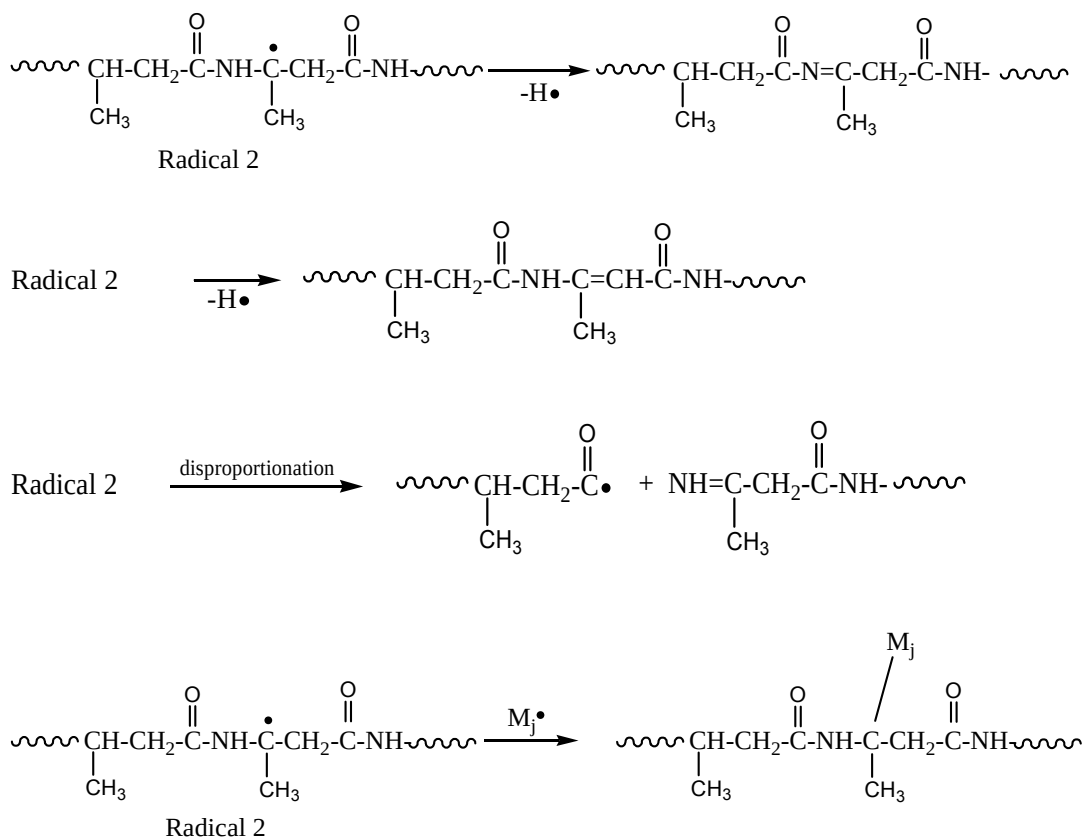


Figure.6.60. Probable decay mechanisms of Radical 2. M_j denotes any macromolecular radical

As remembered in the section of the characterization of pristine and irradiated 3mN3, inherent viscosities of pristine and irradiated polymers in air and nitrogen were determined and 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 observations, it may be deduced that the crosslinking reactions proposed above for both radicals are more likely to take place than the others.

As stated in the section of characterization of pristine and irradiated 3mN3, the decrease in the relative intensity of only NH proton in ^1H -NMR spectrum of

3mN3 irradiated in air had been attributed to decrease in the absolute amount of all type of protons (NH, CH, CH₂ and CH₃) simultaneously. The mechanisms and types of radicals proposed above are in conformity with the results of ¹H-NMR and viscosimetric analysis.

6.10.5. Decay Kinetics

Figure.6.6 shows the change of normalized concentrations of both radicals in nitrogen at room temperature with time.

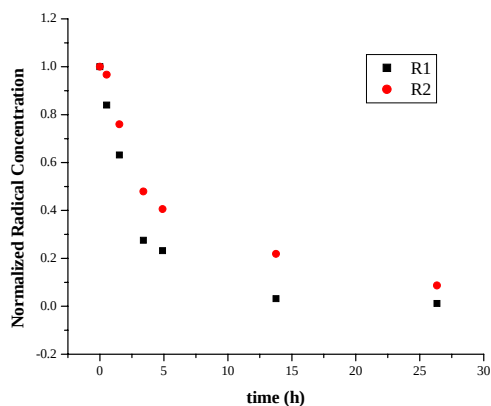


Fig.6.61. Change in the normalized concentration of 3mN3 radicals in nitrogen

As can be seen easily, the radical 2 is more stable than radical 1. Both radicals decay fast at the first stage of the storage (until about 5 hours), and then decay slower. This behavior may be explained considering the semi-crystalline structure of 3-methyl nylon 3 as in the case of N3 and 2mN3.

To complete our understanding of the decay behavior of the radicals better, $\ln(\text{radical concentration})$ versus time and inverse of the radical concentrations versus time were plotted for each radical as shown in Figure.6.62.

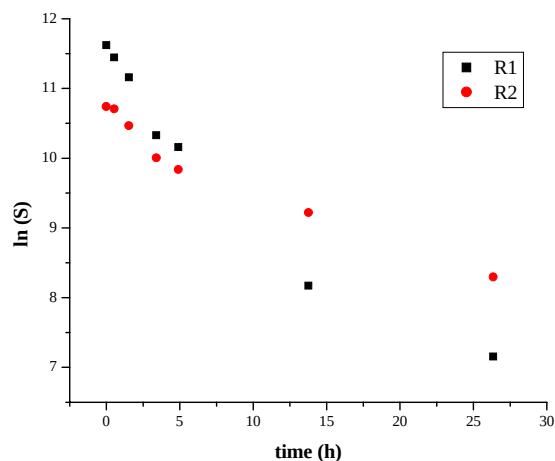


Fig.6.62. Plots of $\ln$ (Radical concentration) versus time

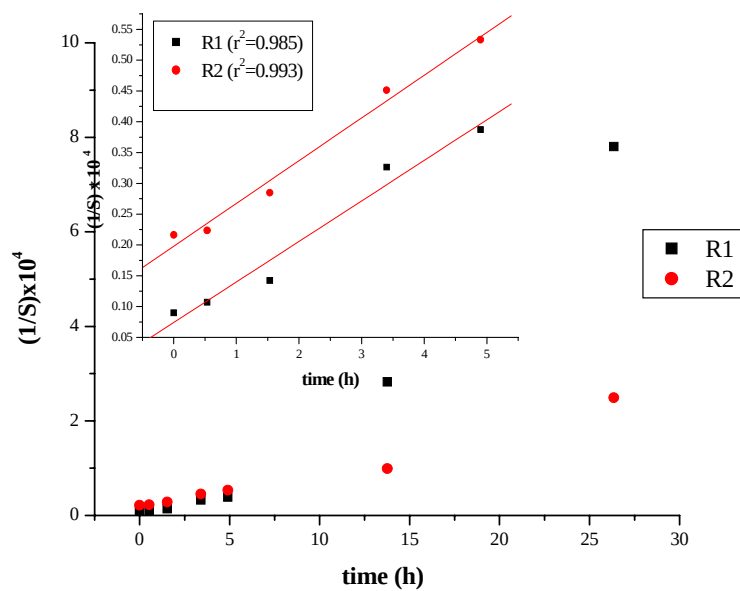


Fig.6.63. Plots of inverse of radical concentration versus time

As the plots in above figures yield straight lines in the initial stage of decay (expanded region), it is possible to say that the decays follow second order reactions.

7. CONCLUSIONS

Nylon3, 2-methyl nylon3 and 3-methyl nylon3, synthesized through base-catalyzed hydrogen transfer polymerization of corresponding monomer, were characterized by FTIR, NMR, elemental analysis, DSC and TGA. The spectroscopic and thermal properties of the polymers were found to be as in the related literatures.

Gamma ray induced radicals of N3 and 3mN3 could not be characterized by ESR spectroscopy due to the low stability of the primary radicals of the polymers when the irradiation was performed in air at room temperature. However gamma ray induced radicals of 2mN3 were stable enough in air and at room temperature to characterize them, their long-term stabilities were not seemed to be enough to use them as ESR/radiation dosimeter material.

When gamma irradiations of N3 and 3mN3 were carried out in nitrogen at room temperature, the radiation induced radicals of each polymer were able to be characterized by ESR spectroscopy.

N3 has two types of radiation induced primary radicals; a radical (Radical 1) generated by removal of hydrogen from the carbon atom next to the amide group and a radical (Radical 2) generated by removal of hydrogen from carbon atom next to the carbonyl group. The Radical 1 transforms to a relatively long lived radical (Radical 3) with unpaired electron on the oxygen atom.

2mN3 has only one type of radiation induced primary radical (Radical 2) formed by the abstraction of hydrogen from the carbon atom next to the

carbonyl group. But, the primary radical transforms to another radical (Radical 1) through disproportionation reaction and then the secondary radical transforms to a relatively long lived radical (Radical 3) with unpaired electron on the oxygen atom.

3mN3 has two types of radiation induced primary radicals; a radical (Radical 1) generated by removal of hydrogen from the carbon atom next to the amide group and a radical (Radical 2) generated by removal of methyl from the carbon atom next to the amide group.

Relative abundances of the radicals generated by irradiation of N3 in nitrogen were determined as R1:32%, R2:49% and R3:19% by simulation of the ESR spectrum recorded immediately after irradiation.

Relative abundances of the radicals generated by irradiation of 2mN3 in nitrogen were determined as R1:13%, R2:76% and R3:11% by simulation of the ESR spectrum recorded immediately after irradiation.

Relative abundances of the radicals generated by irradiation of 3mN3 in nitrogen were determined as R1:74.7% and R2:25.3% by simulation of the ESR spectrum recorded immediately after irradiation.

However viscosimetric studies of pristine and N3 irradiated in air showed that chain-scission dominates over crosslinking due to the peroxydation chain reactions, there is a competition between chain-scission and crosslinking in case of nitrogen.

Viscosimetric studies of pristine and 2mN3 irradiated in air and nitrogen showed that chain-scission dominates over crosslinking in both cases.

As a result of viscosimetric studies on pristine and irradiated 3mN3, crosslinking dominates slightly over chain-scission in both medium.

Kinetic study on the radicals of N3 showed that both radicals follow apparently a first-order decay.

Decay behavior of the radicals of 2mN3 however did not reveal a clear order.

Kinetic study on the radicals of 3mN3 showed that both radicals follow a second-order decay.

Considering the intensities of ESR spectra recorded immediately after irradiation of polymers in nitrogen, radiation chemical yields of the radicals of polymers may be arranged as $2mN3 > 3mN3 \approx N3$.

Usage of 2mN3 as an ESR/radiation dosimeter material may be possible by modification of its properties such as crystallinity, molecular weight and using it with a binding material.

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