CHAPTER-1

INTRODUCTION

1.1 Introduction

PU serves the mankind in its various roles such as flexible foam, rigid foam, elastomers, surface coatings and adhesives. It is a versatile, responsive and long-lasting fabricated material that can replace paint, cotton, rubber, metal or wood in various applications across all fields. It tough is like fiberglass, squishy like upholstery foam, possessive like varnish, elastic like rubber or sticky like glue. Since it was invented during the 1940s, polyurethane had been broadly used for the various items like baby toys to airplane wings and it was adapted for contemporary technology. With a global market of approximately six million tons per annum, the polyurethane industry covers a diverse business area with its multitude of applications. In 2010, the global market for polyurethanes was estimated at 13,650.00 kilo tons and is expected to reach 17,946.20 kilo tons by 2016. North America, Asia-Pacific, and Europe dominate the polyurethane market and together accounted for 95% of the global polyurethane demand in 2010. North America and Western Europe are mature markets and are expected to grow at a sluggish rate. However, Asia-Pacific, Eastern Europe and South America are expected to drive the demand for polyurethanes in the coming decade. The furniture and interior industry dominated the polyurethane market, accounting for 28.01% of the total demand in 2010.[1] the second largest end-use of polyurethanes is in construction industry, which accounted for 24.98% of the overall market in 2010. Electronic appliances, however, are the fastest growing market for polyurethanes. Polyurethane demand for electronic appliances is expected to grow at 7.3% to 2011. As per Global Industry Analysts, the global market for foamed plastics (polyurethane) is projected to reach 9.6 million tons by the year 2015, driven by resurgent demand from construction, furniture and bedding, and automotive markets. The need for low-cost and long-lasting materials and rising significance of energy efficiency in appliances and buildings is expected to foster growth in the foamed plastics market[2].

PU is categorized as a polymer molecule that consists of a series of repeating smaller units called monomers based on its chemical structure. It is manufactured by combining two types of monomers i.e. a di-isocyanate and a diol, through a poly-addition reaction. This makes a basic material which can be stretched, smashed or scratched and will remain fairly indestructible. Depending on the different di-isocyanate and diol or polyol constituents, the resulting polyurethane might be in the form of a liquid, foam or solid. Each form has its own advantages and limitations and finds application in various end uses as given in Table 1.01.

Table 1.01: Uses of PU depending upon the properties of the end product

Uses	**Reasons**
Cushioning	Low density, flexibility, resistance to fatigue
Shoe soles	Flexibility, resistance to abrasion, strength, durability
Building panels	Thermal insulation, strength, long life
Artificial heart valves	Flexibility and bio stability
Electrical equipment	Electrical insulation, toughness, resistance to oils

1.2 History of Polyurethane

More than half a century ago, plastic industries were working with polymerization and polycondensation processes to produce plastics. In 1937 the German scientist Otto Bayer, also known as “father” of polyurethane, and his co-workers discovered a third process, the so called polyaddition reaction, where the polyaddition of a diisocyanate to a diol in the presence of a catalyst proceeds completely to a polyurethane under mild conditions without the formation of undesired byproducts. In 1937’s, the plastic industries had in their disposal the third important synthesis route for the production of macromolecular organic materials[3]. During World War II, polyurethane was used in small scale for aircraft coating, but it was not until 1952 that polyisocyanates became available in the market. In 1954, a commercial production of flexible foam began, based on toluene diisocyanate (TDI) and polyester polyols. The invention of these foams was thanks to water accidentally introduced in the reaction mixture. These materials were also used to produce rigid foams, gum rubber, and elastomers. In 1956, DuPont et al. had introduced the polyether polyols, poly (tetramethylene ether) glycol) by polymerization of tetrahydrofuran[4]. In 1957, BASF and Dow introduced the less expensive polyalkylene glycols. These polyether polyols offered technical and commercial advantages such as low cost, ease of handling, better hydrolytic stability and quickly supplanted polyester polyols in the manufacture of polyurethane goods. And over the years, a lot of successful achievements on polyurethanes were followed. Polyurethane (PU), is actually another name for the family of chemicals known as the urethane polymers, which are composed of two principal raw materials such as isocyanates and polyols, brought together with catalysts and a variety of additives. This reaction produces a basic material whose variations can be stretched, smashed, or scratched, and remain indestructible. Depending on the different isocyanates and polyol constituents, the resulting polyurethane might take a liquid, foam, or solid form, each with advantages and limitations. Polyurethane might be hard, like fiberglass, squishy like upholstery foam, protective like varnish, bouncy like rubber wheels, or sticky like glue. Since its invention in the 40s, the polyurethane has been used in everything from baby toys to airplane wings, and continues to be adapted for contemporary technology.

1.3 Properties of Polyurethane

1.3.1 ***Wide range of hardness and high load bearing capacity***

Polyurethane has a high load capacity in both tension and compression. Polyurethane may undergo a change in shape under a heavy load, but will return to its original shape once the load is removed with little compression set in the material when designed properly for a given application.[5]

1.3.2 Flexibility

Polyurethanes perform very well when used in high flex fatigue applications. Flexural properties can be isolated allowing for very good elongation and recovery properties.[6]

1.3.3 *Abrasion & Impact Resistance*

For applications where severe wear prove challenging, polyurethanes are an ideal solution even at low temperatures.[7]

1.3.4 Tear Resistance

Polyurethanes possess high tear resistance along with high tensile properties.[8]

1.3.5 Resistance to Water, Oil & Grease

Polyurethane's material properties will remain stable (with minimal swelling) in water / oil / grease. Polyether compounds will last many years in subsea applications.[9]

1.3.6 ***Electrical Properties***

Polyurethanes exhibit good electrical insulating properties.[10]

1.3.7 Wide Resiliency Range

Resilience is generally a function of hardness. For shock-absorbing elastomer applications, low rebound compounds are usually used i.e. resilience range of 10-40%. For high frequency vibrations or where quick recovery is required, compounds in the 40-65% resilience are used. In general, toughness is enhanced by high resilience.[11]

1.3.8 Strong Bonding Properties

Polyurethane bonds to a wide range of materials during the manufacturing process. These materials include other plastics, metals, and wood. This property makes polyurethane an ideal material for wheels, rollers, and inserts.[12]

1.3.9 Ability to withstand in Harsh Environments

Polyurethane is very resistant to temperature extremes, meaning harsh environmental conditions and many chemicals will not cause material degradation.[13]

1.3.10 Mold, Mildew & Fungus Resistance

Most polyether based polyurethanes do not support fungal/mold/mildew growth and are therefore highly suitable for tropical environments and FDA applications. Special additives can also be added to reduce this in polyester materials as well.[14]

1.3.11 Color Ranges

Varying color pigments can be added to polyurethane in the manufacturing process. Ultraviolet shielding can be incorporated into the pigment to provide better color stability in outdoor applications.[15]

1.4 Applications for Polyurethane

The polyurethanes are mainly used in seven areas such as rigid foam which is 25% of all polyurethane production, 11% PU used for automotive furniture (moulded foam), 6% used as elastomer, for adhesive purpose 6% PU used, 3% in coating, 31% as flexible foam for household purpose and rest 18% includes shoes, fibers etc.

1.4.1 Apparel

Scientists discovered the polyurethanes that could be made into fine thread, they were combined with nylon to make more lightweight, stretchable garments. Over the years, polyurethanes have been improved and developed into spandex fibers, polyurethane coatings and thermoplastic elastomers. Because of today's advances in the polyurethane techniques, the manufacturers preferred the broad range of polyurethane apparel from man-made skins and leathers used for garments, sports clothes and a variety of accessories.[16]

1.4.2 Appliances

The most common use for polyurethanes in major appliances is rigid foams for refrigerator and freezer thermal insulation systems. Rigid polyurethane foam is an essential and cost-effective

Table 1.02: Comparison of Advantages of Polyurethane with Conventional Materials

vs. Rubber	**vs. Metal**	**vs. Plastic**
High abrasion resistance	Lightweight	High impact resistance
High cut & tear resistance	Noise reduction	Elastic memory
Superior load bearing	Abrasion resistance	Abrasion resistance
Thick section molding	Less expensive fabrication	Noise reduction
Colorability	Corrosion resistance	Variable coefficient of friction
Oil resistance	Resilience	Resilience
Ozone resistance	Impact resistance	Thick section molding
Radiation resistance	Flexibility	Lower cost tooling
Broader hardness range	Easily moldable	Low temperature resistance
Castable nature	Non-conductive	Cold flow resistance

Low pressure tooling	Non-sparking	Radiation resistance

Material that can be used for meeting required energy ratings in consumer refrigerators and freezers. The good thermal insulating properties of rigid polyurethane foams result from the combination of a fine, closed-cell foam structure and cell gases that resist heat transfer.[17]

1.4.3 Automotive

Polyurethanes have found interesting applications in automobiles for examples throughout the cars. In addition to the foam that makes car seats comfortable, bumpers, interior "headline" ceiling sections, the car body, spoilers, doors and windows. Polyurethane also enables manufacturers to provide drivers and passengers significantly more automobile "mileage" by reducing weight and increasing fuel economy, comfort, corrosion resistance, insulation and sound absorption.

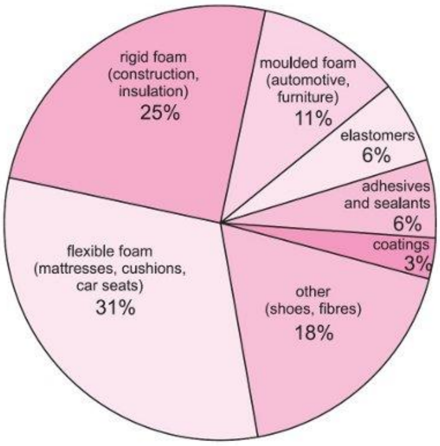


Figure 1.0 Applications for Polyurethane

1.4.4 Building and Construction

Today's homes demand high-performance materials that are strong, yet lightweight; perform well, yet are easily installed; and are durable, but also versatile. Polyurethane helps conserve natural resources and helps preserve the environment by reducing energy usage. With its excellent strength-to-weight ratio, insulation properties, durability and versatility, polyurethane is frequently used in building and construction applications. Both the affordability of these versatile materials and the comfort they provide homeowners have made polyurethane components part of homes everywhere.[18]

1.4.5 Composite Wood

Polyurethanes play a major role in modern materials, such as composite wood. Polyurethane-based binders are used in composite wood products to permanently glue organic materials into oriented strand board, medium-density fiberboard, long-strand lumber, laminated-veneer lumber and even strawboard and particleboard.[19]

1.4.6 Electronics

Often referred to as “potting compounds,” non-foam polyurethanes are frequently used in the electrical and electronics industries to encapsulate, seal and insulate fragile, pressure-sensitive, microelectronic components, underwater cables and printed circuit boards. Polyurethane potting compounds are specially formulated by developers to meet a diverse range of physical, thermal and electrical properties. They can protect electronics by providing excellent dielectric and adhesive properties, as well as exceptional solvent, water and extreme temperature resistance.

1.4.7 Flooring

Either as a foam underlay or on top as a coating, polyurethanes can make the floors we walk on every day more durable, easier to maintain and more aesthetically pleasing. Using flexible polyurethane foam as a carpet underlay in residential or commercial applications can significantly increase the lifespan of the carpet, protect its appearance, provide added comfort and support and can reduce ambient noise. Polyurethane is used all over the house. In floors, flexible foam padding cushions your carpet. In the roof, reflective plastic coverings over polyurethane foam can bounce sunlight and heat away, helping the house stay cool while helping reduce energy consumption.[20]

1.4.8 Furnishings

Polyurethane, mostly in the form of flexible foam, is one of the most popular materials used in home furnishings such as furniture, bedding and carpet underlay. As a cushioning material for upholstered furniture, flexible polyurethane foam works to make furniture more durable, comfortable and supportive.[21]

1.4.9 Marine

Millions of Americans enjoy boating each year. Part of boating's ongoing popularity is thanks to improvements in boating technology, to which polyurethane materials make an important contribution. Polyurethane epoxy resins seal boat hulls from water, weather, corrosion and elements that increase drag, affect hydrodynamics and reduce durability.

1.4.10 Medical

Polyurethanes are commonly used in a number of medical applications, including catheter and general purpose tubing, hospital bedding, surgical drapes, wound dressings and a variety of injection-molded devices. Their most common use is in short-term implants. Polyurethane use in medical applications can be more cost-effective and provide for more longevity and toughness.[22]

1.4.11 *Packaging*

Polyurethane packaging foam (PPF) can provide more cost-effective, form-fitting cushioning that uniquely and securely protecting items that need to stay safely in place during transit. PPF is widely used to safely protect and transport many items, such as electronic and medical diagnostic equipment, delicate glassware and large industrial parts. A versatile on-site solution for many packaging challenges, PPF can save time and be more cost-effective by providing a custom-fit container with each shipment.

1.4.12 Elastomers

Some polyurethane is categorized as an elastomer. It has elastic properties while maintaining some rigidity, which is beneficial for items such as the wheels of a dolly, which must absorb shock without compressing too much. Polyurethane can be extremely flexible when used as a foam insulator in construction or a foam cushion in upholstery. It can be deformed over and over and still maintain its original shape. In other words, it has what is called structural memory.

1.4.13 Thermoplastics

Other polyurethane is a thermoplastic that resembles other kinds of plastic, metal or fiberglass. Thermoplastics are rigid and smooth, with a sealed surface that is impermeable to water. These are used when strength and durability are important, such as in seats at an airport terminal or packaging crates on a truck. Some polymer thermoplastics are difficult to recycle, but they can be reused.

1.4.14 Other Uses

Polyurethane can be found in every room of the house and in practically every building. Since this material became popular during World War II, the polymer has protected, reinvented, joined or transported countless items. It seals surfaces such as wood, metal and paint to protect them from rot, corrosion or fading. As an adhesive, polyurethane resists moisture and heat, so it is ideal for use in the sun or underwater. It also insulates walls, temperature-controlled vehicles and consumer coolers.

1.5 Categorization of Polyurethane on the Basis of End Uses

1.5.1 Flexible Foam:

Of all the polyurethane products, flexible polyurethane foam has the largest production and is most widely used. During flexible polyurethane foam formation, water reacts with the isocyanate group and produces carbon dioxide gas. The carbon dioxide gas will provide volume for

bubble expansion and occupy over 95% of the final volume of the product. Flexible polyurethane foam (FPF) is used as cushioning for a wide variety of consumer and commercial products including furniture, carpet cushion, in transportation, in bedding, in packaging, as textiles and fibers including leather products, shoe uppers, tents, life rafts, labels, hand bags, insulation liners and more. FPF usage consists mostly of slab stock, which is used primarily for carpet cushion and furniture. Most of the FPF is used by the transportation industry for automotive interiors and other purposes.

1.5.2 Rigid foams:

The term "rigid polyurethane foam" comprises two polymer types: Polyisocyanurate formulations, and polyurethane formulas. There are distinct differences between the two, both in the manner in which they are produced, and in the performance of the results.

Polyisocyanurate Foams

Polyisocyanurate foams (or "trimer foams") are generally low density, insulation-grade foams, usually made in large blocks via a continuous extrusion process. These blocks are then put through cutting machines to make sheets and other shapes. Polyisocyanurate foams have excellent insulating value, good compressive-strength properties, and temperature resistance up to 300 degrees F. They are made in high volumes at densities between 1.8 and 6 lbs per cubic foot, and are reasonably inexpensive. Their stiff, brittle consistency and their propensity to shed dust (friability) when abraded can serve to identify these foams.

Polyurethane Foams

Polyurethane foams are considerably different and more useful in composite constructions. These foams are made in large blocks in either a continuous-extrusion process, or in a batch-process. The blocks are then cut to make sheets or other shapes. They are sometimes also individually molded into discrete part-shapes.

Polyurethane polymer foams can be made considerably tougher and less-friable than the polyisocyanurate foams, mostly at the expense of some modulus and high-temperature strength properties. Nevertheless, these foams can be useful (depending on formulation) to temperatures as high as 275 degrees F, while retaining a substantial portion of their strength and toughness. This allows them also to be used in panel applications along with high-temperature curing pre-pregs, cured in ovens or autoclaves.

Typical applications include use as an edge close-out for honeycomb aircraft-interior panels, structural shapes such as transom cores, bulkhead core, stringers, motor-mounts etc. in FRP boat building, impact-limiters and crash-pads, RTM cores, mold-patterns and plugs, sports-equipment core material, and composite tooling.

1.5.3 Polyurethane Elastomer:

The expanding universe of thermoplastic elastomers (TPEs) includes several classes of materials whose common character is close replication of the elastic properties of natural rubbers combined with the easy processability of thermoplastics. TPE families are based on styrenes, polyolefins, polyesters, polyurethanes, thermoplastic vulcanizates (TPVs) and other materials.

The types of polyurethane (PU) elastomers commercially available include RIM- (reaction injection-molding-) processed microcellular polymers, cast and poured elastomers made by mixing and casting reactive liquid components, sprayed polyurethane elastomers and thermoplastic elastomers (TPUs) in a form suitable for conventional thermoplastic processing. Polyurethane elastomers are noted for their durability, flexibility (even at low temperatures), strain, abrasion resistance, shock absorbency and chemical resistance. Their physical properties can be wide variety of end uses by adjusting the mix and nature of the raw materials. Since they are generally expensive and most different elastomers, they are utilized basically as a part of requesting applications, for example, car guard covers/sashes/trim, strong tires, modern rollers, shoe soles, game boots and different mechanical products.

Amid the conjecture period, China will keep on being the biggest worldwide maker of footwear and the biggest customer of PU elastomers for this part. The biggest part of the Europe, Middle East and Africa (EMEA) polyurethane elastomers business sector is in footwear/microcellular frameworks. In spite of the migration of the shoe business to the Asia Pacific locale, PU interest for footwear in EMEA is still critical.

1.5.4 Polyurethane Adhesive:

Polyurethane adhesives are those glues that are made of urethane polymers with chemical based of isocyanate gathering, polyurethane adhesives are otherwise called elastic adhesivess, due they have an exceptional flexibility and lengthening before the crack happens (up to 600%), furthermore like epoxy glues exist unbending polyurethane adhesivess, because of the high break resistance introduced by these cements around 25 MPa. The versatile polyurethane adhesives are cured by polyaddition responses, taking a marginally reticulated structure with properties of an elastomer material; rigid polyurethane adhesives are and in addition cure by polyaddition however they additionally gain a high crosslink structure of thermoset material.[23]

There are 3 different types of polyurethane adhesives or glues:

- 2 component Polyurethane adhesives (Pur 2C)
- 1 component Polyurethane adhesives curing by heat (Pur 1C - heat) - Rigid polyurethane
- 1 component Polyurethane adhesives curing by moisture (Pur 1C - moisture) - Elastic polyurethane

Mono component polyurethane adhesives

Aadhesive 1 component can be elastic or rigid adhesives, depending on the structure of thermoset or elastomer that acquires the adhesive once it has been cured.[24]

The elastic polyurethane adhesives are those cured by the action of moisture; however the rigid polyurethane adhesives are those that are cured by heat input.

Mechanical properties of Pur 1C-moisture are as follows (i) they are flexible and elastic materials (ii) strength about 8 MPa to normal stress (iii) Maximum elongation over 600%

Chemical properties of Pur 1C-moisture are (i) Poor resistance to ultraviolet radiation (ii) Less resistance to chemicals than silicone (iii) It can be painted (iv) It is necessary to use primers and activators to ensure adhesion.

Typical properties of 1C Pur cure by heat.

Mechanical properties rigid adhesives are (i) strength about 15 MPa to normal stress (ii) Maximum elongation over 20% (iii) High resistance to fatigue.

Chemical properties are (i) Poor resistance to ultraviolet radiation (ii) They can be painted (iii) some modified adhesives can absorb oils.

Two components polyurethane adhesives:

Basic components of 2C Pur and poly reaction are resin–polyols with low molecular weight and hardener - low molecular weight prepolymers with isocyanate finishes.[25] Mechanical characteristics of elastic polyurethane adhesive are (i) Elastomer structure. (ii) Strength is about 8 Mpa. (iii) Maximum elongation over 600%. (iv) Very good resistance to creep (long exposure to static loads). Mechanical characteristics of rigid polyurethane adhesive are (i) Thermoset structure ii) strength about 25 Mpa iii) maximum elongation over 50%. Chemical properties of two components polyurethane adhesives are (i) They are sensitive to radiation U.V. (ii) Less resistance to chemicals that epoxy adhesives (iii) They can be painted.

1.5.5 Polyurethane Sealants

Synthesized through the response of glycol and an isocyanate, polyurethane is a natural compound with especially great dampness and erosion resistance qualities. Polyurethane sealant is helpful in both mechanical and business applications. Also, polyurethane is regularly utilized as substantial obligation cement, and in addition a covering.[26] A polyurethane sealant may be squeezed, layered, splashed, or brushed onto joints, yet the most widely recognized technique for application is with a caulk firearm. Most sealants are sold in 10-ounce (295.74 ml) tubes that will fit the normal caulking weapon. And being impervious to dampness, chemicals, and consumption, polyurethane sealant is noted for its adaptability. A typical issue with joints is the extension and constriction of the joint. Polyurethane, with its inalienable versatility, is especially impervious to breaking because of development of the joint materials. These sealants are available as either one- or two-component compounds. Since the typical residential user is typically looking for one that is easy to use, the basic residential product has only one component. This means there is no need to mix ingredients before they can be used. The common polyurethane sealant is hydrocarbon-based. With the advances in water-based polyurethane innovation, then again, successful water-based, or latex, sealants and coatings are presently accessible. These items are noted for their low-scent, low-variable natural compound (VOC) substance, and simplicity of utilization and cleanup. A quality sealant will stick to brick work, wood, solid, steel, aluminum, vinyl, and most plastics. It’s adaptable, yet strong complete secures these powerless materials, as well as, when utilized as a covering, gives a glimmering, flaw free complete, also. Clearly, legitimate application systems must be utilized to accomplish the wanted results. Polyurethane coatings work particularly well as a hostile to destructive on metal items. A few specialists even suggest utilizing it over powder covering for securing metal, however a textured completion, which numerous individuals require, is hard to accomplish.

1.5.6 Polyurethane Thermoplastic:

Thermoplastic polyurethane (TPU) is any of a class of polyurethane plastics with numerous properties, including flexibility, straightforwardness, and imperviousness to oil, oil and scraped area. In fact, they are thermoplastic elastomers comprising of straight portioned piece copolymers made out of hard and delicate sections.[27] TPU are shaped by the response of: (1) di-isocyanates with short-chain diols (alleged chain extenders) and (2) di-isocyanates with long-chain diols. The for all intents and purposes boundless measure of conceivable mixes producible by shifting the structure and/or atomic weight of the three response mixes takes into consideration a tremendous assortment of distinctive TPU. This permits urethane scientific experts to tweak the polymer's structure to the wanted last properties of the material. TPU has numerous applications including car instrument boards, caster wheels, force devices, donning products, therapeutic gadgets, drive belts, footwear, inflatable pontoons, and an assortment of expelled film, sheet and profile applications. TPU is additionally a well-known material found in external instances of versatile electronic gadgets, for example, portable phones.[28]

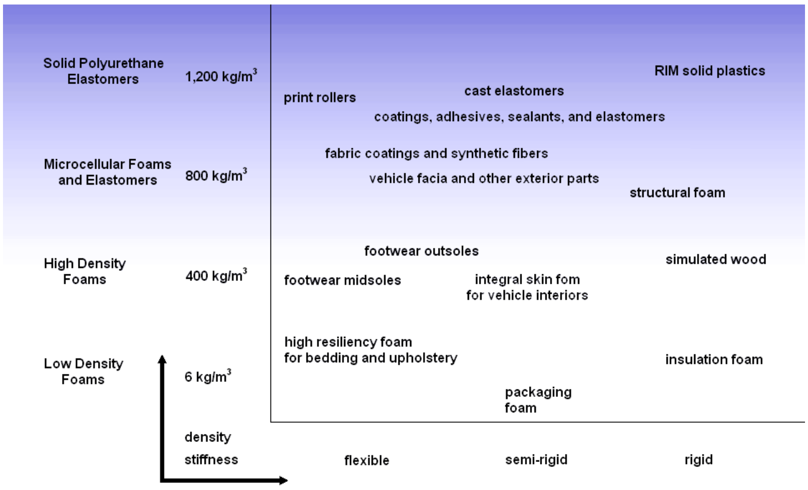


Figure 1.2 different Categories of Polyurethane

1.6 Origin of Research Problem

Among all polymers polyurethanes have a very wide range of polymers depending upon its method of preparation and the raw materials used These are formed by the polyaddition reaction, generally when a monomer containing di-isocyanates reacts with another monomer containing diols. The monomeric component i.e di or polyols can be obtained from plant seed oils. The vegetable oils are saturated and unsaturated ester which has some free double bonds and hydroxyl group. These hydroxyl groups are not enough to produce enough good mechanical properties in resulting polyurethane material. Some chemical modification are required the Hydroxyl value of these oils.

The use of Di-isocyanates is not safe towards health and environment. The exposure to isocyanate causes irritation of skin and mucous membranes, chest tightness, and difficulty in breathing. Isocyanates include compounds classified as potential human carcinogens and known to cause cancer in animals. The main effects of hazardous exposures are occupational asthma and other lung problems, as well as irritation of the eyes, nose, throat, and skin. Later on a new methodology was developed to achieve the urethane that was free from the use of di-isocyanate as raw material. The di-isocyanate and diol were replaced by Di-cyclic carbonate and diamine respectively. The ring opening of cyclic carbonate by amine gives urethane unit in chain. In this methodology the naturally occurring unsaturated oils first converted into their corresponding epoxide and then insertion of Carbon dioxide under vigorous condition in presence of catalyst give cyclic carbonate. The yield of cyclic carbonate is not that much good and the use of hydrogen peroxide, acids and reaction makes it expensive. Other hand the generation of the waste material during of Epoxidation is highly acidic which is due to formic acid that make water acidic.

Glycerol is generally used for enhancing the hydroxyl value of oils. Since glycerol is trihydroxy compound and there are many studies where the glycerol carbonate was reported to be synthesized from glycerol and epoxides. The major problem with glycerol carbonate is isolation due to high miscibility of both glycerol and glycerol carbonate in water. Moreover, these methods need expensive resins and catalyst. Taking all these issues under consideration, this studies aims to synthesize a glycerol base new monomer for the Non Isocyanate polyurethane formation (NIPU). Glycerol is a very nice naturally as well as waste material of the various industries. Glycerol is used in some medical purpose also but with its very high purity level. The huge availability and biocompatibility of Glycerol attracts very much. So we have been attracted to utilize this huge available material for better mankind application.

1.7 Objective of the Research Work

The aim of this present project is to develop the new methodology for the **"Synthesis of Glycerol Based Novel Monomer for Non Isocyanate Polyurethane (NIPU)"** During this project work I have utilize glycerol to synthesize new monomer for NIPU preparation. Here I summaries my objectives the Research programme.

The objectives of my works are:

(a) Synthesis of Glycerol Carbonate (4-(hydroxymethyl)-1, 3-dioxolan-2-one)

(b) Characterization of Glycerol Carbonate

(c) Synthesis of Monomer: Bis ((2-oxo-1,3-dioxolan-4-yl)methyl) (methylene bis(4,1-phenylene)) dicarbamate

(d) Characterization of Monomer

(e) Reaction of Monomer with Various Amines and Conformation of Urethane (-NH-COO-) by IR spectroscopy

CHAPTER-2

POLYURETHANE CHEMISTRY

Bayer and co-workers discovered polyurethanes (PUs) having modular-like polymer structure with diverse properties over 75 years ago (Figure 1).[29] PUs are in the class of compounds called “reaction polymers”, which could be achieved by the polymerization reaction between monomers such as di- or polyisocyanates and polyols. The polymerization reaction usually requires either base catalyst such as DABCO, DBU, TEDA, DMCHA, DMEA etc or UV light irradiation.[30a,b] However, polyurethane was also achieved by catalyst free methodology from the highly reactive monomers.[31] Polyurethanes are the only class of polymers that exhibit elastomeric, thermoplastic, and thermoset properties depending on their chemical composition. In 2011, global polymer consumption reported that 14 out of 280 million tons (that is ≈ 5%) were found to be the raw materials of polyurethane such as polyisocyanates and polyols.[32]

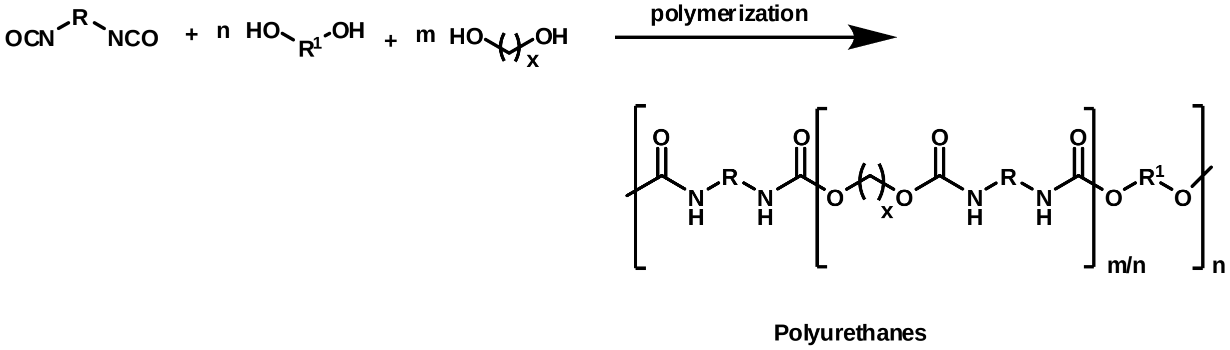


Figure 2.00 General structure of polyurethanes. (If m = 0, linear and single-phase; if m = 1, 2, phase separated).

PU can be classified in to two types on the basis of monomers used for the polymerization.

(i) Isocyanate based polyurethane (ii) Non-isocyanate based polyurethane

2.1 ISOCYANATE POLYURETHNAES:

Isocyanate based polyurethane were synthesized by polymerization reaction between either aromatic di-isocyanates such as toluene diisocyanate (TDI) isomers including 2,4-TDI (1) and 2,6-TDI (2), and methylene diphenyl diisocyanate (MDI) isomers including 4,4'-MDI (3), and

2,4'-EDI (4) or aliphatic di-isocyanates including hexamethylene di-isocyanate (HDI, 5), isophorone diisocyanate (IPDI, 6), and hydrogenated MDI (H12MDI, 7) and polyols.[33]

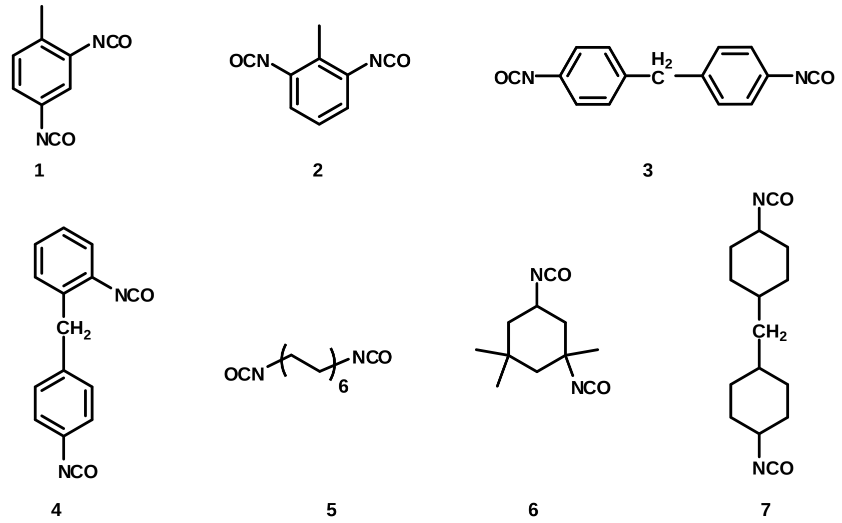


Figure 2.1 Commonly Used Di-isocyanates

The natural source of polyols from renewable oils including castor, soybean, peanut, sunflower oils etc. were considered to be sustainable precursors for PU synthesis. However, these oils have very few hydroxyl groups in their chains and could be improved by chemical modifications such as transesterification with glycerol, ethylene glyocol, polyethelene glycol etc. Castor oil is a source of ricinoleic acid, occurred from seeds of the castor oil plant (*Ricinus communis*) (Figure 2.2).[34] Ricinoleic acid is a unusual 18-carbon monounsaturated fatty acid with hydroxyl functional group on the 12th carbon and a *cis*-double bond at 9,10th carbons. The unique property of ricinoleic acid is further chemical modification on these functional groups, which is not possible with other renewable oils. The ricinoleic acid is a major constituent (85-95%) of castor oil, and the remaining fatty acids are stearic acid dihydroxystearic acid, linoleic acid, palmitic acid, α-linolenic acid, oleic acid are in very minor (15-5%) as shown in Table 1.[35]

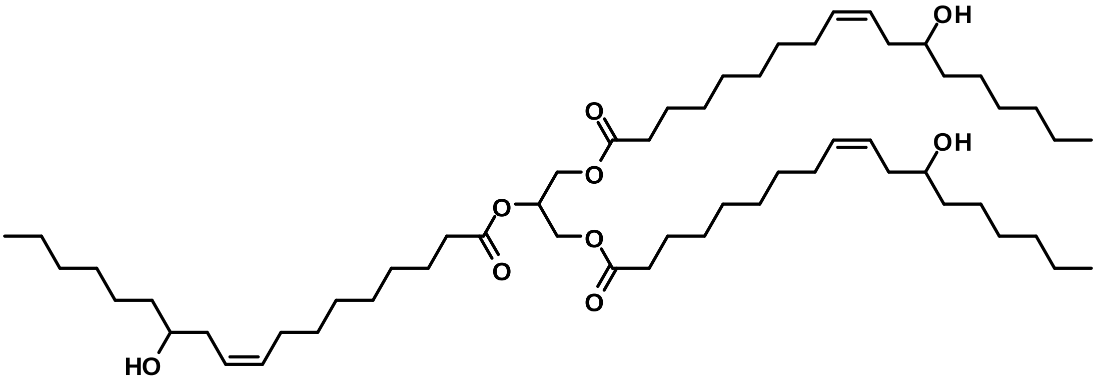
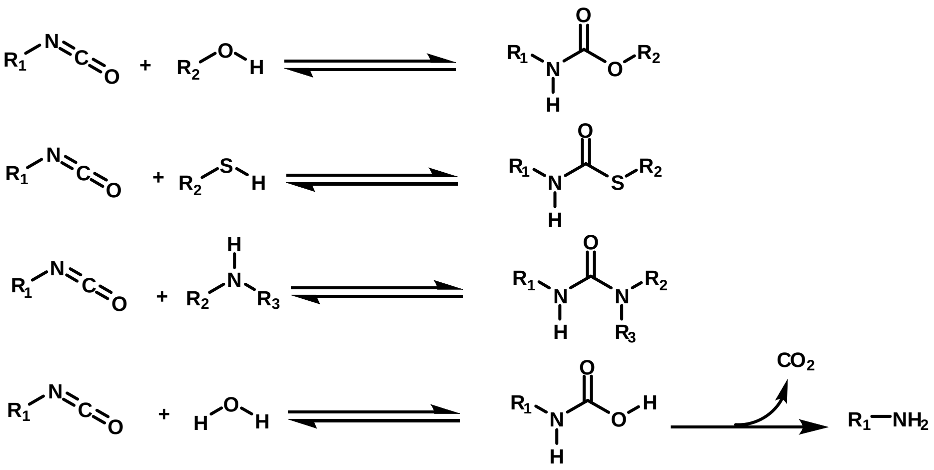


Figure 2.02: Structure of Ricinoleic Acid

Table 2.01: Average Composition of Castor Seed Oil/Fatty Acid Chains

Acid name	Average percentage (%)
Ricinoleic acid	85 – 95
Stearic acid	0.5 – 1
Dihydroxystearic acid	0.3 – 0.5
Linoleic acid	1 – 5
Palmitic acid	0.5 – 1
α-Linolenic acid	0.5 – 1
Oleic acid	2 – 6
Others	0.2 – 0.5

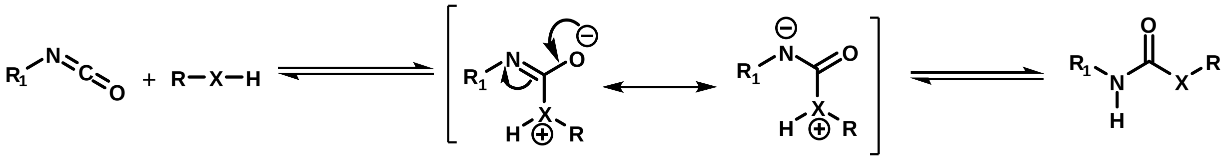
The hydroxyl functionalization of olefinic bonds in unsaturated acids of renewable oils including soybean, canola, sunflower, and peanut could be achieved by epoxidation methodology. The possible side reactions of isocyanate with substrates having active proton are as shown in the Scheme 2.1.[36]



Scheme 2.1: Possible Reactions of Isocyanate

2.1.1 MECHANISM OF POLYURETHANE FORMATION

The monomers of PU such as diisocyanate and polyols have reactive centers by means of which they bind covalently to each other to obtain strong polymeric chains. Carbonyl carbon of isocyanate group acts as an electrophile and alcoholic oxygen of polyols acts as nucleophile. Base catalyst is required to enhance the reaction between these two substrates to produce urethane. However, in case of highly reactive monomers, the reaction proceeds without catalyst. The plausible mechanism of either catalyst free or base catalyzed urethane formation is as shown in Scheme 2.2. First nucleophilic addition of RXH on isocyanate group results anionic species, which further undergoes rearrangement to afford urethane. The both of these two steps are reversible.[37]



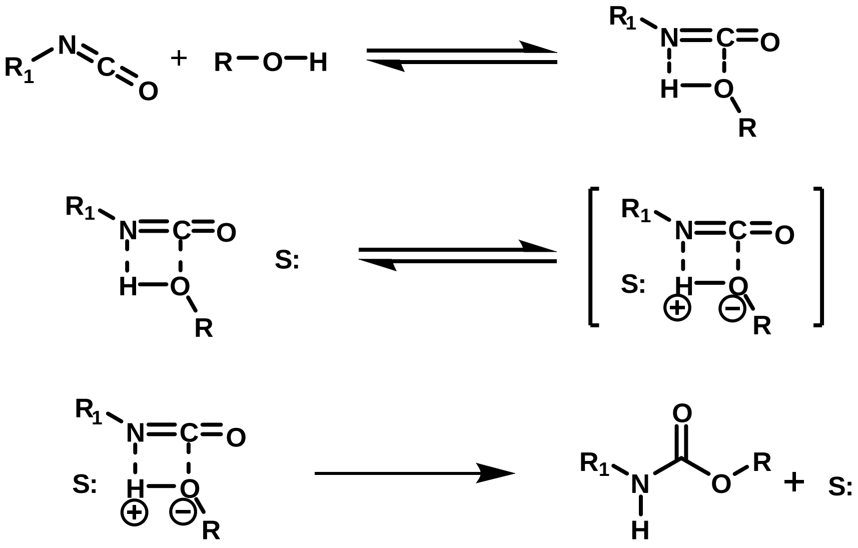
X= O, S, NH

R_1= Alkyl, Aryl substituents

R_2= Alkyl, Aryl substituents

Scheme 2.2 Plausible Mechanism of Urethane Formation

Chang *et al.* proposed a plausible mechanism, where solvent is also participating in the reaction. This mechanism involved in three steps, first and second steps are reversible and third step is irreversible to afford the urethane. In the first step, isocyanate interacts with alcohol to give a four membered cyclic structure which is stabilized by solvent molecules in the second step. Finally the urethane can be obtained with the release of solvent molecule (Scheme 2.3).[38]

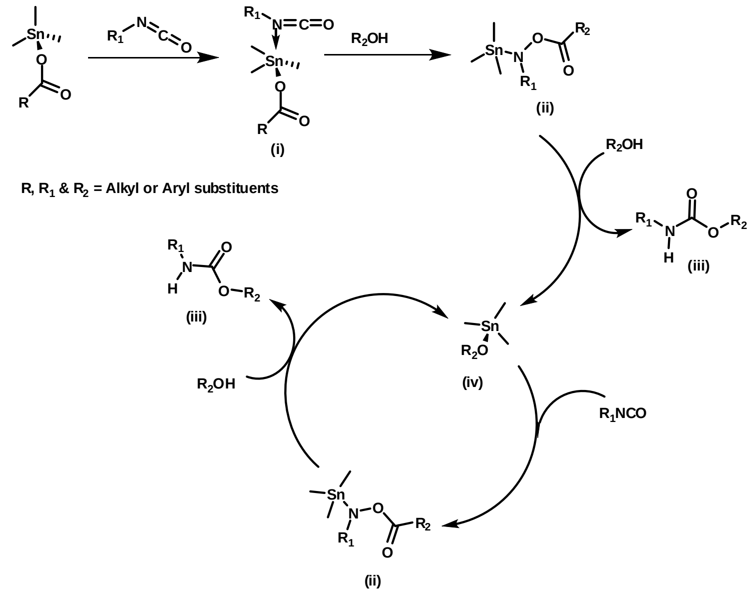


R_1 & R_2 = Alkyl, Aryl substituents

S = Solvent

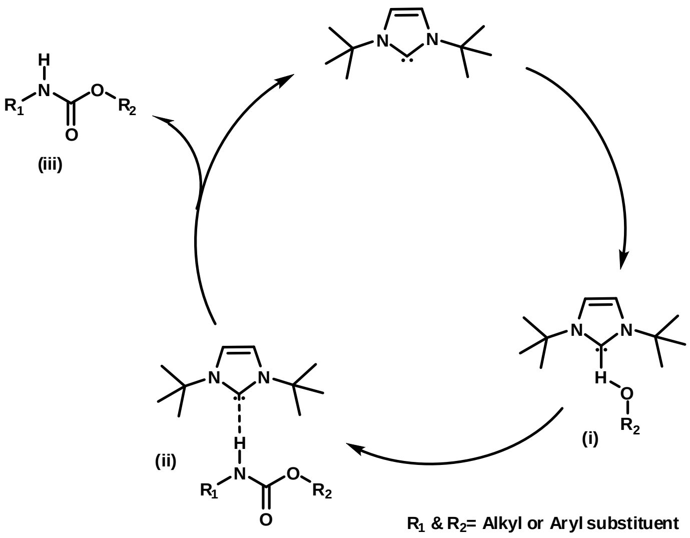
Scheme 2.3: Plausible Mechanism of PU

Bloodworth and Davies studied the effect of organotin catalyst for polymerization reaction to afford PU and its mechanism of formation. The plausible mechanism involves the formation of organotin complex with isocyanate, followed by attacking of alcohol to rearrange to afford the urethane.[39]



Scheme 2.4: Organotin Complex Catalyzed Urethane Formation

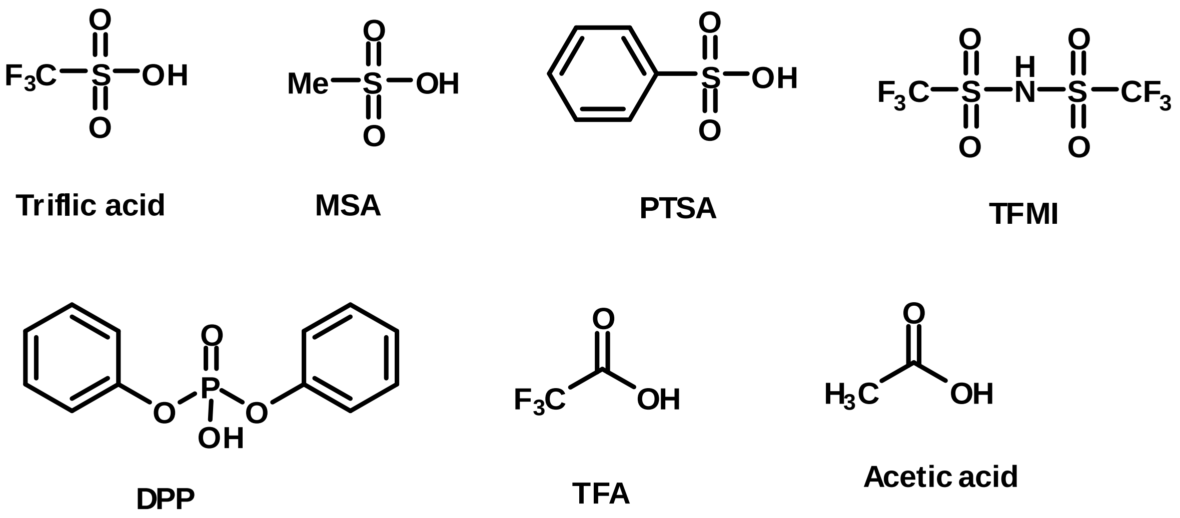
Coutelier *et al.* investigated the use of N-heterocycle carbene catalyst for the synthesis of urethane and PU. In this protocol carbene center activates the hydydoxyl hydrogen to form the intermediate (i). The isocyanate is then attacked by intermediate (i) to afford the urethane (iii). (Scheme 2.5).[40]



Scheme 2.5: *N*-Heterocycle Carbene Catalysed Urethane Formation

2.1.2 *Organic Acid-Catalyzed Polyurethane Formation via a Dual-Activated Mechanism:*

In 2013, Haritz *et al.* reported the organic acid catalyzed polymerization of poly (ethylene glycol) and hexamethylene diisocyanate to afford the polyurethane. Among the various screened organic acid catalysts (Figure 2.3), the sulfonic acid was found to be more efficient to afford polyurethane with high molecular weight. Moreover, the dual activation of sulfonic acid catalyst was supported from the molecular modeling study.[41] The mechanism of organic acid catalyzed formation of polyurethane involved via O-activated and N-activated formation of urethane from isocyanate and alcohol.



Triflic acid

MSA

PTSA

TFMI

DPP

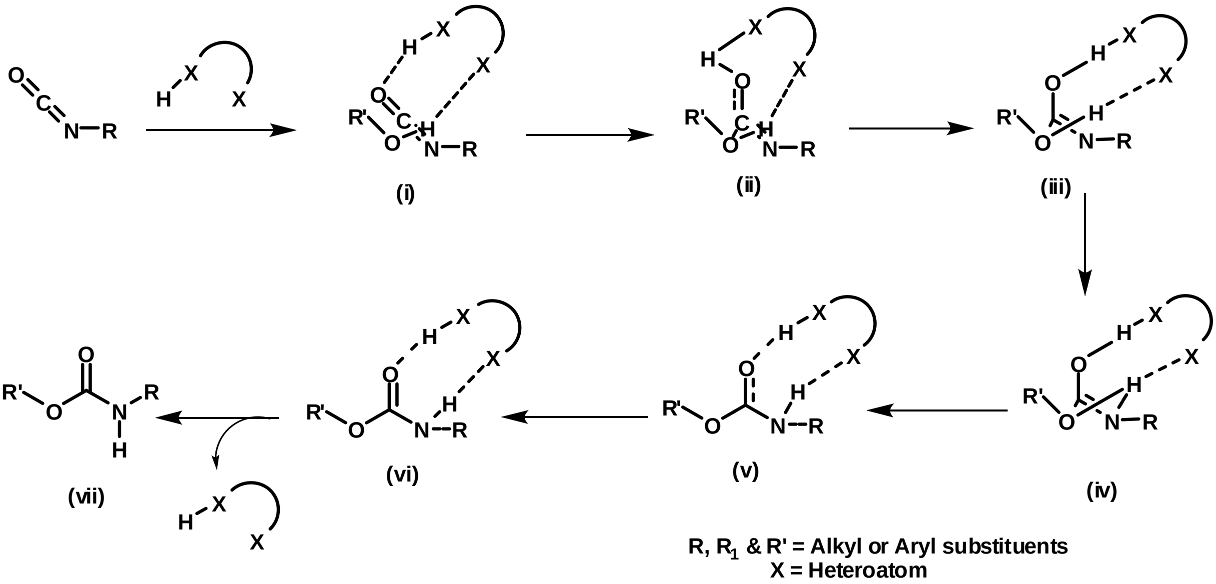
TFA

Acetic acid

Figure 2.03: Structures of Organic Acid Catalysts

O-Activated Urethane Formation:

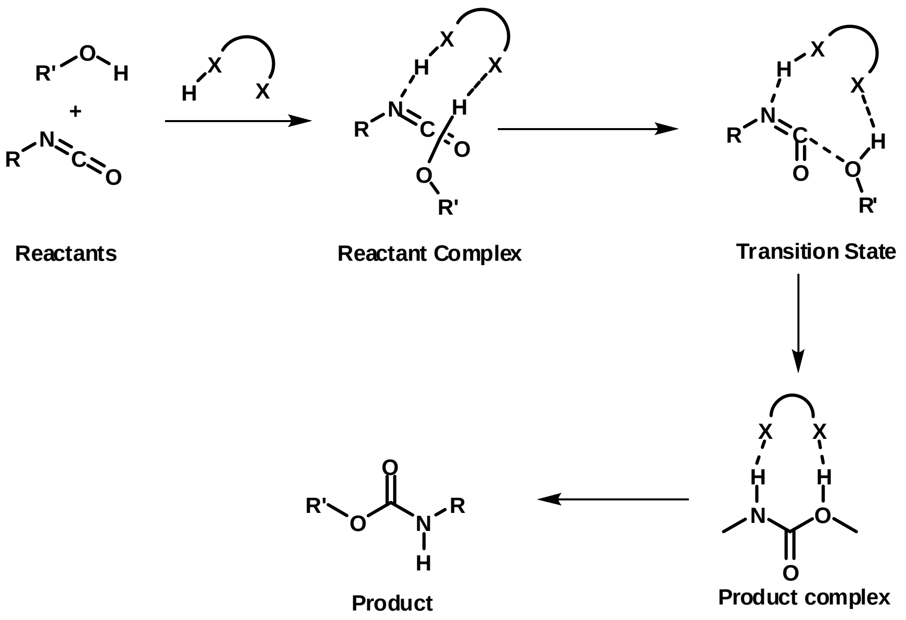
In this methodology, the organic acid catalyst interact with the oxygen atom of isocyanate group while on the other hand another hetero atom of catalyst attract the proton of alcohol to afford the complex (i) & (ii) (scheme 2.6). Nucleophilic oxygen of alcohol attacks on electron deficient carbon of isocyanate to form a covalent bond in the transition state (iii). The alcoholic proton in complex (iii) abstracted by nitrogen atom of isocyanate group to afford intermediate (iv). Finally, urethane can be obtained by the rearrangement of intermediate (iv) as shown in Scheme 2.6.



Scheme 2.6: Organic Acid Catalyzed O-activated Polyurethane Formation

N-Activated urethane formation:

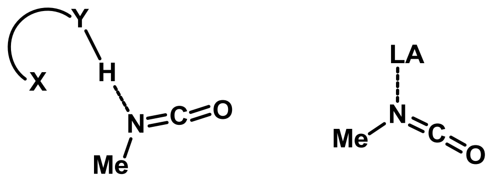
The *N*-activation was achieved by organic acid catalyst for the formation of urethane. In this method, the nitrogen atom of isocyanate group abstracts the proton from acid catalyst followed by abstraction of alcoholic proton by heteroatom of organic acid catalyst to form reactant-acid catalyst complex. The reactant complex converts into product complex *via* transition state to afford urethane as shown in Scheme 2.7.



Scheme 2.7: Organic Acid Catalyzed N-activated Urethane Formation

Activation of electrophilicity of carbonyl carbon of isocyanate ($\mathrm{Me{-}N{=}C{=}O}$ *)*

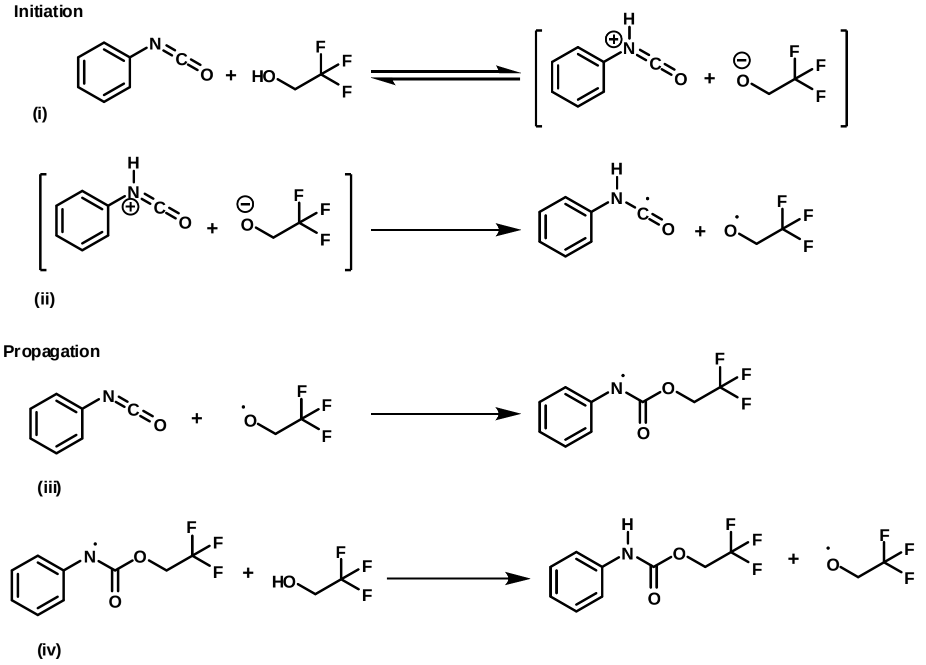
The sp hybridized carbon atom of isocyanate molecule is covalently flanked between more electronegative nitrogen and oxygen atoms. Since the oxygen atom is more electronegative than nitrogen, the flow of electron takes place more towards oxygen than the nitrogen atom. Due to inductive effect of these atoms, the carbon atom becomes electrophilic. The electrophilicity of the carbon atom depends on the electronegativity of nitrogen or oxygen atoms of isocyanate group. The nitrogen and oxygen both have tendency to share their non bonding electrons to electron deficient species like Lewis acid (Scheme 2.8). The oxygen atom of isocyanate coordinates with Lewis acid, which results in the increase of electrophilicity of carbon attached to oxygen atom.



Scheme 2.8: Interaction of Lewis Acid with Isocyanate Group

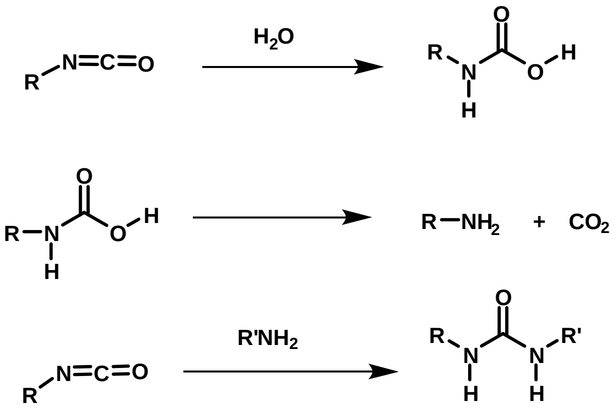
2.1.3 Activation of Extremely Weak Nucleophiles through Photochemical Irradiation

Recently, Marquet *et al.* reported the synthesis of fluorinated urethanes and polyurethanes under photochemical conditions.[42] the initiation step is reversible and involves the transfer of proton from alcohol to isocyanate to afford an activated complex (i) (Scheme 2.9). The radical formation takes place due to the transfer of electrons from ions. The polyfluoroalkoxy radical is found to be a key intermediate for the radical chain mechanism. In the propagation stage, the reaction between alkoxy radical and isocyanate gave carbamate radical, which further reacts with fluorinated alcohols to afford fluorinated urethane and alkoxy radical.



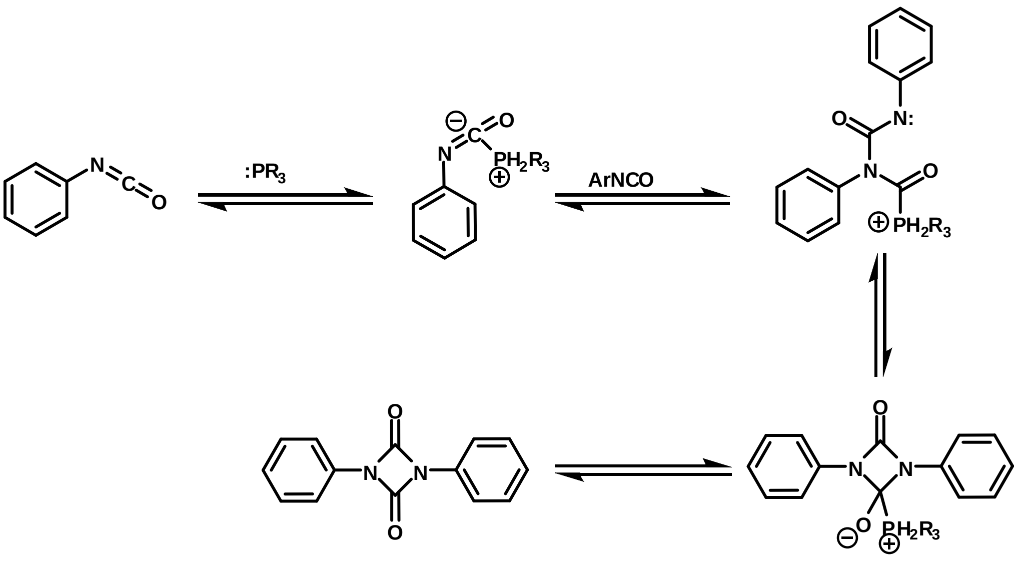
Scheme 2.9: Plausible Mechanism for Formation Polyurethane under Photochemical Condition

Blowing reaction: Isocyanate reacts with water to give carboxylic acid which decomposes into carbon dioxide and amine diffusion. Trapping of CO_2 into polymeric chain creates voids in the bulk of material, is called as “cell”. During this reaction, some blowing characteristics appears in the resulting material hence the reaction is known as blowing reaction (Scheme 2.10).[43]



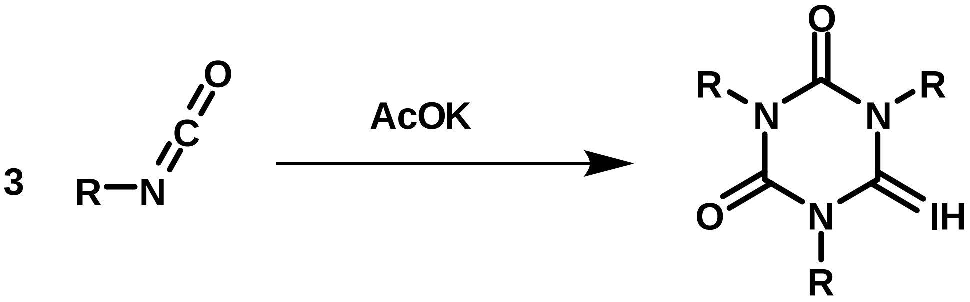
Scheme 2.10: Blowing Reaction of Isocyanate

2.2 Phosphene catalyzed dimerization reaction of Arylisocyanate:[44]



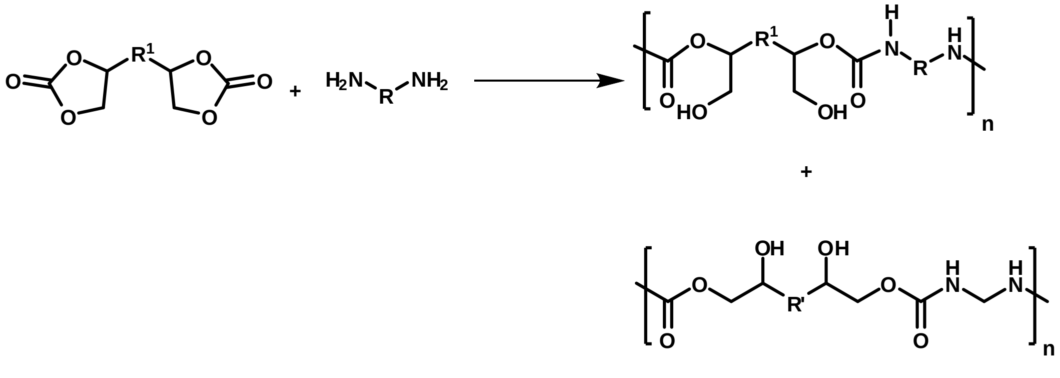
Scheme 2.11: Phosphene Catalyzed Dimerization Reaction

2.3 ISOCYANATE TRIMERISATION REACTION: Some specific catalysts such as potassium acetate, tris dimethylaminomethyl phenol etc promotes the trimerisation reaction among three molecules of isocyanate to afford the heterocyclic isocyanurate compounds. This reaction produces isocyanuric foams. However, in case of excess isocyanates the formation of highly cross linked polymers is also observed. The obtained structures contain urethane groups from the reaction of hydroxyl group with isocyanate, along with this isocyanuric ring.[45]



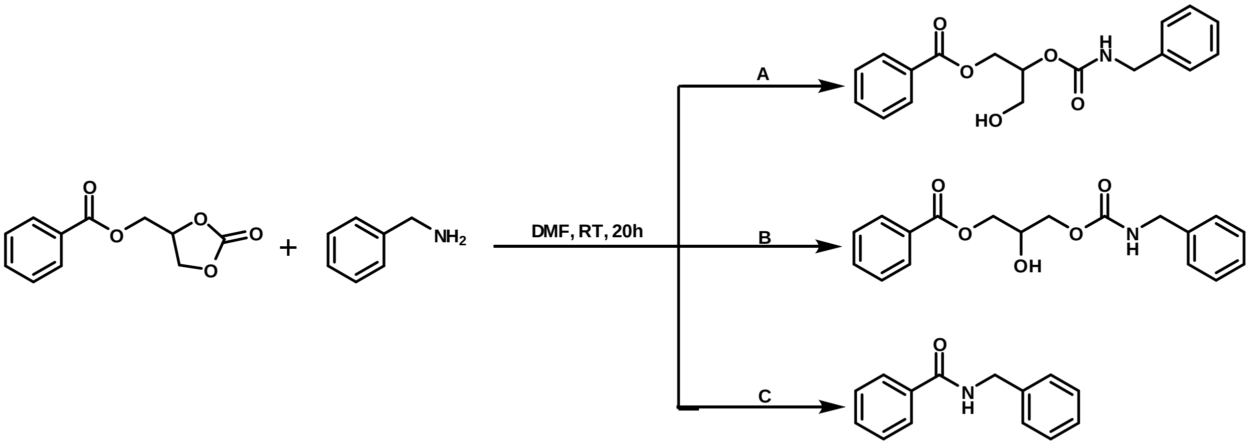
Scheme 2.12: Isocyanate Trimerisation Reaction

2.4 REACTANTS USED FOR NIPU PREPARATION: Polyurethane skeleton was made by another method, where the conventional reactants were replaced by diamine and dicyclic-carbonate. In 1957, Groszos *et al.* patented a novel non isocyanate methodology for the synthesis of polyurethane.[46] In this method, dicyclic carbonate and diamines were used as monomers to afford the non isocyanate polyurethane. These monomers are highly reactive in such a way that the cyclic carbonate ring could be possible to open with either primary or secondary amines in the absence of catalyst at room temperature. The diamine reacts with dicyclic carbonate to afford the original polymer skeleton with free hydroxyl group that could not obtained by common isocyanate and alcohols. The dicyclic carbonates can be synthesized from renewable oils including soybean, peanut, sunflower oils and naturally occurring or derived epoxides etc.



Scheme 2.13: Polyurethane from Dicyclocarbonate and Diamines

2.4.1 Mechanism involved in NIPU synthesis: Endo *et al.* investigated the formation urethane from (2-oxo-1, 3-dioxolan-4-yl) methyl benzoate as nonfunctional cyclic carbonate and benzyl amine. Although, however they did not observe the aminolysis product formation, but interesting to find two isomeric products, which results from ring opening of cyclic carbonate (Scheme 2.14).[47]



Scheme 2.14: Mechanism for NIPU Synthesis

The mechanistic studies with the support of theoretical calculations reveal that the secondary hydroxyl group containing compound (B) predominates over primary hydroxyl group containing compound (A) due to its stability. In case of dicyclic carbonate, the ratio of these two products obtained were determined by substituents introduced α methylene. An electron withdrawing group favours the reaction towards opening of cyclic carbonate ring in such a way to afford 2^0 hydroxyl group containing compound.[48] Molar mass and chemical structure of amine governs the reactivity: α & β-electron-withdrawing substituents, aromaticity and molar mass lower the reactivity.

Reactivity: Kotzev et al. studied the reaction between laprolate and various amines to determine a pattern of reactivity of amines with cyclic carbonate. The decrease in reactivity of amine in solvent free condition was explained by the amine concentration dropping off as the molar mass of the amines increases.[49] The results reveal that the usage of catalyst or raising reaction temperature could improve the product formation and they proposed a scale for structure activity relationship.

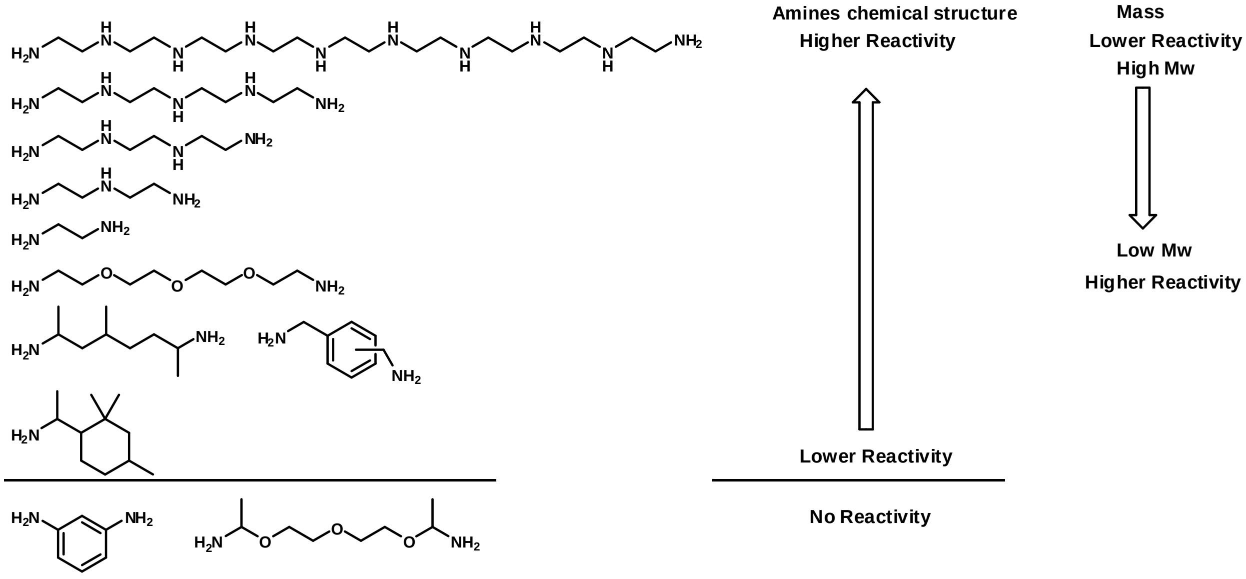


Figure 2.04: Proposed Scale for Structure Activity Relationship

Larger Cycles: Endo et al. investigated the reactivity of different ring size cyclic carbonates including five and six membered cyclic carbonates from epoxy/CO_2 and malonate /triphosgene respectively. The reaction of six membered cyclic carbonate with 4, 9-dioxadodecane-1, 12-diamine was found to be 20 and 10 times more reactive than five membered cyclic carbonate at 30 °C and 70 °C respectively. In the continuation of these studies, Guillaume *et al.* synthesized seven membered cyclocarbonates from levunilic & itaconic acids as starting material. Rather than NIPU, these carbonates were used for ring opening metathesis polymerisation (ROMP) to prepare polycarbonates.[50]

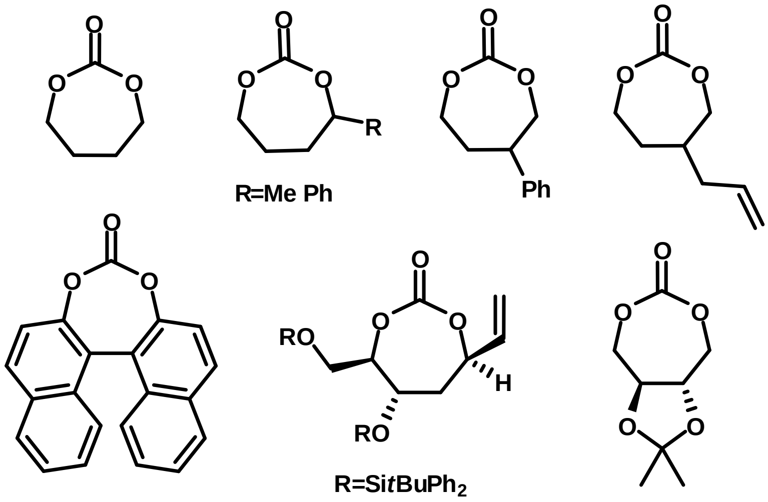
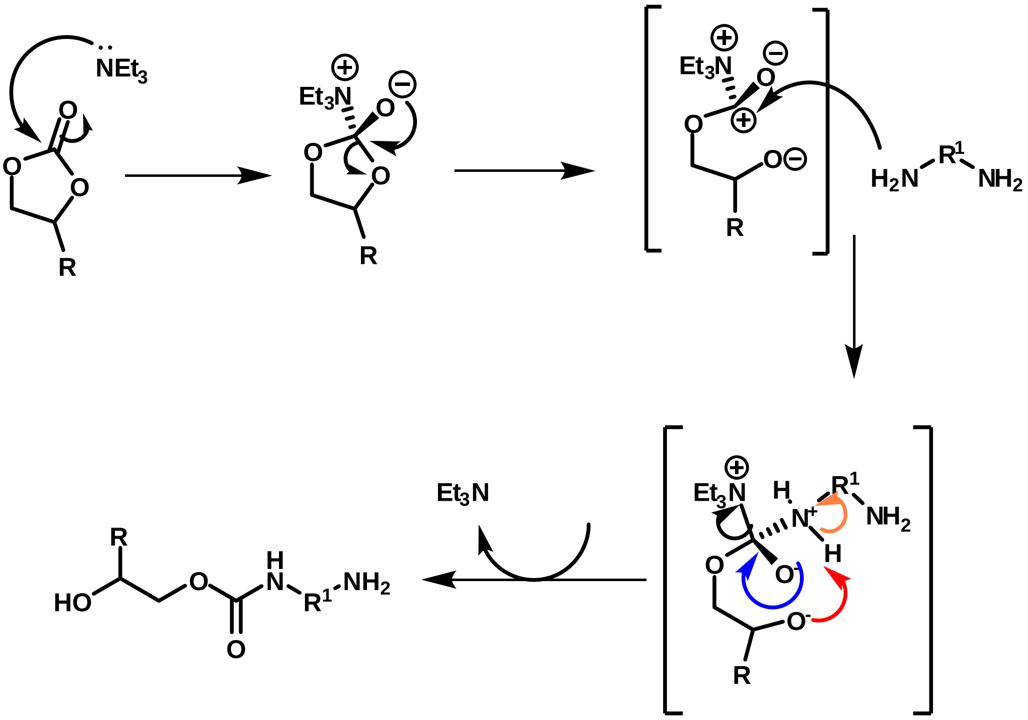


Figure 2.05: Structures of Seven Membered Cyclocarbonates

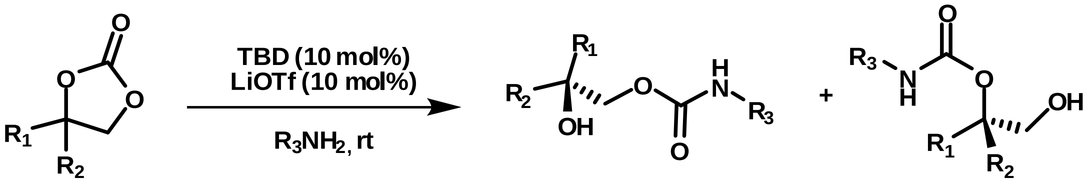
Ring opening metathesis: Kotzev *et al.* reported the plausible mechanism for base catalyzed ring opening metathesis for synthesis of urethane from cyclic carbonate and amine.[51]



Scheme 2.15: Ring Opening Metathesis for Urethane Formation

In the mechanism, triethyl amine acts as a base catalyst, which attacks on electrophilic carbonyl carbon of cyclic carbonate to form a covalent bond. The sp^3 tetrahedral carbon reversibly gets converted into sp^2 carbon results in ring opening of cyclic carbonate. The nitrogen atom of diamine attacks on electron deficient carbonyl carbon to form a covalent bond. The rearrangement of alkoxide ion resulted in the formation of urethane.

Recently, Scheidt *et al.* reported a triazabicyclodecene/lithium triflate (TBD/LiOTf) catalyzed ring opening method for the synthesis of urethane and polyurethane. Triazabicyclodecene was used as catalyst and lithium triflate as co-catalyst.[52]



Scheme 2.16: TBD/LiOTf Catalyzed Formation of Polyurethane

They proposed the plausible mechanism for TBD/LiOTf catalyzed synthesis of polyurethane as depicted in Figure 2.06. Initially, the lithium ion gets coordinated with sp^2 nitrogen atom of the TBD (v) to bring equilibrium between complex and free starting materials (i). On other hand, the Li ion coordinated with the carbonyl oxygen of cyclic carbonate to activate the opening of cyclic carbonate ring by TBD (ii) and (iv) followed by attacking of amine to afford urethane product.

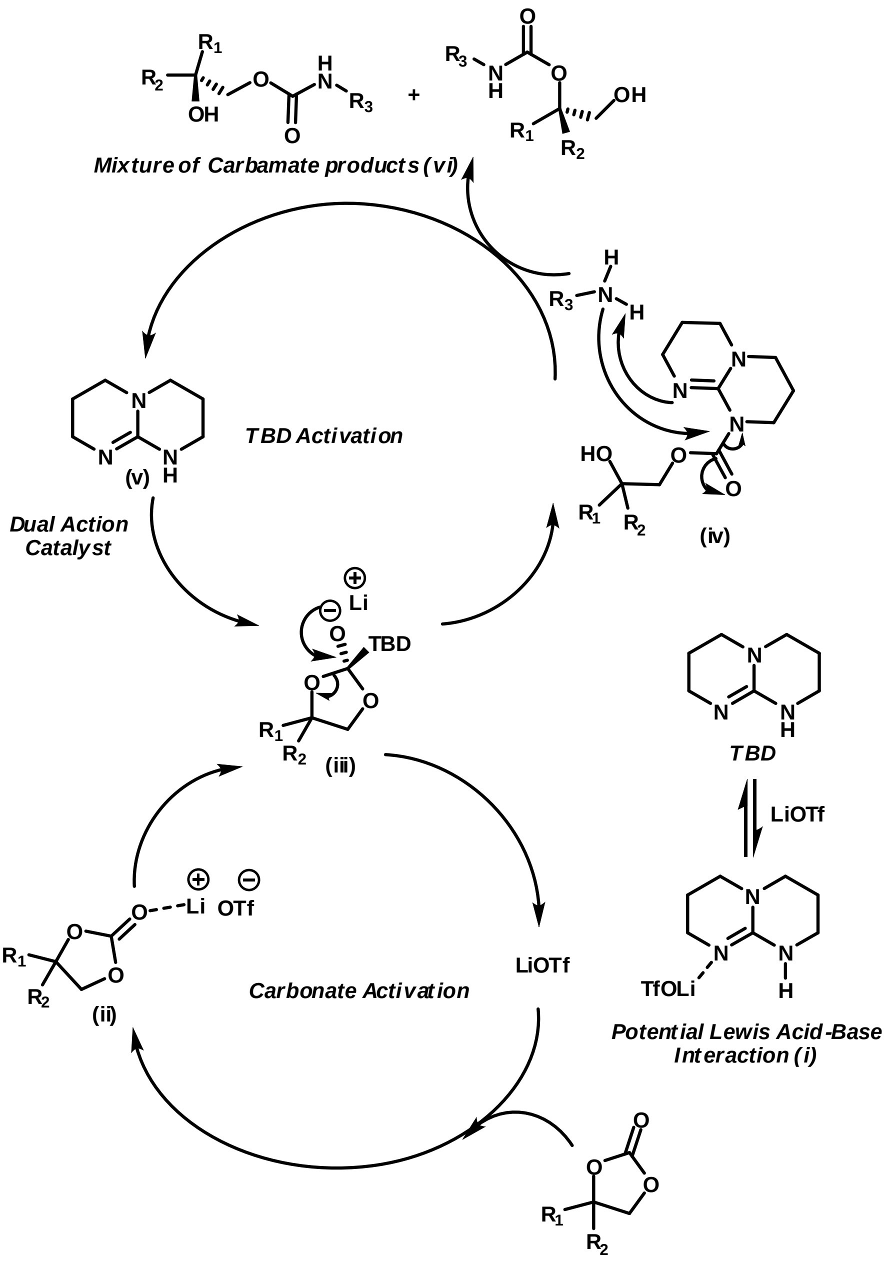
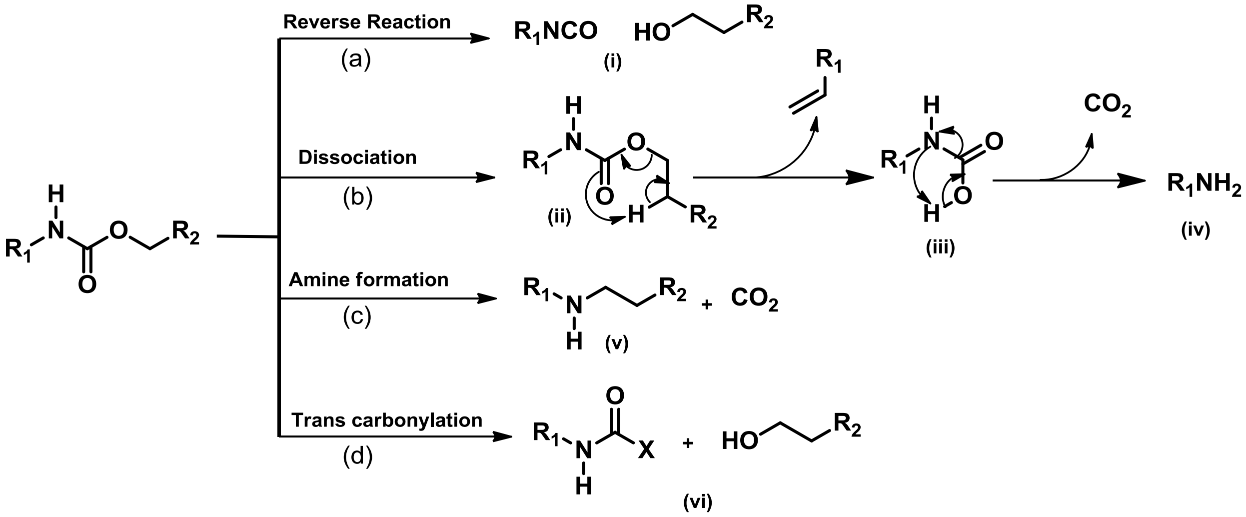


Figure 2.06: Plausible Mechanism for TBD/LiOTf Catalyzed Synthesis of Polyurethane

Polyurethanes are chemically as well as biologically degradable polymers. The chemical degradation of PU follows the four types of mechanism as shown in Scheme 2.17. (a) In reverse reaction of urethane, the formation of monomers such as isocyanate and alcohols can be possible (b) The dissociation mechanism involves the formation of alkene, amine and release of carbon dioxide (ii, iii & iv). (c) Moreover, amines can also generate during the release of CO_2 from urethane. (d) Trans-carbonylation process involves the formation of amide and alcohol. Biodegradability of polyurethanes mainly depends on their accessibility towards enzyme degradation including reactive chemical functional groups, molecular orientation, crystallinity and cross-linking etc.[53-55]



Scheme 2.17: The Chemical Degradation of PU

CHAPTER –3

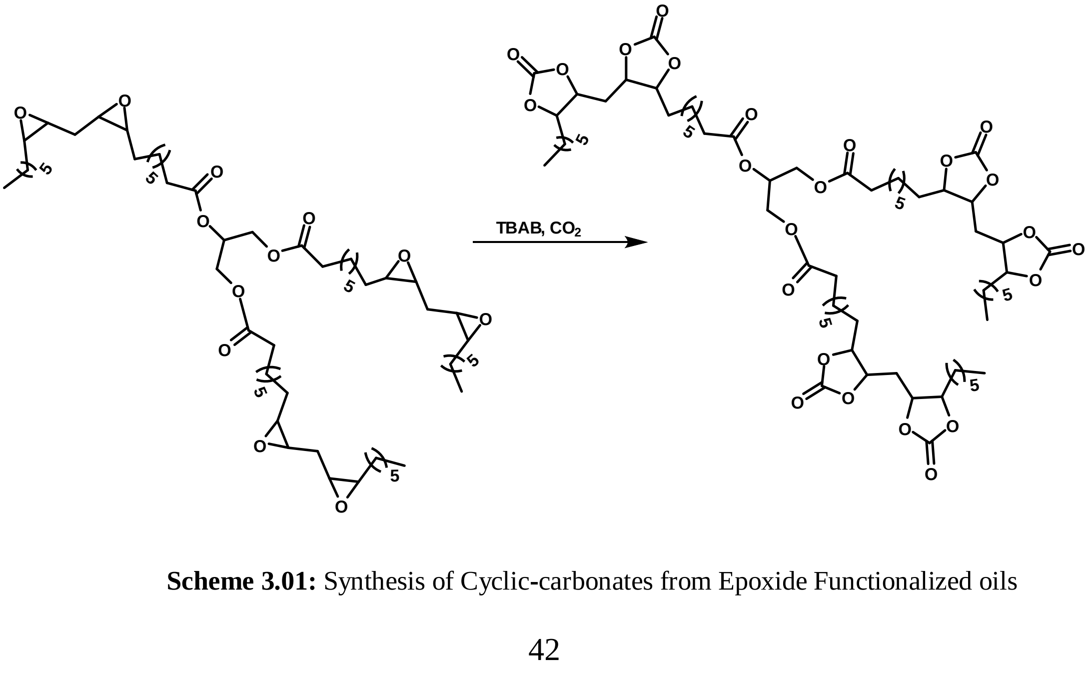
LITERATURE REVIEW:

NON ISOCYANATE POLYURETHANE (NIPU)

3.1 Introduction

Non-isocyanate polyurethanes (NIPU) can be synthesized from the reaction between dicyclic carbonate and diamines.[56] NIPU has been attracted the great attention in both academic and applied research areas due to its green approach of isocyanate free preparation and their excellent properties.[57] Cyclic carbonates are non-toxic and bio-degradable green intermediates for the synthesis of NIPU. The polyurethane obtained from this methodology has linear network with new hydroxyl groups at β-position of carbonyl functional group of urethane. NIPU is moisture insensitive to the moisture present in the surrounding environment. This methodology is very easy to handle and NIPU could be obtained from commercially available diamines and cyclic carbonates, readily obtain from the chemical modification of natural organic molecules. Till date, several research groups have developed various methodologies to make cyclic-carbonate from different sources.[58]

Moritz and Mulhaupt have developed methodology for production of linseed and soybean oil-based polyurethanes. In this methodology, the epoxydized linseed and soybean oils were converted into carbonated vegetable oil under the pressure of 10 to 30 bar at 140 °C temperature in presence of TBAB catalyst.[59]



Scheme 3.01: Synthesis of Cyclic-carbonates from Epoxide Functionalized oils

The product formation was confirmed by ^{1}HNMR and FT-IR spectroscopy techniques as shown in Figure 3.01. In ^{1}HNMR spectra, the epoxy protons show the signals at $\delta = 2.80$ - 3.20 ppm, which gets disappeared by appearing of a new signals at around $\delta = 4.50$-5.10 ppm. The changes in NMR spectrum at epoxide proton reveal the changes in epoxide functional group (Figure 3.01a). FT-IR shows an appearance of the new absorbance peak at 1801 cm^{-1}, which corresponds to carbonyl functional group as shown in Figure 3.01(b).

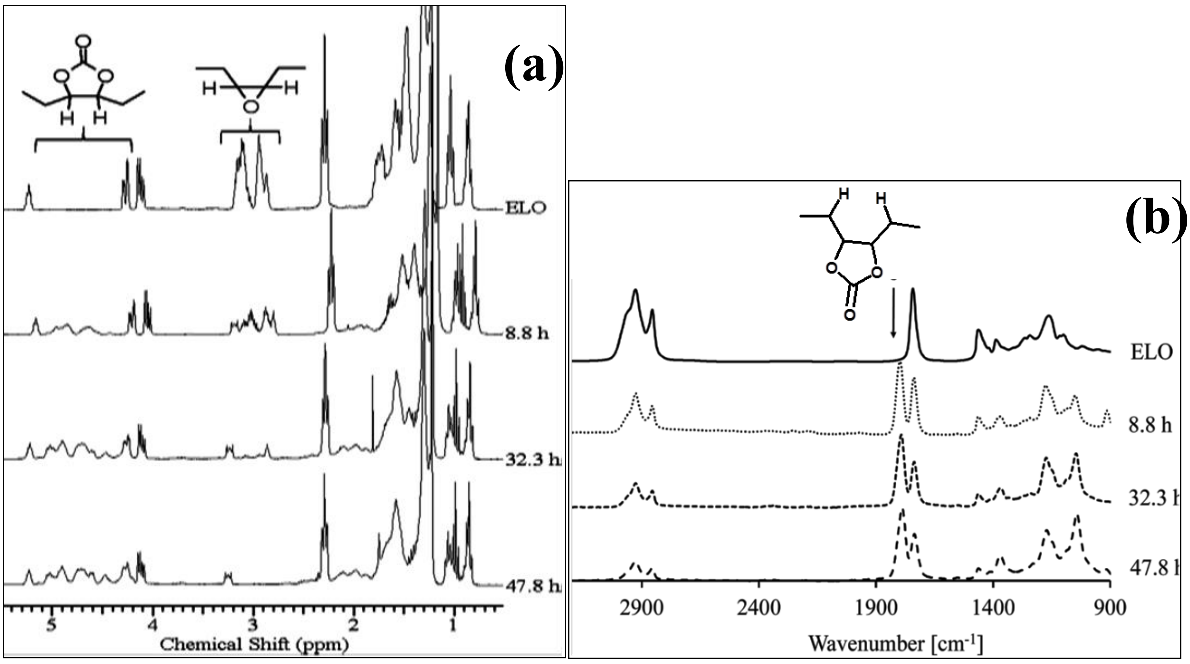
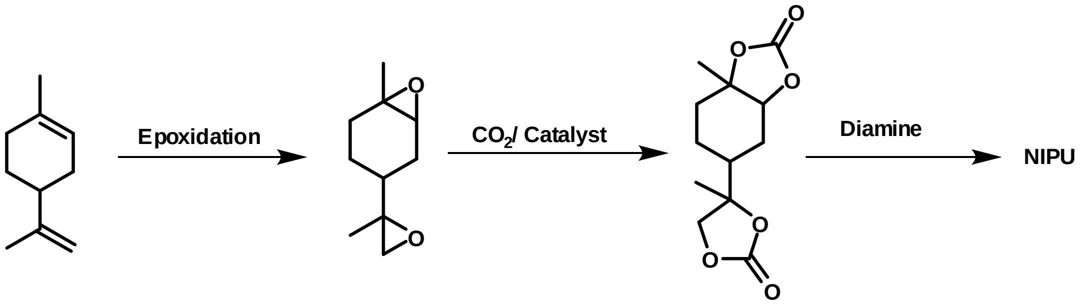


Figure-3.01: Comparison of (a) HNMR and (b) FT-IR of epoxide and Cyclic-Carbonate

3.2: Cyclic limonene dicarbonate as a new monomer for non isocyanate olig and polyurethanes (NIPU) based upon terpenes:

Extensive research has been reported on non isocyanate polyurethane based on chemical modification of plant oil. There have been very few reports on the synthesis of polyurethane from terpenes as precursors. The double bond of terpenes is useful functional group for the preparation of cyclic carbonates *via* epoxidation followed by polymerization with diamines as shown in Scheme 3.02. Limonene is a terpene obtained from citrus fruits.[60] Orange peels contain around 90 wt% of (*R*)-limonene. Limonene has two double bonds in its structure, one is exocyclic and another one is endocyclic. In this methodology, the limonene was used as starting material to synthesize the cyclo-carbonate. Limonene dioxide was reacted with CO_2 under 30 bar pressure in presence of TBAB as catalyst at 120-140 °C. The progress of reaction was monitor by ^{1}H-NMR and FTIR spectroscopy as depicted in Figure 3.02.[61]



Scheme 3.02: Synthesis of NIPU from terpene derivatives

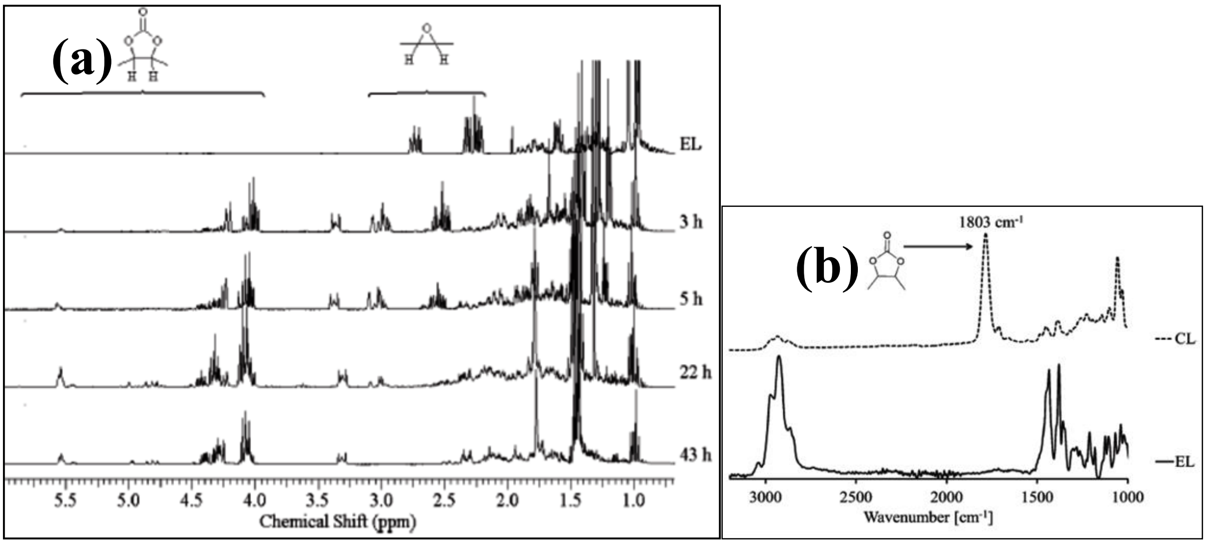


Figure 3.02: (a)^{1}H-NMR and (b) FTIR spectra of epoxide and cyclic-carbonates

In Figure 3.02, the formation of cyclic carbonate was conformed from disappears of epoxide protons at δ = 2.25-3.10 ppm and appears of cyclic carbonate protons at δ = 4.0-5.50 ppm in ^{1}H-NMR spectroscopy as shown in Figure 3.02 (b). Further it was conformed from the FT-IR spectra, the carbonyl absorption peak at 1803 cm^{-1} corresponds to cyclic carbonate as shown in Figure 3.02 (b).

The ring opening of CL with n-butyl amine (BA) that is polymerization reaction was monitored by FTIR spectroscopy as shown in Figure 3.03. The results reveal that polyurethane was obtained after 24 h. The decrease in the intensity of carbonyl peak at 1803 cm^{-1} and increase in the intensity of peaks corresponds to amide functional group.

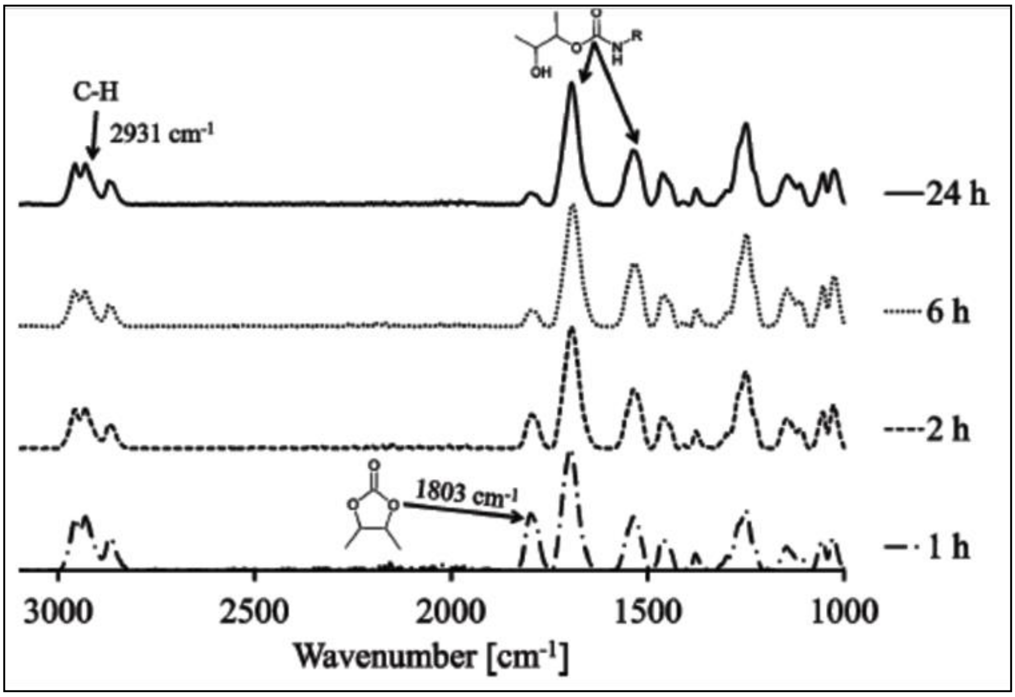
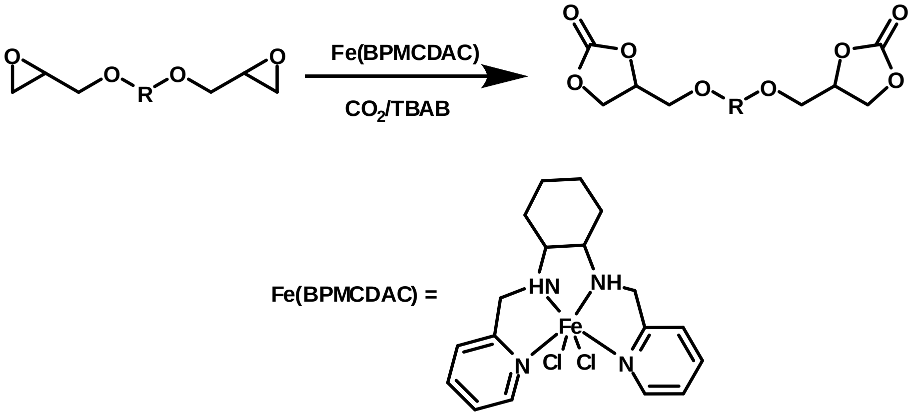


Figure 3.03: Comparative study of FT-IR spectroscopy

3.3 Quantitative synthesis of bis(cyclic-carbonate)s by iron catalyst for non-isocyanate polyurethane synthesis

Yusheng and Wang *et al.* reported the synthesis of NIPU using Iron based catalyst and TBAB for coupling of CO_2 with epoxide to obtain the cyclic-carbonate.[62]The advantages of this method include lower reaction time and require low temperature and pressure. The active site of the catalyst is Iron, which is environment friendly substitute for toxic metals like Co, Cr etc.

Under solvent free condition, the diglycidyl ether could be completely converted into the biscyclo-carbonate under relatively mild condition and purified by flash column chromatography.



Scheme 3.03: Iron complex catalyzed synthesis of biscyclo-carbonate

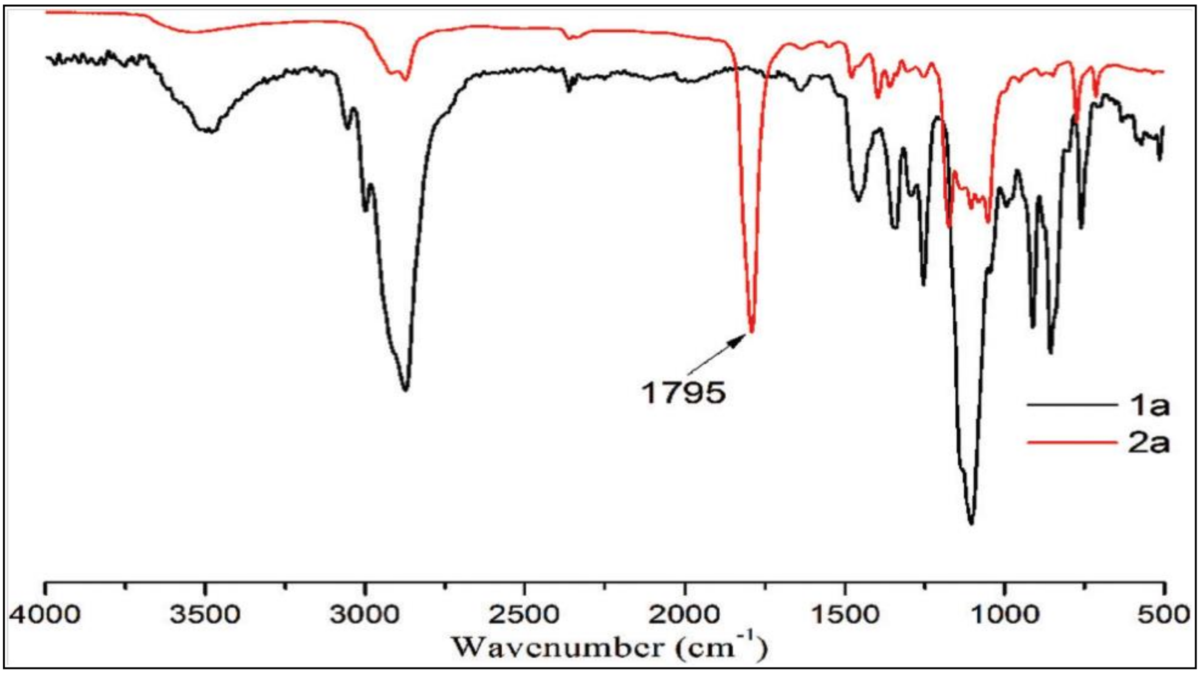


Figure 3.06: FT-IR spectra of epoxide and dicyclic-carbonate

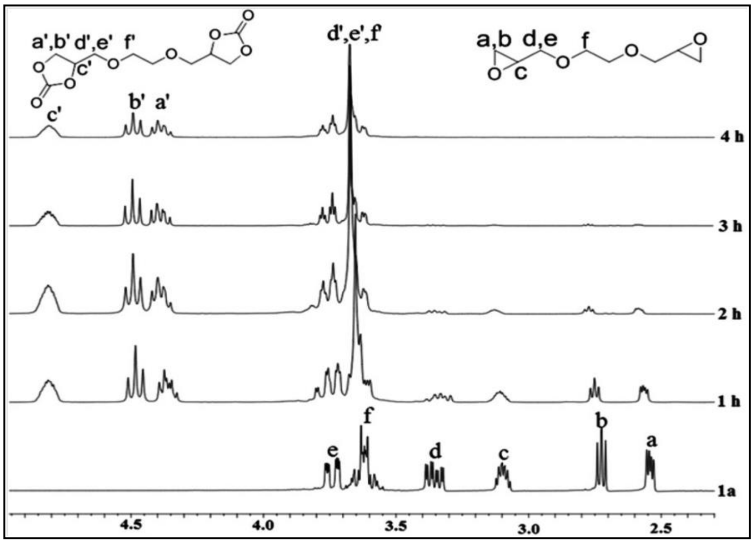
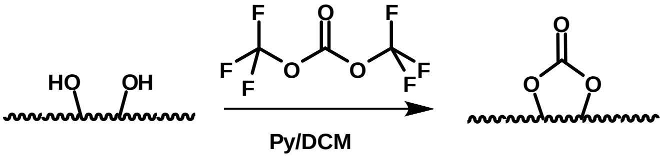


Figure 3.05: ^{1}H NMR spectra of epoxide and dicyclic-carbonate

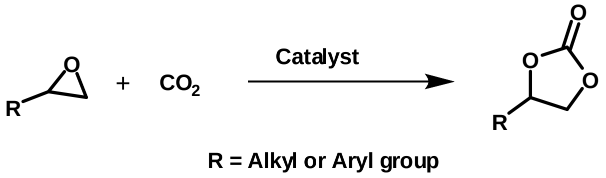
3.04: The cyclic-carbonate was obtained by phosgenation of aliphatic or aromatic diols under excess pyridine. However, the use of phosgene is not safe, and this method is generally avoided (Scheme 3.04).[63]



Scheme 3.04: Synthesis of cyclo-carbonates by phosgenation of diols

3.05 Synthesis of cyclo-carbonate by the insertion of CO_2 into oxirane:

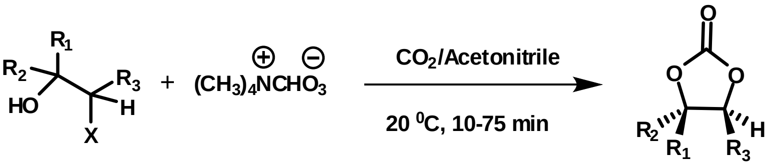
There are many catalysts have been developed by means of which an epoxide can be converted into its corresponding five membered cyclic carbonate (Scheme 3.05). Since CO_2 used as reactant in this method, is much better and widely used to make cyclic carbonate.[64] However, this method has drawbacks such as required high temperature and pressure. To overcome the aforementioned problems, graphene oxide (GO) was used as catalyst.



Scheme 3.05: Synthesis of cyclo-carbonate by the insertion of CO_2 into oxirane

3.06: Synthesis of cyclo-carbonate from halohydrins:

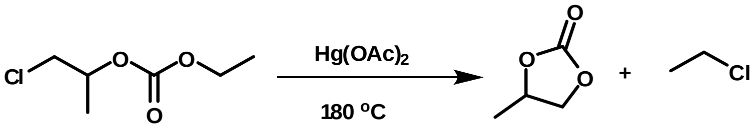
Recently, new methodologies have been developed for the synthesis of alicyclic carbonates from the reaction of halohydrin with tetramethylammonium hydrogen carbonate (Scheme 3.06). CO_2 was used as the carbonylating agent in the presence of acetonitrile solvent at room temperature.[65]



Scheme 3.06: Synthesis of cyclo-carbonate from halohydrin

3.07 Synthesis of cyclic carbonate from halogenated carbonate:[66]

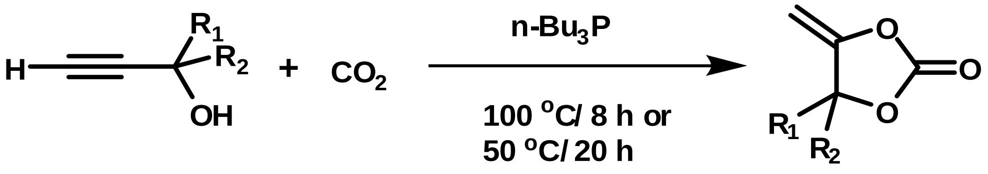
Halogenated carbonates when treated with mercury acetate, results cyclic carbonate along with alkyl halide.



Scheme 3.07: Synthesis of cyclic carbonate

3.08 Synthesis of cyclic carbonate from substituted propargyl alcohols:

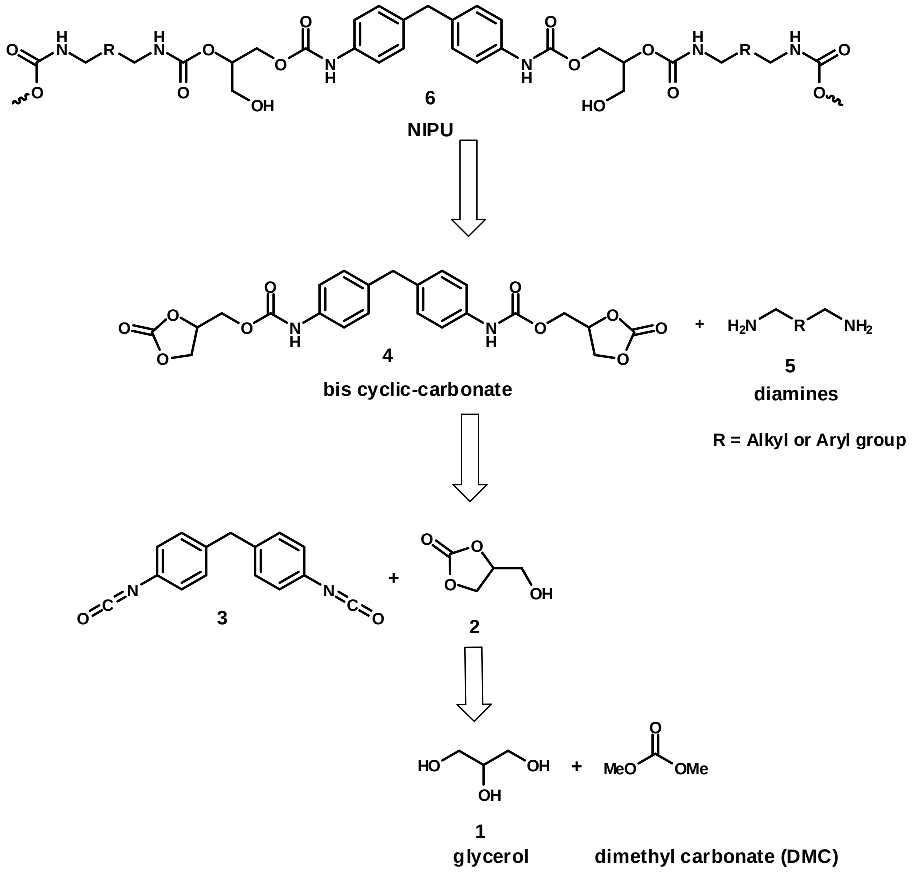
Phosphene catalyzed conversion have been reported by .Propargyl alcohols can be converted into their corresponding α methylene cyclic carbonate by the reaction of CO_2. This procedure needs more time at lower temperature while in reverse condition it will take less time.[67]



Scheme 3.08: Cyclic carbonate from Propargyl alcohols

3.09 Gaps in Literature:

The monomer used for Polyurethane synthesis as reported in literature shows either dicyclic carbonate or Isocyanate and can only results polyurethane when reacts with diamine and diols respectively. In this present work we have made a navel glycerol based monomer which will always give polyurethane either reacts with any di anion. The overall analysis is given below in Scheme 3.09.



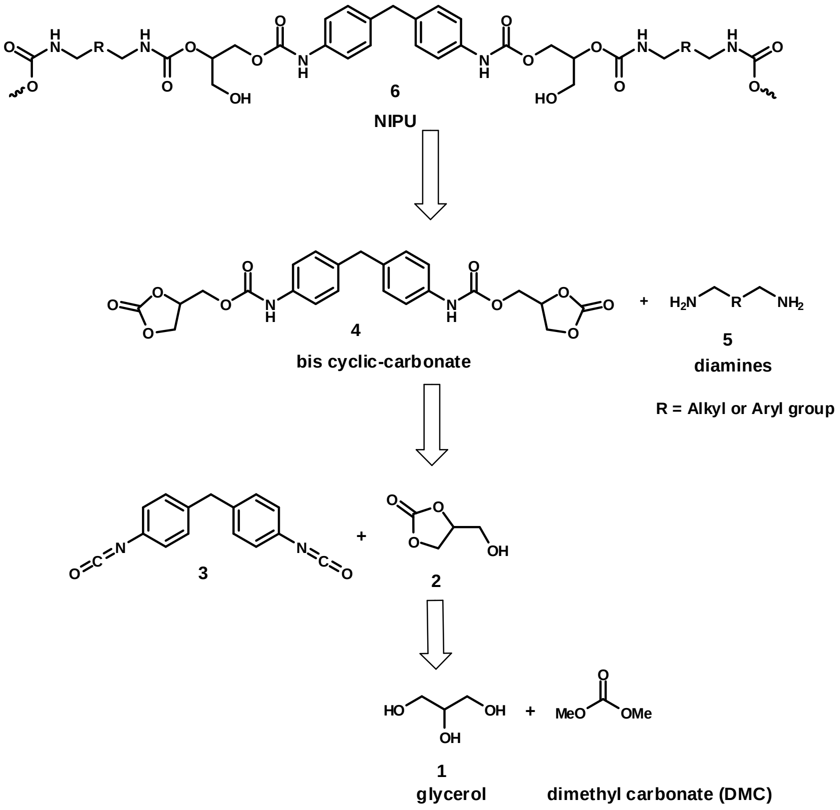
Scheme 3.09 Approch for synthesis

CHAPTER-IV

EXPERIMENTAL WORK

4.1 Retro synthetic approach for analysis of monomer of polyurethane

In present investigation, we studied a novel synthetic route for the formation of non-isocyanate polyurethanes as shown in retrosynthetic analysis (Scheme 4.01).



Scheme 4.01. Retrosynthetic analysis of NIPU from glycerol carbonate

The target novel polymers i.e NIPUs **6** could be obtained from the DBU catalyzed polymerization reaction between novel bis-glycerol carbonate monomer **4** and various commercially available aliphatic and aromatic diamines **5**.The monomer **4** could be obtained from DBU catalyzed reaction between diphenyl methane di-isocyanate (MDI) **3** and glycerol carbonate.

4.2 Experimental section

The chemicals used in these experiments were purchased locally as well as Sigma-Aldrich. Fourier transform infrared (FT-IR) spectra were recorded on Perkin Elmer and the samples were prepared by mixing the samples with KBr. The ^{1}H and ^{13}C NMR spectra were measured on a JeolSpectrospin spectrometer at 400 MHz and 100MHz respectively using TMS as a internal standard.

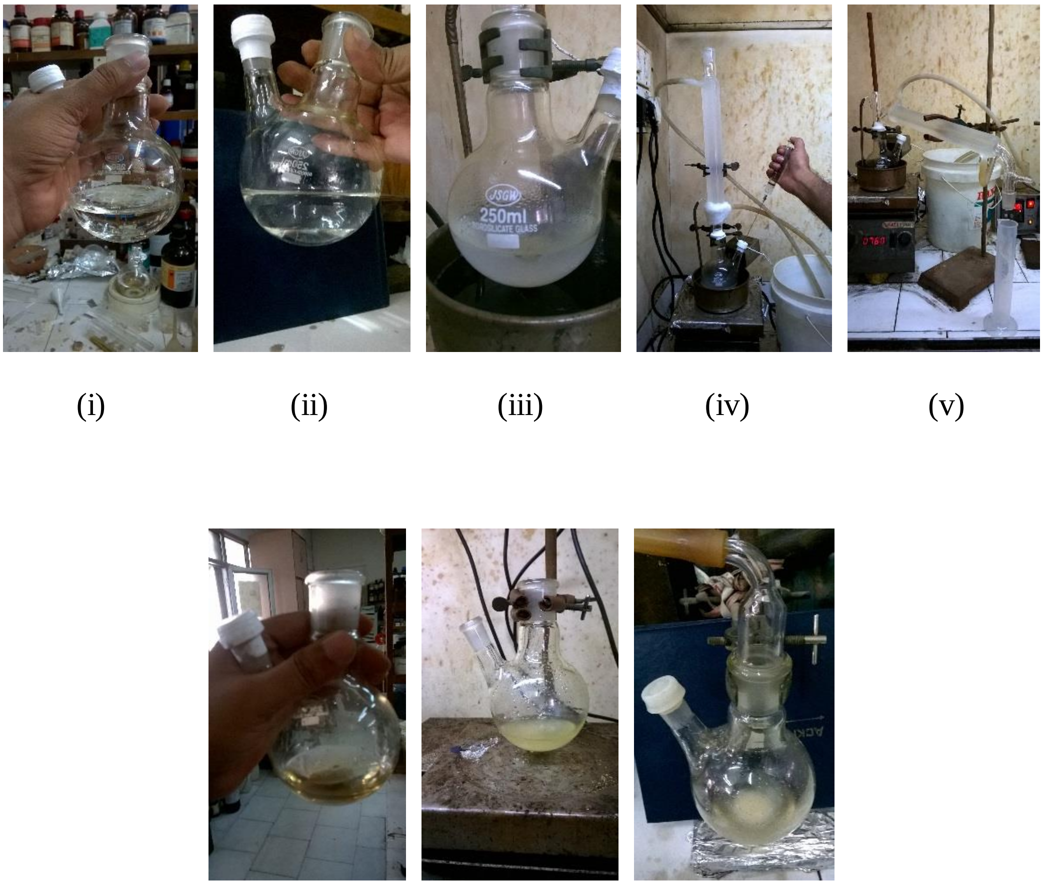
4.2.1 Chemicals used

Table 4.1 List of chemical used for experiment

S.N	**Chemical name**	**Supplier**
1.	Glycerol	Spectrochem
2.	Dimethyl carbonate	Sigma-Aldrich
3.	Sodium Hydroxide	Spectrochem
4.	Phosphoric acid	Spectrochem
5.	MDI	S.L. Ltd,(India)
6.	Ethyl acetate	Spectrochem
7.	Hexane	Spectrochem
8.	Silica gel	Spectrochem
9.	Piperazine	Sigma-Aldrich
10.	1,2-Diamonopropane	Sigma-Aldrich
11.	1,2-Diaminocyclohexane	Sigma-Aldrich
12.	m-Phenylenediamine	Sigma-Aldrich
13.	Chloroform-d^6	Sigma-Aldrich
14.	DMSO-d^6	Sigma-Aldrich

4.2.1 Experimental Procedure

(a) Typical procedures for the preparation of glycerol carbonate (2): Glycerol (23 g) and dimethyl carbonate were added in a 50 ml dried two necked round bottom flask equipped with reflux condenser and magnetic bar to form two phases. The mixture was stirred vigorously for 30 min followed by dropwise addition of 2.5 ml of methanolic solution of NaOH. The mixture was refluxed at 120-130 ^{o}C, till the formation of colourless and clear solution. Distilled off the excess DMC and MeOH formed during the course of reaction. Cool the solution and acidified with H_3PO_4 and maintain the pH around 3. Filter the resulting solution through silica plug to afford the glycerol carbonate (2).



(i) (ii) (iii) (iv) (v)

(vi) (vii) (viii)

Figure 4.02 Conversion of Glycerol into Glycerol carbonate

The Figure 4.02 shows the progress and steps involved in this synthesis. Figure (i) DMC in rb (ii) Glycerol in DMC (iii) Complete setup of reaction (iv) Reaction starts (v) Removal of excess DMC and Methanol (vi) concentrated crude. (vii) Acidified crude with white suspension (viii) after acidification with 85% phosphoric acid shows white precipitate.

(b) Synthesis of bis((2-oxo-1,3-dioxolan-4-yl)methyl) (methylene bis(4,1-phenylene)) dicarbamate: The obtained glycerol carbonate (2) was taken in round bottom flask under nitrogen environment and followed by addition of MDI (1 eq), mixture of 4-(hydroxymethyl)-1,3-dioxolan-2-one/propane-1,2,3-triol (2.1 eq) and DBU (0.1 mol%) and stirred the mixture vigorously for 15-20 minutes in water bath. Two phases were appeared and the mixture was diluted with chloroform and filter through neutral alumina to remove the solid polymer formed. The excess solvent was removed under reduced pressure to afford the bis ((2-oxo-1,3-dioxolan-4-yl)methyl) (methylene bis(4,1-phenylene))dicarbamate. The completion of reaction was confirmed by IR spectroscopy.

Yield 75%; Light yellow gummy liquid

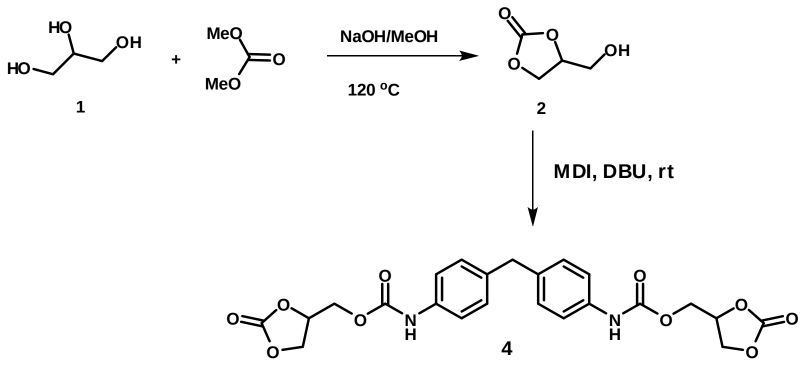
(c) General Procedure for synthesis of polyurethanes NIPUs (6a-6d): Diamine (5a-5d) (89 mg, 1 mmol) was added in an 25 ml round bottom flask containing the dicarbonate monomer 4 (486 mg, 1 mmol) and DBU (7.6 mg, 1 mol%). The reaction mixture was heated at 50 ^{o}C under stirring and the progress in reaction was monitored by the IR spectroscopy to afford the NIPU polymers as yellow gummy liquids.

CHAPTER-V

RESULT & DISCUSSION

Characterization, Result & Discussion

Initially, we prepared bis-glycerol carbonate monomer **4** using DBU catalyst protocol as shown in Scheme 4.02. However, there have been various methods reported for the synthesis of glycerol carbonate **2**, either from 2-oxiranemethanol or glycerol. But the later one has attracted great attention over the last 20 years due to its wide reactivity, implying numerous applications and to valorize glycerol, which is widely available as a major bio-based by-product from the manufacturing of biodiesel and other chemicals. With the inspiration of green chemistry principles, we performed reaction between glycerol and dimethyl carbonate in the presence of methanolic solution of NaOH as a catalyst at 120 ^{o}C temperature. To our delight, the reaction proceeded smoothly to afford the desired glycerol carbonate **2**. The crude reaction mixture was analyzed from ^{1}HNMR and FT-IR spectroscopy techniques as shown in Figure 4.01 and Figure 4.02 respectively. The formation of cyclic carbonate was conformed from the presence of CH_2 and CH protons at $\delta = 4.00\text{-}3.90$ ppm and $\delta = 4.51\text{-}4.50$ ppm respectively. In FT-IR spectrum, the absorption band at 1761 cm^{-1} was further confirmed the presence carbonyl functional group of cyclic carbonate. The absorption peak at 3400 cm^{-1} corresponds to hydroxyl group of glycerol (Figure 4.03). However, glycerol was also present as a minor impurity along with the desired glycerol carbonate **2.**



Scheme 4.02: Synthesis of bis-glycerol carbonate monomer (**4**)

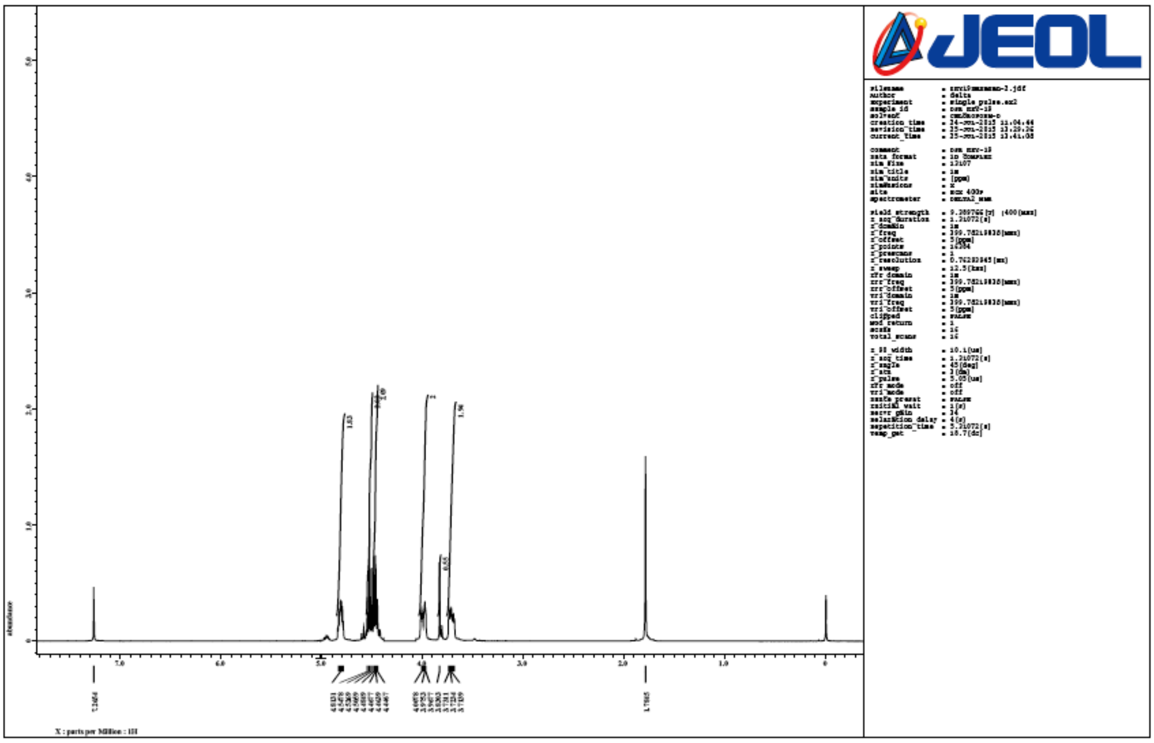


Figure 4.01: ^{1}HNMR spectrum of crude glycerol carbonate (**2**)

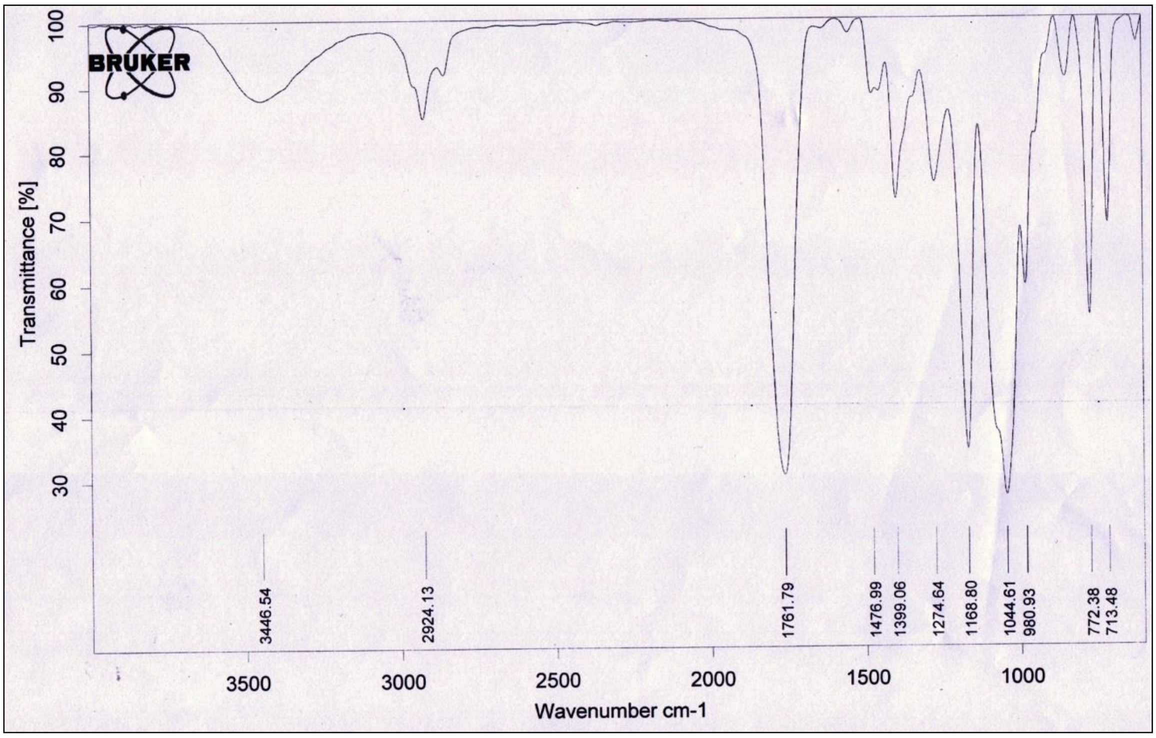


Figure 4.02: FT-IR spectrum of crude glycerol carbonate (**2**)

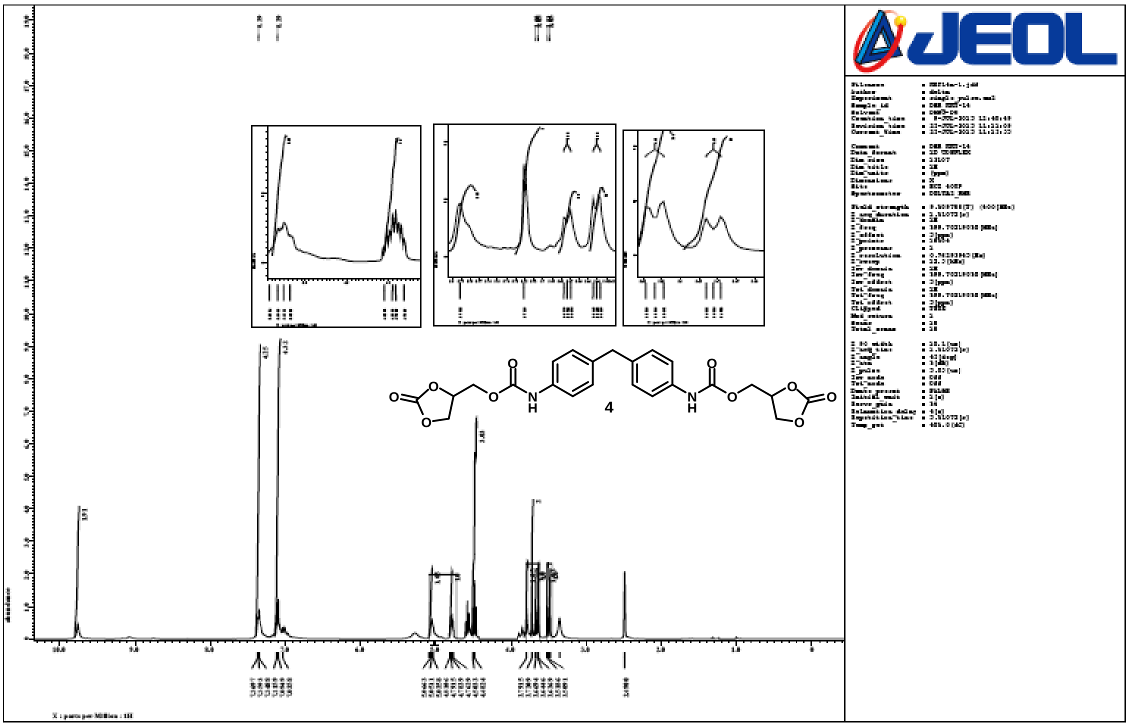


Figure 4.03: ^{1}HNMR spectrum of bis-glycerol carbonate monomer (**4**)

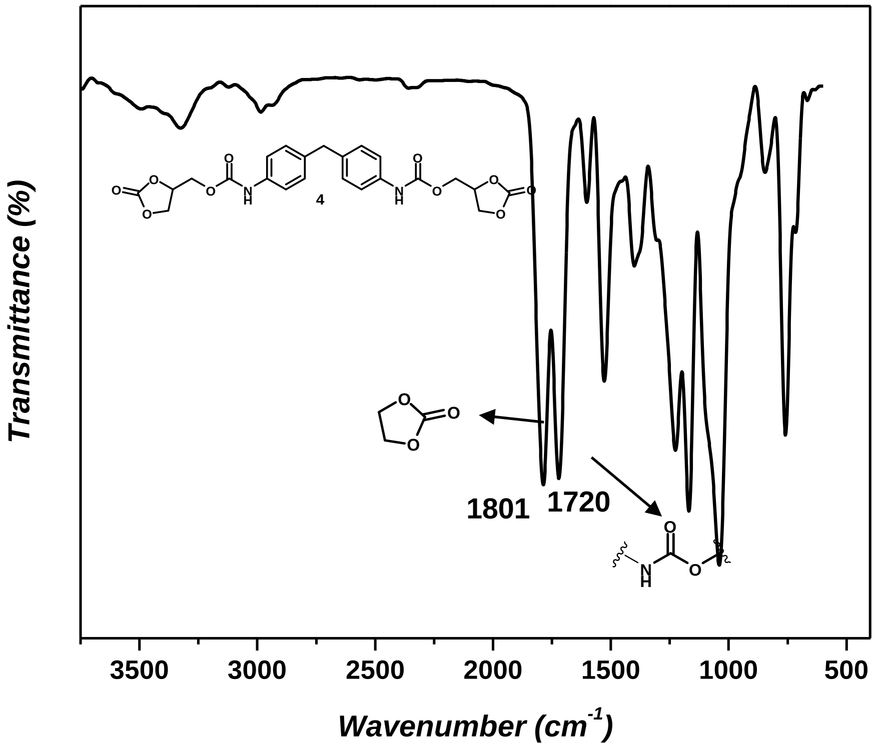
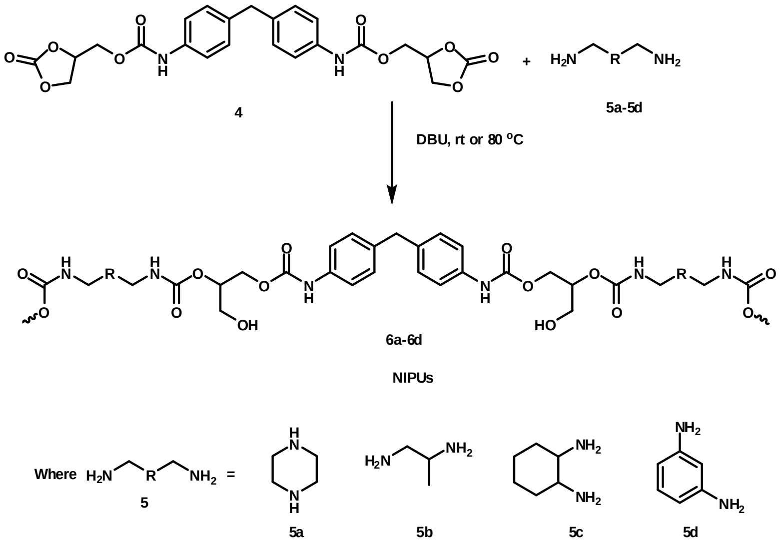


Figure 4.04: FT-IR spectrum of bis-glycerol carbonate monomer (**4)**

We proceeded for further step with this mixture of carbonate **2** and glycerol **1**. The diphenylmethane diisocyanate (MDI) **3** and DBU was added to this mixture and left for stirring at room temperature under inert condition. The bis-glycerol carbonate monomer **4** was obtained as light yellow gummy liquid along with the white solid, which was formed by polymerization reaction of minor impurity glycerol **1** and MDI. At this stage, the monomer **4** was purified and characterized from ^{1}H and ^{13}C NMR, FT-IR spectroscopic techniques. The characteristic protons of monomer **4** such as NH of amide, CH and CH_2 of cyclic carbonate and CH_2 of benzyl protons were conformed from chemical shift at $\delta = 9.8$ ppm, 4.82-4.71 ppm, 3.50-4.01 ppm, and 3.71 ppm respectively as shown in Figure 4.04. The presence of characteristic functional groups such as carbonyl of cyclic carbonate and carbonyl of urethane were confirmed from the absorption bands at 1801 cm^{-1} and 1720 cm^{-1} respectively.

With these interesting results in our hand, we studied the application of novel monomer **4** for synthesis of non-isocyanate polyurethanes (NIPUs) as shown in Scheme 4.03.



Scheme 4.03: Synthesis of various non-isocyanate polyurethanes (NIPUs)

Initially, we performed polymerization reaction between bis-glycerol carbonate monomer (**4)** and piperazine **(5a)** as a diamine in the presence of DBU base catalyst at room temperature to afford the polymer NIPU (**6a)**. The progress in reaction was studied by analyzing reaction mixture at different time intervals i.e 1-5 min by using FT-IR spectroscopy technique as shown in Figure 4.05. The results show as the reaction time increased from 1 to 5 min, the decrease in transmittance of carbonyl functional group of cyclic carbonate at 1787 cm^{-1} and increase of transmittance at 1696 cm^{-1} corresponds to carbonyl functional group of polyurethane (Figure 4.05).

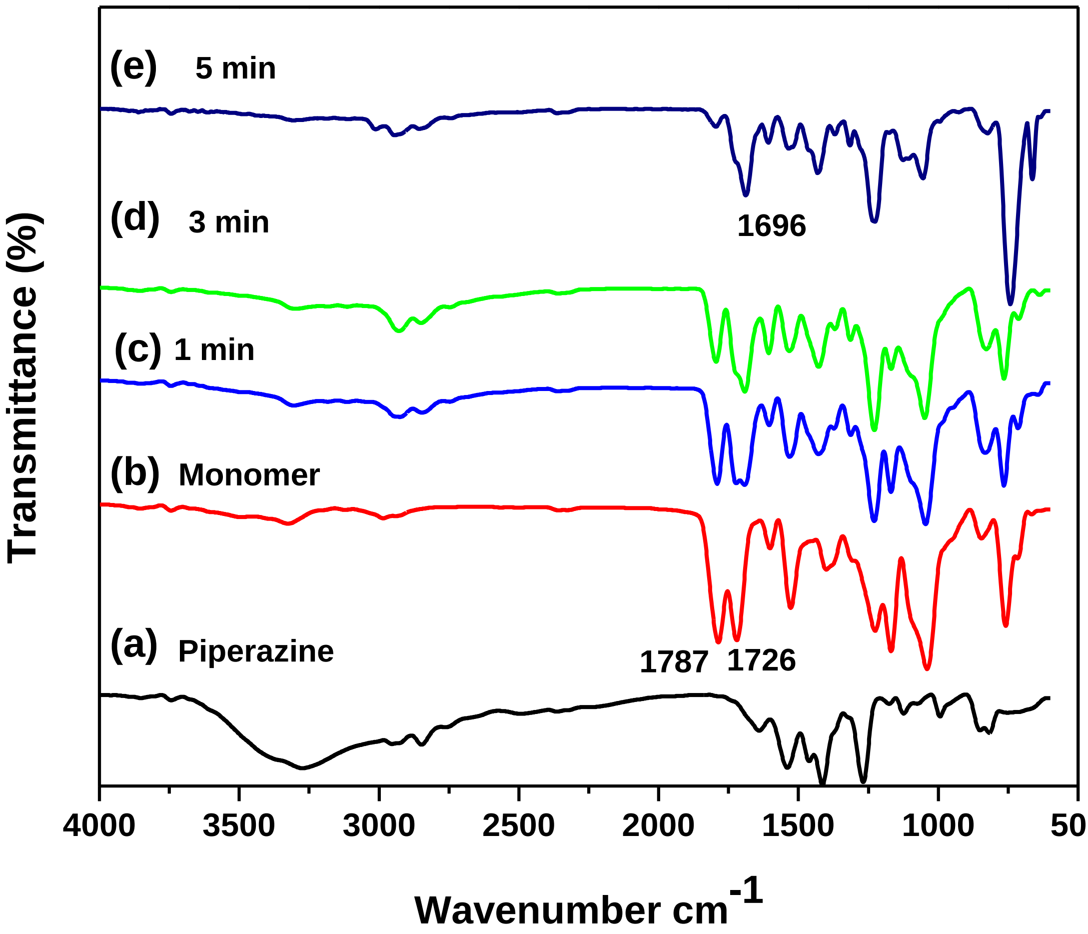


Figure 4.05: FT-IR spectra for formation of NIPU **6a** from monomer **4** and piperazine **5a**

To check the wide applicability of present method, we studied role of other aliphatic diamines such as 1,2-diaminopropane **5b** and 1,2-diaminocyclohexane **5c** and aromatic diamine **5d** for the polymerization reaction of cyclic carbonate monomer **4** as shown in Scheme 4.03.

The synthesis of NIPU **6b** was achieved from the polymerization reaction between bis-glycerol carbonate monomer **4** and 1,2-diaminopropane **5b** in the presence of DBU as a base catalyst at room temperature. The progress in reaction was studied by analyzing reaction mixture at different time intervals i.e 5-15 min by using FT-IR spectroscopy technique as shown in Figure 4.06. The results showed that the polymerization reaction was exothermic and proceeded smoothly within 15 min. With the increase of reaction time from 5 to 15 min, the transmittance of carbonyl functional group of cyclic carbonate at 1797 cm^{-1} was decreased as shown Figure 4.06

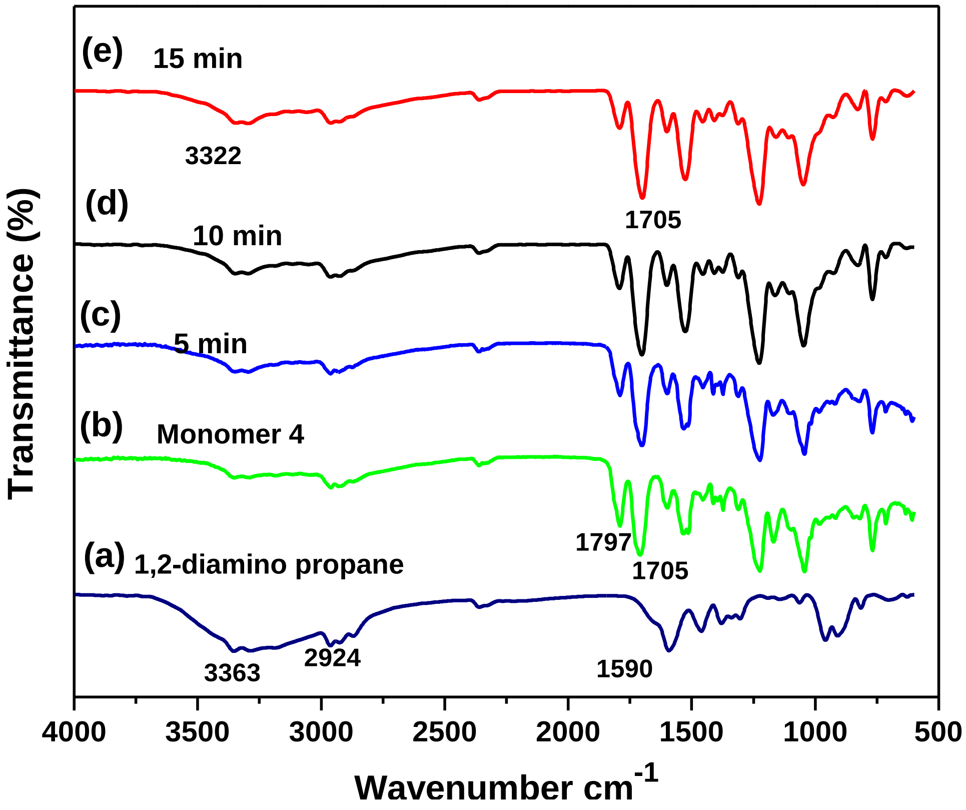


Figure 4.06: FT-IR spectra for NIPU **6b** from monomer **4** and 1,2-diaminopropane **5b**

. Moreover, the formation of NIPU polymer was conformed from the presence of absorption band at 1705 cm^{-1} which corresponds to carbonyl functional group of polyurethane (Figure 4.06).

We further extended our study for the synthesis of NIPU **6c** from the polymerization reaction between bis-glycerol carbonate monomer **4** and 1,2-diaminocyclohexane **5c** in the presence of DBU as a base catalyst at room temperature. The progress in reaction was studied by analyzing reaction mixture at different time intervals i.e 5-15 min by using FT-IR spectroscopy technique as shown in Figure 4.07. The results showed that the polymerization reaction was very slow. Even after 15 min, the absorption band of carbonyl functional group of cyclic carbonate was observed at 1796 cm^{-1} with equal intensity with carbonyl functional group of polyurethane. We analyzed the reaction mixture after 2h by FT-IR spectroscopy, the results shows that decrease of cyclic carbonate was observed at 1797 cm^{-1} with the formation of NIPU **6c** from absorption band at 1704 cm^{-1} which corresponds to carbonyl functional group of polyurethane (Figure 4.07a).

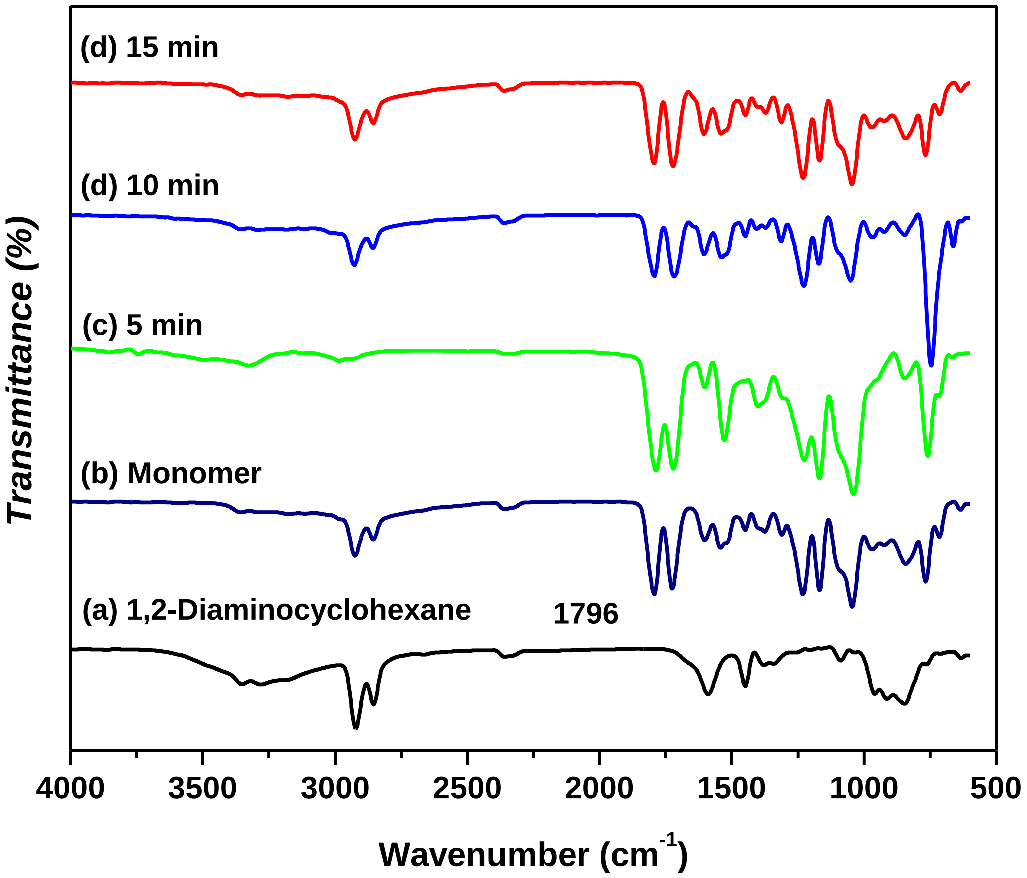


Figure 4.07: FT-IR spectra for NIPU **6c** from monomer **4** and 1,2-diaminocyclohexane **5c**

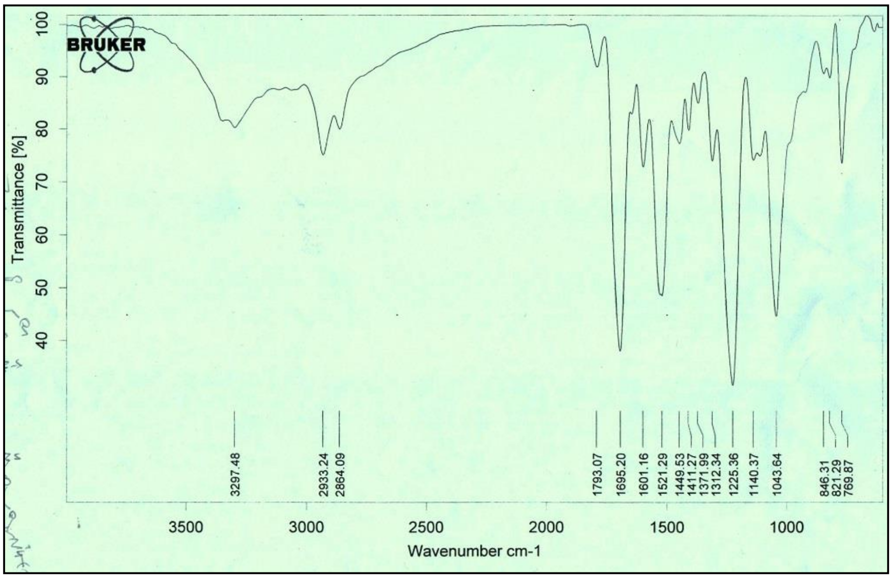


Figure 4.07a: FT-IR spectra for NIPU **6c** after 2h

CHAPTER-VI

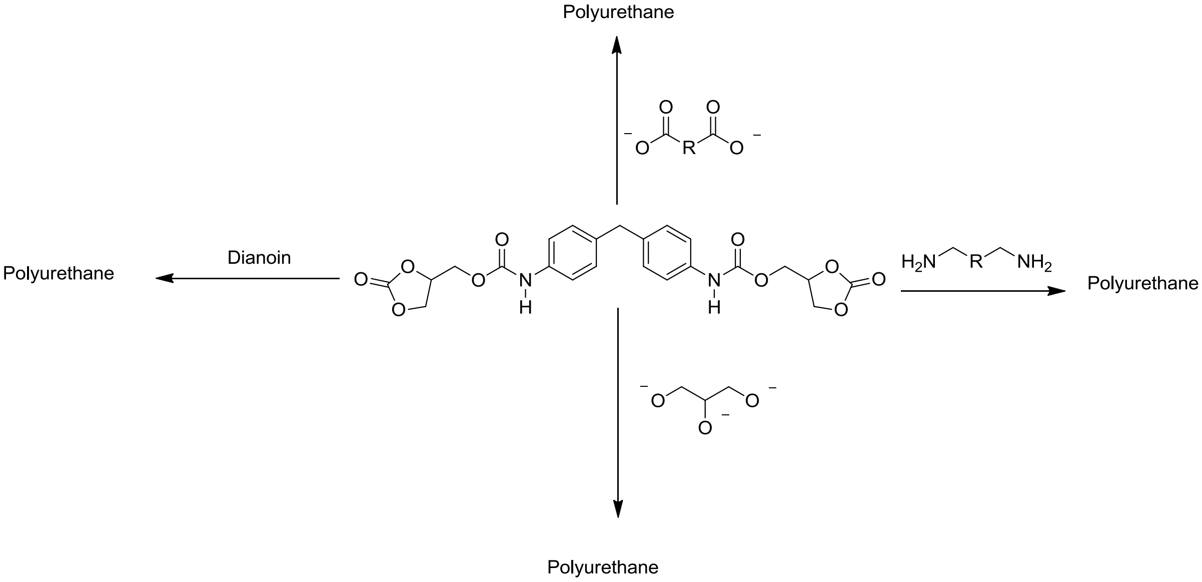
CONCLUSION AND FUTURE WORK

CONCLUSION

In this present work we had developed a methodology for utilization of glycerol in Polyurethane synthesis. We have synthesized a noval glycerol based monomer bis((2-oxo-1,3-dioxolan-4-yl)methyl) (methylene bis(4,1-phenylene)) dicarbamate with multi-functional group that can act as monomer for PU synthesis. The monomer that was synthesized, has two functional groups; cyclic carbonate as well as N-H group. As the N-H group is not that much active under normal condition, so diamines are used for NIPU synthesis and conversion of cyclic carbonate into urethane group. The formation of Polyurethane was confirmed by FT-IR spectroscopy.

SCOPE FOR FUTURE WORK:

In the present investigation, we have developed a new methodology for glycerol based novel monomer. The basic idea of development was the synthesis of a monomer which has potential to replace isocyanate based polyurethane with a novel non isocyanate polyurethane (NIPU) which is environment friendly. The presence of two urethane units in its skeleton makes it more attractive. Literature suggests that the cyclic carbonates if opened by amine can give urethane but in our protocol the monomer will give always polyurethane whether its cyclic carbonates will be opened by amine or other nucleophiles as shown by the scheme ( ) . The resulting polymer contains many functional groups like Hydroxyl, Amine, and Carbonyl etc. which can act as the sites for binding the drug molecules and has potential to be used as a target drug delivery agent, which is very challenging. In future I am planning to explore my research with this molecule in the field of Biotechnology for drug delivery.



Scheme 6.1: Polyurethane from the reaction of bis ((2-oxo-1, 3-dioxolan-4-yl) methyl) (methylene bis (4, 1-phenylene)) dicarbamate with various other precursor

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