

**SYNTHESIS OF TRIGLYCERIDE BASED
URETHANE MACROMERS AND THEIR USE IN
COPOLYMERIZATION**

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AUGUST 2006

**TRİGLİSERİD TEMELLİ ÜRETAN MAKROMERLERİN
SENTEZİ VE KOPOLİMERİZASYONDA
KULLANIMI**

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LIST OF ABBREVIATIONS

FRP	: Free radical polymerization
AIBN	: Azobis isobutyronitrile
MVI	: Methyl vinyl isocyanate
NCO	: Isocyanate
PG	: Partial glyceride
DBTDL	: Dibutyl tindilaurate
TGU	: Triglyceride based urethane
PTGUST	: Copolymerization of triglyceride based urethane and styrene
St	: Styrene
FTGU	: Film of triglyceride based urethane
FTGUST	: Film of copolymer of triglyceride based urethane with styrene
FPSt	: Film of polystyrene
DMSO	: Dimethyl sulfoxide
CDCl₃	: Chloroform
¹H-NMR	: Nuclear magnetic resonance
FT-IR	: Fourier transform infrared
DSC	: Differential scanning calorimetry
GPC	: Gel permeation chromatography
TGA	: Thermogravimetical analysis
CAM	: Contact angle meter
IPN	: Interpenetrating polymer networks
NLO	: Nonlinear optical
HPUR	: Hydrophilic polyurethane

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LIST OF SYMBOLS

M_n	: Number average molecular weight
k_a, k_d	: Rate constants of activation and deactivation steps of the initiation in radical polymerization
r	: Monomer reactivity ratio
M	: Monomer

SYNTHESIS OF TRIGLYCERIDE BASED URETHANE MACROMERS AND THEIR USE IN COPOLYMERIZATION

SUMMARY

As surface coating industry is growing rapidly in these years, studies related with synthesis of renewable natural resources based materials are also increasing rapidly. Modifying surface coatings by triglyceride oils develop materials to get advanced film characteristics. Oils are reacted to vinyl monomers directly or after functionalized by hydroxyl groups they are reacted to monomers such as dianhydrides, diisocyanates to form polymeric materials. Synthesized products are used as a polymer compound to prepare solvent based surface coatings.

In this thesis, oil based urethane macromers containing vinyl bonds were synthesized. First triglyceride oils were converted to di- and mono-glycerides and then reacted with methyl vinyl isocyanate. In the second step homopolymerization and copolymerization of triglyceride based urethanes with styrene were carried out via free radical polymerization. Urethanes and polymers synthesized were characterized by spectroscopic methods as $^1\text{H-NMR}$, FT-IR and gel permeation chromatography and film properties were examined.

TRİGLİSERİD TEMELLİ ÜRETAN MAKROMERLERİN SENTEZİ VE KOPOLİMERİZASYONDA KULLANIMI

ÖZET

Günümüzde yüzey kaplama endüstrisi hızla gelişirken yenilenebilir doğal kaynak bazlı malzemelerin hazırlanmasıyla ilgili çalışmalar da hızla artmaktadır. Yüzey kaplayıcıların trigliserid yağlarla modifiye edilmesi malzemeye gelişmiş film özellikleri kazandırmaktadır. Polimerik malzemeler hazırlamak için yağlar direkt olarak vinyl monomerleriyle yada hidroksil gruplarıyla fonksiyonlandırıldıktan sonra dianhidrit, diizosiyanat gibi monomerlerle reaksiyona sokulmaktadır.

Bu çalışmada vinil bağı içeren yağ bazlı üretan makromerleri sentezlenmiştir. İlk olarak yağların trigliserid yapısı , di- ve mono- gliserid yapısına dönüştürülmüş, daha sonra çalışmada sentezlenen metil vinil izosiyanat ile reaksiyona sokulmuştur. İkinci aşamada trigliserid bazlı üretanların homopolimerizasyonu ve stirenle kopolimerizasyonu serbest radikal polimerizasyonu ile gerçekleştirilmiştir. Sentezlenen üretanlar ve polimerler ¹H-NMR, FT-IR gibi spektroskopik yöntemler ve jel geçirgenlik kromatografisi ile karakterize edilmiş ve film özellikleri incelenmiştir.

1. INTRODUCTION

Polyurethanes are a class of polymers which have versatile applications. They can be tailored according to their application as an adhesive, an additive, a catalyst or a coating material. In recent decades, there has been an increased demand for urethane materials. Polyurethanes have been extensively used in biomedical applications [1, 2]. There are several studies that indicate vegetable oils can be used as integral parts of urethane materials. Triglycerides are the main component of vegetable oils, such as linseed oil, soybean oil, etc. Triglyceride oil based polymers are an economical and environmentally friendly alternative to petroleum for biodegradable polymer synthesis [3].

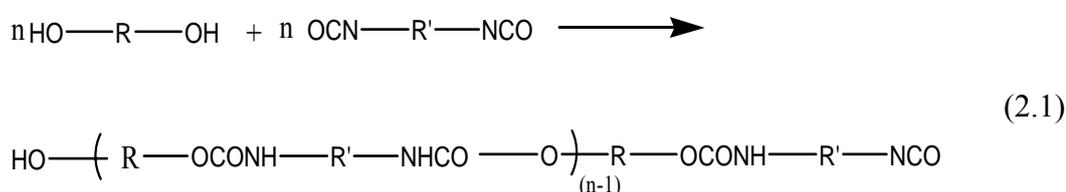
Plant oils, with a few exceptions such as castor oil, cannot be easily converted into polymers in their original form. There are numerous ways of chemically modifying the unsaturated sites on the fatty acids, many of which can be used to make polymers. Various polymerization techniques have been employed, including cationic, thermal, and free radical polymerization [3,4,5]. Among these techniques, free radical polymerization has distinct advantages over other polymerization methods, such as tolerance to trace impurities, less stringent conditions, and also to be able to polymerize a wide range of monomers [6]. The triglycerides derived plants extensively can be reacted with monomers such as maleic anhydride [4], isocyanate [7] forming a monomer capable of polymerization by free-radical polymerization [8]. The main reaction responsible for final curing appears to be an oxidative polymerization by virtue of the double bonds present on the fatty acid chain [8].

2. THEORETICAL PART

2.1. Urethane And Polyurethane Chemistry

2.1.1 Introduction

The synthesis of polyurethanes is usually presented as proceeding via the formation of carbamate (urethane) linkages by the reaction of isocyanates and alcohols [9]. The reaction is shown below.



The general structure or bond that forms the basis of this chemistry is the urethane linkage shown in Figure 2.1.

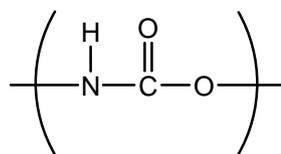


Figure 2.1 : Basic urethane

The first urethanes involved the reaction of isocyanate with simple alcohols and amines. They were of sufficient economic value to foster the development of a number of isocyanates, including the aromatics that play dominant roles in modern polyurethanes [10].

Properties of particular representatives of this group of polymers are greatly dependent on their chemical structure. Variation of the ratio of reagents introduced into the reactions allow obtaining of polymers with different concentration of elastic and rigid blocks, and different density of intermolecular hydrogen bonds [11]. Thus, products with different hardness and elasticity are formed, which allows production of an assortment of materials with different mechanical properties. As a general rule,

the isocyanates are hard segments that impart rigidity to the polymer. The polyol is the so-called soft segment.

But in any case, the feature of the structure of segmented polyurethanes, firstly, combination of the presence of elastic fragments and strong intermolecular interaction, provides for their quite good mechanical properties [12].

The reaction conditions depend on the polyol and the isocyanate. The amount of isocyanate required is calculated from the hydroxyl content of the polyol. Typically the isocyanate is slowly added to the polyol with continuous stirring at ambient temperature and then heated to 65 to 125 °C. An exotherm is evident, and the viscosity slowly builds as the reaction proceeds [10].

Urethane coupling reactions are catalyzed by molecules such as dibutyltin dilaurate, $\text{Bu}_2\text{Sn}[\text{OC}(\text{O})(\text{CH}_2)_{10}\text{CH}_3]_2$, in which the tin atoms coordinate to the terminal oxygen of the isocyanate group and facilitate attack by the oxygen atom of a hydroxyl group on the isocyanate carbon atom. Other catalysts include triethylenediamine (Dabco) or other Lewis bases. These also catalyze the reactions of the isocyanate groups with to give carbon dioxide which forms the bubbles in foam rubber [13].

2.1.2 Isocyanates

Isocyanates, the esters of isocyanate acid, were first synthesized by Wurtz in 1848. Prominent nineteenth century scientists, such as Hofmann and Curtius, studied the chemistry of isocyanates, but it took almost a century until it was recognized that diisocyanates are ideally suited to undergo addition polymerization reaction with polyester or polyether diols to form polyurethanes [14].

Isocyanates of the general structure shown in Figure 2.2 react vigorously with amines, alcohols, and carboxylic acids.

The main chemical feature of isocyanates is their high reactivity toward nucleophiles such as alcohols, phenols, and, amines. However, in certain situations this high reactivity can pose problems, particularly toward moisture [15].

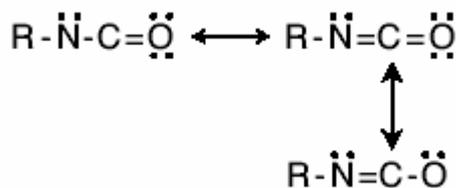


Figure 2.2 : Resonance structure of isocyanates

Isocyanates are divided into mono- and di-isocyanates. The monoisocyanates are subdivided into alkyl and aryl isocyanates; unsaturated isocyanates; halogenated alkyl and aryl isocyanates; carbonyl, thiocarbonyl and imidoyl isocyanates; sulfur isocyanates; phosphorus isocyanates; and inorganic isocyanates. The diisocyanates are also divided into aliphatic diisocyanates and aromatic diisocyanates [14].

Among the diisocyanates that are commonly used in polyurethane synthesis the following should be quoted:

- Toluene diisocyanate (TDI), usually a mixture of toluene-2,4- and toluene-2,6-diisocyanate (80:20)
- Methylene-*bis*-diphenyl diisocyanate (MDI)
- Cyclohexane diisocyanate (CDI)
- Hexamethylene diisocyanate (HMDI)
- Isophorone diisocyanate (IPDI)

The molecules are toluene diisocyanate (TDI) and its isomers and methylene-*bis*-diphenyl diisocyanate (MDI) in monomeric and polymeric forms (see Figure 2.3). As a general rule, TDI makes flexible polyurethanes and MDI produces stiffer polymers [10].

Aliphatic diisocyanates are used in the manufacture of color-stable polyurethanes for coatings and elastomer applications. The major aliphatic diisocyanates are hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI), cyclohexane diisocyanate (CDI).

The most important application for monoisocyanate is their use as monomers for polyurethanes. The reactive isocyanate is also used to dry solution-based polyurethane coatings.

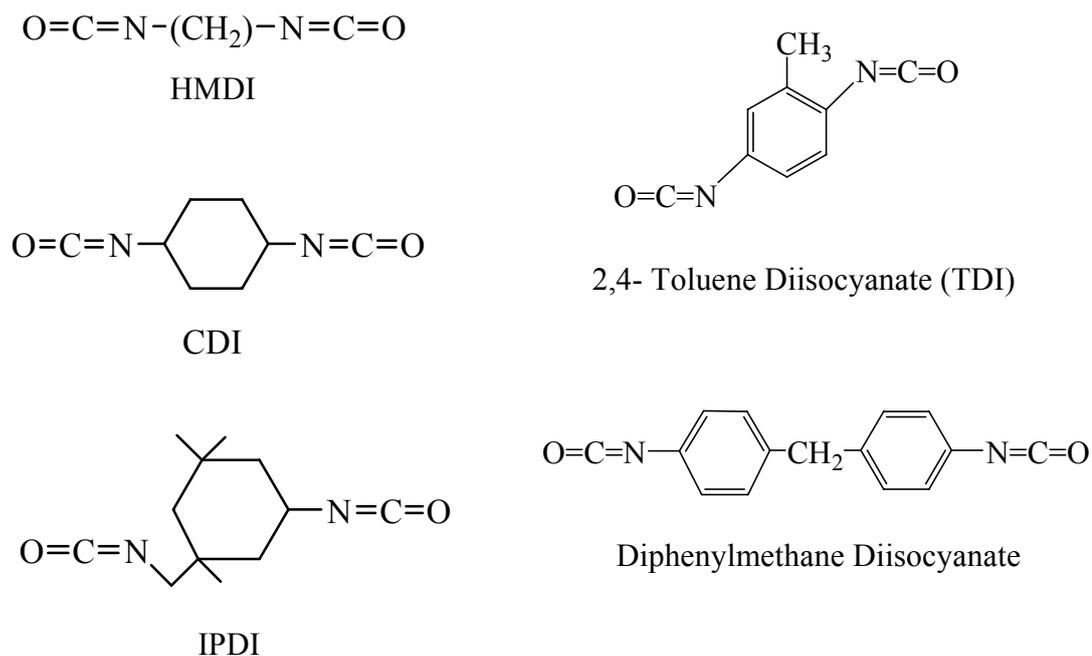


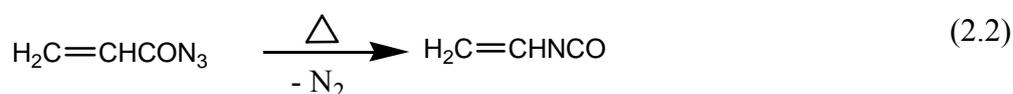
Figure 2.3 : Most common commercial diisocyanates

Monoisocyanates are predominantly used as intermediates in the manufacture of agricultural and pharmaceutical products, such as herbicides, insecticides and oral hypoglycemic agents, and they are also useful blocking agents for functional group, which can be interest in peptide chemistry. The aromatic isocyanates used as building blocks for agricultural chemicals include phenyl isocyanate and halogen substituted phenyl isocyanates [14].

2.1.2.1 Vinyl isocyanates

Phosgenations of some imines and nitriles are useful methods to synthesize vinyl isocyanates. Also, the dehydrohalogenation of halogenated isocyanates and the Curtius rearrangement are other useful methods for the synthesis of unsaturated isocyanates.

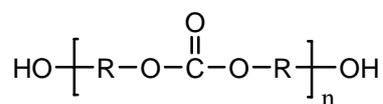
The thermolysis or photolysis of unsaturated carboxylic acid azides is perhaps the most common method of synthesis of unsaturated isocyanates. The reaction can be conducted by thermolysis or photolysis. For example, vinyl isocyanate is obtained in 86 % yield in the thermolysis of the corresponding carboxylic acid azide [14].



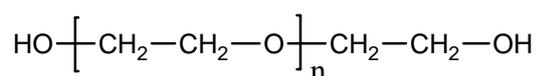
2.1.3 Polyols

Since the early days of polyurethane discovery, the technology has focused on isocyanate reactions with polyesters or polyethers. These reactions are responsible for the growth of the polyurethane industry. The polyesters of interest to polyurethane chemists terminate in hydroxyl groups and are therefore polyols produced by the polycondensation of dicarboxylic acids and polyols. An example is a polyol with a polycarbonate structure. The polyethers are more easily designed when the polarity of the backbone is important. For instance, one can use polyethers to construct polyurethanes that are hydrophilic or hydrophobic or react to water at all levels between these extremes. Polyethers permit the development of biocompatible and hemocompatible devices. Lastly, they are more hydrolytically stable and so are more appropriate for environmental studies [10].

Modified soy-based plant oil polyols, an economical and environmentally friendly alternative to petroleum for biodegradable polymer synthesis [16], are also successfully incorporated as a replacement for conventional polyols to produce polyurethane [2].



polyester polyol



polyethylene glycol

Figure 2.4 : Some polyols

2.1.4 Application of Polyurethanes

It is important to mention that most polyurethanes are useful because of their physical properties, and the breadth of applications is remarkable. They can be stiff enough to be used as structural members and soft enough for cosmetic applicator sponges. They can serve as the wheels of inline skates or cushions for furniture. In these applications and hundreds of others, the chemistry can be summed up as a combination of hard segments and soft segments with varying degrees of cross-

linking. Changes in a limited number of component parts allow a wide variety of products to be made [10].

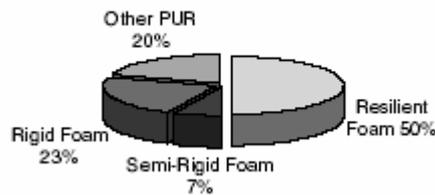


Figure 2.5 : Polyurethane usage by type

One of the great benefits of polyurethane is versatility. With only slight changes in chemistry, one can make products ranging from soft furniture cushions to automobile bumpers and infinite numbers of other products. Depending on the application, a polyurethane chemist can vary density and stiffness to achieve acceptable product performance. Figure 2.5 covers soft foams, rigid foams, and other polyurethanes.

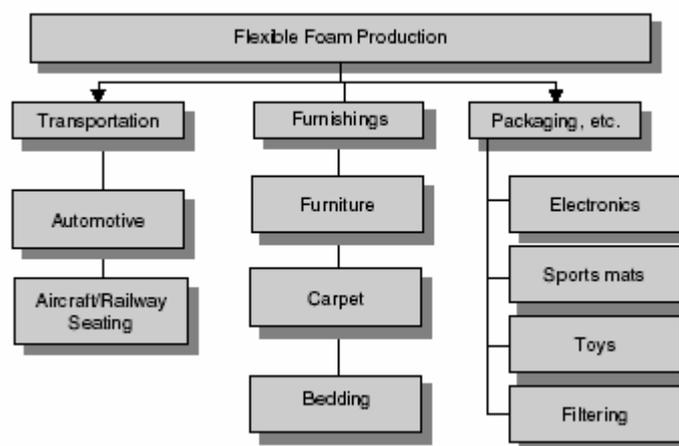


Figure 2.6 : Uses of flexible foam

Rigid foams are used for structural and insulation uses while the flexible materials are used for a vast variety of applications as seen in Figure 2.6. The versatility of polyurethane positions the product as unique in the polymer world because of the breadth of applications. It is supported by a description of the independent variables of density and stiffness and the range of products based on the primary attributes of polyurethanes. See Figure 2.7

Polyurethanes are also a class of biopolymers, because they consist of peptide groups , N-H-C(O), as natural polymers such as proteins and peptides.

Polyurethanes have been extensively used in biomedical applications. They are widely used in the development of medical devices for tissue and blood contact, such as mammary prosthesis, vascular catheters, artificial heart diaphragms and valves.

It is well known that polymers such as polyurethanes are susceptible to microbial attack. Polyurethanes can be degraded by many types of fungi and bacteria, mainly hydrolysis of the $-NHCOO$ groups, when they are exposed to the atmosphere or are used as an adhesive or a coating in the biomedical artefacts [1].

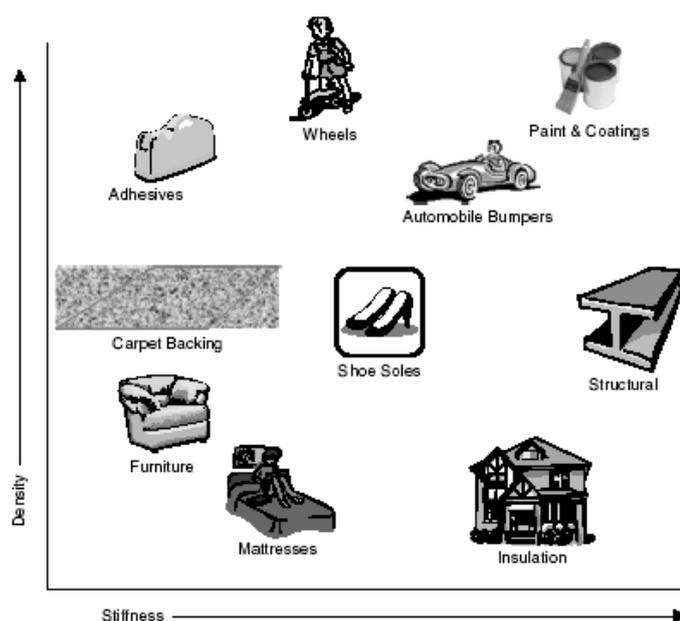


Figure 2.7 : Uses of polyurethane based on physical properties

One grade of polyurethane used for its chemistry has come to be known as hydrophilic polyurethane (HPUR). Unlike common polyurethanes, however, HPUR is used as a drug delivery system, in wound care products, for fragrance and soap-delivery systems, as a component in a host of medical devices, as a semipermeable membrane in protective fabrics, and as specialized growing media for high-value plants. What makes HPUR unique is that it is never used for structural reasons to provide strength and resilience. It is used because its compatibility with water-based systems is essential for the proper functioning of the devices and compounds in which it is contained.

The size of the HPUR market belies its importance, at least as a surrogate for the use of polyurethane as a chemical. Its simplest model absorbs water, but in more

complex associations, microorganisms can colonize because of a property known as biocompatibility.

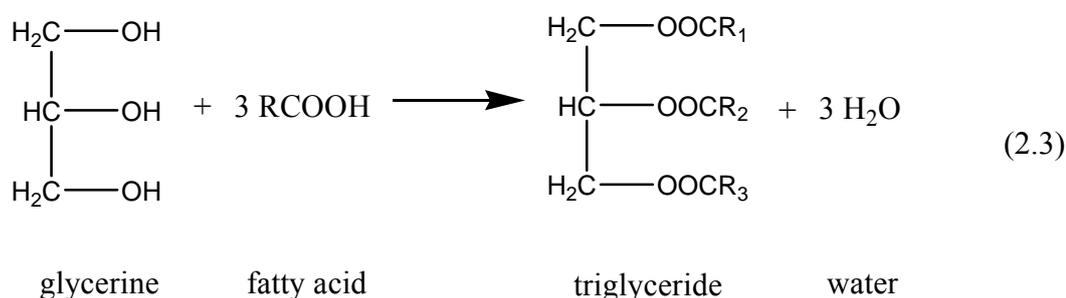
Combining the aforementioned characteristics with a functionalized surface offers a product designer a unique platform for drug delivery, development of hybrid artificial organs, advanced plant growth media, and biofilters, flow-through solvent extraction, and a host of other applications. Put another way, while reticulated foam is essentially (but not entirely) inert, it exerts effects on the environment within its structure. The application of certain techniques can produce profound effects by changing the inert surface of the structure [10].

2.2 Overview of Triglyceride Chemistry

2.2.1 Basic Oil Chemistry

The main component of oil is triglyceride, which is a compound composed of one glycerine and three fatty acid molecules. Fatty acids in most commonly found natural oils vary in alkyl chain length, ranging from 4 to 22 carbons, and also in degree of unsaturation, ranging from total saturation to 1, 2, 3, or 4 double bonds.

When triglycerides have three identical fatty acids, they are called simple or monoacid triglycerides. When triglycerides contain more than one type of fatty acid, they are called complex or mixed triglycerides. The majority of oils are made up of complex mixture of triglycerides [17].



Polymers derived from chemically modified triglycerides, have long been used in coatings, polyurethane foams, also as plasticizers and toughening agents in other polymeric systems.

Linseed oil has a significant fraction of linolenic acid which gives the oil good drying and adhesion. But it also suffers from a strong propensity to yellowing. The new variety LINOLA has a 4% linolenic content as opposed to 55-70%, which could rekindle interest in this type of oil. The majority of oils are made up of complex mixture of triglycerides [5].

2.2.2 Oxidation Mechanism of Oils

Oxidation is specifically referred to as the chemical reaction of atmospheric oxygen attacking the fatty acid chains of triglyceride molecules.

Oil oxidation is a free radical chain reaction which proceeds with the following sequence of reactions :

1. formation of free radical,
2. formation of hydroperoxide,
3. decomposition of hydroperoxide and formation of oxidation products [5].

As shown in Figure 2.8 for the specific case of linoleic esters, the first stage of this polymerization consists of an abstraction of a hydrogen atom from these reactive sites induced by a free radical. The resulting radicals react with ambient oxygen to give peroxy radicals.

The rate of drying reflects essentially the rate of termination, that is, the rate of chain extension leading to a crosslinked product and is a function of double bond contents of the oil for the standard atmospheric conditions which imply a constant oxygen concentration.

The “iodine number” (expressed as the grams of iodine consumed by 100 grams of oil) reflects the degree of unsaturation because the C=C double bonds are determined analytically by titration with I_2Cl_3 . Iodine numbers below 100 reflect a nondrying aptitude in terms of applications (the polymerization is too slow). Iodine numbers between 100 and 150 indicate a modest degree of unsaturation and a relative slow, but often acceptable, capacity to dry. Oils possessing iodine values higher than 150 are used as drying oils in most applications. Thus, linseed oil has an iodine number around 180. The extent of unsaturation is not the only parameter that determines the capacity of oils to dry, the other one being the specific mutual position of the unsaturations, namely whether they are conjugated or not, the former structure being

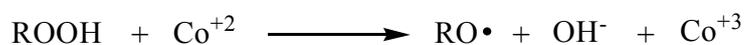


Figure 2.9 : Oxidative polymerization reactions

2.2.3 Functionalization of triglycerides

The rich chemistry that the triglyceride structure of plant oils possesses makes them ideal for making polymers [5]. Plant oils, with a few exceptions such as castor oil, cannot be easily converted into polymers in their original form [16]. There are numerous ways of chemically modifying the unsaturated sites on the fatty acids, many of which can be used to make polymers as seen Figure 2.10 [3,4,5].

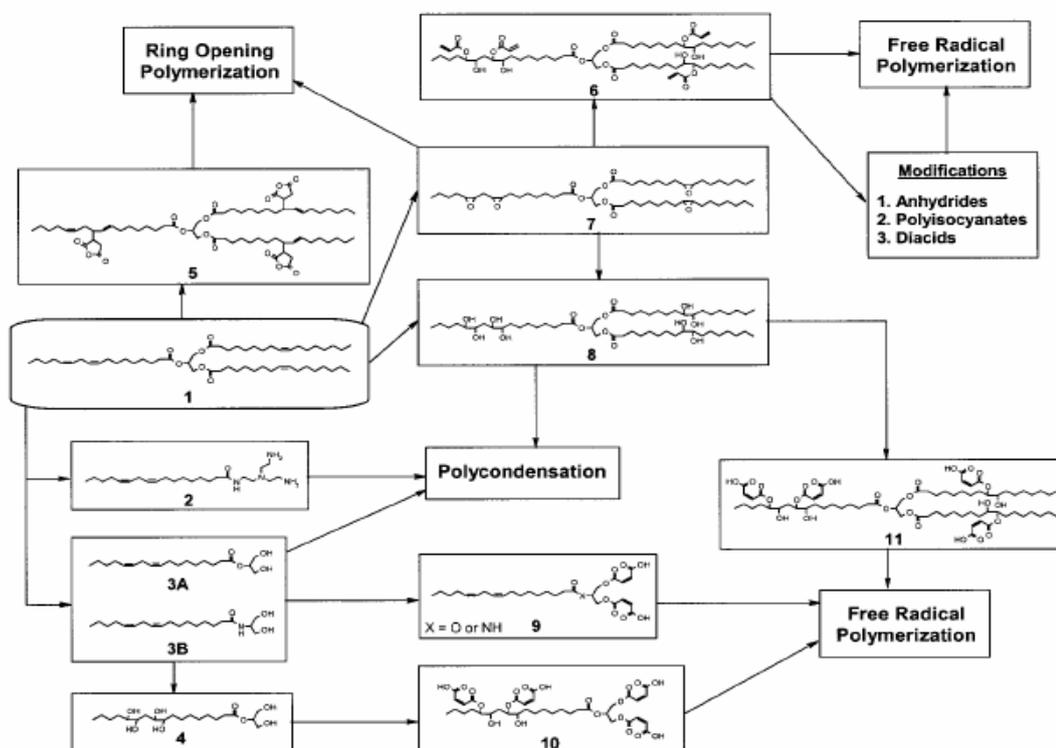


Figure 2.10 : Functionalization of triglyceride

In structures 5, 6, 7, 8, and 11, the double bonds of triglyceride are used to functionalize the triglyceride with polymerizable chemical groups. From the natural triglyceride, it is possible to attach maleates(5) [5] or convert the unsaturation to epoxy (7) [18] or hydroxyl functionalities (8) or attach vinyl [19] and acrylate [20] functionalities to the epoxy and hydroxyl functional triglycerides [4].

The second method for synthesizing monomers from triglycerides is to convert the triglyceride to monoglycerides through a glycerolysis (3A) reaction. The product is generally a mixture of mono- and diglycerides, as illustrated in Figure 2.11. Monoglycerides have found much use in the field of surface coatings, commonly referred to as alkyd resins, because of their low cost and versatility. In those application, the double bonds of the monoglycerides are reacted to form the coating.

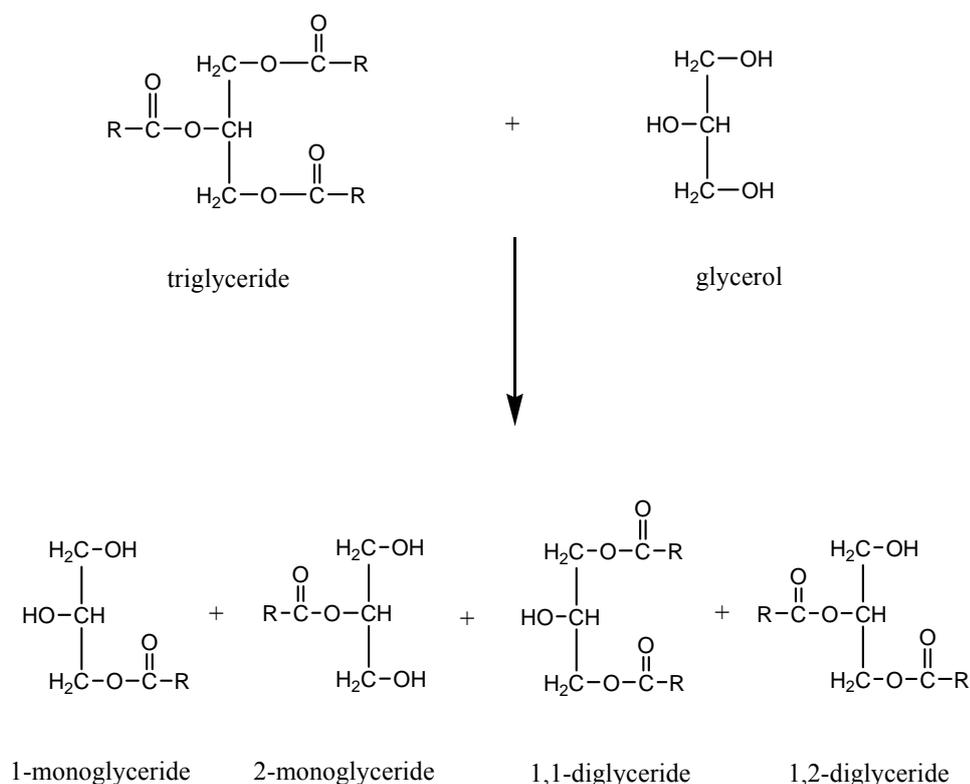


Figure 2.11 : Glycerolysis of triglycerides to form mixture of mono- and diglycerides [4]

However, monoglycerides are also able to react through the alcohol groups via polycondensation reactions with a comonomer, such as a diacid, epoxy, anhydride [4], or isocyanate [8]. In addition to their application triglyceride oils have been utilized quite extensively to produce inks, plasticizers, lubricants, and agrochemicals [4].

The third method is to functionalize the unsaturation sites as well as reduce the triglyceride into monoglycerides. This process can be accomplished by glycerolysis of an unsaturated triglyceride, followed by hydroxylation (4) or by glycerolysis of a hydroxy functional triglyceride [4].

2.2.4 Polymerization of Triglycerides

Various oils and chemical pathways for functionalization of triglycerides have been studied.

These oils are polymerizable by attack on the unsaturation through a free radical mechanism; reactivity of the hydroxyl, keto, epoxy, and the other groups; and after hydrolysis, reaction of the carboxylic and glycerol groups [21].

Both conjugated and nonconjugated drying oils react in the presence of a free radical initiator with such unsaturated monomers as styrene, vinyltoluene, and acrylic esters. High degrees of chain transfer result in the formation of a variety of products, for example, low molecular weight homopolymer of the monomer, short-chain graft copolymers, and dimerized drying oil molecules. The reaction of drying oils with such monomers is not commercially important, but the same principle is used to make modified alkyds. Linseed oil modified with cyclopentadiene has found fairly sizeable commercial use. The product is inexpensive and dries faster than linseed oil. However, its odor and dark color limit its application [22].

2.2.5 Advantages and disadvantages of triglyceride oils

The rich chemistry that the triglyceride structure of plant oils possesses makes them ideal for making polymers [5]. Developing polymer synthesis from plant oils provides a chance to synthesize polymers with the desired qualities [16].

Plant oils are easily degradable by lipase enzymes; thus, the potential biodegradability of these plant oil based polymers for certain applications is another advantage for the use of plant oils instead of petroleum [5]. Triglyceride oil based polymers are an economical and environmentally friendly alternative to petroleum for biodegradable polymer synthesis [16].

Plant oils are found in abundance in all parts of the world, making them an ideal alternative chemical feedstock [5]. Industrially, triglycerides are excellent examples of renewable resources [20].

However, the organic solvents used cannot be completely removed from the products, and they have usually have deterrent effects on polymer quality and cost [16].

Some synthetic problems remain. For example, shrinkage during free radical polymerization and the replacement of expensive comonomers are a couple of current problems which require solutions. Another disadvantage is their tendency to yellowing [12].

2.2.6 Triglyceride Oil Based Polyurethanes

Biopolymers from renewable natural resources have become increasingly interesting because of their low cost, availability, and possible biodegradability. A wide range of naturally occurring biopolymers, cellulose, and starch are already available for material applications. With rapid advances in our understanding of fundamental biosynthetic pathways and methods to modulate or tailor these pathways through genetic engineering, a variety of biopolymers have been derived from polysaccharides, proteins, lipids, and polyphenols, and specialty polymers have been produced by bacteria, fungi, plants, and animals. Meanwhile, new biopolymers may be obtained from low molecular weight natural substances containing various functionalities by the synthetic polymerization methods widely used for petroleum-based monomers.

Natural oils (plant oils and marine fish oils) possess a triglyceride structure with highly unsaturated fatty acid side chains. The multiple C-C bonds make these biological oils ideal monomers of natural origin for the preparation of biopolymers.

One of the major efforts in this field has taken advantage of either the original C-C bonds of soybean oil, tung oil, corn oil, and linseed oil, or the C-C bonds of soybean oil derivatives. The other major process has involved the conversion of plant oils into polyols by epoxidizing the C-C bonds of the triglyceride oil, followed by oxirane ring opening of the epoxidized oil. The plant oil-derived polyols are then further reacted with diisocyanates to produce polyurethanes.

Various polymerization techniques have been employed, including cationic [19], thermal, and free radical polymerization [12].

Plant oils which are triglycerides of fatty acids have a number of excellent properties which can be utilized for producing polymeric materials such as polyurethanes.

The biobased polyurethanes are prepared through condensation polymerization of plant oil polyols and diisocyanates.

Most of these urethane polymers are lightly cross-linked materials with low thermo-mechanical and physical properties. Rigid polyurethanes with higher compressive strength and oxidative and thermal stability are prepared from hydroxylated soybean oil, glycerol and isocyanates. The literature abounds with examples of polyurethanes prepared from castor oil and various aliphatic and aromatic diisocyanates. These castor oil based polyurethanes [23,24] and the castor oil modified with linseed and tung oil [22] have been used in IPNs and semi-interpenetrating polymer networks SIPNs with other petroleum based vinyl monomers such as acrylates, methacrylates, acrylamides, and methacrylamides or by condensing with novalac resin and a phenolic resin prepared from cardanol and furfural [5].

Urethane modified polyetheramide resins can be used as an anticorrosive coatings material [25]. Linseed oil based urethane alkyd resins have good solvent resistance, hydrolysis resistance and superior abrasion performance. Uralkyds are adapted to waterborne application and new polyurethane dispersions with drying oil modification [26, 27]. In the form of foamed polyurethane rubber, polymerized castor oil is utilized in seat cushions [21].

However, polyurethanes from soybean oil have good thermal, oxidative and weather stability, and can be used as a matrix in composite materials [28].

Trilinolein, low-saturation canola oil, and soybean oil polyurethanes displayed excellent mechanical properties and higher glass transition temperatures compared to polyurethanes from epoxidized and hydroformylated polyols of the same functionality [29].

Poly(urethane amide) resins were synthesized from Nahar seed oil showed better performance of the poly(urethane amide) resins compared to polyester or polyesteramide resins of the same oil [30].

2.2.7 Applications of Triglycerides

Natural oil triglycerides have been employed for a long time as a feedstock for paints, coatings, lubricants, etc. In recent years, important advances in the synthesis of structural polymeric materials from these natural oils have been made. Recent work on soy oil-based polymers reveals that in most cases the specific mechanical properties of the biopolymers are comparable to widely used plastics, including polyethylene, polystyrene, and unsaturated polyesters. Various complex structures, such as tubes, panels, and automotive parts, that are currently made from petroleum-based plastics might be replaced by these soy oil plastics. The soy resins can also be fabricated into biocomposites with high strength fillers. These biocomposites possess much higher mechanical properties and thus may find applications where engineering plastics are currently being widely used.

The good damping properties of some of the soy oil biopolymers may greatly broaden their applications. Damping materials, which reduce unwanted noise and prevent vibration fatigue failure, have found numerous applications in the aircraft, automobile, and machinery industries. There are many conventional polymers presently being used commercially for damping, including asphaltics, polyurethanes, polyvinyl acetate, acrylics, natural rubber, SBR, and silicone rubber. Multicomponent polymeric materials, such as interpenetrating polymer networks (IPNs), constitute a new class of advanced damping materials. These IPNs are capable of efficient damping over wide temperature and frequency ranges. The good damping soy oil polymers show damping characteristics similar to the IPNs.

Shape memory polymers, such as heat-shrinkable tubing and films, have been widely used in cable and wire as well as the medical and packaging industries. Due to their low cost, easy processibility, and large variations in starting materials, shape memory polymers also possess great potential as materials for civil engineering, machinery manufacturing, electronics and communications, household materials, etc. Shape memory soy oil plastics are a new class of shape memory materials. More importantly, these materials are the first shape memory polymers prepared from renewable natural resources. Thus, the new soy oil plastics have certain advantages over petroleum-based shape memory polymers, and have definitely broadened the variety and applications of these functional materials [12].

2.3 Free Radical Polymerization (FRP)

Free radical reactions are of importance in a wide variety of commercial applications. Polymers prepared by free radical means are used in manufacture of numerous products, such as fabrics, surface coating and paints, plastics, packaging, spectacle and contact lenses and surgical devices [31]. Free radical polymerization has distinct advantages over other polymerization methods, such as tolerance to trace impurities, less stringent conditions, and also to be able to polymerize a wide range of monomers.

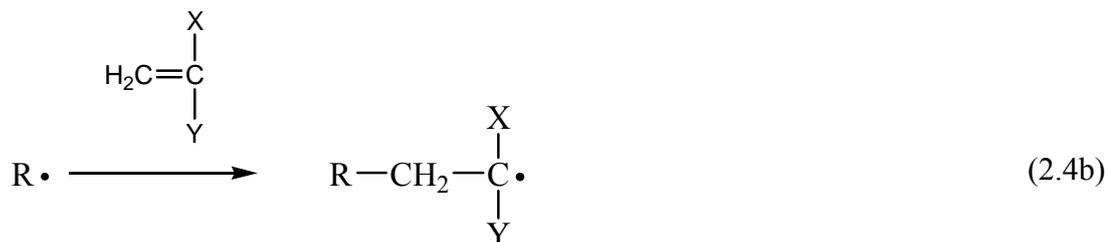
2.3.1 Steps of the Polymerization Process

Free radical systems are characterized by three main steps:

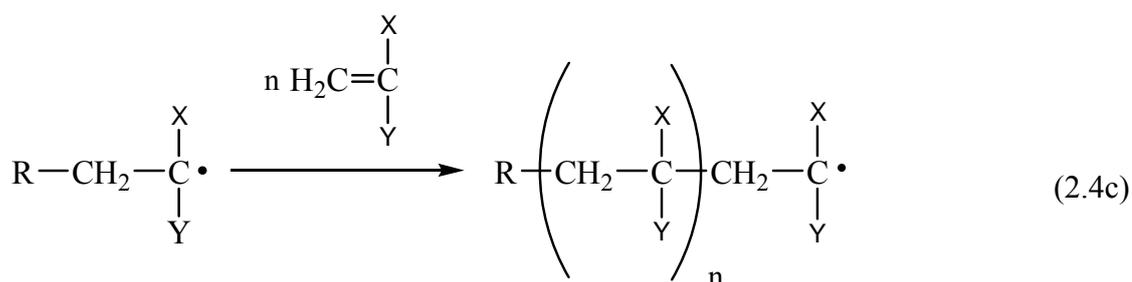
1. initiation,
2. propagation,
3. termination.

Initiation occurs from the reaction of an initiator-derived radical center with the monomer molecule. The propagation or growth reaction consists of the rapid addition of monomer molecules to the radical species. In this step reaction is repeated many times. Usually, it occurs in head-to-tail fashion, because the free radical formed is more stable. However, as with initiation, alternatives are possible and head-to-head, and tail-to-tail modes occur. Usually to minor extents. The propagating radical may be terminated finally by either combination or disproportionation reactions in last step. Where the termination step occurs by combination, a head-to-head linkage is formed and this is shown to have a different stability from the normal head-to-tail linkage. Where the termination occurs by disproportionation, an unsaturated chain end and a fully saturated chain end are formed. Many monomers show both types of termination: thus in methyl methacrylate, disproportionation is approximately twice as rapid as combination at room temperature and increases in importance as the temperature is raised. On the other hand, styrene and acrylonitrile radicals terminate predominantly by combination.

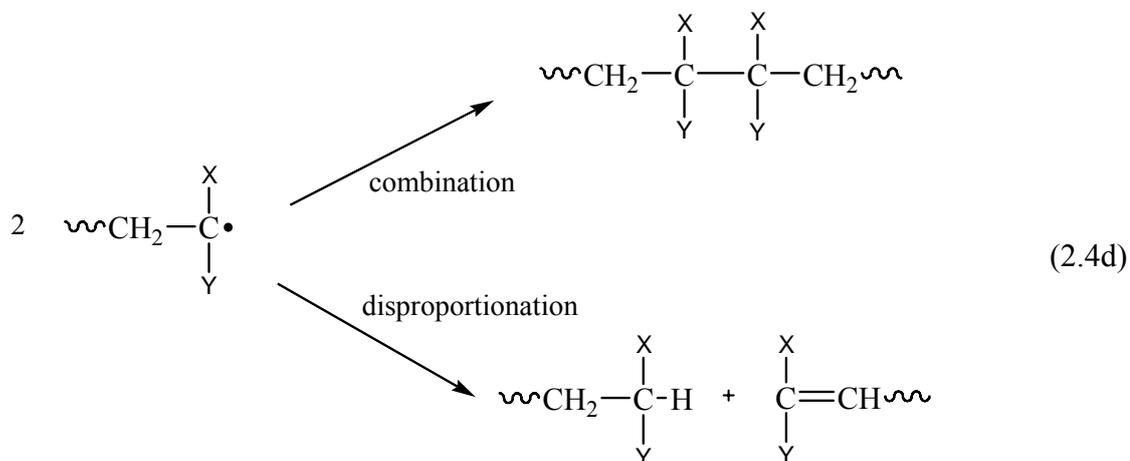
Initiation



Propagation

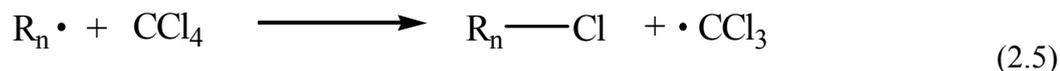


Termination



Atom (often hydrogen) abstraction from saturated molecules is a well-known reaction of free radicals and, as would be expected, is important in free-radical polymerization. It leads to the chain-transfer process, which brings about the cessation of the growth of a propagating radical and at the same time produces a new small radical which may propagate. A great variety of species can participate in

chain transfer agents. Chain transfer, therefore, occurs widely; it commonly involves reaction of growing chains with monomer or solvent or other additive and is well established for polymers and some initiators. Atoms other to hydrogen, notably halogens (except fluorine), may be transferred. Transfer to carbon tetrachloride is illustrated in 2.2.



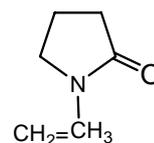
2.3.2 Monomers

A wide variety of unsaturated organic compounds can be induced to undergo free-radical polymerization. Some of these are listed in Table 3.2. In general, the monomer structure can be represented by the formula $CH_2 = CHR$, where the group R is an organic unit, a halogen or pseudo-halogen ligand (such as $C \equiv N$), or even an inorganic residue. A few suitable monomers have the formula $CH_2 = C(R)(R')$, in which two substituent groups are attached to the α -carbon atom [32].

Table 2.1 : Monomers for free-radical polymerization

Styrene	$CH_2 = CHPh$
α -Methylstyrene	$CH_2 = C(Me)Ph$
1,3-Butadiene	$CH_2 = CH-CH = CH_2$
Methyl methacrylate	$CH_2 = C(Me)COOMe$
Vinyl esters	$CH_2 = CHOCR$
Ethylene	$CH_2 = CH_2$
Vinyl chloride	$CH_2 = CHCl$
Vinylidene chloride	$CH_2 = CCl_2$
Tetrafluoroethylene	$CF_2 = CF_2$
Acrylonitrile	$CH_2 = CHC \equiv N$
Acrylamide	$CH_2 = CHCONH_2$

N-Vinyl pyrrolidone



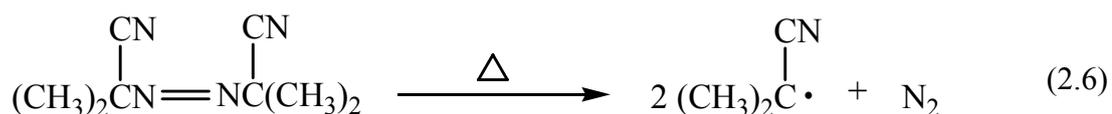
2.3.3 Initiators

Polymerization of a reactive vinyl monomer is initiated by free radicals having sufficiently high activity. These may be generated from initiators in diverse ways, among which thermal or photochemical intramolecular bond cleavage, redox reactions, and photochemical hydrogen abstraction are the commonest, but other processes such as use of γ -radiation or electron beams find applications.

2.3.3.1 Thermal Initiators

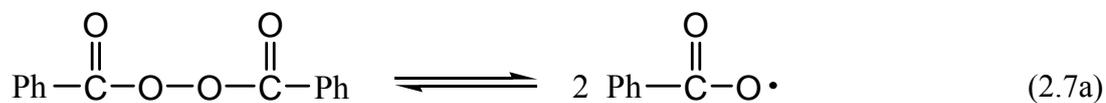
Azo Initiators

Azo compounds, $RN=NR$, such as azobisisobutyronitrile, decompose thermally to give nitrogen and two alkyl radicals, as shown in reaction (2.6). Azo compounds are useful and popular thermal initiators because they offer a wide range of useful operating temperatures [32].



Peroxy Compounds

Benzoyl peroxide is a well-established initiator of polymerization. Like other peroxides, the primary step in the thermal decomposition is scission of the $-\text{O}-\text{O}-$ bond to give two acyloxy radicals. A number of secondary processes may follow ; in addition to reacting with monomer, benzoyloxy radicals may recombine or undergo β -scission to phenyl radicals and carbon dioxide. Further, recombination reactions giving biphenyl and phenyl benzoate may then occur.



Silver Alkyls

All the free radical initiators discussed above are appropriate only for polymerizations carried out at room temperature or above. However, silver alkyls

have been used to initiate radical polymerizations at temperatures as low as -20 to -60°C. Ethylsilver, for example, is believed to decompose by reaction shown in (2.8).



2.3.3.2 Redox Initiation

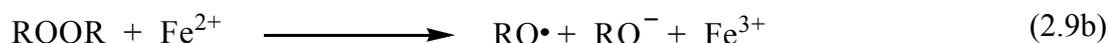
Many oxidation-reduction reactions produce free radicals that can be used to initiate polymerization. This type of initiation is referred to as redox initiation or redox catalysis. A prime advantage of redox initiation is that radical production occurs at reasonable rates over a very wide range of temperatures, including 0-50 °C an even lower, depending on the particular redox system. This allows a greater freedom of choice of the polymerization temperature than is possible with the thermal dissociation of initiators. This redox initiation can be arranged to proceed quickly under mild reaction conditions and is particularly useful for low and ambient temperature radical polymerization.

Some of the common redox systems are described below.

(a) Peroxides in combination with a reducing agent are a common source of radicals, for example, the reaction of hydrogen peroxide with ferrous ion :

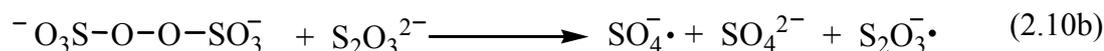
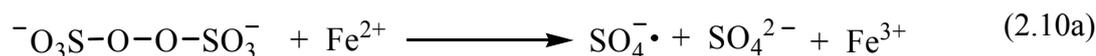


Ferrous ion also promotes the decomposition of a variety of other compounds including various types of organic peroxides:



Other reductants such as Cu^+ , Co^{2+} , Cr^{2+} , V^{2+} , and Ti^{3+} can be employed in place of ferrous ion in many instances.

(b) The combination of a variety of inorganic reductants and oxidants can be used to initiate radical polymerization, for example, redox systems with persulfates as the oxidant:



(c) A combination of inorganic oxidant and organic reductant initiates polymerization, usually but not always by oxidation of the organic component, for example, the oxidation of an alcohol by Ce^{4+} , or by V^{5+} , Cr^{6+} , Mn^{3+} .



2.3.3.3 Photoinitiators

Photoinitiators for free radical polymerization fall into two classes: those which on irradiation undergo intramolecular bond cleavage with radical generation and those which when photoexcited abstract hydrogen atoms from H-donors and so form radicals.

2.4 Free Radical Chain Copolymerization

Chain polymerization can be carried out with mixtures of two or more monomers to form polymeric products that contain two or more different structures in the polymer chain. This type of chain polymerization process in which two monomers are simultaneously polymerized is termed a copolymerization and the product is a copolymer.

From the technological viewpoint, copolymerization of two monomers is an effective way of altering the balance of properties of commercial polymers. While polymerization of a single monomer is relatively limited as to the number of different products make polymer with specifically desired properties. Thus by variations in the nature and relative amounts of the two monomers in a copolymerization, an almost unlimited number of products with different properties can be synthesized [6].

2.4.1 Binary Copolymer Equation

The simplest quantitative statistical treatment for the determination of copolymerization composition, which is generally referred to as the terminal model, was first hypothesized by Dostal in 1936 and later elucidated by others. The terminal

model is based upon the assumption that the chemical reactivity of a propagating polymer chain is independent of the size or composition of the chain and is only influenced by the active end group. Though the terminal model is dependent on several assumptions and may not be the most accurate model to describe a copolymer process, it is relatively simple to apply and provides a facile starting point when evaluating copolymerizations of various monomer pairs. When two monomers, M_1 and M_2 are copolymerized by free radical methods, four reactions are feasible according to the terminal model:



Where k_{11} is the rate constant for the addition of a propagating chain ending in M_1 adding to monomer M_1 (2.12), k_{12} is the rate constant for the addition of a propagating chain ending in M_1 adding to monomer M_2 (2.13), and so on. The rate constants can then be expressed in terms of the monomer reactivity ratios, r_1 and r_2 , where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. Monomer reactivity ratios may either be experimentally determined or estimated and for free radical polymerizations are generally independent of initiator and solvent with only slight temperature dependence.

The terminal model also provides a useful means to approximate copolymer compositions that are dependent on such factors as the comonomer feed ratio and the reactivities of the comonomers according to model. The Mayo-Lewis equation (2.16), which is derived from the terminal model using the assumption of the steady-state radical approximation, can be used to describe the instantaneous copolymer composition:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1 [M_1] + [M_2]}{[M_1] + r_2 [M_2]} \quad (2.16)$$

2.4.2 Types of Copolymerization

Depending on the values of r_1 and r_2 , and of the r_1r_2 product three types of copolymerizations can be recognized [6].

Ideal Copolymerization

When $r_1r_2 = 1$, the two different types of propagating chain ends both add preferentially to one of the monomers, and is described as ideal copolymerization.

Random Copolymerization

When $r_1 = r_2 = 1$ due to the equal reactivity of the monomers toward both types of propagating chain ends and the resulting copolymer composition will directly reflect the comonomer feed.

Alternating Copolymerization

When $r_1 = r_2 = 0$, is referred to as alternating copolymerization. It means that the monomer is incapable of undergoing homopolymerization and its radical prefers to add exclusively to the other monomer. This leads to alteration of two monomer units along the copolymer chain.

Block Copolymerization

When $r_1 > 1$; $r_2 > 1$, it results in a tendency to form blocks of both monomers. The tendency of each radical to add its own type of monomer would increase and the two types of monomers would simultaneously homopolymerize in each other's presence. However, such reactivity combinations are not known in free radical polymerization.

The mechanism of most typical copolymerizations fall somewhere between the extremes of ideal copolymerization and alternating copolymerization [6].

3. EXPERIMENTAL WORK

3.1. Materials

3.1.1. Purification of Materials

3.1.1.1. Monomers

Styrene (St) (Fluka)

Washed with aq. 5% to remove inhibitors, then water, dried with CaH_2 several hours and distilled under reduced pressure ($50\text{ }^\circ\text{C}$ / 25 mmHg). Middle fraction was collected and immediately used.

Methylmethacrylate (MMA) (Fluka)

Washed with aq. 5% to remove inhibitors, then water, dried with CaH_2 several hours and distilled under reduced pressure.

Ethylene glycol (Merck)

Dried with MgSO_4 and distilled under reduced pressure.

3.1.1.2. Solvents

p-xylene (Merck)

Purified (and dried) by fractionally distillation from sodium.

Toluene (Lachema and Lab Scan)

Refluxed and dried with CaH_2 and distilled from sodium.

Isopropyl alcohol (Lab Scan)

Refluxed with Na_2SO_4 for several hours and then distilled and dried further with CaH_2 .

Pyridine (Merck)

It was used without further purification.

Methanol (Lab Scan)

It was used without further purification.

Ethanol (Lab Scan)

It was used without further purification.

Diethyl ether (Akkimya)

It was used without further purification.

Potassium hydroxide (Merck)

It was used without further purification.

3.1.1.3. Other Chemicals and Reagents

Methacryloyl chloride (Aldrich)

It was used without further purification.

Sodium azide (Merck)

It was used without further purification.

Di-n-butylamine (Merck)

It was used without further purification.

Hydrochloride acide (Aldrich)

It was used without further purification.

Sodium carbonate (Merck)

It was used without further purification.

Brom phenol blue indicator (Aldrich)

It was used without further purification.

Acetic anhydride (Merck)

It was used without further purification.

Phenol phthalein indicator (Merck)

It was used without further purification.

AIBN (Aldrich)

Recrystallized from ethanol prior to use.

Benzoyl peroxide (Aldrich)

It was used without further purification.

Lead-Naphthanate (Polisan)

It was used without further purification.

Cobalt octeate (Polisan)

It was used without further purification.

Sulphuric acid (Merck)

It was used without further purification.

Sodium Sulphate (Merck)

It was used without further purification.

3.2. Equipments**3.2.1. Nuclear Magnetic Resonance Spectroscopy (NMR)**

¹H-NMR analysis were recorded on a Bruker 250 MHz Spectrometer.

3.2.2. Gel Permeation Chromatography (GPC)

GPC analyses were carried out with a set up consisting of the Agilent Zorbax pump and refractive-index detector (Model 1100) and Agilent Guard column and three Zorbax PSM Columns (60S, 300S, 1000S). THF was used as the eluent at a flow rate of 0,5 ml/min at 30⁰C. The molecular weights of the polymers were calculated with the aid of polystyrene standards.

3.2.3. Infrared Spectroscopy (FT-IR)

Infrared spectra were recorded on Shimadzu 8300 spectrophotometer.

3.2.4. Differential Scanning Calorimeter (DSC)

The glass transition temperatures of the copolymers were measured by differential scanning calorimetry (TA DSC Q10) in a flowing nitrogen atmosphere at heating rate $10\text{ }^{\circ}\text{C} / \text{min}$.

3.2.5. Thermogravimetric Analysis (TGA)

Thermal gravimetric analysis was performed on a TA TGA Q50 instrument.

3.2.6. Contact Angle Meter (CAM)

The contact angle was measured by KSV CAM200 instrument.

3.3. Synthesis of Chemical Compounds

3.3.1 Synthesis of Methyl Vinyl Isocyanate

39 g (0.6 mole) sample of sodium azide is dissolved in 140 ml of water and cooled to ca. $-10\text{ }^{\circ}\text{C}$. Then 42 g (0.4 mole) of methacrylic acid chloride in 140 ml of xylene is added slowly. So that the reaction temperature does not exceed $-5\text{ }^{\circ}\text{C}$. After complete addition of acid chloride, the mixture is stirred at $0\text{ }^{\circ}\text{C}$ for 1 hour. Then the organic phase of the two-phase reaction mixture is separated and washed once with saturated sodium carbonate and twice with ice water. Before this solution is used further, it is dried carefully over sodium sulfate. To decompose the acid azide, 10 ml of xylene is put into flask and heated to $80\text{ }^{\circ}\text{C}$. The solution of azide is added slowly, and the nitrogen evolution is controlled. After the reaction is complete, the product is separated by distillation. The crude products has a boiling point between 61 and $72\text{ }^{\circ}\text{C}$ (lit. $69\text{ }^{\circ}\text{C}$) and is distilled freshly before every polymerization. In the remaining reaction mixture residues isocyanate are destroyed by adding a small amount of propylamine [32, 33]. (Yield: 20%)

MVI was synthesized according to the procedure in Figure 3.1.

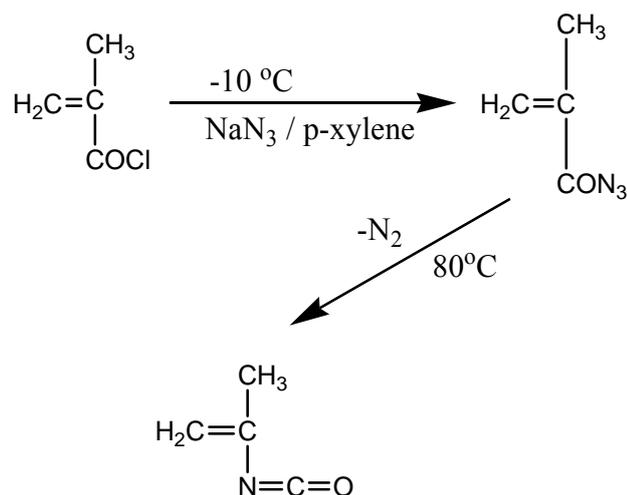


Figure 3.1 : Synthesis of MVI

The structure of MVI was confirmed by FT-IR and $^1\text{H-NMR}$ spectroscopy, respectively.

Figure 3.2 presents the FT-IR spectra of MVI. In the IR spectra, absorptions were observed at 2993 (-CH), 2251 (-N=C=O), 1651 (C=C-N) cm^{-1} and overtones of symmetric stretching band of NCO were observed 1443-1373 cm^{-1} .

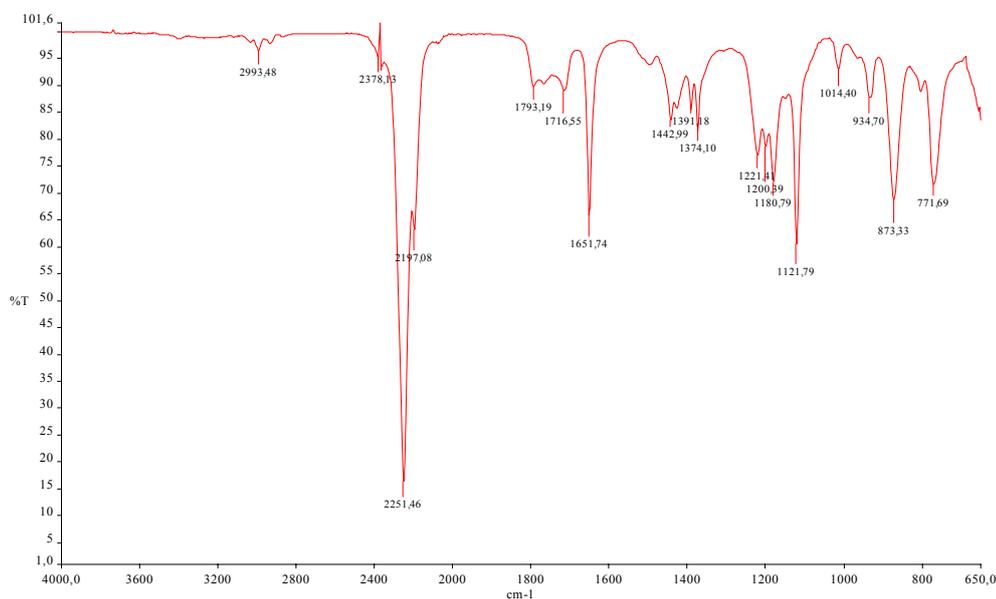


Figure 3.2 : FT-IR spectra of MVI

MVI was further characterized by $^1\text{H-NMR}$, as shown in Figure 3.3, measured with CDCl_3 as an external reference. Signals due to the characteristic protons of alkyl group were found at $\delta = 4,55$ and $4,68$ ppm, three protons of methyl group were found at $1,9$ ppm.

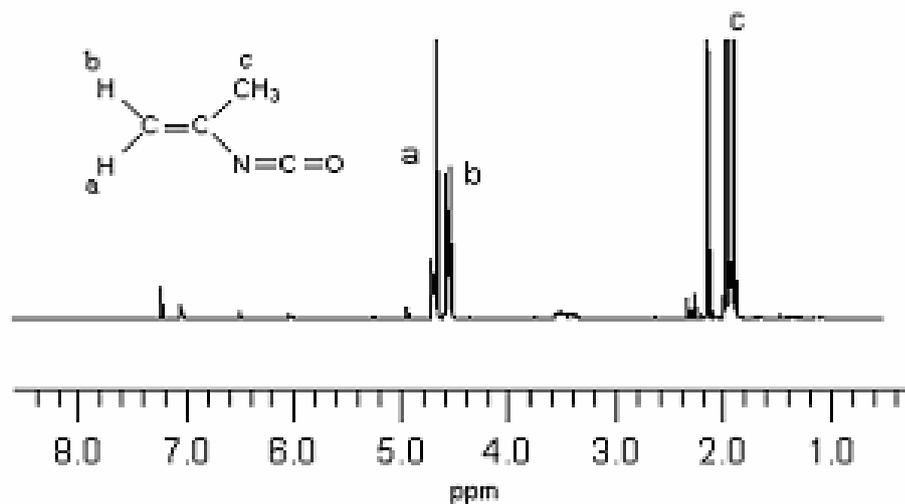


Figure 3.3 : $^1\text{H-NMR}$ spectrum of MVI

3.3.1.1 Determination of Free Isocyanate Content

Approximately 0.1 g of MVI which containing 50.6 % NCO was dissolved in the toluene in a 100 ml volumetric flask and made up to volume with toluene and mixed. 10 ml of this solution was taken into a 250-ml erlenmeyer flask. 15 ml of dry toluene was added and dissolved, then 25 ml of 0.1 *N* di-*n*-butylamine solution was added and was continued swirling for 15 min with stopper in place. 100 ml of isopropyl alcohol and 4 to 6 drops of bromphenol blue indicator solution were added and the solution was titrated with 0.1 *N* hydro chloric acid to a yellow end point. Run a blank titration including all reagents above but omitting the specimen. The NCO content was calculated as follows:

Calculations

$$\text{NCO, \%} = \frac{[(\text{B-V}) \times N \times 0.0420]}{W} \times 100 \quad (3.1)$$

where:

B = volume of HCl for titration of blank, ml,

V = volume of HCl for titration of the specimen, ml,

N = normality of HCl, *N*,

0.0420 = milliequivalent weight of the NCO group,

W = grams of specimen weight, g [34].

3.3.2 Synthesis of 2-hydroxyethyl isopropenylcarbamate

To follow the progress of reaction to synthesize urethanes containing vinyl bond, first methyl vinyl isocyanate was reacted with ethylene glycol as a model compound.

Synthesis was carried out in a 250 ml three-neck round-bottom flask equipped with magnetic stirrer, addition funnel, N₂ inlet, and thermometer. Ethylene glycol (EG) (7 mmol) and toluene, 33% of EG, were added into the flask and methyl vinyl isocyanate (7 mmol) was added dropwise to the reaction mixture and stirred, followed by addition of dibutyltin dilaurate (DBTDL) of 0.14 % of EG at room temperature under N₂ atmosphere and stirred. The flask was replaced into the oil bath at 65 °C. The disappearance of the NCO stretching band at 2256 cm⁻¹ was followed by using FT-IR spectroscopy.

3.3.3 Preparation of Partial Glycerides (PG)

Partial glycerides was prepared by glycerolysis reaction between each triglyceride oil and glycerol. Thus, in order to obtain partial glycerides with higher hydroxyl value, 120 g of triglyceride oil (linseed oil) and glycerol 12 % of oil were heated to 218 °C, and calcium hydroxide 0.1 % of the oil, was added. Temperature was raised to 232 °C and the reaction was continued at this temperature for one hour nitrogen atmosphere. The content of the reaction flask was dissolved in diethyl ether, washed with water, dried over sodium sulfate, and the solvent was removed [35]. Hydroxyl value of Glycerolysate was determined.

¹H-NMR spectrum of PG was taken in CDCl₃ as shown in Figure 3.4. Signals due to the characteristic protons of olefinic CH of fatty acids (-CH=CH-) and CH of glycerol (-CH-O-C(O)-) around 5,3 ppm, CH₂ of glycerol (-CH₂-O-C(O)-) at 4,3-4,0 ppm and 3,7-3,5 ppm, hydroxyl of glycerol (-CH₂-OH and -CH-OH) at 3,9-3,6 ppm was observed. The signals originating from fatty acid were found at 2,7 ppm (double allylic CH₂), 2,3 ppm (α-CH₂-C(O)-O-), 2,1-1,9 ppm (allylic CH₂), 1,6 ppm (β-CH₂-CH₂-C(O)-O-), 1,2 ppm (methylene), 1-0,8 ppm (CH₃) [36].

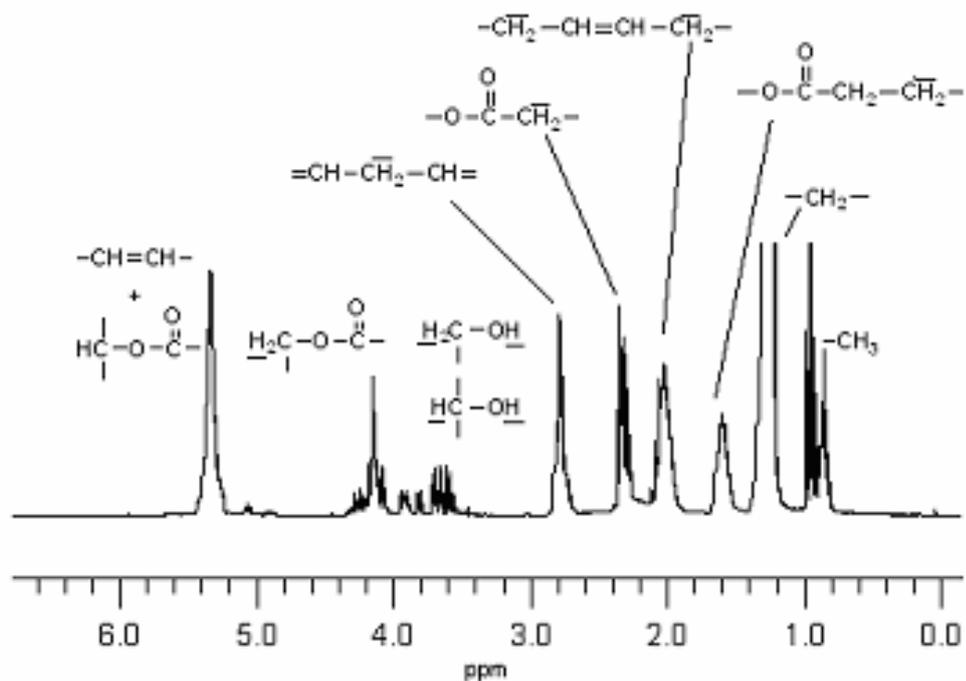


Figure 3.4 : ¹H-NMR spectrum of PG

FT-IR spectra of PG is given in Figure 3.5. In the IR spectra, absorptions was observed at 2923 (-CH), 3473 (-OH), 1741 (C=O) cm⁻¹.

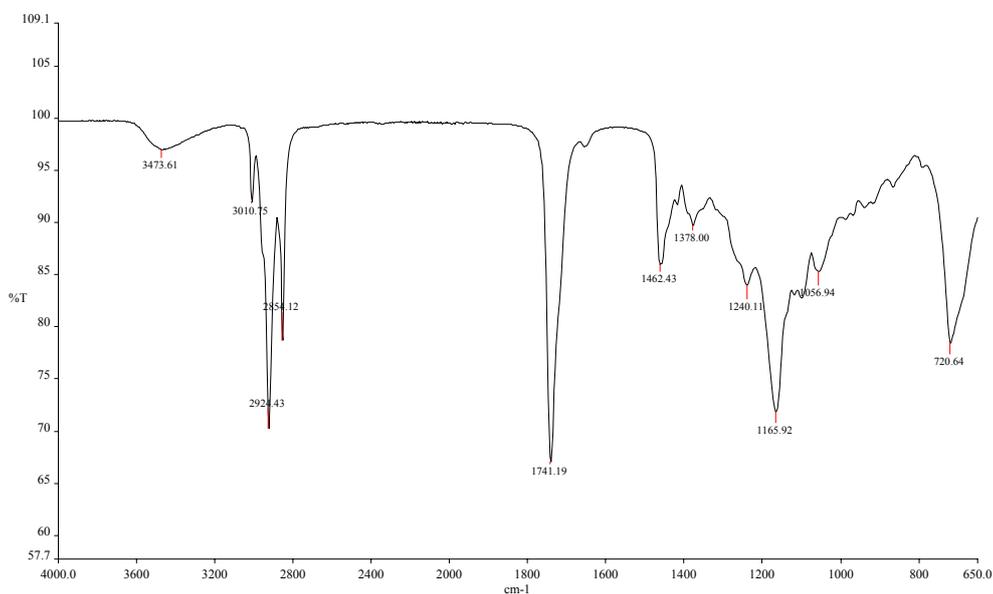


Figure 3.5 : FT-IR spectra of PG

3.3.3.1 Determination of Hydroxyl Value

Hydroxyl Value:

Hydroxyl value is the number of mg of potassium hydroxide required to neutralize the amount of acetic acid capable of combining by acetylating with 1 g of PG. To prepare acetylating agent 25 g dry acetic anhydride was dissolved in the pyridine in a 100 ml volumetric flask and made up to volume with pyridine and mixed. In the experiment approximately 1 g of PG was placed into the flask. The air condenser was attached and 5ml of acetylating agent was added through air condenser. The flask was replaced in the oil bath which is kept at 95-100 °C. The flask must not be immersed more than 1 cm deep in the bath. After 1 hour, the flask was removed from the bath, cooled and 1 ml of distilled water was added through the condenser and mixture was shaken. The flask was placed again in the oil bath for 19 minutes in order to convert quantitatively the anhydride to acetic acid and to decompose anhydrides of fatty acids or mixed anhydrides which may be formed. The flask was allowed with the contents to cool to room temperature, 5 ml 96 % ethanol was added, rinsing the condenser and the neck of the flask, and the mixture was titrated with 0,5 N ethanolic potassium hydroxide solution, using phenolphthalein as indicator. Carry out a blank determination simultaneously in the same way [37].

$$\text{Hydroxyl value} = \frac{56.1 \times N \times (V_2 - V_1)}{W} + \text{Acid value} \quad (3.2)$$

where:

W = weight of sample, g,

V₁ = volume of potassium hydroxide used in test, ml,

V₂ = volume of potassium hydroxide used in blank, ml,

N = normality of potassium hydroxide, N.

Acid Value:

Acid value of a PG is the number of mg potassium hydroxide required to neutralize 1 g of PG. In the experiment approximately 1 g sample was dissolved by 30 ml xylene (50 %)-ethyl alcohol (50 %) solution and titrated by KOH dissolved in alcohol and calculation was made by equation 3.1[37].

$$\text{Acid value} = \frac{56.1 \times N \times V}{W} \quad (3.3)$$

where:

N = normality of potassium solution, N ,

V = volume of potassium hydroxide solution used, ml,

W = weight of PG sample, g.

3.3.4 Synthesis of Triglyceride Oil Based Urethane (TGU)

At room temperature under N_2 atmosphere PG and toluene, 33 % of PG, were added to flask and stirred. MVI based on around 1.1 mol ratio for $-NCO$ to $-OH$ groups was poured slowly into the reaction mixture. Then, DBTDL of 0.14 % of PG was added and continued stirring. The flask was replaced into the oil bath at $65\text{ }^{\circ}\text{C}$. Until NCO peak disappeared, the NCO stretching band at 2256 cm^{-1} was followed using FT-IR spectroscopy. The process was also monitored using ^1H -NMR spectroscopy.

3.3.5 Copolymerization of Triglyceride Oil Based Urethane and Styrene (PTGUST)

To a schlenk tube equipped with magnetic stirrer, vacuum and dry nitrogen was applied 3 times, then 0.8 g urethane (1.1 ml), 0.4 g styrene (0.44 ml) and 1.2 mg AIBN as an initiator were added under nitrogen respectively. The reaction mixture was bubbled by nitrogen to remove dissolved gases and then the tube was immersed in an oil bath and held by thermostat at $65\text{ }^{\circ}\text{C}$. The polymerization was performed for 4, 8, 12 hours.

Copolymerization of triglyceride oil based urethane and styrene was also carried out in the presence of benzoyl peroxide as a radical initiator at $85\text{ }^{\circ}\text{C}$ for 12 h. 4.5 g urethane (5 ml) and 2.5 g styrene (2.47 ml) and 5.1 mg benzoyl peroxide were added into a schlenk tube under nitrogen respectively.

The polymers were precipitated in methanol below $0\text{ }^{\circ}\text{C}$. Then unreacted urethane was extracted by stirring the crude product in ethanol at room temperature for 24 hour.

3.3.6 Radical Homopolymerization of TGU

The radical initiated homopolymerization of triglyceride based urethane was carried out in the presence of AIBN as a radical initiator in toluene. In a sample procedure, to a schlenk tube equipped with magnetic stirrer, vacuum and dry nitrogen was applied 3 times. 3.5 g of triglyceride based urethane was mixed with toluene then 0.042 g AIBN was added, purged with N₂, and heated to 85 °C for 9 h. The polymer was precipitated in methanol below 0 °C.

3.3.7 Film Formation via Radical and Oxidative Copolymerization of TGU with Styrene

Triglyceride based urethane (0,68 g) was mixed with 50% of its own weight of styrene (0,34 g) and toluene (8 times of TGU, 9 ml) to give a yellow colored transparent solution at room temperature under N₂ atmosphere. Benzoyl peroxide (0.15%) was added, the mixtures were purged with N₂ for 10 min. Then lead naphthenate (0.18 %) and cobalt octeate (0.018 %) were added to polymer sample and the sample was mixed for 24 h. The sample with controlled thickness was molded on teflon coated glass into a steel ring with 11 cm diameter from toluene solution. Film from toluene solution was evaporated at room temperature for 9 days.

3.3.8 Film Formation via Radical and Oxidative Polymerization of TGU

1 g TGU and 9 ml toluene were mixed at room temperature under N₂ atmosphere. Benzoyl peroxide (0.15%) was added, the mixtures were purged with N₂ for 10 min. Then lead naphthenate (0.18 %) and cobalt octeate (0.018 %) were added to polymer sample and the sample was mixed for 24 h. The sample with controlled thickness was molded on teflon coated glass into a steel ring with 11 cm diameter from toluene solution. Film from toluene solution was evaporated at room temperature for 9 days.

3.3.9 Film Formation via Radical Polymerization of Styrene

0.55 g styrene and benzoyl peroxide (0.15%) was added into a tube. The reaction solution was bubbled by nitrogen and then the tube was immersed in an oil bath and held by thermostatet at 85 °C. Viscosity increased at the end of the 2 h and polymer was cold and solved in 5 ml toluene. The sample was molded on teflon coated glass into a steel ring with 11 cm diameter from toluene solution. Film from toluene solution was evaporated at room temperature for 3 days.

4. RESULTS AND DISCUSSIONS

In this thesis, urethane macromers containing vinyl bond was synthesized from partial glyceride mixture and methyl vinyl isocyanate. Polymerization and copolymerization of synthesized triglyceride based urethanes with styrene was carried out through vinyl bond via free radical polymerization.

4.1 Synthesis of Methyl Vinyl Isocyanate (MVI)

In this study methyl vinyl isocyanate was synthesized to employ for the synthesis of urethane macromer in the second stage.

The crude product was distilled freshly before every urethane reaction and it was determined by the wet method using di-n- butyl amine that free isocyanate content of the product was calculated as 45%. Yield of MVI was found 20%.

4.2 Synthesis of 2-hydroxyethyl isopropenylcarbamate

Urethane macromers as a model compound was first synthesized by the reaction of MVI and ethylene glycol. Reaction scheme is given in Figure 4.1. This reaction was monitored using FT-IR spectroscopy by following the NCO stretching band at 2256 cm^{-1} .

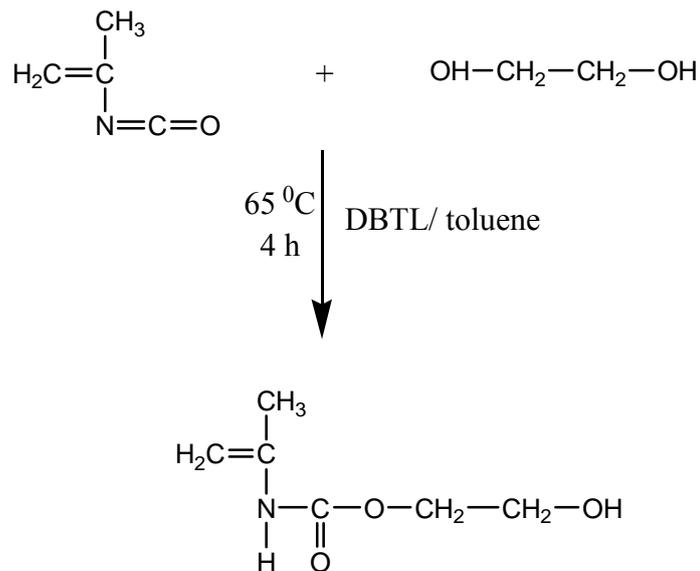


Figure 4.1 : Reaction of 2-hydroxyethyl isopropenylcarbamate

The structure of urethane was confirmed by FT-IR and $^1\text{H-NMR}$ spectroscopy, respectively. Figure 4.2 presents the FT-IR spectra of urethane.

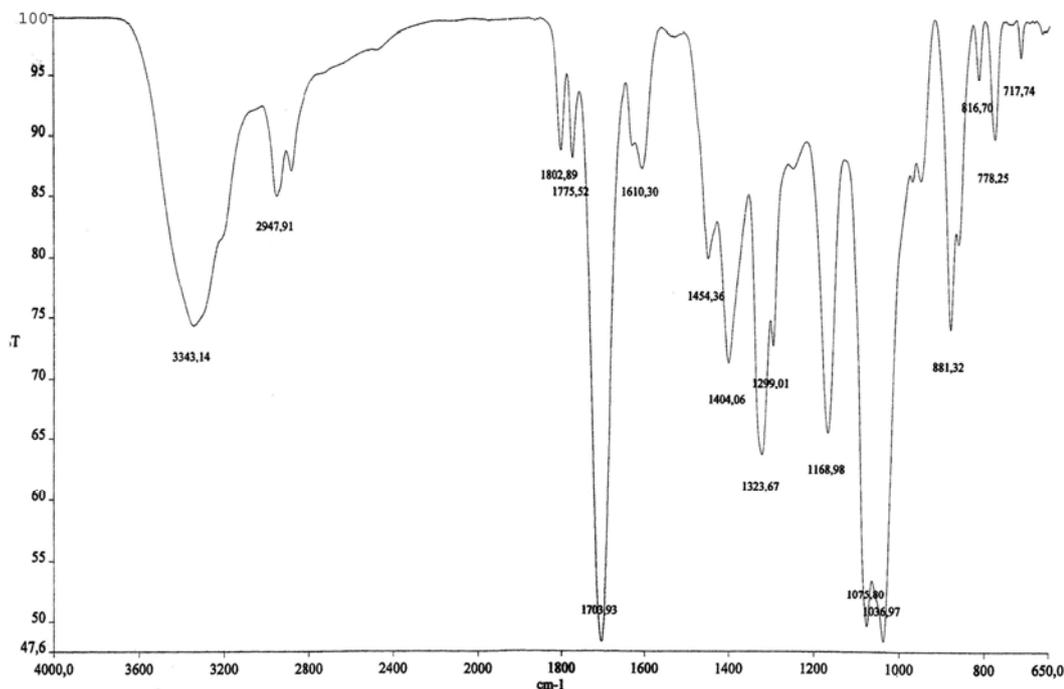


Figure 4.2 : FT-IR spectra of 2-hydroxyethyl isopropenylcarbamate

In Figure 4.2, the IR spectra of the urethane showed strong absorption around 3343 cm^{-1} due to N-H groups, sharp peak at 1703 cm^{-1} due to urethane carbonyls, and medium peak at 1651 due to vinyl bond (C=C). Other absorptions were observed at 2947 (-CH), 1610 (-NH), 1168 (-C-N), 1075 (C-O) cm^{-1} .

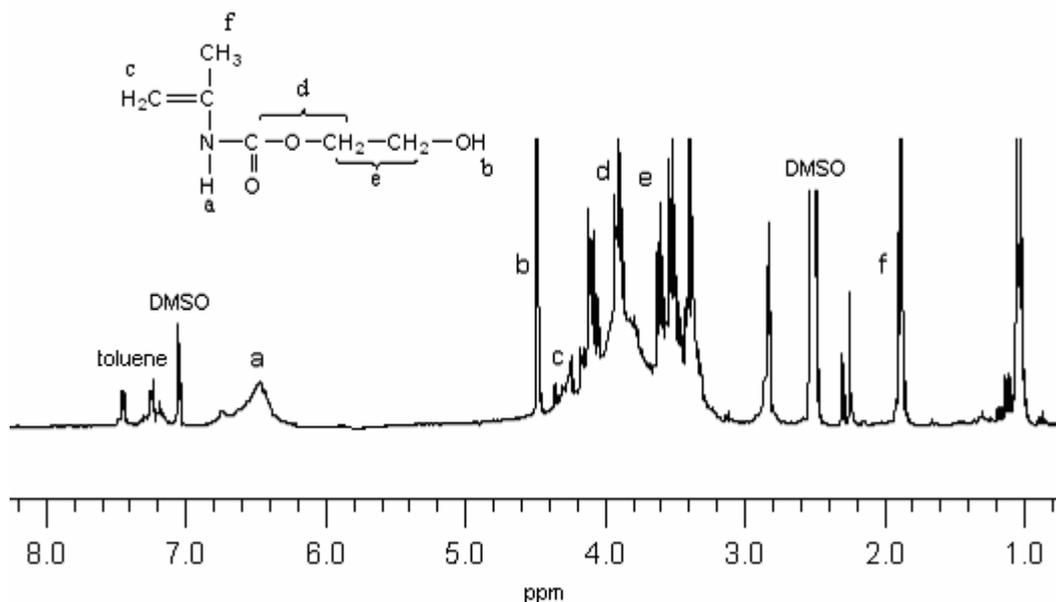


Figure 4.3 : $^1\text{H-NMR}$ spectrum of 2-hydroxyethyl isopropenylcarbamate

$^1\text{H-NMR}$ spectrum of urethane was taken in DMSO-d_6 as shown in Figure 4.3. Signals due to the characteristic protons of urethane at 6,46 ppm, protons of vinyl group were found at $\delta= 4,4$ and 4,2 ppm, three protons of methyl group from MVI were found at 1,88 ppm. According to the spectrum, the signals originating from ethylene glycol were discerned at 4,48 ppm ($-\text{OH}$), 4,1-3,8 ppm ($-\text{C}(\text{O})\text{OCH}_2$), and around 3,62 ppm ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$).

4.3 Synthesis of Partial Glyceride (PG)

In order to synthesize triglyceride based urethane, partial glyceride mixture was synthesized by glycerolysis reaction of linseed oil and glyceride. It was determined that hydroxyl value was 159,4.

4.4 Synthesis of Triglyceride Based Urethane(TGU)

In this part, urethane was synthesized by the reaction of PG and MVI as shown in Figure 4.4.

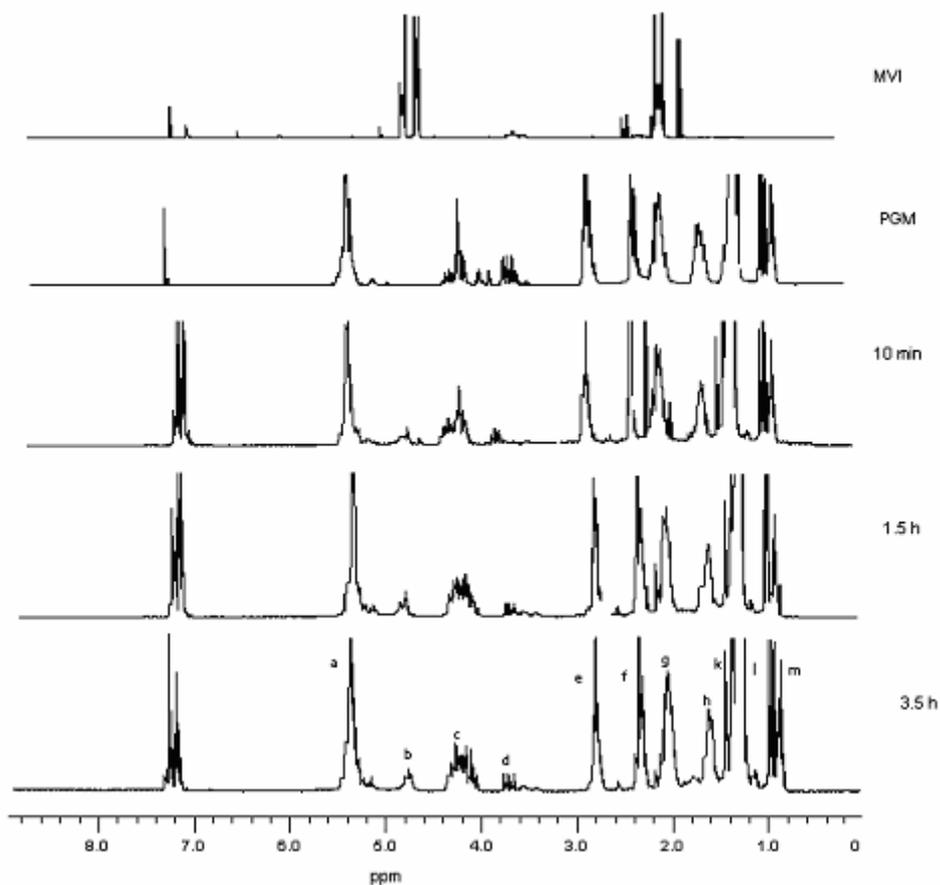


Figure 4.6 : Monitoring reaction progress of TGU using ^1H -NMR spectroscopy

As seen Figure 4.6, signals of hydroxyl protons at 3,9-3,6 ppm disappeared with time, and signal of urethane proton at 4,77 ppm appeared. Signals due to the characteristic protons of alkyl group appeared at $\delta = 4,55$ and 4,68 ppm shifted to lower magnetic field through the urethane signal. These protons were characterized by D_2O exchange and urethane proton was disappeared and signals of alkyl protons at 4,7 and 4,8 ppm were appeared. Figure 4.7 and 4.8 shows ^1H -NMR spectrum of TGU and that of after D_2O exchange, respectively.

As seen Figure 4.9, absorptions was observed at 3374 cm^{-1} (-NH stretching), 3010 cm^{-1} (-CH stretching), 1740 cm^{-1} (carbonyl of ester and urethane), 1604 cm^{-1} (-NH deformation) , 1225 cm^{-1} (C-N bending), 1082 cm^{-1} (C-O-C assym.).

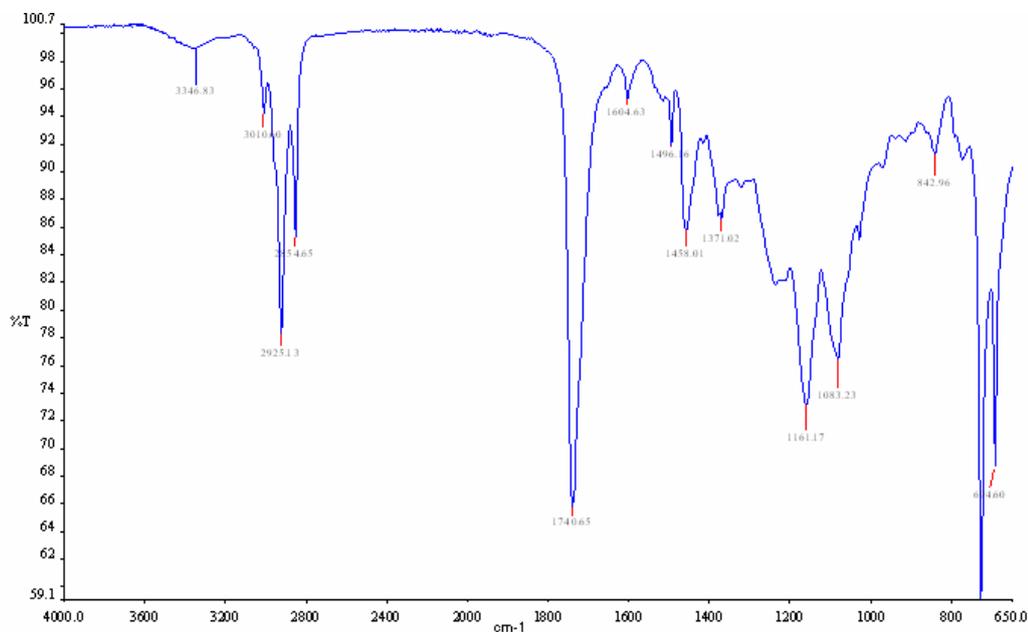


Figure 4.9 : FT-IR spectra of TGU

4.5 Copolymerization of TGU and Styrene (PTGUST)

Copolymerization of triglyceride based urethane was carried out with styrene via free radical polymerization in the presence of AIBN, which has been shown in Figure 4.10.

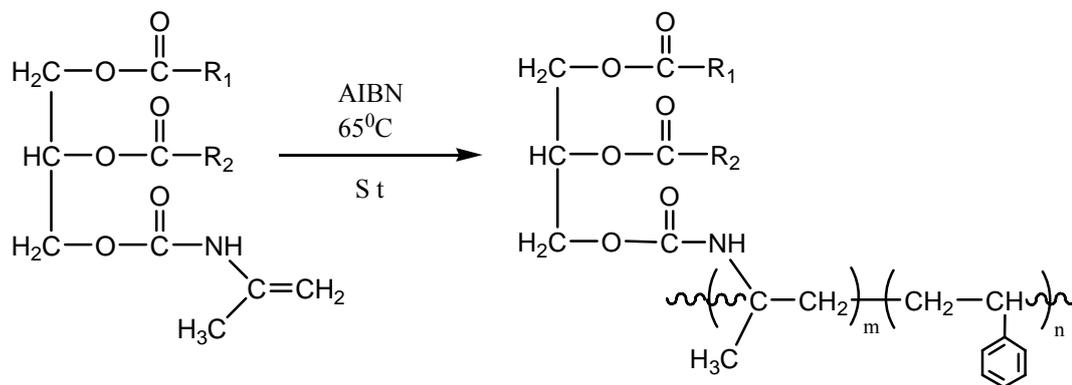


Figure 4.10 : Reaction of PTGUST

The polymerization was performed for 4, 8, 12 hours at 65°C . Typical results concerning the copolymerization of TGU and St are presented in Table 4.1.

Table 4.1 : Copolymerization* of TGU with styrene at 65⁰C

Run	Time (h)	Conversion %	^a Mn (g/mol)
1	4	< 10	4125
2	8	<10	3822
3	12	< 10	4392

*Triglyceride based urethane : [0,54] mol/lt , Mn: 950 g/mol

Styrene : [2,49] mol/lt

AIBN : [5x10⁻³] mol/lt

Temperature : 65 ⁰C

^aDetermined by GPC

As seen Table 4.1 while molecular weight of TGU is 950 g/mol, that of copolymer for 4 h is 4125 g/mol. The resulting copolymers have molecular weights between 3822 to 4392 g/mol. However molecular weight of the copolymers does not show significant difference with varying reaction time and conversions were limited to 10% . Copolymers were also purified by extraction with ethanol to remove unreacted TGU.

In Figure 4.11 GPC traces of TGU, PTGUSt before and after extraction are shown. After extraction PTGUSt shows unimodal molecular weight distribution. Its peak at low elution volume was ascribed to the copolymer and there was no clear peak at high elution volume pertaining to the unreacted TGU.

The copolymerization of TGU and St was also carried out at 85 ⁰C for 12 h as stated in section 3.3.5. In this case the molecular weight of the extracted copolymer was increased to 5960 g/mol compared to the initial TGU (907 g/ mol).

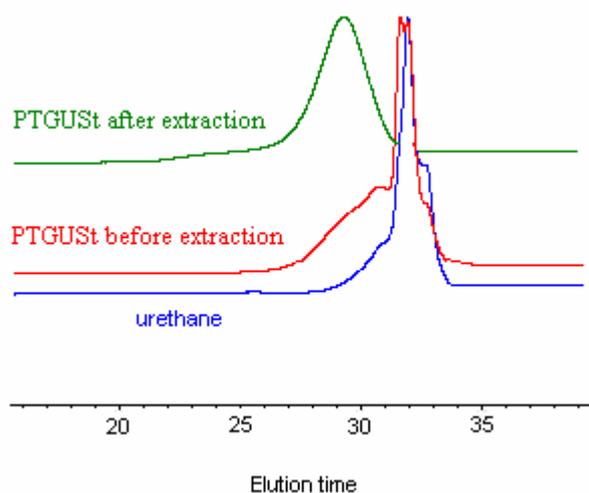


Figure 4.11 : GPC traces of TGU, PTGUST before and after extraction

The structure of PTGUST was confirmed by FT-IR and $^1\text{H-NMR}$ spectroscopy, respectively. Figure 4.12 presents the FT-IR spectra of PTGUST. The large number of absorptions between 1500 and 2000 cm^{-1} indicates C-H overtones of aromatic bonds of styrene, other characteristic peaks of styrene were found at 663 cm^{-1} (aromatic C=C), 757 cm^{-1} (aromatic C-H). The FT-IR spectra of the copolymer showed strong absorption around 1736 cm^{-1} due to the presence of both ester and urethane carbonyls, N-H stretching at 3448 cm^{-1} , N-H deformation at 1061 cm^{-1} , and C-H stretching at 3026 cm^{-1} .

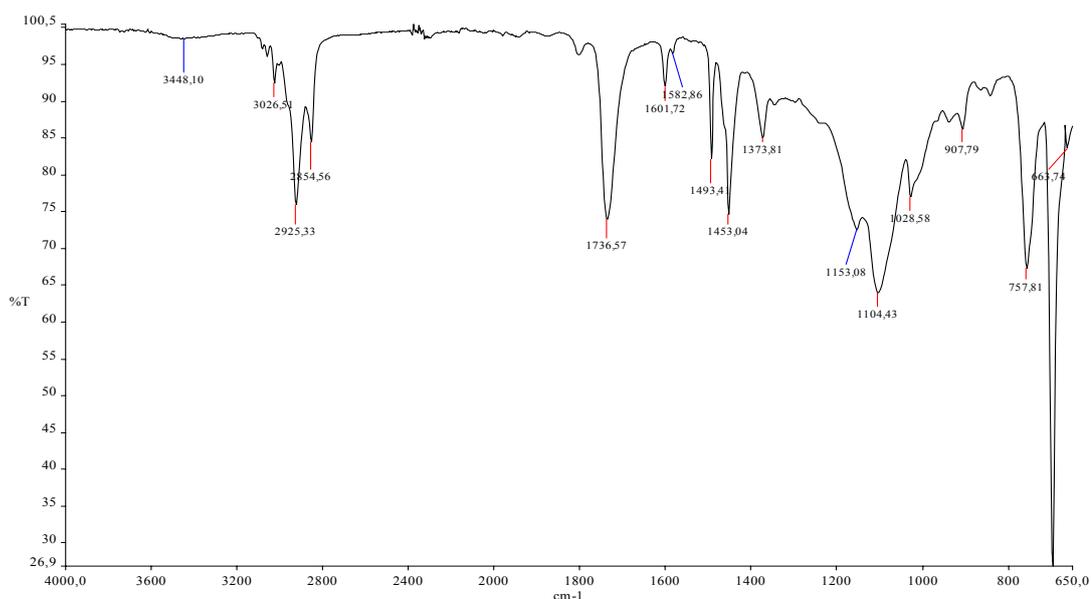


Figure 4.12 : FT-IR spectra of PTGUST

The $^1\text{H-NMR}$ spectra of PTGUST was taken in CDCl_3 as shown in Figure 4.13. The signals of aromatic and $(-\text{CH}_2-\text{CH})$ protons due to styrene at 6,5-7,0 ppm, and around 1,8 ppm was found, respectively. Although signals of urethane and methyl protons due to MVI was not detected clearly as they interfere with other signals in this area. Signals due to the characteristic protons of PG observed at 5,3 ppm (olefinic CH of fatty acids $(-\text{CH}=\text{CH}-)$), and CH of glycerol $(-\text{CH}-\text{O}-\text{C}(\text{O})-)$, 4,1 ppm (CH_2 of glycerol $(-\text{CH}_2-\text{O}-\text{C}(\text{O})-)$), 2,7 ppm (double allylic CH_2), 2,3 ppm ($\alpha\text{-CH}_2\text{-C}(\text{O})\text{-O-}$), 2,1-2,0 ppm (allylic CH_2), 1,6 ppm ($\beta\text{-CH}_2\text{-CH}_2\text{-C}(\text{O})\text{-O-}$), 1,2 ppm (methylene), 1,0-0,8 ppm (CH_3) prove copolymerization of TGU and St.

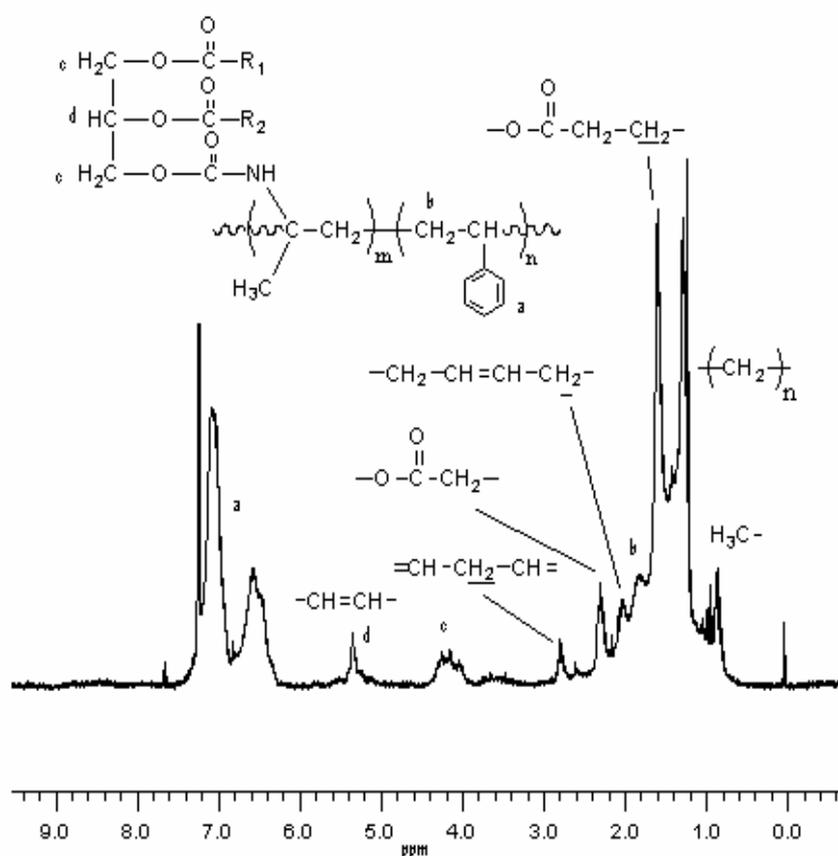


Figure 4.13 : $^1\text{H-NMR}$ spectrum of PTGUST

4.6 Radical Homopolymerization of TGU

Homopolymerization of the triglyceride based urethane was also carried out in the presence of AIBN as radical initiator in toluene at 85 °C. At the end of 9 h homopolymer was precipitated in methanol below 0 °C. Conversion of homopolymer was 54,24% with Mn: 966 g/mole. However we could not separate homopolymer from the unreacted TGU as the solubilities of both were similar. Figure 4.14 shows GPC chromatograms of TGU and corresponding homopolymer.

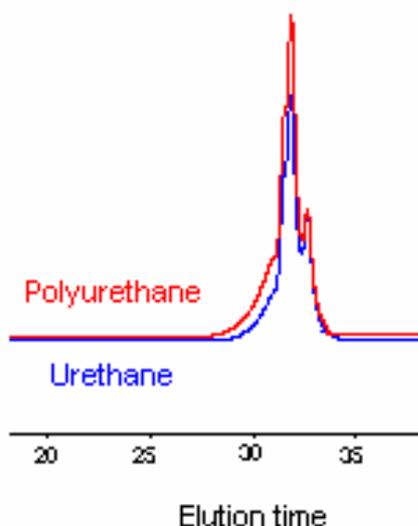


Figure 4.14 : GPC traces of TGU, PTGU

4.7 Film Properties of TGU, Copolymer of TGU with Styrene and PSt

In order to investigate the film properties of TGU, films of TGU and its copolymer with styrene were prepared via radical polymerization in the presence of benzoyl peroxide. Lead naphthenate and cobalt octeate were used as catalysts in the oxidative polymerization reaction. Additionally the film of PSt was prepared. After removing toluene, the films were dried completely. Their thermal and surface properties were investigated.

TGU and its copolymer gave yellow colored transparent films as shown in Figure 4.15. Film of FTGUS_t also indicated elastomeric properties. The film of PSt was transparent and brittle.

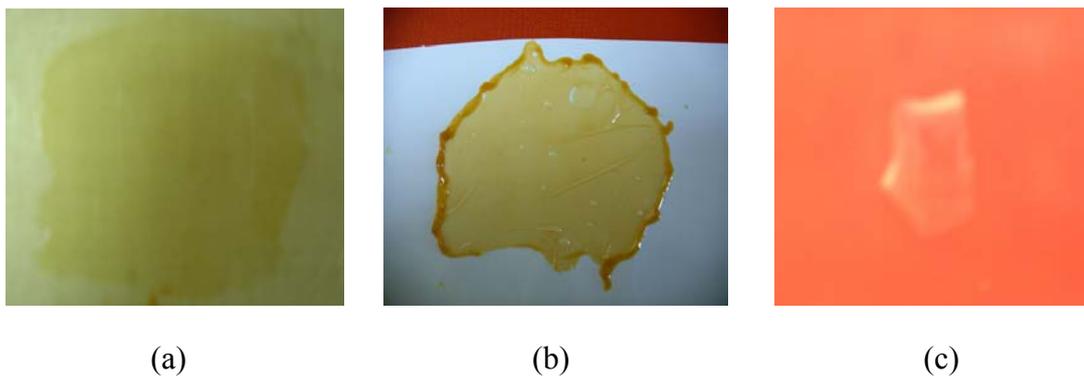


Figure 4.15 : Photos of transparent films; (a) FTGU (b) FTGUST (c) FPSt

In order to show not to undergo homopolymerization of styrene in copolymerization reaction, first the film of PSt was dissolved in toluene, and then TGU was added into this solution and mixed. In a few minute PSt participated, and a heterogeneous mixture was obtained. This led us to conclude that TGU with styrene undergo copolymerization during film formation.

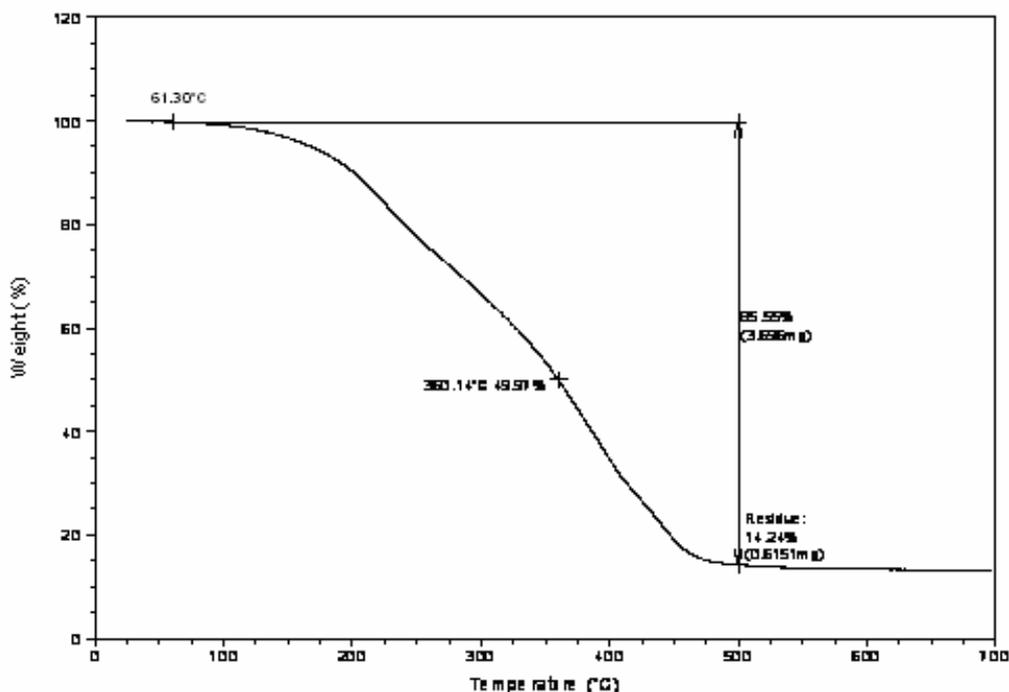


Figure 4.16 : TGA thermogram of FTGU

TGA was carried out in a nitrogen stream at a heating rate of 20 °C/min for analysing thermal stabilities of the polymers. Figure 4.16, 4.17, 4.18 show TGA curves for polymers and copolymer. The temperature at 50 % residue of FTGU, FTGUST and FPSt were 360.14, 369.11, 384.91 °C, respectively. As given in Table 4.2

degradation temperature of copolymer of TGU with styrene was higher than its homopolymer, because of the rigidity of styrene due to benzene ring.

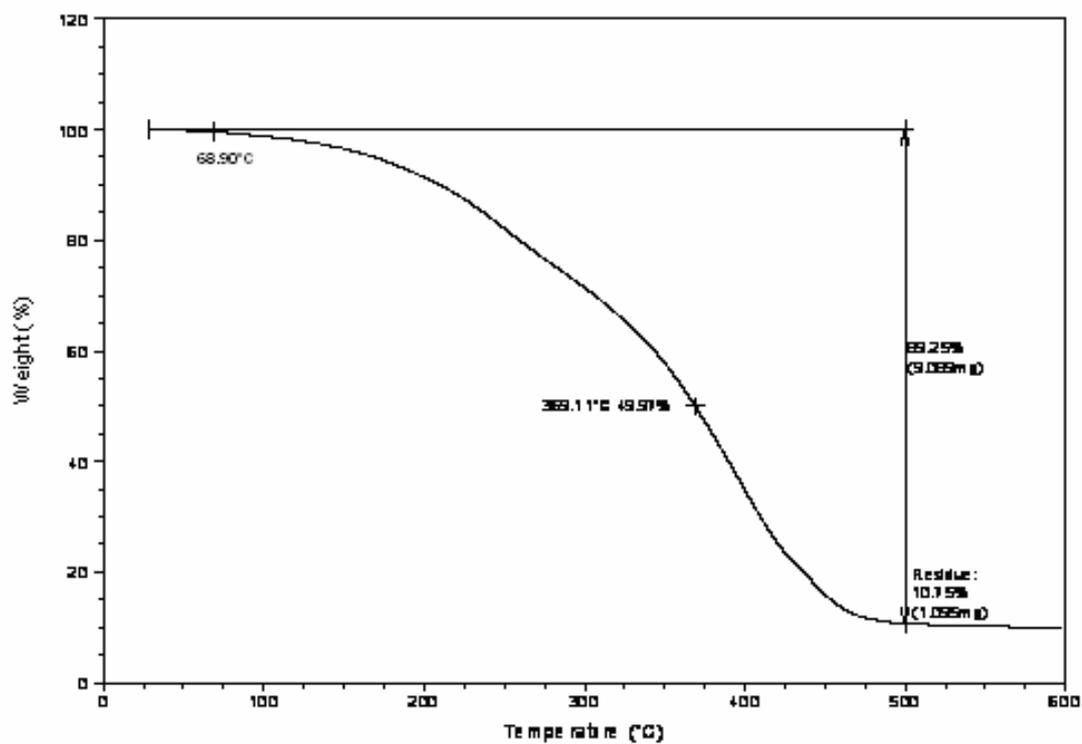


Figure 4.17 : TGA thermogram of FTGUST

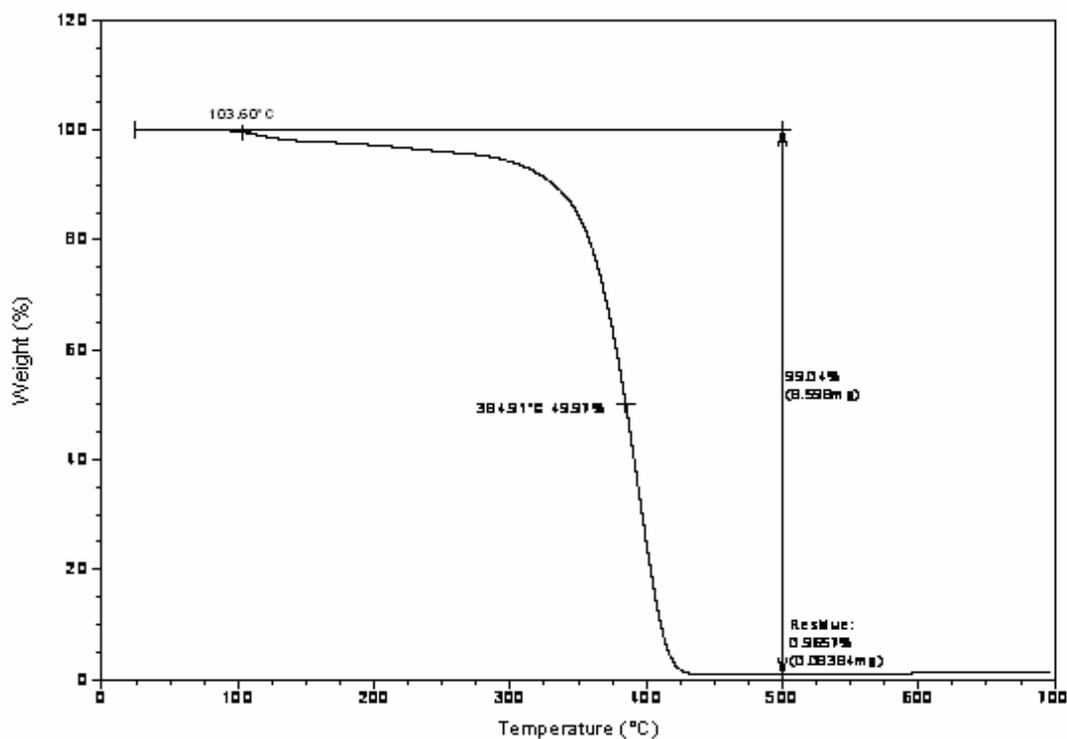


Figure 4.18 : TGA thermogram of FPSt

Table 4.2 : Thermal and hydrophobicity properties of FTGU, FTGUS_t and FPSt

Sample	T ^a (°C)	Contact angle ^b (degree)
FTGU	360.14	66.97
FTGUS _t	369.11	71.72
FPSt	384.91	85.86

^a temperature at residue 50 %, determined by TGA

^b determined by contact angle meter

The hydrophobicities of FTGU, FTGUS_t and FPSt were determined by the measurement of water contact angles formed by droplets with 5 µl under air. As contact angle of FTGU was 66.97 degree, that of FPSt was 85.86 degree. However, FTGUS_t was measured as 71.72 degree. This values shows that FTGU was more hydrophilic than FTGUS_t. Styrene caused to increase the contact angle. FPSt was more hydrophobic than the others.

5. CONCLUSIONS

The triglyceride based urethane macromers containing vinyl bond were synthesized. In order to synthesize triglyceride based urethane, partial glyceride mixture was synthesized by glycerolysis reaction of linseed oil and glyceride, and then reacted with methyl vinyl isocyanate.

Polymerization and copolymerization of triglyceride based urethanes with styrene was carried out through vinyl bond via free radical polymerization. Molecular weight of the copolymers does not show significant difference with varying reaction time and conversions were limited to 10%.

Films cast from the solutions of TGU or copolymers were tested for oxidative polymerization and film forming capacity was examined. Degradation temperature of FTGUSt was higher than FTGU, because of the rigidity of styrene due to benzene ring. FTGU also was more hydrophilic than FTGUSt. Styrene caused to increase the contact angle. FPSt was more hydrophobic than the others.

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