CONTROLLED DEGRADATION OF DIENE ELASTOMERS:
Photo-controlled degradation of natural rubber

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DEDICATED TO

MY BELOVED PARENTS

AND

TEACHERS

DECLARATION

Certified that the work incorporated in thesis **"CONTROLLED DEGRADATION OF DIENE ELASTOMERS: Photo-controlled degradation of natural rubber"** submitted by Mr. SHAILENDRA SINGH SOLANKY was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged.

(R. P. SINGH)
Research Guide

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ABSTRACT

This thesis presents the results of controlled degradation of natural rubber, natural rubber latex and polybutadiene. The role of hydrogen peroxide is to generate hydroxyl radicals to produce hydroxyl-chain ends, but the addition of titanium dioxide is a new approach in the chain cleavage of natural rubber in the solution to get end functionalized oligomers (telechelics). Functionality was estimated ~ 2 during the photo-controlled degradation of natural rubber, especially in combination of H_2O_2 and TiO_2. It was proposed that hydrogen peroxide and/or allylic hydroperoxides act as photoinitiators and produce hydroxyl radicals and/or alkoxy radicals.

Epoxidation of natural rubber was carried out using methyltrioxorhenium as a catalyst in biphasic system. The natural rubber with degree of epoxidation ranging from 12 – 48 % were obtained. The advantage of using the biphasic system is the protection of the sensitive epoxides that remain in the organic phase and are not in contact with the aqueous acidic phase. It has been shown that using perbenzoic acid, chloroperbenzoic acid and monoperthalic acid, good epoxidized rubber yields were achieved but due to high acidity, epoxy groups may be acidolyzed and converted into carbonyl ester, ether or cyclic compounds while using methyl trioxorhenium as a catalyst, side reactions were not observed.

Metathesis reaction of natural rubber using bis(tricyclohexyl phosphine) benzylidine ruthenium (VI) dichloride (Grubb's catalyst), a highly reactive catalyst, is also a way to degrade the natural rubber. We found that viscosity average molecular weight of natural rubber decreases with the progress of the reaction temperature. Dichloromethane was found suitable solvent for metathesis of natural rubber. It is also possible to get desired molecular weight of natural rubber by adjusting the reaction temperature and suitable solvent in metathesis reactions.

We tried to get a route for functional polymers using a mixture of cyclooctadiene and/ or 1,5-dimethyl-1,5-cyclooctadiene and the chain transfer agent (2-methyl but-2-ene-1,4-diacetate and / or but-2-ene-1,4-diacetate) using a Ruthenium carbene complex. With the increase of catalyst concentration from 0.1 mg to 0.3 mg, no change in the yield of the functionalized polymer occur. The reaction temperature, 50°C, was optimum in case of polymerization of cyclooctadiene and cis-2-buten-1,4-diacetate.

Studies of the ozone on diene rubbers were of the fundamental importance in understanding the natural rubber degradation mechanism. The basic ozonolysis products of natural rubber were ozonides, epoxides, methyl ketone and aldehydes which were characterized by FT-IR and NMR spectroscopies. The thickness of natural rubber also plays an important role during ozonolysis. The thinner films get crosslinked faster then the thicker one. It was assumed that when ozone penetrated through the thin natural rubber film, it attacks on the surface and reaches towards inner layer faster than the thicker films therefore, the thin films get crosslinked faster then the thicker one for longer ozonolysis.

Conventional diphenyl diamine antiozonants are widely used in the protection of rubber. Recent developments in the rubber technology have resulted in rubber products with extended service life and therefore, require commensurate protection from ozonolysis. Therefore, there exists a need of new and efficient antiozonants offering extended protection from ozone. The newly synthesized antiozonants relate to a composition comprising an amine and benzotriazole and / or hindered phenol that is prepared in two-step process. The synthesized novel antiozonants as well as antioxidants may give better stability to polymers, specially rubbers to protect them from ozone. The stability of these compounds in rubbers can be studied by photo / thermal / ozone degradation.

ABBREVIATIONS

λ	Wavelength
ADMET	Acyclic Diene Metathesis
AIBN	Azo bis(isobutyro nitrile)
BPO	Benzoyl peroxide
cm^{-1}	Wavenumber
CTA	Chain Transfer Agent
CTPB	Carboxy Terminated Polybutadiene
DRC	Dry Rubber Content
ENR	Epoxidized Natural Rubber
F_n	Number Average Functionality
FT-IR	Fourier Transform Infrared
HTNR	Hydroxy Terminated Natural Rubber
HTPB	Hydroxy Terminated Polybutadiene
LNR	Liquid Natural Rubber
LR	Liquid Rubber
M	Molar
M_n	Number average molecular weight
M_v	Viscosity average molecular weight
MTO	Methyl trioxorhenium
nm	Nanometer
NMR	Nuclear Magnetic Resonance
NR	Natural rubber
NRL	Natural Rubber Latex
PBD	Polybutadiene
PDA	Phenylene diamine
R.T.	Room temperature
ROMP	Ring Opening Metathesis Polymerization
SBS	Styrene butadiene styrene
TLNR	Telechelic Liquid Natural Rubber
TLV	Threshold Limit Value
UV	Ultra violet
VPO	Vapour pressure osmometer
W	Watt

ABSTRACT

ABBREVIATIONS

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INTRODUCTION

CHAPTER II

SCOPE AND OBJECTIVE OF THE PRESENT STUDY

CHAPTER III

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SYNOPSIS

The thesis entitled **CONTROLLED DEGRADATION OF DIENE ELASTOMERS: Photo-controlled degradation of natural rubber** is divided into nine chapters.

The elastomers are important commercial materials and constitute one of the fast moving frontiers of polymer science. During last four decades, radiation chemistry has been and still is an active area of polymer research. Photo-irradiations initiate ionization and radical formation in polymers which may result in degradation, functionalization, modification and/or crosslinking.

In spite of extensive literature on the degradation of natural and synthetic elastomers[1-4], scanty work is carried out on controlled degradation specially on natural rubber and polybutadiene. Attempts have been made to introduce desired functional groups in elastomers/oligomers[5-7]. The controlled degradation will be used as an efficient method to develop new materials by functionalization[5,6], selective oxidation[7], ozonization[8] and epoxidation[9-13] by modifying diene elastomers. The proposed study is targeted to investigate the mechanism of controlled degradation and functionalization of diene elastomers/oligomers.

The degradation of natural rubber to form liquid natural rubber (LNR) has been carried out under various experimental conditions viz. mechanical[14], thermal[15,16] and chemical methods. It is difficult to control the molecular weight and structure of the resulting liquid natural rubber by mechanical and thermal methods. Basically, LNR is prepared by oxidative chain scission of the natural rubber but there are other methods also in literature to make LNR.[17-19] LNR technology has entered into a new era with the development of LNR bearing reactive terminal groups which are capable for further chain extension reactions. The high-energy radiation/photo-irradiations initiate ionization and radical formation in polymers which may result in degradation, modification, functionalization and/or crosslinking.

Tires, automotive components, electrical insulation, belts, theater seats, building materials, footwear, rubber bands, tennis balls, surgical gloves, artificial hearts and refrigerator linings etc are only a sampling of a huge and growing list of products that are completely or partly made of rubber.

Reactive oligomers[20-22,7] such as terminally functionalized (telechelic) oligomers and macro monomers are attracting interests as intermediates for use in various fields, viz. binders for solid rocket propellants, adhesives, tackifiers, lubricating oil additives, polyurethane elastomers and vulcanizing mixture for tyres as well as for surface coatings, reactive injection molding have been synthesized for specialty block and graft copolymers.

OBJECTIVES OF THE PRESENT STUDY

The objectives of present study are:

1. To generate reactive end-functional groups in the oligomers (telechelics) that can be used for developing desired properties in the substrate.
2. Controlled photo-degradation study of natural rubber and polybutadiene
3. To quench the photo-degradation after achieving desired functional group
4. To explain the reaction kinetics and mechanism of photo-controlled degradation
5. Epoxidation of natural rubber in biphasic medium:

   MTO based epoxidation system, already known as an effective catalytic system for the epoxidation of normal olefins, proved to be extremely efficient for the epoxidation of high molecular weight natural rubber. Polymers with degree of epoxidation ranging from 12 – 48% were obtained. The degree of epoxidation could be controlled by the amount of hydrogen peroxide added.
6. Specific chain cleavage by metathesis
7. Optimization of reaction parameters
8. Ozonolysis of natural rubber
9. Synthesis of novel antiozonants/antioxidants

OUTLINE OF THE THESIS

Chapter I

This introductory chapter explores with a discussion of various types of degradation in polymeric substrates. This chapter delivers a comprehensive literature incorporating the significant work done by prominent scientists in this area. Chain cleavages resulting from oxidative (periodic acid coupled with epoxidation), photo-oxidative and metathesis reactions are discussed. The general background on the mechanisms of photo-degradation and photo-stabilization has also been discussed.

Chapter II

The objective and scope of the present investigation are described in this chapter.

Chapter III

This chapter deals with the photo-controlled degradation of natural rubber (NR), natural rubber latex (NRL) and polybutadiene (PB). We attempted to elucidate the chain cleavage mechanisms during hydrogen peroxide catalyzed photo-oxidative degradation of high molecular weight natural rubber, natural rubber latex and polybutadiene which was described as producing liquid rubbers. NR/NRL/PB is photolyzed in toluene solution (2.5 wt.%) in a photoreactor at 30°C under atmospheric air and nitrogen, separately, with a 400 W medium pressure mercury vapour lamp ($\lambda = \geq 290$ nm) with constant stirring in the presence of hydrogen peroxide and/or titanium dioxide. The decrease in viscosity-average molecular weight (M_v) was determined by viscosity measurements/VPO. The effect of various reaction parameters is also discussed in details. The functional groups generated in polymeric chain after controlled degradation are evaluated using FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopic methods.

Chapter IV

This chapter presents the results of epoxidation of natural rubber in biphasic medium using methyltrioxorhenium (MTO) catalyst[23,24]. MTO based epoxidation system, already known as an effective catalytic system for the epoxidation of normal olefins, proved to be extremely efficient for the epoxidation of high molecular weight natural rubber. In a typical epoxidation reaction, 0.1 g of purified natural rubber was dissolved in 20 mL dichloromethane. MTO [2.306 mg (0.0093 m moles)] followed by hydrogen peroxide was added dropwise in the natural rubber solution. The reaction temperature was controlled by water-bath as the reaction was strongly exothermic. The completion of the reaction was indicated by the discoloration, aliquots were withdrawn at different time intervals and the natural rubber precipitated with methanol, dried under vacuum until constant weight. The epoxidation depends upon the concentration of hydrogen peroxide. The 11-50% epoxidation was achieved by adjusting H_2O_2/MTO concentration. The degree of epoxidation could be controlled by the amount of hydrogen peroxide added. The epoxidation was characterized by ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopy.

Chapter V

Metathesis reaction of natural rubber was carried out using Ruthenium catalyst [$RuCl_2(=CHPh)(PCy_3)_2$ (Grubb's catalyst)]. Metathesis reaction is a catalytically induced reaction in which C=C undergo cleavage and reforming. This chapter presents the results of metathetical degradation of natural rubber. The reactions were conducted on a 0.2 to 0.3 gm scale in an nitrogen purged dry box. Only few works on metathesis degradation of polyisoprene structure are described in literature. Ruthenium catalyst stable towards oxygen and moisture was used to carry out metathesis to obtain low molecular weight epoxidized natural rubber.[25]

Chapter VI

This chapter presents the result of 1,5-dimethyl-1,5-cyclooctadiene in presence of derivatives of cis-2-butene-1,4-dioate: an allylic difunctionalized chain transfer agent (CTA) to get end functionalized products using Grubb's catalyst. A neat mixture of 1,5-dimethyl-1,5-cyclooctadiene and CTA can be treated using a ruthenium based metathesis catalyst to yield difunctional product (telechelics). Deprotection of the resulting acetate end-functionalized natural rubber/polybutadiene unit was performed with number average functionalities close to 2.0. The robust nature of Ruthenium catalyst allows the use of high monomer to catalyst ratios.

Chapter VII

To date, the use of controlled ozonolysis for the production of telechelic LNR from natural rubber has not been reported. This chapter presents the results in which polymer solution is bubbled with ozone gas for a period of time and subsequently treated with an oxidizing or reducing agent to yield oligomers bearing reactive oxygenated end groups.[26,27] The effect of film thickness of natural rubber in ozonization is also studied. Unstretched films of natural rubber were exposed to ozone gas. The effect of reaction time and film thickness was studied. The ozone reaction with unstretched natural rubber films differ with depth. The viscosity of the ozonized natural rubber increases followed by decrease, suggesting the formation of crosslinks and chain cleavage, respectively.

Chapter VIII

This chapter deals with the synthesis of novel antiozonants based on para-phenylene diamines and it's derivatives. These molecules are characterized by FT-IR and ^{1}H NMR spectroscopic methods. Rubbers are susceptible to degradation by oxygen under an additional influence of UV light, ozone or heat. The term antiozonant denotes any additive that protects rubber against ozone degradation. Ozone cracking occurs whenever an elastomer/rubber (having unsaturation in backbone) is elongated and exposed to ozone. Unstretched rubber is also attacked but not cracked. Cracking starts from the rubber surface. Chain cleavage starts and new high stress surface is exposed, continuation of this process results in cracking. It can be prevented by using waxes (paraffin and microcrystalline type), inert polymers and chemically reactive antiozonants.[28] Some of the antiozonants are derivatives of 2,2,4-trimethyl-1,2-dihydroquinoline, thiourea, substituted pyrroles and N, N'-derivatives of p-phenylenediamine.

Chapter IX

This chapter summarizes the results and describes the salient conclusions of the study.

APPENDIX- I

1. Cyclic reactions in natural rubber under uv irradiation.
2. The temperature dependent changes in the relative concentrations of hydrophobic and hydrophilic moieties at the natural rubber/water interface are detected as increasing the entropic influence of chain extension which is associated with natural rubber elasticity. The magnitude of this effect depends on the cross-link density and the degree of oxidation of the surface of natural rubber.

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CHAPTER I

INTRODUCTION

1.0 INTRODUCTION

The elastomers are important commercial materials and constitute one of the fast moving frontiers of polymer science. During last four decades, radiation chemistry has been and still is an active area of polymer research. Photo-irradiations initiate ionization and radical formation in polymers which may result in degradation, functionalization, modification and/or crosslinking.

In spite of the extensive literature on the degradation of natural and synthetic elastomers[1-4], scientific community has also worked on controlled degradation of the diene elastomers such as natural rubber, polybutadiene etc. Attempts have been made to introduce desired functional groups in elastomers/oligomers[5-7]. The controlled degradation has been used as an efficient method to develop new materials by functionalization[5, 6], selective oxidation[7], ozonization[8] and epoxidation[9-13] by modifying diene elastomers. The proposed study is targeted to investigate the mechanism of controlled degradation and functionalization of diene elastomers/oligomers.

1.1 ELASTOMERS

The term elastomer is the modern word to describe material that exhibits rubbery properties (that can recover most of its original dimensions after extension or compression). Ever since, the pioneering work of Staudinger[14] in early 1900, has been accepted that such rubbery behaviour results from the fact that the material is composed of a mass of long chains, flexible polymer molecules upon extension stretching of such materials, the individual long chain molecules are partially uncoiled but will coil up again when the force is removed because of its kinetic energy.

1.1.1 Rubbers

The term rubber is a very nebulous one. Rubber can be substantially deformed under stress but recovers quickly to near its original shape when the stress is removed. Polymers are materials consisting of long chains of molecules and include plastics, rubbers and fibers. The main distinction between rubber and plastics is viscoelasticity, that is, it has both elastic and viscous properties. Although natural rubber source is Hevea brasiliensis but other rubbers are such as styrene butadiene rubber (SBR), polybutadiene (PBD), isoprene (man made "natural rubber"), nitrile rubber, butyl rubber, ethylene propylene diene monomer (EPDM), polychloroprene, silicone rubber, fluoro elastomers, urethane, epichlorohydrin (ECO), hydrogenated nitrile rubber, polynorbornene rubber and polysulphide rubber.

Natural rubber for example has excellent abrasion resistance and tensile strength, so it is incorporated in the tire as a tread. Butyl rubber on the other hand is known for its excellent permeation resistance and is an excellent material for tubes and the inner liner of a tire. Nitrile rubber is known for excellent chemical resistance and PBD has a high resiliency.

1.1.2 Natural rubber

The Hevea brasiliensis tree accounts for over 99% of the world's natural rubber production.[15] Columbus and others early explorers observed the use of rubber (Hevea brasiliensis) as plastic balls, containers and waterproof footwear. Gutta-purcha, a plastic product obtainable from trees in Malaya has been used successfully for submarine cables as a result of a recommendation made by Faraday in the early part of the nineteenth century. The English term 'Rubber' was coined by Joseph Priestly in 1770 since the material could erase pencil marks. The chemical name of natural rubber is polyisoprene since it is a polymer of isoprene. Faraday in 1821 found that natural rubber has an empirical formula of C_5H_8 and in 1860 Greville Williams recognized that rubber was a polymer of isoprene. Goodyear reacted natural rubber with sulfur to obtain vulcanized rubber in 1839. The vulcanization process for the production of soft rubber was patented by Hanock in England in 1843 and by Goodyear in the U.S.A. in 1844. Charles Goodyear's brother, Nelson, used larger amounts of rubber to produce hard rubber (ebonite). He patented this process in 1851.

The polymer chains in natural rubber have a perfectly cis-1,4 structure. Natural rubber occurs as particles dispersed in an aqueous serum called latex[16] which is found in the vessels of the tree. To harvest the latex, a 0.8 cm deep groove is made into the tree from which the latex bleeds out from the vessels, flows down along the cut until it reaches a spout and finally drops into a collection[17]. The flexibility, elasticity and durability of the natural and synthetic rubbers have made them choice materials for products like cushion shocks, soften blows, dampen vibrations, transmit power and perform in many other ways. Some other applications are i.e. tires, automotive components, the Goodyear blimp, electrical insulation, conveyor belts, hose to carry liquids, seals for machinery, adhesive on transparent sticky tape, adhesive for surgical, masking, rubber printing rolls, bottle nipples, rubber bands, threads, tank linings shoe soles, escalator handrail, theater seats, building materials, footwear, tennis balls, surgical gloves, artificial hearts and refrigerator linings etc.[18] The outstanding strength of natural rubber has maintained its position as the preferred material in many engineering applications. It has a long fatigue life and high strength even without reinforcing fillers. Other than for thin sections, it can be used at ~ 100 °C. It can maintain flexibility down to - 60 °C if compounded for some specific purpose. It has good creep and stress relaxation resistance and is low cost. Its chief disadvantage is its poor oil resistance and lack of resistance to oxygen and ozone, although these latter disadvantages can be ameliorated by chemical protection.

1.1.3 Natural rubber latex

Natural rubber latex (Hevea latex) is a cytoplasmic system containing rubber and non-rubber particles dispersed in an aqueous serum[19, 20]. It is milky liquid and fairly mobile even when containing as much as 60% of rubber. This fluid, usually white but occasionally buff-yellow or slightly grayish and quite mobile. This arises from the nature of dispersions in contrast to solutions. The size of the particles dispersed in a liquid profoundly affects the physical properties of that liquid. Portions of the constituents of latex are dissolved in the liquid but the amount is too small to make such differences. Small discrete particles in liquid containing substances in solution attract to their surface a part of these substances. They are said to form an adsorption layer on the surface of the dispersed particles and the nature of the layer controls the behaviour of the dispersion. A tenuous layer of proteins with which lecithins may be associated and other substances surrounds the latex particles.

Apart from major constituents, latex contains a variety of other substances which present in minute proportion are exceedingly active. Thus, latex freshly coagulated with acid, if untreated with preservatives, soon acquires a dull bluish surface colouration which turns dark brown when the rubber is dried. This is caused by oxidaze enzyme which absorbs oxygen from the air with the formation of substances of phenolic character and strong staining properties. The natural rubber latex composition has a dispersed phase, non-rubber materials in the serum and adsorbed non-rubber materials.

1.1.3.1 Properties of natural rubber latex

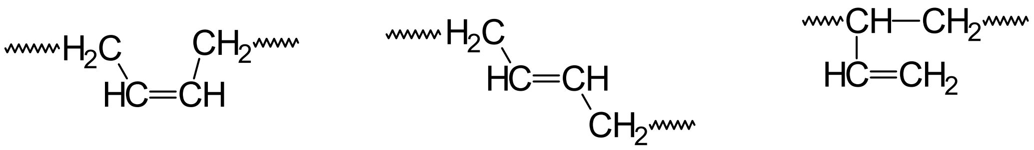
NRL is a highly specified material with main properties such as dry rubber content (DRC), non-rubber solids (NRS), viscosity, potassium hydroxide number, alkalinity determination, conductivity, creaming of NRL, filterability, the mechanical stability time number etc. Particle size determination of natural rubber latex is a specific characteristic. The particles are polydispersed and have a wide range of diameters from 0.25 to 5 μm. The average size is roughly 0.25 and 0.8 μm but it differs with method of determination. The particle size distribution of rubber latex is supposed to be substantially constant in a batch.[21] The wide range of particle size in NRL gives a low viscosity and high DRC. The modern technique of photon correlation spectroscopy permits rapid determination of particle size.

The advantages of using latex mixtures over rubber solutions for dipping purposes are numerous and important. The same facts apply to several other applications of latex and these are conveniently grouped together here for further consideration i.e. painting, spraying, paper making applications, road surfacing and flooring compositions, manufacturing of knife handles, artificial bones and ivory etc. The concentrated latex is used for the production of gloves, condoms, catheters, balloons, glues, foam rubber, carpet backing etc.

1.1.4 Polybutadiene

Polybutadienes are obtained primarily from the interaction of 1, 3-butadiene with a variety of initiators and catalysts.[22, 23] Polybutadiene materials range from general purpose, non crystallizing rubbers,[24, 25] highly crystalline plastics[22], liquid and castable resins etc.[26] The variety of polybutadiene products arises from state-of-the-art synthetic control that results in a variety of molecular architectures and a wide range of molecular weights. Differences in microstructure determine the properties of solids and liquids. Moderately high molecular weight polymers are solids, while low molecular weight polymers are liquids. Further modification of the resulting polymers by subsequent chemical reactions results in other useful and/or potentially useful products. On polymerizing 1,3-butadiene, the resulting polymer contains double bonds, which may exist as one of the three isomers: cis-1,4; trans-1,4 and vinyl as shown in Structure 1.1.

Cis-1, 4 polybutadiene crystallizes upon being stretched and thus has high tensile strength. It has excellent flexibility at low temperatures. It possesses low hysteresis, excellent dynamic properties and outstanding resilience, tear strength and abrasion resistance. As compared to natural rubber cis-1, 4 polybutadiene has low tack and strength. There have been reports that their properties can be improved by appropriate choice of initiation systems or by slight modification of the polymer.[23] Also, the processability of polybutadiene is inferior, it has poor resistance to oil, gasoline and hydrocarbon solvents and very little resistance to heat and ozone.



cis-1, 4- PB trans-1, 4- PB vinyl-1, 2- PB

Structure 1.1

1.2 POLYMER DEGRADATION

The degradation of polymers involves several chemical and physical processes accompanied by small structural changes, which lead to significant deterioration in useful properties of the polymeric materials. Degradation is an irreversible change, resembling the phenomenon of the metal corrosion. Degradation of the polymers is a very crucial aspect, which affects their performance in daily life. Throughout the life of a polymer, it encounters different kinds of degradation at various stages starting from the reactor where a polymer is synthesized, in extruder where it is processed, during service life and after its failure when it is discharged into the environment. The knowledge of the degradation mechanism has led to development of more efficient stabilizers for better stabilization. On the other hand, this knowledge also helped for development of some sensitizers to produce degradable plastics. A new emerging field, controlled degradation of commodity polymers is gaining much more importance these days. Many useful products like, well-defined telechelic oligomers and even monomers recoveries could be achieved by using the phenomenon of controlled degradation.

Thus, degradation of polymers is always not an unwanted phenomenon. Enough care has to be taken to check it otherwise it can be harmful to performance of a polymer and can lead even to safety hazards of fire and toxicity but if properly controlled, it can be used for producing new and better materials. Based on the factors causing the degradation, various types of degradations are such as photo-oxidative degradation,[27] radiation induced degradation,[28] metathetic degradation,[29] thermal,[30] chemical,[31] hydrolytic,[32] mechanochemical,[33] biodegradation,[34] degradation due to natural weathering,[35, 36] metal induced degradation,[37] microbial degradation[38] and enzymatic degradation[39] etc.

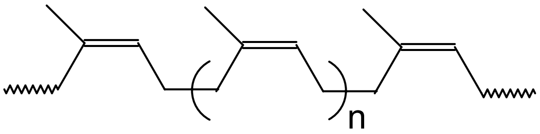
1.3 PHOTO-DEGRADATION / OXIDATION OF NATURAL RUBBER AND NATURAL RUBBER LATEX

Kambara *et al.*[40] studied the oxidation of natural rubber and determined the structure product of oxidized natural rubber using sulphuric acid. Newton *et al.*[41] the influence of wavelength of UV radiation on natural rubber and checked the stiffness. Wavelengths longer than about 540 mμ have only an insignificant effect on stiffening. L. d'Or[42] found that the concentration of the carbonyl group is related exponentially to the temperature and derived the equation using oxidized natural rubber and studied by IR spectrometry. Homans[43] studied the oxidation process in latex of Hevea brasiliensis. Paul[44] observed that the amino acid content of the serum of degraded latex is the governing factor in the heat sensitivity of latex. Shu *et al.*[45] studied the oxidation of natural rubber and presented the mechanistic way of oxidation. During the reaction pathway, saturated ketones were assumed to be formed from α-glycols by dehydration and then it was converted to γ-valerolactone. The kinetics of raw natural rubber was accomplished by oxidative method.[46]

Stafford[47] observed the oxidation of rubber in light. Flint[48] controlled the undesirable viscosity increase in latex compounds. The kinetics of the oxidation of rubber was studied under the influence of light. The curves of the amount of oxygen absorbed with time showed that the rate of oxidation remain constant. In a comparative study in 12 hrs exposure, 55 % and 6- 8 % unsaturation was decreased in photo-oxidation and in thermal oxidation, respectively.[49] Ruck[50] heated natural rubber at high temperature to get liquid vulcanizable, oil and heat resistant degradation products useful in the manufacturing of anticorrosive coatings and binding agents for synthetic resins etc. Donald[51] found that the degree of crosslinking does not affect heat deterioration as specified by chemical changes, upon reaction of rubber vulcanizates with decamethylene azoformate (vulcanizing agent). Watson[52] studied specific viscosity values of degraded natural rubber in solution using different solvents in the presence and absence of oxygen and at different temperatures.

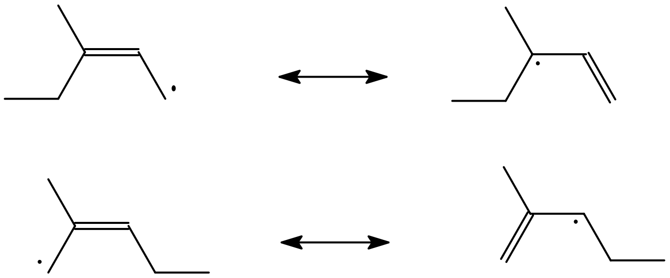
Shelton[53] observed the effect of temperature on the rate of oxidation of rubber at 50-100°C. It was found that the absorption of oxygen increased initially with temperature and then remained constant for longer period. Tkac[54, 55] studied the effect of light and reaction kinetics in the ageing of natural rubber by IR spectroscopy. Samples are not characterized well. Ecker[56] determined tensile strength of degraded natural rubber. Lacau[57] oxidized natural rubber in toluene solution of different concentration at 80 - 140°C under different pressure of oxygen to show mechanism of scission of high polymers containing double bonds. Dolgoplosk[58] studied oxidation-reduction systems on natural rubber using Fe (III) naphthenate and hydrogen peroxide. Raamsdonk[59] studied properties of natural rubber at higher temperatures in the presence and in absence of oxygen. The results showed that changes can be thermal or oxidative and tensile strength was estimated. Schelle[60] described the application of oxidative degradation of natural rubber vulcanizates at different elongations and temperatures. Bevilacqua[61] studied the chain scission in the oxidation of Hevea and studied the effect of temperature on it. It was observed that the scission efficiency increased with the temperature but the ratio of acid formed to scission was remaining constant. Chemie[62] studied degradation of natural and synthetic rubbers at higher temperatures using salt mixtures. Vulcanized natural rubber and raw rubber possess similar oxygen requirements to produce scission but vulcanized samples oxidize more rapidly than raw rubber.[63]

Tkac and coworkers[64] correlated the degree of crosslinking and the degradation of natural rubber. Donel[65] studied the effect of curing system on rubber oxidation and physical degradation was followed by determination of the volume of oxygen absorbed. Catalyzed oxidative degradation of natural rubber networks by electron irradiation at elevated temperatures in presence of benzoyl peroxide was studied.[66] Natural rubber was auto-oxidized in air, in sun light, in UV light and then heated to estimate the viscosity and solubility measurements.[67] Peter[68] described a linear structure (Structure 1.2) of polyisoprene as follows:



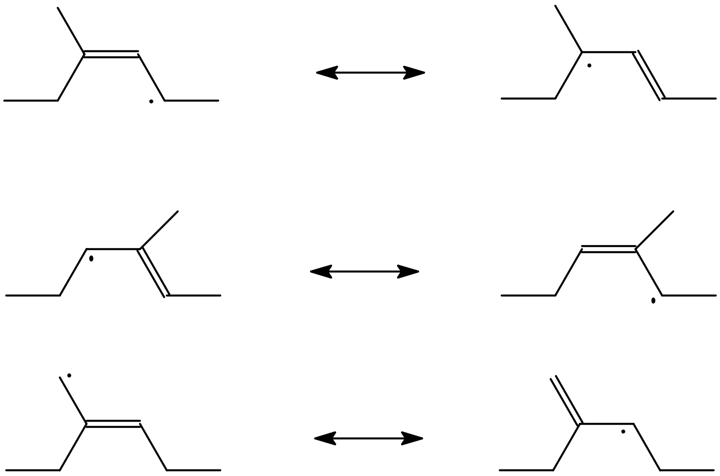
Structure 1.2

where all the monomer units contain one double bond. Therefore, it follows that radicals formed by a single C-C or C-H bond scission can be of allyl, alkyl or vinyl radical type. Formation of allyl radicals require less energy then the other types. There is a possibility of two different types of allyl radicals as shown in Scheme 1.1:



Scheme 1.1

It was also proposed that there are chances to form three different allyl radicals by hydrogen abstraction as shown in Scheme 1.2:



Scheme 1.2

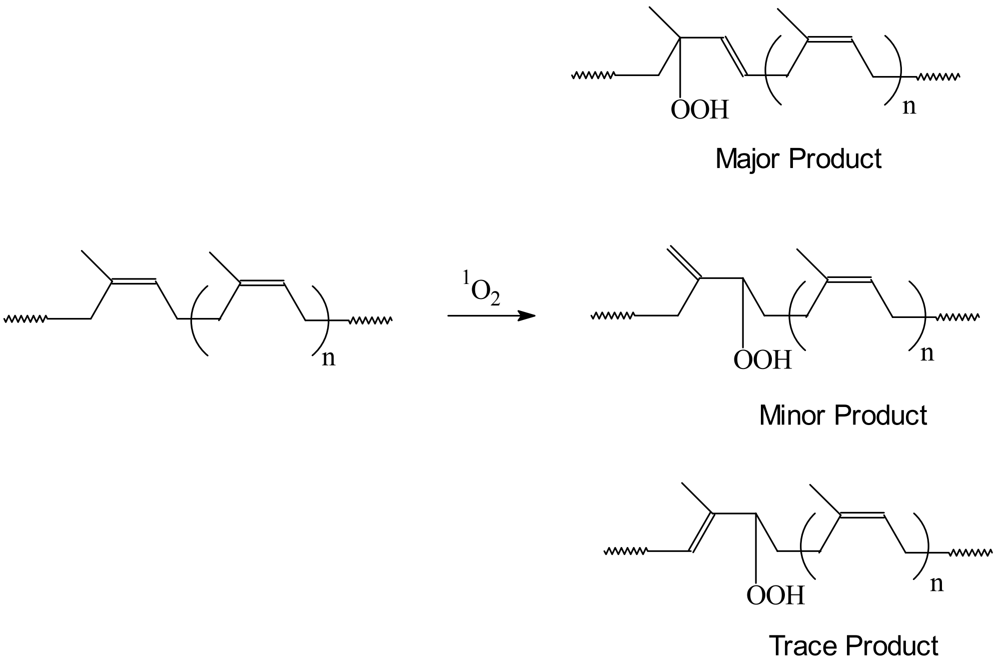
The weight loss of natural rubber on heating in oxygen and nitrogen and in vacuum was measured and it was observed that at 130°C, the weight suddenly decreases.[69] Das *et al.*[70] studied the ageing of natural rubber and determined the sol / gel ratio by two competitive processes. On ageing, the amount of soluble rubber increases as a result of depolymerization and this was followed by oxidative degradation of the fragments. The effect of irradiation in vacuum was studied on the crosslinking behaviour of purified Hevea.[71] Under the influence of oxygen, ozone, light, heat and with heavy metal compounds, rubber undergoes certain chemical and physical changes due to chain cleavage and crosslinking reactions.[72] General mechanism of crosslinking and chain scission in rubbers using high energy radiation was studied.[73]

The low molecular weight oxidative products of Hevea at moderate temperature were accompanied by the formation of formic acid and levulinaldehyde and antioxidants did not make much difference in chain scission.[74, 75] Gamma irradiation on natural rubber was studied by evaluating the mechanical stability, viscosity, pH, swelling ratio and hydroxyl number of latex.[76] Kozai[77] found that viscosity decreases upon exposure of rubber solution to light in air. Foxley[78] studied the action of various classes of chemical compounds as peptizers for rubber solutions to check the degradation. The extent of latex degradation was determined by a colour reaction between latex and picric acid. The colour is ascribed to a reduction of picric acid by thiol groups formed by enzymatic action.[79] Decrease in total amount of unsaturation and cis - trans isomerization in natural rubber under the influence of Ti halides and Al alkyls was studied.[80] Cyclization reactions were also observed in the system. Purified natural rubber was heated with dicumyl peroxide for 1 h at 140°C and was characterized by swelling and Tg measurements.[81] Iyer and coworkers[82] studied the depolymerization of natural rubber in presence of sunlight and air. Bayer[83] studied the rubber degradation products in the presence of oxygen. Morand[84] studied the photodegradation of natural rubber using xenon discharge lamp. Sensitizing effect of thiobenzene[85] and nitroso compounds[86] in the photo-degradation process of diene polymers was studied using 313 mμ and 254 mμ light followed by viscosity changes in the rubbers.

Uraneck[87] prepared telechelic elastomers in emulsion and solution systems. Hydroxy telechelic polymers were similarly prepared in solution by reaction of Lithium -telechelic polymers with ethylene oxide or oxygen and curing of the polymers with a combination of di-isocyanates and peroxides. The iron catalyzed degradation of natural rubber latex foam occurred in the aqueous solutions at low pH and was inhibited by the addition of 8-hydroxyquinone and phenolic antioxidants into the rubber.[88] Alina *et al.*[89] studied the modified natural rubber and its methyl methacrylate copolymer via UV irradiation. Hydroxy terminated oligomers were synthesized by refluxing the isoprene, methanol and a 30% hydrogen peroxide solution for 6 h in a steel reactor at 98°C. Yield was 49- 59%, having molecular weight of 1,500 – 4,000 and 1.46 – 3.36% end functionalized hydroxyl group.[90] Voigt *et al.*[91] found two possible mechanisms for the oxidative chain cleavage of rubber, one in which the primary oxygen attack at both allylically activated α-methylene groups and in the second the attack occurs preferentially on the α-methylene group next to the methyl substituted carbon. The photodegradation of vulcanized rubber was accomplished by xenon lamp with suitable monochromators in air and vacuo.[92] Low energy UV and ESR measurements were conducted and established that simple chain scission was the most likely means of breakdown in polydienes.[93] Degradation during vulcanization / storage, the mechanical action, heat, oxygen and ozone were reviewed.[94]

Kenkichi and coworkers[95] studied the degradation of crosslinked rubbers and developed a method to calculate the degradation rate. A more specific solution to determine rate equations of thermal decomposition of polymers by random scission was achieved.[96] The sensitivity spectrum of rubber in sun light ($\lambda > 300$ nm) determined by variations at 30°C of the initial rate of oxidation or chain scissions as a function of the wavelength of incident light, showed several maxima in the near UV. These maxima are approximately equidistant and the space between them differed only slightly according to the polydienes (polyisoprene, polybutadiene and butadiene-styrene copolymer) in the crude or vulcanized state.[97] Cis-trans isomerism and cyclization was proved by IR and NMR analysis in natural rubber, synthetic rubber and in polybutadiene during thermal degradation.[98] The kinetics of photo-oxidation involving singlet oxygen were studied with and without antioxidants (N-phenyl-N'-cyclohexyl-p-phenylenediamine) and observed that uptake of oxygen suppressed completely during photo-oxidation.[99]

Ng *et al.*[100] observed that reaction of singlet oxygen with cis-1, 4-polyisoprene generated cis-1, 4-poly (isoprene hydroperoxide) as shown in Scheme 1.3. The kinetics and mechanism of the photolysis of this polymer-singlet oxygen adduct had been studied at 313 nm in solution in the absence of oxygen. The primary quantum yield for photolysis of the polymer hydroperoxide was 0.8. The subsequent radical induced chain decomposition of the hydroperoxide was observed.



Scheme 1.3

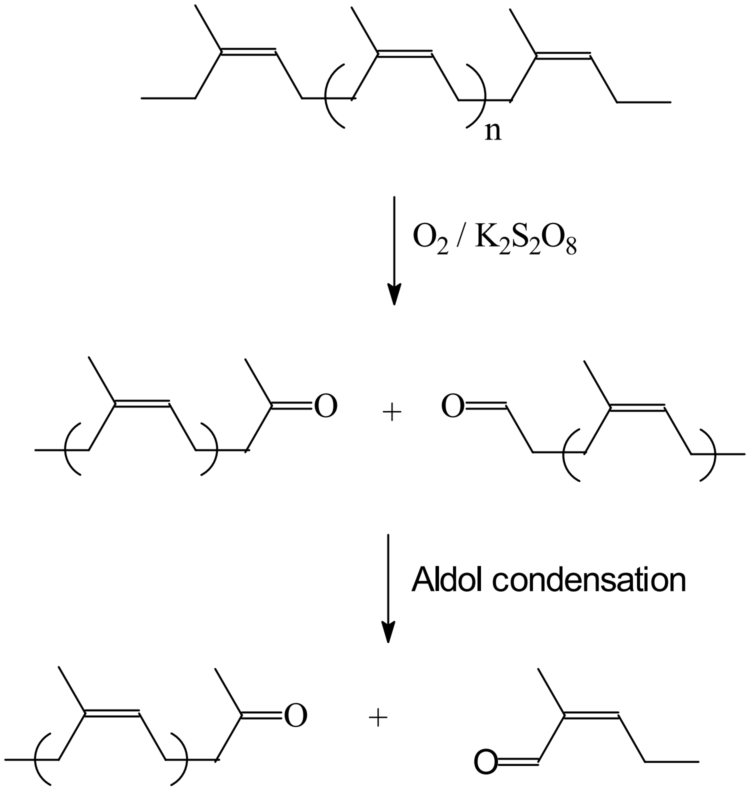
Geminal selectivity in singlet oxygen reactions were carried out by Clennan and coworkers[101] where replacement of hydrogen on tetramethyl ethylene with a variety of functional groups which react preferentially with singlet oxygen by abstraction of a *geminal* hydrogen to form allylic hydroperoxides. The oxidative degradation of rubber in presence of oxygen with radical initiator i.e. AIBN at 80°C proceeded by decomposition of peroxide radicals. The degradation rate in the presence of oxygen was greater than that in argon by an order of magnitude.[102] The photolysis of natural rubber was in vacuum with UV light having wavelength of 147 or 123.6 nm, resulted in consumption of double bonds and formation of intermolecular crosslinking. The photolysis of the rubbers at 147 nm was accompanied primarily by free-radical crosslinking, whereas at 123.6 nm ionic-molecular crosslinking mechanism predominated. The quantum yield at 123.6 nm is considerably higher. A mechanism of the photolysis was also proposed.[103]

The kinetics and mechanism of oxidative degradation of natural rubber was studied in the presence of various antioxidants. Scission of the polymer chain occurs at the hydroperoxide decomposition stage without yielding reactive free radicals.[104]

Natural rubber films were irradiated under ambient conditions and generation of hydroperoxy, hydroxyl group, ketones, aldehydes, epoxides and carboxyl groups. Viscometric measurements showed that chain scission predominates over crosslinking. Photo-oxidation kinetics studied for films containing oxygen quenchers i.e. 1,2-diazobicyclo (2,2,2)-octane and diphenyl-para-isobenzofuran showed that singlet oxygen was not responsible for the initiation of the environmental photo-oxidation of cis-1,4-polyisoprene.[105] Effect of phenyl hydrazine on natural rubber was studied by Barros.[106] Accelerated oxidation by phenyl radical generation and in-situ decomposition of hydroperoxides, allowed to explain the formation of epoxidized and hydroxylated units.

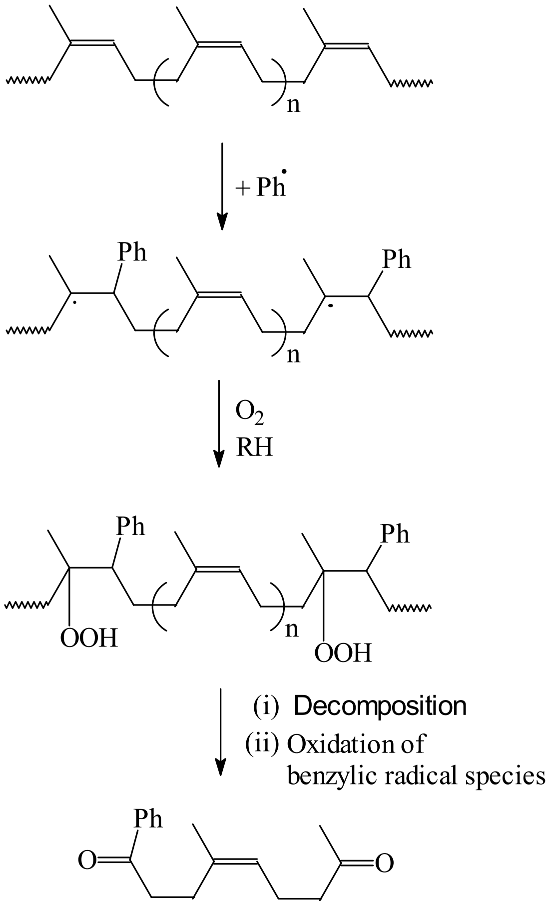
The degradation in the molecular weight of natural rubber latexes is applicable to alkaline latexes and useful in preparing free-flowing, storage-stable powdered rubbers. The latex was treated with oxygen in inert gases or with peroxides.[107] Synthesis of photo-crosslinkable elastomers by chemical modification of liquid natural rubber was prepared with maleic anhydride. Liquid natural rubber was obtained by controlled degradation of natural rubber in latex state using phenyl hydrazine / oxygen system.[108] The depolymerization of natural rubber in the latex stage to produce hydroxyl-terminated liquid natural rubber was reported.[109] Stabilized latex was treated with aqueous hydrogen peroxide and subsequently irradiated in sunlight. The product was isolated, purified and subjected to chemical and spectroscopic analyses. The molecular weight was reduced and the stereo regularity of the rubber was retained. The product contained hydroxyl terminal group but no details were given about the number average functionality. New evaluating methods of environmental stress degradation and weathering of plastics and rubbers were proposed.[110]

Chloranil[111] used to induce degradation in polyisoprene. Tangpakdee *et al.*[112] suggested the novel method for preparation of low molecular weight natural rubber latex. Low molecular weight natural rubber (LNR) and LNR latex was prepared by oxidative degradation of deproteinized natural rubber (DPNR) latex in the presence of 1 phr of $K_2S_2O_8$ and 15 phr of propanal, by shaking at 60°C as shown in Scheme 1.4. The LNR was a telechelic polymer containing aldehyde and ketone groups at both terminals as determined by NMR and molecular weight analysis.



Scheme 1.4

Lemaire[113] reviewed photochemical oxidative degradation of diene elastomers. Reyx *et al.*[7, 114] studied the chain cleavage reaction to study the transformation of high-molecular weight polymers in well-defined oligomers. The mechanism of the phenyl hydrazine accelerated oxidation of rubber in the latex phase was described as shown in Scheme 1.5. The control of oligomers with respect to their average molecular weights, molecular weight distributions and chain-end microstructures implies the control of the cleavage reaction with respect to its yield, its regiospecificity and its chemical specificity. Among several examples of efficient uses of this principle for the preparation of liquid oligomers from unsaturated polymers, attention is focused on controlled oxidative degradation of rubber and on metathetical controlled degradation of 1,4-polydienes and polyalkenamers. The epoxidation of rubber and periodic acid cleavages of epoxides in the latex phase were interpreted referring to the influence of the biphasic medium. The results were in agreement with interfacial blocky epoxidation by the water-soluble reagent and interfacial arrangement of the epoxidized block to be cleaved. Finally, the metathetical degradations resulting from back-bitting cyclization and cross metathesis with acyclic alkenes were presented as preparative methods to get well-defined cyclic oligomers and telechelic oligomers (i.e., terminally functionalized oligomers).



Scheme 1.5

Vinod *et al.*[115] carried out the degradation of natural rubber-aluminium powder composites and studied the effect of heat, ozone and high energy radiation on degradation. Surface adhesion and mechanical properties of natural rubber cast films have been investigated by atomic force microscopy (AFM) before and after UV irradiation. Good agreement was obtained for as-received surfaces with bulk measurements. The photochemistry predicts chain scission events which are likely to account for the observed softening of the polymer.[116]

1.4 PHOTO-DEGRADATION OF POLYBUTADIENE

The photo-degradation of polybutadiene was carried out many researchers in early years.[117, 118] Golub[119] observed that polybutadiene in solid state undergoes photochemical cis-trans isomerization in the absence of deliberately added sensitizer when irradiated with Kr 1236 or Hg 2537 radiation. Anderson[120] studied the isomerization of trans-polybutadiene by high-energy irradiation in an inert atmosphere. Functionally terminated polybutadiene preparation by free radical polymerization was reviewed by Frech.[121] Berlin[122] studied the inhibition effects in thermal and photo-oxidative degradation of cis-1, 4-polybutadiene with pyrolyzed anthracene. The changes in the polybutadiene were studied when exposed to 290-400 nm irradiation in air and in oxygen. Polybutadiene rubber films were exposed to radiation of long wavelength ($\lambda > 300$ nm). Products resulting from the photo-oxidation of polybutadiene rubber have been identified using various techniques such as FT-IR and UV spectroscopy and chemical derivatization reactions. The decrease of oxygen permeability during irradiation of polybutadiene films makes it necessary to study the vacuum photo-thermal decomposition of hydroperoxides also. The results show that when oxygen can diffuse through the irradiated film, photo-oxidative reactions occur implying the formation of hydroperoxides, α, β - unsaturated species and finally saturated carboxylic acid.[124,]

Oxidation of cis-1, 4-polybutadiene by singlet and molecular oxygen was described by Schopov[125] where polybutadiene was treated with UV radiation in air without using any photosensitizer and resulted in a free radical process. On exposure to UV radiation, β-carotene was found an efficient inhibitor for the oxidation of PB by singlet oxygen as it enhanced the free radical oxidation. Adam *et al.*[126, 127] carried out the photo-oxidation of polybutadiene where hydroperoxides at the allylic position (3410 cm^{-1}) were observed. The carbonyl region of the IR spectra of photo-oxidized PB showed two absorbance bands at 1696 and 1710 cm^{-1}, ascribed to α, β-unsaturated ketones. The decrease of oxygen permeability during photo-oxidation implied that oxygen could no longer diffuse through the surface layers consequently the photo-oxidation stopped. Accelerated photodegradation of cis-1, 4-polybutadiene was carried out in presence of hydrogen peroxide in benzene solution. Efficient photo-degradation was achieved and mechanism was suggested.[128] The mechano-chemical degradation of polybutadiene in solution phase by ultra-high speed stirring was investigated in order to obtain information concerning the influence of some parameters on the reaction. It was observed that the type of solvent and temperature, especially very low temperature (-40°C), have the most important influence on the degradation.[129] The effect of 1,3-diphenylisobenzofuran (sensitizer) was studied on the photo-oxidative degradation of cis-1,4-polybutadiene in solid and solution medium.[130]

Comparative studies were performed on polybutadiene with molecular oxygen, singlet oxygen, atomic oxygen and ozone. The products were characterized by UV and IR spectroscopy.[131] Lala *et al.*[132] studied the role of hydroperoxides in photo-oxidative degradation of cis-1, 4-polybutadiene. The photodecomposition of Me_3COOH, $PhCMe_2OOH$ and 2,5-dimethyl-2,5-dihydroperoxyhexane in cis-1, 4-polybutadiene films and solutions was studied by IR spectroscopy and gel permeation chromatography to elucidate the role of hydroperoxides in the photo-oxidative degradation of *cis*-1,4-polybutadiene. The free radicals formed by photo-decomposition of the hydroperoxides lead to appreciable chain scission and / or crosslinking in *cis*-1, 4-polybutadiene and initiate free radical oxidation. Radiation induced changes in the structure of cis-1, 4-polybutadiene were observed and studied by Burnay.[133] The formation of intermolecular crosslinks and intramolecular cyclic structures were observed during the irradiation. The decay processes are described by first order kinetics. Paoli *et. al.*[134] carried out the photo-oxidation kinetics of polybutadiene films containing singlet oxygen quenchers. The nonparticipation of singlet oxygen in the photo-oxidation of polybutadiene was observed.

The mechanism of photo-degradation of 1,2-polybutadiene which was irradiated with UV light of wavelength 312 nm was investigated by FTIR-ATR and thermal analysis. DMA and DSC measurements showed that the 3-dimensional networks were formed between 1,2-polybutadiene main chains by UV irradiation. FTIR-ATR spectra indicated that the vinyl groups in the side-chains of 1,2-polybutadiene was produced by the decomposition of main chains according to Norrish II type photodegradation.[135] Photo-oxidation of polybutadiene was studied by UV, IR and NMR spectroscopy.[136]

1.5 LIQUID NATURAL RUBBER

Depolymerized natural rubber with sufficiently low viscosity and good flow at room temperature, is termed as 'liquid natural rubber'. It is soluble in most organic solvents except alcohols and lower ketones. It is used as a rubber softener, lubricating oil additive, binder in the grinding wheels, cement of brush bristles, in corrosion resistant paints, sealant for pipe joints, an insulating material for low power electrical components and in the manufacturing of printing rollers and battery boxes.[137, 138] There are four different types of depolymerized rubbers:[139]

(i) Rubbers which reduce the weight average molecular weight to within the range of 4,00,000 - 10,00,000. The goal is to reduce the internal viscosity of the starting material and to minimize and eliminate the gel formation in order to obtain the material which is more easily processed in the factories.

(ii) Rubbers fairly degraded Mw in the range of 1,50,000 – 4,00,000. These materials are soft and sticky with adhesive properties and used as basic elements for the industrial latex - adhesives.

(iii) Extensively degraded materials, which are highly viscous liquids named "liquid rubbers" (LR).

(iv) Essentially completely degraded rubbers with molecular weight below 500. They are obtained by pyrolysis methods and are interesting from a chemical point of view since they make it possible to understand the exact nature of the connections contained in the polymer, however, no current commercial use.

1.5.1 Methods of degradation to get liquid natural rubber

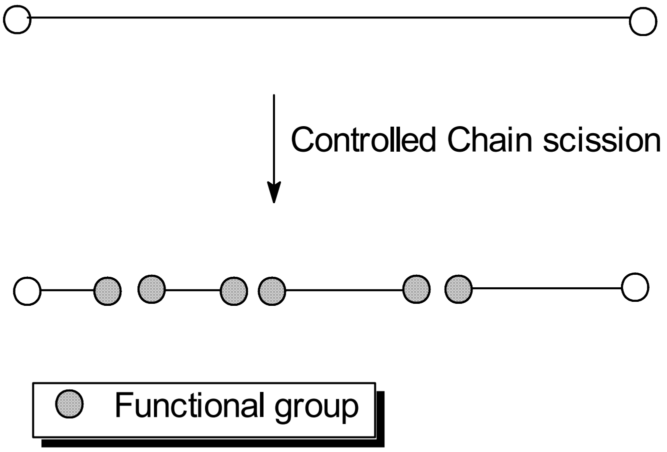
Hardman[140] commercialized the production of liquid rubber from natural rubber in 1923. This material was made by extensive mechanical mastication at elevated temperatures in air (an oxidative depolymerization). The product was highly viscous liquid which did not entirely fulfill the immediate objectives and challenges. Most of the methods used for preparation of liquid rubbers are the chewing and the pyrolysis which were generally done in the solid form of the natural rubber.

In 1930 Stevens and coworkers[141] led to the production of liquid natural rubber (Rubbone) by an entirely chemical route. The material was a viscous adhesive of yellow colored and contained an oxygen rate from ~ 10% (0.001 - 0.6% of hydroperoxides, 0.3% of carbonyls, 0.6% - 1.5% of esters, 3.3% - 4% of aldehydes and ~ 6% of ketene functional groups but this process was not commercialized. Later on, Pike[142] included plasticizers during mastication and commercialized the process. Since 1970s, the Japanese firm,[143] marketed a range of liquid synthetic polyisoprene. This liquid synthetic rubber was made by controlled polymerization of isoprene monomer with high purity.[144] It should be noted that many ameliorations concerning the ingredients of liquid rubber currently gave better vulcanized rubbers with better mechanical properties and could be used for the manufacturing of films / adhesives and coatings. In general, the methods developed for the preparation of liquid natural rubber discussed above, do not give reactive terminal groups, therefore, it does not show good mechanical properties owing to the presence of a high proportion of elastically inactive chain ends.[145] The applications of such liquid natural rubbers are limited only to products like heat resistant finishes, insulators for electrical components, brush-bristle cements, binders, battery boxes, printing rollers, additives in lubricants, corrosion resistant coatings, processing aids such as rubber softener in conventional rubber compounding etc.[146]

The present technology of liquid rubber opened a new era with the development of telechelic liquid natural rubber possessing reactive end functional groups which can be used for chain extension. Liquid natural rubber bearing reactive terminal groups is later referred to as telechelic liquid natural rubber (TLNR).

1.6 TELECHELIC POLYMERS

Telechelic polymers are of great interest, mainly because they provide the means for further reactions to give modified polymers with controlled properties.[146-149] The term telechelic came from the Greek word *tele / telos* means far and chelos means claw, thus describing the molecule as having two claws far away from each other; i.e. at the extremities of the chain, able to grip something else, has been proposed by Uraneck and coworkers[150] in 1960 to describe the polymers having two terminal functional groups. Telechelic (terminally functional) polymers are the polymers that carry reactive end groups. A telechelic polymer is, therefore, characterized by the nature of the polymer chain, the nature of the functional groups and the number of these groups. The usual telechelic polymer is a linear molecule having two equal functional end groups. Polymers containing only one functional end group are not, in a strict sense, telechelics but are for obvious reasons frequently considered as special members of this category of reactive polymers which plays reactivity toward another functional group. It means that a polymer may be telechelic under certain conditions but not telechelic under others. The term 'functionality' and the functionality of the end group should not be combined because if the polymer is having more than two functionalities, i.e. branched or star shaped structures, it will be functional polymer. Consequently, the really telechelics are those having only two functional groups at the chain end as shown in Scheme 1.6. The polymers, having only one functional group at the chain end are called monotelechelic or semitelechelic.



Scheme 1.6

Due to their low molecular weight, telechelics are easy to melt, have low viscosity and can be mixed with additives and fillers without providing high energy. It can also be transformed into high molecular weights polymers or model networks. Telechelic polymers are conventionally prepared by anionic polymerization, group transfer polymerization, cationic polymerization, radical polymerization, stepwise polymerization and controlled polymer chain scission. The controlled scission of polymer chains offer the potential for making telechelic 'oligomers' from any high molecular weight polymer regardless of its mode of synthesis. This method has, until now, been rather little explored. Oligomers are short chain polymers, the name originates from the Greek words 'oligo' means few and 'mer' means part. The dividing line between oligomers and polymers is a somewhat arbitrary one but is best considered as corresponding to a region beyond which the bulk physical and mechanical properties of the polymer no longer depend significantly on chain length.

Basically, the oligomerization starts from a high molecular weight polymer to a limited degradation and controlling the range and manner of chain scission such that oligomers are produced having desired average molecular weight and end functional groups (functionality). The advantages of controlled degradation are:

(i) It is applicable to a wide range of polymers
(ii) Predetermination of the scission points
(iii) Engineering of various functionality at the chain ends
(iv) Desired functionality achievement

The other methods such as photo-irradiation, heating, chemical degradation and physico-chemical degradation etc are also prevalent to obtain telechelic oligomers[149] but desired specific functionality and regioselectivity is not possible by these methods, moreover, the process consists essentially in the breaking of double bonds which needs high energy.

1.6.1 Synthetic routes of telechelic polymers

Almost all classical synthetic methods for the preparation of polymers have been used for the telechelics:

1.6.1.1 Anionic polymerization

The ability to synthesize addition polymers of predetermined molecular weights and of narrow polydispersity, was virtually created by the development of anionic living polymer technique by Szwarc[151] in late 1950. The usual strategy is to initiate polymerization with a suitable anionic initiator (high concentration relative to monomer) to keep chain length short and then to terminate the resulting living oligomeric anion with a terminating agent which introduces the required end group.[152]

1.6.1.2 Cationic polymerization

Carbocationic polymerizations of vinyl monomers do not generally proceed smoothly to give living polymers which can be end capped to give telechelics with high degree of functionality. Lewis acids in addition to boron tri chloride are also effective in promoting polymerization and other olefins such as β-pinene, can also be converted to telechelics.[153]

1.6.1.3 Group transfer polymerization

A recent advance, which enhances the possibilities for synthesizing telechelic polymers, is the development of group transfer polymerization. GTP is suitable for the polymerization of selected monomers specially methacrylates and acrylates.[154]

1.6.1.4 Free radical polymerization

Radical methods, unfortunately suffer from a number of disadvantages. In particular, the introduction of functional groups during initiation, either by using an appropriately functionalized radical initiator or an initiator, gives a radical of the appropriate functionality. The chain termination takes place exclusively by the combination of radicals if the resulting polymer chains contain two-end functional groups.[155]

1.6.1.5 Step growth polymerization

Step growth polymerizations are defined as polymerizations in which each individual bonding step must be separately activated. The oligomers synthesized by step growth polymerization suffer from the disadvantage of broad molecular weight distributions.[156]

1.6.1.6 Chain scission

Telechelic oligomers with terminal ketone and / or carboxylic groups, can be obtained by specific oxidative double bond cleavages of 1, 4-butadiene, 1, 4-isoprene or other unsaturated units in the homopolymers and copolymers. The chain scission offers the potential of making telechelic oligomers from high molecular weight polymers. The disadvantage of chain scission method is its randomness / distribution. Oxidative cleavage[157], hydrolysis[158], ozonolysis[159] and reductive chain scission[160] are widely employed reactions in the formation of telechelic oligomers.

1.6.1.7 Metathesis

Metathesis of unsaturated polymers belongs to the same group of reactions as metathesis of low molecular weight olefins, ring opening metathesis polymerization or acyclic diene metathesis. In the typical reaction of metathesis, the scission of double bond occurs followed by a recombination of alkylidine groups. High activity catalyst is also important in metathesis.[161]

1.6.1.8 Thermal degradation

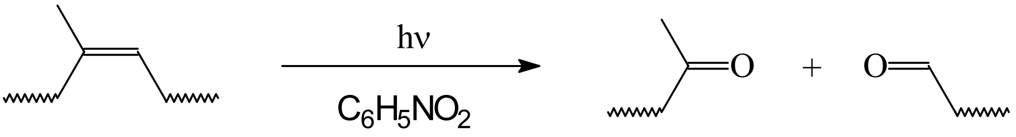
Saturated polymers can suffer chain scission on heating under pyrolytic conditions, giving rise to two radicals which undergo rearrangements. Thermal degradation has been used as the first step in preparing ethylene-propylene based hydroxy-telechelics, having functionality 1.7. This method consists of thermal degradation of ethylene propylene rubber followed by ozonolysis and reduction using alkyl aluminum compound.[162, 163]

1.6.2 General methods of degradation to obtain telechelic liquid rubber

Telechelic liquid natural rubber (TLNR) can be defined as a low molecular weight natural rubber having number average molecular weight of 10^2- 10^4, approximately and having reactive terminal groups capable of being used in further chain extension and crosslinking. The development of methods for the preparation of TLNR was started two decades ago. Basically, the methods involve controlled degradation or depolymerization of the natural rubber backbone via oxidative chain scission by either photochemical or chemical routes. The methods which have been developed on controlled degradation or depolymerization of the chains of natural rubber via an oxidizing scission by photochemical or chemical way. Three main categories are marked to classify these methods:

1.6.2.1 Photo-chemical method

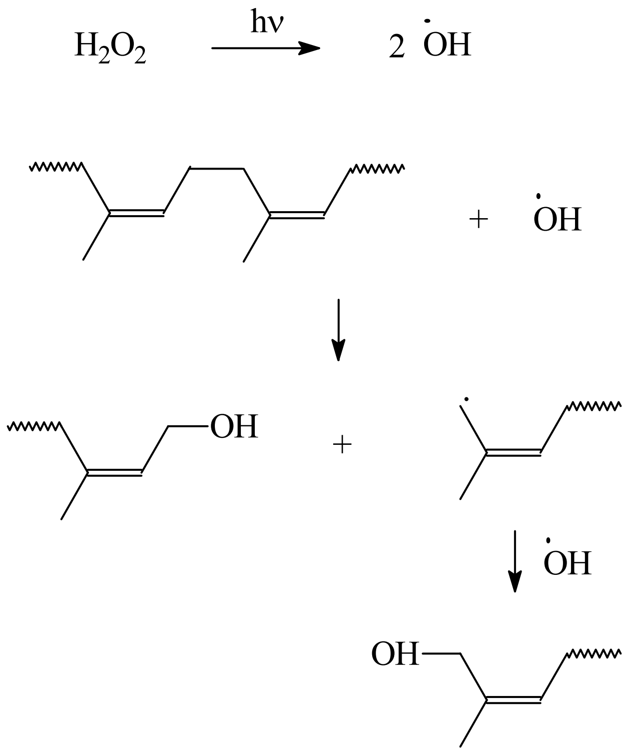
It is known that light having a wavelength of 600 to 300 nm, which is equivalent to an energy of 200 – 400 Kj/mol and therefore, comparable of cleaving the covalent bond of certain substances resulting in free radicals. Under suitable controlled conditions, these free radicals produced can be used to cleave polymer chains to offer telechelic oligomers. Cunneen[164] first explored controlled degradation of natural rubber by photochemical chain scission for the preparation of TLNR. Natural rubber was irradiated with UV light in the presence of nitrobenzene to get carboxy terminated natural rubber, having M_n 3,000 as shown in Scheme 1.7. However, no details were mentioned about mechanism of the reaction, characterization of oligomers and as well as about number average functionality.



Scheme 1.7

Tillekeratne *et al.*[165] utilized sunlight to get TLNR. In this method, natural rubber was first mixed with a photosensitizer using an open mill to get a thin sheet which was exposed to sunlight to achieve carboxy terminated natural rubber having M_n 2,000 – 8,000. However, no details for the appropriate reaction mechanism as well as the functionality were given. The oligomer was also not characterized.

Ravindran and coworkers[6] studied controlled degradation of natural rubber to yield telechelic liquid natural rubber as shown in Scheme 1.8.[5]



Scheme 1.8

In addition to that, a comparison of the degradative effects of UV radiation and sunlight was made. It was found that sunlight as well as UV light degrades the natural rubber in toluene. The functionality was determined using hydroxyl number in the reaction products and it was 1.93 - 1.97 whereas sunlight gave slightly poor functionality. Joseph *et al.*[109] depolymerization the natural rubber in latex form by sun light and hydrogen peroxide, leading to the production of hydroxy terminated natural rubber having number average molecular weight 7,600 after 50 hrs irradiation. The functionality was determined ~2. However, no percentage yields and no details of type and number of functionalities were reported. Abdullah and coworkers[166] studied the controlled degradation of natural rubber in presence of benzophenone in solution phase to yield telechelic liquid natural rubber having weight average molecular weight 10,000 - 50,000. However, the number average functionality was not determined. The mechanism of the reaction leads the chain scission and formation of end products.

1.6.2.2 Oxidation in presence of specific reagents to cleave the double bonds

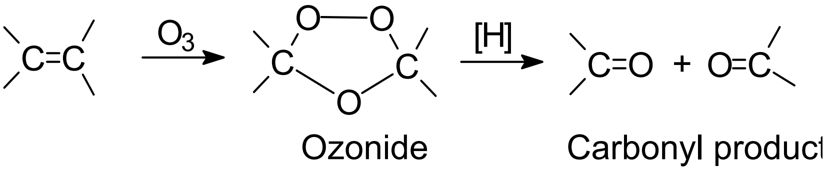
1.6.2.2.1 Ozonolysis

Studies of the action of ozone on diene rubbers were of the fundamental importance in the understanding the structure of natural rubber. Ozonization is still a key tool for the elucidation of molecular structure and monomer sequences in the polymer and is widely used to characterize the structures of various rubbers to make telechelic oligomers.

The problems of ozone attack and antiozonant protection continue to be the subject of great importance. The ozone attack on the rubber causes chain-scission and the formation of various decomposition products such as ozonides, polymeric peroxides, hydroperoxides, lactones, esters and aldehydes etc.

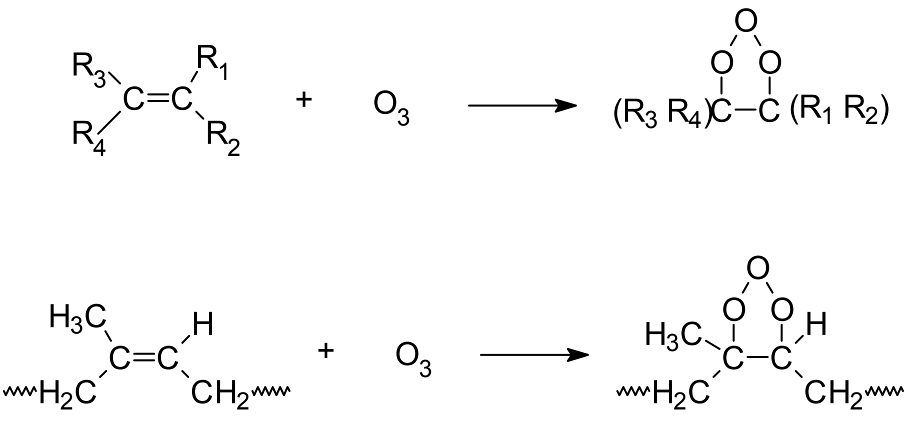
1.6.2.2.1.1 Ozone reactions with double bonds

Ozonolysis is a reaction of alkenes with ozone, producing an ozonide. This ozonide is subsequently reduced and causes cleavage around the double bond, with oxygen attached to each carbon from the double bond. The reaction Scheme 1.9 is shown below:



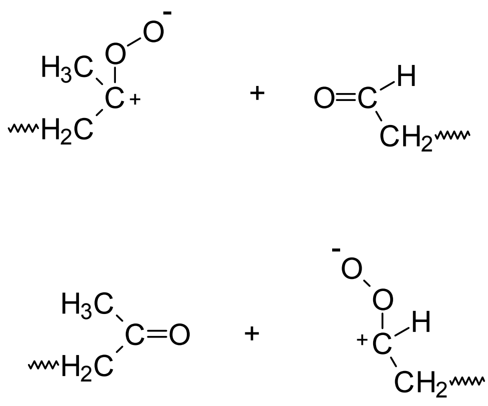
Scheme 1.9

At present the classical mechanism of the reaction of ozone with isolated double bonds proposed by Criegee[167-172] is widely accepted (Scheme 1.10):



Scheme 1.10

Ozone reacts with the double bond as shown in Scheme 1.10, to form 1,2,3-trioxalane (primary ozonide) as shown in Scheme 1.11. The rate of this reaction is dependent on the structure of the double bonds and on the number, electron donating properties and size of the attached R groups.



Scheme 1.11

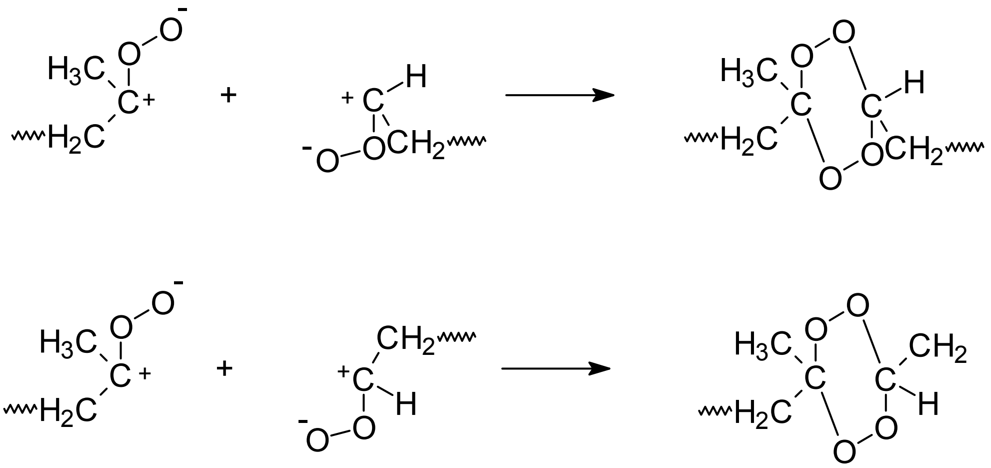
In the case of two substituents, the trans-isomer reacts faster than the cis- one. Two and more adjacent groups can change the mechanism of the reaction to 1,2-cycloaddition or to a triangular transition state, thus forming peroxides and epoxides. Electrons donating attached groups always increase the rate of the reaction but bulky groups hinder the free movement of ozone to the double bonds and therefore, decrease the reaction rate.

The primary ozonide is very unstable and rapidly decomposed to zwitterion, carbonyl oxide (CO) and carbonyl moiety. The cleavage of O-O bond will depend on the primary ozonide geometry, electronic structure and environment. The configuration of the carbonyl oxide formed is closely related to the number, size and electronic properties of the substituents.

In the next step the carbonyl oxide reacts with the carbonyl moiety to form 1,2,4-trioxalane (ozonide) as shown in Scheme 1.12:

Scheme 1.12

The last carbonyl oxide can react outside the kinetic cage with the so-called participating solvent (methanol, water, acetone etc.) or with "foreign" ketones, aldehydes, alcohols and so forth, thus forming hydroxy-ethers or other ozonides. The carbonyl oxide can also react with another carbonyl oxide to form complex oxygen-containing dimeric or oligomeric products as shown in Scheme 1.13:



Scheme 1.13

Harries[173] showed that natural rubber reacts rapidly with ozone and that both the molecular weight and the bromine number decrease. We studied the reaction of ozone with rubbers both in solution and under conditions of the elastic state.

1.6.2.2.1.2 Ozonolysis of natural rubber

Experiments to demonstrate the catalytic effect of light were made both in the sunlight and under artificial light. Light of short wavelength is most effective in producing surface oxidation and in general the amount of oxidation varies with the intensity of light. Ozone is the active cause of cracking but it has no effect on unstrained rubber. The cracking could be prevented by using copper salts to catalyze surface oxidation. Crabtree *et al.*[174] studied the soft vulcanized rubber and found that ozone attacks and affects rubber only under stress and is checked to a considerable degree by addition of certain hydrocarbon waxes as long as the stress is static. Alekpero[175] studied the effect of naphthenic acid on the ozone resistance of rubbers. He found that ozone resistance was improved with increasing concentration of additive and its molecular weight. Andries *et al.*[176] studied the ozonization of a vulcanized natural rubber and observed degraded rubber layer containing ozonides and carbonyl compounds on the surface and characterized it by ATR spectroscopy.

Odinokov *et al.*[177] did ozonization of an unsaturated carbon chain polymer, such as cis-1, 4-polyisoprene in inert organic solvent at –70°C to 30°C, followed by reduction by lithium aluminum hydride. Oligomeric α, ω-glycol was produced at the end of the reaction. Glycol yield was increased and ozone consumption decreased by carrying out the ozonization in the presence of lower alcohols. Miller *et al.*[178] studied the ozonolysis on polyisoprene popcorn polymer at dry ice temperature. The volatile reaction products were collected in a dry ice cooled trap and analyzed. They found water, formic acid, acetic acid and levinaldehyde. Ariffin[179] and coworkers studied the ozonolysis of deproteinized natural rubber in chloroform-ethanol at -30°C and the subsequent reduction of the ozonides by sodium borohydride in aqueous ethanol at 50°C, gave 1,4-pentanediol and γ-valerolactone. The potential use of this ozonolysis-reduction procedure is discussed, especially its use in determining and localizing groups involved in storage crosslinking of natural rubber.

Mathew[180] studied the ozone cracking of NR and NR/EPDM blend by scanning electron microscopy. Rasumovski *et al.*[181] told that the ozonization of unsaturated rubber is governed by the diffusion of ozone from the gas phase into the polymer. Razumovskii *et al.*[182] reviewed the basic reactions of ozone with saturated, unsaturated polymers, various synthetic and natural rubbers. They explained the nature of functional groups, unstable intermediates, the protection of unsaturated rubber vulcanizates against ozone, antiozonants reaction mechanism, the possibility of polymer modifications by ozone and the protection of articles by atmospheric ozone action. Keller *et al.*[183] reviewed the mechanisms of rubber oxidation and ozonation, types of antioxidants and antiozonants and methods of studying the oxidation and ozone resistance of rubbers. Robert *et al.*[184] modified the natural rubber and nitrile rubber by grafting with styrene or butyl acrylate, by immersing into polystyrene or poly(butyl acrylate) solution or by mixing with neoprene rubber (in case of natural rubber) or with butyl rubber (in case of nitrile rubber) followed by heating at 150°C in the presence of morpholine disulfide. The modified rubbers showed a significantly higher resistance to O_3 and HCl than the non-modified samples. Ho[185] described a mechanistic study of hydrocarbon diene elastomers by ozonation as shown in Figure 1.1. A study of the effects of ozonation on butadiene and isoprene and several related hydrocarbon rubbers showed that rubbers containing di-substituted double bonds (e.g., cis-1, 4-polybutadiene) gave crosslinked as well as chain scission products in nonpolar solvents whereas those containing tri-substituted double bonds (e.g., cis-1,4-polyisoprene) gave chain scission products only. Both types of rubbers gave only chain scission products in polar solvents. It is clear from Figure 1.1 that amount of crosslinked gel is directly proportional to the amount of ozone absorbed and the yield of it is unaffected by the temperature during ozonization. The effect of ozonides of mono-olefins and the solvent effect implied that the chain scission involved an attack of a second ozone molecule on the pre-formed ozonide and the crosslinking was due to an attack of the biradical carbonyl oxide on the rubber. It is shown in Schemes 1.14 and 1.15.

Plaumann *et al.*[186] suggested two methods, ultrasound and ozonolysis which were used to degrade cis-polyisoprene. Perera *et al.*[187] studied the fragmentation of epoxidized natural rubber by ozonization and the ozonized mixture was analyzed by GC/MS. Clough *et al.*[188] investigated gamma-radiation degradation of SBR and nitrile rubber in the presence of air. Using a recently developed modulus profiling technique, it is shown that the degradation of these materials is very heterogeneous through the sample thickness. There is a broad, parabolic shaped modulus profile through the sample interior, together with a dramatic change in modulus in the surface regions.

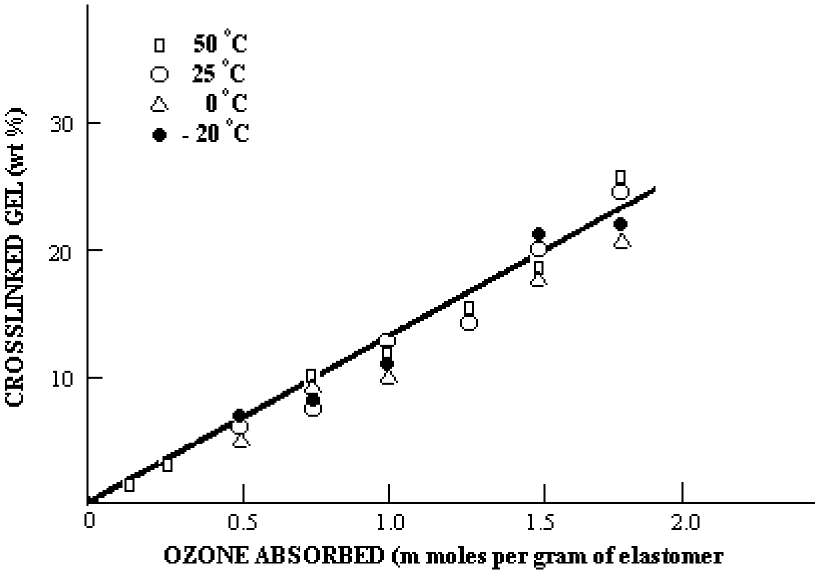
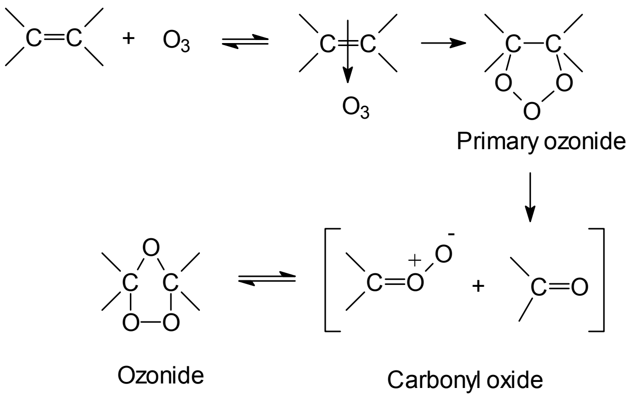
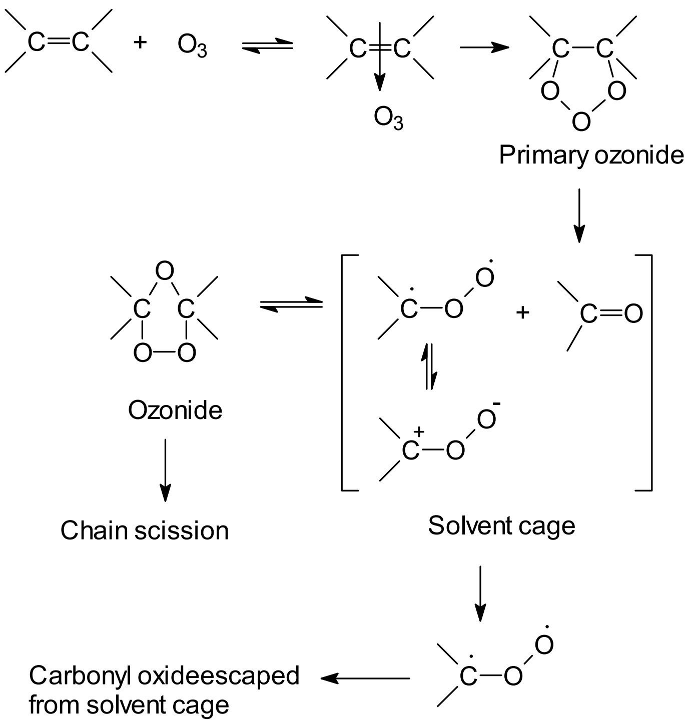


Figure 1.1: Relationship between amount of ozone absorbed and crosslinked gel during ozonization of cis-1, 4-polybutadiene in hexane at different temperatures.



Scheme 1.14



Scheme 1.15

Vogel *et al.*[189] described the ozonolysis of cis-1,4-polyisoprene, cis-1,4-polybutadiene and trans-1,4-polychloroprene rubber surfaces and characterized by FT-IR spectroscopy. Razumovskii *et al.*[190] showed that physico-chemical principles govern the aging of elastomers under the action of atmospheric ozone. The complex process of ozone degradation of elastomers was considered as a physico-chemical system. Parker *et al.*[191] described a hydrogenated elastomeric polymer latex by (a) combining an unsaturated polymer in latex form with an oxidant selected from oxygen, air, and hydrogen peroxide followed by a reducing agent selected from hydrazines and their hydrates and with a metal ion activator, (b) heating the mixture to a temperature from 0°C to the reflux temperature of the reaction mixture, (c) treating the mixture with ozone in an amount and under conditions which are sufficient for the ozone to react with residual polymer unsaturation to form an ozonated latex of elastomeric polymer having one terminal aldehyde end group, (d) treating the ozonated latex with hydroxylamine in an amount and under conditions which are sufficient to convert the aldehyde end groups to oxime end groups to form an oximated polymer latex.

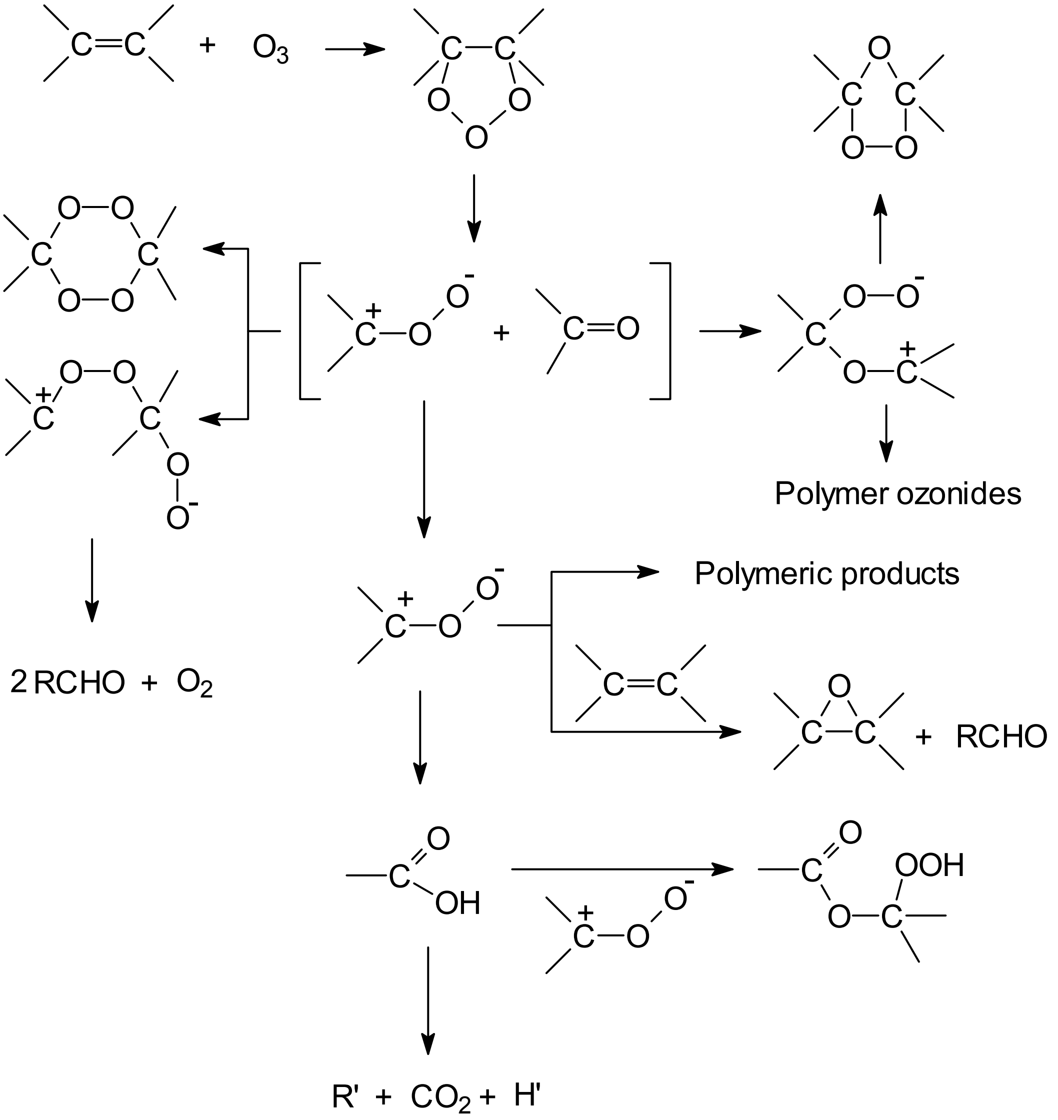
Thomas *et al.*[192] studied modification of diene rubbers by ozone. The filler-rubber interaction of diene rubbers is improved, resulting in tire treads with better roll resistance. Han Sang[193] studied the surface degradation characteristics of silicone rubber which is used as the weathershed material of polymer insulators under natural environmental condition. Rakovskii *et al.*[194] studied the mechanism of crack formation in rubbers under the effect of ozone. The formation and growth of cracks in natural, isoprene, butadiene and SBR rubbers under the effect of ozone were studied using reflection-light optical microscopy. Parker *et al.*[195]studied the ozonolysis of rubber latexes for removal of residual hydrazine. An emulsion of vulcanized rubber latex containing residual hydrazine is subjected to ozonolysis under sufficient ozone to react with the vulcanized rubber and the residual hydrazine to produce latex of soluble elastomer having a reduced level of residual hydrazine. Frank *et al.*[196] studied the formation of hydrogen peroxide in the ozonolysis of isoprene and simple alkenes under humid conditions.

Criegee's[167-169] three-step mechanism has been widely accepted. The first step is the formation of a primary ozonide. In most cases, it is a concerted cycloaddition of alkene to ozone. The second step is the fragmentation of the primary ozonide into a carbonyl oxide and a carbonyl compound. Carbonyl oxide is the core of Criegee's mechanism. The ratio of carbonyl oxide to carbonyl compound depends on the structure of the alkene. The third step is recombination of the carbonyl compound with carbonyl oxide. Besides newly formed carbonyl compound, other already existing carbonyl groups can also react with carbonyl oxide. Carbonyl oxide can also react with compounds bearing active proton, such as water, alcohols, organic acids and amines. Anachkov *et al.*[197] studied ozonolysis of 1,4-cis-polyisoprene and 1,4-trans-polyisoprene in solution using carbon tetrachloride. By means of IR and ^{1}H NMR spectroscopies, it was established that the basic ozonolysis products of both elastomers are ozonides, ketones and aldehydes. The ozonide: ketone:aldehyde ratio established by NMR spectra was 40:37:23 and 42: 39:19 for 1,4-cis-polyisoprene and 1,4-trans-polyisoprene, respectively. In addition to the specified functional groups, epoxide groups were also found, their amount being 8 and 7 % for 1,4-cis-polyisoprene and 1,4-trans-polyisoprene, respectively, in relation to reacted ozone.

1.6.2.2.1.3 Kinetics of primary ozonides

Saloman *et al.*[198] studied the correlation between the structure of elastomers and the mechanism of their degradation by ozone. The ozone sensitivity is roughly proportional to the number of double bonds. Razumovskii *et al.*[199] determined the rate constants for reaction of ozone with polymer solutions in carbon tetrachloride at 20 °C and it was 7.5 x 10^5 for natural rubber and studied the rate constants for the reactions of ozone with triphenyl phosphite and triphenylphosohine at several temperatures[200].

Nangia and coworkers[201] studied the thermo chemistry and kinetics of ozonization. To explore the reaction pathways for ozonation reactions, empirical methods of transition-state theory were used. For unsaturated compounds, all three steps in the formation of stable ozonides are fast and concerted processes. These are (a) primary ozonide formation, (b) cleavage of primary ozonide into carbonyl oxide plus aldehyde or ketone, and (c) recombination of carbonyl oxide with aldehyde (or ketone) to produce stable ozonide. The exothermicities of steps (a) and (c) are shown not to lead to hot molecular effects in liquid state but can do so in gas reactions. These exothermicities do lead, however, to important self-heating in ozonation of olefins. Razumovskii *et al.*[202] studied the kinetics of absorption by elastomers, using ozone by butyl, natural, neoprene, SKD, SKI-3 and SKS-30 ARKP rubber vulcanizates in a small glass compartment for diffusion-controlled. Anachkov *et al.*[203] studied the decrease in molecular weight of three different grade of nitrile rubber samples, containing, respectively, 20, 28 and 39 mol % of acrylonitrile, during their ozonization in solution. By comparing the functional groups obtained during ozonolysis of the C=C bonds with the amount of the ozone consumed, it was found that ~1 mol of ozonides or 2 mol of aldehydes were formed from 1 mol of reacted ozone. The degradation mechanism of nitrile rubber by ozonization was shown in Scheme1.16. Nor *et al.*[204] studied the kinetics of chain scission and major changes in functional groups of natural rubber (NR) during ozonolysis in chloroform at 0°C. Reduction in molecular weight occurs most noticeably in the first minute of ozonolysis to give products with a bimodal distribution of molecular weight. After 20 minutes of ozonolysis, the number average molecular weight (M_n) falls to less than 900 and the molecular weight distribution becomes close to unimodal again. These findings are interpreted in terms of an initial, rapid, diffusion-controlled process of ozonolysis, during which polymeric ozonides and peroxides (and possibly also hydroperoxides) are formed, followed by a slower second stage during which the ozonides and peroxides are cleaved, possibly by reaction with further ozone, to give oligomers with various oxygenated end groups.



Scheme 1.16

1.6.2.2.1.4 Sequence length distribution

Tanaka *et al.*[205] studied the sequence length distribution in butadiene-styrene rubber (SBR) after ozonolysis and characterized by GPC method. Tanaka and coworkers[206] studied the sequence distribution of styrene units in vulcanized styrene butadiene rubber (SBR) and analyzed by high-resolution gel-permeation chromatography (GPC). The GPC fractions, corresponding to long styrene sequences, the residual 1,4-butadiene units, as measured by ^{1}H NMR, decreased from 77 to 47 % as the ozone increased from 3.7 to 80% of the required amount. Razumovskii *et al.*[207] studied the kinetics of the decrease in stress (Dp) in isoprene rubber vulcanizates at 22°C and in an ozone concentration of 1.8-7.3 x 10^{-8} mol/L and the kinetics of degradation of the rubber macromolecules in solution. The number of ruptured macromolecules increased linearly with time, whereas the time dependence of Dp was more complex.

1.6.2.2.1.5 Formation of functionalized oligomers

Allison *et al.*[208] studied ozonolysis on purified samples of Hevea brasiliensis, nitrile and neoprene rubbers. They observed hydroxyl and carbonyl groups at 2.9 and 5.8 nm. Stephens[209] obtained low molecular weight hydroxyl terminated oligomers upon passing ozone gas for 75 minutes in cis-1,4-polyisoprene solution at room temperature. Fujio *et al.*[210] obtained high molecular weight 1,4-conjugated diene which were reductively ozonolyzed to give hydroxyl terminal low molecular weight polymers, which were treated with lithium aluminum hydride or sodium borohydride to give polyesters which are useful in coatings, adhesives or synthetic rubbers. Gordienko *et al.*[2111] studied the ozonization of rubber into mixture of ozone-oxygen containing 2.5-3.0 mg/L ozone, followed by reduction with lithium aluminum hydride and obtained cis-1,4 type diol with molecular weight distribution of 2.9 – 4.8. Odinokov *et al.*[212] prepared the oligomeric hydroxy-terminated 1,3-diene polymers with cis-1, 4-configuration by ozonolysis of high-molecular weight 1,3-diene polymers by bubbling an O_3-O_2 mixture in a solution of 1,3-diene polymers in hydrocarbon solvent containing methanol and subsequent reduction of the ozonide product. Rabek *et al.*[213] studied effect of molecular oxygen, singlet oxygen, atomic oxygen and ozone on cis-1,4-polybutadiene using UV and IR spectroscopies. They found chain scission in all cases.

Beresnev *et al.*[214] ozonized the butyl rubber in $C_{12}H_{26}$ at 20°C and the COOH- and ketone group-terminated oligomers were obtained. Pyridine increased the yield of

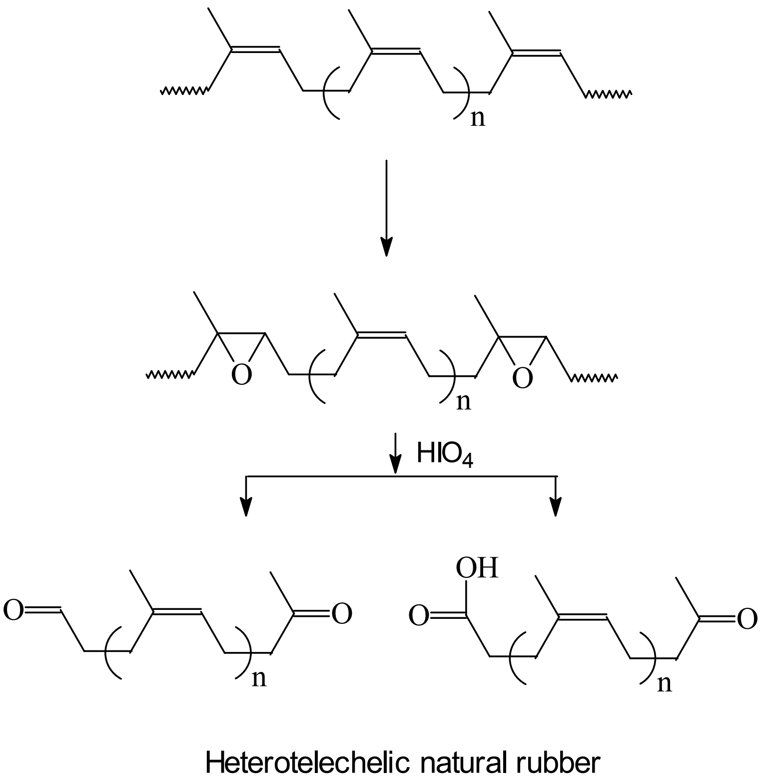
COOH-terminated oligomers presumably due to interaction with bipolar ions and isomerization. Tanaka *et al.*[215] prepared cis-conjugated-diene telechelic oligomers with narrow molecular weight distribution. Beresnev *et al.*[216] obtained oligodienes with narrow molecular weight distribution by ozonolysis of diene rubbers (cis-1,4-polyisoprene and cis-1,4-polybutadiene) at ozone concentration 10-12 mg/L in a reactor. Macias *et al.*[217] described the low-molecular-weight polyisobutylenes with terminal reactive groups. Toshio *et al.*[218] suggested that the polymers containing CH=CH or CR_2=CH (R= H, alkyl or aryl) groups were ozonized and reduced with trivalent phosphorus compounds (triphenyl phosphinne) to give the end functionalized aldehyde groups with average molecular weight between 500 - 50,000.

1.6.2.3 By ruthenium tetraoxide

Ruthenium tetraoxide is a very powerful oxidizing agent. It is soluble in almost all solvents. To carry out the reaction in organic solvents, continuation of ruthenium dioxide - peracetic acid is preferred but periodate also can be used with phase transfer catalyst. The carbon - carbon double bonds are rapidly oxidized by ruthenium tetraoxide. Starting from butyl rubber, a carboxyl ketonic ditelechelic poly(isobutylene) was formed. Diketonic telechelic was obtained from 2,3-dimethyl butadiene / isobutylene copolymer. The reduction of these oligomers can be carried out by using lithium aluminium hydride to yield telechelics. The functionality of the oligomers produced by this method depends on the configuration of diene units, linked in the polymer.[219, 220]

1.6.2.4 Cleavage of Epoxidized polydiene

Epoxidation is an alternative modification of natural rubber. Epoxidized units can be cleaved by selecting a suitable oxidizing agent to get homo/hetero-telechelic oligomers as shown in Scheme 1.17. Potassium periodate was used to cleave the epoxidized units.



Scheme 1.17

However, the molecular weight and polydispersity are higher than expected.[221, 222]

1.6.2.5 Oxidizing agents

The systems based on chromium reagents provide oxidation in unsaturated polymers with simultaneous cleavage.[223] Permanganate-periodate based mixtures exhibit high selectivity and reactivity. It can even be used in the presence of primary hydroxyl functions that are inert in these reactions.[224] Periodates have been used with osmium tetra oxide as a classical system. Limitation of this system is that the osmium tetra oxide can not be solubilized in many solvents.[225] Fuming nitric acid was used to demonstrate that the nitro groups are primary and it can be converted into carboxylic functions on treated with hot concentrated sulphuric acid which gives carboxy terminated poly(ethylene). Nitric acid oxidation was carried out on high density poly(ethylene) to yield nitrated dicarboxy telechelic poly(ethylene).[226]

1.6.2.6 Redox or oxidation-reduction systems

The redox method is also a sophisticated method for the synthesis of end-functionalized polymers/oligomers. The oxidizing agent *i.e.* organic peroxides, hydrogen peroxide, ferric chloride - oxygen etc upon coupling with a reducing agent *i.e.* hydrazines, sulphanilic acid etc, were used to depolymerize natural rubber to telechelic natural rubber Natural rubber was treated with phenyl hydrazine to get end functionalized natural rubber. Controlled degradation of natural rubber latex was accomplished using phenyl hydrazine and oxygen to yield carboxy terminated natural rubber. Model molecules have also established the formation of end functionalization in this way.[227, 7]

1.6.3 Examples of telechelic liquid rubbers:

A list is enclosed of telechelic liquid rubber in Table 1.1.

Table 1.1: Telechelic liquid rubbers

Serial No.	Rubber	Nomenclature
1	Hydroxy telechelic Polybutadiene	HTPB
2	Carboxy telechelic polybutadiene	CTPB
3	Hydroxy telechelic natural rubber	HTNR
4	Carboxy telechelic natural rubber	CTNR
5	Bromo telechelic polybutadiene	BTPB
6	Acrylonitrile-butadiene hydroxy telechelic	HTNBR
7	Acrylonitrile-butadiene carboxy telechelic	CTNBR
8	Acrylonitrile-butadiene telechelic amine	ATNBR
9	Acrylonitrile-butadiene telechelic vinylic	VTNBR
10	Styrene-butadiene hydroxy telechelic	HTSBR

1.6.4 General characterization /analysis of telechelic oligomers

Various methods[228, 229] are known to produce functional polymers having functional groups at both ends 'telechelics'. Telechelic oligomers are of use in several technological spheres like surface coatings, adhesives as well as in reactive injection mouldings and extrusion. Functionally terminated low molecular weight natural rubber are also currently used in sealants, adhesives, to make block and graft copolymers etc and can be used as a binder for rocket propellants also.

Functionality is defined as the average number of reactive groups per molecule and thus became a most important property of the prepolymers. Earlier functionality was determined by dividing molecular weight by equivalent weight but error was found more than 5% in this system. Probably, it is the most important single parameter which determines the nature of the oligomeric chains. Number average molecular weight was determined by VPO and functionality was calculated:

$$F_n = \frac{M_n \text{ x Hydroxyl number}}{4000}$$

where hydroxyl number is in mg (NaOH) / g (polymer). Molecular weight of NaOH = 40 = 40,000 (mg)

1.6.4.1 Fourier Transform-Infrared spectroscopy

Infrared absorption is suitable for quantitative estimation of end groups after being calibrated with polymers of known end group content. Hydroxyl group appears in the range of 3600- 3200 cm^{-1} as broad band due to association with hydrogen bonds.[230] It is shown that the IR quantification of the free hydroxyl absorption at 3640 cm^{-1} using long path liquid cells in dilute carbon tetrachloride solution in conjugation with number average molecular weight determination is a convenient method for analysis of hydroxyl functionality of linear tri-arm star PIB.[231] The reaction with aromatic isocyanates such as toluene sulphonyl isocyanate has been used and disappearance of this group was checked by FT-IR spectroscopy.[232]

1.6.4.2 Nuclear magnetic resonance spectroscopy

^{1}H NMR allows a direct determination of hydroxyl groups as we can check the proportionality between signals and the number of protons. Generally the analysis requires multiple accumulation of the spectrum. Using trimethyl silylchloride for hydroxy telechelic polymer, it is easy to find out the hydroxyl protons as each alcoholic proton will be replaced by nine protons which can be easily identified by NMR spectroscopic method.[233-235] Mauler *et al.*[236] described the functional group determination technique by ^{1}H NMR using phenyl or naphthyl isocyanate as reagents. By using a totally deuterated monomer technique, the fraction of the cyano-isopropyl end group in radical polymerization with azobis(isobutyronitrile) was reported with ^{1}H NMR spectroscopy.[237]

1.6.4.3 Ultra violet spectroscopy

The alcoholic groups do not absorb in UV and a chemical modification of chain extremities is required.[238, 233] UV-visible spectroscopy was used to determine carboxyl and amine end groups in Nylon 66 by using a radio-reagent. This method was compared with that of Waltz and Taylor in which samples are titrated with potassium hydroxide in hot benzyl alcohol to a phenolphthalein end point. The results showed excellent agreement for these condensation polymer samples.[239]

1.6.4.4 Dye detection test

Carboxyl and strong acid end groups were detected by dye partition and dye interaction techniques. Dye detection tests are also suitable for detecting hydroxyl, amino, quaternary ammonium and halogen groups.[240] Ghosh *et al.*[241] determined the end group functionalization by means of dye interaction technique.

1.6.4.5 Titration method

The hydroxyl groups are generally determined by esterification in which the OH group are treated with acetic anhydride or acetyl chloride in pyridine.[242-244, 236] Carbonyl group was determined by titration method by dissolving the sample in pyridine under nitrogen and titrating with 0.02 N sodium methylate to thymol blue end point.

1.6.4.6 Potentiometrically and Conductometrically

The acidic and basic end groups, such as polyesters, polyamides and polyethers were determined by either potentiometrically or conductometrically. Comparison of these methods for determining carboxyl and amine groups shows that the latter is more precise than the former.[245] Potentiometric titration in nonaqueous media was carried out to determine phenolic hydroxyl end groups in polysulfones.[246]

1.6.4.7 Gas chromatography and Size exclusion chromatography

High-resolution pyrolysis-gas chromatography and size-exclusion chromatography (SEC) or Gel Permeation Chromatography also have been applied to analyze the polymer end groups.[247] The number-average molecular weights, determined from GPC of the prepolymers, were compared with number average functionality values obtained by titration of the end carboxyl group.[248] A dual-detector GPC was used to determine the molecular weight and functionality averages and distributions on hydroxy terminated polybutadiene.[233]

1.6.4.8 Elemental analysis

End functionality was determined by calculating the data on the basis of elemental analysis.[249]

1.6.5 Types of end functionalization

The terminal transformation of telechelics gives not only the access to polymers with changed functional groups but also to new compounds with changed properties. Thus, tailor made telechelic polymers and well-defined derivatives may lead to broader use in different fascinating areas. There is a long list of end functionalized telechelics i.e. hydroxyl terminated, carboxy terminated, halogen terminated, phosphonated terminated, ether terminated, tosyl terminated, carboxylic acid ester terminated and many more. Some of them are:

1.6.5.1 Hydroxyl terminated

Hydroxyl terminated means the presence of one hydroxyl group at each end of the oligomeric / macromolecular chain. These reactive chain ends can be further used for chain extension. Various methods are available in literature to synthesize hydroxyl terminated/ telechelic polymers using azo compounds[250, 251], peroxides[252], photoinitiators[253], Fe (II) / Hydrogen peroxide system[254], UV light with hydrogen peroxide[5, 6, 109, 255] Hydroxyl terminated soluble polymers were prepared by reacting carboxyl terminated nitrile rubber (1.2 equivalent) and 2-amino-1-ethanol (1 equivalent) in toluene at 150°C until 90% carboxyl group reacted and stripped in vacuum to get the product.[256]

Low-viscosity liquid diene polymers were prepared in high yield by treating conjugated dienes with hydrogen peroxide in the presence of carboxylic acids. Thus, 1, 3-butadiene, iso-propanol, hydrogen peroxide and acetic acid were taken and stirred for 90 minutes at 125° to get 69.1% OH-terminated polybutadiene (average molecular weight 1670, OH content 1.26 mili equivalent /g).[257] Hydroxyl-terminated natural rubber (HTNR) was prepared by the depolymerization of masticated natural rubber in the presence of hydrogen peroxide in toluene. Probable mechanism leading to the formation of side-reaction products was proposed based on the analytical data.[258]

1.6.5.2 Carboxy terminated

A method for preparing a crosslinked rubber was formulated having improved hysteretic properties which exhibit reduced rolling resistance. This composition is based on an elastomer matrix comprising at least a diene elastomer including a carboxylic acid function at one or both chain ends and a reinforcing filler where the diene elastomer[259] molecular weight is > 80,000 g/mole. Application of thin layer chromatography separation of polymers by difference in end-group showed that these liquid rubbers had functionalities >2.0, indicating that the termination mechanism in this polymerization was predominately by coupling reaction.[260]

1.6.5.3 Amine terminated

Amine-terminated reactive liquid polymers can be prepared by using corresponding carboxy-terminated liquid butadiene and nitrile rubbers and diamines and used as impact modifiers in epoxy resins.[261] Amine-terminated styrene - butadiene rubber (SBR) or nitrile rubber was prepared by amination of chlorine - terminated rubbers and could be cured to vulcanizates with good chemically and water resistant.[262]

1.6.5.4 Nitrosodiphenylamine terminated

A composition prepared by mixing rubber with oligomeric nitroso diphenylamine-terminated cis-1, 4-polyisoprene in toluene or an isopentane-toluene mixture was a two-component system in which there was no chemical interactions between the nitrosoamine groups of the oligomer and rubber.[263]

1.6.5.5 Epoxy terminated

An epoxy-terminated adduct was prepared by blending an epoxy resin with tri-phenylphosphine, butadiene/acrylonitrile rubber and carboxy-terminated rubber at 100°C for 3 hrs.[264]

1.6.5.6 Silyl terminated

The silyl group terminated rubbers provide vulcanizates with excellent heat resistance, water resistance, weatherability and flexibility. The polymeric main chains are composed of liquid rubber and / or hydrogenated liquid rubber residues with terminal silyl groups.[265]

1.6.5.7 Isocyanate terminated

The isocyanate terminated rubber were synthesized which contain fewer heterogeneous inclusions and form vulcanizates with improved quality.[266]

1.6.5.8 Bromine terminated

Bromine terminated polybutadiene rubber was prepared by emulsion polymerization of butadiene in the presence of carbon tetrabromide as chain-transfer agent. When the amount of carbon tetrabromide, emulsifier and initiator was 20, 5 and 3.5 - 4.5 %, respectively, at 60 – 75°C (polymerization temperature) for 18 - 24 hrs, the conversion was more than 90 %. The average functionality of the rubber was ~2.[267]

1.6.5.9 Maleimido terminated

An amino-terminated butadiene-acrylonitrile copolymer[268] was chemically modified into a Maleimido terminated rubber which can be used as a toughening agent for an unsaturated polyester resin.

1.6.5.10 Chlorobenzoate terminated

Carbon black filled injection moldable rubbers were manufactured from chlorobenzoate terminated butadiene oligomer[269], chlorobenzoate-terminated butadiene-styrene oligomer or acrylonitrile-chlorobenzoate-terminated butadiene oligomer which were characterized by adequate tensile strength, hardness, high fatigue strength, crack and heat resistance methodologies.

1.6.5.11 Hydrocarbyl (thio)phosphites terminated

Solution-polymerized diene rubbers were terminated with hydrocarbyl (thio)phosphites.[270] The phosphite terminated polymers can be added to carbon black filled and oil extended tread stocks for high resilience, low hysteresis and improved tensile strength.

1.6.5.12 Organometallic terminated

Uncoupled, linear butadiene rubber was terminated by Bu_3Sn-, Ph_3Ge- or Ph_3Pb- groups[271] which produced highly improved properties in gum stocks or filler-containing stocks without increasing the rubber molecular weight. Thus, butadiene was polymerized in cyclohexane in the presence of terminating agent (Bu_3SnCl) with a multilithium catalyst prepared by treating divinylbenzene with Butyl lithium.

1.6.5.13 Vinyl terminated

Vinyl terminated[272] stable polymers can be achieved by treating carboxy terminated nitrile rubber with glycidyl methacrylate in the presence of carboxylic acids having pKa 2.5b- 5.0 to yield.

1.6.5.14 Vinylidene terminated

Vinylidene-terminated rubber[273] can be obtained by treating carboxy terminated nitrile rubber with glycidyl in the presence of acrylic acid at 95°C for 6 hrs.

1.6.5.15 Ester terminated

Ester terminated telechelic polymers were synthesized by the acyclic diene metathesis (ADMET) polymerization of 1,9-decadiene with ester-containing mono olefins using ruthenium based Grubbs catalyst.[274]

1.6.5.16 Bio-active terminated

As some telechelics have inert backbones, it will be interesting to modify the terminal chain ends with biologically active molecules in order to obtain compounds with changed and desired properties. The compound 3-(5-fluorouracil-1-yl) propionyl chloride does not show any anti-tumour activity but when coupled with monomethoxy poly(ethylene glycol), enhances the antitumor activity. Interestingly, the antitumor activity increased with the chain length of the telechelic introduced for a range of 'n' in between of 1 and 113.[275]

1.6.6 Applications of telechelic oligomers

The synthesis of telechelic polymers and their utilization for the design of new macromolecular architectures has become a scientifically and industrially very emerging and interesting field. The uses of telechelics are as starting blocks for segmented copolymers. It is useful to make thermoplastic elastomers as well as a large number of speciality polymers. Segmented copolymers lead to polymeric emulsifiers, adhesion promoters, surface modifiers and compatibilizers etc. Coupling reactions between different polymers via their end groups provide the possibility to prepare polymer networks containing different segments. Unique physical properties can also be obtained by composing of more than two different segments to synthesize linear multi segmented copolymers. The great interest in telechelic polymers resides in the fact that such polymers can be used, generally together with suitable linking agents, to carryout three important operations:

(i) chain extension of short chains to long ones using bifunctional linking agents

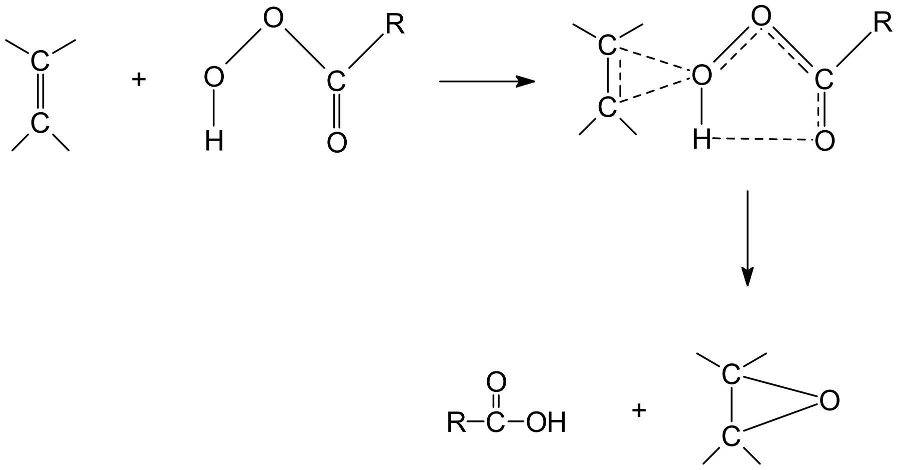
(ii) network formation by multifunctional linking agents

(iii) block copolymers formation by combination of telechelics with different backbones

The use of liquid precursors which can be end-linked to the desired network, offers not only processing advantages but in some cases, also better properties of the end product.

1.7 EPOXIDATION OF NATURAL RUBBER

The epoxidation chemistry of rubbers using peroxy acids is well documented in the literature.[276-282] The mechanism proposed by Barlett[283] is generally accepted and involves electrophilic attack of the peroxycarboxylic acid on the double bond with the formation of a bicyclic transition state as shown in Scheme 1.18.

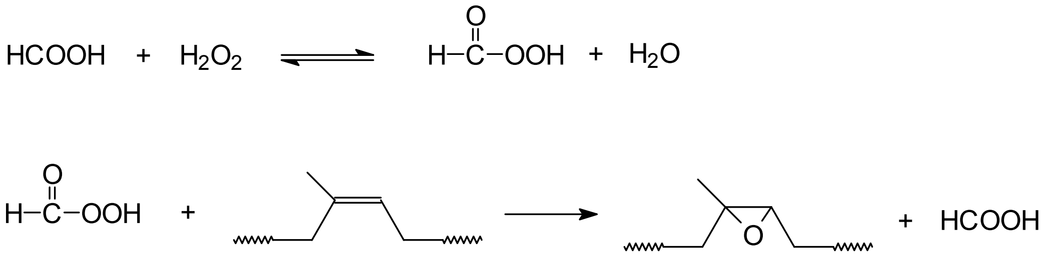


Scheme 1.18

Badran *et al.*[284] studied the in-situ epoxidation in natural rubber and 1,4-*cis*-polybutadiene using hydrogen peroxide and acetic acid in the presence of *p*-

$MeC_6H_4SO_3H$ as catalyst. Gelling[285] stabilized the natural rubber latex with a nonionic alkoxylate surfactant and treated with *in-situ*-formed performic acid at 60°C for 23 hrs followed by addition of 2,5-di-tert-pentylhydroquinone as stabilizer and heated for 1 h to get epoxidized natural rubber latex (ENR 50). A titration method[286] of determining low-level epoxidation in cis-1,4-polyisoprene was performed with generating of HBr in-situ by treatment of Et_4NBr with $HClO_4$. Natural rubber was epoxidized with peracetic acid to 25, 50 and 75 mole % epoxidation. At low levels of epoxidation, simple diols and hydroxy acetates were formed. However, at higher epoxidation, 5-membered cyclic ethers were formed. At 100 mol % modification, the white, amorphous thermoplastic product consisting almost entirely of furan structures was observed.[287]

Ng *et al.*[288] reported that due to high acidity of formic acid, the oxiranes readily changed into hydroxy formate and glycol. In most cases, the latex coagulated within 2 hrs of reaction and further THF rings were formed as the side reactions. Burfield and coworkers[289] studied natural rubber latex epoxidation by bromohydrin intermediates, H_2O_2 - catalyzed systems and in-situ peracetic acid. The peracetic acid was found most suitable reagent for epoxidation of latex. The randomness of epoxidation in natural rubber was determined using IR spectroscopy and differential scanning calorimetry methods.[290, 291] Gan and coworkers[292] studied the kinetics of stabilized epoxidized natural rubber latex at 3, 15 and 25°C. The samples were characterized by gravimetric, DSC, IR and NMR analysis. The rate determining step of the epoxidation was the formation of performic acid (Scheme 1.19).



Scheme 1.19

The effect of acid concentration and other reaction parameters on epoxidation of natural rubber latex were studied. The kinetics of the reaction and effect of acid concentration were studied in depth.[293, 294] The kinetics of epoxidized natural rubber [295] and cyclized rubbers were studied and compared. The epoxidation reaction of natural rubbers was found of second order. The purified natural rubber and synthetic isoprene rubber were epoxidized using *m*-chloroperbenzoic acid. The rubbers were tested for an accelerated storage hardening test in the presence of *glycine*.[296, 297] The aggregative stability of natural rubber latex stabilized by a nonionic surfactant (Verol S-15) was studied in the presence of formic acid during in-situ epoxidation. The epoxide contents were characterized by by IR and ^{1}H-NMR. The solubility and gel content in various solvents demonstrated that epoxidation led to increasing gel content at high epoxide levels.[298] The aggregative stability of natural rubber latex (NRL) was studied in the presence of 1.7-5.0 part per hundred rubber (phr) of nonionic surfactant and HCl. The reaction is fast and of high efficiency, leading to pure epoxidized natural rubber (ENR) products having up to approx. 50 mol% epoxide groups. At high epoxide level, the epoxidation leads to increase the gel content of product.[299]

Perera *et al.*[300] studied furanized rubber by NMR spectroscopy. Effect of latex concentration on the extent of epoxidation of natural rubber was evaluated by determining the physical properties. It was found that the epoxidation rate increased with increasing latex concentration.[301] The epoxidation of natural rubber using H_2O_2 and formic acid was hindered by adventitious iron (II).[302] Roy and coworkers[303] observed the effects of agitation, mode of addition of reagents, secondary acid and neutralization techniques on epoxidized natural rubber latex (ENRL). FT-IR spectroscopy was used in the determination of the degree of epoxidation of epoxidized natural rubber, the vinyl content of the unreacted products and byproducts.[304] The accumulation of a gel phase in the epoxidized polyisoprene latexes is strongly depend on acidity of the reaction medium and on the particle size. The epoxidation was carried out using formic acid and hydrogen peroxide. Comparison of the degree of swelling of the gel phase in a hydrocarbon solvent and in a solvent which is capable of acting as a hydrogen bond acceptor demonstrated that the gelation is due to the result of secondary interactions between the polymer chains.[305] Derouet *et al.*[306] studied the chemical modification of 1,4-polydienes by dialkyl (or aryl) phosphates and evaluated in terms of improved flame resistance. The pervaporation separation and the swelling behavior of chlorinated hydrocarbon / acetone mixtures were investigated using natural rubber (NR) and epoxidized natural rubber (ENR) membrane with 25 and 50 mole %

epoxidation, respectively. The swelling degree increases with increase in the epoxidation level. Li[307] synthesized the epoxidized natural rubbers (ENRs) with different epoxide percentage by suitably increasing the reaction temperature and reducing the dosage of formic acid and hydrogen peroxide. Zhang *et al.*[308] prepared the epoxidized butadiene rubber, natural rubber, isoprene rubber and styrene-butadiene rubber by in-situ epoxidation using alkyl hydroperoxide in the presence of a complex catalyst of Mo, W, V or Ti metal.

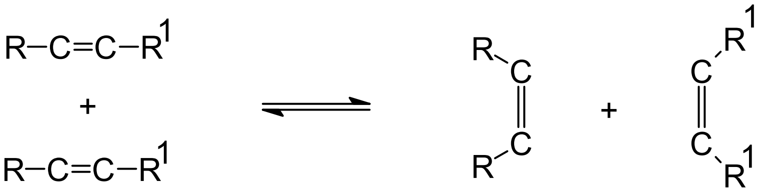
1.7.1 Epoxidation in biphasic medium

There are a few references in literature on epoxidation of natural rubber in biphasic medium[309] where the catalysts were chloro- or acetato-manganese (III) tetraphenylporphyrin in association with NaOCl and PhIO. This transformation in aqueous dichloromethane and / or PhIO(s)-CH_2Cl_2 was monitored by ^1H NMR and IR spectroscopy. In both the cases, the transformation to the polyepoxide was completed within a few hours. Yadav *et al.*[310] demonstrated the epoxidation of styrene with aqueous H_2O_2 by using synergism of heteropoly acid (HPA) and phase-transfer catalyst (PTC) in a biphasic system. Styrene was converted quantitatively to styrene oxide with 100 % selectivity in ethylene dichloride at 50°C. The effects of various parameters were studied on the rate of reaction. Dodeca tungstophosphoric acid and cetyldimethyl benzylammonium chloride were found to be the best HPA and PTC combination, respectively, for the epoxidation. At higher temperature, decomposition of hydrogen peroxide was observed. The epoxidation of polybutadiene[311] was carried out in biphasic system (H_2O_2 / dichloromethane) with methyltrioxorhenium. This system presented a high selectivity of epoxidation without significant change in the molecular weight of the polymer.

Bach *et al.*[312] studied epoxidation of alkenes with o - ethylperoxycarbonic acid generated in situ in an alkaline biphasic solvent system. Later Daniel and coworkers[313] studied olefin epoxidation by a manganese (III) (porphyrin)-ascorbate in a biphasic system. Arias *et al.*[314] carried out the epoxidation of alkenes with trichloroacetonitrile/hydrogen peroxide in a neutral biphasic solvent system. There is an extensive literature available on epoxidation of olefins in biphasic medium with various methods.[315, 316]

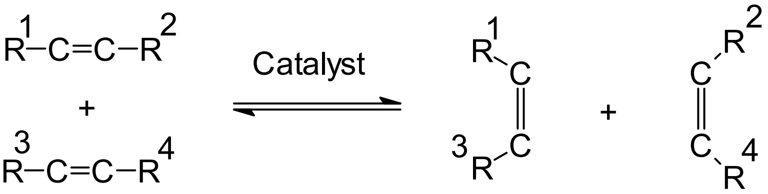
1.8 METATHESIS: A GENERAL VIEW

Olefin metathesis is the reaction that interchanges the alkylidine fragments existing at the carbon - carbon double bond in the starting olefin with formation of higher and lower members of this series of compounds.[317, 318] The word metathesis is a Greek word and means transportation of interchange. It is the metal catalyzed redistribution of carbon – carbon double bonds (Scheme 1.20):



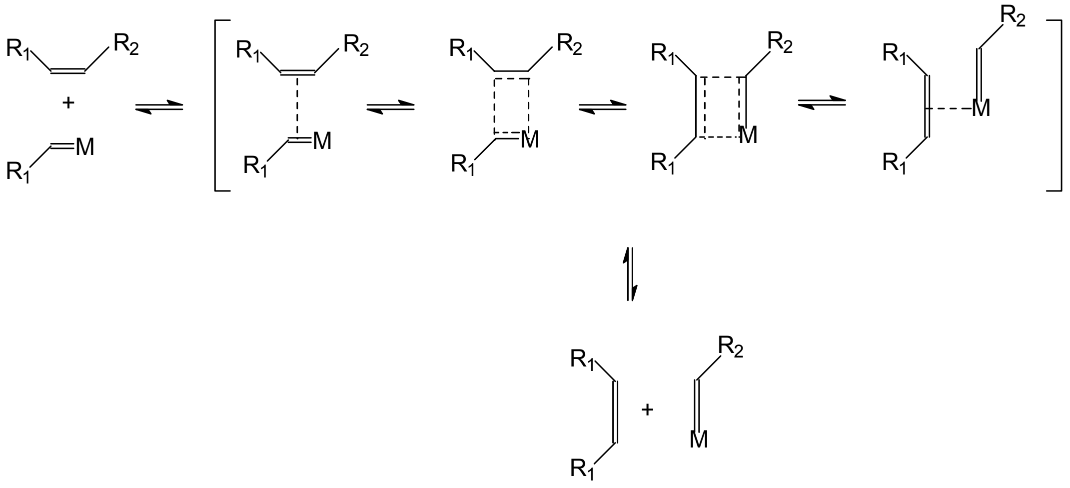
Scheme 1.20

This process takes place in the presence of a wide range of catalysts derived from transition metal salts, preferably in association with organometallic compounds. The specific metallacarbenes derived from tungsten, molybdenum and ruthenium are more specific and efficient catalysts while rhodium, iridium and osmium have also been used.[319] The reaction occur between two different olefins, giving rise to other two new olefins, is called cross metathesis (Scheme 1.21).



Scheme 1.21

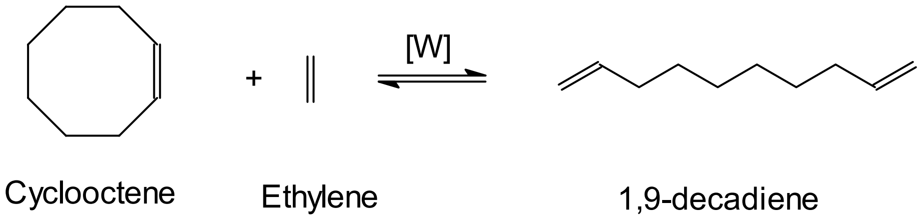
The metathesis reaction occurs through a metallacarbene-metallacyclobutane mechanism involving a [2+2] Cycloaddition of the metallacarbene to the olefin to form intermediate, metallacyclobutane (Scheme 1.22).[317, 320] This intermediate product can either revert to the starting material or open in a productive manner.



Scheme 1.22

1.8.1 Ring Opening Metathesis

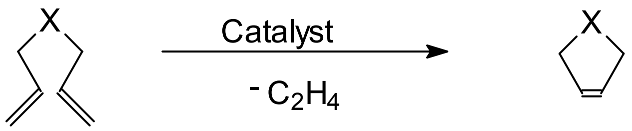
The cleavage of cycloolefins by ring opening metathesis with acyclic olefins in the presence of appropriate metathesis catalyst to produce linear dienes from cycloolefins as shown in Scheme 1.23.[321, 322] The reaction needs controlled conditions *i. e.* catalyst, reactant, temperature etc.



Scheme 1.23

1.8.2 Ring Closing Metathesis

The ring closing metathesis reaction has recently become a versatile route for the synthesis of cyclic compounds in the polymer and organic chemistry.[323] The reaction can be applied to unconjugated dienes which form carbocyclic compounds and to heteroatom containing dienes leading to heterocyclic compounds using suitable catalysts (Scheme 1.24).[324, 325]

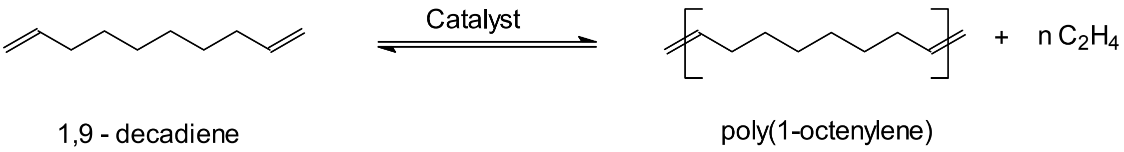


where X = O, N, C

Scheme 1.24

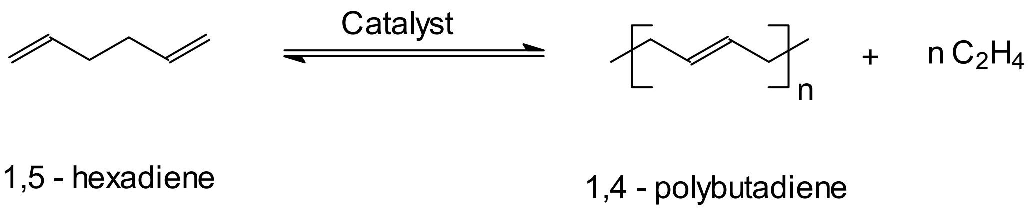
1.8.3 *Acyclic Diene Metathesis*

Acyclic diene metathesis polymerization is a viable synthetic route for high molecular weight polymers. A wide variety of unsaturated polymers and copolymers can be prepared using metathesis catalysts (Scheme 1.25).[326, 327]



Scheme 1.25

1,4-polybutadiene has been synthesized by the metathetic condensation polymerization of 1,5-hexadiene as shown in Scheme 1.26.[328]



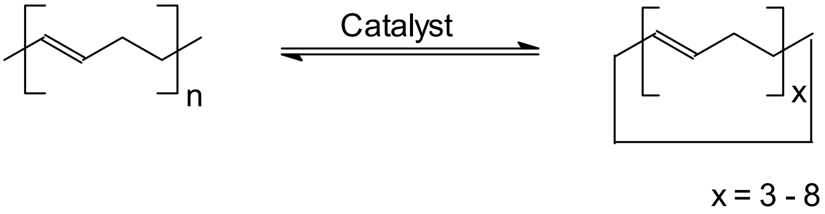
Scheme 1.26

1.8.4 *Metathetic Degradation of Unsaturated Polymer*

There are three ways for the degradation of unsaturated polymers by metathesis reaction, using metathetic catalysts:

1.8.4.1 Intramolecular Degradation

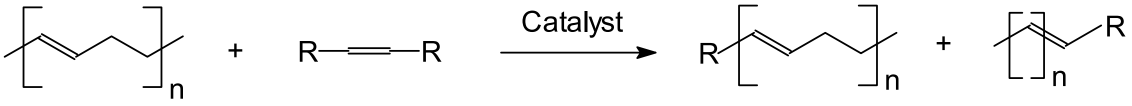
It is the intramolecular degradation of linear unsaturated polymers to macrocyclic oligomers by tungsten hexachloride based catalysts. 1,4-polybutadiene gives a series of unsaturated macrocycles with the number of repeating units, ranging from 3 to 8 as shown in Scheme 1.27:[329]



Scheme 1.27

1.8.4.2 Intermolecular degradation

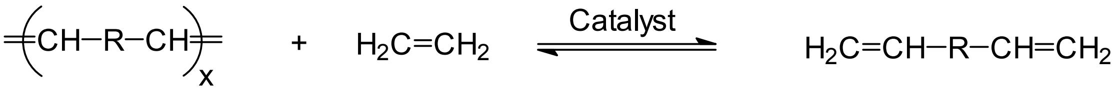
Unsaturated polymers react with linear olefins to give low molecular weight products by controlled chain scission using metathesis catalyst as shown in Scheme 1.28:[330]



Scheme 1.28

1.8.4.3 Acyclic Diene Metathesis Depolymerization

The polymers can be degraded to low molecular weight oligomeric units by using metathetic catalysts[331] as shown in Scheme 1.29:



Scheme 1.29

1.8.5 Metathetic Degradation of natural rubber and polybutadiene

Kumar *et al.*[332] studied the kinetics of metathetic degraded 1,4-polybutadiene. Crosslinked cis-1,4-polybutadiene was treated with metathesis catalysts (WCl_6-Me_4Sn) with trans-4-octene. Hummel and coworkers[333] studied the metathesis degradation of polymers using Grignard-Wurtz reaction in that partially hydrobrominated 1,4-polybutadiene and α-brominated polyoctenylene were treated with RMgBr where R = pentyl, iso-Pr, cyclohexyl, benzyl, 4-methylbenzyl, Ph, 4-methylphenyl, 4-ethylphenyl, 3,4-dimethylphenyl, 2,4,6-trimethylphenyl, 4-chlorophenyl, 4-fluorophenyl, 4-methyloxyphenyl, 3,4-dimethoxyphenyl and 2-thienyl. In addition, partially hydrobrominated 1,4-polybutadiene was treated with RMgBr, where R = 2-methylbenzyl, 3-methylbenzyl and 4-isopropylphenyl. Polymers were metathetically degraded with 4-octene using WCl_6/Me_4Sn as a catalyst. The low molecular weight products were separated by gas chromatography and identified by mass spectrometry. Metathetic degradation of rubbers has been reviewed in literature.[334-336] Some other copolymers were also degraded using metathesis catalysts.[337]

Co-metathesis reactions[338] of 1,5-cyclooctadiene were carried out with di-methyl-3-hexenedioate, 4-octene and 1,5-hexadiene for comparative study. The experimental distribution of the telomers was compared with theoretical values. The reactivity of 1,5-cyclooctadiene double bonds was found higher than that of the other types of double bond. The possibilities of weight control of the degraded 1,4-polybutadiene were also studied. Alimuniar *et al.*[339] studied the metathetic degradation of natural rubber. Metathesis reactions were carried out using WCl_6 and $(Me)_4Sn$ in chlorobenzene. Marmo *et al.*[340, 341] synthesized perfectly difunctional high-molecular weight telechelics by ADMET depolymerization of polybutadiene with 1,4-bis(trimethylsilyl)-2-butene. The α,ω-vinyl-terminated butadiene oligomers[342] can be synthesized by the cross-metathesis of ethylene and high molecular weight 1,4-polybutadiene, catalyzed by the complex $RuCl_2(=CHPh)(PCy_3)_2$ (Grubb's catalyst). The effect of varied ethylene pressure is studied in order to obtain the highest conversion to the monomer 1,5-hexadiene. 1,4-polybutadiene was depolymerized with ethylene using Ru catalyst in bulk and in solution phase. Linear and cyclic butadiene oligomers with n = 1 - 7 (for linear) and n = 2 - 7 (for cyclic) were obtained.[343]

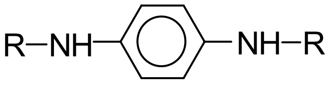
Hillmyer *et al.*[344] accomplished the polymerization of cyclooctadiene (COD) in the presence of 1,4-diacetoxy-2-butene (chain transfer agent) by a ruthenium metathesis catalyst (Grubb's catalyst). Deprotection of the resulting acetate end-functionalized polybutadiene was performed, leading to 1,4-hydroxy telechelic polybutadiene (HTPBD) with number average functionalities ~ 2.0. The effect of vinylsilane on metathetical degradation and functionalization of 1,4-polybutadiene was studied in the presence of vinyltriethoxysilane and ruthenium catalysts.[345] Computational study of metathesis degradation of rubber was also carried out.[346]

1.9 STABILIZATION OF RUBBERS BY ANTIOZONANTS

The polymers undergo degradation at various stages of their production and service life. Exposure of most polymers to the natural and induced environmental conditions, UV radiation, either alone or in combination with oxygen, heavy metal etc profoundly deteriorates the mechanical properties of most polymers. Small quantities of additives called 'stabilizers' are added into the polymer matrix to retard degradation or depolymerization and to impart long-term outdoor stability to the polymer. The stabilizers quench the electronic excitation energy associated with specific chromophores as a result of photon absorption. It has been established that antiozonants, light screeners, UV absorbers, antioxidants, peroxide decomposers, radical scavengers and excited-state quenchers effectively help in achieving polymer stabilization. The commonly used polymer stabilizers are listed below.

The term antiozonant denotes any additive that protects rubber against ozone degradation. Ozone cracking occurs whenever an elastomer/rubber (having unsaturation in backbone) is elongated and exposed to ozone. Unstretched rubber is also attacked but not cracked. Actually ozone cracking is a physico-chemical phenomina.[347] Cracking starts from the rubber surface. Chain cleavage starts and new high stress surface is exposed, continuation of this process results in cracking.

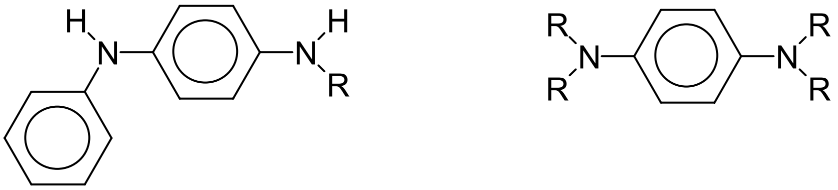
It can be prevented by using waxes (paraffin and microcrystalline type), inert polymers and chemically reactive antiozonants.[348] Some of the antiozonants are derivatives of 2,2,4-trimethyl-1,2-dihydroquinoline, thiourea, substituted pyrroles and N,N'-derivatives of p-phenylenediamine (p-PDA).



Structure 1.3

p-Phenylene diamines are subdivided into three classes:

i) N, N'-dialkyl -p- phenylenediamine
ii) N-alkyl- N'-aryl -p- phenylenediamine
iii) N, N'-diaryl -p- phenylenediamine

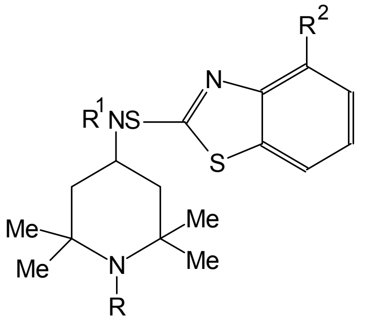


Structure 1.4

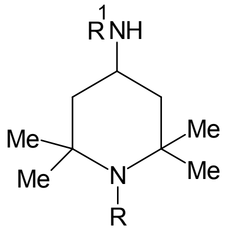
Derivatives of i) are liquid, not easy to handle and rapidly destructed by oxygen. They become dark red to purple discoloration. Derivatives of ii) are solids with low melting points. These are excellent antiozonant and are slowly de-structured by oxygen. Derivatives of iii) are active antiozonants but solubility is very poor. These are most stable towards oxygen.

Several theories were given for the mechanistic action of antiozonant on rubbers such as Scavenger theory, Protective theory, Re-linking theory etc. According to Scavenger theory, the antiozonant covers and diffuse the rubber/elastomer surface so that ozone can not react to the polymer directly.[349] Protective film theory states that antiozonant reacts with ozone and form a thin layer on the elastomer surface.[350] In spite of these theories, scavenger mechanism is the most important model to be the principal mechanism of antiozonant protection. Ozone attacks on antiozonant and gives numerous products of antiozonant like nitro, nitroso and amides compounds.[351] Edelstein[352] carried out microscopic studies.

Merten *et al.*[353] studied the phenylenediamine stabilizers for diene rubbers. William[354] described the synthesis of selenium-containing para-phenylenediamines, a novel antidegradants for natural rubber. Albert *et al.*[355] studied the behavior of p-phenylenediamine and its N,N'-disubstituted derivatives in three vulcanized rubbers with ozone and found that amine ozonization products play an important role in the protection of rubbers from ozone. Parr[356] suggested new antiozonants for natural rubber based on novel selenium-containing p-phenylenediamines. 2,2,6,6-Tetramethyl-4-[(2-benzothiazolylthio)amino]piperidines (I) compounds [R = H, alkyl; R^1 = (cyclo)alkyl, alkenyl, alkynyl, aryl; R^2 = H, Me], antiozonants for rubbers, were prepared by reaction of the aminopiperidines (II) with the appropriate 2-benzothiazolethiols[357] as shown in Structure 1.5.



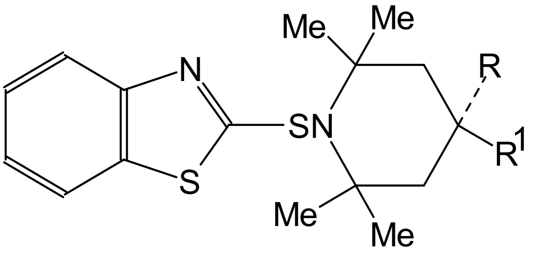
I



II

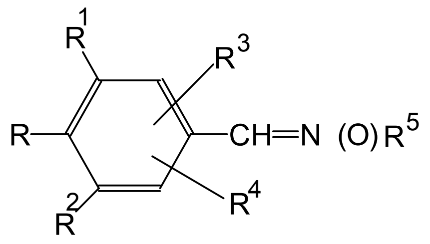
Structure 1.5

The 2-(2,2,6,6-tetramethyl-1-piperidinylthio)benzothiazoles compound[358] (Structure 1.6) where RR^1 = O; R, R^1 = H, HO; H, MeO; H, octadecyloxy; H, AcO; H, dodecanoyloxy), useful as vulcanization accelerators imparting ozone stability, were prepared from benzothiazole-2-thiol.



Structure 1.6

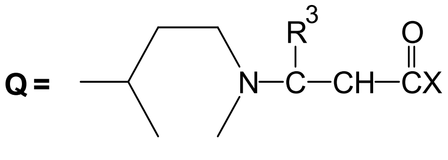
Scott et al.[359] described that C-substituted or unsubstituted aryl-N-substituted or unsubstituted nitrones (Structure 1.7) are useful as antifatigue agents or antiozonants for rubbers where R is an electron acceptor group, R^1 and R^2 are the same or different and each is an (un)substituted alkyl or alkoxy group, R^3 and R^4 are the same or different and each is H or an unsubstituted alkyl or alkoxy group, and R^5 is an (un)substituted branched or cycloalkyl group.



Structure 1.7

Brueck *et al.*[360] studied the action of antiozonants in rubber. A combined scavenger/protective film mechanism was responsible for the protective effect of the non-staining antiozonant bis(1,2,3,6-tetrahydrobenzaldehyde) pentaerythritol acetal in neoprene rubber. Bernard and coworkers[361] described that lactams with 5 to 22-membered rings and 1-2 lower alkyl or phenyl substituents are non-staining antiozonants for natural and synthetic rubbers. Braun and coworkers[362] found ozone-induced degradation of elastomers. Ozonization of 1,4-polybutadiene and 1,2-polybutadiene rubber in solution caused a sharp and weak decrease in the intrinsic viscosity, respectively.[363] Wheeler[364] suggested the triazine derivatives as antiozonants for diene rubbers. The stabilized diene rubbers are useful for belts, air springs, hoses, roofing membranes etc.

Tachi and coworkers[365] described the unsaturated amine antioxidants i.e. $XCOCH{:}CR^3NR^1R^2$ (Structure 1.8) (R^1, R^2 = H, aralkyl, alkenyl, cycloalkyl or alkoxy-, OH-, NH_2-, SH-, CO_2H-, CN-, Q- or $XCOCH{:}CR^3NH$-substituted $C_{1\text{-}18}$ alkyl, cyclic alkylene or oxydiethylene residue; R^3 = $C_{1\text{-}15}$ alkyl or cyclic alkylene residue with X; X = $C_{1\text{-}5}$ alkyl, alkoxy, amino, Me, Ph, halo) as useful discoloring-resistant antiozonants for rubbers.

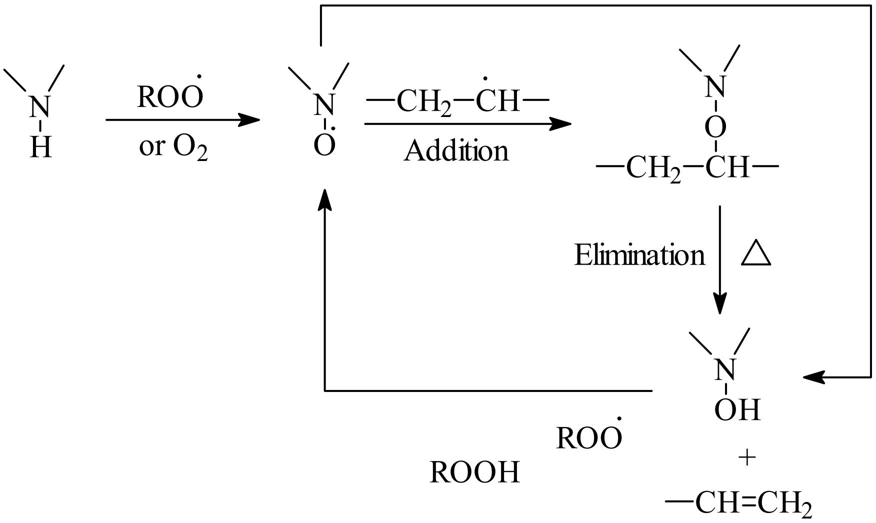


Structure 1.8

Wideman and coworkers[366] used polymeric diphenyldiamines as antiozonants in diene polymers and found that they are capable of accelerating the curing of diene polymers also. These compounds are prepared by reacting *p*-$PhNHC_6H_4NHR$ (R = C_{3-16} alkyl, C_{5-12} cycloalkyl) with vinyl ethers. Bomal *et al.*[367] found that silicones bearing phenylenediamine groups of specified structure are efficient antiozonants for rubbers, especially those subjected to dynamic stress in the presence of ozone.

Humplik and co workers[368] prepared 3,9-bis(methylbicyclo[2,2,1]hept-5-en-2-yl)-2,4,8,10-tetraoxaspiro-[5,5]undecane, a new cyclic pentaerythritol acetal, useful as nonstaining antiozonant for natural and/or synthetic rubber when used alone or in combination with microcrystalline wax. Besska *et al.*[369] prepared 4-aminodiphenylamine which is useful as an intermediate in preparation of alkylated derivatives as antioxidants.

Waxes are generally unreactive but are used as antiozonant also. It migrates to the surface of rubber and forms a protective film, which acts a protective film/physical barrier to the ozone. Paraffinic waxes give better protection at lower temperature. Wax films are easily ruptured. The protection of elastomer by waxes is improved by addition of chemical antiozonants.[675] Waxes have a low solubility in rubber below their melting point but at higher temperatures disperse well in the compound.[370] Lin *et al.*[371] found that natural rubber is slightly more stable to UV and thermal aging than guayule or isoprene rubber, although the presence of carbon black tends to nullify the differences between the degradation behavior of these vulcanizates. The presence of an antioxidant in the formulation is more effective than the origins of the gums in controlling the degradation behaviour. Lattimer[372] discussed the ozone-induced degradation of rubbers and the characteristics of antiozonants. Scott[373] suggested the catalytic cycle (Scheme 1.30) of antioxidant activity. The cycle is:



Scheme 1.30

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CHAPTER II

SCOPE AND OBJECTIVES OF THE PRESENT INVESTIGATION

2.1 INTRODUCTION

Reactive oligomers such as terminally functionalized (telechelic) oligomers and macro monomers are attracting interests as intermediates for use in various fields, viz. surface coatings, adhesives, reactive injection moulding and synthesis of speciality block and graft copolymers. Numerous investigations have been carried out for the synthesis of telechelic polymers using polymerization methods.[1-3] They are also prepared by the cleavage of macromolecular chains of high molecular weight polymers using the well-known conventional methods.[4-7] In recent years, an effective alternative method for the production of telechelic oligomers from high molecular weight polymers has been investigated. Besides, the cleavage of macromolecular chains other specific reactions such as ozonolysis or metathesis[8-10], competition between the control of chain cleavage and/or crosslinking during oxidative degradation were also utilized.

Elastomeric materials are especially sensitive to photo-oxidative degradation. The extensively degraded materials are viscous liquid called 'liquid rubbers'.[11, 12] The extremely controlled exposure of diene elastomers to UV irradiation produces distinct types of degraded products.[13, 14] In this process, polymer of desired molecular weight and functional groups can be obtained by suitable choice of oxidizing agent and exposure time.

Controlled chemical degradation[15, 16] of polymers is efficient to reduce the molecular weight of polymers and allowing less expensive manufacturing and obtaining well defined reactive telechelic oligomers. However, to gain a better understanding of the specific mechanisms associated with biphasic medium, requires a study of more selective reactions *i.e.* selective oxidation reactions[17] and the specific chain cleavage by metathesis.[16-20]

2.2 OBJECTIVES OF THE PRESENT INVESTIGATION

The objective of the present investigation is to study the controlled degradation of diene elastomers, especially natural rubber. This would provide a basic understanding of the functionalized polymers by photo-degradation / ozonolysis / metathesis reactions.

The following aspects of degradation have been studied:

1. To generate reactive end-functional groups in the oligomers (telechelics) that can be used for developing desired properties in the substrate.

2. Photo-degradation study of natural rubber, natural rubber latex and polybutadiene.
3. To quench the photo-degradation after achieving desired functional group.
4. To explain the reaction kinetics and mechanism of photo-controlled degradation.
5. To study the epoxidation of natural rubber in biphasic medium using methyltrioxorhenium.
6. To study the specific chain cleavage in natural rubber / model compounds by metathesis using Grubb's catalyst.
7. To optimize the reaction parameters.
8. Ozonolysis of natural rubber to get functionalized polymer.
9. To design and synthesize novel antiozonants as well as antioxidants.

2.3 APPROACHES

2.3.1 Controlled degradation studies of elastomers

2.3.1.1 Detailed photo-products formation during photo-irradiation of natural rubber, natural rubber latex and polybutadiene will be studied by FT-IR and NMR spectroscopy.

2.3.1.2 Photo-controlled functionalization of natural rubber was studied by FT-IR and NMR spectroscopy. The viscosity average molecular weights and number average molecular weights were determined by viscosity and VPO measurements, respectively.

2.3.1.3 Functionality of natural rubber was determined by Acetylating method.

2.3.1.4 Natural rubber was epoxidized in biphasic medium using methyltrioxorhenium as a catalyst and characterized by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The side reaction products *i.e.* carbonyl ester, ether or cyclic compounds[40] of commercial epoxidized natural rubber (ENR) were compared with the newly synthesized ENR.

2.3.1.5 Metathetic degradation of natural rubber / model compound are studied using bis(tricyclohexyl phosphine) benzylidine ruthenium (VI) dichloride [Grubb's catalyst] as catalyst of different concentration. The reaction was carried out at room temperature and at 50 and 60°C. The reaction products were characterized by NMR spectroscopy.

2.3.1.6 The basic ozonolysis products of natural rubber were ozonides, epoxides, methyl ketone and aldehydes which were characterized by FT-IR and NMR spectroscopy.

2.3.2 Synthesis of novel antiozonants

2.3.2.1 The newly synthesized antiozonants relate to a composition comprising an aromatic amine and a benzotriazole / hindered phenol that is prepared in two-step process. The synthesized novel antiozonants as well as antioxidants may give better stability to polymers, specially rubbers to protect from ozone. The antiozonants were characterized by NMR and IR spectroscopy.

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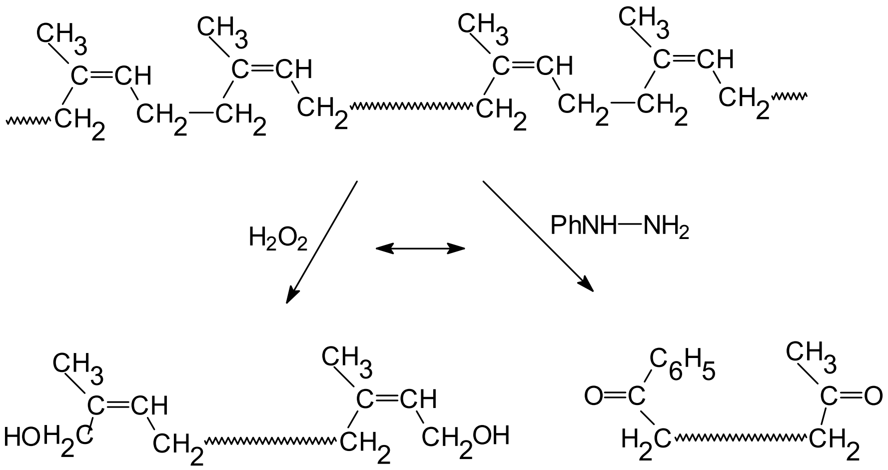
CHAPTER III

PHOTO-CONTROLLED DEGRADATION OF NATURAL RUBBER, NATURAL RUBBER LATEX AND POLYBUTADIENE

3.1 INTRODUCTION

Reactive oligomers such as terminally functionalized (telechelic) oligomers and macromonomers are attracting interests as intermediates for use in various fields, viz. surface coatings, adhesives, reactive injection moulding and synthesis of speciality block and graft copolymers. Numerous investigations have been carried out for the synthesis of telechelic polymers using polymerization methods.[1-3] They are also prepared by the cleavage of macromolecular chains using the well-known conventional methods.[4-7] In recent years, an effective alternative method for the production of telechelic oligomers from high molecular weight polymers has been investigated. Besides, the cleavage of macromolecular chains other specific reactions such as ozonolysis or metathesis[8-10], competition between the control of chain cleavage and/or crosslinking during oxidative degradation were also utilized.[10, 11] Although there are few reported investigations, still the later method (cleavage of macromolecular chain) (Scheme 3.1) was rather explored especially for the control of phenylhydrazine-accelerated thermo-oxidation[12, 13] and hydrogen peroxide catalyzed photo-oxidation[12-16] of natural rubber (NR) for the production of ketone-terminated and hydroxy-terminated telechelic liquid natural rubbers (LNRs), respectively.

In the first method, the improvement in chain cleavage by phenylhydrazine acceleration was explained by the phenyl radical initiation producing phenyl-ketone and methyl- ketone chain ends. In the second method, the role of hydrogen peroxide is to generate hydroxy radicals ($^{\cdot}$OH) to produce hydroxyl-chain ends but the addition of titanium dioxide (TiO_2) is a new approach in the chain cleavage of NR in the solution. The TiO_2 catalyzed photo-oxidation generates hydroxy radicals[15] on its surface which produces hydroxy-terminated end groups. This chapter presents results for photo-oxidative degradation of natural rubber, natural rubber latex (NRL) and cis-1,4-polybutadiene (PB) using different systems *i.e.* H_2O_2/THF/TiO_2 and H_2O_2/TiO_2/THF under air and nitrogen using toluene as a solvent.



Scheme 3.1: Photo-oxidation of natural rubber

3.2 EXPERIMENTAL

3.2.1 *Materials*

Natural rubber [NR] ($\overline{M}_v = 2.82 \text{x} 10^5$) and natural rubber latex ($\overline{M}_v = 1.75 \text{ x } 10^5$) were supplied through the courtesy of Dr. S. Thomas, M.G.University, Kottayam, Kerala. cis-1,4-polybutadiene ($\overline{M}_w = 3 \text{ x } 10^5$) and Berol (surfactant) were supplied through the courtesy of Prof. D. Reyx and I. Campistron, Laboratoire De Chiemie Organique Macromoleculaire, Faculte des Sciences, Univesite Du Maine, Cedex, France. H_2O_2 (30 wt %) and TiO_2 (anatase) were obtained from M/s. S.D. Fine Chemicals Ltd. Toluene, acetone, pyridine and tetrahydrofuran were of reagent grades and used after distillation.

3.2.2 *Reaction procedure*

3.2.2.1 Photo – controlled degradation of natural rubber

A 2.5 wt % solution (105 ml) of purified NR was prepared in toluene. The homogeneous NR solution was photolysed in a closed photoreactor (Pyrex glass) under air and nitrogen atmosphere, separately, under constant and efficient stirring (600 rpm) with the help of 400 W medium pressure mercury vapour lamp. The temperature was maintained at 30 ±1°C by a circulating water bath. Aliquots were withdrawn at different time intervals and the rubber was precipitated with acetone and dried under vacuum. For photo-controlled degradation, three different experiments were carried out by taking NR solution with H_2O_2 (5ml) [**A**], 1 % w/v TiO_2 [**B**] and H_2O_2 (5ml) + 1 % w/v TiO_2 [**C**], respectively. THF (25ml) was also added in H_2O_2-NR systems to homogenize the solution.

3.2.2.2 Photo – controlled degradation of natural rubber latex

Natural rubber latex (30 % DRC) was stabilized by Berol (3 % w/w). For photo-controlled degradation, three different experiments were carried out by taking NRL solution with H_2O_2 (5ml) [**D**], 1 % w/v TiO_2 [**E**] and H_2O_2 (5ml) + 1 % w/v TiO_2 [**F**], respectively. The advantage of choosing natural rubber latex is that the hydrogen peroxide is miscible in latex, therefore, the process can be carried out in a homogeneous medium. Rest of the reaction conditions were kept same as stated for natural rubber.

3.2.2.3 Photo – controlled degradation of polybutadiene

A 2.5 wt % solution (105 ml) of purified cis-1,4-polybutadiene (PB) was prepared in toluene. For photo-controlled degradation, three different experiments were carried out by taking PB solution with H_2O_2 (5ml) [**G**], 1 % w/v TiO_2 [**H**] and H_2O_2 (5ml) + 1 % w/v TiO_2 [**I**], respectively. When H_2O_2 was present, 25ml THF was also added to homogenize the solution. THF (25ml) was also added in H_2O_2-PB systems to homogenize the solution. Rest of the reaction conditions were kept same as stated for natural rubber.

3.3 ANALYSIS

3.3.1 FT-IR Analysis

FT-IR spectra were recorded from thin films obtained by evaporating 1.0 wt % solution of the oxidized rubber, latex and polybutadiene, which were dried to constant weight, with PERKIN-ELMER 16 PC spectrophotometer at room temperature.

3.3.2 NMR Analysis

^1H and ^{13}C NMR spectra were recorded using Bruker AC 200 and 300 spectrometers (time acquisition: 22.048 sec., temperature: 24°C, number of transient: 512 etc) operating at 200 MHz and 300 MHz, respectively. $CDCl_3$ (Aldrich 99.8 % D) was used as solvent.

3.3.3 Molecular weight determination

Viscosity-average molecular weights ($\overline{M}_v$) of controlled and oxidized rubbers were determined in dried toluene (0.016 wt %) at 25 ± 0.1°C using an Ubbelohde viscometer and the Mark-Houwink-Sakurada equation:

$[\eta] = K.\ \overline{M}_v^{a}$

where $K = 5x10^{-4}$ and $a = 0.667$ for natural rubber

Number-average molecular weights ($\overline{M}_n$) of controlled degraded rubbers and polybutadiene were determined in dried toluene (0.016 wt %) at 25 ± 0.1°C using vapour pressure osmometer.

3.4 RESULTS AND DISCUSSION

3.4.1 Natural rubber

Viscosity-average molecular weights (M_v) and number average molecular weight (M_n) were determined by viscometer and vapour pressure osmometer, respectively, at different intervals of irradiation time for the control, H_2O_2/ THF, TiO_2 and combination of H_2O_2 and TiO_2 / THF systems (Tables 3.1 and 3.2). We observed a continuous decrease in $\overline{M}_n$ and $\overline{M}_v$ with irradiation time.

H_2O_2 generates hydroxy radicals upon U.V. irradiation. The hydroxyl (3600-3200 cm^{-1}) and carbonyl (1850-1550 cm^{-1}) peaks, in FT-IR spectra (Figures 3.1 and 3.2), are formed during the depolymerization process by oxidative cleavage of the rubber molecules. Upon addition of H_2O_2 in NR solution, FT-IR spectra showed the gradual increase in the peak intensity in the hydroxyl region with irradiation time. A broad band with a maximum of 3280 cm^{-1} and a shoulder at 3450 cm^{-1} appeared during U.V. irradiation. After 63 h irradiation, decrease in the peak of hydroxyl group is observed which may be due to the simultaneous generation of carbonyl groups and /or crosslinking. A low intensity peak at 1730 cm^{-1} is observed upon 12 h of U.V. irradiation (Figure 3.1B) and it increases slightly on further irradiation. In Figure 3.2D, a broad hump appeared which may be due to adventitious oxidation during isolation of the product.

Table 3.1: $\overline{M}_n$ of photo-degraded natural rubber (in air)

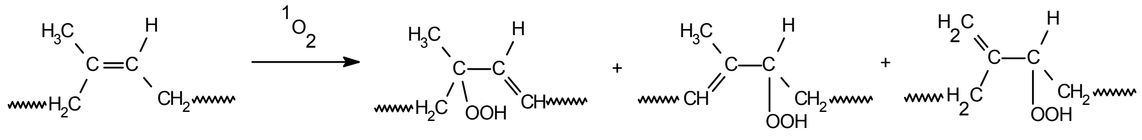
Irradiation Time (h)	**Number average molecular weight (x $10^{3)}$**			
	NR	NR+H_2O_2	NR+TiO_2	NR+H_2O_2+TiO_2
0	282	282	282	282
36	8.3	1.11	2.37	2.19
63	7.2	1.02	1.86	1.58

Table 3.2: $\overline{M}_n$ of photo-degraded natural rubber (in nitrogen atmosphere)

Irradiation Time (h)	**Number average molecular weight (x $10^{3)}$**			
	NR	NR+H_2O_2	NR+TiO_2	NR+H_2O_2+TiO_2
0	282	282	282	282
36	9.9	6.3	4.63	5.67
63	6.1	3.26	4.21	5.03

In nitrogen atmosphere, there is a gradual but less intense, broad hydroxyl region which increases upto 36 h and then decreases, which may be due to the formation of epoxy group in the oxidative degraded polymer chain (Figures 3.3 and 3.4). No changes were observed in the carbonyl region.

These results are quite similar to those previously observed in the photo-oxidation of rubber in the presence of oxygen in which allylic hydroperoxides[17] (3400 cm^{-1}), which are generated due to singlet oxygen reaction according to the "ene" reaction mechanism but no evidence of carbonyl absorption as shown in Scheme 3.2:



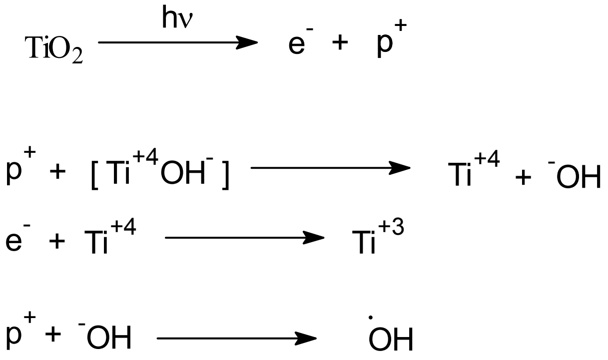
A **B**

with possible cis or trans configuration

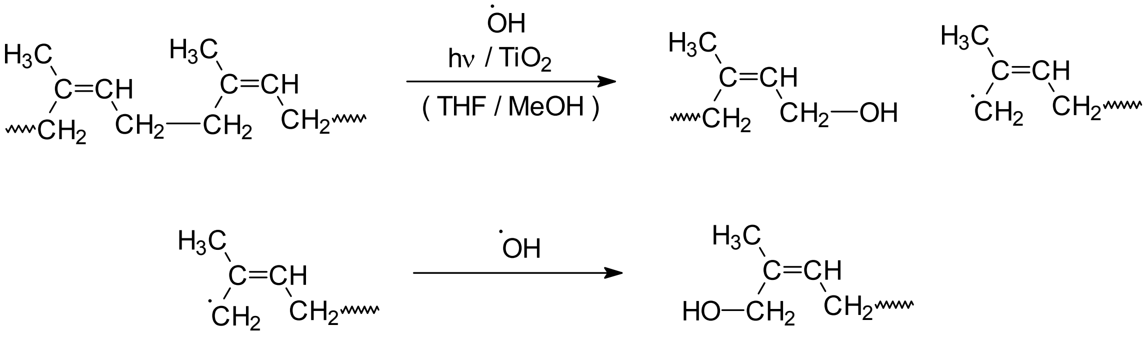
Scheme 3.2

In this context, the chain cleavages would be the result of hydroperoxide decomposition through O–O photolysis[18, 19] and fragmentation of the resulting alkoxy radicals. However, the classical auto-oxidation involving both alkoxy and hydroxy radicals initiating species would concomitantly occur to produce allylic hydroxyl and carbonyl species. In fact, these hydroperoxides would act as photoinitiators. Due to the relative importance of the oxidation by this process, it was not possible to discriminate the eventual terminating -OH groups resulting from the H_2O_2 as a photo-catalysis.

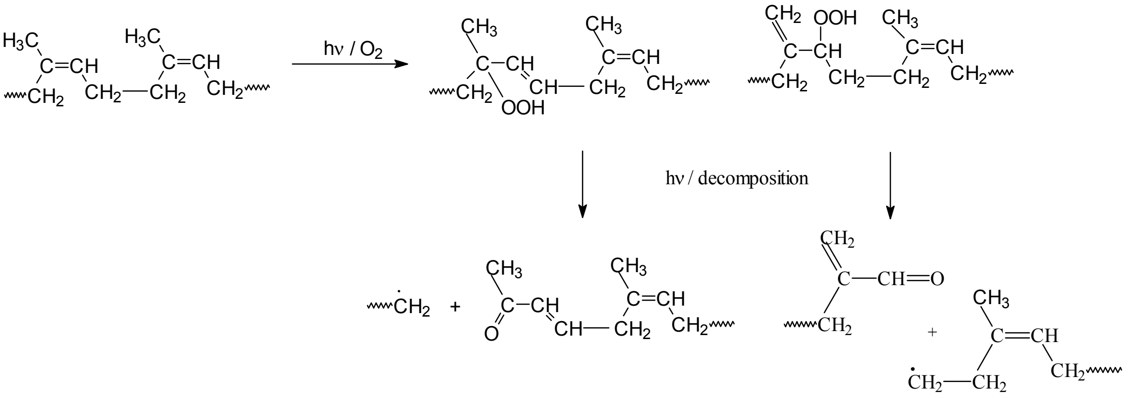
In case of NR solution in **B**-system, the hydroperoxide accumulates up to 12 h (Figure 3.1) and thereafter is the fast decomposition (63 h) due to photocatalytic[20, 21] effect of TiO_2. The absorbed U.V. radiation below 370 nm releases electrons and +ve holes in the TiO_2 crystals, some of which diffuse into the surface, resulting in the production of free radicals, which can attack the polymer causing the classical oxidative degradation (Schemes 3.3 to 3.5). In this case, the carbonyl peak (1730 cm^{-1}) is maximum due to the fast decomposition of hydroperoxides on longer irradiation (63 h). Under nitrogen atmosphere, we observed continuous increase in hydroxyl region (Figure 3.5), which is attributed to the accumulation of hydroxyl groups onto TiO_2 surface (due to the screening effect of the pigment)[21] as they are not decomposed due to lack of free hydroxyl groups formed in the presence of air.



Scheme 3.3



Scheme 3.4: Formation of Hydroxy- terminated functional groups



Scheme 3.5: Generation of carbonyl / aldehyde / carboxylic functional groups

In the case of combined effects of TiO_2 (1 % w/v) and H_2O_2 (Figure 3.2) in **C**-system, the hydroperoxides accumulate up to 24 h due to simultaneous catalysis of H_2O_2 and after that similarly, the fast decomposition was observed. The broad hydroxyl region increases (under nitrogen) with irradiation time. A broad band with a maximum at 3280 cm^{-1} and a shoulder at 3448 cm^{-1} (Figure 3.4) appears during U.V. irradiation. There is no change in the carbonyl region, except the peak at 1660 cm^{-1} which decreases gradually with irradiation time.

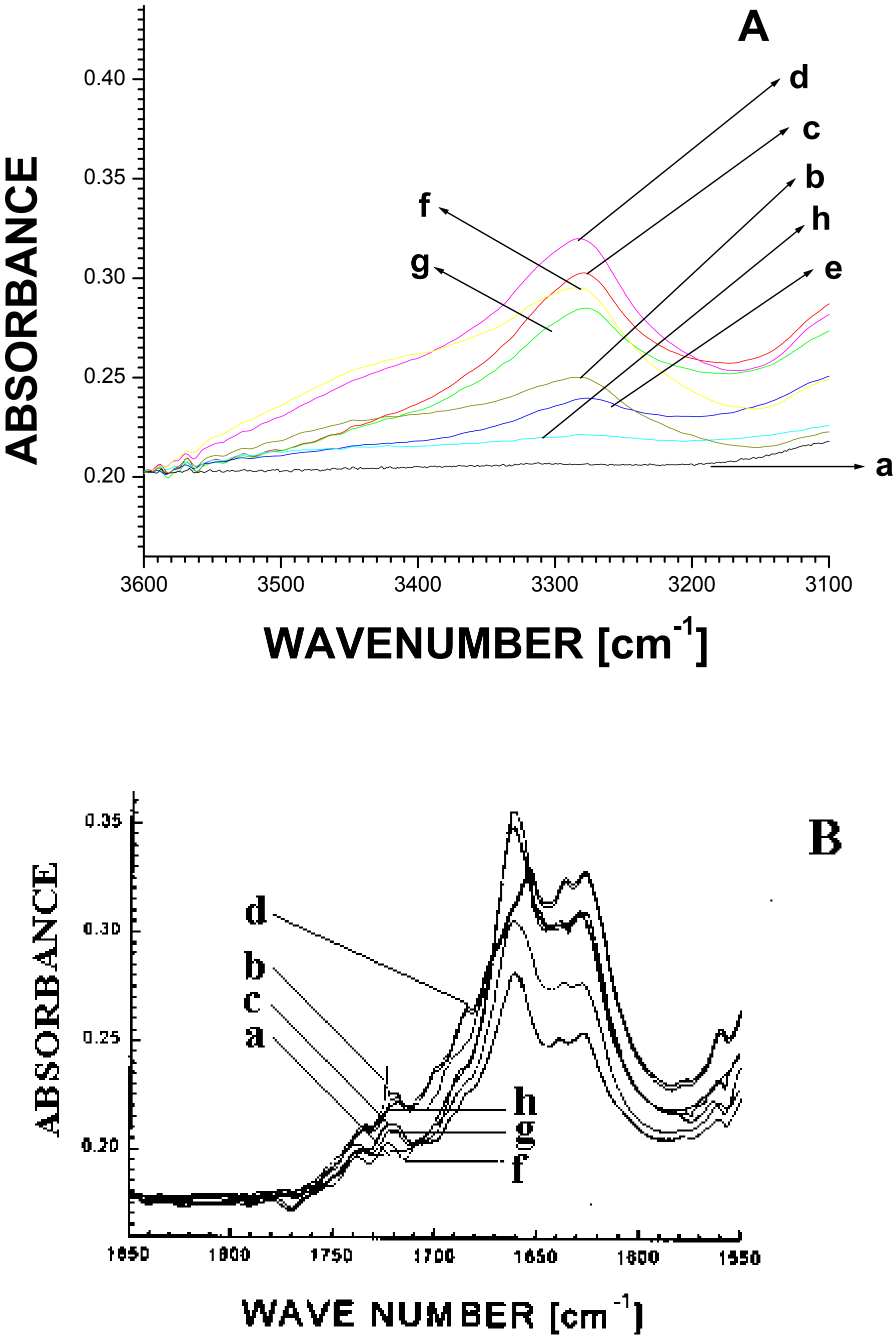
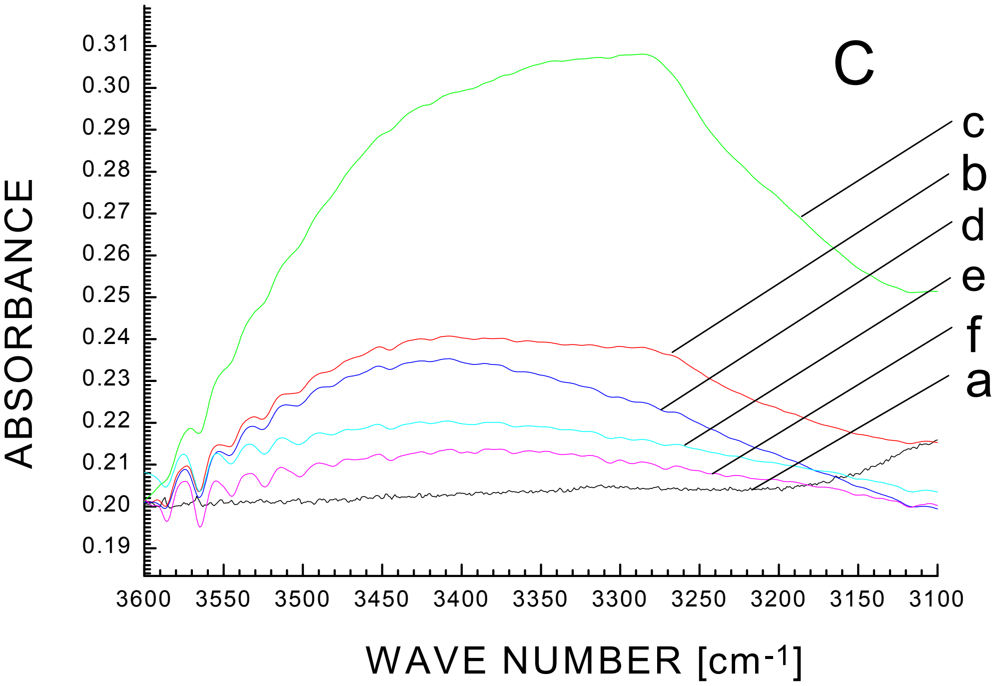


Figure 3.1: FT-IR spectral changes in the (A) hydroxyl and (B) {except **e**} carbonyl regions of U.V. irradiated natural rubber in presence of hydrogen peroxide [I]**:** **a**: control, **b**: 12 h, **c**: 48 h, **d**: 63 h, **e**: 78 h, and titanium dioxide [II]**:** **f**: 12 h, **g**: 48 h, **h**: 63 h.



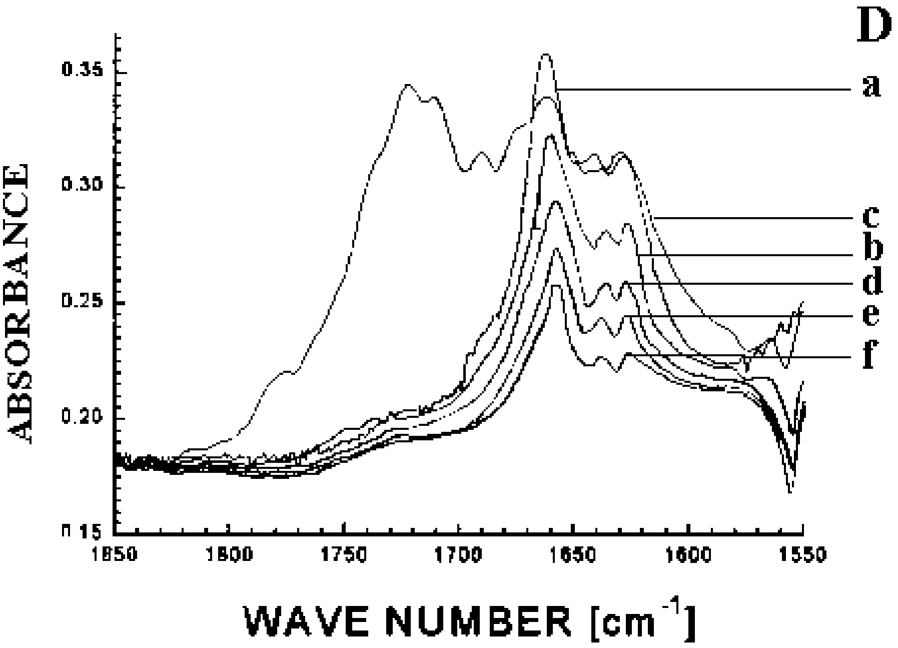


Figure 3.2: FT-IR spectral changes in the (C) hydroxyl and (D) carbonyl regions of U.V. irradiated natural rubber in presence of combination of hydrogen peroxide and titanium dioxide [III]**:** **a**: control, **b**: 12 h, **c**: 24 h, **d**: 36 h, **e**: 48h, **f**: 63 h.

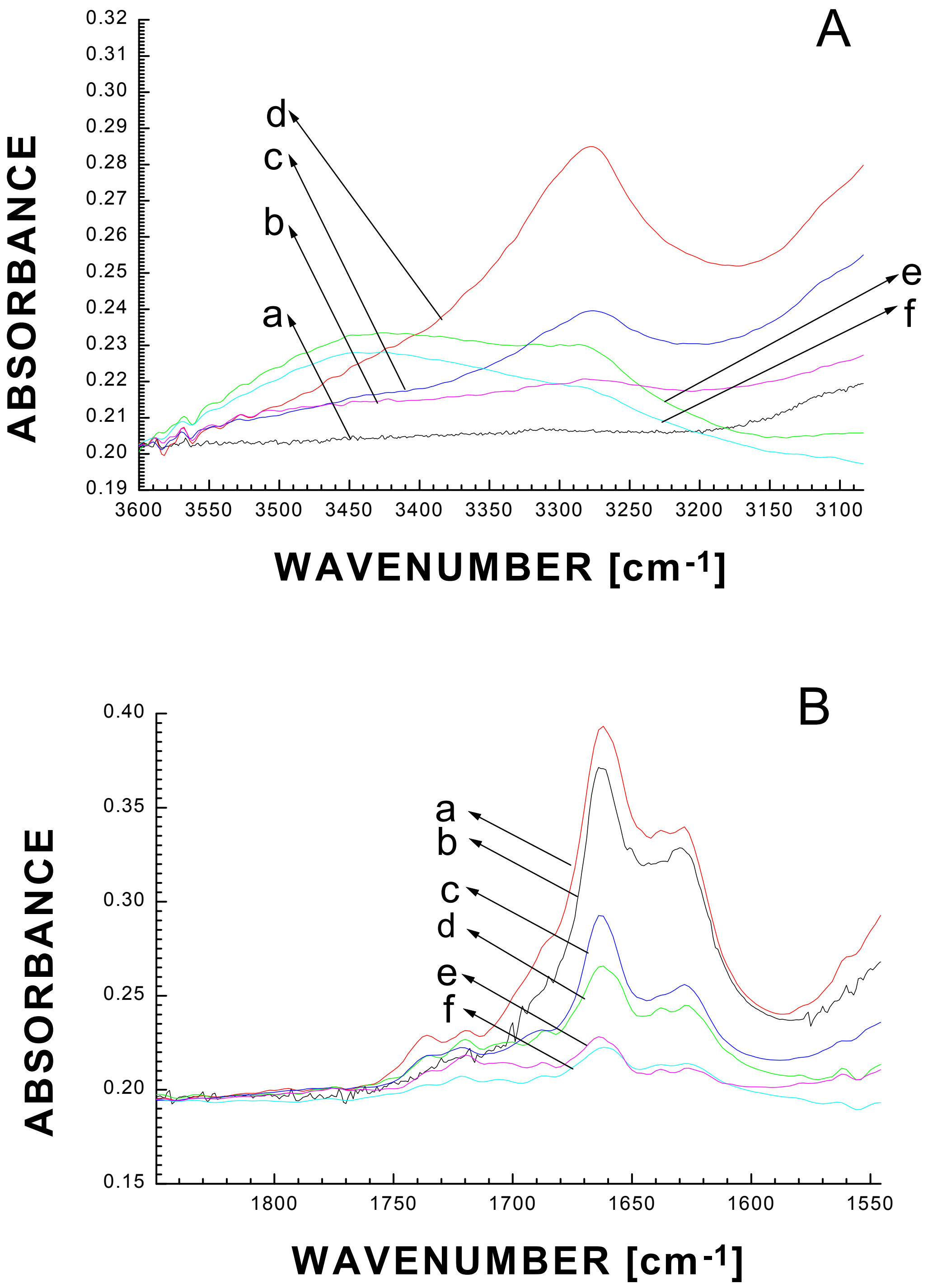
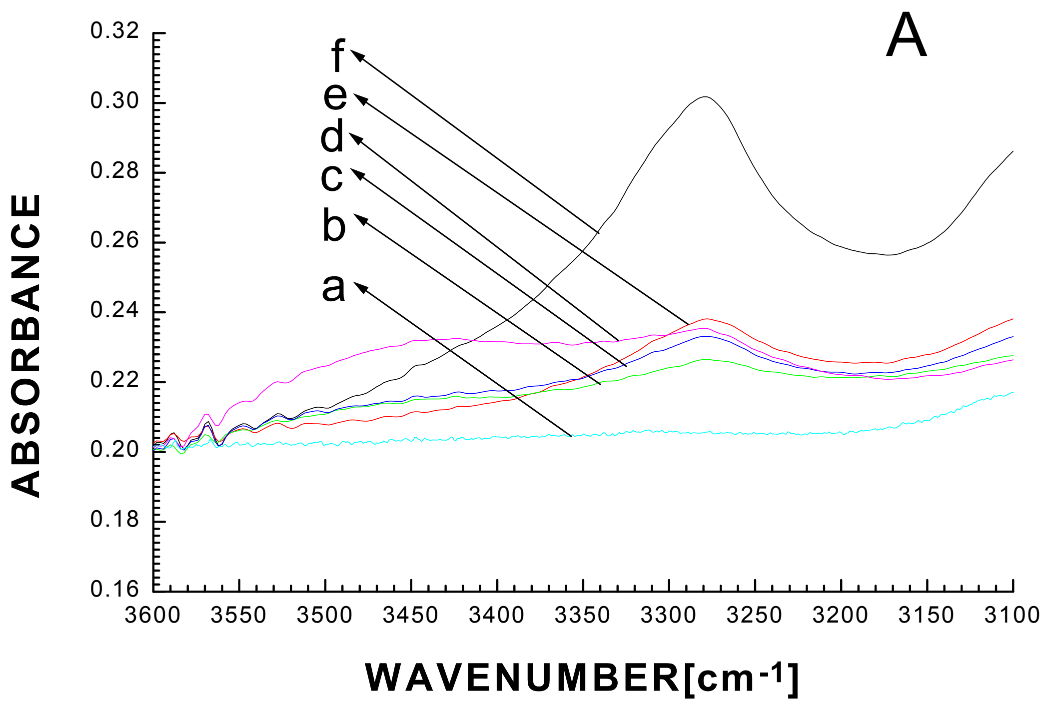


Figure 3.3: FT-IR spectral changes in the (A) hydroxyl and (B) carbonyl regions of U.V. irradiated natural rubber in presence of hydrogen peroxide (under nitrogen atmosphere)**:** **a**: control, **b**: 12h, **c**: 24h, **d**: 36h, **e**: 48h and **f**: 63 h.



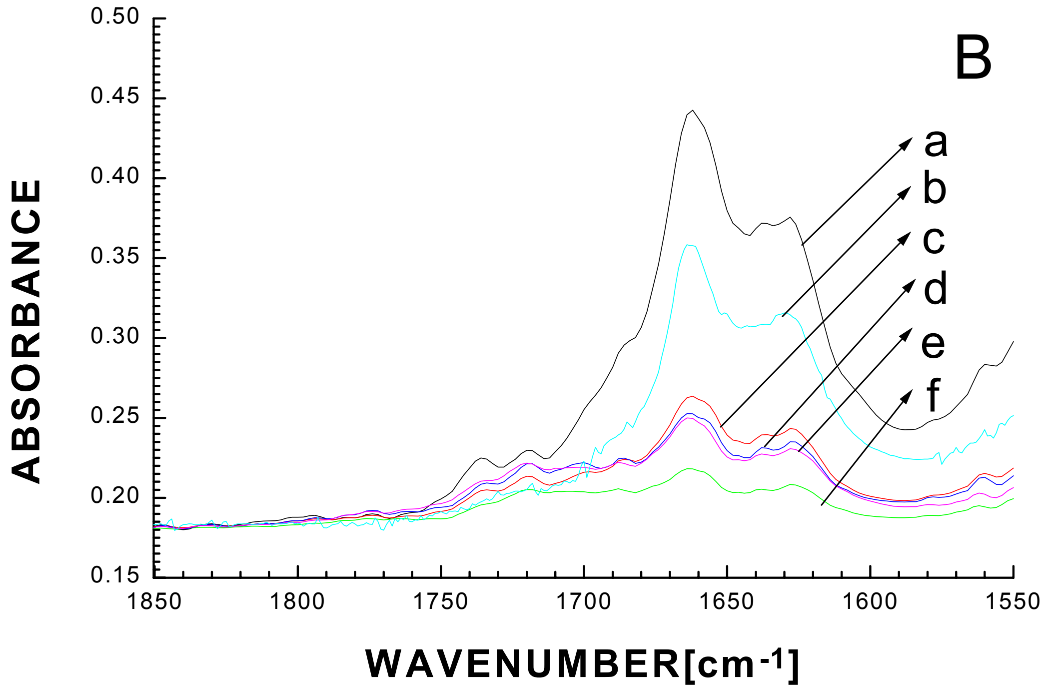


Figure 3.4: FT-IR spectral changes in the (A) hydroxyl and (B) carbonyl regions of U.V. irradiated natural rubber in presence of combination of hydrogen peroxide and titanium dioxide (under nitrogen atmosphere)**:** **a**: control, **b**: 12h, **c**: 24h, **d**: 36h **e**: 48h and **f**: 63h.

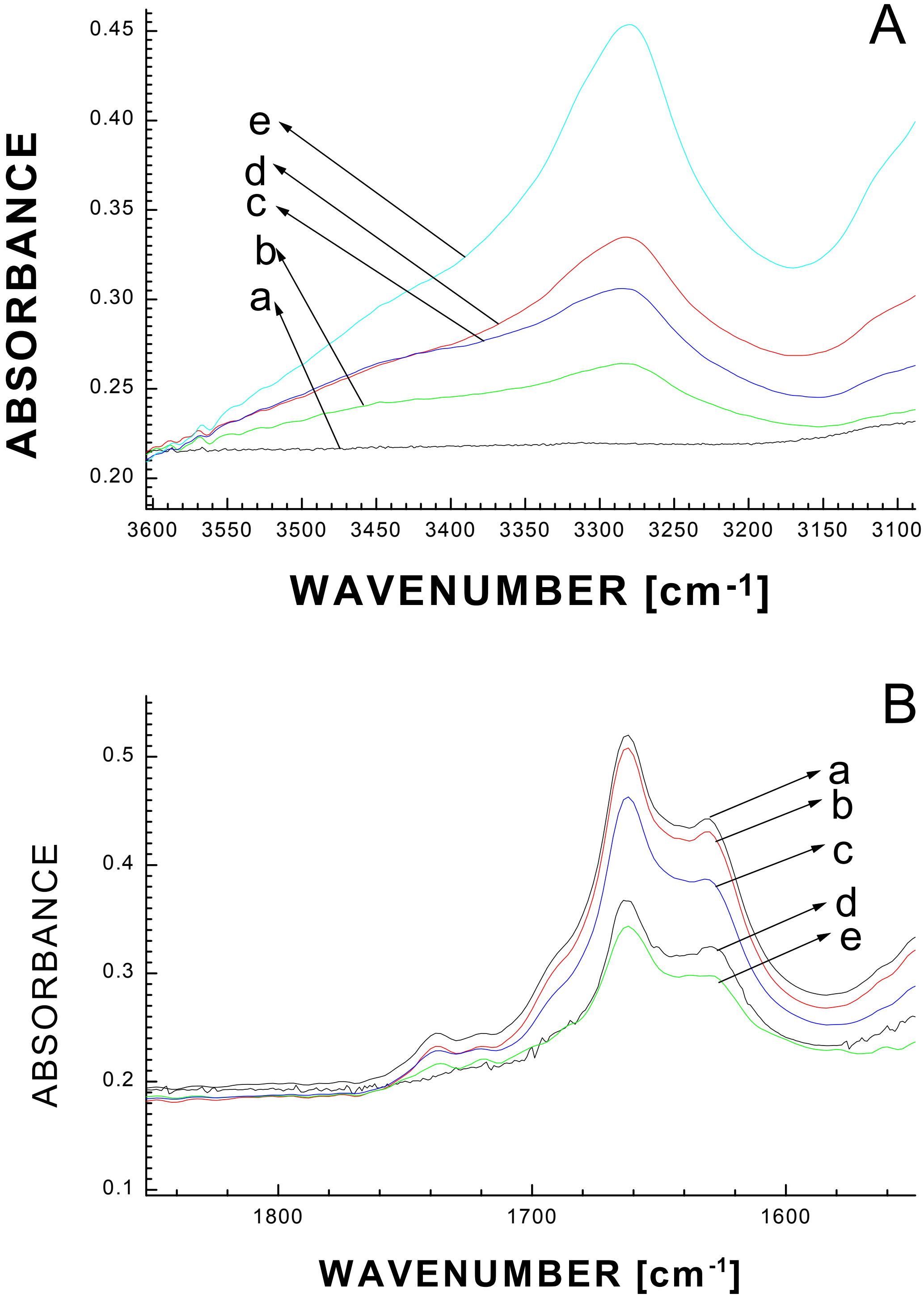
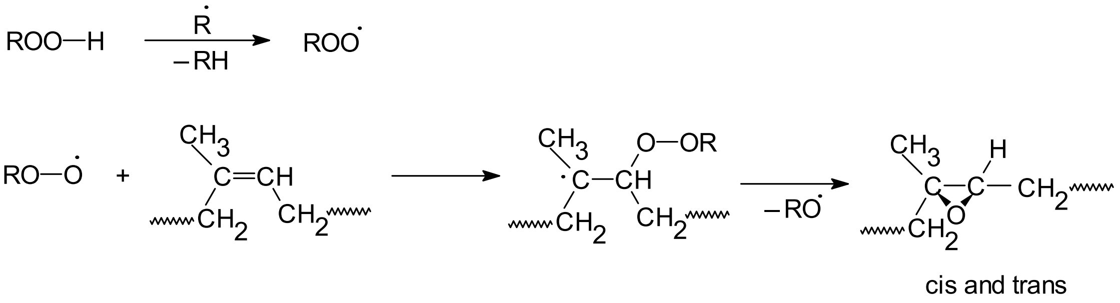


Figure 3.5: FT-IR spectral changes in the (A) hydroxyl and (B) carbonyl region of U.V. irradiated Natural Rubber in presence of titanium dioxide (under nitrogen atmosphere)**:** **a**: control, **b**: 12h, **c**: 36h, **d**: 48h and **e**: 63h.

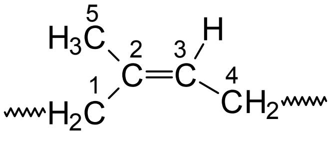
The free radical mechanism occurrence makes possible the double bond epoxidation by addition of peroxy radical and elimination of alkoxy radical as shown in Scheme 3.6.[12, 13, 16] The previous detection of epoxidized units in H_2O_2 -catalyzed photo-degradation of liquid natural rubber[16] is a supplementary argument for a photoinitiated radical oxidation process.



Scheme 3.6

In each case, ^{1}H and ^{13}C NMR spectra presented preponderantly the *cis* 1,4-polyisoprene signals. The ^{1}H NMR (Figures 3.6, 3.7 and 3.8) and ^{13}C NMR spectra in $CDCl_3$ at 24°C lead further support to the above conclusion. ^{1}H NMR $\delta = 1.63$ ppm (-CH_3, 3 H); $\delta = 2.05$ ppm (-CH_2-C=C, 4 H) and $\delta = 5.1$ ppm (vinylic proton). The signal due to hydroxyl proton in the hydroxy methyl group is observed at ~ 4.15 ppm[22], but in our studies this peak is quite clear at 3.5- 4.0 ppm under air as well as nitrogen atmosphere. In addition to that, after 48 h exposure (nitrogen) two more signals at 1.27 and 2.70 ppm, denote *trans* and *cis* epoxides,[16] respectively (Figure 3.7) and the intensity of signals increases with irradiation time (Figure 3.8). The signal at 1.30 ppm increases with irradiation time which is assumed due to some impurities.

The ^{13}C NMR spectra indicate ^{13}C shieldings typical of *cis*-1,4-polyisoprene at the following positions: C^1 $\delta = 32.19$, C^2 $\delta = 135.10$, C^3 $\delta = 125.03$, C^4 $\delta = 26.38$ and C^5 $\delta = 23.27$ as shown in Structure 3.1:



Structure 3.1

We have also noticed the appearance of a small signal at 27.09 ppm (Figure 3.9) upon irradiation for 36 h with combined effect of TiO_2 (1 % w/v) and H_2O_2. This mild peak besides the sharp signal of allylic methylene at 26.4 ppm could be due to a small amount of *trans* 1,4- isoprene units. Two signals were observed after 48 h in the case of the combination of H_2O_2 and TiO_2 (nitrogen) at 64.40 ppm and 60.76 ppm (Figure 3.10), due to partially epoxidized NR. The peaks at δ = 63.49 (air)[14, 15] after 18 h (Figure 3.11) and δ = 63.48 (nitrogen) after 24 h (Figure 3.12) are quite evident which are due to α -carbons (allylic-1- alcohol) attached to the hydroxyl groups and hence can correspond to an α-hydroxy methyl group/hydroxy terminated functional groups.

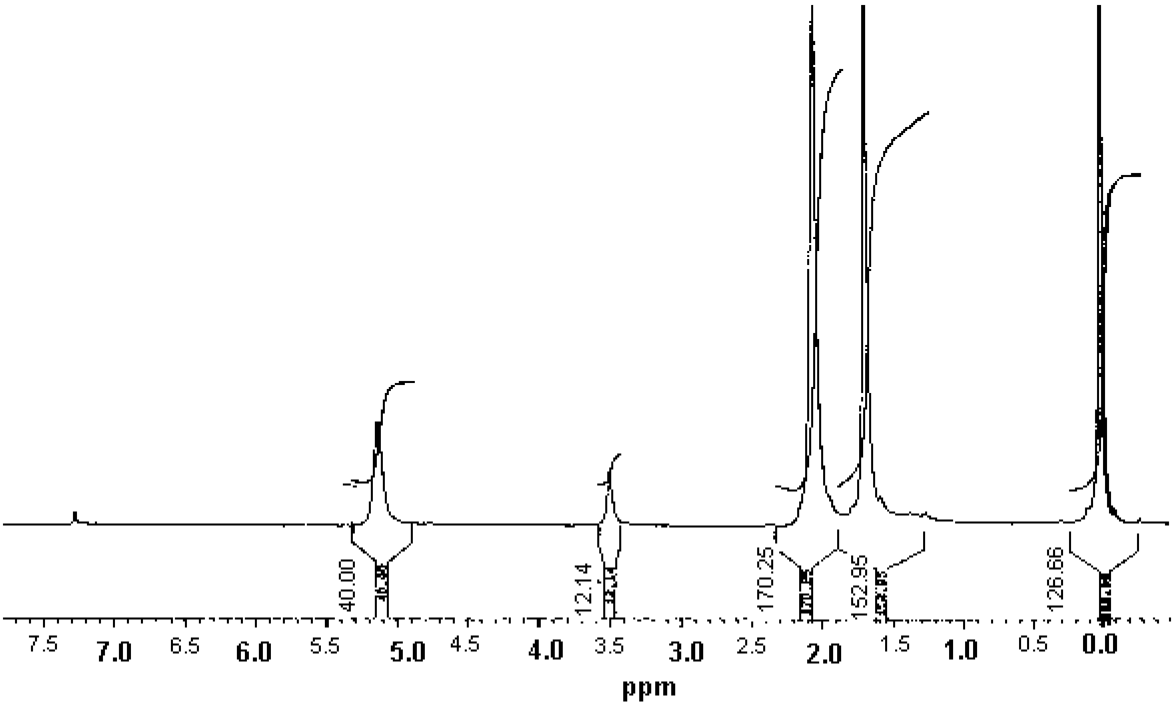


Figure 3.6: ^1H NMR spectrum of degraded Natural Rubber after 18 h U.V. exposure (under air) in $CDCl_3$ solution.

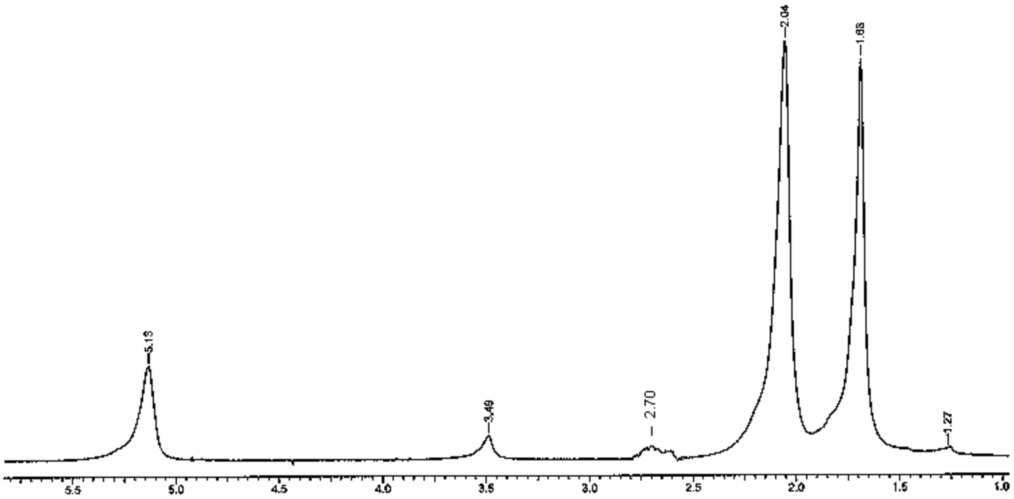


Figure 3.7: ^{1}H NMR spectrum of degraded natural rubber after 48h U.V. exposure (under nitrogen) in $CDCl_3$ solution.

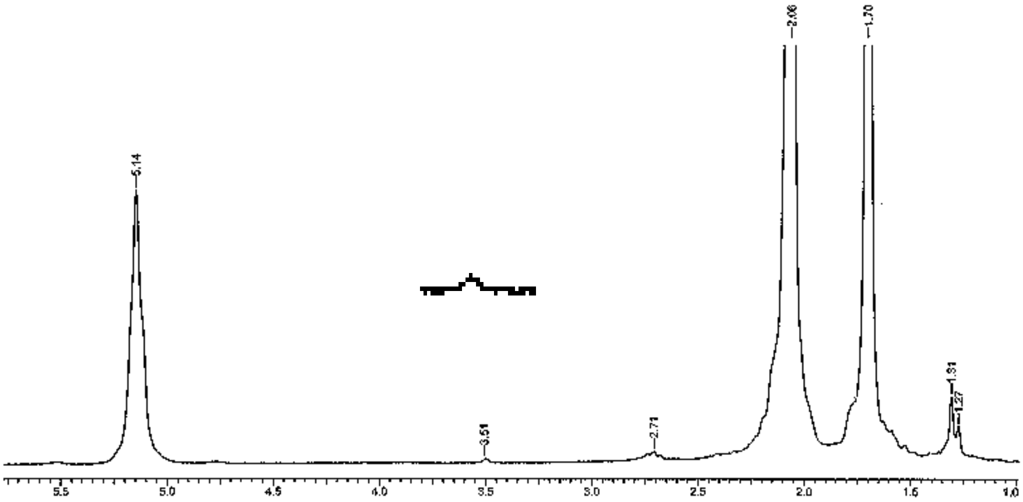


Figure 3.8: ^{1}H NMR spectrum of degraded natural rubber after 63h U.V. exposure (under nitrogen) in $CDCl_3$ solution.

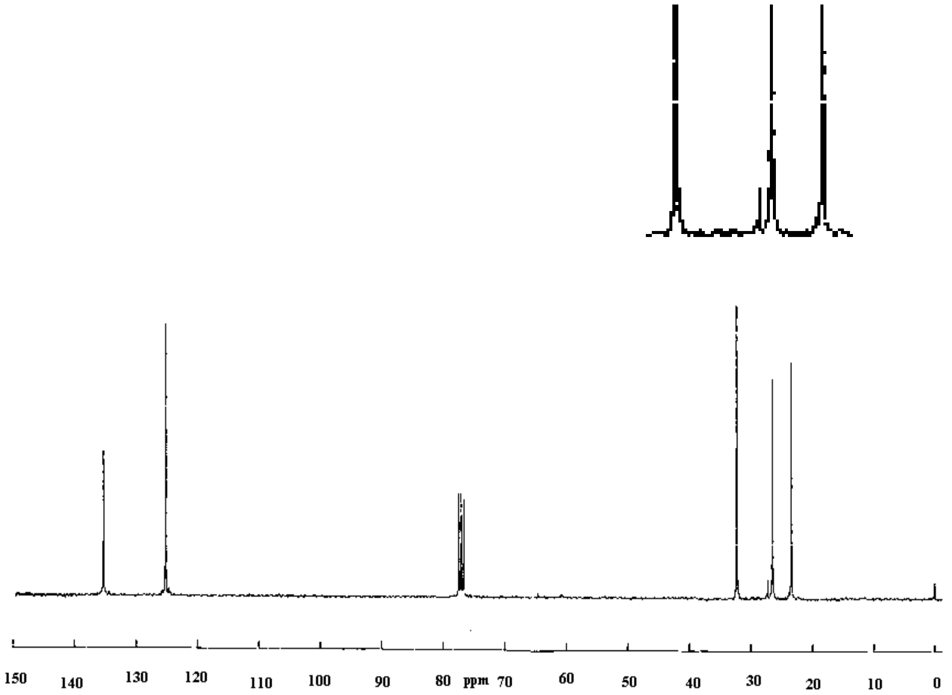


Figure 3.9: Combined effect of titanium dioxide and hydrogen peroxide on degraded natural rubber after 36 h U.V. irradiation (under air) ^{13}C NMR spectra.

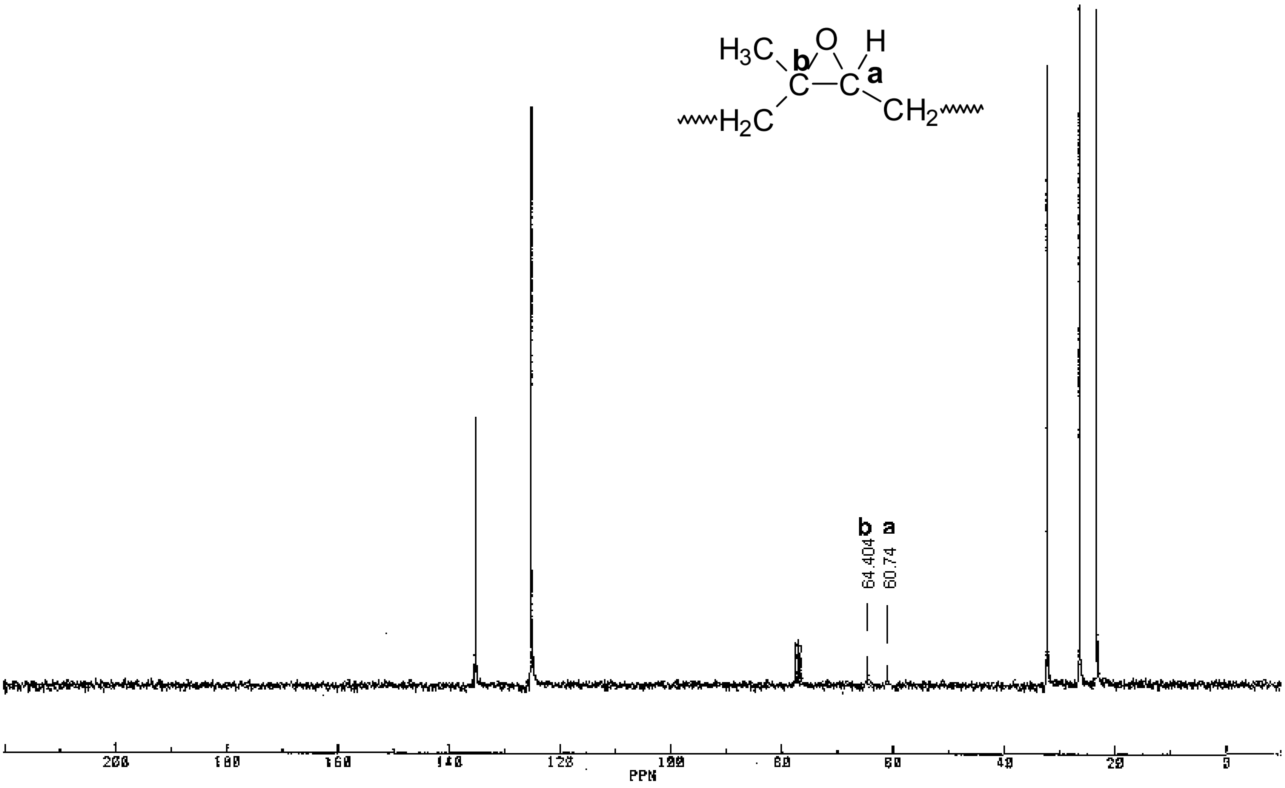


Figure 3.10: Partially epoxidized natural rubber formation due to combined effect of titanium dioxide and hydrogen peroxide on degraded N.R. after 48h U.V. irradiation (under nitrogen) ^{13}C NMR spectra.

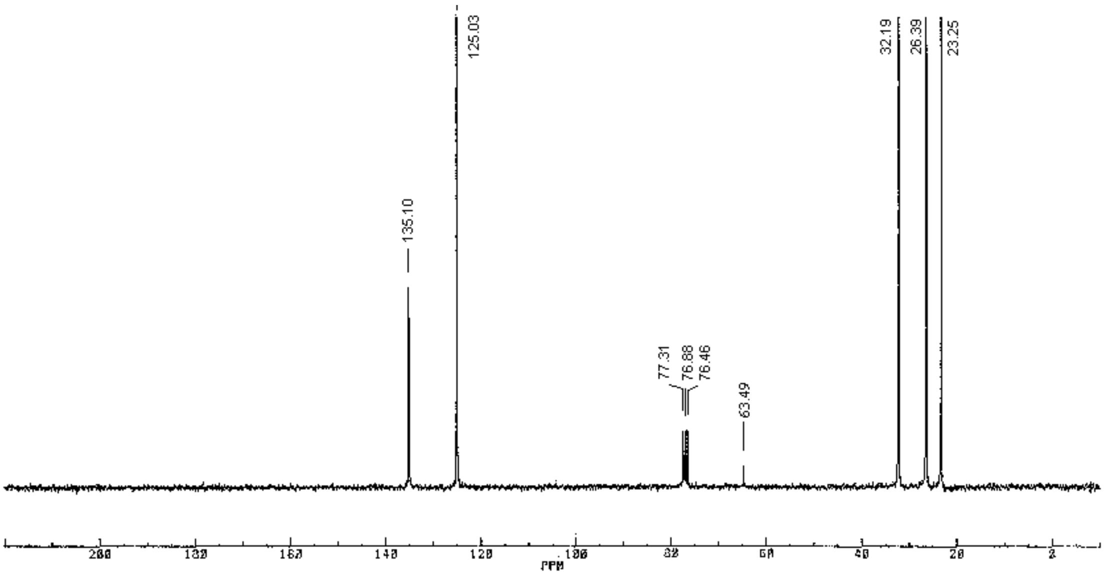


Figure 3.11: ^{13}C NMR spectrum of degraded natural rubber after 18h U.V. exposure (under air) in $CDCl_3$ solution.

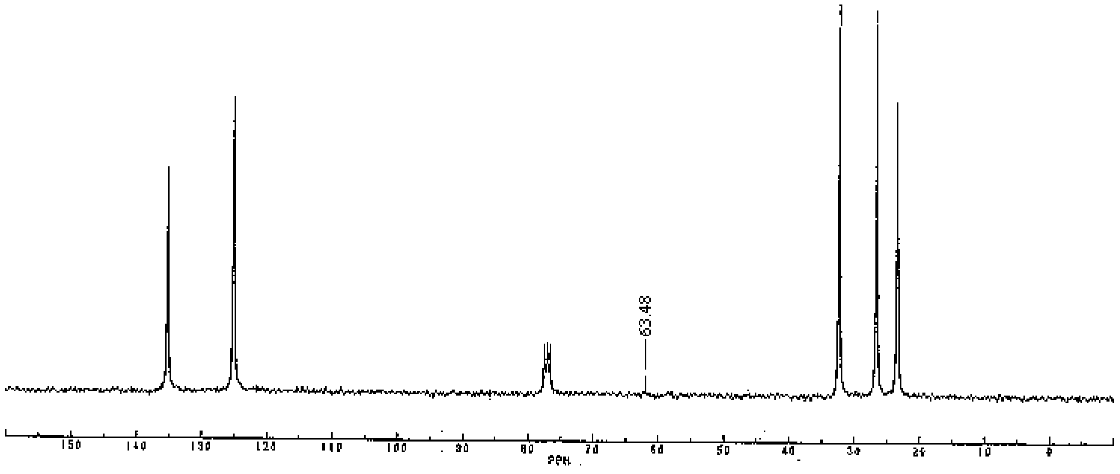


Figure 3.12: ^{13}C NMR spectrum of degraded natural rubber after 24h U.V. exposure (under nitrogen) in $CDCl_3$ solution.

In all the earlier schemes, a free-radical mechanism has been suggested for the degradation of NR. These free radicals interact with the labile α- C-H bond, abstracting the proton and leaving macroradicals behind. The peroxides are formed by the interaction of these radicals with O_2 and decomposed to yield various degradation products containing hydroxyl, carbonyl and carboxy groups at the chain ends. We also observed that after purification and drying, further solubilization of the photoproduct in varying solvents was often difficult and sometimes a part of it was insoluble. This can be explained by crosslinking resulting from subsequent reactions involving hydroperoxide decomposition.

3.4.2 Natural rubber latex

Our results for functionalized natural rubber latex using these systems showed the expected dependence of hydroxyl group and molecular weight on the photocatalytic agent but the functionalities obtained were often variable. The addition of oxidizing agent and co-catalyst may constitute an essential feature for more correct functionality. Under photochemical conditions, H_2O_2 generates free hydroxy radicals. The hydroxyl (3600- 3200 cm^{-1}) region, in FT-IR spectra (Figures 3.13), is formed during the depolymerization process by oxidative cleavage of the natural rubber latex molecules in

D -system. Upon addition of H_2O_2 in NRL solution, FT-IR spectra showed a broad band at 3280 cm^{-1} and a shoulder at 3450 cm^{-1} during U.V. radiation. The band intensity of 3280 cm^{-1} decreased after 12 h of irradiation and then again increased till 63 h. It was expected due to the generation of epoxy group in the latex molecules. It was evidenced by the disappearance of the shoulder (3450 cm^{-1}) in FT-IR spectra as well as the formation of a new peak at 1.26 ppm in ^1H NMR spectra (Figure 3.14). The epoxide groups may be formed in the latex under UV irradiation as shown in Scheme 3.6. ^1H NMR spectrum showed a peak at 3.5 ppm, indicating hydroxyl proton in the hydroxy methyl group after 63 h of UV irradiation.

In case of NRL solution in **E**-system, the hydroperoxide accumulates up to 12 h (Figure 3.15) and then there is a fast decomposition (63 h) due to photocatalytic[14, 15] effect of TiO_2. ^1H NMR spectrum shows a very little noise at 3.6 ppm of hydroxyl proton in the hydroxy methyl group after 63 h UV irradiation.

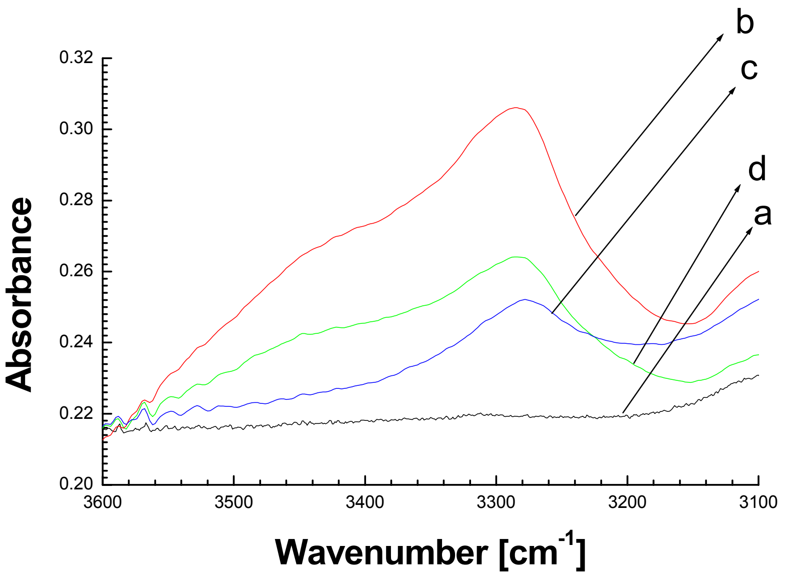


Figure 3.13: FT-IR spectral changes in the hydroxyl region of UV irradiated NRL with H_2O_2 [**D**-system]; a: control, b: 12 h, c: 36 h and d: 63 h.

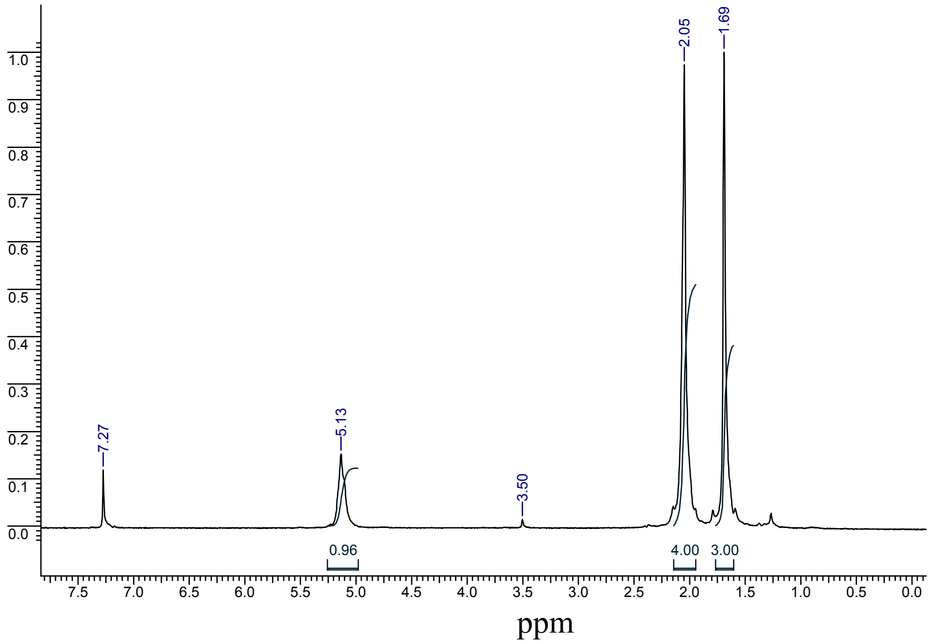


Figure 3.14: ^{1}H NMR spectrum of degraded NRL with H_2O_2 after 63 h UV irradiation.

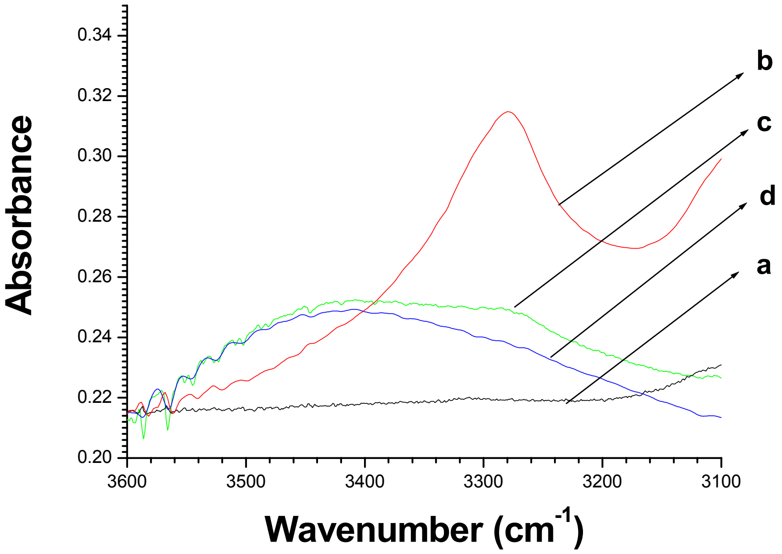


Figure 3.15: FT-IR spectral changes in the hydroxyl region of UV irradiated NRL with TiO_2 [**E**-system]; a: control, b: 12 h, c: 36 h and d: 63 h.

In case of combined effects of TiO_2 (1 % w/v) and H_2O_2 (**F**- system), ^{1}H NMR shows the peak at 1.29 ppm, indicating the protons of the methyl group on the oxirane ring in cis position. Figure 3.16 shows that intensity of this peak increased with exposure time. The peak intensity at 3.49 ppm (Figure 3.17) increases with irradiation. The ^{1}H NMR spectrum does not show the integration of two hydroxyl protons but the hydroxyl group estimation by acetylation method gave the functionality 1.85. It shows that there may be some side reactions also during irradiation.

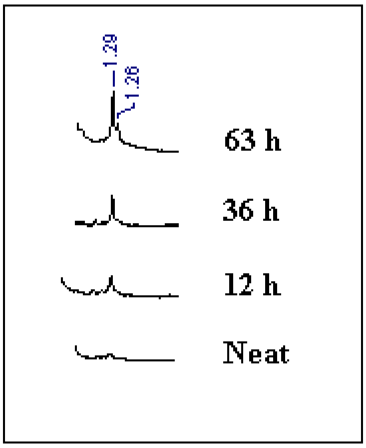


Figure 3.16: ^{1}H NMR spectral view of epoxide group pattern of the degraded natural rubber latex under UV irradiation in combination of H_2O_2 + TiO_2.

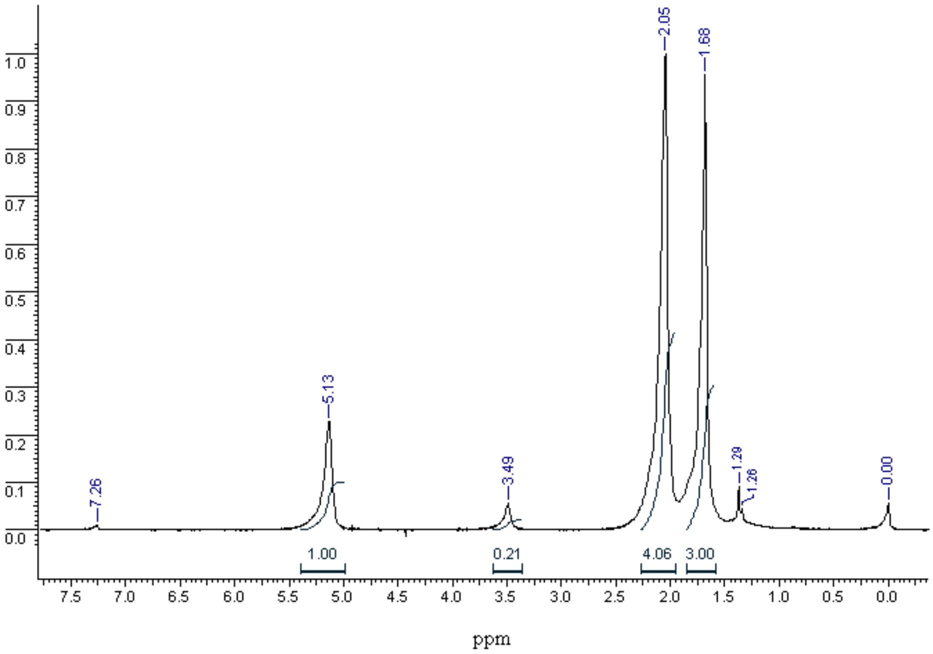


Figure 3.17: ^{1}H NMR spectra of degraded NRL in combination of H_2O_2 + TiO_2 after 63 h UV irradiation.

Number average molecular weights were taken at different intervals of irradiation time for the control, **D-**system, **E-** and **F**-systems (Table 3.3). We observed a continuous decrease in $\overline{M}_n$ with irradiation time.

Table 3.3: $\overline{M}_n$ of photo-degraded natural rubber (in air)

Irradiation Time (h)	**Number average molecular weight (x 10^3)**			
	NRL	NRL+H_2O_2	NRL+TiO_2	NRL+H_2O_2+TiO_2
0	175	175	175	175
36	7.9	5.27	6.45	3.28
63	7.4	3.11	4.36	1.46

3.4.3 Polybutadiene

Photo-degradation of polybutadiene initiates with the chain-scission free radical generation and then hydroxyl and hydroperoxy radicals attack on the hydrogen atom in the allylic position. Hydroperoxides are unstable and can initiate further decomposition of polybutadiene.[23-26] Formation of a strong absorption band in the range 3600 – 3200 cm^{-1} is a characteristic for hydroxyl and / or hydroperoxy groups. Decrease of the cis-CH=CH absorption peak (1654 and 738 cm^{-1}) may be the result of reduction/ consumption of the double bonds during photo-degradation. Moreover, a weak band at 892 cm^{-1} appears due to epoxide group. We did not find any change in the carbonyl region (1710-1680 cm^{-1}). By measuring viscosities, we have found that the molecular weight of polybutadiene decreases with irradiation time but the number average functionality was very high.

In scheme-**G and H**, it was observed that hydroxyl / hydroperoxy groups region (stretching vibration region) 3600- 3200 cm^{-1} with maximum at 3350 cm^{-1}, increases with time (Figures 3.18 and 3.19) and no change in the carbonyl region (Figure 3.20) was observed. The ^{1}H NMR spectra of polybutadiene (Figure 3.21) shows the peaks at δ = 2.09 ppm (-CH_2-, 4H) and δ = 5.39 ppm (vinylic protons, 2H). The signal due to hydroxyl proton in the hydroxy methyl group is observed as a noise after 63 hrs at 3.6-3.8 ppm. We did not find any other impurity and/or side reactions such as epoxy groups etc (Figure 3.22).

In case of combined effects of TiO_2 (1% w/v) and H_2O_2 (**I**-scheme), ^{1}H NMR shows the peak at 3.76 ppm which increases with irradiation time (Figures 3.23 and

3.24). The peak at 1.26 ppm, indicates the protons of the methyl group on the oxirane ring at cis-position and it increases with time.

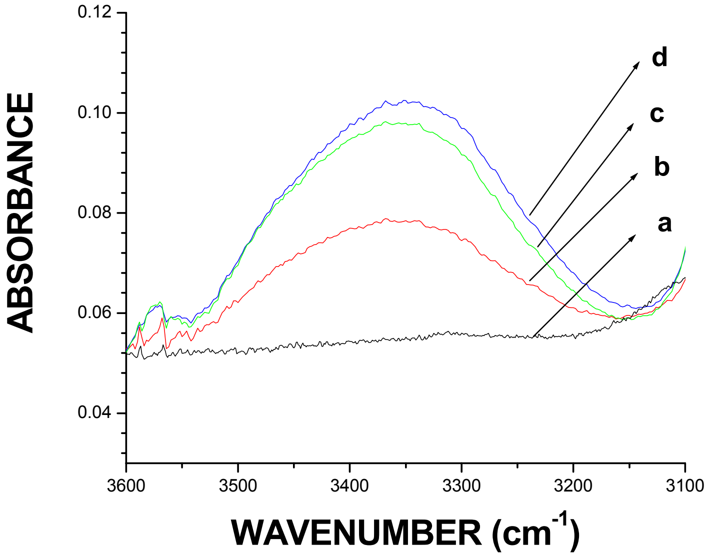


Figure 3.18: FT-IR spectral changes in the hydroxyl region of UV irradiated polybutadiene with H_2O_2 [**G**-system]; **a**: control, **b**: 12 h, **c**: 36 h and **d**: 63 h.

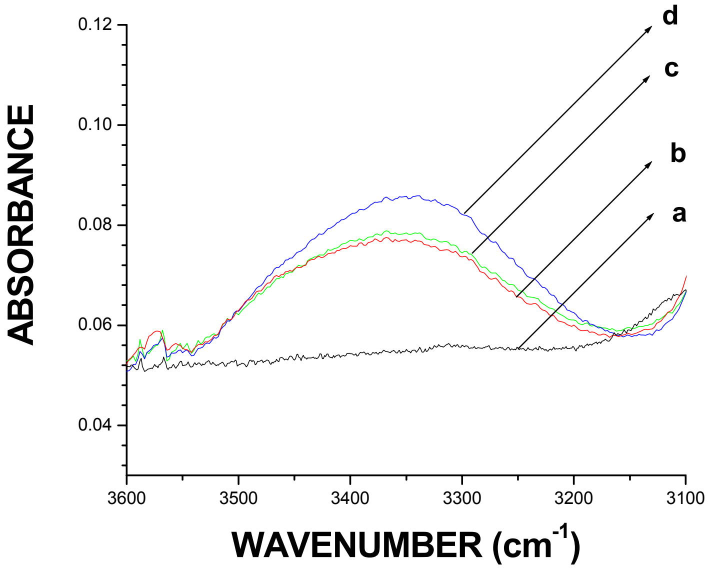


Figure 3.19: FT-IR spectral changes in the hydroxyl region of UV irradiated polybutadiene with TiO_2 [**H**-system]; **a**: control, **b**: 12 h, **c**: 36 h and **d**: 63 h.

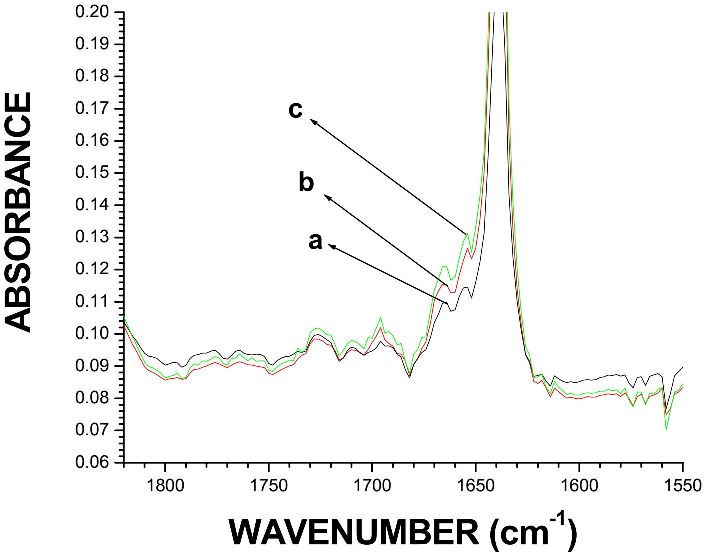


Figure 3.20: FT-IR spectral changes in the carbonyl region of UV irradiated polybutadiene with H_2O_2 [**G**-system]; **a**: 12 h, **b**: 36 h and **c**: 63 h.

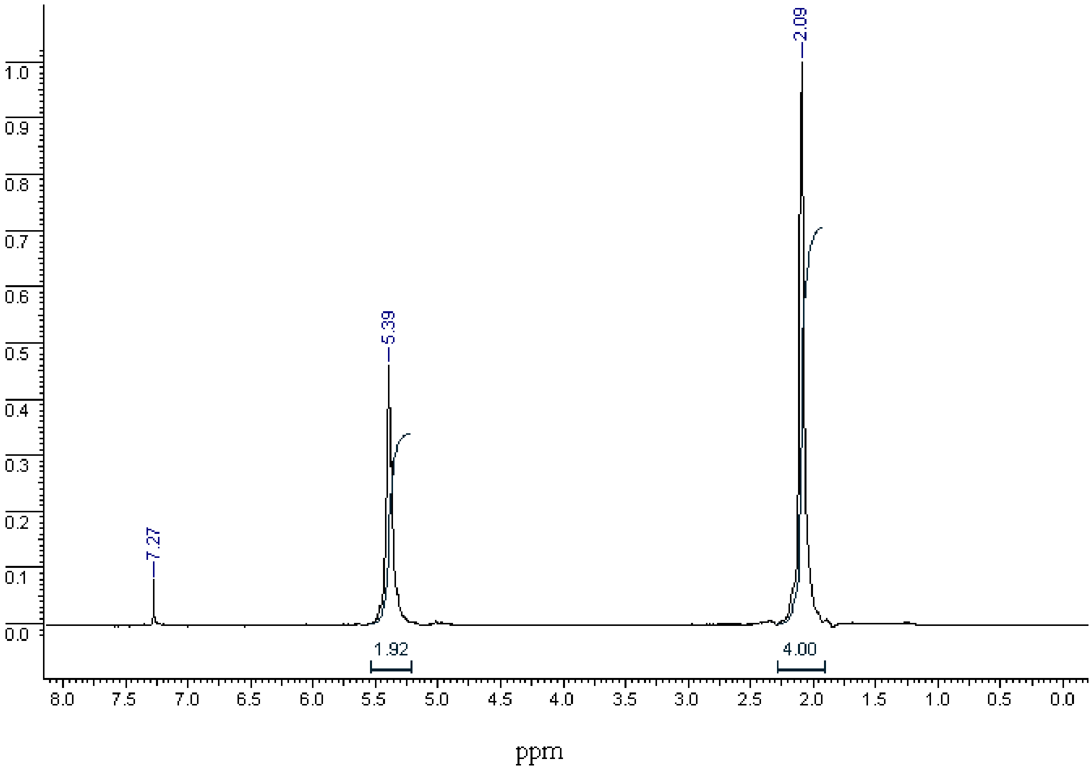


Figure 3.21: ^{1}H NMR spectrum of cis-1, 4-polybutadiene.

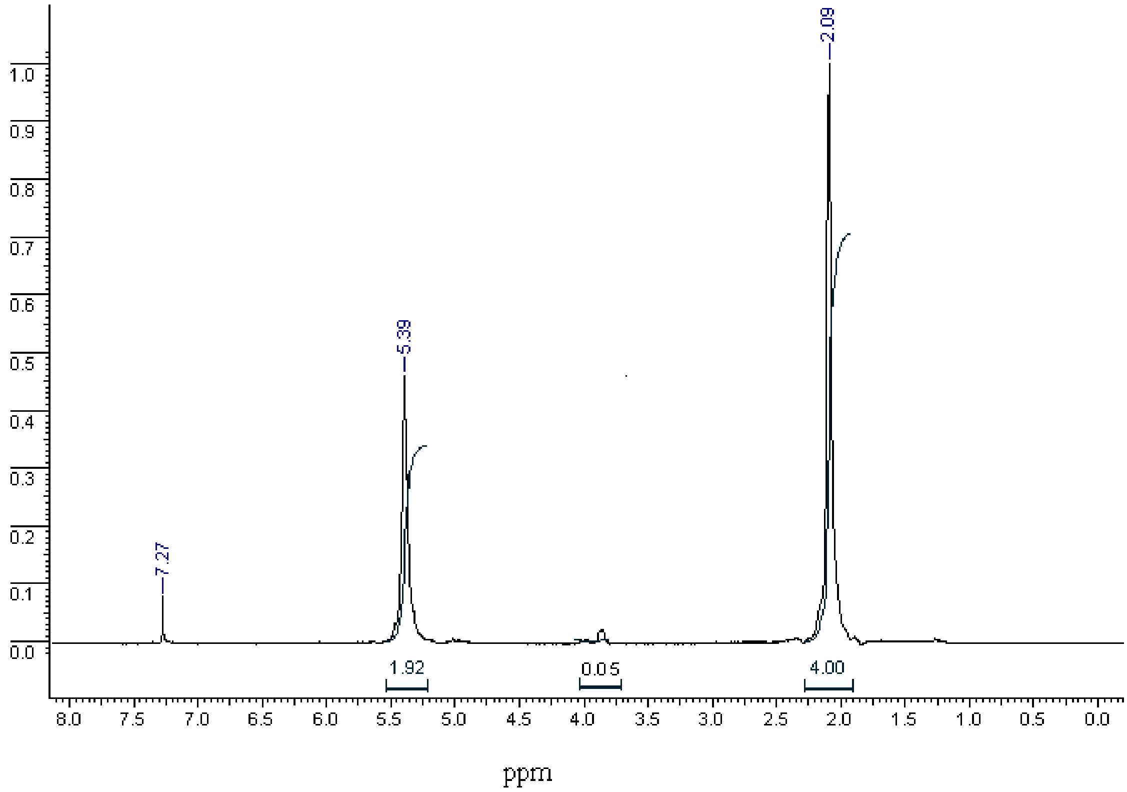


Figure 3.22: ^{1}H NMR spectrum of cis-1, 4-polybutadiene with TiO_2 [**H**-scheme] after 63 h UV irradiation.

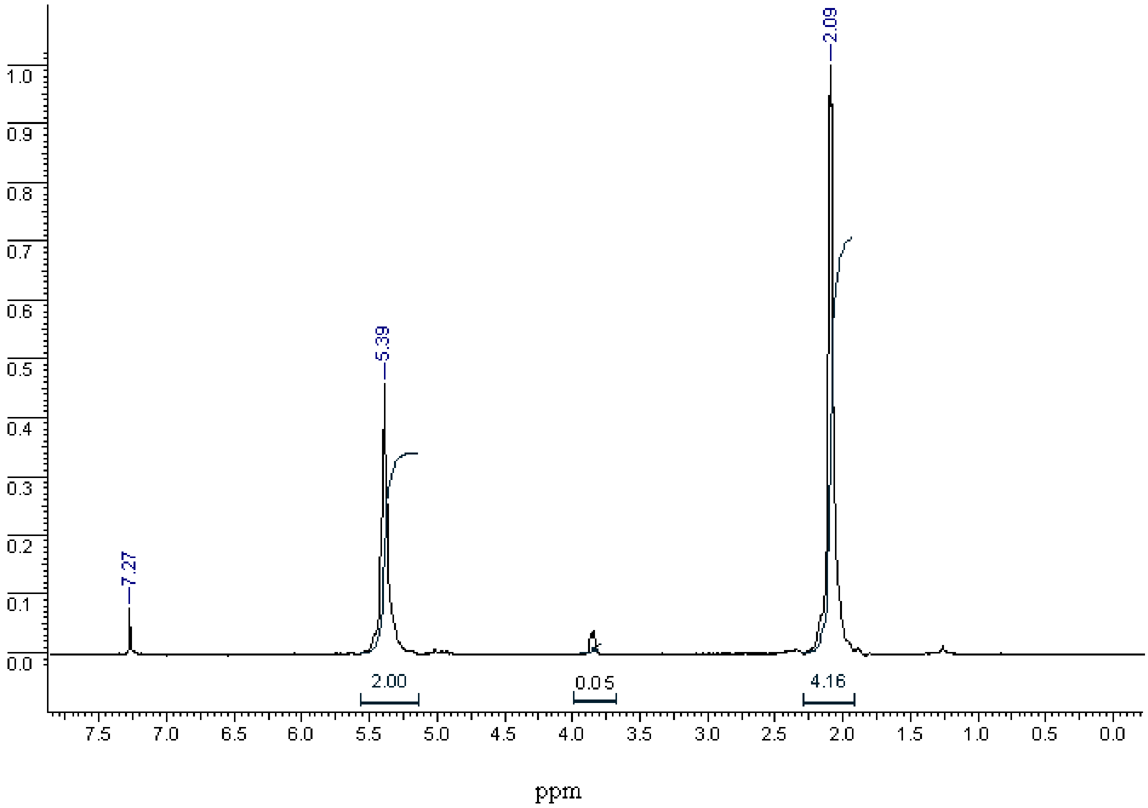


Figure 3.23: ^{1}H NMR spectrum of cis-1, 4-polybutadiene with H_2O_2 and TiO_2 [**I**-scheme] after 12 h UV irradiation.

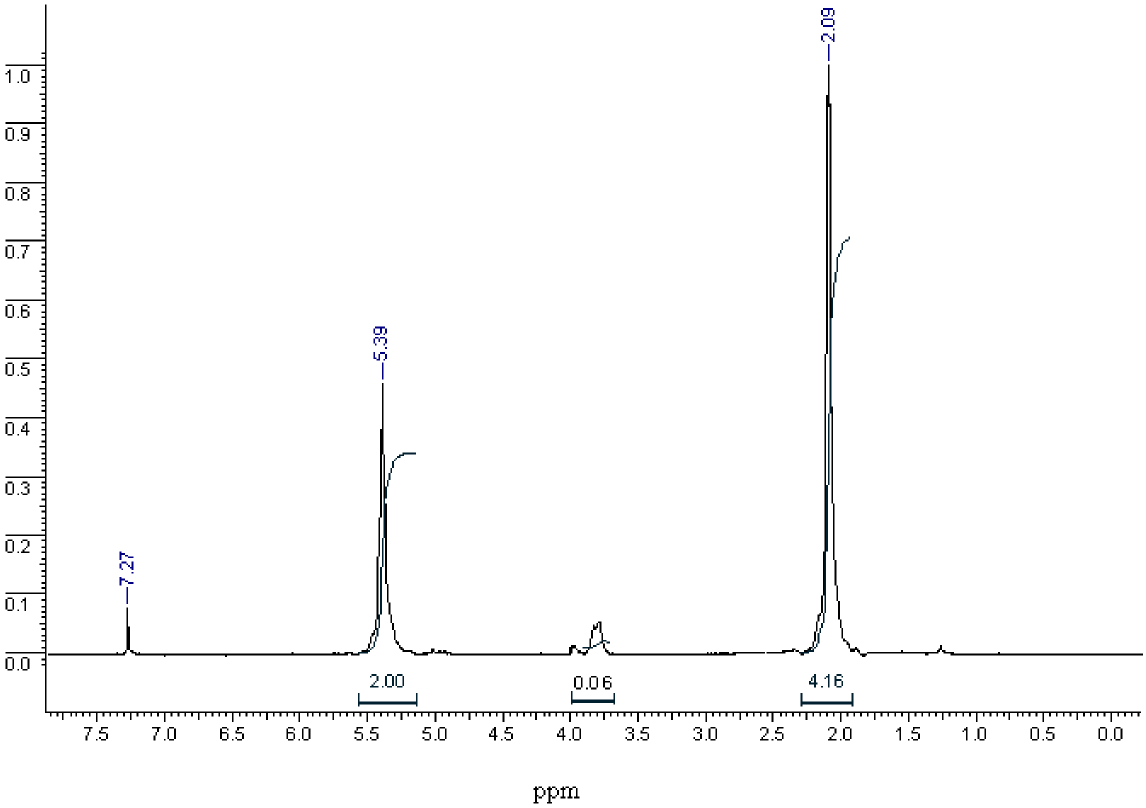


Figure 3.24: ^{1}H NMR spectrum of cis-1, 4-polybutadiene with H_2O_2 and TiO_2 [**I**-scheme] after 63 h UV irradiation.

3.4.4 Functionality determination of natural rubber

The functionality of the telechelic oligomers has a greater significance itself.[27, 28] Properties such as viscosity of the fine solids loaded mixture and the strength of the cured propellant are greatly affected by the functionality of the polymer. Probably, it is the most important single parameter which determines the nature of the oligomeric chains. The hydroxyl numbers per unit were calculated by acetylation method (Table 3.4).[29-32] Fundamentally, the number average functionality of a polymer molecule is the ratio of the number of functional groups to the number of macromolecules. We can say that the ratio of the number of functional groups present in the polymer to the number of moles of polymer molecules. Number average molecular weight was determined by VPO and functionality was calculated:

$$\overline{F_n} = \frac{\overline{M_n} \times \text{Hydroxyl number}}{4000}$$

where hydroxyl number is in mg (NaOH) / g (polymer).

A high value of functionality and randomness was observed in case of photo-degradation of neat natural rubber (Figure 3.25). The addition of oxidizing agent and co-catalyst may constitute an essential feature for accurate functionality measurement.

Functionality was estimated ~ 2 in scheme-**C** as shown in Figure 3.25. It was proposed that hydrogen peroxide and/or allylic hydroperoxides act as photoinitiators and produce hydroxyl radicals and/or alkoxy radicals. The results show that functionality ~ 2 was achieved after 63 hrs of photo-irradiation of natural rubber (Figures 3.25 and 3.26) while in initiated irradiation, it was very low. The proton adjacent to the oxygen at the end groups can be detected at $\delta = 3.4 - 3.8$ ppm in natural rubber, natural rubber latex and polybutadiene. Errors are, however, conceivable if more than one OCH_2- group present at the chain end.

Table 3.4: Determination of hydroxyl number in the photo-degraded natural rubber

Samples	**Irradiation time (h)**	**Hydroxyl number**	
		In air	**In nitrogen**
NR	Neat	0.015	0.015
	36	11.71	4.96
	63	13	16.32
NR +H_2O_2	36	68.1	11.17
	63	74.5	--
NR+TiO_2	36	20.59	12.52
	63	38.49	--
NR+H_2O_2+TiO_2	36	32.14	11.8
	63	49.87	14.2

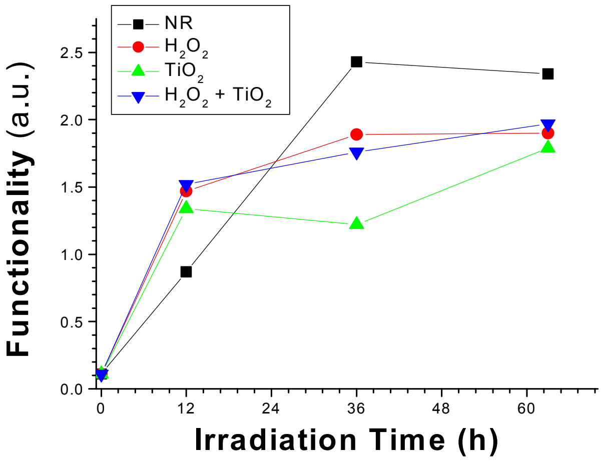


Figure 3.25: Rate of functionality in degraded natural rubber with irradiation time (in air).

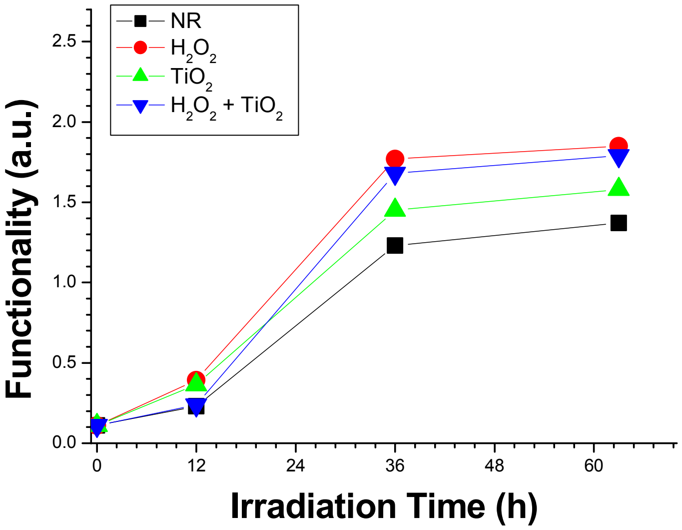


Figure 3.26: Rate of functionality in degraded natural rubber with irradiation time (in nitrogen atmosphere).

3.5 CONCLUSIONS

Since, in the presence of atmospheric air, reactions involving oxygen can not be prevented, namely oxidation by singlet oxygen and radical-induced auto-oxidation resulting from hydrogen peroxide and hydroperoxide photolysis, leading to the formation of hydroperoxy, hydroxyl, carbonyl and epoxide groups. The segregation/identification of the chain-end-oxidized microstructure is difficult, therefore, the mechanism of the chain cleavage is difficult to propose definitively. Thus, the mechanism by H_2O_2 photolysis and the hydroxyl radical-induced chain cleavage[7, 8] could not be evidenced and it will be implied to characterize the resulting allylic alcohol chain ends. A free-radical mechanism has been suggested for the degradation of natural rubber. These free radicals interact with the labile α-hydrogen (C-H bond), abstracting the proton and leaving macroradicals behind. The peroxides are formed by the interaction of these radicals with O_2 and decomposed to yield various degradation products containing hydroxyl, carbonyl and carboxy groups at the chain ends.

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CHAPTER IV

EPOXIDATION OF NATURAL RUBBER IN BIPHASIC MEDIUM USING METHYLTRIOXORHENIUM

4.1 INTRODUCTION

Epoxidized natural rubber (ENR) is a derivative of natural rubber produced by chemical modification. Such materials have been reported in the literature since 1922, including an epoxidized synthetic polyisoprene.[1-10] However, a huge range of conflicting properties were reported in literature for these materials.[11-13]

The properties of the de-oxidized dienes that result from epoxidation of polydienes, have led to increasing interest over the past years. Actually, epoxidation is a relatively old form of modification but the new form deliberately set out to establish a commercially viable material. Although the material is based upon natural rubber and retains many of its characteristics, some of the new properties are distinctly similar to several of the specialty synthetics, such as nitrile rubber. ENR is far more resistant to hydrocarbon oils than unmodified natural rubber and offers excellent damping properties. The polymerization of a monomer, already epoxidized, has the disadvantage and usually many side reactions occur.[10] The most promising route to epoxidation seems to be the direct introduction of oxygen atom across the double bonds of polydienes. The system commonly used to epoxidize polydienes, is the in-situ formation of peracids, obtained by the reaction of acetic or formic acid with hydrogen peroxide.[4, 5, 7, 10, 14] Nevertheless, some unreacted acid is often still present at the end of the reaction thus reducing the stability of the epoxidized polymer. The products are free from secondary ring-opened structures such as diols and furans but an excessive reaction temperature or too low pH can result in these groups forming in ENRs.[15]

Epoxidation reactions are stereospecific and thus ENR is a cis-1, 4-polyisoprene with epoxide groups randomly situated along the polymer backbone.[16] The techniques such as NMR, IR or differential scanning calorimetry (DSC) can be used to determine the epoxide content of epoxides natural rubber.[17] However, analysis employing tetramethyl ammonium bromide or hydrochloric or hydrobromic acids give low values as these reagents initiate ring opening of adjacent epoxide groups.[18]Attempts have been carried out to epoxidize the polydienes with catalytic systems based on metals such as Molybdenum, Tungsten, Manganese and with oxidants such as hydrogen peroxide or organic hydroperoxides.[19-21] A number of efficient and useful catalysts for oxidation have discovered over recent years.[22-24] Amongst them, methyltrioxorhenium (MTO) is a versatile and highly active catalyst which has gained increasing importance for the activation of hydrogen peroxide in oxidation reactions such as epoxidation and sulphur oxidation (sulphoxidation).[25-28] The MTO is a peculiar appealing catalyst for oxygen transfer from hydrogen peroxide to olefin owing to the efficiency and selectivity of such reactions as shown in Scheme 4.

Hermann *et al.*[29] for the first time, used MTO for epoxidation in combination with hydrogen peroxide (H_2O_2). The catalytic reactions performed by MTO, particularly epoxidation, have been thoroughly documented.[30-34] Methyltrioxorhenium combined with hydrogen peroxide, is a very active and selective catalytic precursor for the epoxidation of olefins (functionalized or not).[35] It can be used in homogeneous or biphasic systems. The advantage of using the biphasic system is the protection of the sensitive epoxides that remain in the organic phase and are not in contact with the aqueous acidic phase. In some cases, when the epoxide is extremely sensitive to acidic media, the reaction may be performed using bipyridine to reduce the pH of the solution or in pyridine. In this study, we describe the results using MTO as the catalytic precursor for the epoxidation of cis-1,4-polyisoprene in a biphasic system, dichloromethane as the solvent and hydrogen peroxide as oxidant.

4.2 EXPERIMENTAL

4.2.1 Materials

Methyltrioxorhenium (MTO) was purchased from Aldrich. Natural rubber ($\overline{M}_v = 2.82 \times 10^5$) was supplied through the courtesy of Dr. S. Thomas, M.G.University, Kottayam, Kerala. Hydrogen peroxide 30%v/v was supplied by M/s. S.D. Fine Chemicals Ltd. All other solvents were of A.R. grade and used after distillation.

4.2.2 Reaction Procedure

In a typical epoxidation reaction, 0.1 g of purified natural rubber was dissolved in 20 mL dichloromethane. MTO (2.306 mg) followed by hydrogen peroxide was added dropwise in the natural rubber solution. The reaction was controlled by water-bath as the reaction was strongly exothermic. The completion of the reaction was indicated by the discoloration, aliquots were withdrawn at different time intervals and the natural rubber precipitated with methanol, dried under vacuum until constant weight. At the completion of the reaction, sodium carbonate was added to decompose the catalyst, extracted with ether and washed with small amount of water. The samples were characterized by ^{I}H, ^{13}C NMR and FT-IR spectroscopic methods.

4.3 ANALYSIS

4.3.1 FT-IR Analysis

Epoxidized natural rubber and kinetics of epoxidation were studied by FT-IR (Fourier Transform Infrared Perkin Elmer16 PC spectrometer).

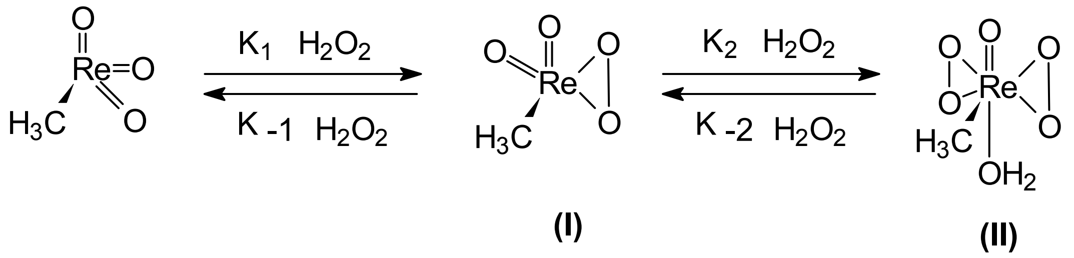
4.3.2 NMR Analysis

Epoxidized products were characterized by ^{1}H and ^{13}C NMR spectroscopy (Bruker AC 200 MHz; time acquisition: 22.048 sec., temperature: 24°C and number of transient: 512 etc). $CDCl_3$ (Aldrich 99.8 % D) was used as solvent.

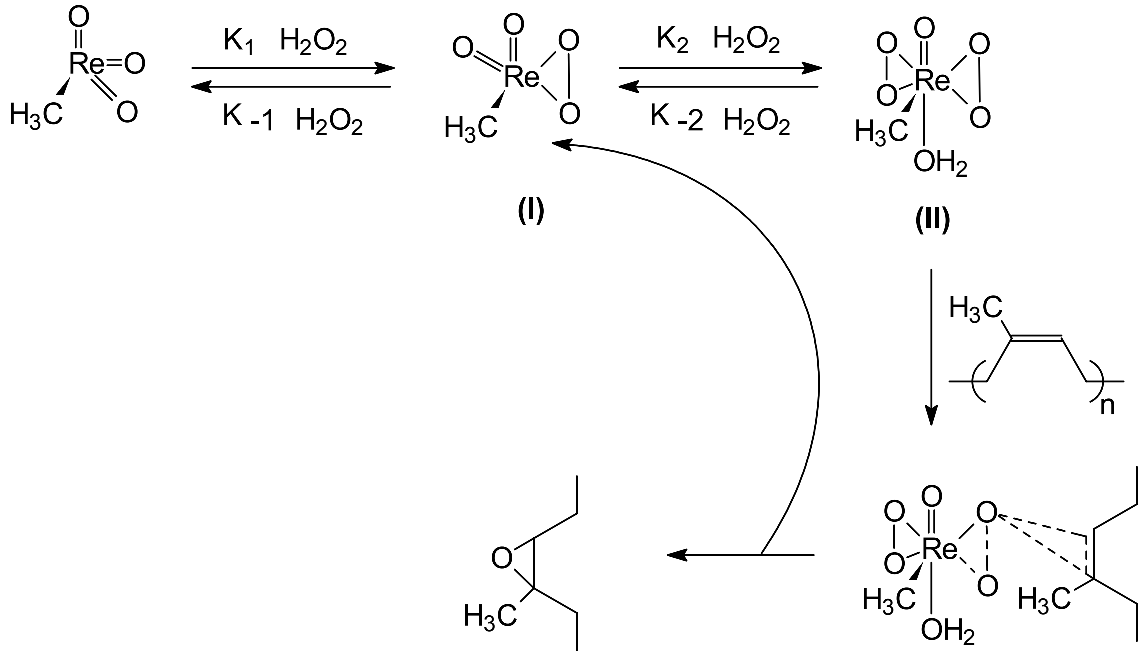
4.4 RESULTS AND DISCUSSION

The experiments with the biphasic system were intended to determine the optimal ratio of MTO, relative to the amount of available double bonds. The amount of catalyst had already proved to be effective in the total epoxidation of normal olefins. After total consumption of hydrogen peroxide, a conversion of 20% with 100% selectivity in epoxide was achieved[36]. It has been shown that using perbenzoic acid[37], chloroperbenzoic acid[38] and monoperthalic acid[39], good yields of epoxidized rubbed were achieved but due to high acidity, epoxy groups may be acidolyzed and converted into carbonyl ester, ether or cyclic compounds[40-47] while using methyl trioxorhenium catalyst, side reactions were not observed.

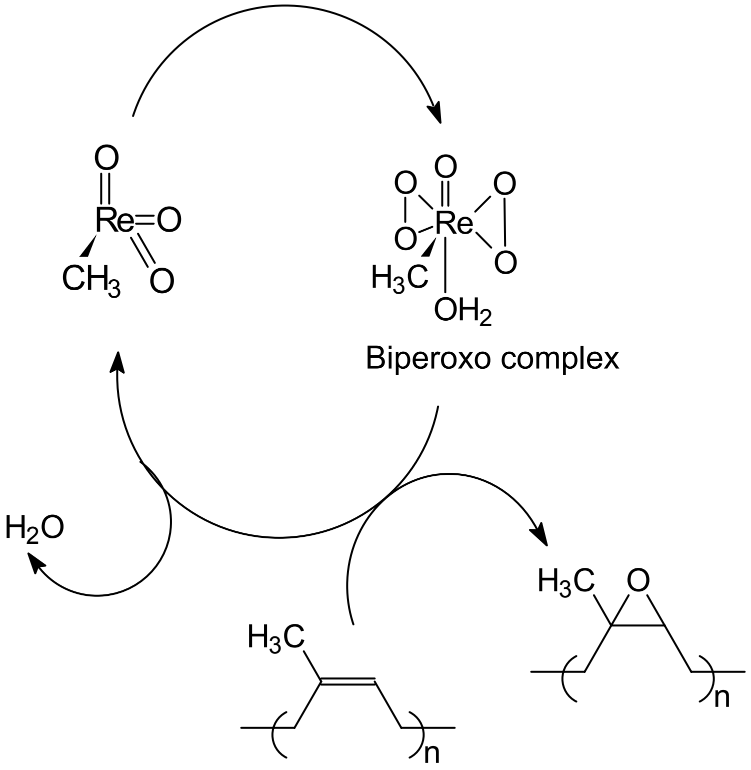
Epoxidation occurs in the initial stages of the reaction between the substrate (I) or (II) as shown in the Schemes 4.1 – 4.4.



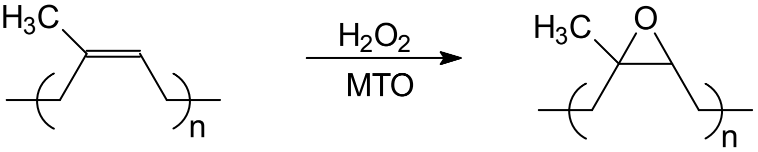
Scheme 4.1



Scheme 4.2



Scheme 4.3



Scheme 4.4

It has been well documented that two peroxorhenium compounds exist in equilibrium with MTO and H_2O_2..[48] The relative contributions of (I) and (II) depend on the concentration of hydrogen peroxide. Oxides of transition metals in high oxidation states are common reagents and catalysts for olefin oxidation.[49, 50] Hermann *et al.*[51] elucidated the active species of the catalytic system [H_2O_2/MTO] and described the first isolated peroxo-metal complex with a metal-alkyl group that was stable to hydrolysis and to peroxide. The rhenium (VII) peroxo complex (substrate II in Scheme 1) which could be isolated in solid state, is the active species in the olefin epoxidation which is catalyzed by MTO. In contrast, the monoperoxo complex does not react significantly with olefins. In the process, the catalyst (MTO) in presence of H_2O_2 forms monoperoxo complex. In excess of hydrogen peroxide (2 equivalent), substrate I gives substrate II which is the active species and more stable under the catalytic conditions for the epoxidation in this system.

4.4.1 Effect of Methyltrioxorhenium concentration (%)

Taking into account that a highly epoxidized polydiene is undesirable due to its low solubility and high glass transition temperature, the ratio of methyltrioxorhenium (MTO) to double bond has been reduced to 0.1 %. Under these conditions and with the addition of 20 % hydrogen peroxide, 12 % epoxidation was achieved. Since the maximum degree of epoxidation desired is about 50 %, we used 0.5 % MTO for further reactions for lower degree of epoxidation, however, this amount can be reduced. The effect of epoxidation of natural rubber using H_2O_2 (20 %) as a function of MTO is shown in Figure 4.1.

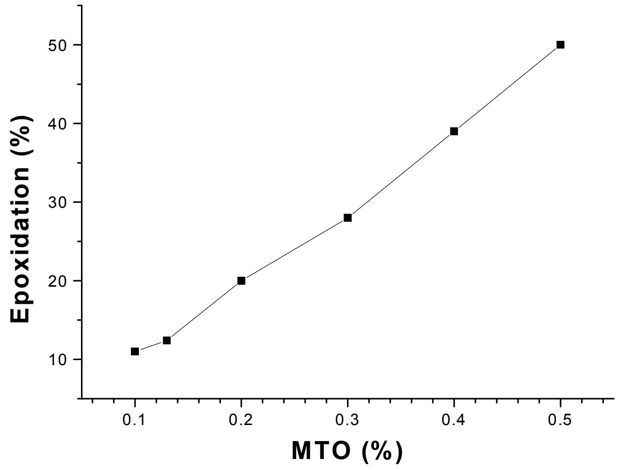


Figure 4.1: Effect of epoxidation of Natural Rubber using H_2O_2 (20 %) as a function of MTO.

4.4.2 Epoxidation of natural rubber at various parameters

For the reaction with more oxidant, a longer time is necessary in order to achieve the attempted degree of epoxidation. The use of 60 % hydrogen peroxide led to a product that was insoluble in standard solvents and could not be spectroscopically characterized. In all the cases, epoxidation occur very effectively and selectively, which is in agreement with results obtained for epoxidation systems as shown in Table 4.1.

Table 4.1: Epoxidation of natural rubber at various parameters using methyltrioxorhenium

Sr. No.	H2O2 (%)	MTO (%)	Reaction Time (min.)	Reaction Temp. (°C)	Epoxidation (%)
1	20	0.1	20	35	11
2	20	0.13	20	35	12.4
3	20	0.13	30	35	12.8
4	20	0.13	60	35	12.8
5	30	0.13	40	35	12
6	50	0.13	55	35	12
7	20	0.2	30	35	20
8	20	0.3	30	35	28
9	20	0.4	30	35	39
10	30	0.5	45	35	50
11	60	0.4	100	35	--

The ^{1}H NMR showed the presence of the peaks at 1.27 ppm (methyl group on the oxirane ring) in cis position and the peak at 2.71 ppm as the proton on the oxirane ring. The vinylic proton of the natural rubber unit was at 5.1 ppm. As the carbon to carbon double bond was converted to the highly strained cyclic epoxide unit, the tertiary proton of the epoxide ring was shifted to 2.71 ppm. Signals in the FT-IR and ^{1}H NMR spectra showed the presence of epoxy ring (band at 874 cm^{-1}, 1249 and 886 cm^{-1}) relative to the oxirane ring vibration in the FT-IR spectra (Figure 4.2), peaks at 1.7 and 2.7 ppm in ^{1}H NMR (Figures 4.3 to 4.5) and the peaks at 64.6 ppm and 60.6 ppm in ^{13}C NMR spectra (Figure 4.6), assigned to the carbon with the methyl of the oxirane ring at cis and other carbon (with the proton) of the oxirane ring at trans position, respectively[52].

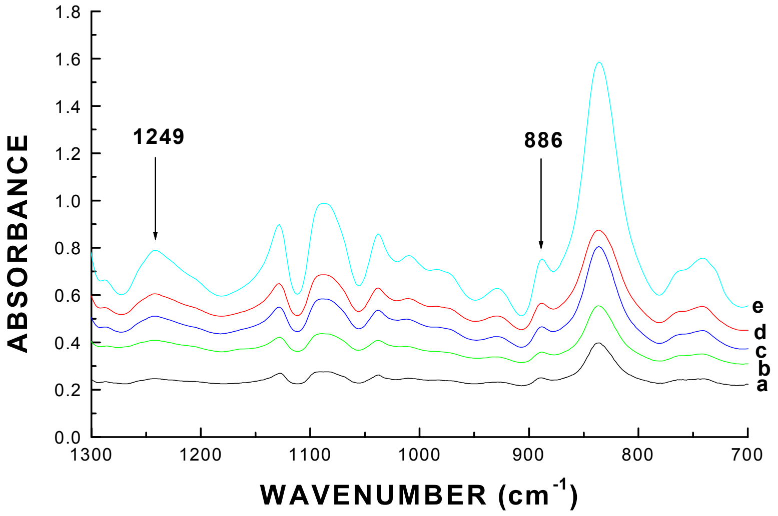


Figure 4.2: FT-IR spectral changes in the epoxidized natural rubber in presence of MTO (0.13 %) and hydrogen peroxide (% v/v)**: a**: Nil, **b**: 20, **c**: 30, **d**: 40 and **e**: 50.

The absence of further new peaks either in FT-IR or ^{1}H NMR spectra shows the high selectivity of this catalyst system. It is important to stress that the catalytic systems, normally used for epoxidation of polydienes, lead to the formation of other functionalized products such as ketones[36] and carboxylic acids, which for the catalytic system presently investigated (epoxy) is the only new functional group.

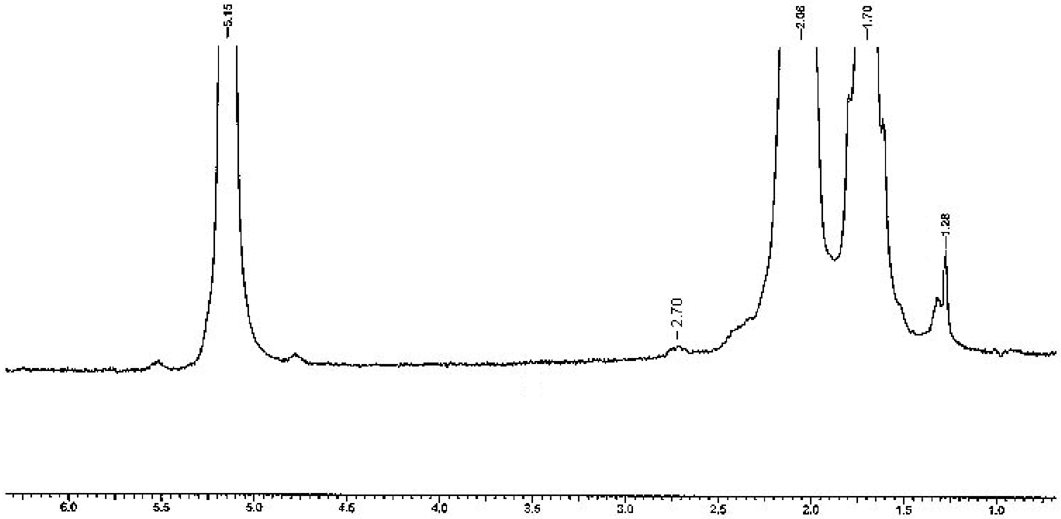


Figure 4.3: ^{1}H NMR spectrum of epoxidized natural rubber (using MTO (0.13 %) and hydrogen peroxide (20%) in $CDCl_3$ solution.

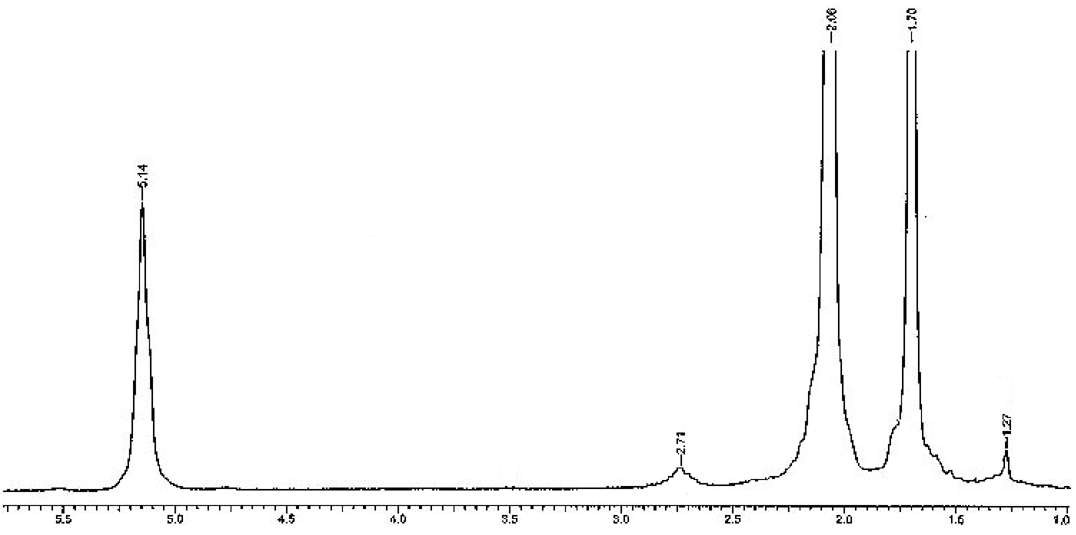


Figure 4.4: ^{1}H NMR spectrum of epoxidized natural rubber using MTO (0.13 %) and hydrogen peroxide (30%) in $CDCl_3$ solution.

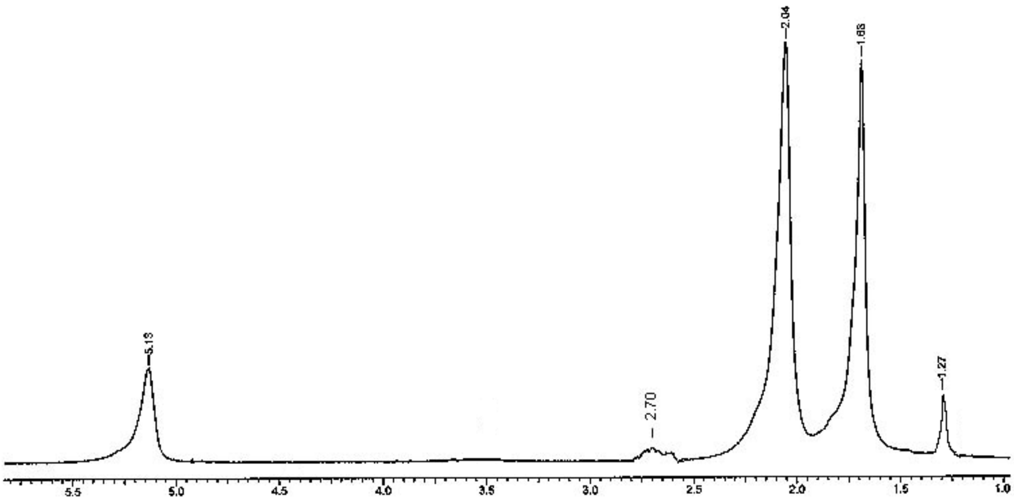


Figure 4.5: ^{1}H NMR spectrum of epoxidized natural rubber using MTO (0.3 %) and hydrogen peroxide (30%) in $CDCl_3$ solution.

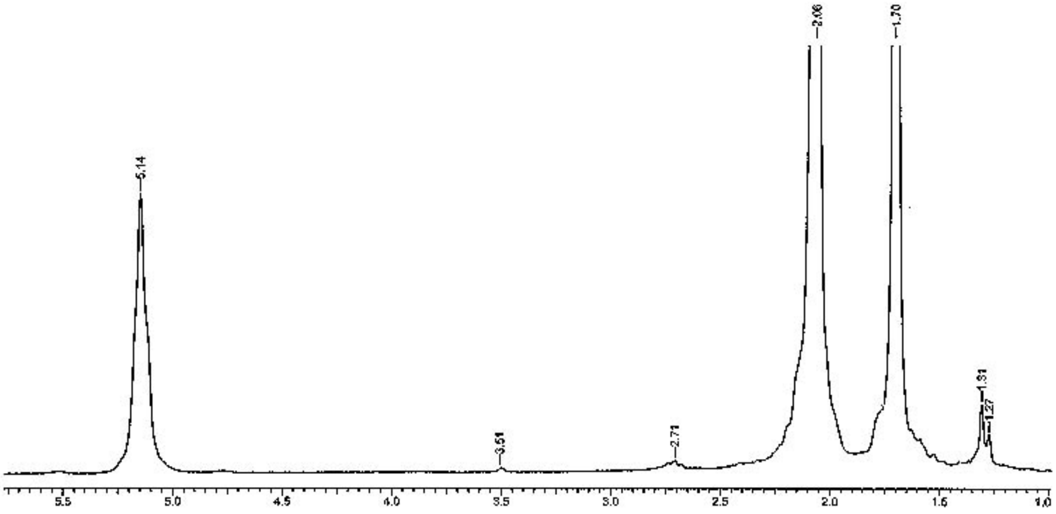


Figure 4.6: ^{1}H NMR spectrum of epoxidized natural rubber using MTO (0.3 %) and hydrogen peroxide (40%) in $CDCl_3$ solution.

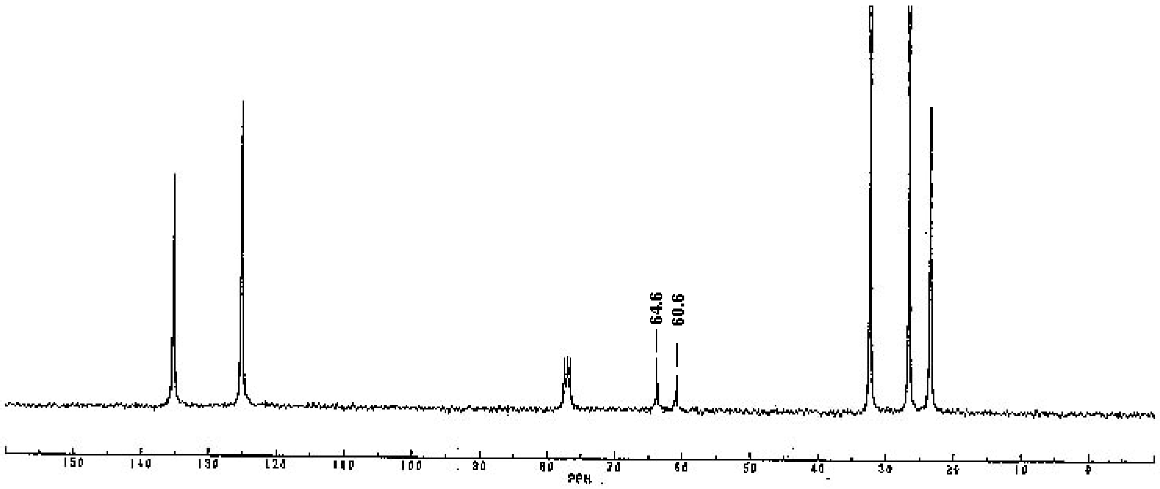


Figure 4.7: ^{13}C NMR spectra of epoxidized natural rubber.

4.5 CONCLUSIONS

MTO based epoxidation system, already known as an effective catalytic system for the epoxidation of normal olefins, proved to be extremely efficient for the epoxidation of high molecular weight natural rubber. Polymers with degree of epoxidation ranging from 12 – 48% were obtained. The degree of epoxidation could be controlled by the amount of hydrogen peroxide.

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CHAPTER V

METATHETIC DEGRADATION OF NATURAL RUBBER

5.1 INTRODUCTION

A high activity of the metathesis catalyst is important for metathetical degradation of unsaturated polymers. Some metathesis catalysts suitable for the ring opening metathetical polymerization of highly strained norbornene are not applicable to metathetic degradation of unsaturated polymers.[1-4] The catalyst action should be sufficiently free from side reactions for metathetic degradation of unsaturated polymers to low-molecular-weight products. Three generations of catalysts have been used for metathetic degradation of unsaturated polymers. In the beginning, tungsten catalysts (especially tungsten hexachloride and its derivatives) and co-catalysts *i.e.* ethyl aluminum dichloride were used.[5, 6] Later, the organoaluminiums were substituted by tetra-alkyltins (*i.e.* tetramethyltin, tetraethyltin).[7-10] Well-defined carbene catalysts of the Schrock or Grubbs type are presently preferred.[11-13]

Metathesis depolymerization[14, 15] using simple alkenes as depolymerization agent was extensively used for analyzing the microstructure of the unsaturated polymers. The advent of acyclic diene metathetical polymerization as a viable synthetic route to high molecular weight linear polymers and copolymers has provoked important examination of metathesis chemistry.[16] Alimuniar *et. al.*[17] studied the metathetic degradation of natural rubber with tungsten hexa-chloride and tetramethyl tin catalyst system. The reaction was catalytically induced in which carbon to carbon double bond undergo cleavage and reform. Metathesis has been used for the polymerization of cyclic olefins to give poly(alkenamers). Metathesis degradation of unsaturated polymers was reported in few reports but feebly descriptive.[18-20] In this chapter, metathetic degradation of natural rubber is studied using bis(tricyclohexyl phosphine) benzylidine ruthenium (VI) dichloride [Grubb's catalyst] as catalyst. The metathetical degradation of high molecular weight unsaturated polymers using specially Grubbs or Schrock catalyst will enhance the low molecular weight polymers/ oligomers.

5.2 EXPERIMENTAL

5.2.1 Materials

Natural rubber ($\overline{M_v} = 2.82 \times 10^5$) was supplied by the courtesy of Dr. S. Thomas, M. G. University, Kottayam, Kerala. The natural rubber was purified three times with toluene and methanol. The Grubbs catalyst 'bis(tricyclohexyl phosphine) benzylidine ruthenium (VI) dichloride' was purchased from Strem Chemicals. Dichloromethane, chloroform, toluene and methanol were supplied by M/s. S.D. Fine Chemicals Ltd. All solvents were of A.R. grade and used after distillation.

5.2.2 General reaction procedure

All the reactions of metathetic degradation of natural rubber were conducted on a 0.2 to 0.5 gm scale in an nitrogen purged dry box. A two necked round bottom flask with magnetic bar was charged with Grubb's catalyst [**(i)** 0.001g, **(ii)** 0.0015 g and **(iii)** 0.003 g]. A 1.0 % natural rubber solution (in dichloromethane / chloroform / toluene) was purged with a vigorous stream of argon through a needle in the round bottom flask with vigourous and constant stirring. The reaction was carried out at room temperature and at 50 and 60°C. Cold water was circulated in the condensor when reaction was carried out at higher temperatures. At the end of reaction, the resulting reaction mixture was allowed to cool to room temperature and poured into 300 mL of methanol dropwise. The polymer was oily, sticky and blakish brown in colour.

5.3 ANALYSIS

5.3.1 FT-IR Analysis

Degraded natural rubber products were studied by FT-IR (Fourier Transform Infrared Perkin Elmer16 PC spectrometer).

5.3.2 NMR Analysis

Degraded natural rubber was characterized by ^1H NMR spectroscopy (Bruker AC 200 MHz; time acquisition: 22.048 sec., temperature: 24°C and number of transient: 512 etc) where $CDCl_3$ (Aldrich 99.8 % D) was used as solvent.

5.3.3 Viscosity average molecular weight

The changes in the $\overline{M}_v$ during ozonolysis were determined in dried toluene (0.016 wt %) at 25 ± 0.1°C using an Ubbelohde viscometer and the Mark-Houwink-Sakurada equation:

$$[\eta] = K. \overline{M}_v^{a}$$

where $K = 5x10^{-4}$ and $a = 0.667$

5.4 RESULTS AND DISCUSSION

Aliquots were withdrawn at different time intervals and the natural rubber was precipitated in methanol and dried under reduced pressure. Viscosity-average molecular weights [$\overline{M}_v$] were determined at different intervals of natural rubber solution. A continuous decrease in $\overline{M}_v$ with time and temperature was observed during metathetic degradation (Figure5.1).

We carried out the metathesis reactions in dichloromethane, chloroform and toluene. Dichloromethane was found most suitable solvent for natural rubber degradation at 60°C. We studied the behaviour of temperature on the reaction. The M_v decreases with time as the temperature rises (Figure 5.1). There was no coagulation in the rubber solution even after 48 h, it shows that chain scission is predominant over crosslinking reactions in metathetic degradation. The catalyst composition was also studied on the metathetic behaviour in rubbers. Since the catalyst is highly reactive, therefore, was used in very small quantity. The different amount of catalyst was used (*i.e.* 0.1 mg, 0.15 mg and 0.3 mg) by keeping constant volume of natural rubber solution in the reaction solution. We observed no change with increasing the amount of catalyst (Figure 5.2). The ^{1}H NMR spectra of degraded rubber do not show any specific changes (Figures 5.3 to 5.5). Alimuniar *et. al.*[17] observed decrease in unsaturation and some cyclization reactions, when natural rubber was treated with tungsten hexa chloride catalyst system. Although, much attention was paid to the protonic species which were produced in the reaction due to some lewis acid nature of the metal halide, but they could not give any mechanism of generation of cyclic products during metathetic degradation.

In another experiment, we took purified natural rubber and catalyst in a round bottom flask under nitrogen atmosphere. The reaction was carried out at 60°C without any solvent medium under argon atmosphere. After completion of 48 h, there was no change in the the $\overline{M}_v$ of reaction product. It is assumed that solvent offers a good homogeneous medium to natural rubber and catalyst to react.

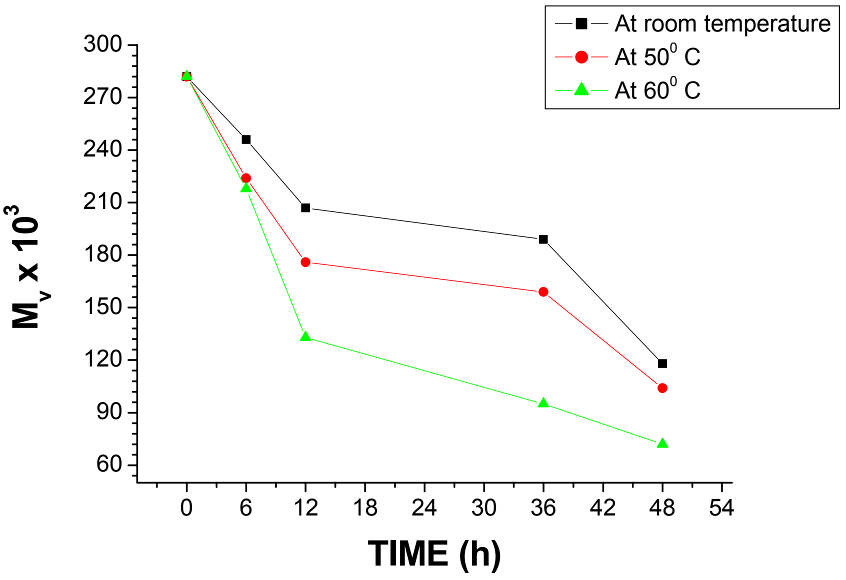

Figure 5.1: Changes in the average molecular weight of degraded natural rubber using grubbs catalyst.

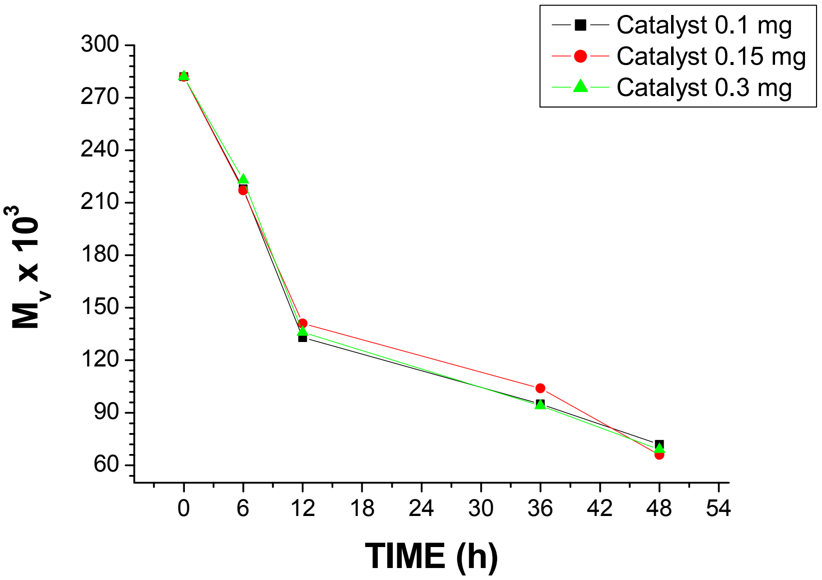

Figure 5.2: The effect of various concentration of Grubb's catalyst on average molecular weight of degraded natural rubber at 60°C.

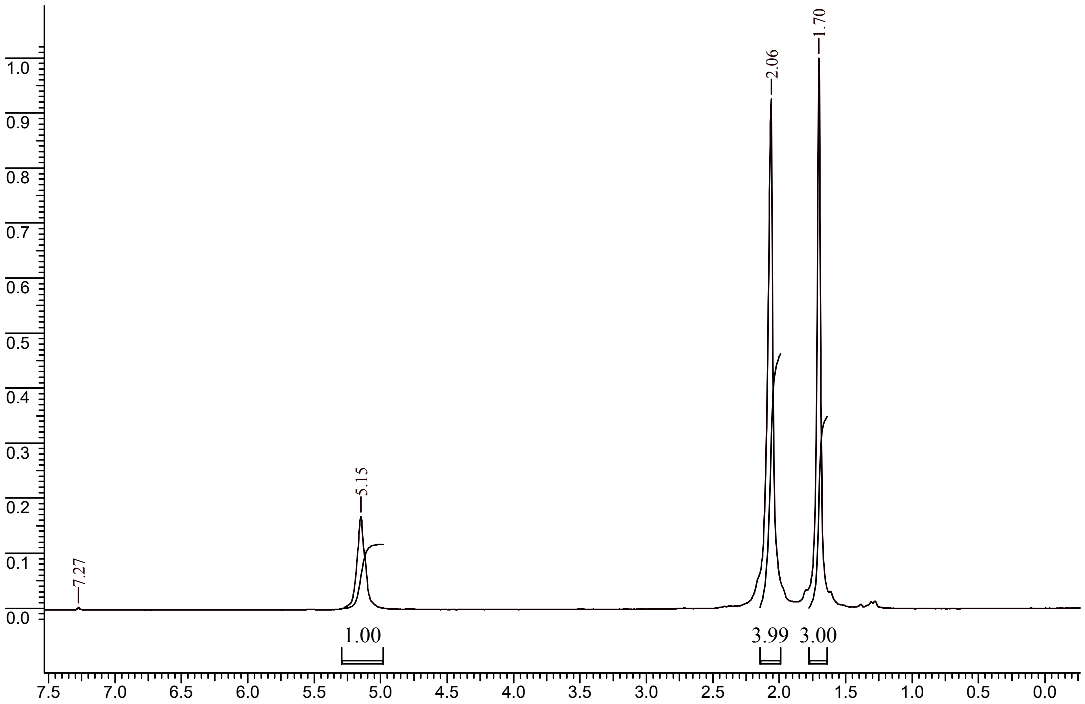

Figure 5.3: ^{1}H NMR spectra of degraded natural rubber containing 0.1 mg catalyst.

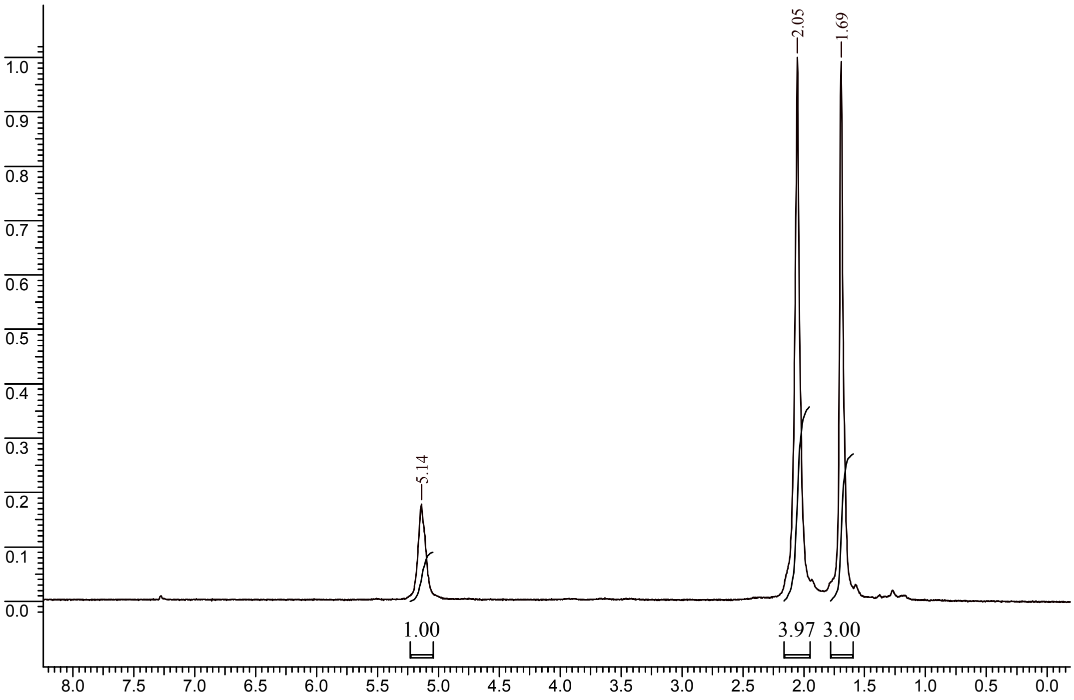

Figure 5.4: ^{1}H NMR spectra of degraded natural rubber containing 0.15 mg catalyst.

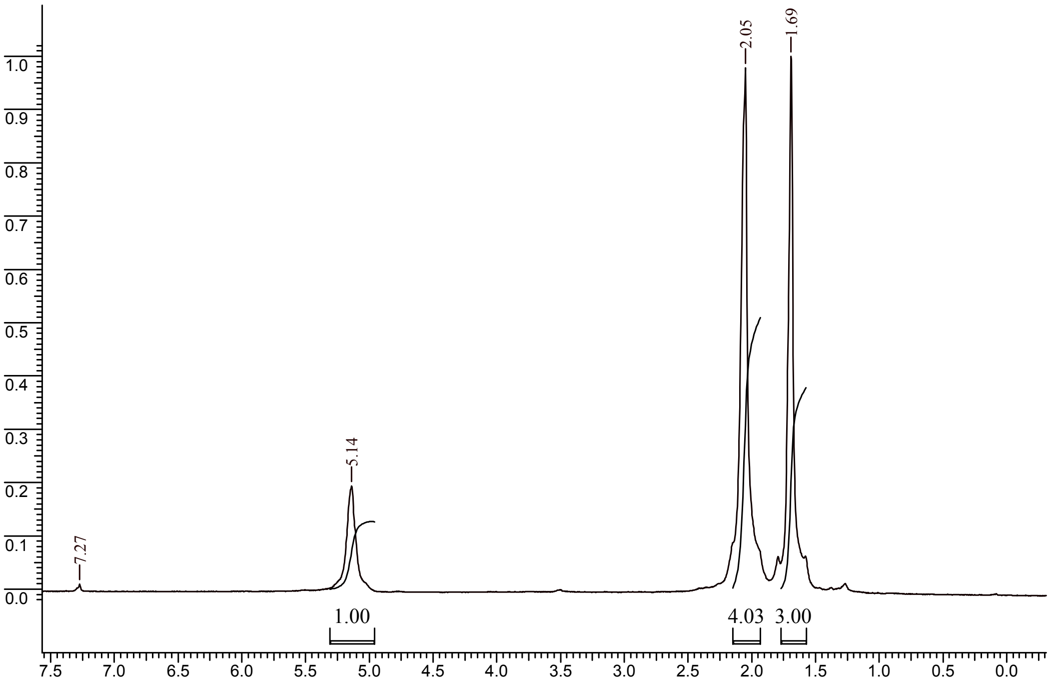

Figure 5.5: ^{1}H NMR spectra of degraded natural rubber containing 0.3 mg catalyst.

5.5 CONCLUSIONS

Metathesis reaction of natural rubber using Grubb's catalyst is also a way to degrade the natural rubber. Viscosity average molecular weight of natural rubber decreases with the progress of the reaction and temperature. Dichloromethane was found suitable solvent for metathesis of natural rubber. It is also possible to get desired molecular weight of natural rubber by adjusting the reaction temperature and suitable solvent in metathesis reactions.

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CHAPTER VI

METATHETIC DEGRADATION USING MODEL MOLECULE

6.1 INTRODUCTION

Over the past several years, there has been an increasing interest in the synthesis of polymers with reactive functional groups at terminal ends.[1, 2] Telechelic hydroxyl, carboxyl, amino natural rubbers (NR)s are excellent examples of such polymers that have been used to make block / graft copolymers.[3, 4] The telechelics impart a major role in the preparation of advanced polymeric materials, because of their functional groups at the chain ends.[5-8] In addition to radical and anionic pathways to telechelic natural rubber, several approaches, involving olefin metathesis have also been explored.[9] In presence of a difunctional chain transfer agent, ring-opening metathesis of cyclooctadiene has been successfully employed.[10] Classical defined catalyst system (tungsten hexachloride/ tertramethyl tin) does not offer good result when functionalized chain transfer agents are used in the reaction. The development of well defined tungsten and molybdenum complexes offered the better understanding of the nature of chain transfer that occurs between growing polymer chains and the chain transfer agent.[11] It was found that neighboring functional groups deactivate the catalyst through coordination effects, therefore, two or more methylene spacers are necessary between the olefin and some functionality in chain transfer agent.[12]

Ruthenium based catalyst[13, 14] (Grubb's catalyst) shows a high tolerance to a wide variety of functional groups. This tolerance power of this catalyst allowed more freedom in the choice of functionality that can be included in chain transfer agent and thus at the end of the polymer chain. Telechelic oligomers can be prepared by a selective cleavage with synchronous functionalization. Recent advances in ring opening metathesis polymerization, acyclic diene metathesis and metathesis degradation in the presence of an appropriate chain transfer agent have been cited in the literature for the preparation of end functionalized polymers.[15-17]

In this chapter we tried to get a route for functional polymers using a mixture of cyclooctadiene and/ or 1,5-dimethyl-1,5-cyclooctadiene and the chain transfer agent (2-methyl but-2-ene-1,4-diacetate and / or but-2-ene-1,4-diacetate) using a Ruthenium carbene complex.

6.2 EXPERIMENT

6.2.1 Materials

1,5-dimethyl-1,5-cyclooctadiene; 1,5-cyclooctadiene; cis-2-butene-1,4-diol and cis-2-butene-1,4-diacetate were purchased from Aldrich Chemicals. Cis-2-butene-1,4-diol was distilled over $CaSO_4$ under vacuum just before use. Solid Ruthenium carbene complex was procured from Strem Chemicals. Mercury (II) chloride, toluene, dichloromethane, chloroform were purchased from S. D. Fine Chemicals Ltd. Ferric acetoacetae was purchased from Spectrachem Ltd. Toluene was distilled and made free from sulphur impurity and distilled over sodium wire. Other solvents were of reagent grade and were used without further purification.

6.2.2 Analysis

6.2.2.1 FT-IR Analysis

Synthesized products were studied by FT-IR (Fourier Transform Infrared Perkin Elmer16 PC spectrometer).

6.2.2.2 NMR Analysis

^{1}H NMR spectra were recorded using Bruker AC 200 spectrometers MHz where $CDCl_3$ (Aldrich 99.8 % D) was used as solvent.

6.2.3 Reaction Procedure

6.2.3.1 Synthesis of hydroxyl functionalized polymer: A possible route

6.2.3.1.1 Synthesis of chain transfer agent

The 1,5-dimethyl-1,5-cyclooctadiene was treated with cis-2- methyl -2- butene-1,4-diacetate, a chain transfer agent (CTA) in the presence of Grubb's catalyst. The synthesis of CTA (cis-2- methyl -2- butene-1,4-diacetate) was followed by polymerization with 1,5-dimethyl-1,5-cyclooctadiene to get functionalized polymer (Scheme 6.1).

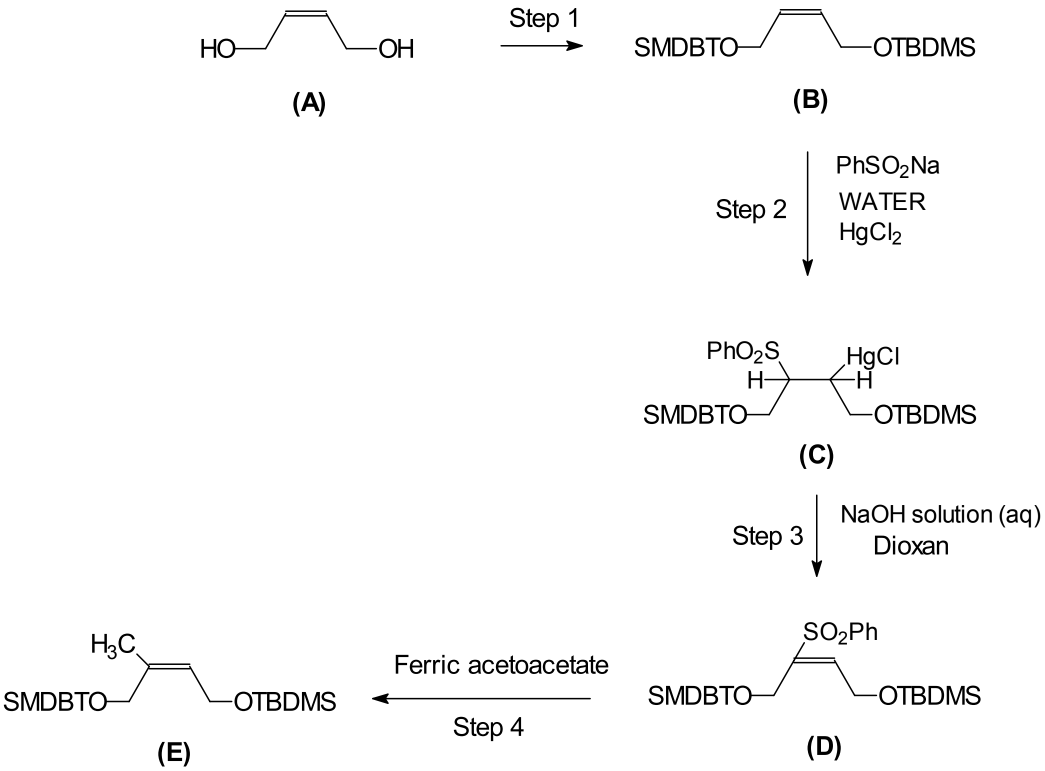
The synthesis of cis-2- methyl -2- butene-1,4-diacetate (CTA) is of four step synthesis (Step 1 to Step 4) and Step 5 is the polymerization reaction.

Step 1: Protection of cis-2-buten-1,4-diol

Cis-2-buten-1,4-diol (0.5 g, 0.00568 moles, 1 equivalent), imidazole (1.35 g, 1 mole, 3.5 equivalent) and 4-dimethyl amino pyridine (0.004 moles) [DMAP] were taken in a two neck round bottom flask with a magnetic bar under strict dry conditions. Dry dichloromethane was added in the round bottom flask with the help of syringe under argon atmosphere. The reaction solution was stirred for 30 minutes. The reaction flask was kept at 0°C and stirred for 15 minutes. In a separate round bottom flask, *tert*-butyl dimethyl silyl chloride (2.5 g, 0.017 moles, 3.0 equivalent) was taken and dry dichloromethane was added by syringe. This solution was transferred into that round bottom flask which contains cis-2-butene-1,4-diol. After some time, precipitation is observed in the reaction solution. It was stirred continuously for 7 h. Distilled water is added and organic layer was separated. The compound is purified by column chromatography with suitable solvent system. The structure of the final product was confirmed by ^{1}H NMR and FT-IR spectroscopy.

^{1}H NMR (δ): 5.56-5.52 (m, C*H*), 4.26-4.17 (m, CH_2), 0.88 (s, $(CH_3)_3$ C), 0.05 {s, $(CH_3)_2$ Si}.

FT-IR (cm^{-1}): C=C stretching (1709 - 1558), Si – CH_3 (s, 1255 and w, 1363)


HO
OH
(A)
Step 1
SMDBTO
OTBDMS
(B)
Step 2
$PhSO_2Na$
WATER
$HgCl_2$
PhO_2S
HgCl
H
H
SMDBTO
OTBDMS
(C)
Step 3
NaOH solution (aq)
Dioxan
SO_2Ph
SMDBTO
OTBDMS
(D)
Ferric acetoacetate
Step 4
H_3C
SMDBTO
OTBDMS
(E)

Scheme 6.1

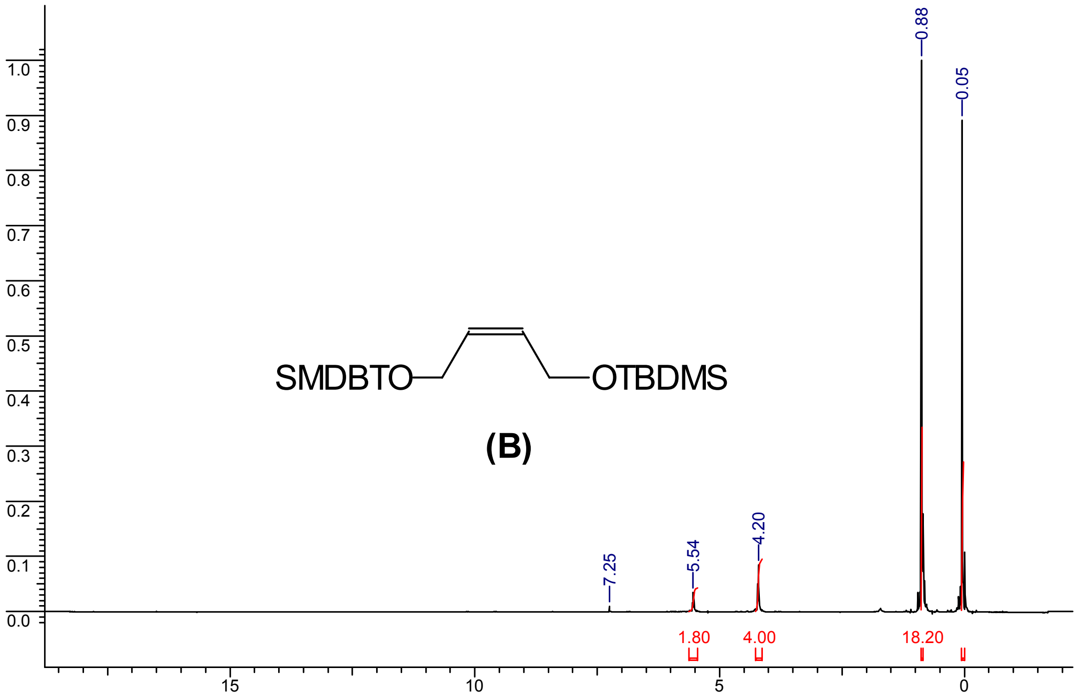


Figure 6.1: ^{1}H NMR spectrum of compound **(B).**

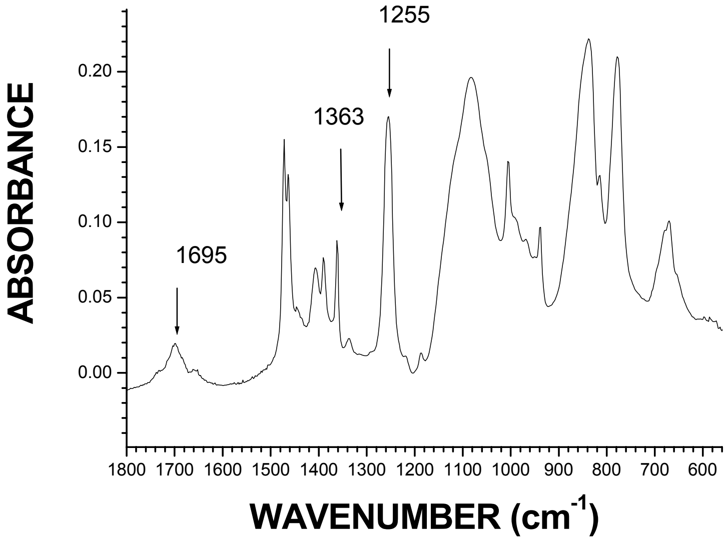


Figure 6.2: FT-IR spectrum of compound **(B).**

Step 2: Reaction of compound (B) with mercury (II) chloride and sodium salt of benzene sulphonic acid:[18]

The compound **(B)** (0.467 g, 0.00147 moles, 1.1 equivalent), mercury (II) chloride (0.364 g, 0.00134 moles, 1 equivalent) and distilled water (16 mL) were taken in a round bottom flask and stirred for 30 minutes. Sodium salt of benzene sulphonic acid (0.275 g, 0.00167 moles, 1.25 equivalent) is added in the reaction mixture and stirred vigorously at room temperature for 50 h. After completion of the reaction, organic phase was separated by dichloromethane. The organic phase contains some white colored fluffy material which is the desired product **(C),** an organometallic compound. It was filtered and the filtrate was evaporated under reduced pressure till constant weight but some impurity still was settled down in the flask which. The dissolved part was separated by syringe and evaporated till constant weight. The yield of compound **(C)** is 35%.

^{1}H NMR (δ): 7.95-7.55 (m, 5H, Ar C*H*), 5.90-5.10 (m, 2H, C*H*), 4.3-3.7 (m, 4H, CH_2O), 0.85 (s, $(CH_3)_3$ C), 0.01 {s, $(CH_3)_2$ Si}.

FT-IR (cm^{-1}): S=O stretching (s, b, 1370 – 1160 and s, b, 1080-1020), C-S stretching (w, 690- 610), Si – CH_3 (s, 1255 and w, 1374)

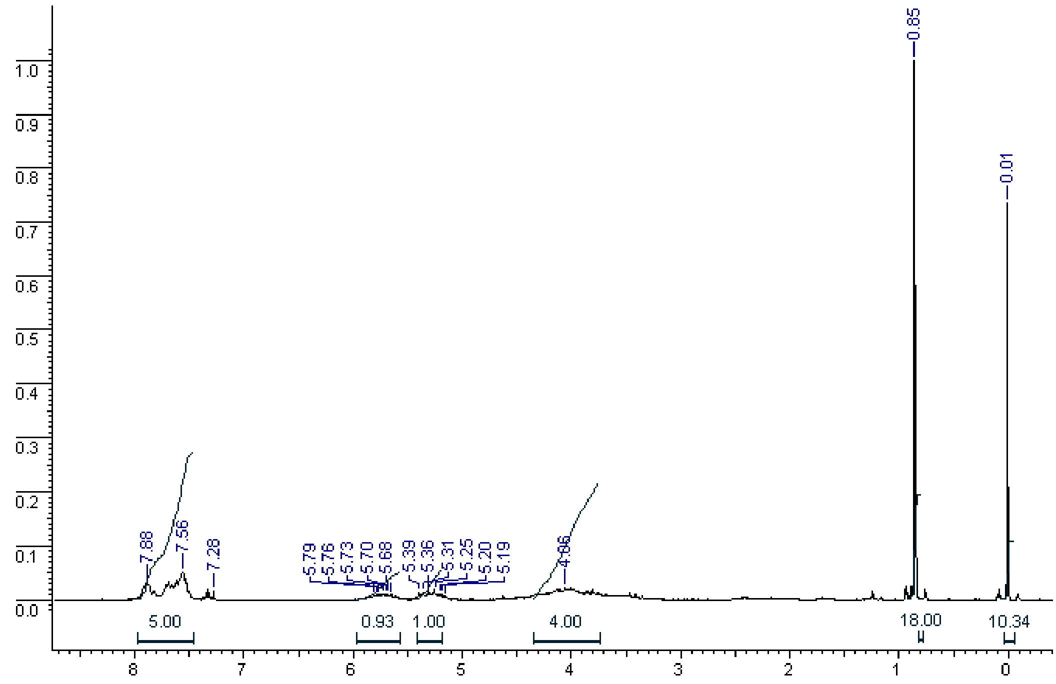


Figure 6.3: ^{1}H NMR spectrum of compound **(C).**

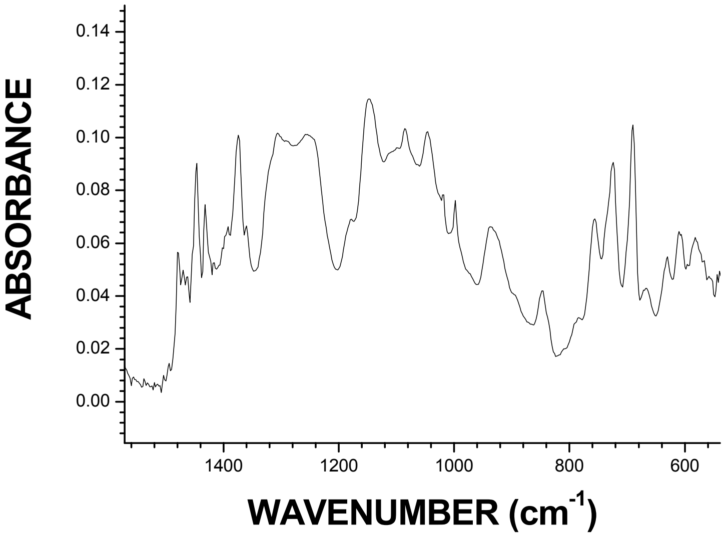


Figure 6.4: FT-IR spectrum of compound **(C).**

<u>Step 3:</u> Demurcurization on double bond

The compound **(C)** (0.5 g) was taken with dioxan-1,4 (7 mL) and stirred. Aqueous solution of sodium hydroxide (50% solution, 12 mL) is cooled and added drop-wise in the round bottom flask with vigorous stirring. The reaction solution was stirred for 21 h at room temperature. As we add the sodium hydroxide solution in the reaction solution, it turns to yellowish followed by greenish coloration. After the completion of the reaction, dioxan-1, 4 layer was separated. The reaction solution was washed with ethyl acetate and water six times and was dried over anhydrous sodium sulphate. The yield of the product **(D)** is 27 %.

^{1}H NMR (δ): 7.70-7.10 (m, 5H, Ar C*H*), 5.80-5.76 (m, 1H, C*H*), 4.02 (s, 4H, CH_2O), 0.83 (s, $(CH_3)_3$ C), 0.02 {s, $(CH_3)_2$ Si}.

FT-IR (cm^{-1}): C=C stretching (1709 - 1558), S=O stretching (s, b, 1370 – 1160 and s, b, 1080-1020), C-S stretching (w, 608), Si – CH_3 (s, 1304 and w, 1370).

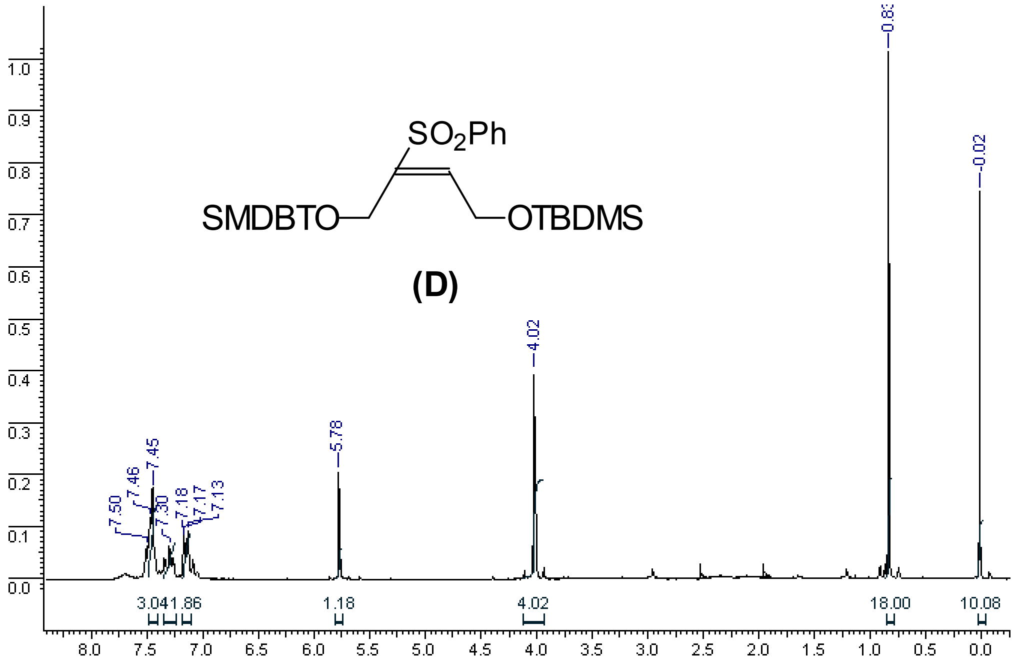


Figure 6.5: ^{1}H NMR spectrum of compound **(D).**

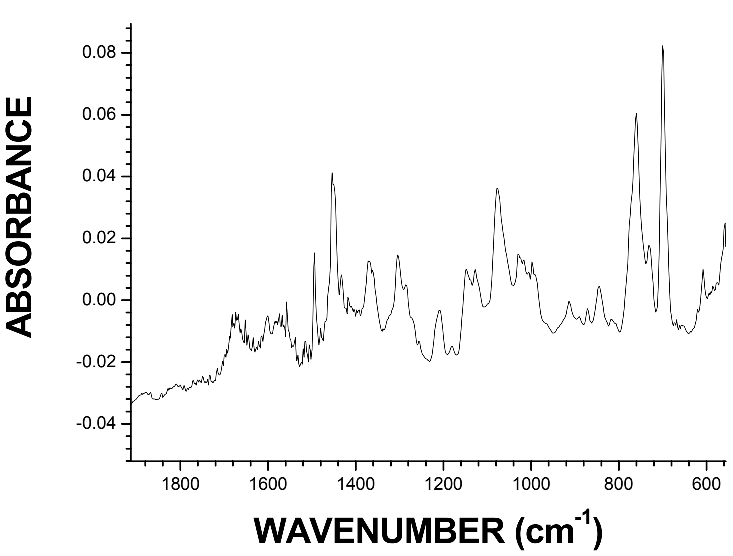


Figure 6.6: FT-IR spectrum of compound **(D).**

Step 4: Methylation on double bond[19-21]

The compound **(D)** (0.050 g, 0.00016 moles) and catalyst (1 %) were dissolved in tetrahydrofuran under argon atmosphere. The Grignard reagent (0.034 g, 0.00028 moles, 1.8 equivalent) [1molar solution in tetrahydrofuran] is then slowly added by syringe. The reaction mixture was stirred for 25 h at 60°C under argon atmosphere. At the end of the reaction, the mixture is hydrolyzed with an aqueous solution of ammonium chloride and extracted with dichloromethane. The organic layer was separated and dried over anhydrous sodium sulphate and filtered. The product was dried till constant weight. The yield of the product **(E)** was poor (11 %), as the reactant was not pure.

^{1}H NMR (δ): 7.70-7.09 (m, 5H, Ar C*H*), 5.80-5.75 (m, 1H, C*H*), 4.16 (s, 4H, CH_2O), 1.76 (s, CH_3), 0.83 (s, $(CH_3)_3$ C), 0.02 {s, $(CH_3)_2$ Si}.

FT-IR (cm^{-1}): C=C stretching (1709 - 1558), Si – CH_3 (s, 1304 and w, 1370).

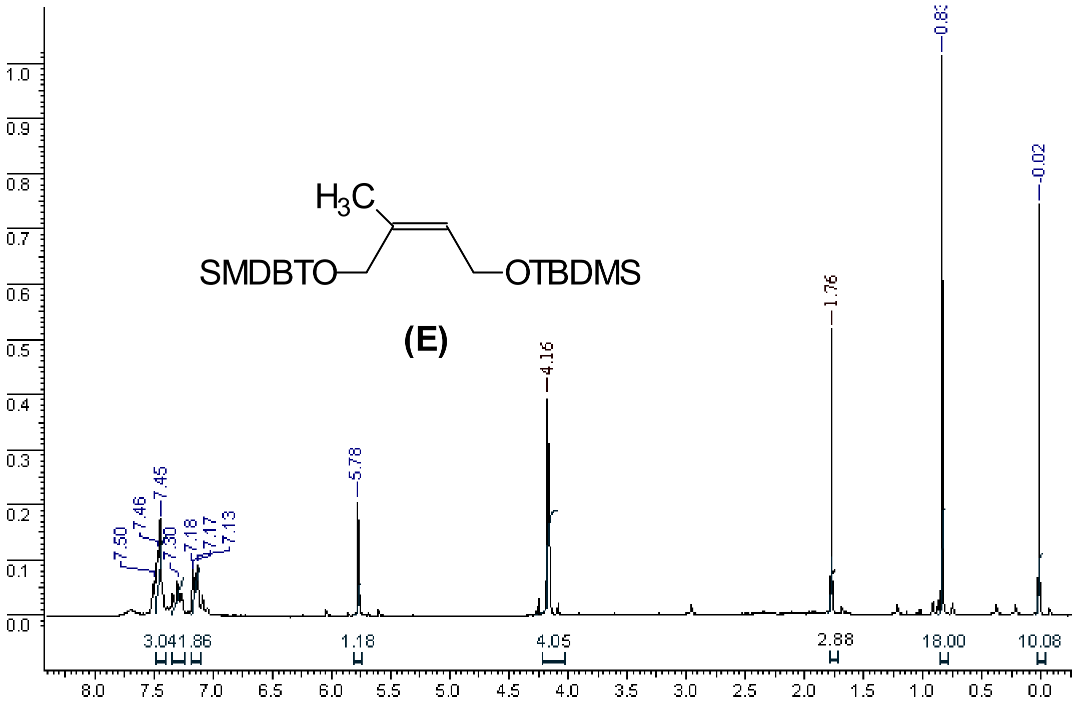


Figure 6.7: ^{1}H NMR spectrum of compound **(E).**

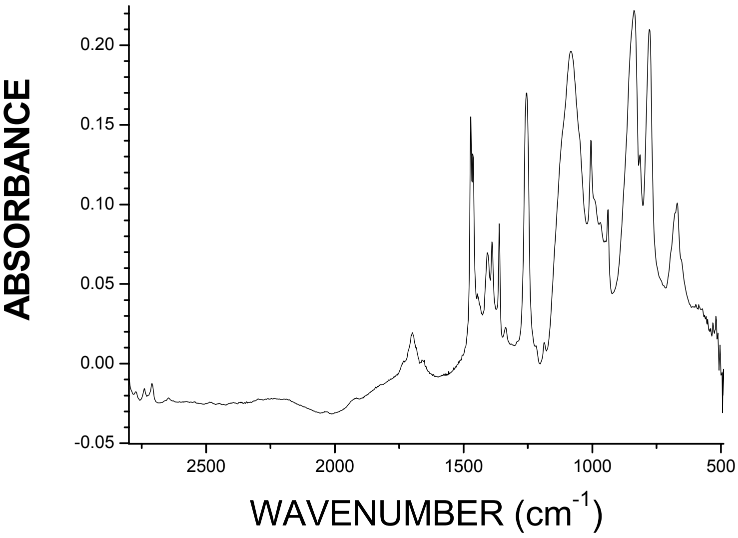


Figure 6.8: FT-IR spectrum of compound **(E).**

Step 5: Polymerization of 1,5-dimethyl-1,5-cyclooctadiene with compound (E)

Grubb's catalyst (0.001 g, 0.0000013 moles, 1 equiv) was taken in a two neck round bottom flask in a dry box. 1,5-dimethyl-1,5-cyclooctadiene **(F)** (1 g, 0.0063 moles, 4880 equiv) with cis-2-methyl-2-butene-1,4-di-OTBDMS **(E)** (0.02411 g, 0.000151 moles, 114 equiv) [solution in dichloromethane) was transferred into the round bottom flask by a syringe under argon atmosphere. The reaction solution was stirred magnetically with constant stirring at 50°C for 6 hrs. Cooled at room temperature and poured the reaction solution into 500 mL methanol. A white colored fluffy material floats in the solution. The product **(G)** was dried under reduced pressure till constant weight. This product was treated with tetra butyl ammonium fluoride (1 equivalent in tetrahydrofuran) and stirred for 5 hrs under strictly dry conditions. The product **(H)** was extracted by dichloromethane and dried under reduced pressure till constant weight (Figure 6.9). The yield of hydroxy terminated polymer **(H)** is 9 %. The reaction scheme is shown in Scheme 6.2.

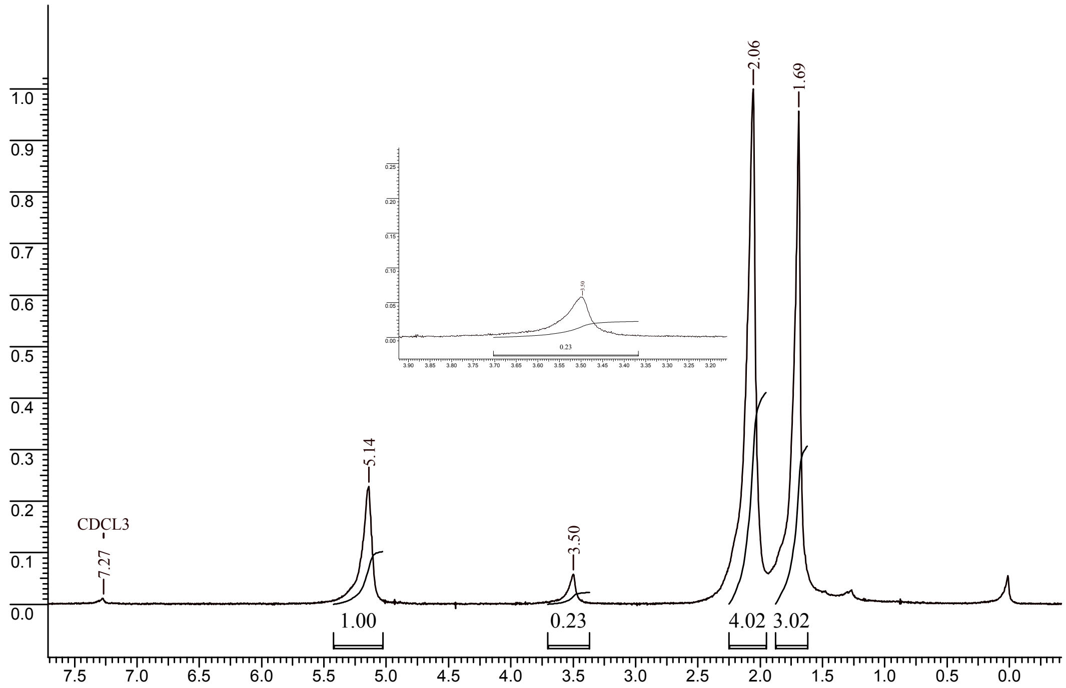
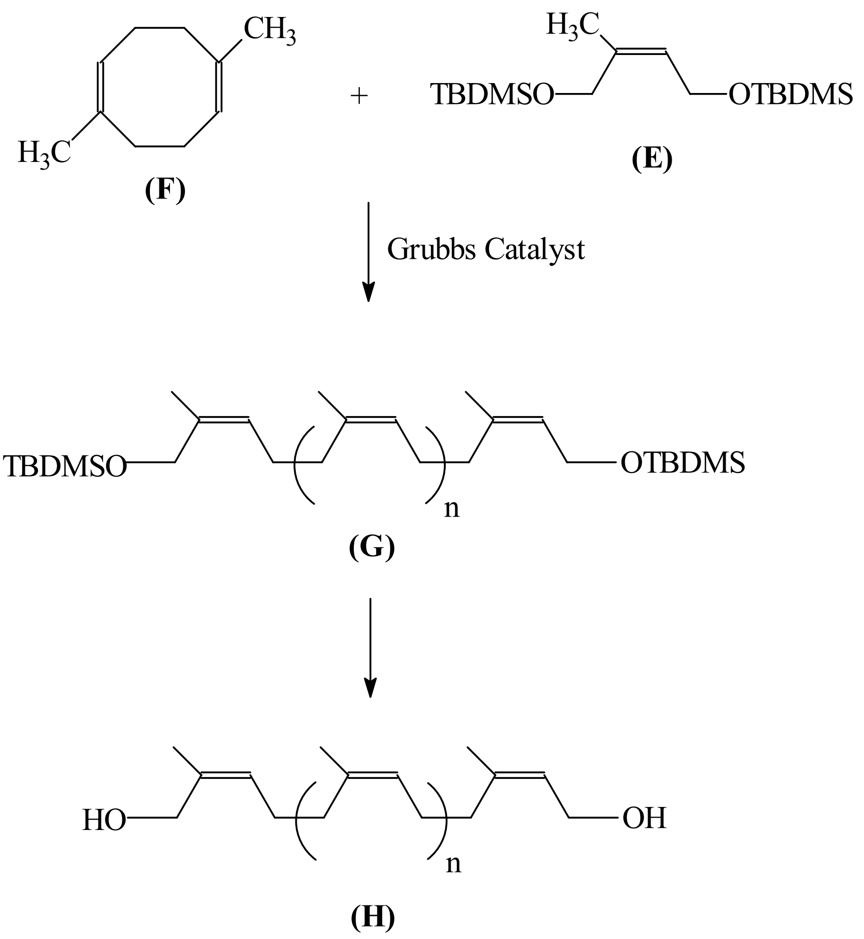


Figure 6.9: ^{1}H NMR spectrum of hydroxy terminated polymer **(H)**.



Scheme 6.2

6.2.3.2 Polymerization of cyclooctadiene in absence of solvent

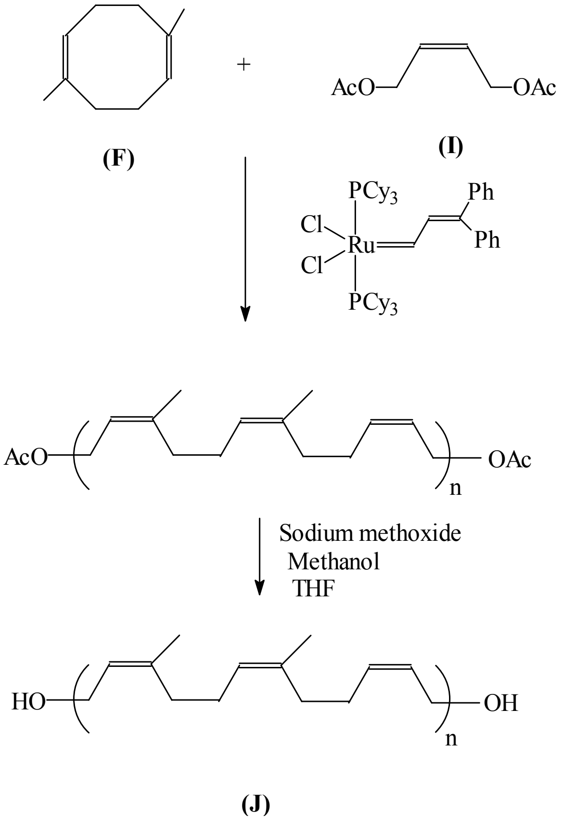
Hillmayer *et al.*[10] have synthesized the hydroxy telechelic polybutadiene by polymerization of cyclooctadiene and cis-2-butene-1,4-dioate using Grubbs catalyst. In this chapter, we studied the polymerization behaviour of cyclooctadiene in absence of any solvent. The catalyst amount was varied by keeping constant ratio of cyclooctadiene and chain transfer agent at 50°C. The effect of polymerization time was also studied during the reaction. The polymerization reaction method is given elsewhere.[10]

6.2.3.3 Polymerization of cyclooctadiene with different solvents

Polymerization reactions of cyclooctadiene and cis-2-butene-1,4-dioate were carried out using Grubbs catalyst in dichloromethane, chloroform and toluene at 50°C for different time intervals. The catalyst concentration effect was studied on the polymerization by keeping the ratio of cyclooctadiene and CTA constant.

6.2.3.4 General polymerization method of 1,5-dimethyl-1,5-cyclooctadiene with cis-2-butene-1,4-diacetate

Grubb's catalyst (0.001 g, 0.0000013 moles, 1 equiv) was taken in a two neck round bottom flask in a dry box. 1,5-dimethyl-1,5-cyclooctadiene (1 g, 0.0063 moles, 4880 equiv) with cis-2-butene-1,4-diacetate (0.02411 g, 0.000151 moles, 114 equiv) [solution in dichloromethane) was transferred into the round bottom flask by a syringe under argon atmosphere. The reaction mixture was stirred magnetically with constant stirring at 50°C for 6 h, cooled at room temperature and poured in 500 mL methanol (acidic, 1 M hydrochloric acid). A brown colored fluffy material **(J)** floats in the solution, hydroxy terminated polybutadiene (Figure 6.10). The yield is 11 %. The reaction Scheme 6.3 is proposed for the same.



Scheme 6.3

6.3 RESULTS AND DISCUSSION

The ^{1}H NMR spectrum of **(H)** shows the peaks at δ = 1.69 ppm (-CH_3, 3 H); δ = 2.06 ppm (-CH_2-C=C, 4 H); δ = 5.14 ppm (vinylic proton); δ = 3.50 ppm (-CH_2– OH) as shown in Figure 6.9. The yield is 9 %.

We studied the polymerization reactions of cyclooctadiene without any solvent medium as the Grubb's catalyst is soluble in cyclooctadiene as well as in cis-2-butene-1,4-dioate. The polymerization reactions were carried out for 5h, 18 h and 40 h at 50°C. Even after 5 h of the reaction, the hydroxy functionalized polybutadiene was obtained with additional small peaks at δ = 1.63 ppm, 1.44 ppm and a broad hump from 1.32 – 1.21 ppm (Figure 6.10) [Yield is 24%]. The peak at 3.8 ppm shows the hydroxyl proton in the hydroxy methyl group. We found that there is no change in the yield of the polymer with time as well as the catalyst ratio which was varied from 0.1 mg to 0.3 mg by keeping constant the cyclooctadiene and cis-2-buten-1,4-diol.

In another experiment, the polymerization of cyclooctadiene with cis-2-buten-1,4-dioate was carried out in different solvent systems, taking dichloromethane, chloroform and toluene with constant amount of catalyst (0.1 mg). We observed that yield of the functionalized polybutadiene is higher ~ 43 % when dichloromethane was used as solvent.

In another experiment, when 1,5-dimethyl-1,5-cyclooctadiene was treated with cis-2-buten-1,4-diacetate using Grubb's catalyst, gives brown colored fluffy material **(J)** in the solution. The fluffy material was separated by spatula and dried under reduced pressure. ^{1}H NMR spectrum of compound (J) shows the peaks at δ = 1.68 ppm (-CH_3, 3 H); δ = 2.04 ppm (-CH_2-C=C, 4 H); δ = 5.13 ppm (vinylic proton) and δ = m, 3.31 to 4.0 ppm (-CH_2– OH) as shown in Figure 6.11.

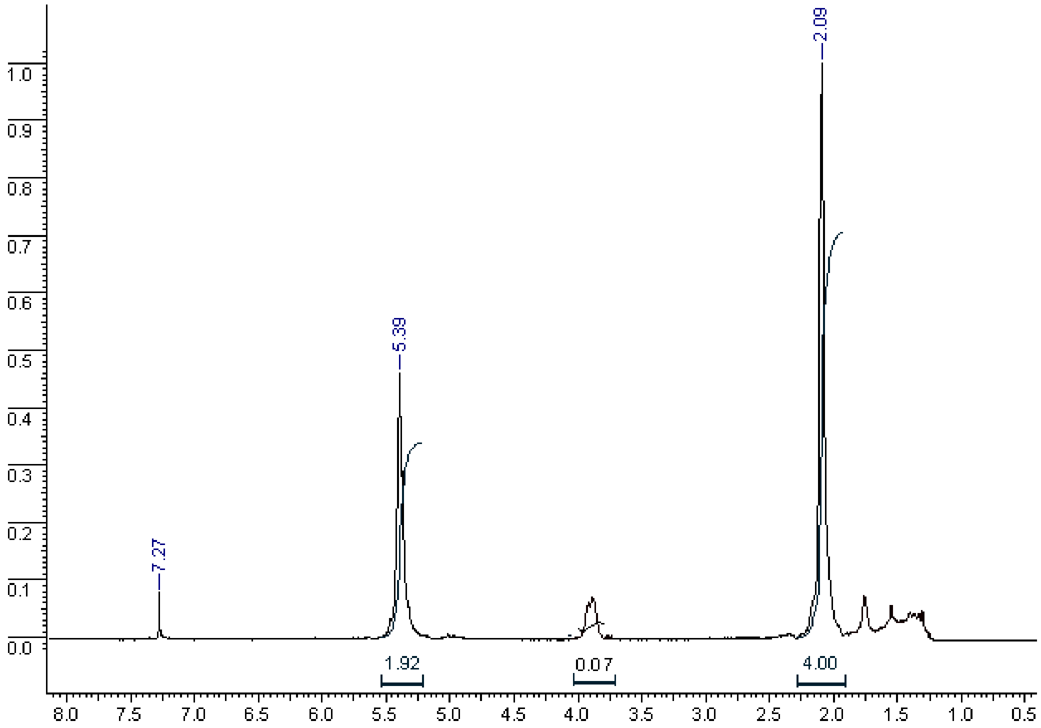


Figure 6.10: ^{1}H NMR spectrum of hydroxyl functionalized polybutadiene**.**

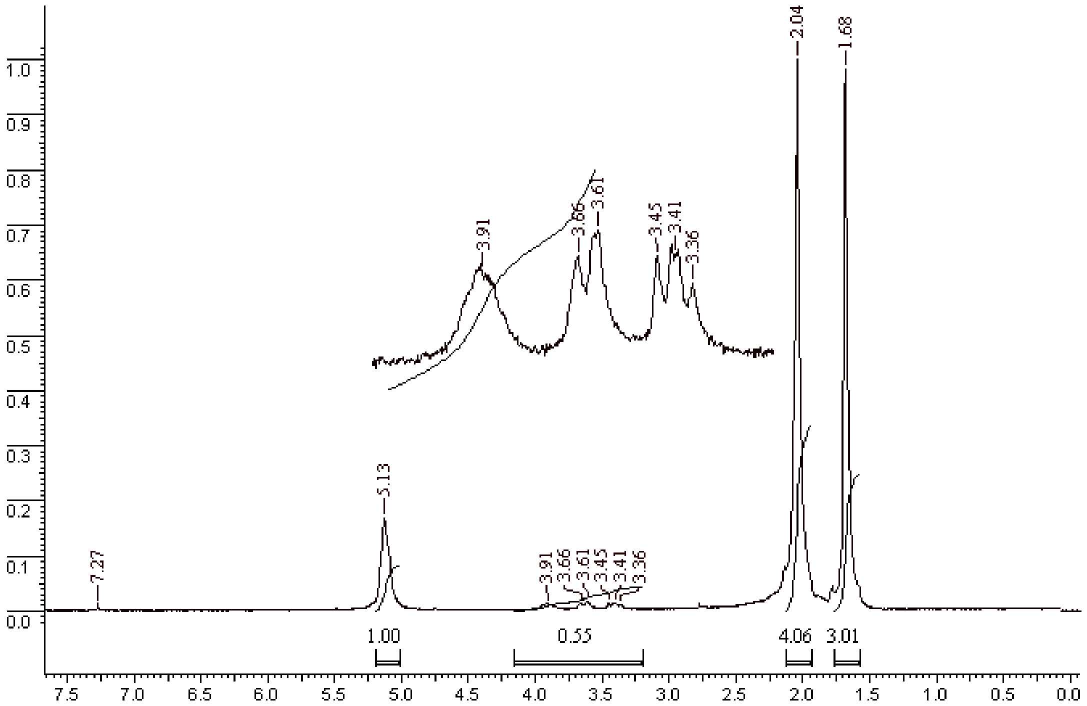


Figure 6.11: ^{1}H NMR spectrum of hydroxy terminated polymer **(J)**

6.4 CONCLUSIONS

The functionalized polymers can be obtained using Grubb's catalyst. Functionalized hydroxy terminated natural rubber (HTNR) was synthesized by polymerization method using Grubb's catalyst. The Grubb's catalyst is highly reactive so it is needed in very small amount in the polymerization reactions. If we increase the amount of catalyst from 0.1 mg to 0.3 mg, no change in the yield of the functionalized polymer occur. The reaction temperature, 50°C was optimum in case of polymerization of cyclooctadiene and cis-2-buten-1,4-diacetate. Dichloromethane was found suitable solvent for these reactions.

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CHAPTER VII

OZONOLYSIS OF NATURAL RUBBER

7.1 INTRODUCTION

Ozone is a highly poisonous, strong odour pale blue coloured gas.[1] Liquid ozone is a deep blue and strongly magnetic. The name ozone came from the Greek word 'ozein' means, "to smell". It is an allotropic form of oxygen having three atoms in each molecule e.g. O_3, naturally occurring in troposphere. It is generated from nitrogen oxides and organic oxides and is emitted as a product of combustion engines or from passing an electric current through air. Ozone is much more active chemically than ordinary oxygen and is a better oxidizing agent. It is used in purifying water, sterilizing air and bleaching certain foods. Ozone is formed in the atmosphere from nitrogen oxides and organic gases emitted by automobiles and industrial sources. It is however, health hazards and may cause serious crop damage in some areas. Ozone is a strong oxidizing agent and is used to treat drinking water for the control of odor and taste, wastewater for control of odor, and many chemical-processing applications. Ozone is also produced in many applications where the corona treaters are used in printing and copying operations.

Studies of the action of ozone on diene rubbers[2-5] were of the fundamental importance in the understanding of the structure of natural rubber. Ozonization is still a key tool for the elucidation of molecular structure and monomer sequences in the polymer and is widely used to characterize the structures of various rubbers to make telechelic oligomers.[6, 7] The problems of ozone attack and antiozonant protection continue to be the subject of great importance.[8] The ozone attack on the rubber causes chain-scission and the formation of various decomposition products such as ozonides, polymeric peroxides, hydroperoxides, lactones, esters and aldehydes etc. Sweeney *et al.*[9] studied ozonolysis in natural rubber solution. Egorova *et al.*[10, 11] studied the micro structural composition of 1,4-units of industrial isoprene rubbers by ozonolysis in carbon tetrachloride, chloroform and dichloromethane at –70 °C and the decomposed ozonides were characterized by chromatographic techniques. Solvent effect on cis-1, 4-polyisoprene rubber ozonolysis was studied at 213 °K in hexane, chloroform and dichloromethane. The degree of polymer degradation during ozonolysis increased with rising dielectric constant of solvents. Plaumann *et al.*[12] suggested two methods, ultrasound and ozonolysis which were used to degrade cis-polyisoprene. Vogel *et al.*[13] described the ozonolysis of cis-1,4-polyisoprene, cis-1,4-polybutadiene and trans-1,4-

polychloroprene rubber surfaces. Ozonolysis of the isoprene rubber was characterized by the formation of methyl ketone groups which ruptured the chain. Additional absorption bands for ozonide and peroxide structures were observed and the intensity of olefinic structure bands decreased rapidly. The ozonized butadiene rubber products were almost exclusively ozonides and peroxides and the bands for carbonyl groups were of small intensity, indicating that chain rupture occurred only to a small extent. The prevailing ozonides and peroxides stopped ozone diffusion and its reaction with double bonds. In all cases, the ozonolysis process was more complex than for ozonolysis of low-molecular weight compounds in solution. Anachkov *et al.*[14] studied ozonolysis of 1, 4-cis-polyisoprene and 1, 4-trans-polyisoprene in solution using carbon tetrachloride. It was established that the basic ozonolysis products of both elastomers are ozonides, ketones and aldehydes and characterized by various techniques. Nor *et al.*[15] studied the kinetics of chain scission and major changes in functional groups of natural rubber during ozonolysis. This chapter is focused on the study of ozone reaction of natural rubber in solution as well as films.

7.2 EXPERIMENTAL

7.2.1 Materials

Natural rubber ($M_v = 2.82 \times 10^5$) was supplied through the courtesy of Dr. S. Thomas, M. G. University, Kottayam, Kerala. Toluene, acetone, tetrahydrofuran and sodium borohydride were supplied by S. D. Fine Chemicals Ltd., India. Ozone gas was generated by Fischer Technology Ozone Generator Model 503.

7.2.2 Reaction Procedure

A 2.5 wt % solution (105 ml) of purified natural rubber (NR) was prepared in toluene and cooled at 0°C in a three necked round bottom flask equipped with a bubbling tube and thermometer with constant and efficient stirring (600 rpm). An oxygen-ozone stream (1.2×10^{-4} mol / Litre, 0.33 Bar and 2.6 Amp) from the ozone generator (ozonizer) was passed into the natural rubber solution by bubbling. Aliquots were withdrawn at different time intervals and the natural rubber was dried under reduced pressure. The ozonized rubber was re-dissolved in tetrahydrofuran and kept at 0°C. Sodium borohydride solution (1.2 %) in tetrahydrofuran was added dropwise for 2 hrs until the reducing agent was present in excess. The reaction solution was taken to room temperature and then heated to reflux for 3 hrs. Distilled water was added cautiously to decompose the excess of sodium borohydride. The organic layer was separated and precipitated in excess of acetone.

In another experiment, natural films were casted as described elsewhere[16] . The natural rubber films of two different thickness ~ (200 microns and 400 microns) sized (2 x 2 inches) and were placed in the round bottom flask with ozone bubbling tube at 0°C. Ozone gas was passed in the flask with internal pressure (0.33 Bar and 2.6 Amp) for 1 h to 7 h.

7.3 ANALYSIS

7.3.1 FT-IR Analysis

IR spectra were recorded using a FT-IR (Fourier Transform Infrared Perkin Elmer16 PC spectrometer).

7.3.2 NMR Analysis

The rubber samples were characterized by ^{1}H and spectroscopy (Bruker AC 200 MHz) where $CDCl_3$ (Aldrich 99.8 % D) was used as solvent.

7.3.3 Viscosity measurements

The changes in the M_v during ozonolysis were determined in dried toluene (0.016 wt %) at 25 ± 0.1°C using an Ubbelohde viscometer and the Mark-Houwink-Sakurada equation:

$[\eta] = K.\ \overline{M_v}^a$

where $K = 5x10^{-4}$ and $a = 0.667$

7.4 RESULTS AND DISCUSSION

7.4.1 Viscosity changes by ozone degradation

Viscosity-average molecular weights were determined at different intervals of ozone bubbling in natural rubber solution (Table 7.1). A continuous decrease in M_v with time was observed faster in early hours of ozonolysis.

Table 7.1: Changes in viscosity average molecular weight of natural rubber after ozonolysis

Serial No.	Time (h)	$\overline{M_v}$ (x 10^3)
1	1	261
2	3	144
3	5	128
4	7	107

7.4.2 Functional groups

The FT-IR spectrum of ozonized natural rubber shows a band at 1084 cm^{-1}. There is only a little difference if we compare the spectra of neat natural rubber with ozonized one (Figure 7.1). The carbonyl noise appears at 1722 cm^{-1} after 2 hrs of reaction but no change in the intensity for longer ozonolysis was observed. The peaks in ^1H NMR spectra arise at 1.27 and 2.70-2.71 ppm indicate the presence of methyl group on the oxirane ring in cis position and the proton on the oxirane ring (Figure 7.2). The peak at 9.78 ppm shows the protons of aldehyde group. The intensity of the peak of 2.71 ppm was higher than the 9.78 ppm. As the ozone gas is passed into the rubber solution, it attacks on double bond and forms the structures as described (Scheme 7.1).[17] There is another possibility to generate ketonic functional group[19-21] at the chain end as shown in Scheme 7.2.[18] ^1H NMR spectrum shows the signal at 2.19 ppm of methyl ketone chain end and the signal of 2.71 ppm (the proton on the oxirane ring) vanishes (Figure 7.3). The behaviour is probably due to the formation of some acidic impurity during ozonolysis which may cause the formation of methyl ketone proton.

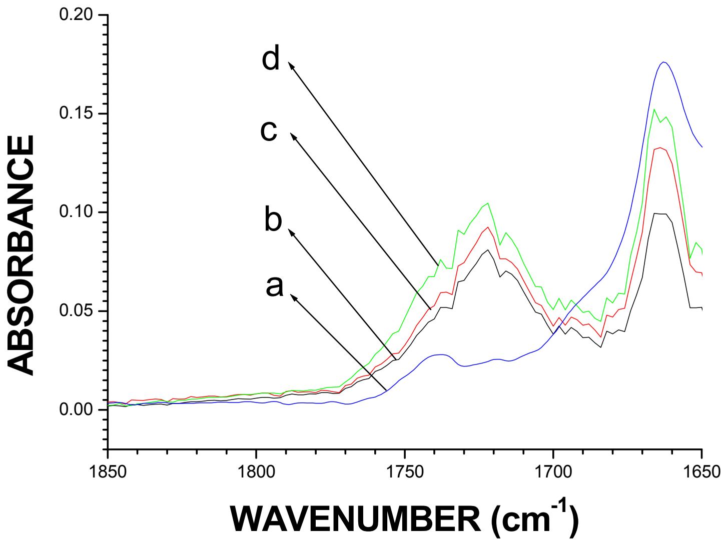


Figure 7.1: FT-IR spectral changes in the carbonyl regions of ozonized natural rubber; (a) control, (b) 2 h, (c) 5 h and (d) 7 h.

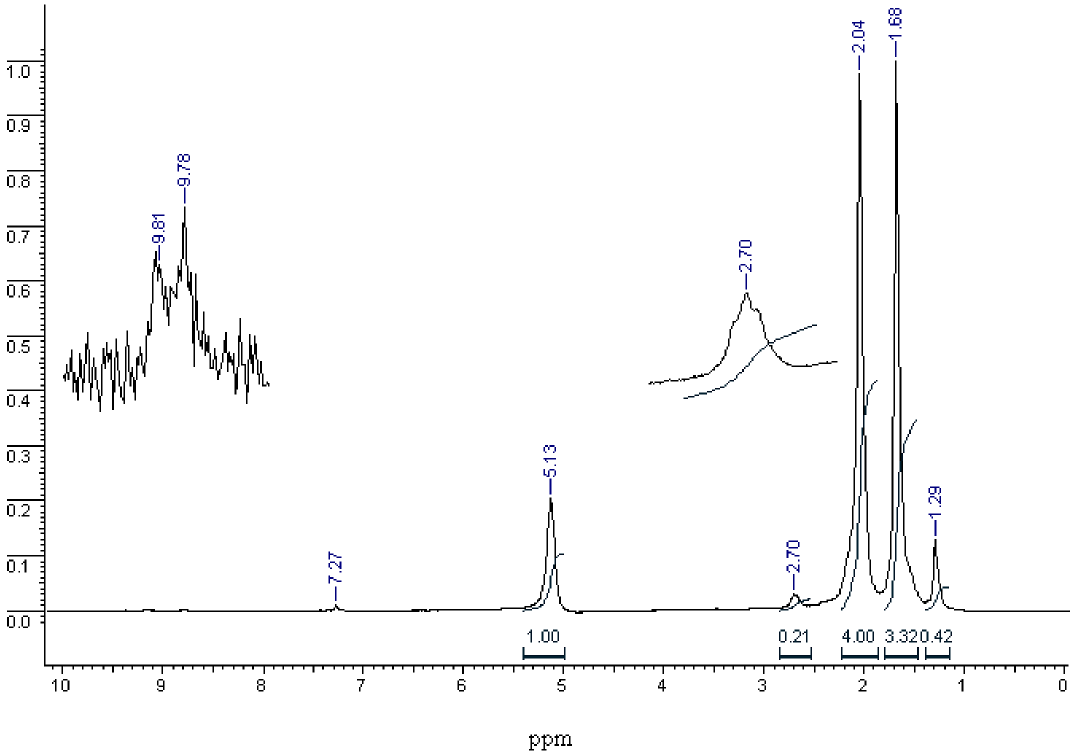
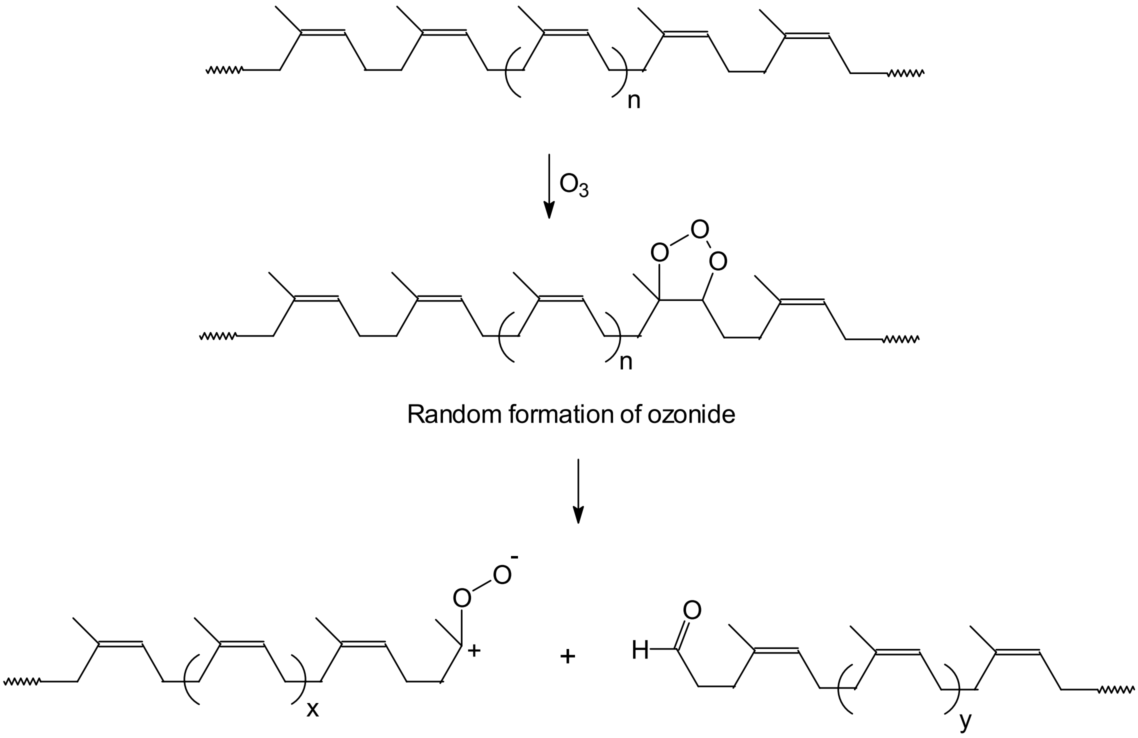
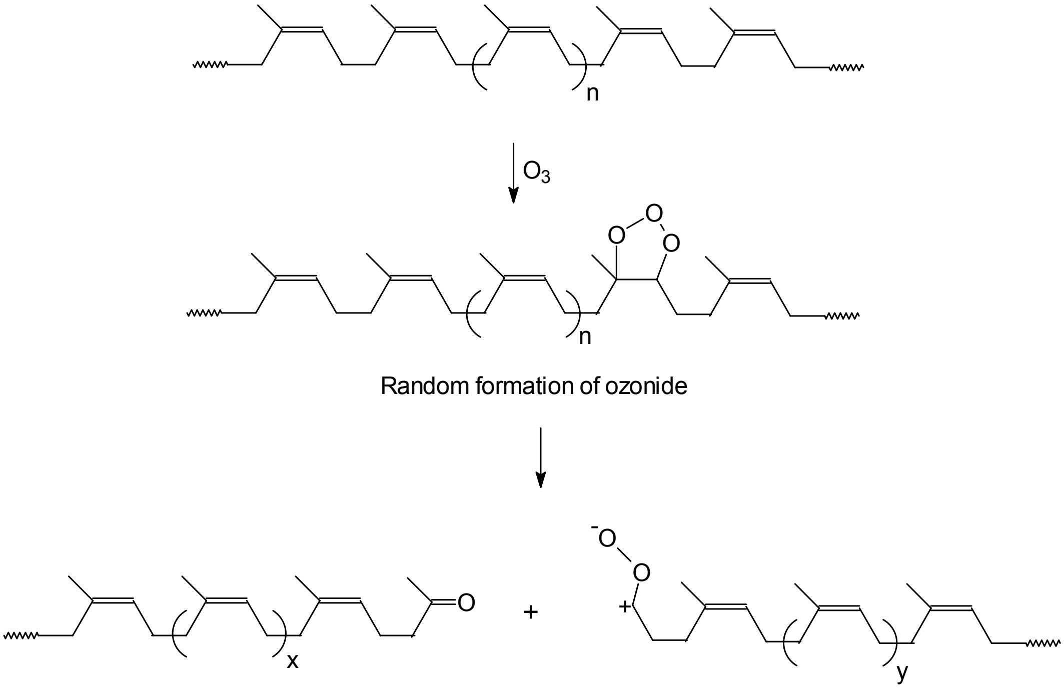


Figure 7.2: ^{1}H NMR spectrum of ozonized natural rubber.



Scheme 7.1



Scheme 7.2

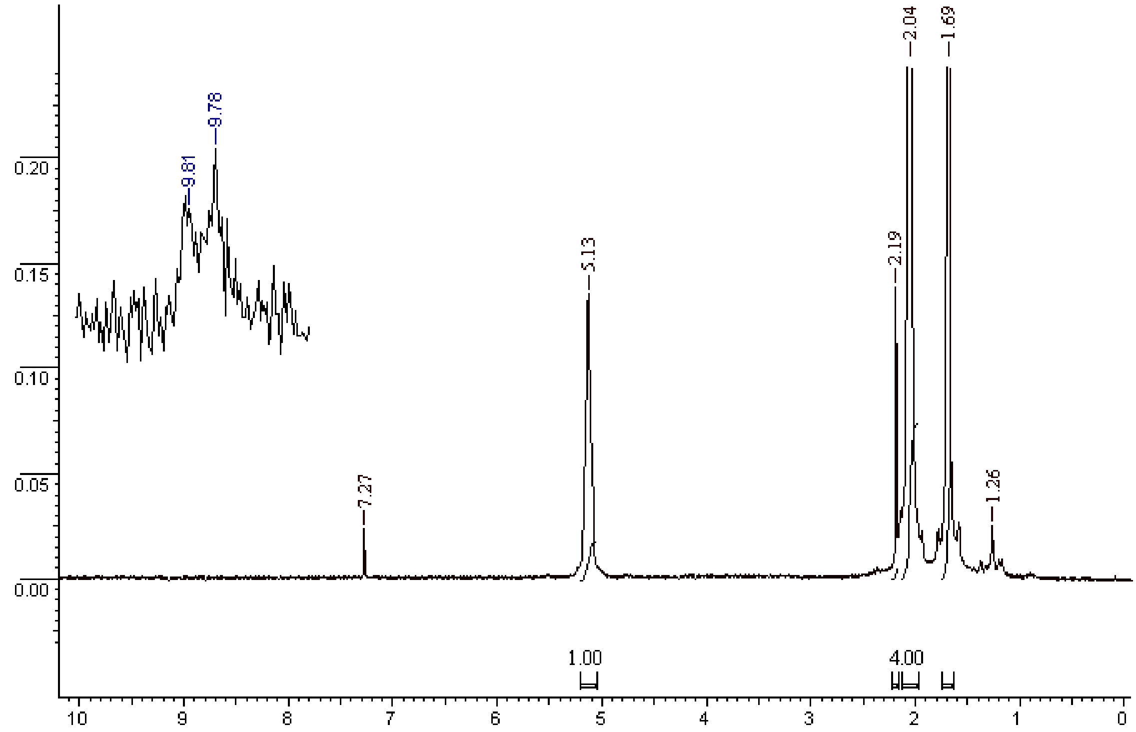


Figure 7.3: ^{1}H NMR spectrum of ozonized natural rubber showing the aldehyde and methyl vinyl ketone protons.

In another experiment, the ozonized natural rubber was treated with sodium borohydride, a valuable reagent for hydrogenation. The formed aldehydes during ozonolysis were reduced by sodium borohydride to get the hydroxyl functionality in the natural rubber. The ^{1}H NMR (Figure 7.4) spectra in $CDCl_3$ lead further support to the above conclusion. ^{1}H NMR $\delta = 1.63$ ppm ($-CH_3$, 3 H); $\delta = 2.05$ ppm ($-CH_2-C=C$, 4 H); $\delta = 5.1$ ppm (vinylic proton) and the signal due to hydroxyl proton in the hydroxymethyl group is observed at ~ 3.6 ppm. A broad hump of hydroxyl region (3600- 3200 cm^{-1}) with a maximum of 3280 cm^{-1} appeared in FT-IR spectra, also supports the presence of hydroxyl group (Figure 7.5).

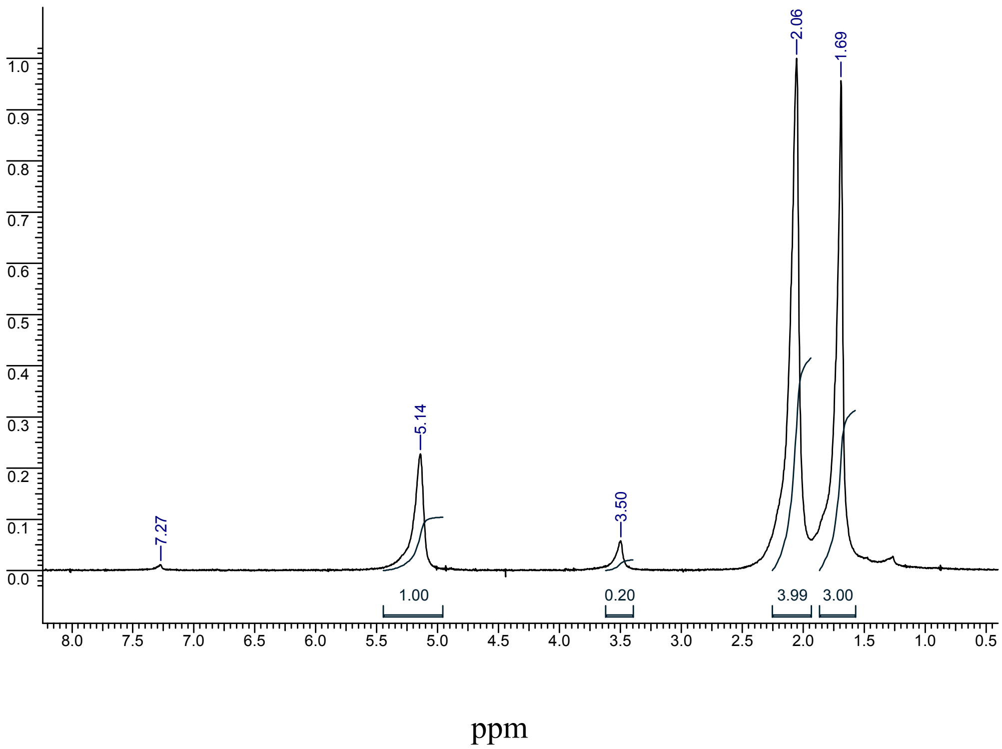


Figure 7.4: ^1H NMR spectrum of hydroxy functionalized natural rubber.

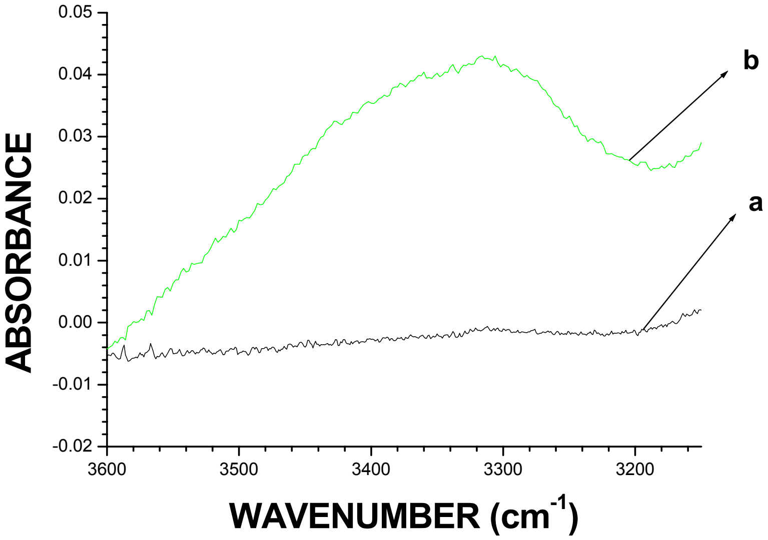


Figure 7.5: FT-IR spectral changes in the hydroxyl regions of natural rubber; (a) control and (b) after treating with sodium borohydride.

In another experiment, we checked the lowering of viscosity average molecular weights of natural rubber films under ozonolysis. The ozone cracking is a physico-chemical phenomina[22-25] and cracking starts from the rubber surface. Chain cleavage is higher in the stressed surfaces but we studied the behaviour of natural rubber film without any stretching in our experiment. We observed that M_v decreases faster in initial hours (Figure 7.6) but after 4 h, the rubber film was not fully soluble in toluene, tetrahydrofuran and carbon tetrachloride. It is proposed that after longer ozonolysis, chain scission takes place and simultaneously crosslinking occurs in the natural rubber. In both the films, the same trend in decrease of molecular weight (M_v) was observed. The thickness of the film was also an important factor during ozonolysis. The weight of the crosslinked rubber film was found 0.4 times more than the thick crosslinked natural rubber. For that, 0.005 g of both crosslinked films were dipped in toluene for 48 h in dark after thorough washing and drying under reduced pressure till constant weight. It was assumed that when ozone penetrated through the thin natural rubber film, it attacks on the surface and reaches towards inner layer faster than the thicker films, therefore, the thin films get crosslinked faster then the thicker one for longer ozonolysis.

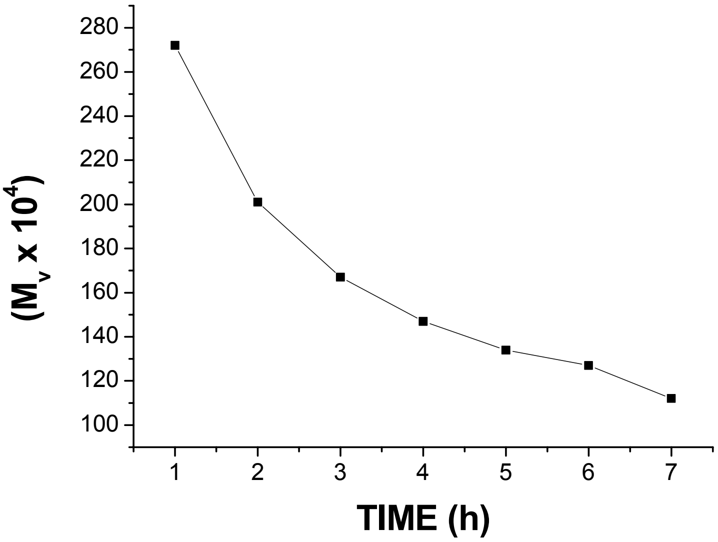


Figure 7.6: Changes in viscosity average molecular weight of unstretched natural rubber films after ozonolysis.

7.5 CONCLUSIONS

Since the formation of ozonide is very random, therefore, it was difficult task to get telechelic oligomers. The basic ozonolysis products of natural rubber were ozonides, epoxides, methyl ketone and aldehydes which were characterized by FT-IR and NMR spectroscopies. The thickness of natural rubber also plays an important role during ozonolysis. The thinner films get crosslinked faster then the thicker one.

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CHAPTER VIII

SYNTHESIS OF NOVEL ANTIOZONANTS AS WELL AS ANTIOXIDANTS

8.1 INTRODUCTION

The degradation of rubber from ozone manifests itself by (i) crack appearing perpendicular to the stress in the rubber and (ii) the appearance of a silvery film on the surface of the article. The attack of ozone is a purely surface phenomenon and the function of the antiozonant depends on the migration to the surface of the rubber article.[1]

Antioxidants are the compounds, which upon addition to the polymers are capable of preventing or retarding the reactions of degradation caused by heat and light energy in the presence of oxygen.[2, 3] Triazines[4] are one of the most important antioxidants, which are used commercially. Monomeric and low molecular weight antioxidants[5] have limitations owing to the migration and leaching. This phenomenon could lead to uneven distribution of antioxidants within the polymeric matrix. Leaching could be even more harmful as the loss of antioxidants from the polymer matrix could lead to extensive thermal and photo-degradation of the substrate. Therefore, in order to prevent the phenomena of migration and leaching, the antioxidants with polymerizing ability are being developed. This particular class of stabilizers would have even distribution within the polymer matrix and also overcome the migration and leaching.[6]
Most thermoplastic polymers and coating compositions are unstable to the extended exposure to ultraviolet light source in atmosphere. The preliminary effect of ultraviolet radiation on polymers is the formation of free radicals on the polymer chain, which react with atmospheric oxygen.[7] This results in the formation of peroxide groups. Furthermore, decomposition of peroxide groups causes formation of carbonyl groups and chain scission. Irradiation in the absence of oxygen causes the increase in crosslinking. In order to prevent or at least retard the damage caused by these factors, stabilizers are added to the plastics.

Conventional diphenyl diamine antiozonants[8-10] are widely used in the protection of rubber. Recent developments in rubber technology have resulted in rubber products with extended service life and therefore, require commensurate protection from ozonolysis. Therefore, there exists a need of new and efficient antiozonants offering extended protection from ozone. Amine containing antiozonants are commonly used in diene rubbers. Common examples of such antioxidants are N,N-di-substituted p-phenylene diamines. There is a continuing need of superior antiozonants to further prolong the useful life of these rubber products.

N, N-di substituted para-phenylene diamines offer protection to polymers such as natural rubber and elastomers against the deteriorous effects of oxygen and ozone. Hindered phenols and benzotriazoles have been used as stabilizers since long.[11-28]. In addition, aromatic amines[29] have also been used as antioxidants based on α-methylstyryl-substituted diphenylamines. In addition, the synergistic blends of hindered phenols and amine antioxidants were studied as stabilizers for polypropylene and polyethylene.[30, 31] The one step acid catalyzed reaction with thiols, formaldehyde and aromatic amines is known in the prior articles.[32-33] Recently, we have reported some novel combination of antioxidants and antiozonants.[34-37]

This chapter contains the synthesis of antiozonants and their use in diene containing polymer. The newly synthesized antiozonants relate to a composition comprising an aromatic amine and a benzotriazole and / or hindered phenol that is prepared in two-step process.

8.2 EXPERIMENTAL

8.2.1 Materials

2,6-di-tert-butyl-4-methyl phenol (BHT) and 2-benzotriazol-2-yl-4-methyl-phenol (Tinuvin P) were received from Ciba-Geigy, Switzerland. Para-phenylene diamine and 2,5-dimethyl-para phenylene diamine were received from Aldrich Chemicals and used as such. Bromine was received from Merck, India.

8.2.2 Analysis

8.2.2.1 FT-IR Analysis

Synthesized products were studied by FT-IR (Fourier Transform Infrared Perkin Elmer16 PC spectrometer).

8.2.2.2 NMR Analysis

NMR spectra were recorded on Bruker AC 200 MHz spectrometer using TMS as an internal standard.

8.2.3 Synthesis of antiozonants as well as antioxidants

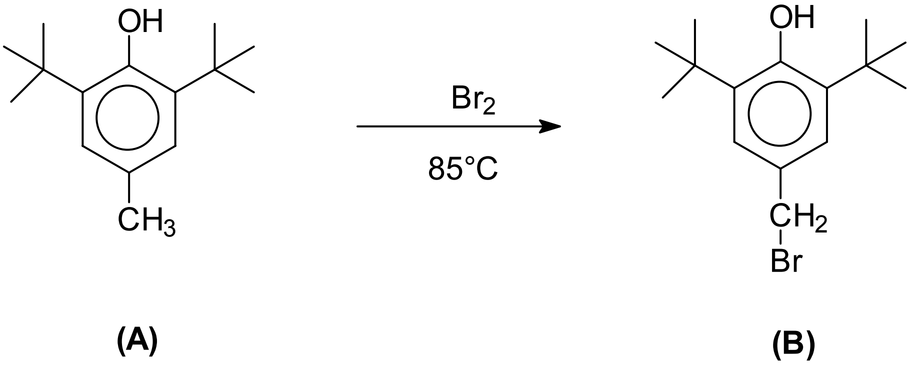
8.2.3.1 *Synthesis of 4-[(4-Amino-phenylamino)-methyl]-2,6-di-tert-butyl-phenol*

The synthesis is carried out in two steps:

(Step-I)

8.2.3.1.1 Synthesis of 4-Bromomethyl-2,6-di-tert-butyl-phenol

4-Bromomethyl-2,6-di-tert-butyl-phenol was prepared from the bromination of 2,6-di-tert-butyl-4-methyl phenol.



In a 250 ml three-necked round bottom flask, 2.5 g (0.0112 mol) of 2,6-di-tert-butyl-4-methyl phenol (**A**) was dissolved in 50 ml of dry carbon tetrachloride. In a separate conical flask 1.83 g (0.589 mL, 0.0115 mol) of bromine was dissolved in 50 ml of dry carbon tetrachloride and solution was transferred to a cylindrical funnel with pressure equalizing tube. Three-necked round-bottomed flask containing solution of 2,6-di-tert-butyl-4-methyl phenol was kept in oil-bath at 85°C. Solution in the flask was continuously stirred with the help of magnetic stirrer. Bromine solution was added, drop-by-drop, from funnel to the flask for a span of 4-5 hours till all the solution was poured out. After that heating was stopped and the final reaction mixture was allowed to cool at room temperature. Product was separated by solvent evaporation. Finally, the product obtained was a viscous yellow liquid and was absolutely pure. The yield of (**B**) was 4.02 g (90 %).

^{1}H NMR (δ ppm): 7.23 **(a)** (s, 2 H); 5.31 **(b)** (s, 1 H); 4.49 **(c)** (s, 2 H); 1.45 **(d)** (s, 18 H).

FT-IR (cm^{-1}): 3600 – 3200, O-H stretching; 1222, C-O stretching / O-H bending; 684 and 571, C-Br stretching

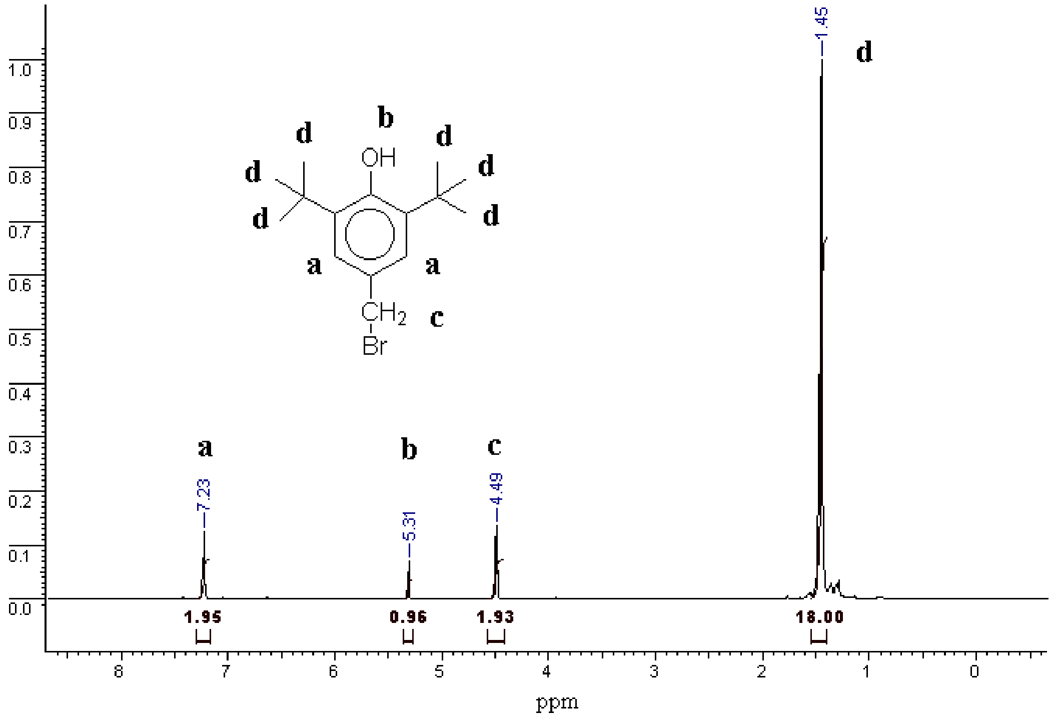


Figure 8.1: ^{1}H NMR spectrum of 4-Bromomethyl-2,6-di-tert-butyl-phenol

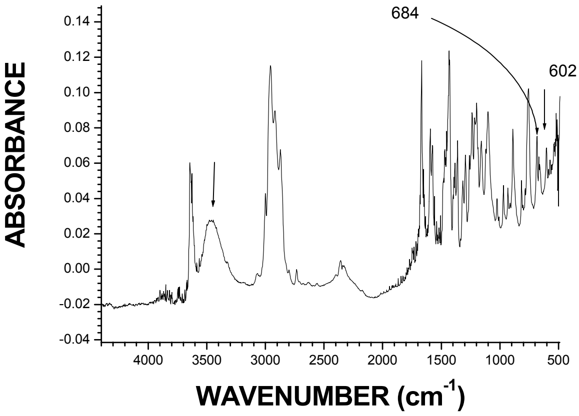
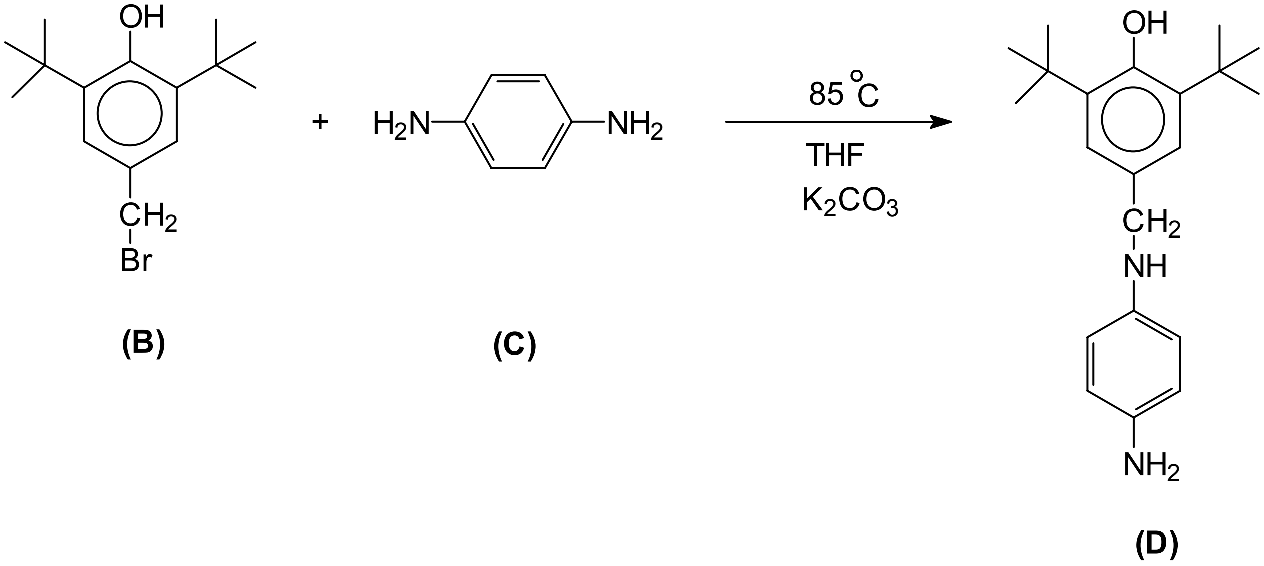


Figure 8.2: FT-IR spectrum of 4-[(4-Amino-phenylamino)-methyl]-2,6-di-tert-butyl-phenol

Step -II

8.2.3.1.2 Synthesis of 4-[(4-Amino-phenylamino)-methyl]-2,6-di-tert-butyl-phenol



4-Bromomethyl-2,6-di-tert-butyl-phenol (2.42 g, 0.011 mole) (**B**) was dissolved in 50 ml dry THF containing potassium carbonate (0.022 mole). In a separate conical flask benzene-1,4-diamine (para-phenylene diamine) (2.376 g, 0.022 mole) was dissolved in 25 mL of THF and solution was transferred to a cylindrical funnel with pressure equalizing tube. Three-necked round-bottom flask containing 4-bromomethyl-2,6-di-tert-butyl-phenol was kept in oil-bath at 85°C. Solution in the flask was continuously stirred with the help of magnetic stirrer. Benzene-1,4-diamine solution was added drop-by-drop, from funnel to the flask in acidic medium for a span of 4-5 hours till all the solution was poured out. After that heating was stopped and the final reaction mixture was allowed to cool at room temperature. The product was purified by column chromatography. The yield of **(D)** was 0.0127 g (85 %).

^{1}H NMR (δ ppm): 7.19 (m, 4 H, ArC*H*), 6.55 (s, 2H, ArC*H*), 5.12 (b, s, 1 H, O*H*), 4.05 (t, 2H, CH_2N*H*), 3.42 (s, 2H, NH_2), 2.01 (b, m, 1H, N*H*), 1.2-1.38 (m, 18 H, tert-butyl)

FT-IR (cm^{-1}): OH and NH stretching (s, 3600 - 3200), ArCH (m, 1622 and 1518).

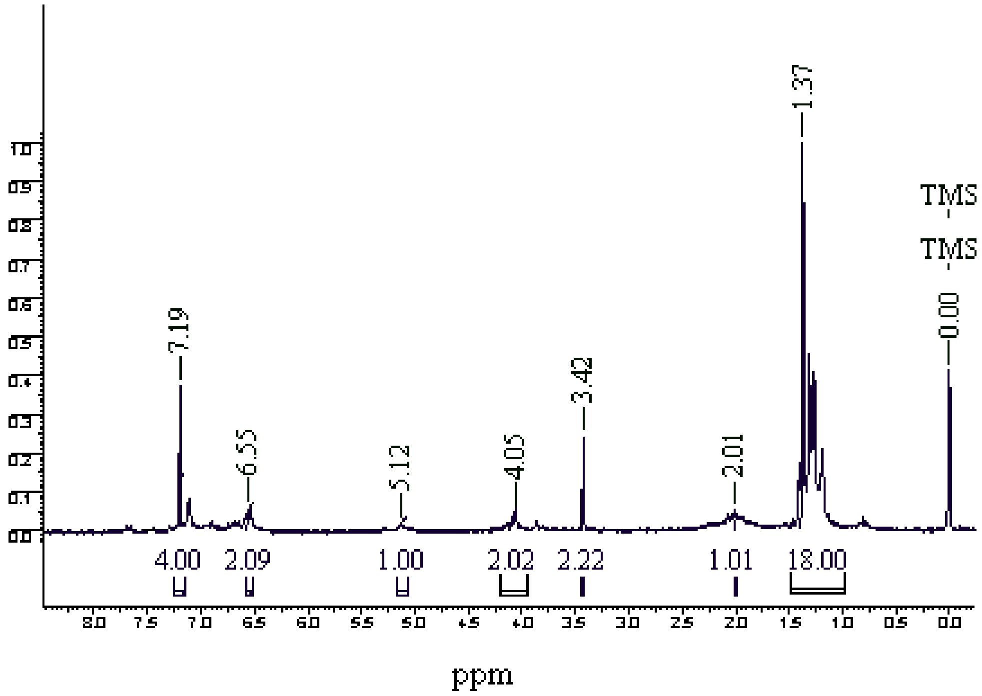


Figure 8.3: ^{1}H NMR spectrum of 4-[(4-Amino-phenylamino)-methyl]-2,6-di-tert-butyl-phenol

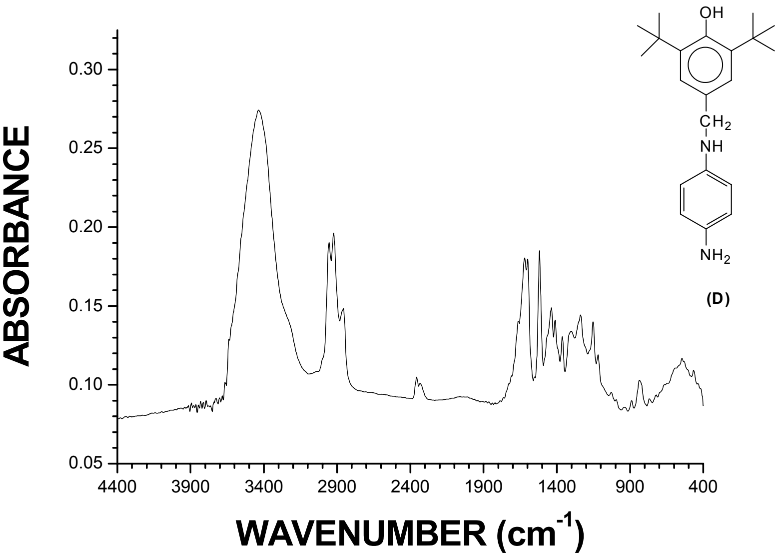
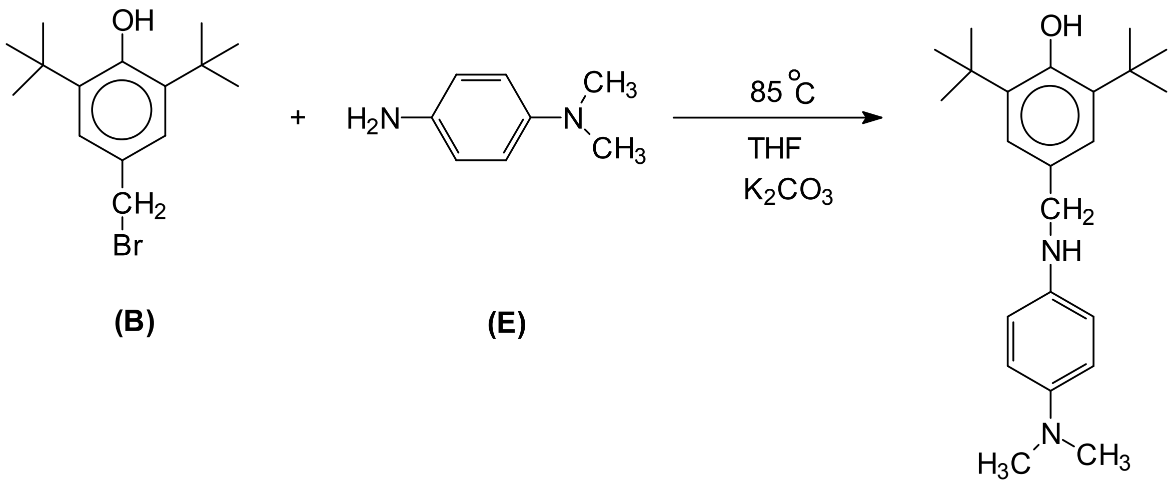


Figure 8.4: FT-IR spectrum of 4-[(4-Amino-phenylamino)-methyl]-2,6-di-tert-butyl-phenol

8.2.3.2 Synthesis of 2,6-Di-tert-butyl-4-[(4-dimethylamino-phenylamino)-methyl]-phenol



(B) **(E)** **(F)**

4-Bromomethyl-2, 6-di-tert-butyl-phenol **(B)** (2.42 g, 0.011 mole) was dissolved in 50 ml of dry THF. In a separate conical flask N, N-dimethyl-benzene-1, 4-diamine **(E)** (2.99 g, 0.022 mole) was dissolved in 25 mL of THF and solution was transferred to a cylindrical funnel with pressure equalizing tube. Three-necked round-bottom flask containing solution of 4-Bromomethyl-2, 6-di-tert-butyl-phenol was kept in oil-bath at 85°C. Solution in the flask was continuously stirred with the help of magnetic stirrer. N, N-dimethyl-para-phenylene diamine solution was added drop-wise, from funnel to the flask in acidic medium for a span of 4-5 hours till all the solution was poured out. After that heating was stopped and the final reaction mixture was allowed to cool at room temperature. The product was purified by column chromatography. The yield of **(F)** is 0.582 g (63 %).

^{1}H NMR (δ ppm): 7.39-7.17 (m, 4 H, Ar C*H*), 6.70 (b, s, 2H, Ar C*H*), 5.15 (b, s, 1 H, O*H*), 4.07 (d, 2H, CH_2NH), 2.76 (s, 6H, $(CH_3)_2$ N), 2.2-2.4 (m, 1H, N*H*), 1.2-1.38 (s, 18 H, tert-butyl)

FT-IR (cm^{-1}): OH and NH stretching (3600 - 3200), ArCH (m, 1622 and 1518).

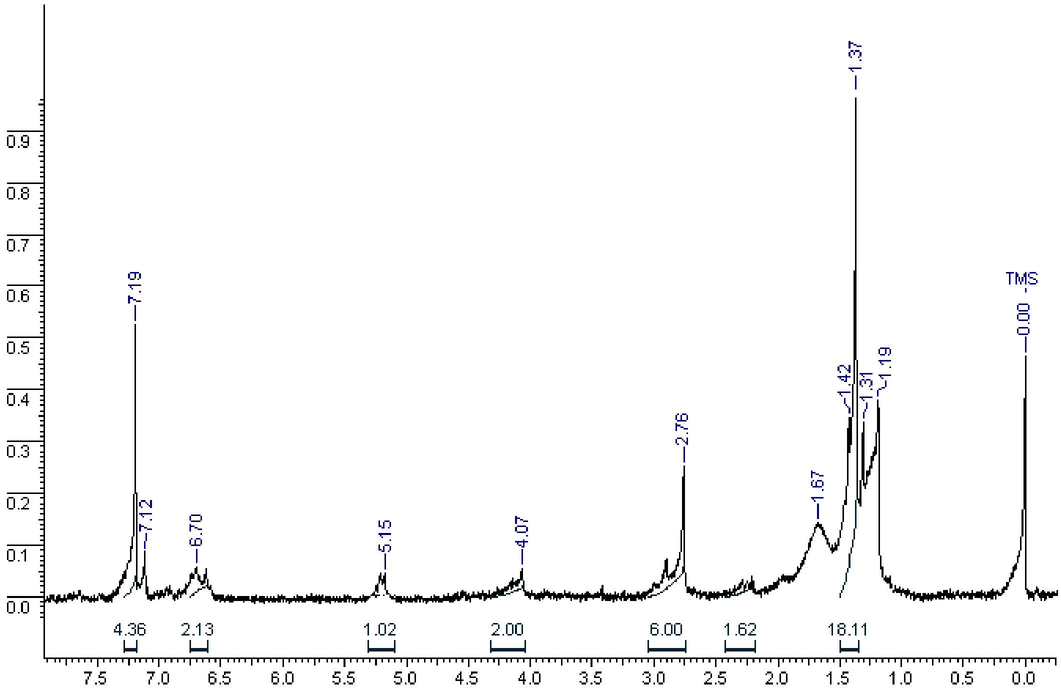


Figure 8.5: ^{1}H NMR spectrum of 2,6-Di-tert-butyl-4-[(4-dimethylamino-phenylamino)-methyl]-phenol

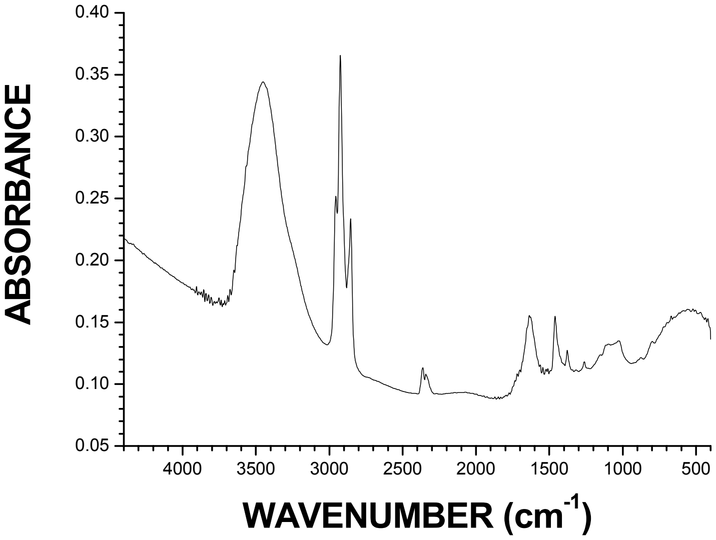


Figure 8.6: FT-IR spectrum of 2,6-Di-tert-butyl-4-[(4-dimethylamino-phenylamino)-methyl]-phenol

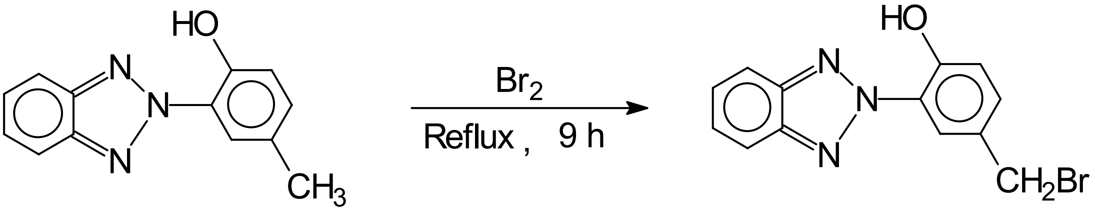
8.2.3.3 Synthesis of 4-[4-amino-phenylamino]-2-benzotriazol-2-yl-phenol

The synthesis is carried out in two steps:

Step-I

8.2.3.3.1 Synthesis of 2-benzotriazol-2-yl-4-bromomethyl-phenol or 2-(2H-Benzotriazole-2-yl)-4-bromomethylphenol

2-(2H-Benzotriazole-2-yl)-4-bromomethylphenol was prepared from the bromination of 2-(2H-Benzotriazole-2-yl)-4-methylphenol. Thanki *et al.*[21, 22] synthesized the product **(J)** with using a radical initiator (AIBN) recently. We synthesized the same **(J)** without using any radical initiator with good yield.



(I) **(J)**

In a 250 ml three-necked round bottomed flask, 2-(2H-Benzotriazole-2-yl)-4-bromomethylphenol **(I)** (4.0 g; 0.0112 mol) was dissolved in 30 ml of dry carbon tetrachloride. In a separate conical flask, bromine (0.748 ml; 0.01176 mole) was dissolved in 45 ml of dry carbon tetrachloride and solution was transferred to a cylindrical funnel with pressure equalizing tube. Three-necked round-bottom flask containing solution of 2-(2H-Benzotriazole-2-yl)-4-bromomethylphenol was kept in oil-bath at 45 °C for 4 hrs and followed by 85°C for 9 hrs. Solution in the flask was continuously stirred with the help of magnetic stirrer. Bromine solution was added, drop-by-drop, from funnel to the flask for a span of 4-5 hours till all the solution was poured out. After that heating was stopped and the final reaction mixture was allowed to cool at room temperature. Product was separated by solvent evaporation. Finally the product obtained was fine white crystalline and was absolutely pure. The yield of **(J)** was 4.071 g (75%) m.p. 169-171°C (incorrect).

^{1}H NMR (δ ppm): 11.47 (s, 1 H, O*H*), 8.47 (d, 1H, Ar CH), 7.97-7.92 (q, 2H, Ar CH), 7.53-7.48 (q, 2H, Ar CH), 7.38 (d, 1H, Ar CH), 4.59 (s, 2H, C*H*$_2$)

FT-IR (cm^{-1}): O-H stretching (s, 3300), C-O stretching (s, 1222), CH_2 wagging (1258), C=N (1620-1680) and C-Br stretching (m, 684).

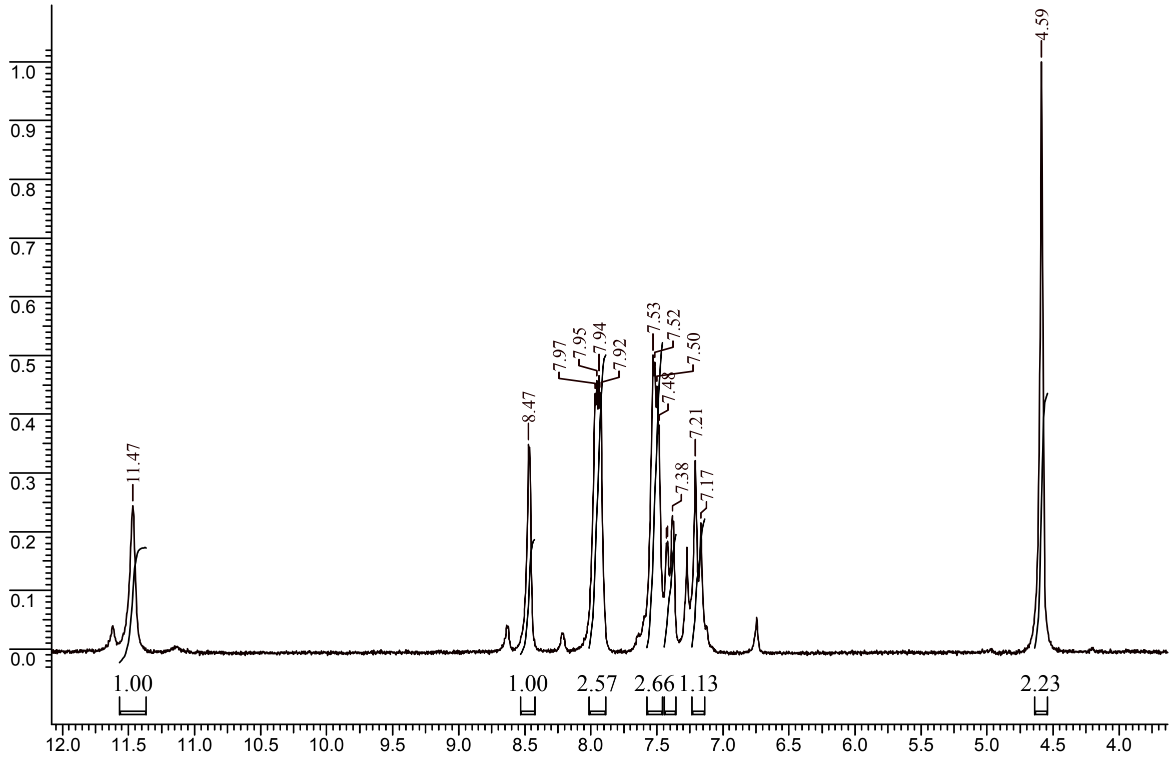


Figure 8.7: ^{1}H NMR spectrum of 2-benzotriazol-2-yl-4-bromomethyl-phenol

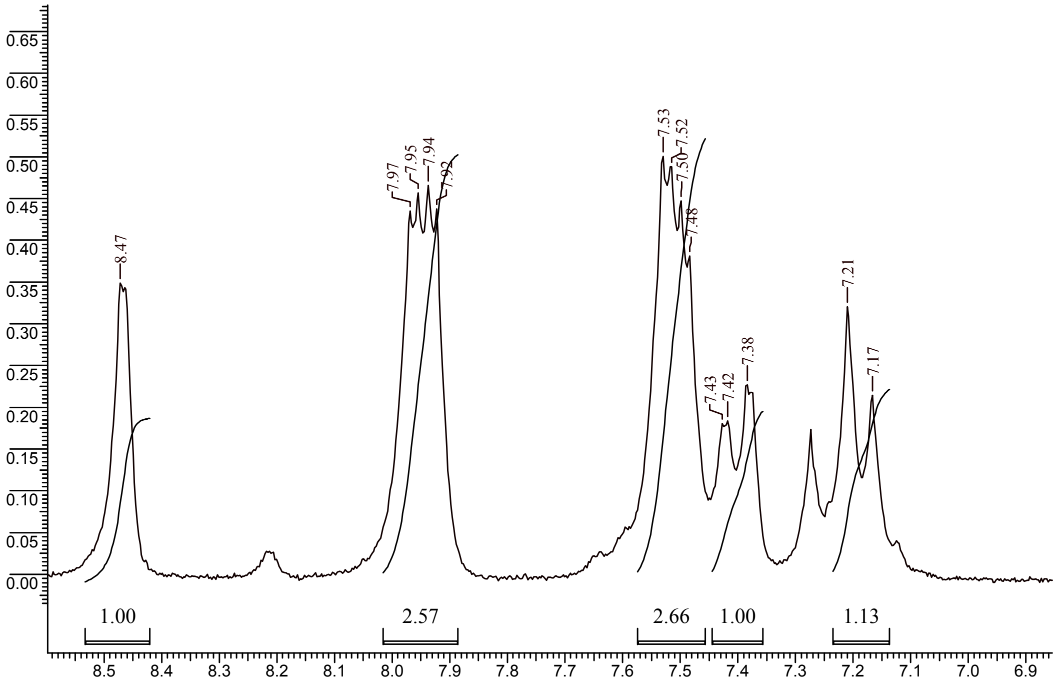


Figure 8.8: ^{1}H NMR spectrum of 2-benzotriazol-2-yl-4-bromomethyl-phenol (enlarged portion)

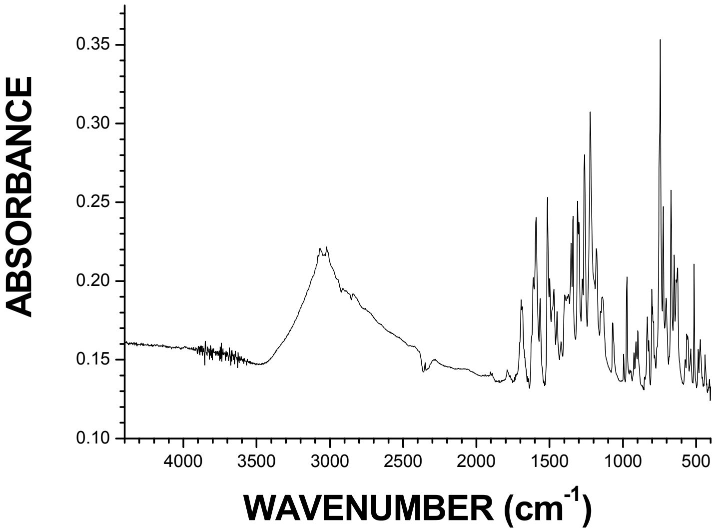
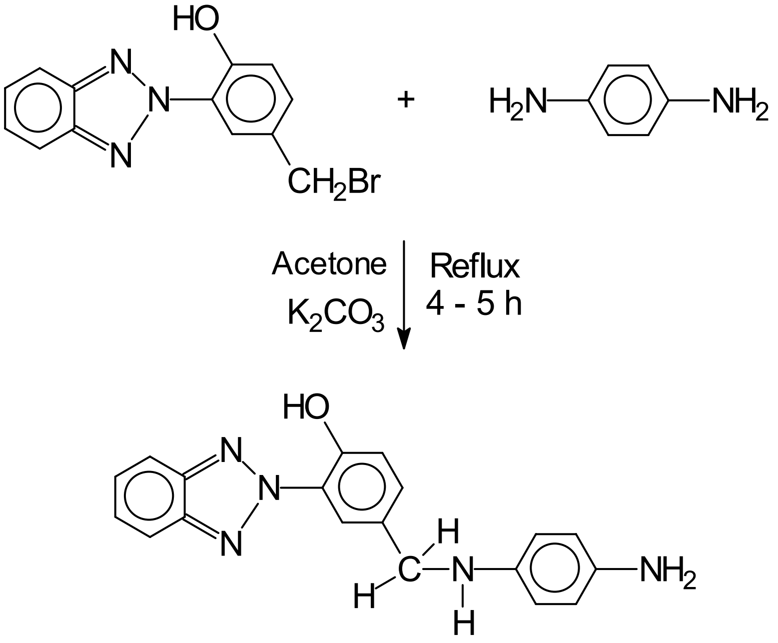


Figure 8.9: FT-IR spectrum of 2-benzotriazol-2-yl-4-bromomethyl-phenol

Step-II

8.2.3.3.2 Synthesis of 4-[4-amino-phenylamino]-2-benzotriazol-2-yl-phenol



Para-phenylene diamine (p-PDA) (2.1 equivalent, 0.373 g, 0.00345 mole), potassium carbonate (2.2 equivalent, 0.50 g, 0.00361 mole) and 25 ml acetone were magnetically stirred in a 100 ml two-necked round-bottom flask. 2-benzotriazol-2-yl-4-bromomethyl-phenol (1 equiv., 0.5 g, 0.00164 mole) was dissolved in 50 ml of acetone and solution was transferred to a cylindrical funnel with pressure equalizing tube. Two-necked round-bottomed flask containing solution of p-PDA was kept in oil-bath at 80 °C. or 2-benzotriazol-2-yl-4-bromomethyl-phenol solution was added drop-wise, from funnel to the flask for a span of 4-5 hours till all the solution was poured out. After that heating was stopped and the final reaction mixture was allowed to cool at room temperature. The product was separated by column chromatography. The yield was 63 %.

^{1}H NMR (δ ppm): 11.47 (s, 1 H, O*H*), 8.60-8.58 (d, 1H, Ar CH), 8.15-8.08 (q, 2H, Ar CH), 7.70-7.65 (q, 2H, Ar CH), 7.45-7.42 (m, 6H, Ar CH), 6.78-6.6 (3 H, m, NH_2, N*H*), 4.48 (s, 2H, Ar CH_2)

FT-IR (cm^{-1}): O-H and NH stretching (s, 3600 – 3300), C-O stretching (1222), CH_2 wagging (1258) and C=N (1620-1680).

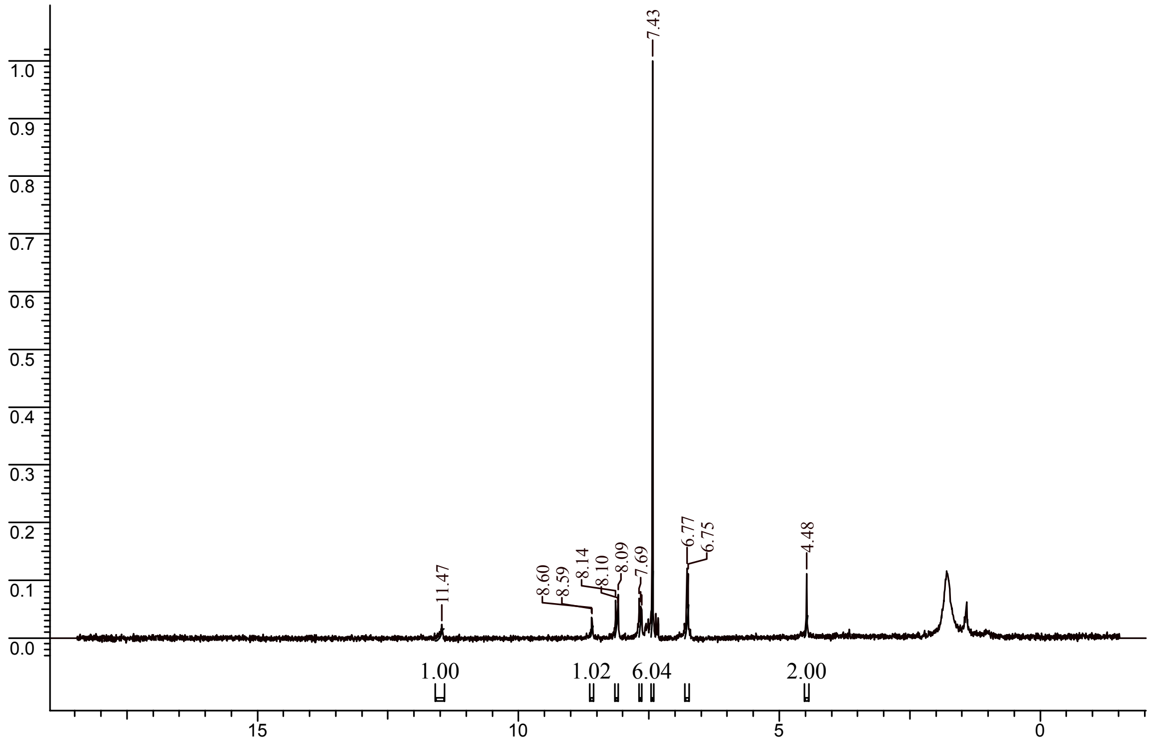


Figure 8.10: ^1H NMR spectrum of 4-[4-amino-phenylamino]-2-benzotriazol-2-yl-phenol

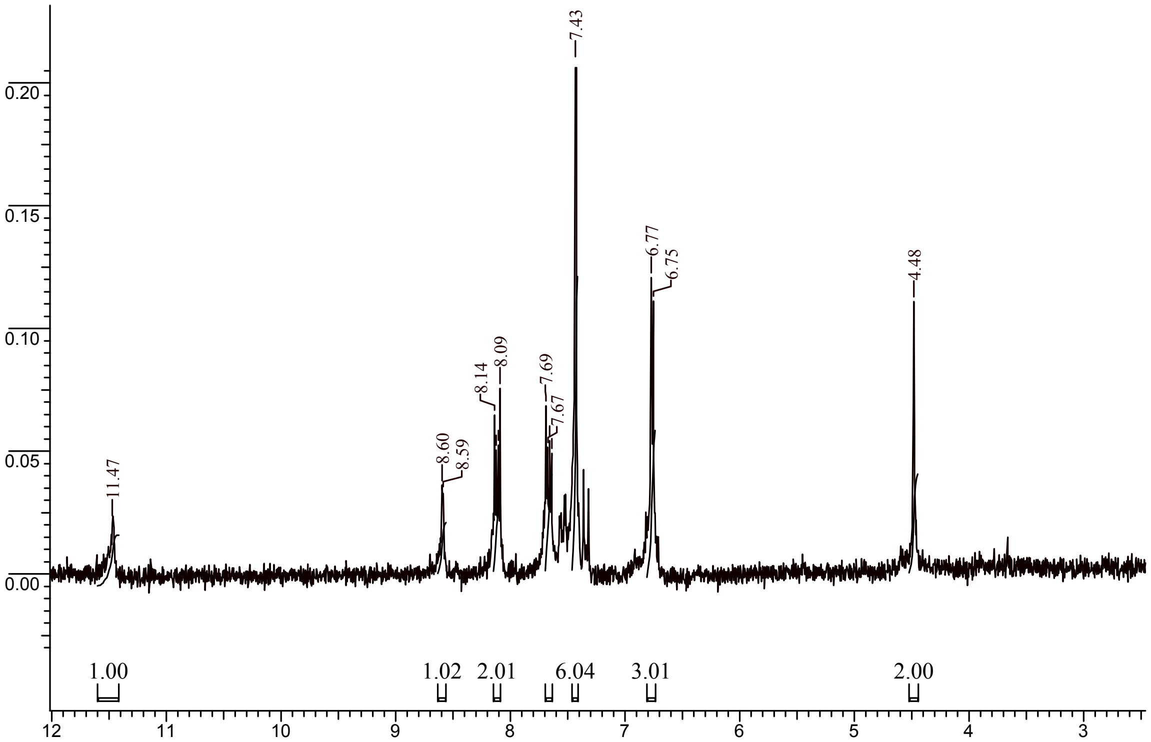


Figure 8.11: ^{1}H NMR spectrum of 4-[4-amino-phenylamino]-2-benzotriazol-2-yl-phenol (enlarged view)

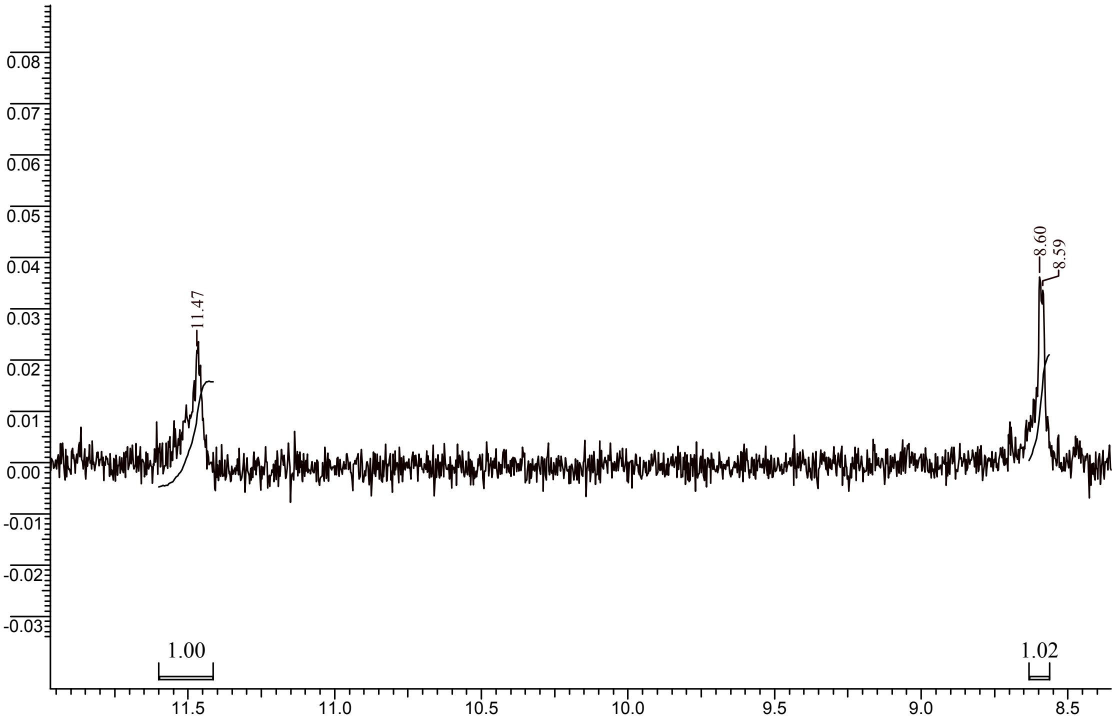


Figure 8.12: ^{1}H NMR spectrum of 4-[4-amino-phenylamino]-2-benzotriazol-2-yl-phenol (enlarged view)

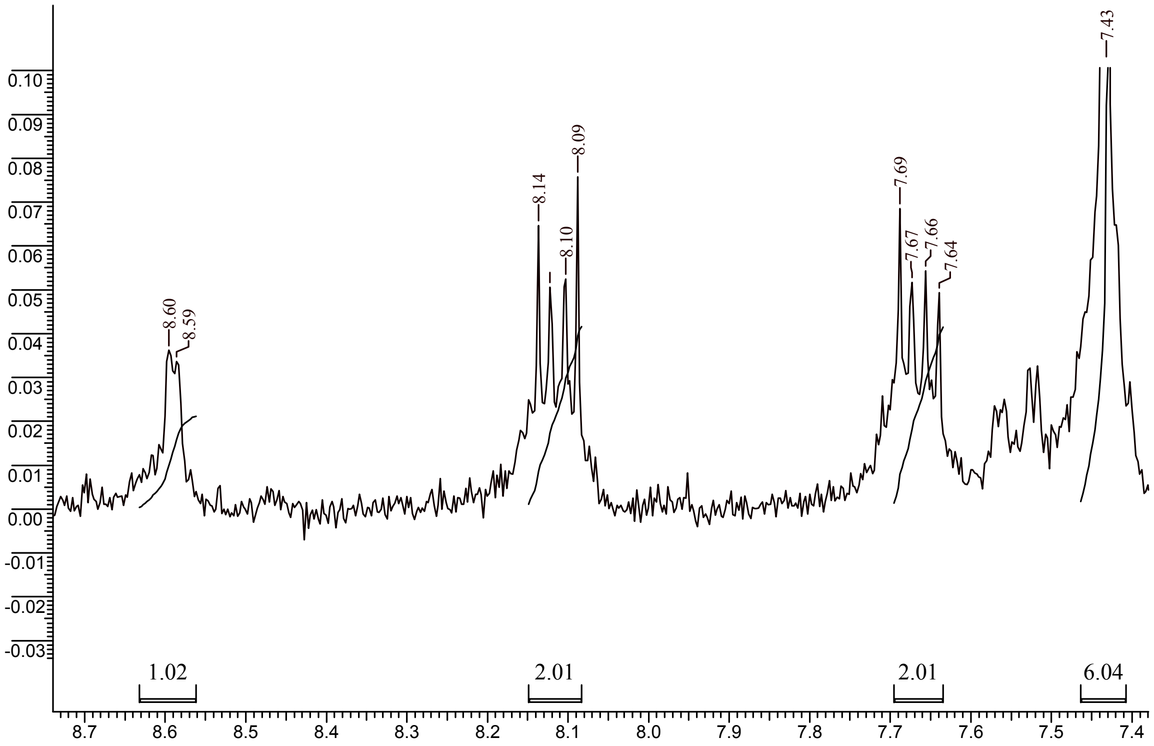


Figure 8.13: ^{1}H NMR spectrum of 4-[4-amino-phenylamino]-2-benzotriazol-2-yl-phenol (enlarged view)

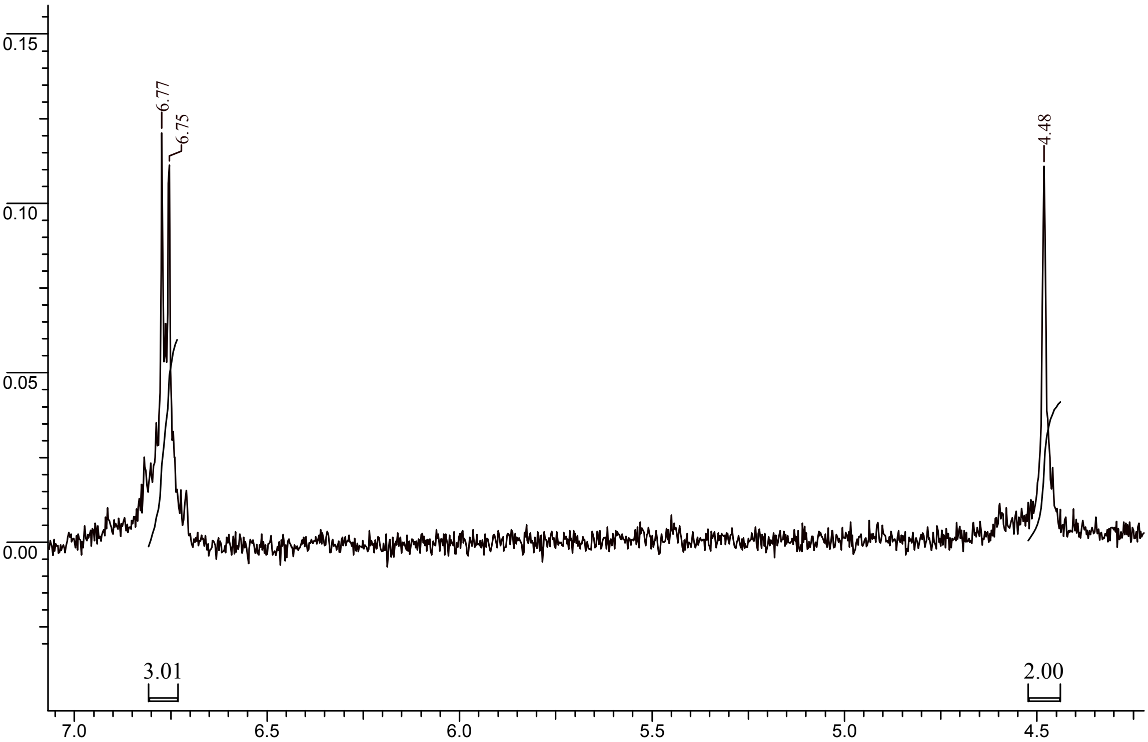


Figure 8.14: ^{1}H NMR spectrum of 4-[4-amino-phenylamino]-2-benzotriazol-2-yl-phenol (enlarged view)

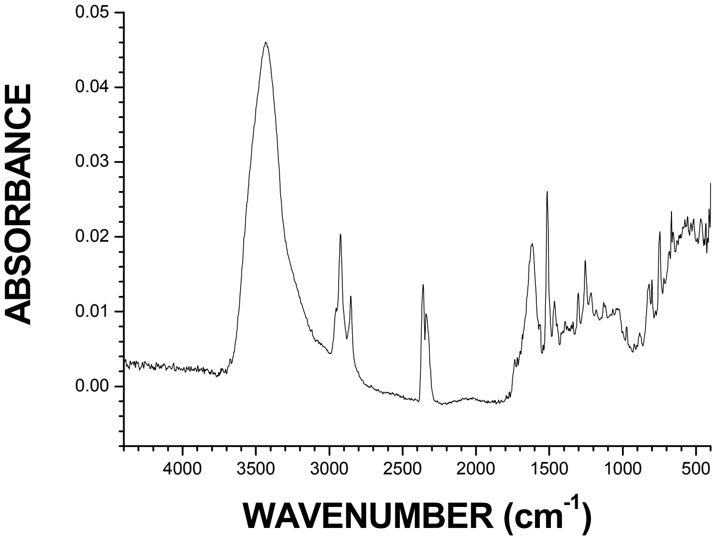


Figure 8.15: ^{1}H NMR spectrum of 4-[4-amino-phenylamino]-2-benzotriazol-2-yl-phenol (enlarged view)

8.3 CONCLUSIONS

The newly synthesized antiozonants relate to a composition comprising an aromatic amine and a benzotriazole and / or hindered phenol that is prepared in two-step process. The synthesized novel antiozonants as well as antioxidants may give better stability to polymers, especially rubbers to protect from ozone. The stability of these compounds on rubbers can be studied by photo / thermal / ozone degradation. The newly synthesized and commercially available antiozonants / antioxidants effect on rubbers are under process.

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CHAPTER IX

SUMMARY AND CONCLUSIONS

In the present investigation, we attempted to elucidate the chain cleavage mechanisms during hydrogen peroxide catalyzed photo-oxidative degradation of high molecular weight natural rubber, natural rubber latex and polybutadiene. A free-radical mechanism has been suggested for the degradation of natural rubber. These free radicals interact with the labile α-hydrogen (C-H bond), abstracting the proton and leaving macroradicals behind. The peroxides are formed by the interaction of these radicals with O_2 and decomposed to yield various degradation products containing hydroxyl, carbonyl and carboxy groups at the chain ends. We also observed that after purification and drying, further solubilization of the photoproducts in varying solvents was often difficult and sometimes a part of it was insoluble. This can be explained by crosslinking resulting from subsequent reactions involving hydroperoxide decomposition. We observed a continuous decrease in M_n and M_v with irradiation time. In nitrogen atmosphere, there is a gradual but less intense, broad hydroxyl region which increases upto 36 h and then decreases, which is attributed to the formation of epoxy groups in the oxidative degraded polymer chain. The free radical mechanism occurrence makes the double bond epoxidation possible by addition of peroxy radical and elimination of alkoxy radical. The ^{1}H NMR shows the signal due to hydroxyl proton in the hydroxy methyl group at 3.5- 4.0 ppm under air as well as nitrogen atmosphere. In addition to hydroxyl group, the epoxy groups were also detected in the degraded rubber. Functionality was estimated ~ 2 in scheme-**C**. It was proposed that hydrogen peroxide and/or allylic hydroperoxides act as photoinitiators and produce hydroxyl radicals and/or alkoxy radicals. The results show that functionality ~ 2 was achieved after 63 hrs of photo-irradiation of natural rubber while in initiated irradiation, it was very low.

Our results for functionalized natural rubber latex using UV irradiation showed the expected dependence of hydroxyl group and molecular weight on the photocatalytic agent but the functionalities obtained were often variable. The addition of oxidizing agent and co-catalyst may constitute an essential feature for more correct functionality.

Methyltrioxorhenium (MTO) based epoxidation system, already known as an effective catalytic system for the epoxidation of normal olefins, proved to be extremely efficient for the epoxidation of high molecular weight natural rubber. Polymers with degree of epoxidation ranging from 12 – 48 % were obtained. The degree of epoxidation could be controlled by the amount of hydrogen peroxide. For the reaction where more oxidant was used, a longer time is required in order to achieve the attempted degree of epoxidation. The epoxidation occur very effectively and selectively, which is in agreement with results obtained for epoxidation systems. Side reactions *i.e.* furans, carbonyl ester, ether or cyclic compounds were also not observed during the reaction.

We carried out the metathesis reactions of natural rubber using bis(tricyclohexyl phosphine) benzylidine ruthenium (VI) dichloride in dichloromethane, chloroform and toluene. Dichloromethane was found most suitable solvent for natural rubber degradation at 60°C. Viscosity average molecular weight (M_v) of natural rubber decreases with the progress of the reaction and temperature. It is also possible to get desired molecular weight of natural rubber by adjusting the reaction temperature and suitable solvent in metathesis reactions.

The telechelics impart a major role in the preparation of advanced polymeric materials, because of their functional groups at the chain ends. In addition to radical and anionic pathways to telechelic natural rubber, several approaches, involving olefin metathesis have also been explored. In the presence of a difunctional chain transfer agent, ring-opening metathesis of cyclooctadiene has been successfully employed. We tried to get a route for functional polymers using a mixture of cyclooctadiene and/ or 1,5-dimethyl-1,5-cyclooctadiene and the chain transfer agent (2-methyl but-2-ene-1,4-diacetate and / or but-2-ene-1,4-diacetate) using a Ruthenium carbene complex.

The ozone attack on the rubber causes chain-scission and the formation of various decomposition products such as ozonides, polymeric peroxides, hydroperoxides, lactones, esters and aldehydes etc. In our studies, the natural rubber solution is bubbled with ozone gas for a period of time and subsequently treated with an oxidizing and / or reducing agent to yield oligomers bearing reactive oxygenated end groups. The peaks in ^{1}H NMR spectra arise at 1.27 and 2.70-2.71 ppm indicating the presence of methyl group on the oxirane ring in cis position and the proton on the oxirane ring. The peak at 9.78 ppm shows the protons of aldehyde group. The intensity of the peak of 2.71 ppm was higher than the 9.78 ppm. We observed a signal at 2.19 ppm of methyl ketone chain end in the natural rubber.

The effect of film thickness of natural rubber in ozonization is also studied. Unstretched films of natural rubber were exposed to ozone gas. The effect of reaction time and film thickness was studied. The ozone reaction with unstretched natural rubber films differ with depth. We also studied the lowering of viscosity average molecular weights of natural rubber films under ozonolysis and found that M_v decreases faster in initial hours but after 4 h, the rubber film was not fully soluble in toluene, tetrahydrofuran and carbon tetrachloride. It is proposed that after longer ozonolysis, chain scission takes place and simultaneously crosslinking occurs in the natural rubber. The thickness of the film was also an important factor during ozonolysis. It was assumed that when ozone penetrated through the thin natural rubber film, it attacks on the surface and reaches towards inner layer faster than the thicker films, therefore, the thin films get crosslinked faster then the thicker one for longer ozonolysis.

N, N-di substituted para-phenylene diamines offer protection to polymers such as natural rubber and elastomers against the deteriorous effects of oxygen and ozone. We synthesized antiozonants as well as antioxidants which may give better stability to polymers, specially rubbers to protect them from ozone. The newly synthesized antiozonants relate to a composition comprising an aromatic amine and a benzotriazole and / or hindered phenol that is prepared in two-step process. The stability of these compounds in rubbers can be studied by photo / thermal / ozone degradation.

SCOPE OF THE FUTURE WORK

1. Cyclic reactions in natural rubber under UV irradiation.
2. The temperature dependent changes in the relative concentrations of hydrophobic and hydrophilic moieties at the natural rubber/water interface are detected as increasing the entropic influence of chain extension which is associated with natural rubber elasticity. The magnitude of this effect depends on the cross-link density and the degree of oxidation of the surface of natural rubber.
3. The telechelic oligomers can be synthesized by ozonolysis of SBS followed by reduction.
4. Metathetic degradation of natural rubber and polybutadiene can be carried out using suitable functionalized alkenes to get functionalized oligomers.

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