STRUCTURAL STUDY OF EPOXIDIZED NATURAL RUBBER (ENR-50) AND ITS DERIVATIVES SYNTHESIZED *VIA* EPOXIDE RING-OPENING REACTIONS USING NMR TECHNIQUES

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By

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Specially dedicated to

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TABLE OF CONTENTS

PAGE

CHAPTER 1: RESEARCH BACKGROUND

CHAPTER 2: NOMENCLATURES

CHAPTER 3: EXPERIMENTAL

CHAPTER 4: STRUCTURAL STUDY OF EPOXIDIZED NATURAL RUBBER (ENR-50) AND ITS CYCLIC ITHIOCARBONATE DERIVATIVE

CHAPTER 5: THE STRUCTURAL STUDIES OF EPOXIDE RING OPENING REACTIONS IN EPOXIDIZED NATURAL RUBBER USING ACETIC ACID AND POTASSIUM HYDROXIDE

CHAPTER 6: SYNTHESIS AND STRUCTURAL STUDIES OF HYBRIDS OF EPOXIDIZED NATURAL RUBBER/TITANIA (ENR/TiO$_2$) AND EPOXIDIZED NATURAL RUBBER/ZIRCONIA (ENR/ZrO$_2$) HYBRIDS

LIST OF FIGURES

LIST OF TABLES

LIST OF SCHEME

PAGE

LIST OF EQUATIONS

LIST OF ABBREVIATIONS

COSY	Correlation Spectrosopy
DEPT	Distortion Enhancement by Polarization Transfer
DSC	Differential Scanning Calorimetry
DTG	Differential Thermal Gravimetric
FTIR	Fourier Transform Infra Red
HMBC	Heteronuclear Multiple Bond Coherence
HMQC	Heteronuclear Multiple Quantum Coherence
JRES	J-Resolved Spectrosopy
NMR	Nuclear Magnetic Resonance
SEM-EDX	Scanning Electron Microscopy-Electron Diffraction X-ray
TEM	Transmission Electron Miscroscopy
TG	Thermal Gravimetric
XRD	X-ray Diffractogram

KAJIAN STRUKTUR GETAH ASLI TEREPOKSIDA (ENR-50) DAN TERBITANNYA YANG DISINTESIS MELALUI TINDAK BALAS PEMBUKAAN GELANG EPOKSIDA MENGGUNAKAN TEKNIK NMR

ABSTRAK

Satu terbitan siklik ditiokarbonat yang terdiri daripada getah asli terepoksida (ENR-50) dan tiga jenis hibrid ENR-50/titania (TiO_2), ENR-50/zirkonia (ZrO_2) dan kompleks ENR-50/stanum (Sn) telah disediakan. Teknik FTIR, 1D NMR; ^{1}H-, ^{13}C-, ^{119}Sn-NMR, 2D NMR; HMQC, HMBC, COSY, TGA, DSC, TEM, SEM-EDX dan XRD telah digunakan untuk mencirikan terbitan dan hibrid ENR. Suatu susunan triad ENR-50 berjaya ditandakan menggunakan teknik NMR dan gabungan terbitan siklik ditiokarbonat ENR-50. Suatu terbitan siklik ditiokarbonat ENR-50 telah disintesis daripada tindak balas ENR-50 dan karbon disulfide (CS_2) dengan kehadiran mangkin 4-dimetilaminopridina (DMAP) pada suhu refluks (47 °C) selama 3 jam. Kedua-dua hibrid ENR/TiO_2 dan ENR/ZrO_2 telah disediakan daripada tindak balas pembukaan gelang epoksida ENR-50 pada keadaan berasid lembut (ENR-50 terawat asid) dan berbes (ENR-50 terawat bes) yang seterusnya ditindak balaskan dengan pemula masing-masing melalui teknik sol-gel pada suhu refluks (60 °C) selama 24 jam. Sumber pemula TiO_2 dan ZrO_2 masing-masing adalah $Ti(OCH_2CH_2CH_3)_4$ dan $Zr(OCH_2CH_2CH_3)_4$. Tindak balas pembukaan gelang ENR-50 dengan terawat asid dan bes masing-masing menggunakan asid asetik dan kalium hidroksida/isopropanol pada suhu refluks (110 °C) selama 3 jam. ^{1}H-NMR menunjukkan bahawa 19.56 dan 16.76% pembukaan gelang epoksida telah berlaku daripada keseluruhan jumlah unit epoksida dalam ENR-50 bagi ENR-50 terawat asid dan bes masing-masing dan disokong oleh spektroskopi FTIR kuantitatif. Pelekatan alkil (R) berlaku pada kedua-dua karbon paling (↑) dan kurang (↓) berhalangan terhadap

gelang epoksida. ^{13}C-NMR menunjukkan lokasi R dalam rantai polimer melalui pertambahan puncak asetat dan ester bagi ENR-50 terawat asid dan puncak eter bagi ENR-50 terawat bes. Nilai T_g bagi ENR-50 terawat asid adalah lebih tinggi daripada ENR-50 terawat bes kerana tahap pembukaan gelang dan lokasi pelekatan R. Pembentukan hibrid ENR/TiO_2 dan ENR/ZrO_2 adalah melalui jaringan C-O-Ti dan C-O-Zr masing-masing. Atom Ti terikat khusus pada karbon kuartet E^6 manakala Zr pada kedua-dua karbon (↑) dan (↓) (iaitu (E^6 dan E^7) pembukaan gelang epoksida. Kedudukan R, Ti dan Zr telah dibuktikan melalui ^{13}C-NMR dan 2D NMR. Nilai T_g hibrid ENR/TiO_2 adalah lebih tinggi daripada ENR/ZrO_2 kerana jenis moeiti takorganiknya. Kompleks hibrid ENR/Sn disintesis daripada pelanjutan tindak balas refluks komposit ENR/$SnCl_2.2H_2O$ (110 °C) selama 3 jam dan dirawat dengan gas CO_2 selama 1 hingga 5 jam semasa campuran tindak balas ini sedang disejukkan. Pembentukannya berlaku melalui pelbagai tahap serangan elektrofilik dan akhirnya menyusun kepada kompleks hibrid ENR/Sn. Pembentukan C-O-Sn berlaku pada karbon kuartet E^6 pembukaan gelang ENR-50.

STRUCTURAL STUDY OF EPOXIDIZED NATURAL RUBBER (ENR-50) AND ITS DERIVATIVES SYNTHESIZED *VIA* EPOXIDE RING-OPENING REACTIONS USING NMR TECHNIQUES

ABSTRACT

A cyclic dithiocarbonate derivatives of epoxidized natural rubber (ENR-50) and three types of hybrids comprising ENR-50/titania (TiO_2), ENR-50/zirconia (ZrO_2) and ENR-50/tin (Sn) complex were prepared. FTIR, 1D NMR; ^{1}H-, ^{13}C-, ^{119}Sn-NMR, 2D NMR; HMQC, HMBC, COSY, TGA, DSC, TEM, SEM-EDX and XRD techniques were used to characterize the ENR derivative and hybrids. A triad sequence of ENR-50 was successfully assigned using NMR techniques consolidated by the cyclic dithiocarbonate derivative of ENR-50. A cyclic dithiocarbonate derivative of ENR-50 was synthesized from the reaction of purified ENR-50 with carbon disulfide (CS_2), in the presence of 4-dimethylaminopyridine (DMAP) as catalyst at reflux temperature (47 °C) for 3 hours. Both ENR/TiO_2 and ENR/ZrO_2 hybrids were prepared from epoxide ring opening reaction of ENR-50 at mild acidic (acid treated ENR-50) and basic (base treated ENR-50) conditions which later reacted with the respective precursors *via* sol-gel technique at reflux temperature (60 °C) for 24 hours. The respective source of TiO_2 and ZrO_2 precursors used were $Ti(OCH_2CH_2CH_3)_4$ and $Zr(OCH_2CH_2CH_3)_4$. The ring opened reaction of ENR-50 with acid and base treated ENR-50 were carried out using acetic acid and potassium hydroxide/isopropanol respectively at reflux temperature (110 °C) for 3 hours. ^{1}H-NMR revealed that 19.56 and 16.76% of epoxide were ring opened from the total amount of the epoxide unit in ENR-50 for acid and base treated ENR-50 respectively and these were supported by quantitative FTIR spectroscopy. The alkyl (R) attachment occured at both most (↑) and least (↓) hindered carbons of the epoxide. ^{13}C-

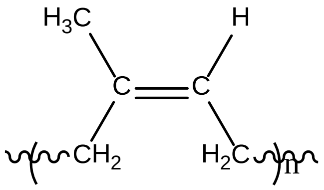
NMR provides the location of R in the polymer chain *via* additional acetate and ester peaks for acid treated ENR-50 and ether peaks for base treated ENR-50. The T_g value of acid treated ENR-50 was higher than base treated ENR-50 due to extent of ring opening and location of R attachment. The formation of ENR/TiO_2 and ENR/ZrO_2 hybrids was via C-O-Ti and C-O-Zr networks respectively. Ti atom was specifically tailored at the quaternary carbon E^6 while Zr atom as at both (↑) and (↓) carbon (E^6 and E^7) of the ring opened epoxide. The structural position of R, Ti and Zr were proven using ^{13}C-NMR and 2D NMR. The T_g value of ENR/TiO_2 was higher than ENR/ZrO_2 hybrid due to types of inorganic moiety. The ENR/Sn complex hybrid was synthesized upon further reaction of ENR/$SnCl_2.2H_2O$ composite at reflux temperature (110 °C) for 3 hours and upon cooling, the reaction mixture was subject to 1 to 5 hours of CO_2 gas treatment. The formation was through various stages of electrophilic attack and finally rearranged to ENR/Sn complex hybrid. The formation of C-O-Sn also occurred at quaternary carbon E^6 of ring opened ENR-50.

CHAPTER 1

RESEARCH BACKGROUND

1.1 Natural Rubber (NR)

Natural rubber (NR) is commercially available in the form of latex from tropical tree *Havea brasiliences*. It is one of the main agricultural commodities of Malaysia (Ismail and Abu Bakar, 2005). The NR comprises of 99% of *cis*-1,4-polyisoprene (Scheme 1.1). The remaining 1% is a mixture of non-rubber components such as protein, amino acid, sugar, fatty acids and other substances (Isayev and Sun, 2007). The high content of *cis*-1,4-polyisoprene in NR, contributes to high degree of crystallization as well as high mechanical properties for NR (Isayev and Sun, 2007).



Scheme 1.1: The *cis*-1-4 polyisoprene

Typically, the *cis*-1,4-isoprene unit sequence can be repeated up to 3000 times (Eng and Ong, 2001). Thus NR behaves like a rubber, resin and plastic (Novesar, 2001). The physical and chemical properties of NR are given in Table 1.1. Based on Table 1.1, NR has high tensile, elongation at break; tear strength and compression properties (Menough, 1985; Novesar, 2001; Thakore 2014). NR is suitable for application at room and medium operating temperature (less than 120 °C). NR has low melting (28 °C) and glass transition temperature, T_g (-75 °C) (Novesar, 2001; Tantatherdtam, 2003).

Table 1.1: Physical and chemical properties of NR (Novesar, 2001)

Physical properties	**Value**
Density, ρ	0.92 g cm^{-3}
Refractive index, *n*	1.52
Stretching coefficient	0.00062 °C^{-1}
Thermal conductivity	0.00032 cal s^{-1} cm^{-3} °C^{-1}
Dielectric constant, ε	2.37
Volume resistance	1015 ohms cc^{-1}
Durometer range (Shore A)	30 – 90
Tensile strength	4000 psi or 28 Mpa
Elongation at break	700 %
Maximum operating temperature	75 – 120 °C
Low temperature operation	-60 °C
Compression set, 24 hours/70 °C	10 – 15%
Tear strength	35 – 44 KN m^{-1}
Chemical properties	**Value**
Melting point, T_m	28 °C
Glass transition temperature, T_g	-75 °C
Resistivity* – weather	good - moderate
Resistivity* – ozone	poor
Resistivity* – acid and alkaline	good
Resistivity* – oil and solvent	poor
Resistivity* – steam	good
Abrasion	good - excellent
Air permeability	good

*Range of resistance evaluation: excellent > good > moderate > poor

Typically NR is not comparable to synthetic polymers in term of oil and solvent resistance as well as gas permeability (Baker, 2001). Therefore, the usage of NR in automotive and manufacturing industry is restricted to certain products such as tyres. While synthetic polymers like polysiloxane is resistant to oil, solvent and heat thus applicable at wide range of operating temperature -100 to 316 °C.

NR tends to degrade when expose to oxygen, ozone, heat, dynamic stress and radiation (Cibulkova *et al.*, 2006). Oxygen molecule is able to diffuse into NR and makes NR susceptible to thermal oxidation. Thermal oxidation involves scission and cross-linking at C=C bond amongst the polymer chain (Bonfils *et al.*, 2001;

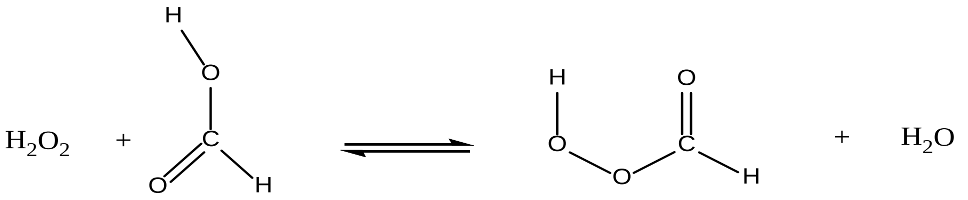
Ngolemasango *et al.*, 2003). The poor permeability of NR to ozone gives opportunity to ozone to react with C=C bond even at relatively low temperature. This caused oxidation reaction to NR. Typically, ozonide and polyperoxide are formed at the main chain of NR (Scott, 1995). Heating leads to NR polymer chains defect and degradation through pyrolysis such as breaking of bonds of the main polymer chains and side groups, elimination of organic group and depolymerization. However, the extend of degradation is relative to the heat applied (Kind and Hull, 2012; Schanabel, 1981). Dynamic stress in NR is loads applied to the NR polymer chains and the ability of NR to returns into its viscoelastic state after the load is relieved. The excess amount of dynamic stress affects the molecular chains rearrangement and reorientation (Eng and Ong, 2001). By radiation, radical is produced at C=C bond and this radical abstracts hydrogen on the carbon atom in α-position to the double bond (Cibulkova *et al.*, 2006).

The prolonged storage of NR under ambient condition caused the progressive increased in Mooney viscosity of NR. This is called ‘storage hardening’ and affects processing behaviour of NR (Eng and Hong, 2001; Chaikumpollert *et al.*, 2011; Isayev and Sun, 2007). Storage hardening changes the molecular weight, molecular weight distribution, molecular structure, and non-rubber components in NR (Chaikumpollert *et al.*, 2011). Generally this reaction involves crosslinking reaction between C=C and the abnormal groups that exist in NR. These abnormal groups include epoxide, ester, aldehyde and lactone that are formed during NR processing. They are present as a very small amount of non-isoprene group and located on the main-chain of NR molecules (Eng and Ong, 2001; Ngolemasango *et al.*, 2003).

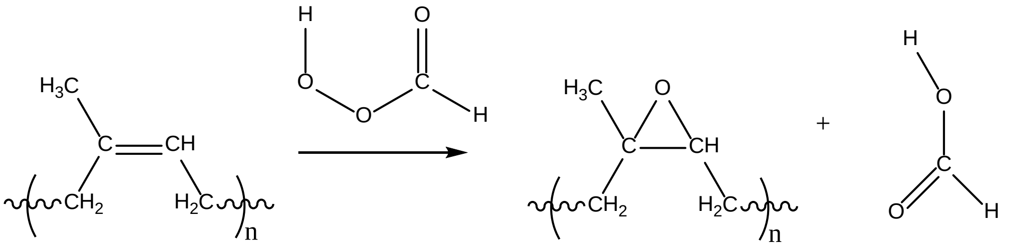
1.2 Epoxidized Natural Rubber (ENR)

1.2.1 Preparation

Epoxidized natural rubber (ENR) was developed to make NR comparable to synthetic polymers (Ismail and Abu Bakar, 2005). ENR is a commercial polymer produced from epoxidation process of NR with formic peroxide or acetic peroxide in a reactor (Gelling, 1991). The chemical reactions between hydrogen peroxide, formic acid and NR are consequently given in Equation (1.1) and (1.2) respectively.



(1.1)



(1.2)

The epoxidation process of NR is carried out in latex phase because it provides relatively low cost route and the reagent can be recycled for a few times (Gelling, 1991). NR latex is stabilized from its acid coagulation by adding anionic surfactant. At the optimum reaction condition, the mole ratio between formic acid and hydrogen peroxide ranges from 0.2 to 0.5 times (Baker and Gelling, 1987). While the optimum temperature for epoxidation process is at 60 to 70 °C to avoid secondary ring opening product of ENR or epoxidized latex such as diol and furan which occurs at high temperature and low pH (Gelling, 1996). The ENR is treated with heat flow before it was dried in hot air (Baker and Gelling, 1987).

There are also several other methods to carry out epoxidation process of NR such as by using oxidizing agent such as acidic, alkaline and selected halogen. The epoxidation of NR with acidic oxidizing agent is a direct process. NR latex is directly reacted with the acidic medium *i.e.* perbenzoic acid, metachloroperbenzoic, peracetic acid, trifluoroperacetic acid or perpropionic acid during coagulation process. While by using alkaline oxidizing agent, the NR latex is reacted with a mixture of hydrogen peroxide and NaOH aqueous solution. Other than that, NR latex is exposed to a direct flow of oxygen gas in the presence of a catalyst *i.e.* Ag to produce ENR. The selected epoxidation process of NR with halogen gas *i.e.* Cl_2 and Br_2 is carried out in the presence of water to produce halohydrin. This is followed by an alkaline treatment to produce ENR (Hogt *et al.*, 1992).

1.2.2 Physical and Chemical Properties

The production of ENR from epoxidation process of NR is a stereospecific reaction. Stereospesific reaction of ENR is the stereochemical outcome of ENR as previously specified. This is due to the random epoxidation process of NR which randomly distributes the epoxide group in the polymer chains while maintaining the *cis*-NR configuration in ENR structure. NR with 4 isoprene units can accommodate 2 epoxides groups without affecting the tensile properties, tear strength and non-strain crystallization (Baker and Geling, 1987).

NMR spectroscopy is well known and reliable method to determine the mole percentage of epoxidation (Baker *et al.*, 1984; Bradbury and Perera, 1985, Gemmer and Golub, 1978, Saito *et al.*, 2007) compared to the other methods such as differential scanning calorimetry, elemental analysis, titration (Burfield *et al.*, 1984) and degradation (Burfield and Gan, 1977). Various epoxide content of ENR is commercially available. However, there are three mole percentages of epoxidation that are considered as standard *i.e.* ENR-10 (10 mole percentage of epoxidation), ENR-25 (25 mol percentage of epoxidation) and ENR-50 (50 mole percentage of epoxidation (Menough, 1985). Above 50 percent of epoxidation level lead to high preparation cost as well as produced non-crystalline rubber with inferior tensile properties. While less than 25 percentage of epoxidation level *i.e.* 10-15% produces rubber with a slight different properties than NR itself (Baker and Gelling, 1985).

The physical properties of ENR are influenced by its mole percentage of epoxidation as tabulated in Table 1.2. The increment in mole percentage of epoxidation of ENR produces ENR with high mechanical strength such as tensile, elongation, hardness and compression set. However, Mooney Scorch value shows a decrement trend. ENR density increases with the increment in epoxide content. This is consistent with additional oxygen atom in the ENR. Therefore the density and viscosity of ENR-50 is higher than ENR-25. The refractive index of ENR-50 and 25 are lower than NR (Menough, 1985).

Higher level of epoxidation increases oil and solvent resistivity of ENR. ENR-50 exhibits better oil resistance than ENR-25 (Menough, 1985). The oil resistivity of ENR is related to its solubility parameter where one mole percentage of epoxide adds 0.131 $(Jm^{-3})^{1/2}$ value of the solubility parameter. At high epoxidation level, ENR is more resistant to non-polar solvent or hydrocarbon and decreases its resistivity in the polar solvent (Baker *et al.*, 1984; Baker and Gelling, 1987). The increment in mol percentage epoxidation of ENR decreases the air (Ismail and Hashim, 1994) and oxygen (Ismail and Ng, 1988) permeability across ENR membrane. Typically, the permeability of air is generally lower than oxygen through ENR membrane. This is due to easy diffusion of oxygen than air into the ENR membrane (Ismail and Hashim, 1994). The air permeability is an important parameter in tire liners industry.

Table 1.2: Some physical properties of NR and the epoxidised (ENR) derivatives (Menough, 1985).

Property	**NR**	**ENR-10**	**ENR-25**	**ENR-50**
Density (mg m^{-3} or g cm^{-3})	0.92	-	0.97	1.03
Refractive index	1.52	1.52	1.52	1.51
Mooney Scorch, Mooney viscosity (min)	23	24	18	14
Tensile strength (psi)	3915	3683	3712	3954
Elongation at break (%)	550	515	580	565
300% Modulus (psi)	1117	1160	972	1262
Hardness, IRHD	59	54	52	58
Resillence (%)	78	73	59	74
Compression set (%)	17	14	15	17
Volume swell during immersion (70 hours & 70 °C)				
ASTM D471; Oil 1	+15	-	+12	+01
ASTM D471; Oil 3 (equivalent to IRM 903)	+78	-	+40	+11

*All compounds were filled with 30 phr of N-220 black by using EV cure system.

The glass transition temperature increases by 1°C per mole percentage epoxidation. Thus ENR-25 shows glass transition temperature, T_g at -48°C and ENR-50 at -18°C. The T_g value affected the resilient properties of rubber at room temperature. Rubber with low T_g value is more resilience than those with high T_g value. This changes the purpose of rubber from general elastomer to a special elastomer (Baker and Gelling, 1985; Menough, 1985). The thermal degradation of ENR-50 under nitrogen gas flow is a single-step reaction. It displays T_{onset} at 348 °C, maximum degradation temperature, $T_{max\ deg}$ at 392 °C and ends at, T_{final} 445 °C. While thermooxidative degradation of ENR-50 under oxygen gas flow is a multi-step reaction. It starts at T_{onset} 246 °C, maximum temperature, $T_{max\ deg}$ 378 °C and ends at, T_{final} 584 °C. However the applied heating rate influences the thermooxidative degradation of ENR (Novesar, 2001; Li *et al.*, 1998).

1.2.3 Structure of ENR

NMR spectroscopy techniques are widely used to characterize various polymers either in liquid or solid state. Characterization using 1D NMR gives structural elucidation on reactive groups and monomer units in the polymer chain. However, the 2D NMR extents detail structural arrangements of the monomer units within the polymer chain. Either or both of these techniques have been applied to ENR-25 (Jeerupun *et al.*, 2004), ENR-50 (Lee *et al.*, 2010; Gelling, 1991; Burfield *et al.*, 1984a; Gelling, 1996; Bhattacharjee *et al.*, 1993; Gan and Ziana, 1997), and ENR-75 (Burfield *et al*., 1984a), and other ENR related compounds (Derouet *et al.*, 2001a; 2001b). However, most of these works fall short of full structural assignments due to the overlapping of signals arising from the randomly distributed isoprene (C) and epoxidized isoprene (E) monomer units (Bradbury and Perera, 1985; Saito *et al.*, 2007). The arrangement of these monomer units in a group of three is called a triad sequence (see Chapter 2).

Thus prior to the advent of the triad sequence, previous workers (Burfield *et al.*, 1984a; Gelling, 1996; Bhattacharjee *et al.*, 1993; Gan and Ziana, 1997; Bradbury and Perera, 1985; Thames and Gupta, 1997) were only able to ascertain the assignments of ^{1}H chemical shifts of methine proton of C and E units but sporadically to either the methyl and or methylene protons of C and E units of the ENR. Saito *et al.* (2007) have reported the use of computer simulation (also Furst and Pretsch, 1990; Pretsch *et al.*, 1992) to predict chemical shifts of these protons and their triad assignments. Gelling (1985), on the other hand, has assigned the triad sequence based on ^{13}C-NMR chemical shifts for ENR-20. However, the assignment deals with certain triad sequences only and the position of carbon represented by the triad sequences was found to be inconsistent. Consequently, Saito *et al.* (2007) have successfully interpreted the ^{13}C-NMR spectra for the ENR related compounds and assigned their triad sequence.

1.3 Reactions of Epoxide

1.3.1 Crosslinking Reactions

ENR contains both epoxide and C=C bond (Gan and Ziana, 1997). Both offer crosslinking reaction(s) with other polymers chains, fillers or other reactive substances. Crosslinking is a process of forming a three-dimensional network structure from a linear polymer by a physical or chemical method (Akiba and Hashim, 1997). Typically the physical methods are vulcanization (Akiba and Hashim, 1997) and high energy electron irradiation (Ratnam *et al.*, 2000a; 2000b; 2001). The vulcanization involves the formation of 3-D polymer network at C=C bond in the presence of sulfur (Akiba and Hashim, 1997). While high energy electron irradiation produces free radical that reacts with the structure of the irradiated rubber. This reaction is also known as irradiation-induced crosslinking and can take place either at epoxide or C=C bond (Ratnam *et al.*, 2001).

The chemical methods are preferred due to their simplicity and low cost such as the acid (Bhattacharjee *et al.*, 1993; Brosse *et al.*, 2000) or alkali treatments (Gan and Ziana, 1997) which modify the epoxide or the C=C bond in the ENR chain. These methods produce covalently bonded network in the polymer system.

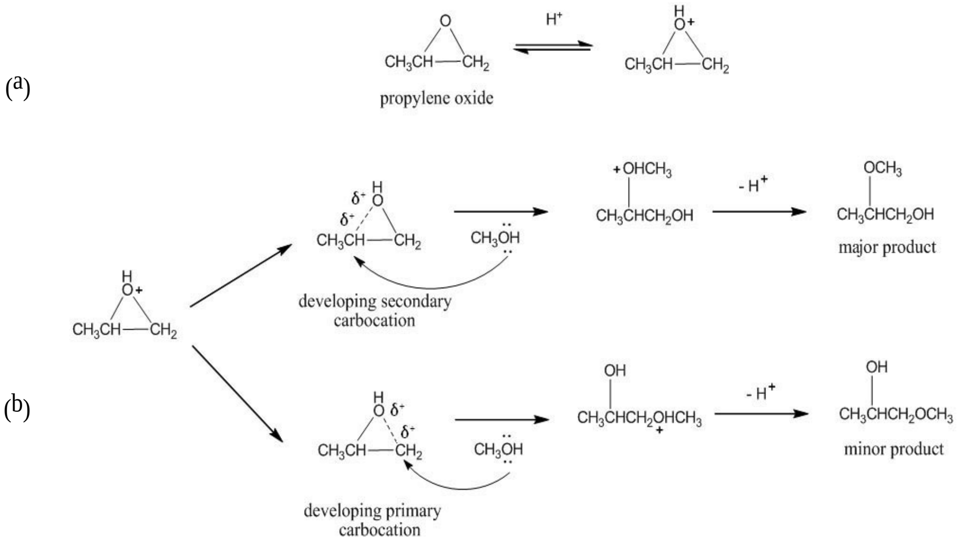
1.3.2 Ring Opening Reactions (RORs)

Epoxide or oxirane is an ether in which the oxygen atom is incorporated into the C=C bond to form a three-membered ring. Ethylene oxide is the simplest form of epoxide. The carbons in an epoxide are very reactive electrophile thus able to react with a variety of nucleophile. The ring strain in the three-membered ring of epoxide is able to relieve through ring opening reaction (Bruice, 2001a). Majority of epoxide reactions are studied in solution and most of the reaction involves the epoxide ring opening and addition of a molecule of reagent (Brosse *et al*., 2000).

In practice, the oxirane ROR is a common reaction during preparation of ENR. The ring opening products varies the properties and application of ENR (Yu *et al.*, 2008). Thus this reaction offers opportunities to functionalize ENR with other reactive substances, fillers or polymers. The oxirane ring is reactive towards nucleophilic reagents such as amine, carboxylic acid, alcohol (Derouet *et al.*, 2001a; 2001b), dibutylphosphate and phosphoric acid derivatives (Derouet *et al.*, 2005).

1.3.2.1 ROR under Acidic Condition

The mechanism of epoxide ring opening is considered under three conditions (i) orientation of ring opening, (ii) stereochemistry of ring opening, and (iii) kinetics of ring opening. The presence of acid accelerates the addition of most nucleophile to the epoxide carbon atoms (Bruice, 2001a). By using propylene oxide to represent the epoxide, Scheme 1.2 shows the protonation of epoxide by acid (H^+). The formation of conjugated acid of the epoxide is a reversible process. The protonated epoxide ($>^+OH$) is then attacked by a nucleophile (CH_3OH) at the most substituted carbon. Thus the carbon-oxygen bond breaks. A covalent bond between nucleophile and the most substituted carbon *i.e* secondary carbon is formed. Thus the partial positive charge is located at the most substituted carbon because this carbocation is more stable than primary carbocation. The products are formed after elimination of a proton (H^+). The major product resulted from the addition of nucleophile at the most substituted carbon while the minor product is from the addition of nucleophile at the least substituted carbon. The pathway of the reaction is partially S_N1 and S_N2. This is because S_N1 reaction involves a carbocation as an intermediate and S_N2 reaction requires a departure of leaving group before the compound is able to attack by the nucleophile (Bruice, 2001a).



Scheme 1.2: (a) The formation of conjugate acid of the epoxide and (b) the attack of nucleophile on one of the epoxide carbon atoms (Bruice, 2001).

ENR is a pH sensitive polymer and favours neutral pH (Baker *et al.*, 1984; Menough, 1985). The exposure of ENR to pH below than 7 (acidic) is able to catalyst the ring opening reaction of epoxide and provides crosslinking amongst the polymer chains through ether groups (Baker *et al.*, 1984; Baker and Gelling, 1985; Menough, 1985). The excessive reaction temperature and too low pH contributes to secondary ring opening reaction of ENR-50 such as diol and furans (Gelling, 1996; Tanrattanakul *et al.*, 2003). Typically acidity and temperature are main factor for the formation of ring opening products i.e hydroxyl-acetates, diols and intermolecular ethers (Yu *et al.*, 2008). The cleavage of epoxide ring under acidic condition involves formation of oxonium ion. Then this oxonium ion is attacked by the nucleophile in a S_N2 displacement that produced β-alkoxy alcohols. However, the addition of nucleophile onto epoxide ring is difficult to obtain under acidic condition due to undesirable side reactions obtained (Derouet *et al.*, 2001b).

The ring opening reaction of ENR-50 using periodic acid will produce heterotelechelic NR. It involves chains scission at the epoxide structure and degradation of ENR chains (Brosse *et al.*, 2000; Phinyocheep *et al.*, 2005). However, periodic acid works as an oxidizing agent due to formation of carbonyl group after prolonged reaction time (Phinyocheep *et al.*, 2005).

A ring opening reaction in acid solution produces formyl ester and an alcohol group (Bradbury and Perera, 1985). Acid catalysed the ring opening of the epoxide and formed ether crosslinked (Gelling, 1991). The acid treatment is more preferred because at neutral pH, the epoxide structure of the ENR is stable towards the epoxide ring opening (Gan and Ziana, 1997). However, at low pH (not less than 3), organic acids such as methacrylic acid (Derouet *et al.*, 1990) and benzoic acid (Gan and Burfield, 1989) and other carboxylic acids (Copeland and Thames, 1994) are capable of inducing epoxide ring opening reactions. Typically the products are ester, alcohol, hydroxyl and diol.

1.3.2.2 ROR under Alkaline Condition

In the common base, a nucleophile attacks the less substituted carbon of the epoxide causing the β-opening at the epoxide ring (Grobelny *et al.*, 2003). While in the rubber processing via vulcanization reaction, the excess of base will cause premature curing and accelerate the reaction. This premature curing is due to the epoxide ring opening reaction under basic condition (Baker *et al.*, 1984; Baker and Gelling, 1985). Hydrolysis of epoxide ring of ENR-50 can occur by boiling ENR-50 in THF for more than 30 minutes under alkaline conditions (Gan and Ziana, 1997).

1.3.2.3 ROR via Alcoholysis

The epoxide ring opening by alcohols are mainly conducted under mild and neutral conditions (Derouet *et al.*, 2001b). However this reaction requires metal catalyst such as metal doped alumina, metal halides, organotin phosphate derivatives and cerium ammonium nitrate (CAN) (Derouet *et al.*, 2001b).

The alcoholysis using CAN catalyst shows the orientation of the reaction is influenced by (i) the size and the nature of the alcohol substituents, (ii) polarity of the solvent, and (iii) the complexing properties of the solvents (Derouet *et al.*, 2001a; 2001b). The alcoholysis of epoxide using various alcohols produces β-alkoxy alcohols. This reaction is regioselective and occurs exclusively at the most hindered carbon. The small size alcohol is more reactive than large size alcohols. The electron drawing substituents on the carbon that bear the hydroxyl group of the alcohols decrease the reactivity of the alcohols. The solvents play an important role on epoxide rearrangement during alcoholysis. In polar (*i.e* DMSO, DMF) and medium polarity solvents (*i.e* THF, dichloromethane) epoxide rearranges into ketone and allylic alcohol. While in non polar solvents (*i.e* benzene, toluene, dioxane) the rearrangement product is allylic alcohol. The alcoholysis reaction is also influenced by complexing power of the solvent. Solvents like dioxane and diglyme are able to solvate cerium ion and deactivate CAN catalyst (Derouet *et al.*, 2001b). The alcoholysis reaction of ENR-20 in dichloromethane (DCM)-alcohol mixture is a slow process. Thus the excess amount of alcohol (i.e. concentration) is necessary to increase the reaction rate besides the reaction temperature. The products are mixture of alkoxylated, ketone and allylic units (Derouet *et al.*, 2001a). Alcoholysis does not generate any crosslinking or cyclization reaction (Brosse *et al.*, 2000).

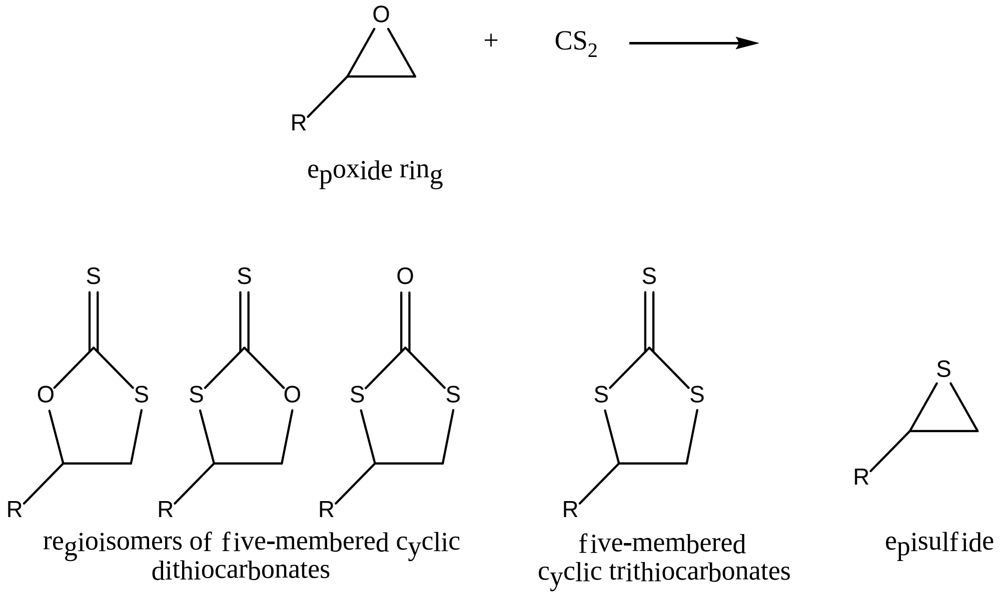
1.3.3 Fixation or Insertion Reactions

1.3.3.1 Insertion of Carbon Disulfide (Thiocarbonation)

Carbon disulfide (CS_2) is abundantly available and a low cost precursor. It is a common sulphur source in organic chemistry and a solvent for various polymers. The CS_2 comprises both electron-donor and electron-acceptor moieties. As electron-donor the CS_2 is able to donate its electron and acts as reducing agent. While as electron-acceptor, CS_2 accepts the electron and acts as oxidizing agent (Ochiai and Endo, 2005).

The reaction between epoxide and CS_2 produces five- and six-membered cyclic thiocarbonates. Typically five-membered cyclic thiocarbonates consists of dithiocarbonates and trithiocarbonates. Dithiocarbonates and trithiocarbonates contain 2 and 3 sulfur atoms in the cyclic structure respectively. There are three regioisomers of five-membered cyclic thiocarbonates as given in Scheme 1.4. These regioisomers present different order of 2 sulfur atoms, 1 oxygen atom and 2 carbon atoms bonded together as a cyclic dithiocarbonates (Motokucho *et al.*, 2001). Episulfide is a sulfur analogue of epoxide. The position of oxygen atom in the epoxide structure (Scheme 1.3) is replaced by a sulfur atom. The five-membered cyclic trithiocarbonates and episulfide are selectively obtained using high temperature experiment *i.e.* 120 °C (Kihara *et al.*, 1995; Motokucho *et al.*, 2001).

Synthesis of five-membered cyclic dithiocarbonates depends on the catalyst and reaction conditions *i.e.* temperature and pressure. It is important to produce a selective intermediate which later produce a selective product (Ochiai and Endo, 2005). The reaction requires a strong nucleophile as catalyst (Shamsuzzaman and Salim, 1997). A 4-dimethylaminopyridine (DMAP), triethylamine (Et_3N) and lithium bromide (LiBr) are common catalysts in this system because they posses lone pair electron to attack the carbon at CS_2. The usage of DMAP or Et_3N as catalyst and water as solvent accelerates Diels-Alder reaction and produces high yield of cyclic dithiocarbonates (Halimehjani *et al.*, 2009). The usage of LiBr as catalyst produces a selective product of cyclic dithiocarbonates which is 5-substituted 1,3-oxathiolane-2-thiones (Ochiai and Endo, 2005; Shamsuzzaman and Salim, 1997). Typically the catalyst prefers to attack at the less substituted carbon of the epoxide. This is due to the regioselectivity, steric and electronic effect (Azizi *et al.*, 2010).



Scheme 1.3: The reaction of epoxide ring with carbon disulfide (Motokuchu *et al.*, 2001).

The single S_N2 is a well known reaction route between epoxide and CS_2. The CS_2 is inserted into the epoxide structure by the ring opening reaction of epoxide by catalyst, nucleophile addition of catalysts to carbon disulfide to form xanthate salts, ring opening of epoxide by xanthate salts, and cyclization in dithiocarbonates synthesis (Ochiai and Endo, 2005). Xanthate salts is a formula of $ROCS_2^-M^+$ (R =

alkyl; M+ = Na^+, K^+). Other typical simple epoxide employed in the reaction with CS_2 such as glycidyl methacrylate and propargyl alcohols (Ochiai and Endo, 2005).

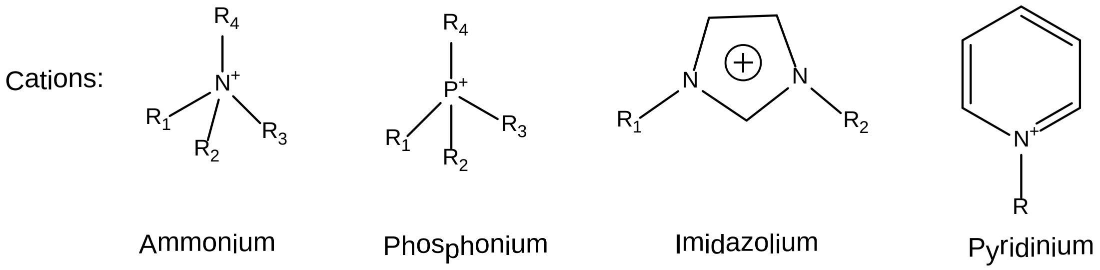
Other reaction involving sulfur nucleophile for the ring opening of epoxide is thiolysis. This reaction produces β-hydroxy sulphide. Various catalysts such as water and Rongalite ® (sodium formaldehyde sulfoxylate, $NaHSO_2.CH_2O.2H_2O$) have been employed (Azizi *et al.*, 2010; Guo *et al.*, 2009).

1.3.3.2 Insertion of Carbon Dioxide (Carbonation)

The coupling reaction of epoxide with carbon dioxide (CO_2) is similar to the synthesis of cyclic dithiocarbonate from the coupling reaction of the epoxide with CS_2 (Kim *et al.*, 2008). The fixation of carbon dioxide (CO_2) to the epoxide group is a way to protect the environment because CO_2 is a primary greenhouse gas. The emission of CO_2 to the atmosphere contributes to global warming (Xiong *et al.*, 2013). As a chemical reactant however, the CO_2 presents numerous advantages such as highly abundant, inexpensive, renewable resources, non-toxic, non-flammable, low chemical reactivity, ease of attainment of its critical conditions, and high diffusion (Supercritical fluids, 2013; Xiong et al., 2013). The cyclic carbonate is widely used as electrolyte solution for lithium ion battery, aprotic polar solvent, monomer for various polymeric material products *i.e* polycarbonates, chemical ingredients in medicine and agricultural product, alkylation agents, engineering plastics, and biomedical devices (Sako *et al.*, 2002; Xiong *et al.*, 2013).

The synthesis of cyclic carbonate via insertion or cycloaddition of CO_2 to epoxide requires the presence of a catalyst in the reaction. Two types of catalyst commonly used in the reaction are homogeneous and heterogeneous catalysts. Homogeneous catalyst possesses good solubility of catalyst, reactant and product because these are in the same phase. The disadvantage of this catalyst is the time consumed during catalyst-product separation. While heterogeneous catalyst provides easy catalyst-product separation and its high thermostability (Kawanami *et al.*, 2003). However at the optimum conditions, both of the catalyst gives high yield, good selectivity and high recyclability. While the examples for heterogeneous catalysts are ionic liquids, alkali metal halides (*i.e.* LiBr), metal oxides, transition metal complexes, salen complex (Wu *et al.*, 2012), and ion exchange resin (Xiong *et al.*, 2013).

Ionic liquid is widely used in the synthesis of cyclic carbonate from CO_2 and epoxide. The ionic liquid can be used as a prominent acid-base catalyst and provides easy penetration of CO_2 gas molecules into the catalyst (Kawanami *et al.*, 2003). This will enhance the reaction rate as well as the product yield. Various types of ionic liquid salts such as quartenary ammonium, phosphonium, imidazolium, and pyridinium cations with inorganic anions are as shown in Scheme 1.4 (Darensbourg and Holtcamp, 1996; Sun *et al.*, 2005).



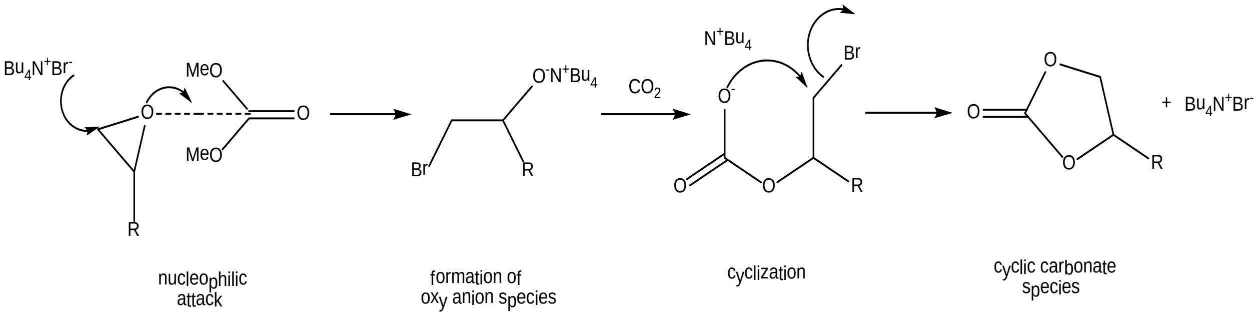
Anions: BF_4^-, PF_6^-, X^- (X = Cl, Br, I), NO_3^-, $CF_3SO_3^-$, $PhSO_3^-$

Scheme 1.4: Ionic liquids used in the synthesis of cyclic carbonate from CO_2 and epoxide (Sun *et al.*, 2005).

Typically, alkali metal halide is solely used or with support *i.e* crown ether or inorganic support. The use of alkali metal salt with crown ether shows the catalytic activity of alkaline metal salt increases with an increased in the anion nucleophilicity and cation diameter (Darensbourg and Holtcamp, 1996). The combination of ionic liquid with other alkali metal halide *i.e* 1-butyl-3-imidazolium tetrafluoroborate/$ZnBr_2$ as co-catalysts is necessary for conversion of styrene oxide to styrene carbonate. This is due to less reactivity of β-carbon atom as compared to propylene oxide and ethylene oxide. Both of the catalyst phases can be separated after the reaction and reused without significant loss in activity (Sun *et al.*, 2005). Basic metal oxides such as magnesium oxide (MgO) are highly active and selective to produce cyclic carbonate from ethylene oxide or propylene oxide and CO_2. Using the same catalyst, cyclic carbonates is an important precursor for transesterification reaction to produce glycol or dimethyl carbonate (DMC) from alcohols (Bhanage *et al.*, 2001).

Polymer supported ionic liquid *i.e* highly crosslinked chloromethylated polystyrene supported quartenary phosphonium salt produces high yield and excellent selectivity of cyclic carbonates. The anchored catalysts on the polymer remain active and produce consistent performances of the catalyst activity (Xiong *et al.*, 2013).

The utilization of non-toxic and non-corrosive solvents such as DMC as a reaction media provides fast and quantitative conversion of cyclic carbonate without side-products. Tetrabutylammonium bromide (TBAB) acts as catalyst. Both can be recovered and reused for subsequent experiment up to six runs. The known reaction mechanism is shown in Scheme 1.5. The reaction involves nucleophilic attack of bromide ion of quaternary salt to the epoxide ring. The ring opening reaction of the epoxide is facilitated by the promoting effect of DMC by non-bonding interaction with the oxygen of the epoxide. An oxy anion species is formed and reacts with CO_2 and subsequent cyclization produces the corresponding carbonate (Kumar *et al.*, 2011).



Scheme 1.5: The proposed reaction mechanism for synthesis of cyclic carbonates using TBAB and DMC (Kumar *et al.*, 2011).

The synthesis of cyclic carbonate under solvent free condition is typically conducted using supercritical CO_2 as both reactant and solvent. Hence it is an alternative route to replace conventional solvents. Supercritical CO_2 enhances the reaction rate because the boundary of vapour-liquid changes to supercritical uniform phase. The supercritical CO_2 property is easily tuned by the applied pressure and temperature. The miscible CO_2 is easy to penetrate and reacts with the epoxide (Kawanami and Ikushima, 2000; Sako *et al.*, 2002).

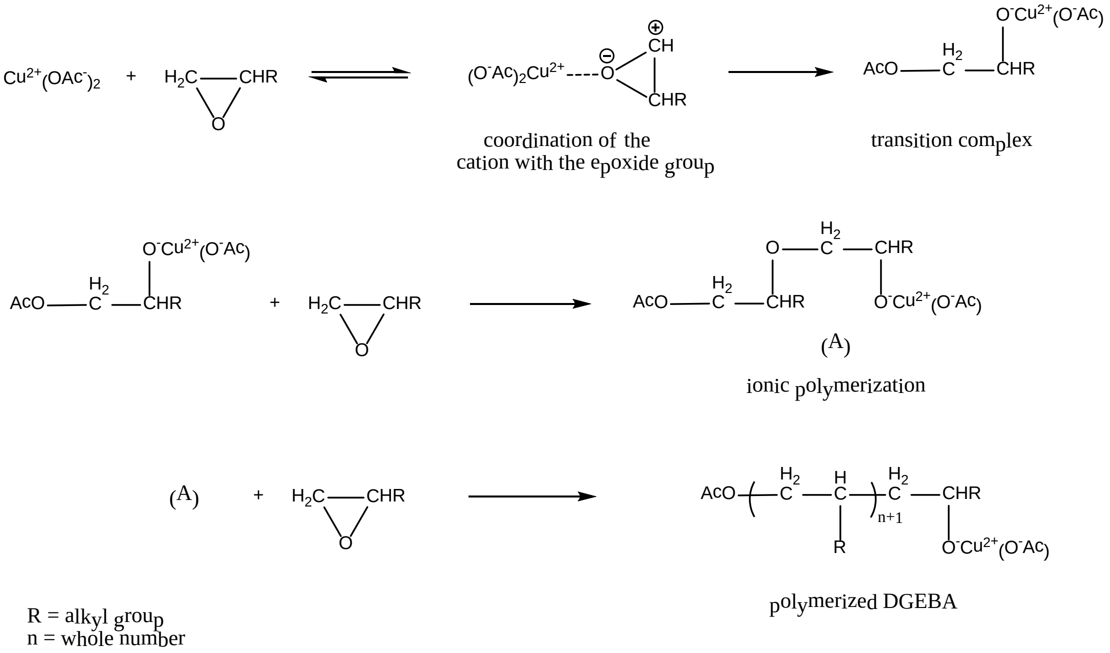
Various types of simple epoxide were used in the cycloaddition reaction such as 2-methyloxirane (Sako *et al.*, 2002), propylene oxide and epichlorohydrin (Xiong *et al.*, 2013). The cycloaddition with industrial epoxide *i.e* diglycidylether of bisphenol A (DER 331) is obtained using ruthenium chloride ($RuCl_3$) as alkali metal halide catalyst supported on co-catalyst of tetraethylammonium bromide (TEAB). At both normal pressure and supercritical CO_2 condition *i.e* pressurized CO_2/Ar gas mixture produces high product conversion and selectivity. While using $RuCl_3$ without any co-catalyst or supported on SiO_2 produces good conversion respectively as compared to TEAB. The use of polyphosphostungstic acid (HPW) as co-catalyst enabled DER 331 to be converted to polycarbonate at similar experimental conditions (Gomes *et al.*, 2008).

The cycloaddition reaction of liquid epoxidized deproteinized natural rubber (LEDPNR) in super critical CO_2 condition in the presence of LiBr catalyst has been reported. The reaction produces novel, natural, organic polymer with the isoprene unit and polar carbonate group in the polymer chains. The removal of catalyst is not necessary because it can be a component in electrolyte media for lithium ion battery (Kawahara and Saito, 2006).

1.3.4 Epoxy/Metal Complex Formation

The coordination of aluminium with the epoxide group is obtained from the reaction of triethylaluminium and diastereomeric 2-methyl-3,4-epoxy alcohol. The cleavage of epoxide is obtained from a formation of tetracoordinated aluminium-oxygen. A stereochemical disposition of the substituents proceeds through a bidentate aluminium complex by promoting the attack at the most substituted epoxide carbon (Torres *et al.*, 2012).

The epoxide group of diglycidyl ether of bisphenol-A (DGEBA) is able to coordinate with the copper cation of copper acetate. Copper acetate works as hardener and later cures DGEBA. It reacts with epoxide of DGEBA through the coordination of the copper cation with the epoxide group and later formed a transition complex. The transition complex acts as initiator of ionic mechanism for the ring opening polymerization of the epoxide as shown in Scheme 1.6. The chelation mechanism depends on the equilibrium process of dissociation of the chelate at a certain particular temperature and a concentration of the copper acetate (Ghaemy *et al.*, 1999).



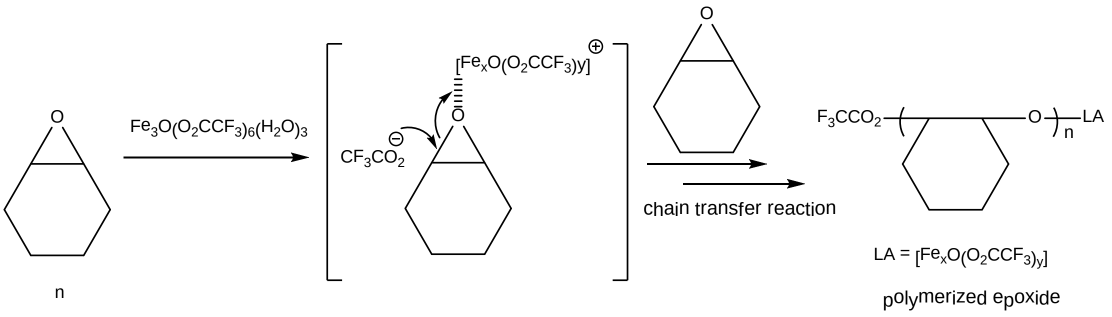
Scheme 1.6: Ring opening polymerization of the epoxide through coordination of the cation with epoxide group (Ghaemy *et al.*, 1999).

A series of copper(II) coordination polymers (CPs) was derived from *bis*-pyridyl-*bis*-urea ligands. These CPs use oxalate, succinate and 2,6-napthalene dicarboxylate as co-ligands in the systems. The CP was used as catalyst for ring opening methanolysis of various simple epoxides such as cyclopentene-oxide, cyclohexene-oxide, styrene oxide, *trans*-stilbene oxide and *cis*-stilbene oxide. The reaction is facilitated by hydrogen bonding interaction between epoxide and functionality of urea as co-ligand. This interaction brings epoxide in close proximity of the catalytic Cu(II) in the CPs structure (Banerjee *et al.*, 2012).

The epoxide group of glycidyl esters of phosphoric acids (GEPs) is cured using various types of rare-earth elements (REE). The cured polymer is optically transparent with required refractive index and high concentration of REE. Anhydrous or hydrated REE chlorides, nitrates and sulphates were used in GEPs production.

The rate of curing process depends on salt content, cation, anion, GEP structure, curing temperature and moisture content. For example, the incorporation of gadolinium salts in GEPs will increase the T_g of the cured polymer while maintaining its hardness (Amirova *et al.*, 2003).

In small amount, mixed-valent iron trifluoroacetate complex $[Fe_2^{III}Fe^{II}(\mu_3\text{-}O)(O_2CCF_3)_6(H_2O)_3]$ is an effective catalyst for a ring opening polymerization (ROP) of epoxide. The employed epoxide monomers are cyclohexane oxide, cyclopentene oxide and epichlorohydrin. The reaction mechanism involves Lewis acid catalyzed anionic polymerization in the presence of a nucleophilic anion. A coordination of $[Fe_xO(O_2CCF_3)_y]^+$ cation with oxygen of the epoxide activates the epoxide ring opening reaction towards nucleophilic addition. While the counter anion $[CF_3CO_2]^-$ functions as a nucleophilic initiator. This reaction is followed by some chain transfer reactions to produce polymerized epoxide as given in Scheme 1.7 (Ertürk *et al.*, 2012).

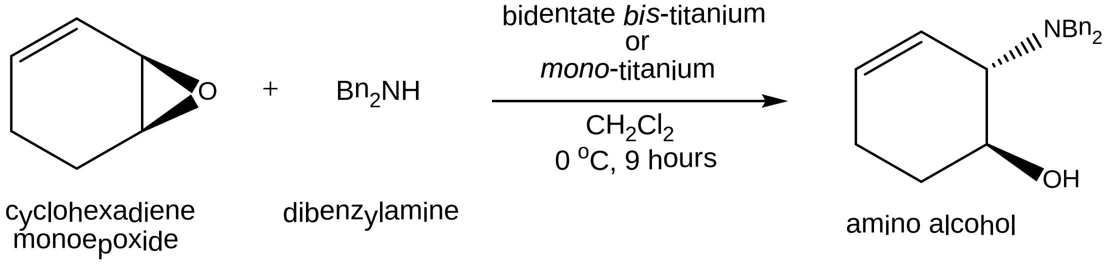


Scheme 1.7: Lewis acid-catalyzed anionic reaction mechanism proposed for $[Fe_3O(O_2CCF_3)_6(H_2O)_3]$ catalyzed epoxide polymerization (Ertürk *et al.*, 2012).

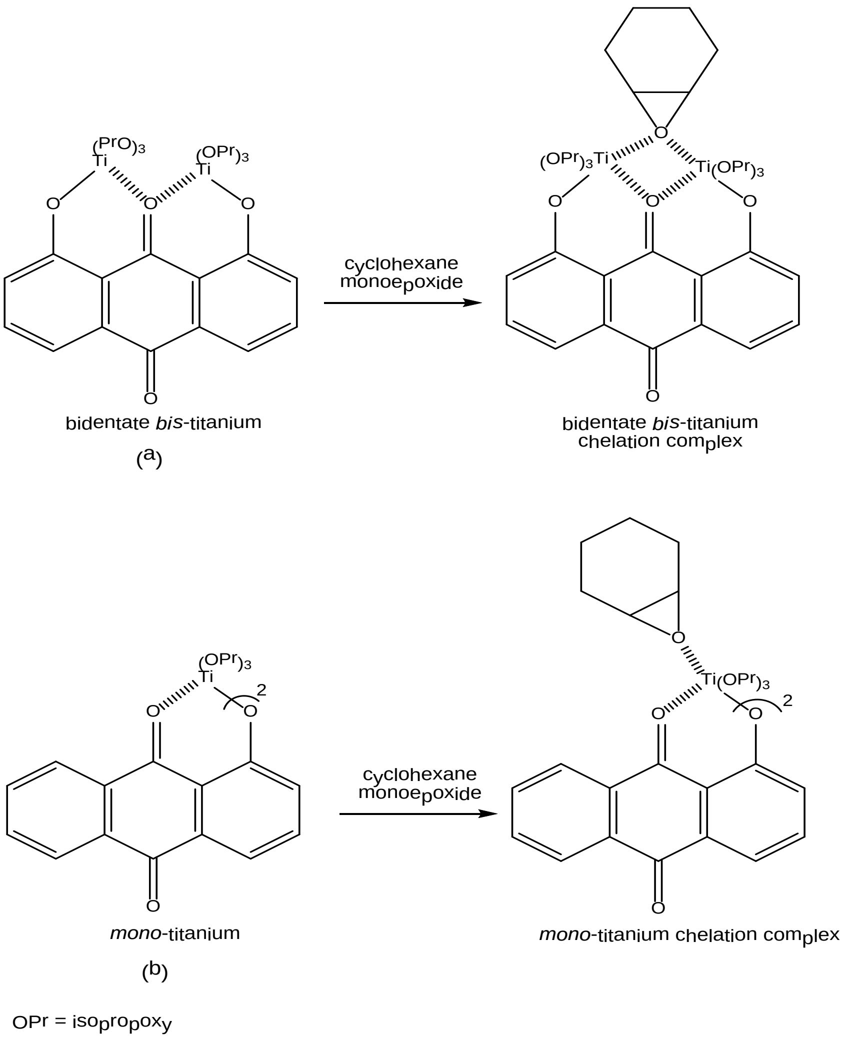
The ROP is carried out using organotin phosphate (Bu_2SnO-Bu_3PO_4) condensate using two types of monomer *i.e* monofunctional and bifunctional epoxide. The steric effect of the monofunctional monomer was studied using monosubstituted and disubstituted epoxide monomers. The ROP results show that the monosubstituted epoxide monomer give high product conversion while disubstituted epoxide monomer was considerably low and produce mixture of products in moderate yield. The ROP reaction using bifunctional epoxide produces polyether with the epoxide ring in the side chain (Iwasa *et al.*, 2008).

The epoxide ring opening of cyclohexadiene monoepoxide with an amine base is obtained using bidentate *bis*-titanium or *mono*-titanium catalyst as shown in Scheme 1.8. The reaction with bidentate *bis*-titanium catalyst produces 73% of amino alcohol while *mono*-titanium produces 3% alcohol under identical reaction conditions. The high catalytic activity of *bis*-titanium catalyst is due to two titanium metal centers in its structure and hence two sites of Lewis acidity as compared to the *mono*-titanium catalyst. Thus, bidentate *bis*-titanium is able to form chelation complex with cyclohexane monoepoxide through double coordination. While *mono*-titanium is through single coordination as shown in Scheme 1.9 (Asao *et al.*, 1998).

The ring opening of epoxide from tetra(2,3-epoxypropoxysilane) with dicyclopentadiene titanium dichloride (Cp_2TiCl_2) is obtained through free radical polymerization combined with coordination polymerization. The free radical species Ti(III) is end-capped at the epoxide ring of the polymer chains. This locates a non-pair electron at most hindered epoxide carbon which later reacts with copolymer through coordination polymerization to produce the 4-armed hydroxyl-functionalized copolymer (Sheng *et al.*, 2014).



Scheme 1.8: Epoxide ring opening of cyclohexadiene monoepoxide using titanium catalysts (Asao *et al.*, 1998).



Scheme 1.9: (a) Bidentate *bis*-titanium and (b) *mono*-titanium catalysts and their respective chelation complex of cyclohexane monoepoxide (Asao *et al.*, 1998).