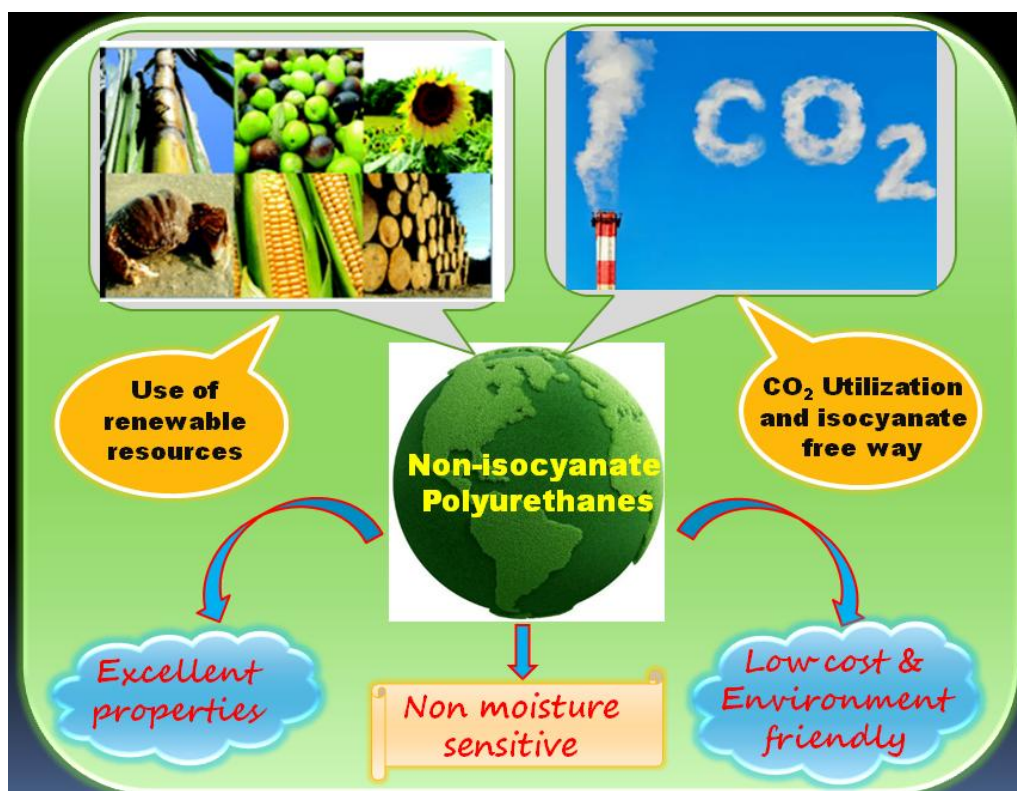# Chapter 1

General Introduction

Motivation and literature review on isocyanate-free polyurethanes from renewable sources by utilizing greenhouse gas CO_2 are described in this chapter.

1.1 Motivation

Polymers are one of the main significant materials which are used in various purposes. Currently, the majority of the polymers are synthesized from fossil-based sources. In respect of the environmental problems and diminution of fossil resources, polymer from renewable resources is receiving remarkable interest in both industrial and academic research [1–3]. The utility of agricultural resource as renewable feedstock has gained tremendous popularity in recent years. For instance, in the chemical industry, the most extensively use sustainable raw materials are vegetable oils, sugars, wood, cellulose, starch and others [4,5].

Out of all, the vegetable oils reveal a favorable path towards the synthesis of renewable chemicals and polymers. They are broadly used in a variety of applications owing to their worldwide availability, less expensive, and eco-friendly [6,7]. Vegetable oils consist of ester and different long chain saturated and unsaturated fatty acids with C=C that can be chemically functionalized into different products. A lot of vegetable oils are used in the production of several polymeric resins like epoxy, polyesteramide and polyurethanes (PUs) etc. [8]. Among the different types of vegetable oil based polymeric resins used in modern day's society, PUs is one of the most significant groups of polymeric materials. PUs with a worldwide production of around 18 million tons in 2016 is used in many applications including coatings, soft or rigid foams, medical devices, adhesives and textile industry due to their tailoring properties [9]. Traditionally, PUs are manufactured by the polymerization reaction between short and long chain polyol and polyisocyanate which are petroleum-based [10]. In recent times, PUs has been synthesized from various bio-based polyols which can compete with the conventional ones. These bio-based polyols are mainly synthesized from different types of vegetable oils like soybean oil, jatropha oil, tung oil, linseed oil and castor oil etc. *via* special chemical modifications like the ring opening of the oxirane groups, ozonolysis, trans-esterification and thiol-ene reactions [11–14].

Meanwhile, isocyanates are very harmful chemicals and prepared from the reaction of an amine with phosgene which is an extremely toxic gas. The isocyanates can cause serious health problems such as respiratory, skin irritation and asthma problems [15,16]. Since isocyanates are petroleum dependent as well as highly toxic chemicals, so from the viewpoint of environment-friendly, health and economy, development of non-

isocyanate PUs (so-called NIPUs) mainly those made from renewable resources is very important. Several methods have been developed to synthesis isocyanate-free PUs. Among them, the most well-known substitute way is the reaction of the cyclic carbonates with amines, which results in the formation of NIPUs with hydroxyls group on the carbon chain [17–20]. The cyclic carbonates are easily obtained by the treating an epoxides group containing compounds with CO_2 [21,22]. CO_2 is considered as one of the major greenhouse gases which cause global warming and the major climatic concerns in the twenty-first century. For this reason, from the perspective of environmental protection, resource utilization and economic, the valorization of CO_2 for the manufacturing of value-added material is extremely beneficial [23–25].

Therefore, the utility of renewable resources and CO_2 are the very essential steps towards sustainable development in the era of depletion of fossil resources and a rising emission of greenhouses gases.

1.2 Classical polyurethanes (PUs)

PUs are an exceptional group of polymeric material which is globally the sixth most extensively used polymer. This unique polymer demonstrates excellent mechanical and physical properties like abrasive resistance, flexibility, chemical resistance, toughness and durability etc. In the 1940s, Otto Bayer (also known as the "father" of PU) and his colleagues developed PU by the reaction of a polyester diol with a diisocyanate [26]. The PUs commonly found application in adhesives, elastomers, coatings and rigid foams by the mid 1950s. The commercialized flexible PU foam was first synthesized from the reaction between polyester polyols and toluene diisocyanate when some amount of water was accidentally introduced into the reaction mixture in the year 1954.

Along with the presence of major repeating unit NHCOO- group (so-called urethane linkage) in PUs, it also contains other groups like ethers, urea, some aromatic compounds and esters [27–29]. Hence, PUs exhibit versatile properties which can be tailored by using different sources from which PUs are synthesized. Besides, by using additives and controlling reaction conditions during the synthesis process, PUs with particular properties can be synthesized for various applications. Based on their properties, PUs can be classified into different classes such as thermoplastic, elastomers, rigid, flexible, waterborne, coating and adhesives (**Fig. 1.1**) [10].
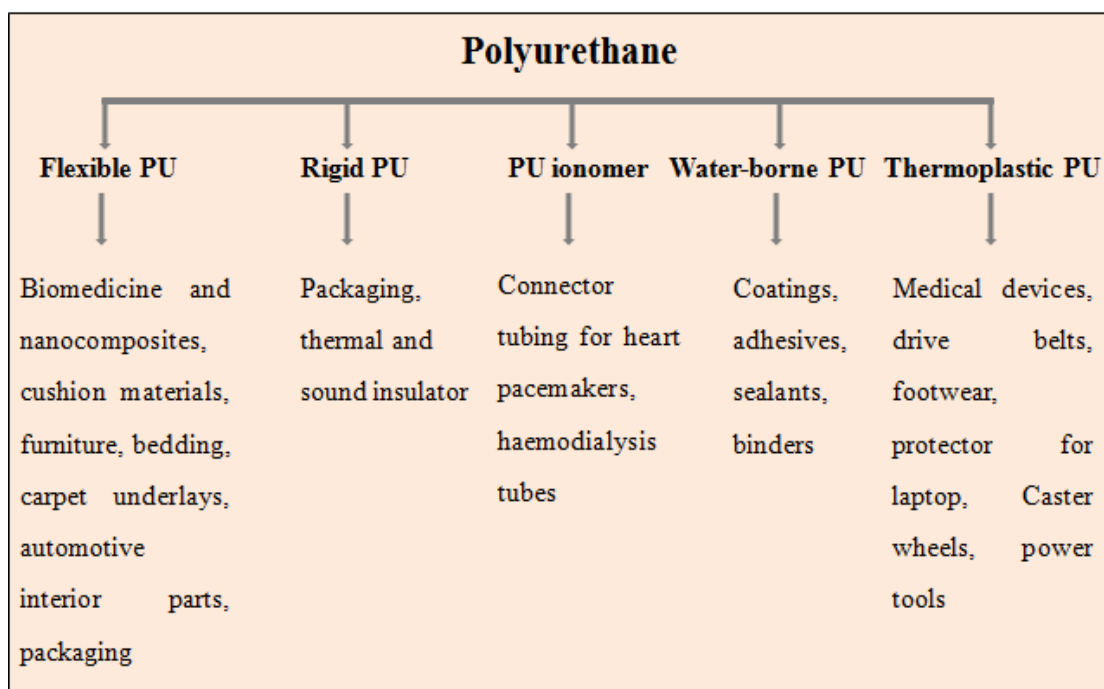
Fig. 1.1: Different types of PUs and their applications [10].

1.2.1 PU market

From its invention, PUs have rapidly developed to one of the most extensively used polymers everywhere in everyday life with a constantly spreading worldwide market. According to Research and Markets, the PUs industry dominates a diverse business area with a global market of approximately 13,650.00 kilotons in 2010 and reached 17,946.20 kilotons by 2016 [31]. With the average yearly growth rates 2.5%, the market demand has been gradually increasing in Europe [32].
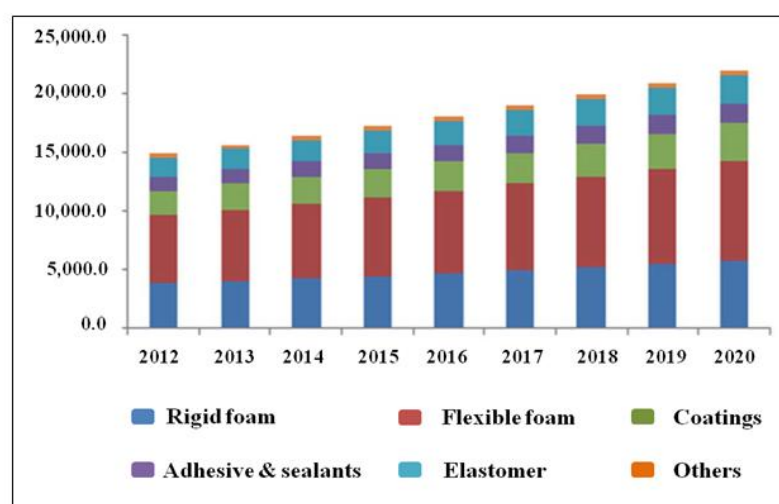

Fig. 1.2: Global production of PUs and an estimated forecast till 2020 [30].

Around 95% of the worldwide PUs requirement was lead by Europe, North America and Asia-Pacific. Mostly PUs market is predominated by furniture and interior industry accounting for 28.01%, followed by the construction industry, which accounted for 24.98% of the total demand in 2010 [31,33]. **Fig. 1.2** shows the global production of different types of PUs and an estimated forecast till 2020.

1.2.2 Chemistry of PUs

PUs are often called "reaction polymers", that can be obtained by the polymerization reaction between polyisocyanates and polyols in the presence of base catalysts like dibutyltin dilaurate (DBTDL), triethylamine (TEA), 1,4-diazabicyclo[2.2.2]octane (DABCO), and diethyltin dicaprylate (DETDC) etc [27]. Various kinds of polyols (**Fig. 1.3**) are used to synthesis PUs which can be synthesized in laboratories. As an example, polyester polyols are mainly synthesized by the reaction of phthalic anhydride or carboxylic acid with a hydroxyl group. The copolymerization of propylene oxide and ethylene oxide in the presence of appropriate polyol precursor yields polyether polyols [35,36]. Nowadays, various types of bio-based polyols for example tannic acid and vegetable oils etc. are used as a sustainable precursors for PU synthesis [37].
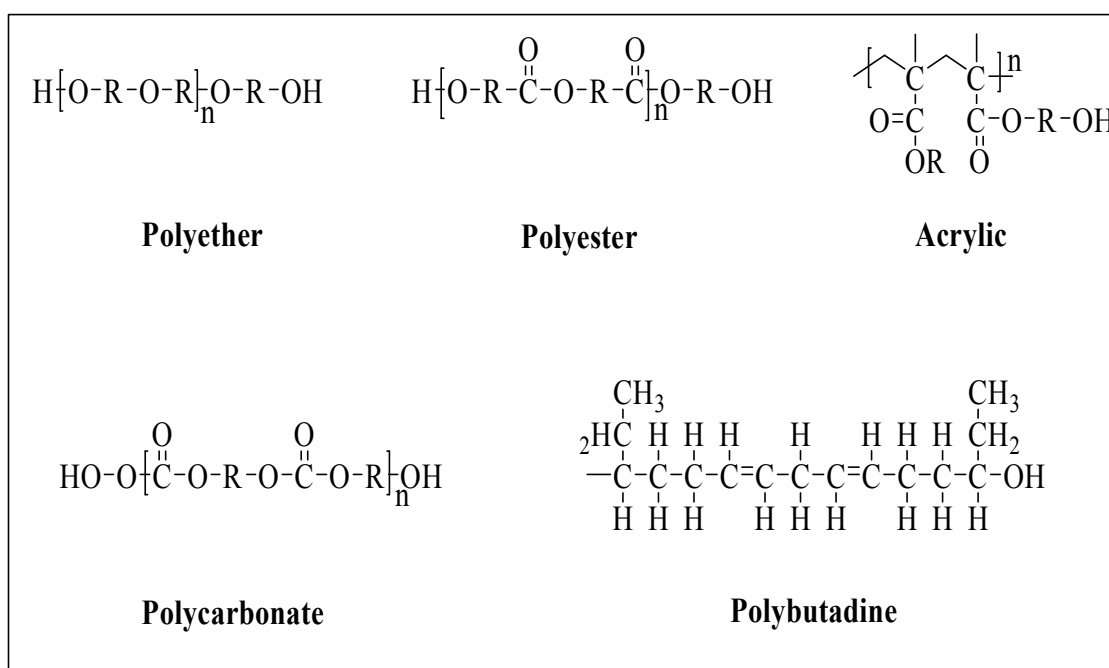

Fig. 1.3: Structure of different types of polyols [34].

The chemical structure of commonly used diisocyanates like hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), toluene diisocyanate (TDI), methylene diphenyl diisocyanate (MDI), dimethyl methylene diphenyl diisocyanate (DMMDI), o-tolidine diisocyanate (TODI), 1, 3 phenylene diisocyanate (MPDI) and dianisidine diisocyanate (DADI) are shown in **Fig. 1.4** [27]. The isocyanates are introduced into the PU synthesis process by preparing PU prepolymer with NCO terminated groups that are produced from the reaction between a polyol and an excess amount of diisocyanate and then this prepolymer is added to another polyol as a chain extender [38]. Due to the slow rate of the reaction, an appropriate catalyst is needed to increase the electrophilic nature of isocyanate and hence get a faster reaction rate. Depending on the types of polyols and isocyanates, the PUs exhibit different properties [27]. Soft and flexible PU foams are made from polyols with high molecular weight and low molecular weight (a few hundred units) respectively. The hard PUs are achieved from short chains isocyanates and polyols with high cross-linking and elastic PUs are acquired by using longer chains polyols and isocyanates with low cross-linking [36].
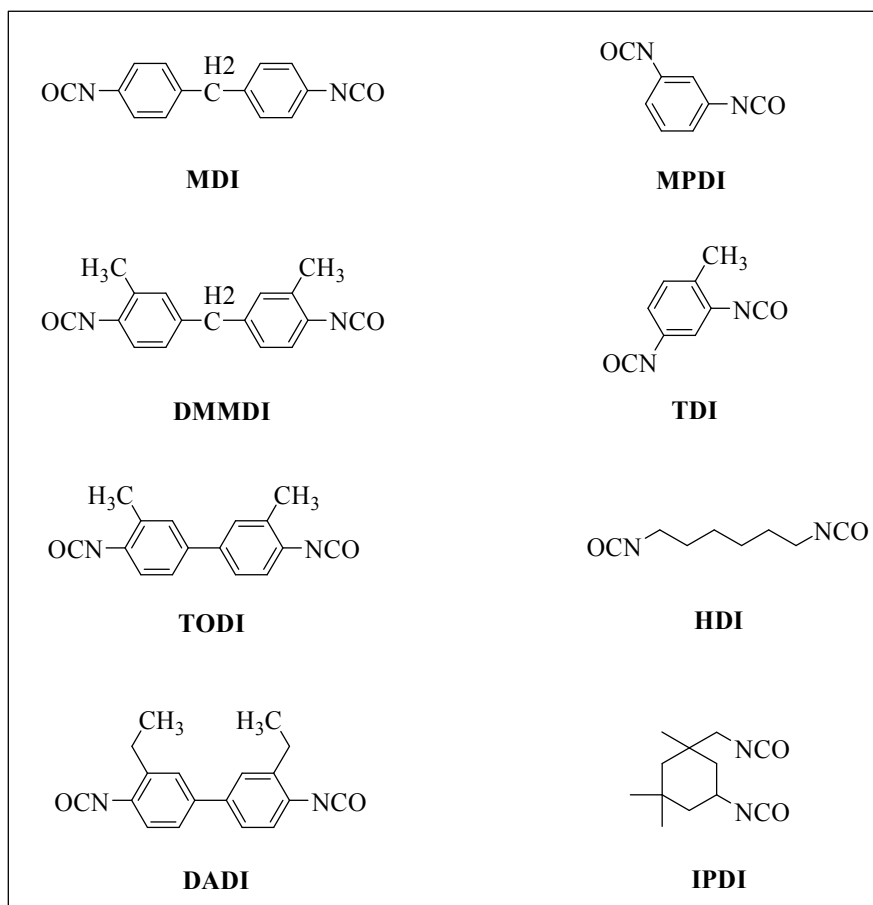

Fig. 1.4: Chemical structures of some essential isocyanates [27].

1.2.3 Drawbacks of classical PUs

For industrial applications, PUs are prepared through a two-step approach called prepolymer method (**Scheme 1.1**). However, the use and production of these isocyanates monomer are associated with serious environmental and health issues. Commonly, the isocyanates are synthesized from amine and phosgene, that is an extremely poisonous gas and contact with it can lead to serious respiratory problems, skin and eye burning, irritation, and even death [15,16]. Regarding the use of isocyanates, even low concentrations can cause very injurious effects on human health like dermatitis, asthma, and acute poisoning. Furthermore, general isocyanates namely MDI and TDI can go into the human body by skin or inhalation, and can quickly react with the functional groups like thiol, hydroxyl and amine groups present in the biomacromolecules which compose the human body [20]. Some isocyanates are recognized as mutagens, carcinogens or toxic and MDI should not be exceeded by 0.10 wt % in a component of mixtures [39,40].
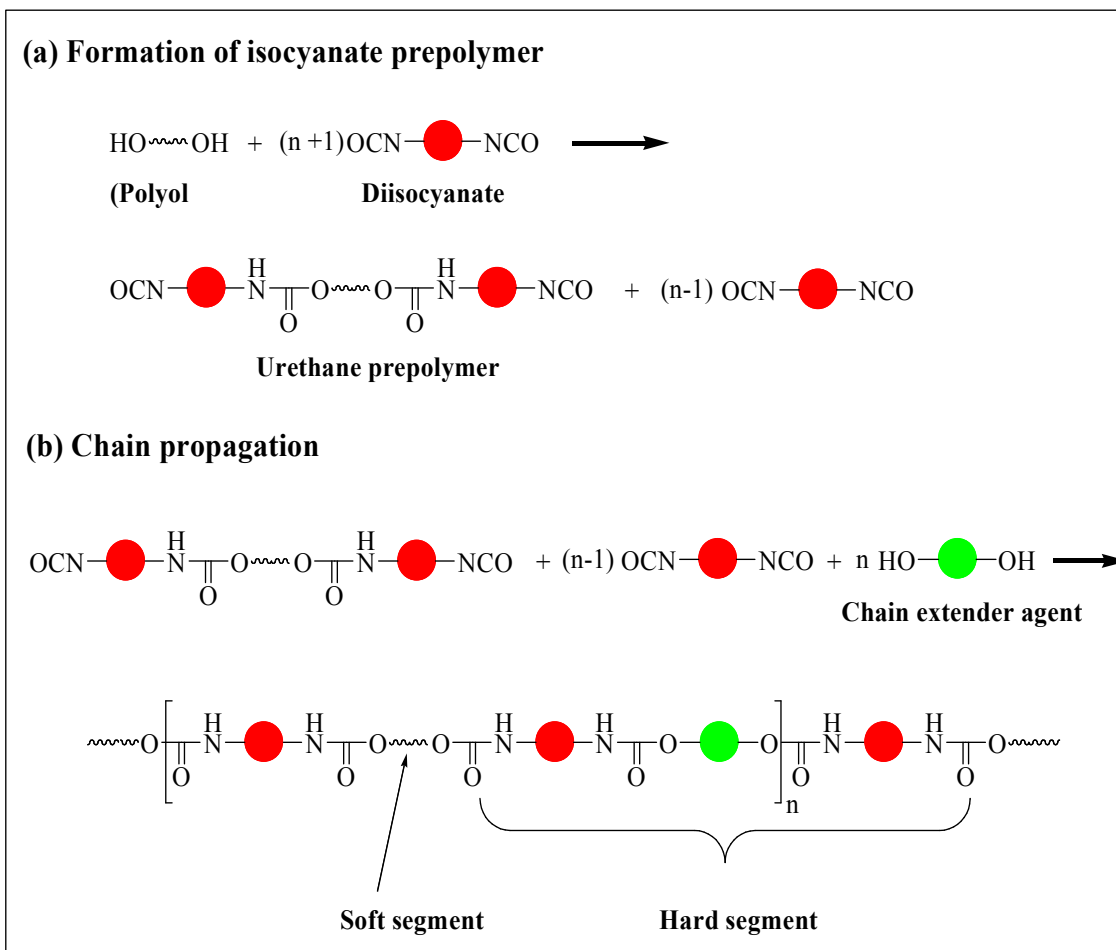
Scheme 1.1: Two-step synthesis of procedure of traditional PU [38].

Due to the electrophilic nature of the isocyanates, they are highly reactive towards the water and other chemical compounds. In general, isocyanate can form urea and CO_2 by irreversible reaction with water resulting in an unusable product [41]. For that reason, during the synthesis of PU, extreme precaution is needed. Many injurious chemicals like amines and isocyanates etc. are produced and released to the environment at the time of recycling and disposal of the isocyanate-based PUs [42].

Therefore, development of an isocyanate-free pathway is most important to prepare PUs, especially from renewable resources.

1.3 Isocyanate-free polyurethanes (NIPUs)

In consideration of environmental and human protection, significant attention has been given to develop eco-friendly approaches for the production of PUs without the use of isocyanate. From the literature reports, four synthesis routes have been developed for the synthesis of NIPUs which are discussed below [40].

#### *1.3.1 Polycondensation method*

In the polycondensation route, NIPUs are mostly synthesized by the reaction between carbamates and alcohols or chloroformates and amines as shown in **Scheme 1.2**.
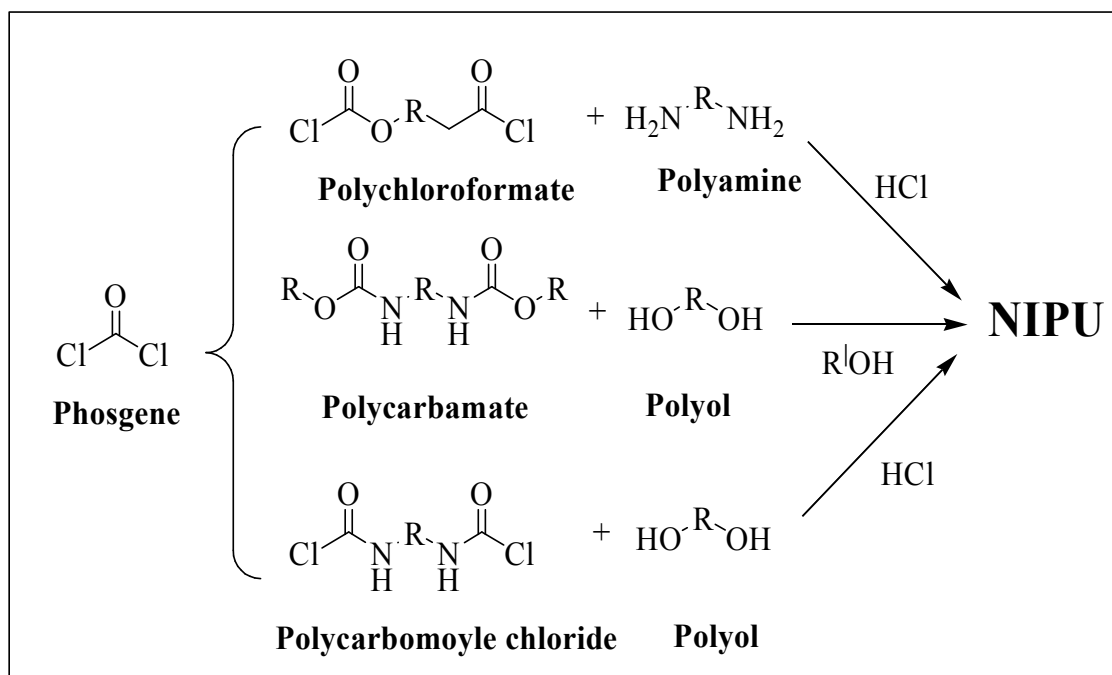
Scheme 1.2: Synthetic approach to NIPUs *via* polycondensation routes.

In 1963, Morgan developed non-isocyanate [n,m]-PUs by using alkylene bis(chloroformate)s and diamines at room temperature [43]. More recently, by utilizing AB-type self-polycondensation reaction More et al. synthesized bio-based NIPU from fatty acid derived acyl azides [44]. However, the use of phosgene as a raw material is the main problems in this method. Additionally, the releases of side products like HCl or alcohols during synthesis are the shortcomings for industrial applications [40].

### 1.3.2 Rearrangement method
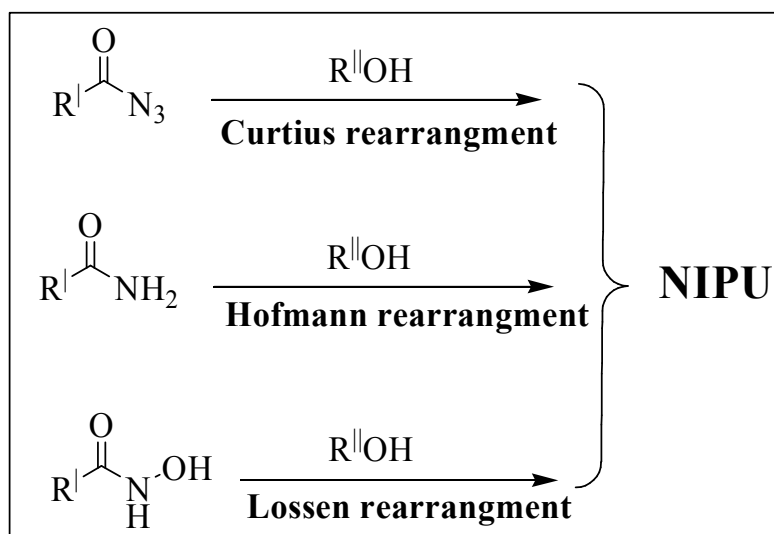
Scheme 1.3: Synthetic approach to NIPUs *via* different rearrangements.

The popular rearrangement reactions namely, the Hoffman, Curtius, and Lossen rearrangement of carboxamides, acyl azides, and hydroxamic azides respectively are used to synthesis NIPUs (**Scheme 1.3**) [45–49]. In these rearrangements, isocyanates are formed as reaction products; consequently, it reacts with alcohols to produce PUs. In 1909, Stoermer first developed aromatic PU by using the Curtius rearrangement of p-hydroxybenzoylazide [50]. While heated acylazides (p-hydroxybenzoylazide), it undergoes the Curtius rearrangement to form isocyanates in non-hydrolytic solvent. The produced isocyanates further react with OH groups of phenol to give polyurethane [51]. Recently, Neumann et al. synthesized NIPU foams in the absence of water *via* Curtius rearrangement [52]. The blowing agent used here was nitrogen which is produced by using the Curtius rearrangement. Although the isocyanate precursor used here is produced through *in situ*, the use of chemicals like carboxamides, acyl azides and hydroxamic azides remains a major problem.

1.3.3 Ring opening polymerization (ROP)

The NIPUs are also synthesized by ROP polymerization of aziridines or aliphatic cyclo-carbamates (**Scheme 1.4**) [53–57]. Generally, strained rings cyclic urethanes are used to obtain straight [n]-PUs (n = 3 or 4). For the first time, Hell and Schneider used cyclic urethanes precursor to polymerize into PUs by using N-Acetyl-2-oxohexamethyleneimine and NaH as a catalysts in the year 1958[58]. Hoecker and his group prepared [n]-PUs *via* ROP polymerization of 6 or 7-membered cyclic urethanes by using organometallic catalyst along with brønsted acids [53,54]. However, these cyclic carbamates are obtained from phosgene. Hence, even though in this method NIPUs are produced with no side-products, the use of cyclic carbamates and aziridines are the main problems to overcome**.**
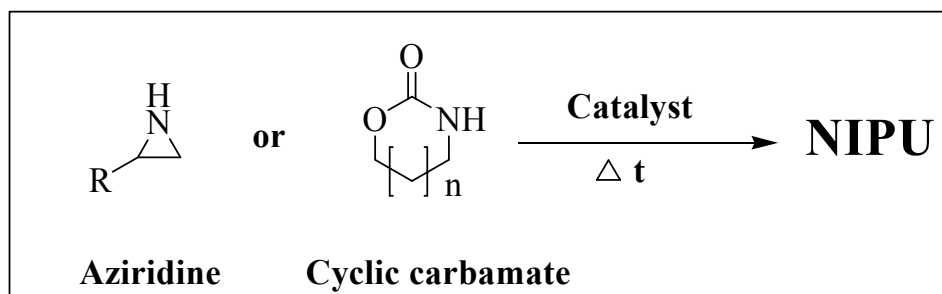

Scheme 1.4: Synthesis of [n]-PU by ROP of cyclic urethane or aziridine.

1.3.4 Polyaddition between cyclic carbonates and amines

Among the non-phosgene and non-isocyanate methods of the NIPUs preparation, the most advantageous and the best possible way is the polyaddition reaction between the polycyclic carbonates and polyamines [59–63]. NIPUs synthesized in this way contain extra primary and secondary hydroxyl groups in the main polymer chain, as shown in **Scheme 1.5** and hence, the resulting polymer is also termed as poly(hydroxyurethanes) (PHUs as well as NIPUs). In 1957, Drechsel and Groszos first developed PHUs (or NIPUs) by using this methods from the cyclic carbonate and amine [64].

Figovsky and his groups suggested a comprehensive list of NIPUs (PHUs) patents that are of tremendous interest to industrial companies [65]. The structure of NIPUs with the additional hydroxyl groups differs from conventional PUs affects the properties of NIPUs [20]. The hydroxyl groups produced in this reaction can formed inter and intramolecular hydrogen bonds and display better thermally stable owing to the

inexistence of unstable biuret and allophanate groups [66]. The NIPUs prepared in this way demonstrate numerous benefits. Here, the cyclic carbonate precursors can be easily obtained by the fixation of CO_2 with an epoxide containing compounds [67–70]. The non-moisture sensitivity as in the traditional methods is also an advantage of this method. Furthermore, the reactive pendant hydroxyl groups of NIPUs can be further by functionalized with chemical and biological functionalities [71].
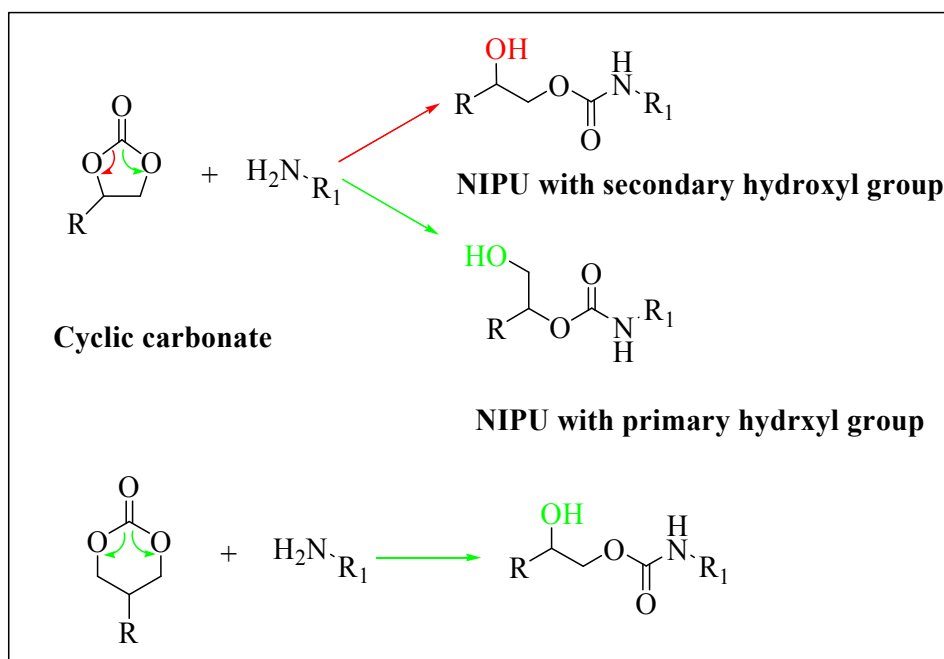
Scheme 1.5: Aminolysis of cyclic carbonate to produce NIPUs.

So, among the different synthetic ways of NIPU synthesis, the polymerization of polycyclic carbonates with amines is the greenest and beneficial one. Moreover, major industries of PUs such as BASF, Huntsman and DOW give serious interest to manufacture NIPU or H-NIPU (hybrid NIPU) by using this technology. Furthermore, recently, Polymate, PPG, Wacker, Henkel, American Cyanamid, Solvay, Kansai Paint, and Hoechst have filed patent applications of NIPUs (or PHUs) [40].

1.3.4.1 Five-membered cyclic carbonates: The precursors for NIPU synthesis

In the polyaddition route, the most important chemicals used for the production of NIPUs are five-membered cyclic carbonate based compounds. However, NIPUs can also be prepared from five and six-membered cyclic carbonates which are highly reactive and their synthesis process usually requires phosgene-like hazardous reagents [72,73]. In early 1933, the group of Carothers first developed various sized cyclic carbonate

intermediates [74,75]. The cyclic carbonates have a lot of applications such as reactive diluents, lithium-ion batteries, surfactants and plasticizers. The five-membered cyclic carbonates are mainly synthesized from halohydrins, halogenated carbonates, diols, substituted propargyl alcohols, olefins, and mostly from epoxy derivatives and CO_2 by using various synthetic approaches [76,77]. The most important methods are shown in **Scheme 1.6.**

It is found that among the different kinds of approaches, the catalytic conversion of epoxy compounds by reacting it with CO_2 is most extensively used to prepare cyclic carbonates. Various research groups have extensively studied a range of catalyst including halogenated salts, metal complexes, ionic liquids, halides, ion-exchange resins, etc. and optimized different reaction conditions [63,77–79]. With regard to environmental and economic concern, this mentioned method possesses various advantages in comparison to other routes. The utilization of greenhouse gas CO_2 instead of the diisocyanates and phosgene is the main advantage of this method.

Recently, various bio-based starting chemical molecules such as vegetable oils, gallic acid, isosorbide, resorcinol, sorbitol, glycerol, vanillin, trimethylolpropane, furfuryl alcohol, tannic acid, cardanol and pentaerythritol have been extensively used to get cyclic carbonates and consequently utilize it to synthesize NIPUs. Some literature reviews on the synthesis of NIPUs from bio-based starting material are discussed below.

Bähr et al. (2012) synthesized novel cyclic limonene (CL) dicarbonate from epoxidized limonene and CO_2 (30 bar) at 140 °C by using tetrabutylammonium bromide (TBABr) and silica supported 4-pyrrolidinopyridinium iodide as a homogeneous catalyst and heterogeneous catalyst respectively. Limonene is originated naturally from greater than 300 plants and by-product of citrus fruits. The prepared CL dicarbonate was used as a precursor for the preparation of a series of NIPUs by using various diamines namely 1,4-butane diamine (BDA), isophorone diamine (IPDA), 1,6-hexamethylene diamine (HMDA), and 1,12-dodecane diamine (DADO) as curing agents. The obtained NIPUs showed satisfactory young's modulus and glass transition temperature (Tg) [80].

Besse et al. (2013) derived isosorbide-based cyclic carbonates from renewable isosorbide by coupling of 0.6 MPa CO_2 pressure with epoxidized isosorbide at 80 ^{0}C. Then, the isosorbide-based cyclic carbonates were cured by various diamines (viz diethylenetriamine (DETA), 1,10 diaminodecane (DA10), IPDA, and jeffamine D-400)

to get NIPUs. The resulting NIPUs displayed degradation temperatures (5% weight loss) between 234 °C and 255 °C and Tg varied from -8 °C to 59 °C. Furthermore, the authors investigated the degradation of these NIPUs by using ATR-FTIR procedure and found that secondary amines and CO_2 were produced during the degradation process [81].
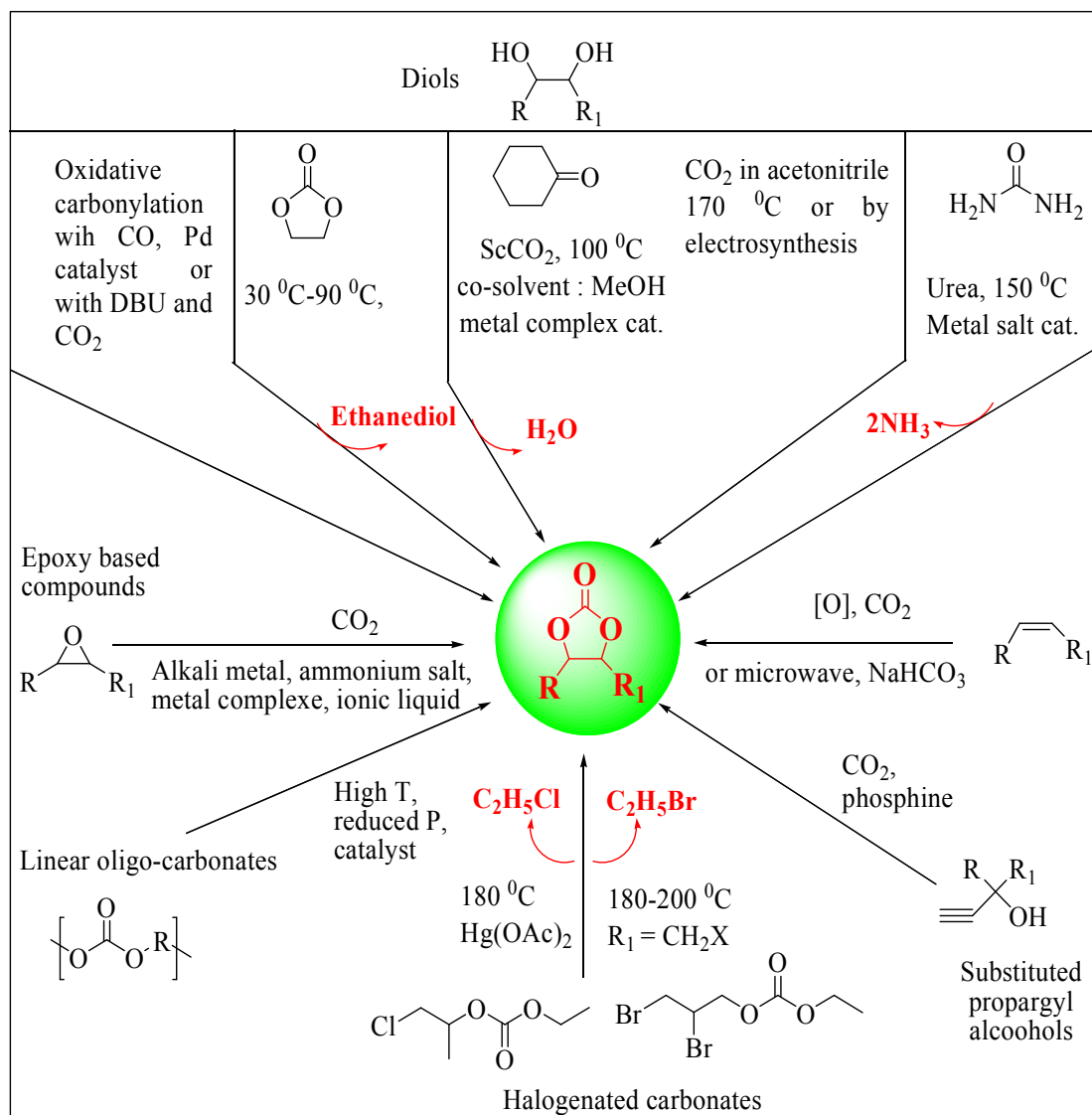
Scheme 1.6: Synthetic methodologies of five-membered cyclic carbonates [76].

Chen et al. (2015), prepared lignin-based cyclic carbonate from CO_2 and lignin, the most abundant naturally occurring aromatic moieties. Firstly, bisphenol was synthesized from creosol and formaldehyde through condensation reaction in the existence of lignosulfonic acid as the catalyst. Finally, NIPUs were prepared by the reaction of cyclic carbonate based on lignin and glycerol with IPDA and HMDA [82].

Blattmann et al. (2016) prepared cyclic carbonates by reacting CO_2 (10 bar pressure) with bio-based trimethylolpropane polyglycidylether (TMPGC) and ethoxylated trimethylolpropane polyglycidylether (EO-TMPGC) at 140 °C. Additionally, in this study, authors prepared fully bio-based stretchy NIPU foams from these resulting cyclic carbonate blends. The rigid trimethylolpropane based cyclic carbonates were blended and curing with HMDA by using fluorohydrocarbon (Solkane 365/227) as a blowing agent without ozone depletion ability. With increasing EO-TMPGC content, the prepared foams became flexible and soft and hence lowered viscosity, Tg and storage modulus [83].

Janvier et al. (2017) utilized renewable syringaresinol (SYR) as the raw material for synthesizing new bio-based based aromatic cyclic carbonate with high purity and yield. Authors revealed that syringaresinol can be used as a greener and safer substitute for the petroleum-based bisphenol A. At this work, syringaresinol based cyclic carbonate was cured with various diamines such as DA10, IPDA and tris(2-aminoethyl)amine (TREN), to obtain bio-based NIPUs. These NIPUs exhibited high molar mass (Mn = 5.4 kg mol^{-1}), Tg varied from 63 to 98 °C and good thermal stabilities (degradation temperatures, Td 5% = 267- 281 °C) [84].

The carbonation of epoxidized soybean oil (ESO) and epoxidized sucrose soyate (ESS) with CO_2 under supercritical conditions were carried out by Yu et al. (2019). The prepared poly(cyclic carbonates) was cured with the multifunctional amine to prepare bio-based NIPU coatings and then optimized the catalyst, solvents and temperature to get the best curing conditions. The addition of a secondary catalyst, i.e. a Lewis acid (LiOTf), and ethyl 3-ethoxypropionate (EEP) as a tailing solvent significantly enhanced the solvent resistance of the coating. Overall, the coating properties of the prepared NIPUs were improved due to the higher functionality of the carbonated sucrose soyate [85].

1.3.4.2 Chemistry of NIPUs

To understand the aminolysis reaction of the cyclic carbonates, a three step mechanism has been suggested by Garipov and his group as shown in **Scheme 1.7** [86,87]. The initial step of the reaction includes a nucleophilic attack on the carbonyl of five-membered carbonate by the amine to form a tetrahedral intermediate which is deprotonated by a second amine in the second step. In the last step, the C-O bond of the

intermediate breaks and results in the formation of urethane groups along with primary and secondary OH groups and the secondary OH group is the more predominant product (**Scheme 1.7, step 3**). Due to the more electron density at the nitrogen atom of the amine, the cleavage of C-O bond is preferred.
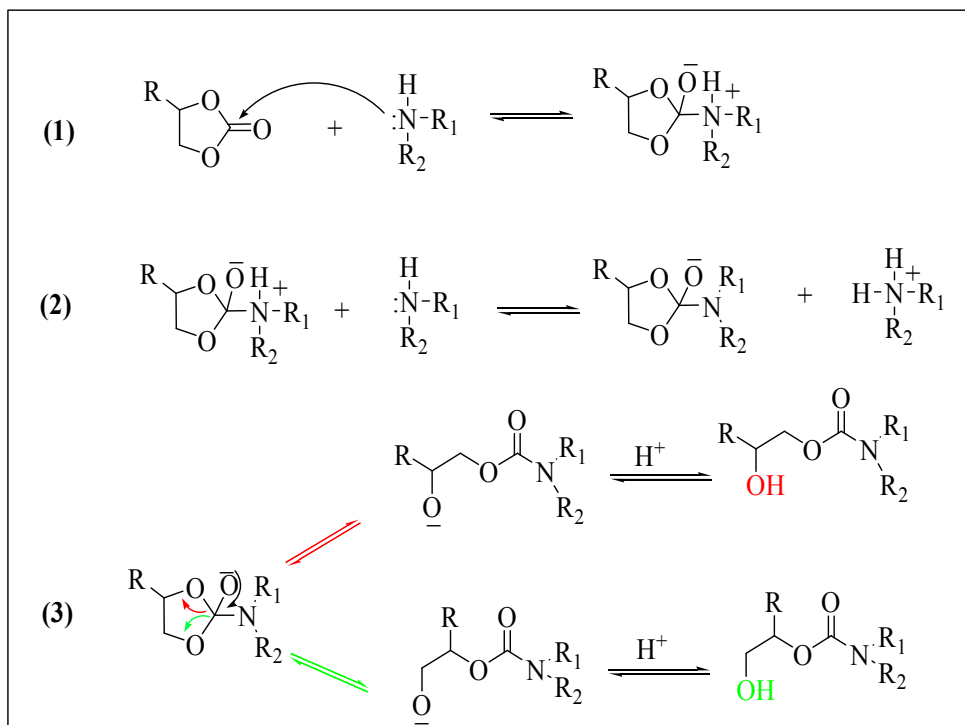
Scheme 1.7: Mechanism of NIPU formation *via* addition polymerization.

Steblyanko et al. found that the ratio of primary to secondary OH group product was in 18: 82 % resulting from the reaction between glycerine carbonate benzoate and benzylamine. Additionally for further confirmation, they had performed theoretical observations and found that enthalpically the NIPUs with secondary OH groups was better favored than the primary OH group by around 1.67 kcal mol^{-1} (primary OH product, $\Delta H_{f(OH)}$ = -8.10 kcal.mol^{-1} and secondary OH product, $\Delta H_{f(OH)}$ = -9.77 kcal mol^{-1}) [88]. On the other hand, only primary OH groups containing NIPUs are achieved when it is derived from six-membered cyclic carbonates (**Scheme 1.5**).

To carry out this polyaddition reaction of cyclic carbonates by amines, various catalysts such as organometallic catalysts, organic catalysts and salts have been used which are shown in **Fig. 1.5**. The Lewis base catalyst can attack on the carbon of carbonyl group which is a good leaving group that can promote the attack of the amine. In contrast, Lewis acidic catalyst can enhance the electrophilicity of the carbonate.

Different types of catalysts such as organometallic, organic and salts have been used to perform the aminolysis reaction [76]. Among all these catalysts, thiourea and triazabicyclodecene (TBD) are the most efficient catalysts for this aminolysis reaction of the cyclic carbonates [89,90].
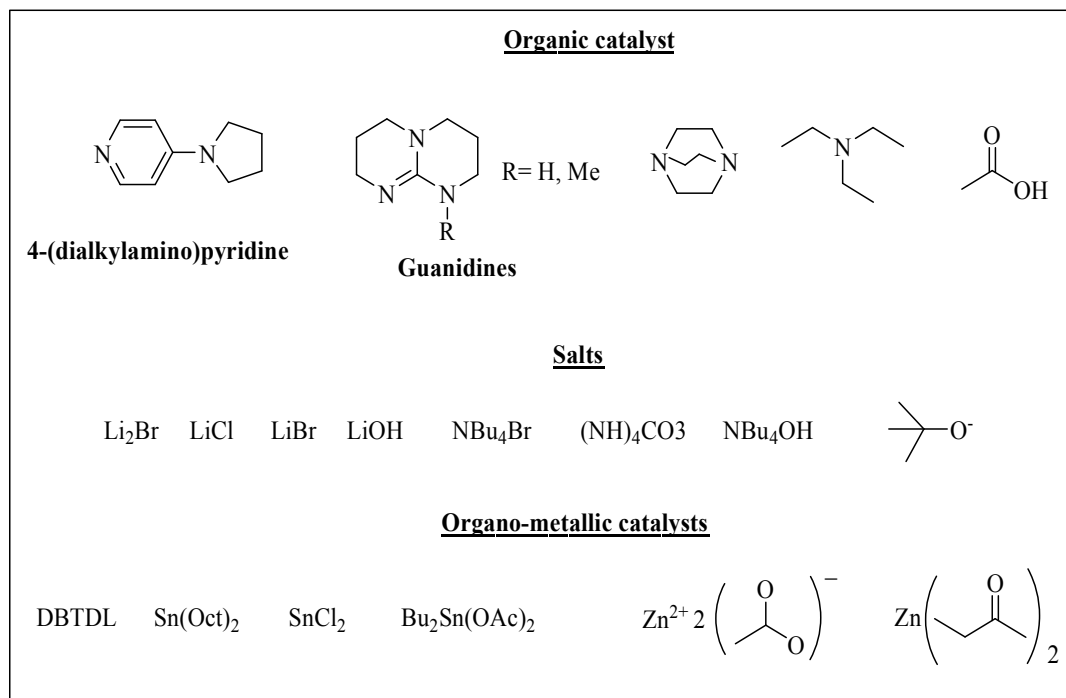

Fig. 1.5: Different types of catalysts used for the aminolysis of cyclic carbonate reaction [76].

The rate of this addition reaction is influenced by various factors, for example temperature, solvent and initial concentration of the reactants. The order of the reaction is second with respect to cyclic carbonate and amine, and the rate of reaction increase with the increment of temperature [91–93]. However, side products are formed above 100 °C [94]. The rate of reaction is also affected by the solvent. In protic solvents, the first step is more rapid and. On the other hand, the first step is the limiting step of the reaction in the case of aprotic solvents.

Several studies observed that the rate of aminolysis reaction of cyclic carbonate is controlled by the chemical structure of the amine. The secondary amines are less reactive towards the cyclic carbonates than the primary amines. Moreover, lower molar mass amines are more reactive than higher molar mass amines [86,94,95]. Various studies have been conducted to examine the effect of substituent of the cyclic carbonate on the

aminolysis of cyclic carbonate reaction rate [96]. Garipov et al. (2003) observed that the presence of electron withdrawing substituents (-I) enhanced the electrophilicity of cyclic carbonate and, hence faster nucleophilic attack of the amine occurred towards the cyclic carbonate. In contrast, the electron releasing substituent (+I) on the cyclic carbonates decreased the electrophilicity of cyclic carbonate and therefore lower the nucleophilic attack of the amine [86].

Another study examined that the size of cyclic carbonate can also control the kinetics of reaction rate. Endo et al. (2001) found that the rate of this aminolysis reaction of cyclic carbonate increased with enlargement in its size [97]. Hence the rate constant of seven, six and five-membered ring containing cyclic carbonates were 0.02, 1.19 and 48.5 L mol^{-1}. Yuen et al. (2016) prepared the first eight-membered cyclic carbonate and revealed that it was more reactive than five, six and seven-membered ring containing cyclic carbonates [98]. This is due to the more ring strain of the larger size carbonates. However, the use of phosgene during the preparation of large size carbonates is the main issue which is toxic reagents. Hence, the use of five-membered cyclic carbonates in NIPU synthesis is more favorable and economic.

1.4 Carbon dioxide as a building block

CO_2 is considered as a one of the main greenhouse gases that is responsible for global warming and the worldwide climate changing. The main sources of CO_2 concentration are combustion of fossil fuels, deforestation, overexploitation and industrialization etc. [99,100]. In the present time, the concentration of CO_2 in the atmosphere has reached around 408 ppm (parts per million) which was around 277 ppm in the starting of Industrial Revolution (around 1760) [100,101]. Therefore, it is urgently required to control its emission, capture and utilization. However, at the same time, CO_2 is much more attractive due to it being non-hazardous, abundant in nature, non-flammable and chemically inactive [99]. So, with respect to the environmental and economic issues, the valorization of CO_2 into value-added products is more advantageous and has received worldwide attention from the scientific society and industries.

Recently, it has been used in various organic molecule syntheses such as cyclic carbonates, urea, salicylic acid, formamides, esters, carbamates and carboxylic acids etc. as a one-carbon building block (C1) [99]. **Fig. 1.6** shows some examples of the

utilization of CO_2 in the preparation of various chemicals. CO_2 is the oxidized form of carbon which is available in abundance due to its kinetic and thermodynamic stability [102–104]. As a result, to activate CO_2, most of the research papers have used very reactive substrates such as epoxides, activated alkynes, alkanes and aziridines, catalysts and varied different reaction parameters. The most important chemicals, five-membered cyclic carbonates are easily prepared by using CO_2. Nowadays, five-membered cyclic carbonates are widely used as a precursor for NIPUs synthesis as it avoids the use of toxic isocyanate [40,42,76,80,83].
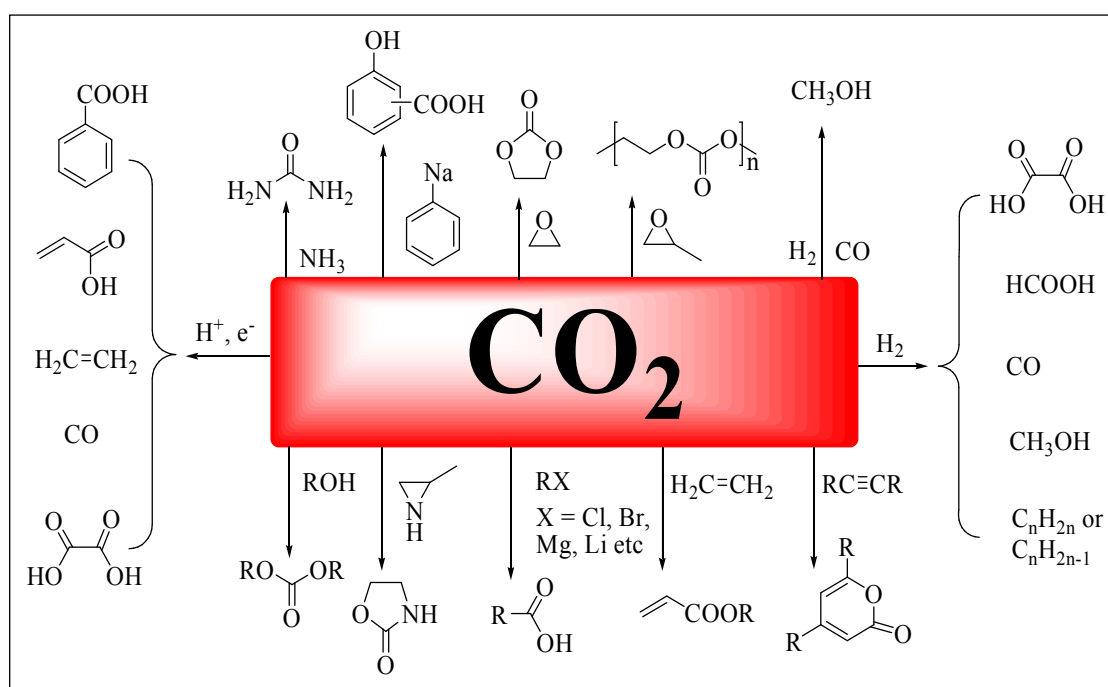
Fig. 1.6: Some examples of utilization of CO_2 as a one-carbon (C1) building block in organic synthesis [42].

1.5 Polymer from renewable resources

1.5.1 Vegetable oil

Recently, in the synthesis of polymer, the utilization of renewable raw materials has received global interest in both industrial and academic field due to the diminution of petroleum resources and environmental awareness. With constant reduction of fossil oil resources and rising emission of greenhouse gases, there is an urgent need to utilize renewable resources towards sustainable development as much as possible [1-3]. In addition, the development of renewable raw materials can fulfill the principles of green

chemistry that minimize the emission of greenhouse gas like CO_2, easily degradable and low toxic. In 2002, the UN World Summit on Sustainable Development was held in Johannesburg which focused on the utilization of renewable raw materials [105]. Among the various types of renewable raw materials, vegetable oils provide a favorable path to bio-based polymers and widely used in coatings and paints for a long time due to the presence of double bonds which can undergo polymerization in contact with air [106,107].
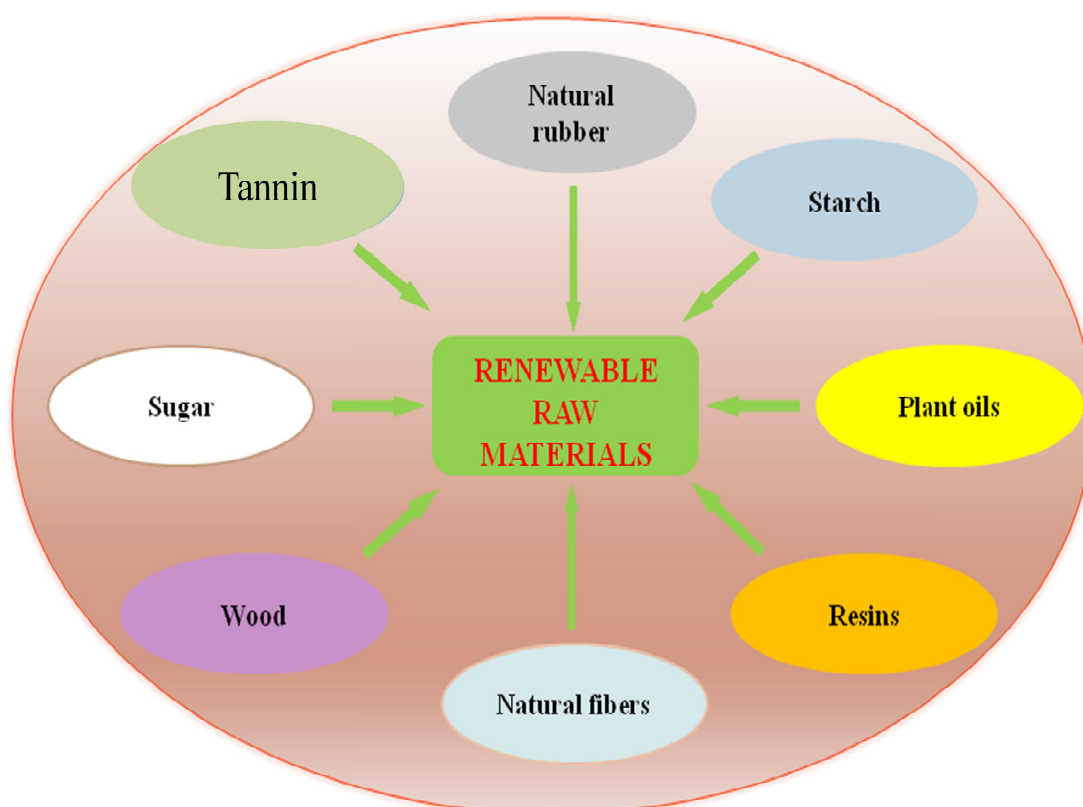
Fig. 1.7: Various types of renewable raw materials used in the plastic industry [42]**.**

Currently, vegetable oils are used in the production of biodiesel that can be used as a replacement for the petroleum-based fuel by catalytic cracking, pyrolysis and transesterification [108]. The annual global production of the main vegetable oils (palm, soybean, rapeseed, cotton, sunflower and coconut) amounted to 84.6 million by end of the 20th century and according to UFOP report, it raised to 195 million tons during the year 2017-18 [3]. In recent years, the amounts of production of vegetable oils and fats produced have risen by about 4% per year [109].

1.5.2 Structures of vegetable oils

Chemically, vegetable oils are tri-esters of glycerol and consist of various long chain fatty acids (**Fig. 1.8**). Different types of fatty acids are present depending on types of the oils and the growing conditions. The majority fatty acids are long chain with double bonds which are mostly in a *cis* configuration [109,110]. The physico-chemical properties of oils depend on the parameters such degree of unsaturation, stereochemistry and conjugation of the C=C bonds and type of fatty acids present on the oil [111]. On the basis of the degree of C=C bonds of oil, which are evaluated by the iodine value (IV), the vegetable oils are categorized into three types: (a) drying oils (IV > 130); example: linseed oil), (b) semi-drying ((100 < IV < 130); example: sunflower oil) and (c) non-drying oils (IV < 100); example: palm kernel oil) [106,109]. The IVs are the quantity of iodine which is reacted with C=C bonds in 100 g of the oil under a particular environment. The composition of different fatty acids of the common vegetable oils is summarized in **Table 1.1** [109,112]. In case of castor oil, the main abundant fatty acid is ricinoleic acid that contains naturally available hydroxyl group which can be easily modified to get various products and in the case of linseed oil, the main constituents are linoleic acid and linolenic.

Table 1.1: Iodine value (IV) and fatty acid compositions of the various vegetable oils:

Vegetable oils	IV (mg/100)	Fatty acids (%)				
		Palmitic	Stearic	Oleic	Linoleic	Linolenic
Soybean	117-143	11	4	23.4	53.3	7.8
Sunflower	110-143	5.2	2.7	37.2	53.8	1.0
Linseed	168-204	5.5	3.5	19.1	15.3	56.6
Cottonseed	90-119	21.6	2.6	18.6	54.4	0.7
Castor	82-88	1.5	0.5	5.0	4.0	0.5
Corn	102-130	10-22	-	11-25	-	-
Olive	75-94	13.7	2.5	71.1	10	0.6
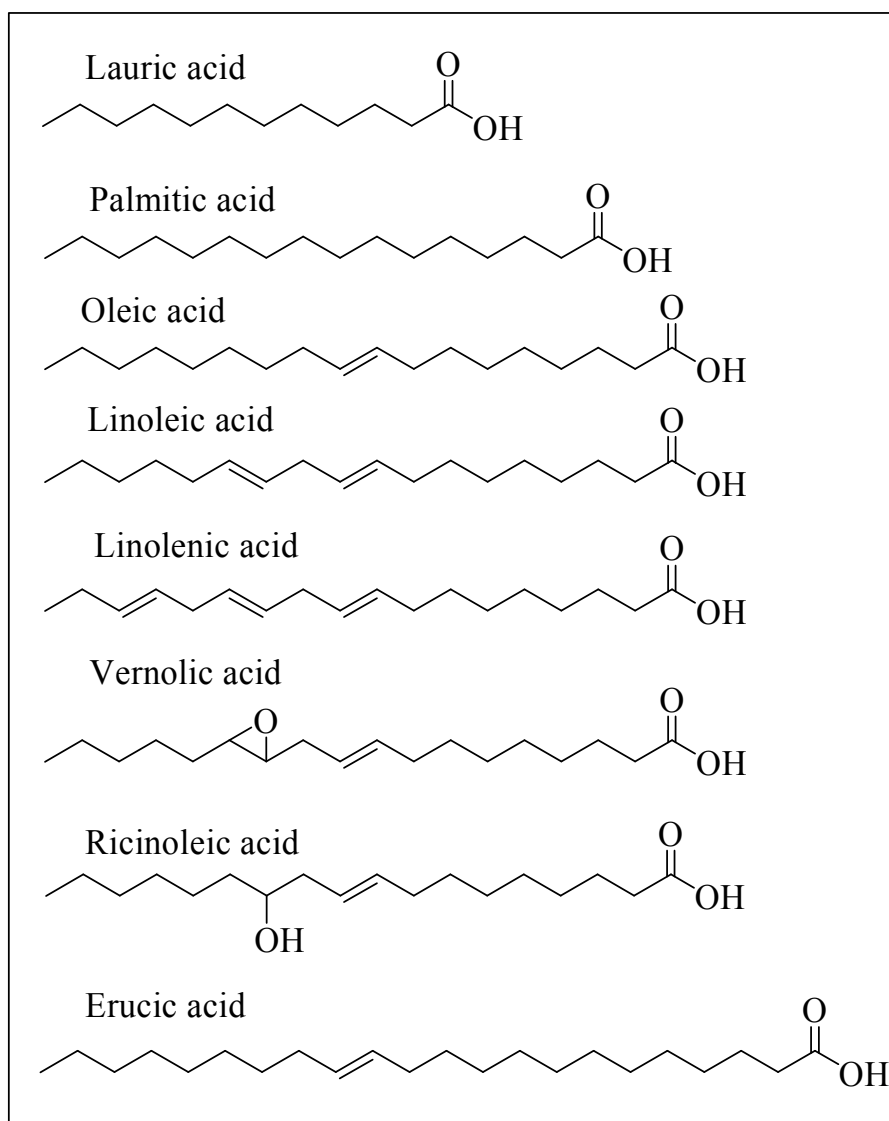
Fig. 1.8: Chemical structures of some fatty acids present in vegetable oils [106,109].

Recently, vegetable oils have been used in preparations of a variety of polymers for applications in many purposes. Some polymeric materials preparing from vegetable oils are discussed below:

Alkyd resins

Alkyd resins are possibly the oldest applications of vegetable oil derived polymer which belongs to the class of polyester. In 1847, for the first time, Berzelius synthesized the polyester resin by a condensation reaction between tartaric acid and glycerol. However, in the year 1921, Kienle familiarized the term alkyd for the oil-modified polyester resin. Generally, alkyd resins are synthesized from a polyol, acid anhydride or polyvalent acid and fatty acid derivatives [113]. The vegetable oils based alkyd resin is

prepared by using the most common method namely monoglyceride process which proceeds through two steps (**Scheme 1.8**) [114–116].

The first step is the alcoholysis of the triglyceride oil to make monoglyceride in the presence of an acidic (para-toluene sulfonic acid) or basic (NaOH, CaO) catalyst. The methanol solubility test is used to confirm the formation of the monoglyceride. The second step involves the reaction of the prepared oil-based monoglycerides with aliphatic or aromatic anhydrides to produce the vegetable oils based alkyd resin.
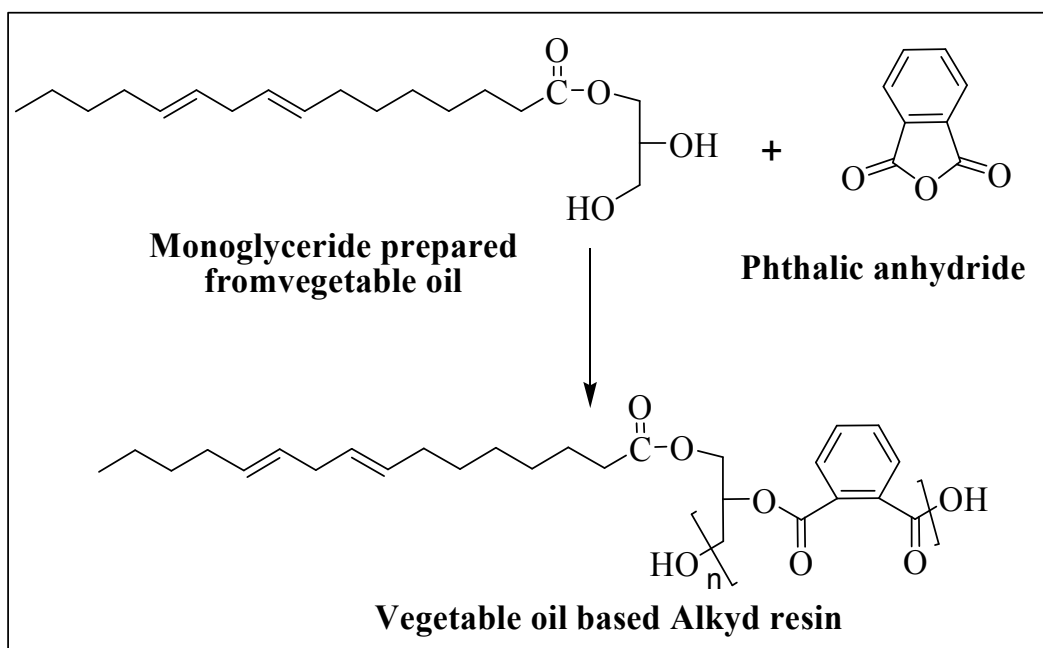
Scheme 1.8: Schematic pathway of synthesis of alkyd resin from vegetable oils.

The vegetable oils based alkyd resin displays better properties as compared to glycerol-based polyester resins. Depending on the type and content of the oil length and anhydrides, the properties of the alkyds are altered. The aromatic polyesters exhibited better stability towards heat and moisture in comparison to the aliphatic one due to the presence of benzene ring. Furthermore, with increasing anhydride content, the drying times of resins decrease. The anhydrides used for preparation alkyd resins are succinic, maleic, phthalic, and glutaric anhydrides [106].

Based on the percentage of oil content in the resins, the alkyd resins are classified as below [113].

i)   Short oil alkyds (oil content below 40%).

ii)   Long oil alkyds (oil contents above 60%).

iii)   Medium oil alkyds (oil contents between 40-60%).

Bora et al. (2014) prepared alkyd resins from yellow oleander oil *via* two step monoglyceride methods by using a different amount of combination of maleic anhydride (MA) and phthalic anhydride (PA). The authors observed that the content of MA have an important role in properties of the prepared resins. They found that the resin with 100% PA exhibited the highest thermal stability and pencil hardness [114].

Gogoi et al. (2014) prepared bio-based alkyd resin from jatropha oil with 100% PA by applying the above mentioned methods. The prepared alkyd was blended with various amount (20, 30, 40 and 50 wt% with respect to the resin) of jatropha oil based epoxy resin (EJO) by using an aqueous citric acid solution as the curing agent. They observed that the thermal stability, mechanical properties and curing times of the resulting alkyd resins enhanced with increased wt% of EJO upon blending. The results of this study suggested that the prepared blends can be used in surface coatings applications [117].

Epoxy resins

Recently, epoxy resin derived from vegetable oils and fatty acids have become one of the most extensively studied polymers, and it can be used as an economical and renewable material for industrial applications. The epoxidation of vegetable oils involve the C=C double bonds, and in some fatty acid like vernolic acid contains naturally occurring epoxy group [8]. The epoxidation of unsaturated fatty acids of the vegetable oils can be performed in a simple procedure by reacting it with hydrogen peroxide (oxidizing agents), molecular oxygen along with chemo-enzymatic reactions (**Scheme 1.9**) [118]. The polymerization of epoxidized vegetable oils is carried out by using a curing agent such as polyamines, polycarboxylic acid, anhydrides as well as polyamides with suitable properties [119]. Epoxidized vegetable oils and fatty acids can be used in paints and coating purposes which mitigate our dependence on petro-based coatings and paints [120].

Sahoo et al. (2018) prepared linseed oil and castor oil based epoxy resins by using hydrogen peroxide as the oxidizing agent. The obtained epoxy resins were cured with bio-based citric acid and compared the properties of cured epoxies with commercial

epoxy resin (diglycidylether of bisphenol A-epoxy). The properties like tensile strength, modulus and thermal stability of the linseed oil based epoxy (ELO) based network were comparatively better than the castor oil based epoxy (ECO). The oil-based epoxies showed almost comparable contact angle and thermal degradation as the commercial epoxy [121].
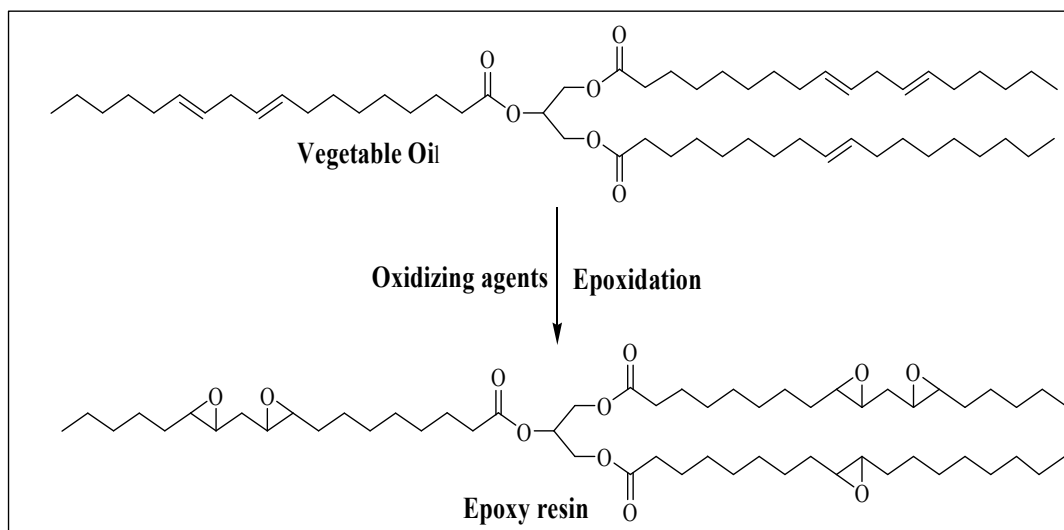
Scheme 1.9: Synthetic pathway of epoxy resins from vegetable oils.

Polyetheramides (PEA)

PEA is an important polymeric material in which amide and ether moieties are present [122]. The amide and ether groups present in the polymeric chain of PEA resins are responsible for good chemical resistance and adhesion. The PEA coatings exhibit good impact resistance, flexibility, hardness as well as improved drying behavior.

The vegetable oils based PEA can be synthesized *via* a two step route (**Scheme 1.10**):

   (i)   Synthesis of vegetable oil amide diols, and
   (ii)   The reaction of amide diols with resorcinol and bisphenol A [123–125].

Akintayo et al. (2011) synthesized albizia benth oil based PEA resin. In the first step, albizia benth oil fatty amide was prepared which was underwent condensation polymerization with bisphenol A to produce PEA resin. In the second step, the prepared PEA was modified with urethane groups which is synthesized by the reaction of free hydroxyl groups of the Albizia benth oil fatty amide and toluene 2,4 di-isocyanate. The synthesized urethane modified PEA demonstrated better chemical resistance, scratch

hardness, flexibility along with air drying characteristics due to the presence of bisphenol A, ether and urethane groups. The authors revealed that the coatings can be used as a promising candidate for anticorrosive coating [125].
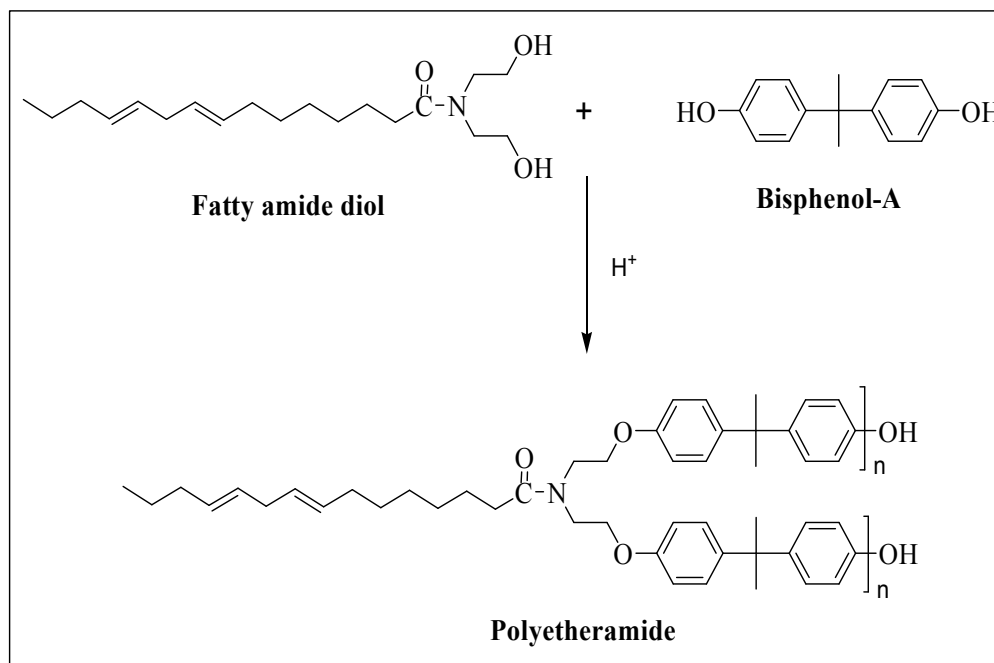
Scheme 1.10: Synthetic pathway of polyetheramide from vegetable oils.

Polyurethanes (PUs)

Recently, different vegetable oils based polyols (**Scheme 1.11**) have been comprehensively utilized directly or after modifications to synthesize PUs [36,37,126]. The vegetable oils oil based polyols are copolymerized with isocyanates to get PUs. These vegetable oils based PUs present a comparable thermal and mechanical properties as compared to petroleum-based PUs, and can be used in various applications as for example flexible foams, hard elastomers and wood adhesives etc.

Varieties of methods have been developed to synthesize vegetable oils based polyols as mentioned below:

(a) **Epoxidation route:** In this method, vegetable oils are first epoxidized by various methods and then the epoxide ring is opened up by reacting it various proton donors such as methanol to produce polyols with large numbers of functionality [127,128].

(b) Ozonolysis route: The C=C bond of vegetable oils can be converted into terminal primary hydroxyl groups by ozonolysis which includes three steps. Initially, an ozonide is formed by the reacting the vegetable oils with O_3. Then, the ozonide is reduced to aldehyde which is further reduced to get polyols. The resulting polyols possess better mechanical properties and Tg [129,130].

(c) Hydroformylation/Reduction route: In this route, the vegetable oils are treated with CO/H_2 (syngas) to synthesize an aldehyde which is furthermore reduced by hydrogen to obtain primary hydroxymethylated functional group in the oil backbone [131,132].

(d) Thiol-ene coupling route: Owing to the presence of electron rich C=C bonds in vegetable oils; it prefers radical addition of various molecules. The vegetable oils have been treated with thiols like mercaptoethanol to give polyols [133,134].
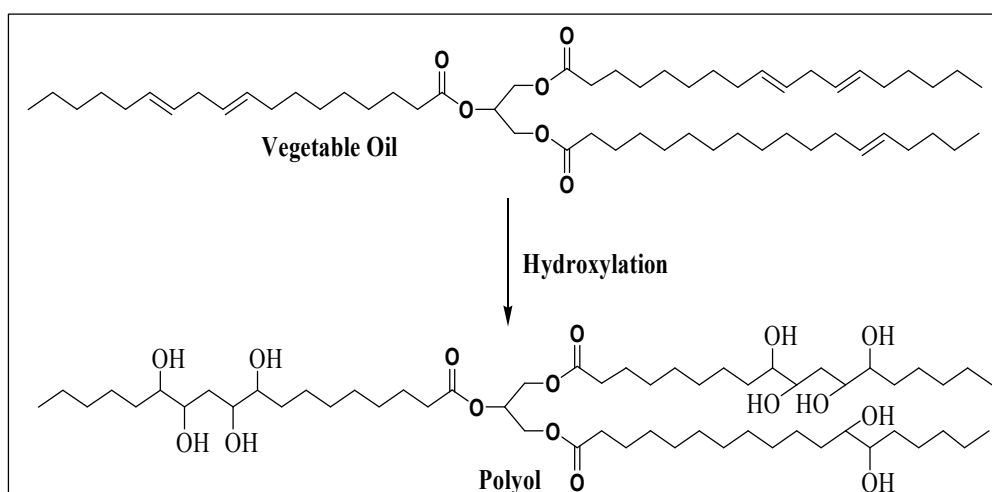
Scheme 1.11: Synthetic pathway of polyols from vegetable oils.

1.5.3 Tannic acid

Tannic acid is a natural occurring compound with catechol functional group and the chemical formula of $C_{76}H_{52}O_{46}$ [135]. It is generally found in plants, legume seeds, fruits, wine, cider, tea and cocoa [136]. Its chemical structure is very complex which consists of a glucose polyester core with five gallic units with 25 terminal phenolic hydroxyl groups (**Fig. 1.9**) [137]. It can be classified as hydrolyzable tannins and proanthocyanidins. It is the second richest natural source of phenolic derivatives after

lignins. Among the aromatic bio-based compounds, tannic acid is an attractive candidate in the area of materials chemistry, which possesses high thermal stability, chemical resistance and toughness. Owing to the presence of a lot of nucleophilic OH group, it can be functionalized to give a variety of polymers like polyols, acrylate resins and epoxy resins [138]. Tannic acid and its derivatives are extensively used for toughening of epoxy resins [139], antibacterial materials and coating purposes [140,141].
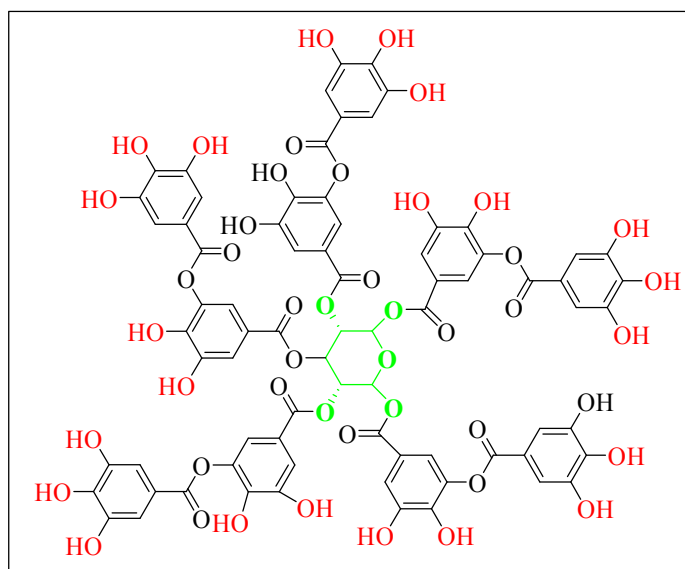
Fig. 1.9: Chemical structure of tannic acid.

1.5.4 Vegetable oil based NIPUs

The applications of vegetable oils have achieved a plenty of interest to synthesize wide variety of polymer for different types of applications. Recently, various epoxidized oils are used to prepare cyclic carbonates, which further react with various amines to obtain NIPUs. Some literature review is discussed below:

Tamami et al. (2004) synthesized soybean oil based five-membered cyclic carbonates (CSBO) by the reaction of epoxidized soybean oil (ESBO) with CO_2 by using TBABr as the catalyst at 110 °C in high yield. They observed a model reaction by the reaction CSBO with n-butylamine in order to get β-hydroxyurethane (NIPUs) group. The authors concluded that the carbonated can readily react with amines to give NIPUs [142].

Li et al. synthesized (2008) CSBO by the reaction between ESBO and CO_2 in the presence of a mixture of $SnCl_4.5H_2O$ and TBABr as a catalyst at the temperature of 120 °C and 1.0 MPa CO_2 for the duration of 20 h. They observed that the catalyst with 1:3

molar of $SnCl_4.5H_2O$ and TBABr demonstrated the most excellent result. Finally NIPUs was synthesized by reacting CSBO with ethylenediamine (EDA) at a temperature of 60-80°C [143].

Javni et al. (2008) synthesized NIPUs by reacting CSBO with different diamines such as EDA, BDA and HMDA at various ratios. They studied the optimal condition of high formation of cyclic carbonate groups from ESBO and found that the prepared NIPUs exhibited better mechanical property than earlier obtained by Tamami et al. for the analogous NIPUs [144].

Bähr et al. (2012) synthesized bio-based NIPUs from soybean and linseed oil. The carbonated soybean and linseed oil (CLSO) was prepared from epoxidized oils by treating CO_2 in presence of a mixture of TBABr and silica-supported 4-pyrrolidinopyridinium iodide (SiO_2-(I)) as a catalyst at temperature 140 °C and pressure 30 bar for 20 h and achieved 100% conversion. Finally curing the mixture of CSBO and CLSO with different diamines in order to obtain NIPUs with better Tg value from 17 °C to 60 ° in contrast to the CSBO/EDA based NIPUs [145].

Jalilian et al. (2015) synthesized soybean oil based NIPU networks with potential application as a biodegradable scaffold. CSBO was synthesized from ESBO and CO_2 gas by using TBABr as an effective catalyst at 110°C. In the final step, NIPUs was synthesized by the reaction of CSBO with various weight ratios of 3-aminopropyl-terminated poly(ethylene glycol) (ATPEG) and EDA with cytotoxicity, biodegradability and non-hemolytic properties [146].

Poussard et al. (2016) synthesized thermosets or thermoplastics NIPUs by melt-blending CSBO and EDA, BDA and 1,5-diaminopentaneamino-telechelic oligoamides. They observed that the NIPU prepared by using CSBO and short diamine exhibited low tensile and thermal properties whereas oligoamides curing NIPUs displayed higher thermal stability and elongation at break (up to 400%) [16].

Malik et al. (2018) synthesized canola oil based five membered cyclic carbonates by using 5,10,15-tris(pentafluorophenyl) corrolato-manganese(III) complex as a novel catalyst and subsequently developed bio-based NIPUs. The time of carbonation reaction was reduced by $1/4^{th}$ by using the mentioned catalyst in comparison to the previous

reported data. The prepared NIPUs demonstrated a tensile strength of 8 MPa and thermally stable up to 200 °C [147].

Mokhtari et al. (2019) prepared bio-based NIPUs by the aminolysis reaction between the cyclic carbonates based on castor and jojoba oil with different diamines (aliphatic or aromatic) with Tg varying from -45 to 20 °C [148].

1.6 Applications of NIPUs

NIPUs have a broad variety of applications due to its display of superior thermal, chemical resistance, porosity and water absorption than the traditional PUs. Here, some examples of applications of NIPUs are discussed.

NIPU obtained from the copolymerization of N-phenylmaleimide and 3-(2-vinyloxyethoxy)1,2-propylene carbonate provide better durability and hardness [149]. In contrast to the conventional PU coatings, the chemical and permeability properties of NIPUs coatings are 1.5 to 2.5 times more resistant. Moreover, waterproof coatings prepared by the reaction between the epoxy and HMDA with monofunctional cyclic carbonate show better water resistance properties. Acrylic based NIPU coatings are excellent ultraviolet-stable which turn into yellow moderately after 200 h ultraviolet irradiation test in comparison to saturated epoxy resin coatings which turn yellow after 100 h [62]. NIPUs can be used in applications of sealing, adhesion and electrical equipment with excellent efficiency. The acrylic-modified NIPUs can be used in the preparation of sealants. This sealant can be cured by ultraviolet radiation and used in indoor or outdoor sealing purposes.

Figovsky et al. (2005) prepared NIPU with excellent adhesion properties on a range of substrates from cyclic-carbonates, amines, acrylate and polyepoxide. The resulting NIPU has good abrasion, weathering and solvents resistance properties and can be cured at a temperature 10-30 °C [150].

1.7 Nanocomposite prospect

Recently, polymer nanocomposites with carbon-based nano-fillers are broadly investigated to establish advanced materials for various potential applications. Polymer nanocomposites are usually a mixture of the polymer matrix with one or more nano-fillers materials which may be organic or inorganic. These fillers can be zero-

dimensional nanoparticles, one- dimensional nanotubes or nanowires and two-dimensional nanosheets [151]. Over the past decades, various nano-fillers such as graphene, carbon nanotubes (CNT), clays, fullerene, metal oxide and polymeric nano-fillers have been extensively used to develop polymer nanocomposites with balanced properties. The performances of the nanocomposites depend on the types of nano-fillers, their dispersion, alignment of nano-fillers within the polymer network and interaction with the polymer chain [152]. Among the different kinds of nano-fillers, carbon-based nano-fillers like graphene, CNT and clays get more attention due to their extraordinary properties [153–158].

Graphene is a two-dimensional planar sheet composed of sp^2-bonded carbon structure which is distinguished as an emerging star in the area of material science [159–161]. It has been making an intense influence in many areas of science and technology such as energy storage and conversion, biotechnology, electronics and particularly the development of composite fiber materials since its discovery in 2004. The exceptional planar structure of graphene provide its significant properties such as excellent mechanical strength, electrical (106 S cm^{-1}), high surface area and electron transport capabilities [151,161,162].

The field of polymer nanocomposites was revolutionized by the discovery of CNT in 1991 by Iijima [163]. Since its discovery, Ajayan et al. prepared the first CNT reinforced polymer nanocomposites [164]. CNT are classified into two types: (a) Single walled nanotubes (SWCNT), in which single graphene layer is rolled into a cylinder and (b) multi walled nanotubes (MWCNT), in which multiple graphene layers stack in the form of cylinders. Depends on the atomic arrangement of CNT, it may be metallic or semiconducting. The CNT based polymer composites are used in defense applications, gas storage devices, sensors, lightweight aircraft applications and energy storage [165–167].

Naturally, clays occur as platelets and consist of stacking of many sheets. It possesses many unique characteristics like mechanical, magnetic and electrical properties, large surface area, high cation exchange capacity and nanometer-sized platelets, with very small cross-sectional area and distinctive structural properties. These exceptional properties of clays make them attractive candidates for reinforcing polymer

nanocomposites [168]. **Fig. 1.10** shows the different types of polymer clay composite [169].
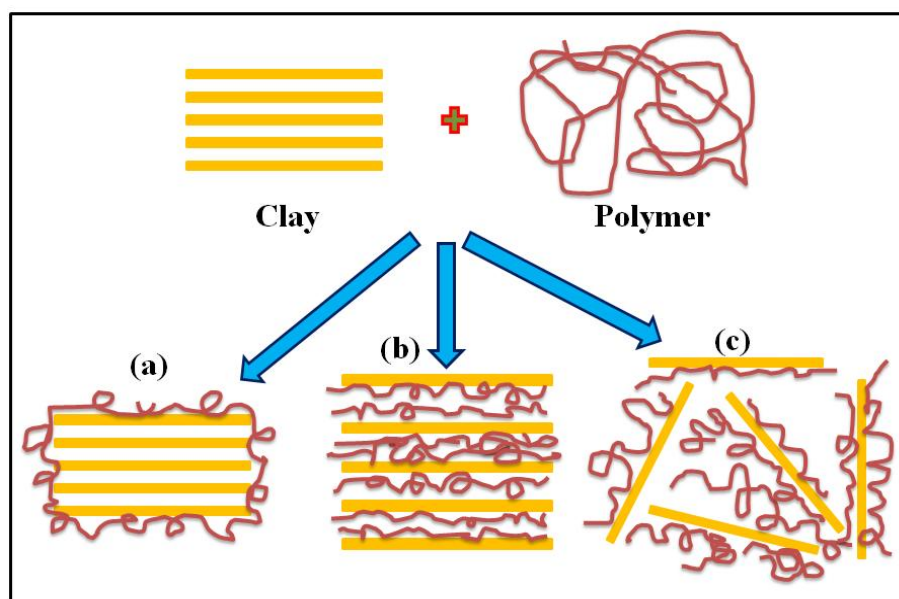

Fig. 1.10: Schematic representation of (a) conventional composite, (b) intercalated composite and (c) exfoliated composite [170].

The properties of the nanocomposite also depend on the methods and conditions of processing. The main processing methods are (a) *in situ* polymerization, (b) solution processing and (c) melt processing [167,170].

(a) ***In situ* polymerization:** This method is associated with the clay/CNT dispersion into the monomer matrix in the absence or presence of solvent. The polymerization reactions are initiated either by radiation or heat or by an appropriate catalyst and monomers are used as the starting materials in lieu of polymers. The benefit of this processing is that the superior interactions and dispersion among the polymeric matrix and CNT *via* the grafting of polymer molecules on surface of the CNT.

(b) **Solution processing:** This method is widely used in the synthesis of composites of CNT and polymer in which polymer and CNT are mixed with a proper solvent such as water, toluene, and chloroform etc and evaporates the solvent after the formation of the nanocomposite films.

(c) **Melt processing:** It is one of the most inexpensive and environmentally friendly approaches of the fabrication of nanocomposites. This processing involves the mixing of the polymer and CNT above the melting point of

polymer to give viscous liquid. The dispersion of CNT is enhanced by shear mixing and this method is generally used for thermoplastic polymers such as polystyrene, polycarbonate and polypropylene etc.

Kathalewar et al. (2013) developed diglycidyl ether of bisphenol-A (GY-250) based NIPU coatings and their nanocomposites with surface treated zinc oxide (ZnO) nanoparticles. They observed the influence of incorporation of ZnO nanoparticles on the properties of the NIPU nanocomposite coatings. The authors found that the properties like scratch hardness and abrasion resistance of the prepared nanocomposites were enhanced as compared to NIPU coatings without ZnO nanoparticles [171].

1.8 Scope and objectives

From the standpoint of sustainable development, the main problem in the PU synthesis is to replace the petro-based PUs by bio-based isocyanate-free NIPUs. NIPUs have been broadly studied in academic and industries research. The NIPUs produced from aminolysis of cyclic carbonate can replace the isocyanate-based PU. Recently, the renewable sources especially vegetable oils have been extensively used to synthesize NIPUs.

Vegetable oils are available worldwide, economic and have many other social advantages. Moreover, they are environment friendly as they are biodegradable in nature. A large number of vegetable oils have been used for the production of different types of NIPUs. However, the vegetable oils based NIPU displays poor mechanical properties due to the flexible nature of vegetable oils and therefore cannot compete with traditional PUs. In addition, due to side reactions, steric hindrance of cyclic carbonates and lower reactivity between amine and cyclic carbonates, NIPUs prepared in this way exhibit low mechanical properties.

Therefore, inspired from the foregoing discussion, the present thesis aims to develop bio-based NIPUs by utilizing sunflower oil, soybean oil, glycerol, tannic acid, and CO_2, and make them appropriate for practical applications like coating, paints, adhesive etc. In this regard, efforts have been devoted to enhance the properties of these NIPUs by blending and reinforcing various nano-fillers.

Objectives of the present investigation:

➢ Synthesis and characterization of sunflower oil based NIPU.

➢ Preparation of blends of sunflower and soybean oil based NIPU with epoxy resin and highly branched cyclic carbonates respectively.

➢ Synthesis of tannic acid based NIPU in order to get better performance of NIPU.

➢ Fabrication of nanocomposites from sunflower oil and tannic acid based NIPU with various types of nano-fillers.

➢ Characterization and determination of the various properties of the prepared nanocomposites.

Plan of work:

To fulfill the above objectives, the following plan of work has been adopted:

➢ Synthesis of five-membered cyclic carbonate by reacting epoxidized sunflower and soybean oil with CO_2 and their characterization.

➢ Preparation of sunflower oil based NIPUs through non-isocyanate path by reacting cyclic carbonate with various types of amines.

➢ Preparation of sunflower oil based NIPU/epoxy resin blends and their nanocomposite with modified graphene oxide (GO).

➢ Synthesis of sunflower oil based NIPU and its nanocomposites with modified MWCNT.

➢ Blending of soybean oil based cyclic carbonate with glycerol based highly branched cyclic carbonates.

➢ Synthesis of tannic acid based NIPU and their nanocomposites with modified clay.

➢ Characterization of the prepared polymers and the nanocomposites using different characterization techniques like FT-IR, NMR, UTM, SEM, XRD and TEM.

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