REPUBLIC OF TURKEY

YILDIZ TECHNICAL UNIVERSITY

GRADUATE SCHOOL OF SCIENCE AND ENGINEERING

SPECTROSCOPIC AND RHEOLOGICAL ANALYSIS OF POLYESTER POLYOLS

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MSc. THESIS

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July, 2021

REPUBLIC OF TURKEY
YILDIZ TECHNICAL UNIVERSITY
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Bahar TAYLANLI

Signature

Dedicated to my mommy

TÜLAY TAYLANLI

ACKNOWLEDGEMENTS

First and foremost, I'd want to give my deepest appreciation to my supervisor, Prof. Dr. Metin TÜLÜ, who guided me through my graduate studies. In addition, I'd like to thank Prof. Dr. Tark EREN for assisting me see things from a different perspective and comprehend new aspects of polymer chemistry.

I'd like to thank Chemists CANBERK YÜKSEL and MESUT GÜRGEN for their assistance with my analysis and synthesis, as well as Dr. MURAT BARANAK for allowing me to conduct my research at Polex Kimya Sanayi ve Ticaret A.Ş.

To My friend MSc chemist KETRİN ZEKİ, for her endless support and helping me through every obstacle I faced during my master's degree and all my friends who have supported me throughout my graduate studies, I want to thank them a lot.

I'd also like to express my sincere appreciation to my lovely friend chemist CANSEN KORKMAZ for always believing in me and supporting me even when I didn't think I'd be successful. Her encouragement and support, even in the most difficult moments, is invaluable.

As a final, I would like to convey my endless gratitude to my dear mother for being my biggest supporter throughout my education life, for her endless trust in me and for always encouraging me. I couldn't have done it without her.

BAHAR TAYLANLI

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LIST OF SYMBOLS

d	Day
°C	Degree Centigrade
g	Gram
h	Hour
min	Minute
rpm	Revolutions per Minute

LIST OF ABBREVIATIONS

ACP	Acrylate Polyol
DABCO	1,4-diazabicyclo [2.2.2] octane
DEG	Diethylene glycol
DMF	Dimetilformamid
MEG	Monoethylene glycol
MHP	Hybrid Polyol
PEP	Polyester Polyol
PET	Polyethylene Terephthalate
PETP	Polyether Polyol
PU	Polyurethane
PUD	Polyurethane Dispersion
SMPUS	Shape Memory Polyurethanes
Tg	Glass Transition Temperature
TPU_s	Thermoplastic Polyurethanes
VC	Virtually cross-linked

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ABSTRACT

Spectroscopic and Rheological Analysis of Polyester Polyols

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MSc. Thesis

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The flammability of polymeric materials is an important restricting factor in their daily usage; therefore, polymer flammability is reduced by adding Flame Retardants (FR). While the flame retardant materials added to the polymer provide safe areas of use against fire, they are also desired to be materials that will provide improvements in terms of tensile bending strength, resistance to impact fractures, flexibility, oxygen or UV resistance. In order to increase the fire resistance of polymeric materials or to provide flame retardancy, some organic or inorganic agents ($Al(OH)_3$, phosphorescent materials, TCPP, TEP) are added at the resin stage. These additives do not chemically bond to the polymer chain, they only take place as a blend and provides FR up to a certain degree of temperature, and they may eventually start to leak or migrate from the polymer after a certain point of degree. Even if it is not exposed too high temperatures, it is known that the additives in plastic materials emerge over a time. Additionally, FRs may cause some weaknesses in the physicochemical properties of the polymeric material.

Borane is one of the important natural sources of our country, and in the current study; it is aimed first to synthesize boron based crosslinker to be used as an alternative to the conventional cross linker (Trimethylolpropane, TMP). Then this cross linker is used for the synthesis of polyesters and consequently polyurethanes. Since it is a part of polymeric backbone and expected to provide better FR and smoke trap properties. Higher mechanical strength, more flexibility and UV resistance are also additional expectations of this study. Trimethylolpropane (TMP) is generally used as a crosslinker in traditional polyester synthesis. Accordingly, in our study, trifunctional (triol) borate ester was synthesized starting from boric acid and mono ethylene glycol (MEG). Then, different polyester polyols were synthesized with this triol. Synthesized polyols were purified by Liquid-Phase Polymer-Based Retention (LPR) Technique and characterized by spectroscopic and chromatographic methods (NMR, ATR, GPC etc.). Finally, different Polyurethanes were synthesized from these polyols, and the effects of boron on the flame retardancy performance and mechanical properties were investigated.

Key words— Polyol, polyurethane, crosslinker, boron, fire retardants.

ÖZET

Poliester Poliollerinin Spektroskopik ve Reolojik Analizi

Bahar TAYLANLI

Kimya Bölümü

Yüksek Lisans Tezi

Danışman: Prof. Dr. Metin TÜLÜ

Polimerik malzemelerin yüksek tutuşa bilirliği, uygulama alanlarını sınırlayan önemli bir faktördür, bu nedenle polimer yapılarına alev geciktiriciler eklenerek tutuşabilirliği azaltılır. Polimere eklenen alev geciktirici malzemeler yangına karşı güvenli kullanım alanları sağlarken aynı zamanda gerilme eğilme mukavemeti, çarpma kırılmalarına karşı direnç, esneklik, oksijen veya UV direnci açısından iyileştirmeler sağlayacak malzemeler olmaları da istenir. Polimerik malzemelerin yangına dayanımına artırmak veya alev geciktirilmesi sağlamak için reçine aşamasında organik veya anorganik bazı ajanlar ($Al(OH)_3$, fosforlu malzemeler, TCPP, TEP gibi) katılır. Bu katkılar polimer zincirine kimyasal olarak bağlanmadıkları için sadece blend olarak yer aldıklarından belirli bir sıcaklığa kadar direnç sağlarlarken sıcaklığın belirli bir noktasından sonra polimerden sızmaya/kusmaya başlarlar. Hatta yüksek sıcaklığa maruz kalmasa bile plastik malzemelerin, içerisindeki katkı maddelerini zamanla salınım yaptıkları bilinmektedir.

Çünkü bu katkılar polimer zincirine kimyasal olarak bağlanmamış sadece blend olarak karıştırılmıştır. Yanı sıra polimerik malzemenin fizikokimyasal özelliklerinde bazı zafiyetlere de yol açabilirler.

Bu çalışmada ülkemizin zengin kaynaklarından türetilen bor bazlı bileşiklerin polimerin gövdesine bağlandığında, partikül yüzeyinde doğal olarak oluşan oksit tabakasının inhibisyonuna sebep olarak polimere alev geciktirici, duman tutucu gibi özellikler kazandırması hedeflenirken yanı sıra yüksek mekanik mukavemet, esneklik ve UV dayanım gibi özelliklerde de iyileşmeler sağlanması beklenmektedir. Geleneksel Poliester sentezinde çapraz bağlayıcı olarak genellikle Trimetilolpropan (TMP) kullanılmaktadır. Buna bağlı olarak bizim çalışmamızda da borik asitten yola çıkılarak üç fonksiyonlu (triol) borat esteri sentezlenmiştir ve Sentezlenen Borlu çapraz bağlayıcı ile farklı polyesterik poliollarin sentezi gerçekleştirilmiştir. Elde edilen polioller Sıvı Fazlı Polimer Bazlı Tutma (LPR) Tekniği ile saflaştırıldıktan sonra spektroskopik/kromatografik yöntemler ile (NMR, ATR, GPC vb) karakterize edilmiştir. Devamında bu poliollardan farklı poliüretanlar sentezlenerek, Borun poliüretan üzerindeki alev geciktiricilik performansı ve mekanik özelliklere olan etkileri incelenmiştir.

Anahtar Kelimeler— Poliol, poliüretan, çapraz bağlayıcı, bor, yangın geciktiriciler.

1
INTRODUCTION

1.1 Literature Review

Polymer chemistry was gradually developing during WWII due to the need for alternative materials useful for combat technology such as warheads and fighter jets. The most important polymer at the time was nylon thus, Professor Otto Bayer was attempting to synthesize a fiber polymer with properties similar to nylon. He coincidentally managed to synthesize the first fiber-forming polyurethane in the laboratory and announced this in early 1937[1]. Since the first polyurethane was developed over 75 years ago, it has been widely used in a variety of fields. Polyurethane synthesis was regarded as a major breakthrough in polymer chemistry, and then the development of polyurethane from various sources began to come to the fore[2].

At the end of January 1938, Rinke et al. and collaborators successfully reacted an aliphatic 1,8-octane diisocyanate with 1,4-butanediol and managed to obtain a low-viscosity melt, which acted as a source to draw polyurethane fibers. A variety of forms of polyurethane could be manufactured from these melt. Yarns and monofilaments that were obtained from their new polymer had got excellent quality. Rinke and Associates received the first US patent for polyurethanes in 1938. (the patent was filed in 1938 and later approved in 1950; Rinke et al., 1950)[3].

DuPont (Edward and Edward, 1943) and ICI (Szycher and Robinson, 1980) were the first to recognize the elastomeric properties of polyurethane, and they began commercial development of the polymer in the 1940s[2]. This elastomer, vulkollan, was synthesized in the 1940s and is the most well-known and advanced polyurethane elastomer in terms of performance. Later, using different methods, this polyurethane elastomer was diversified for a wide range of applications[4].

In 1959, polyurethane VC which is “virtually cross-linked,” was first investigated for biomedical applications and specifically for heart valves[5]. Polyurethane VC is chemically inert, has a water repellent surface, and is resistant to break, abrasion, solvents, and oil. Due to all these properties, it is thought to be ideal for biomedical applications.

A segmented polyurethane grade was developed in the mid-1960s that demonstrated both strong biocompatibility and exceptionally flexible existence in biological solutions at 37°C [6]. The efficiency of this new polymer class ensures its applicability to a wide range of systems, including heart valves, cannulas, catheters, and pacemaker lead wire insulation[7].

In 1993, Michael Szycher and his partner Andrew M. Red obtained a patent for their work on biostable polyurethane products. Polyurethane products with long term biostability with high tensile strength and a low modulus of elasticity are intended to be implanted into a mammal's body for long periods of time without significant degradation of the product, especially as lead for implantable pacemakers, as breast prostheses, as vascular grafts and other such products[8].

Polyurethanes are conventionally synthesized by reacting a polyol (an alcohol having more than two reactive hydroxyl groups per molecule) with a diisocyanate or a polymeric isocyanate in the presence of appropriate catalysts and additives. Since polyurethane can be synthesized by using a wide variety of isocyanates and polyols, a wide range of materials can be created to meet the needs of particular applications[9]. Types of Polyurethane are divided into nine groups such as flexible polyurethane foam, rigid polyurethane foam, coatings, adhesives, sealants and elastomers (CASE), thermoplastic polyurethane (TPU), reaction injection molding (RIM), binders, waterborne polyurethane dispersion (PUDs)[10]. The desired polymer's properties are obtained as the finished product by changing the type or ratio of polyol / isocyanate used, or by adding different additives.

Elastomers, one of the polyurethane groups, are a class of materials that show high reversable deformation. Such activity necessitates highly flexible chains, a low degree of intermolecular contact, as well as the existence of cross-links that

prevent the chains from slipping against their neighbors, resulting in plastic flow[11].

Cross-links can be either chemical or physical. Both of them are used in polyurethane elastomer structures. Chemical cross-linking is formed by trior multifunctional constituents. Chemical cross-links, unlike physical cross-links, cannot be easily destroyed by thermal treatment, except in certain particular variable chemical groups, which form an irreversible network. On the other hand, hydrogen bonding and hard field forming are used to establish physical cross-links. Physically cross-linked polyurethane elastomers are block copolymers consisting of successive rigid and flexible blocks. Because of the differences in polarity and chemical structure, all blocks are classified as "soft" and "hard"[11].

The high flammability of polymer materials is an considerable factor limiting their application, therefore flame retardants provide safe use areas against fire, as well as provide materials with improvements in terms of tensile bending strength, resistance to impact fractures, fluidity, resistance to oxygen or UV rays, fire resistance. It becomes more important as it goes on. Flame Retardants can be classified as phosphorous, halogen-free and brominated flame retardants. The toxic gases emitted to the environment during their release can seriously affect the respiratory tract, and their mixing with the blood causes sudden fainting by blocking the amount of oxygen inhaled. Due to all these reasons, their application has been limited in many countries and alternative fire retardant research are ongoing[12]. In addition, polymers are treated with fire retardants to prevent the polymers from combustion at the high temperatures and to obtain more durable polymers. For this purpose, studies are continuing to obtain ideal fire-resistant polymers.

A group of compounds which can show flame retardant effect is boron-based compound. The use of boron-based compounds as flame retardants goes back to years ago. For example, borax (sodium borate) as the flame retardant is based on two decades ago. Water-soluble sodium borates and borate-boric acid combinations continue to be used in cellulosics and other hydroxyl-containing polymers today. In addition, borates and boric acid can emit water, which serves as

a fuel diluent, a propellant to keep the fuel out of the flame region, a heat sink, and a blowing agent for the glassy intumescent coating. In the same way, Zinc borates are prominent flame and smoke retardants. The majority of zinc borates used in industry are hydrates with well-defined endothermic water release temperatures. Hydrated calcium borate and the aqueous barium borate is also valuable as flame retardant[13]. In addition to the flame retardant effects of boron-based compounds, derivatization studies continue in order to be used as cross-linkers. A new chemistry is being developed to produce more effective crosslinkers than existing compounds, one of which is to produce boron-based cross-linkers through reactions between boron, organometallic intermediates and boron reagents[14].

1.2 Objective of the Thesis

There are various types of flame retardants (such as brominated materials, TCPP, TEP) available that are incorporated into the polymer structure by blending. These flame retardants provide resistance up to a high temperature, but after a certain point of the temperature they begin to leak from the polymer. However, the fire retardants we intend to synthesize are not blended with the polymer. They are directly connected to the chemical structure in the polymer chain. Thus, they are able to withstand higher temperatures and at the same time, the fire retardants are prevented from leaking from the polymers. On the other hand, the flame retardants to be synthesized are boron-based materials, therefore it is expected to supply the polymer structures mechanical strength, chemical resistance and flexibility besides fire resistance. Furthermore, boric acid produced by ETİ, one of the local resources of our country, will be used in the synthesis of products which are more valuable.

1.3 Hypothesis

Boron-based compounds are integrated to the polymer structure in order to give the substance some new properties such as fire retardant, strong resistance, tensile tension, elasticity, and smoke retainer. For this reason, organoboron compounds enhance properties to the structure as additives in polymer synthesis.

On the other hand, polyurethane is a versatile and high performance polymers. The sole of the shoes we wear in our daily lives, the sponge and artificial leather in the seats we sit and the beds we sleep in, the imitation of wood in the decorations of the mirrors and the seats, the insulation material of the refrigerators and the water heater, the console and the steering wheel of the cars, the panels covering the walls and roofs of the factories and cold rooms, polyurethane is used in almost every industrial areas. Therefore, studies are continuing today to improve the polyurethane properties.

In this thesis study, the aim is to obtain polyurethanes containing boron as cross-linker. For this purpose, isocyanate was reacted with boron based polyols which had synthesized via borate ester. It is assumed that the final polyurethanes have a fire resistant, strong resistible, flexible and unbreakable structure.

2
POLYOLS

Polyols refer compounds which have more than two hydroxyl groups, conventionally they do not have other functional groups. Molecules containing three hydroxyl groups is called a triol. If it has got four hydroxyl groups, it is called a tetrol. Polyols are divided into two groups as low molecular weight polyols and polymeric polyols[15].

2.1 Low Molecular Weight Polyols

Sugar alcohols belong in this category. Sugar alcohols exist as crystals moderately non-hygroscopic powders and clear liquids forms. They have resistance to heat and are obtained by hydrogenation of mono-, di-, or oligosaccharides (Figure 1).

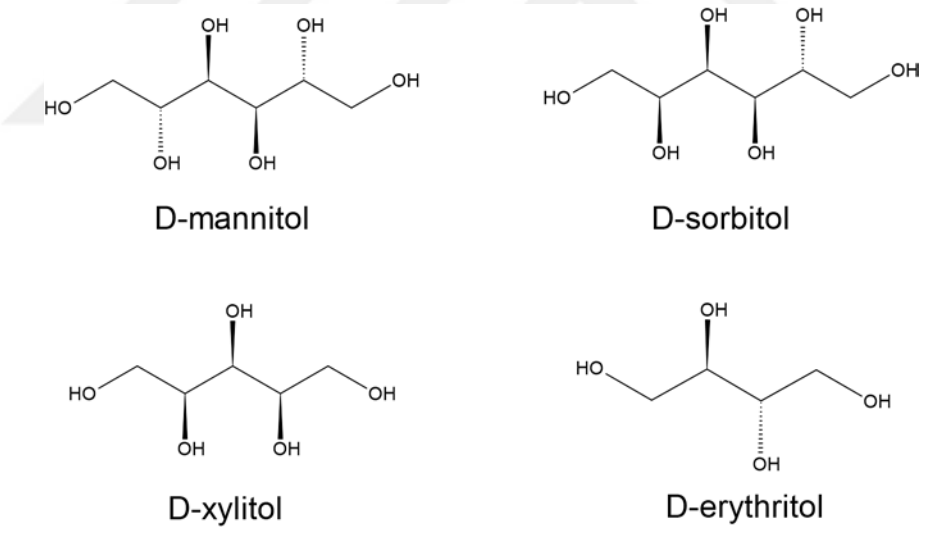


Figure 2.1 Structures of some sugar alcohols which are produced from hydrogenation of monosaccharides[16]

Usage of sugar alcohols is common due to their properties which are not found in other sweeteners. Sugar alcohols's sweetness content is lower than other sugars (Table 2.1), therefore they are so convenient using healthy nutrition and diet

control. On the other side, they are not broken down by bacteria in mouth and hereby they do not cause tooth decay. For this reason, they are seen beneficial for using in chewing gums as a sweetener[17].

Table 2.1 Sweetness ratios of sugar alcohols[17]

Compound	**Relative sweetness**
Polyol[a]	
Xylitol	80-100
Sorbitol	50-60
Mannitol	50-60
Maltitol	80-90
Lactitol	30-40
Isomalt	40-50
Erythritol	60-70
Sucrose[a]	100
a: 10% in H_2O: 20°C	

Sorbitol is used instead of low sugar products. Sorbitol powders or solution is added in special diatary products. It is also useful as moisturizer to extend the shelf-life of baked foods. As for Xylitol, studies in Finland have shown that using xylitol in the diet selectively reduces tooth decay. For this reason, the use of producing chewing gum is common. Besides, adding little amount glycerol to xylitol increases the plastifying qualities and addition of mannitol averts stickiness[17].

Maltitol syrups or combining either isomalt or lactitol are convenient for producing gums as well. Maltitol syrups also supply good shelf-life properties. As for erythritol, it is practical to produce successfully in low-calorie beverages, hard

candies, cookies, biscuits, and cakes. Usage at low proportion of it eliminates bad taste in drinks and giving refreshing feel. In addition, almost 7% of erythritol addition improves storage capacity[17].

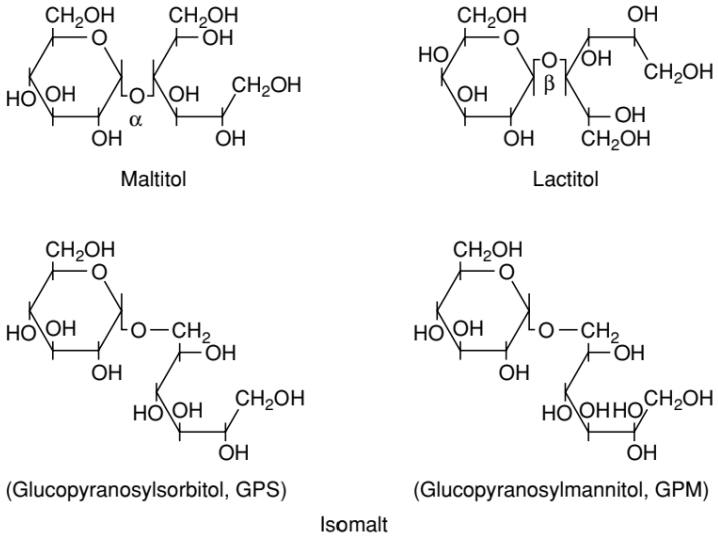


Figure 2.2 Sugar alcohols which are produced from hydrogenation of disaccharides[17]

Sorbitol, mannitol, xylitol and similar polyols have been known for thirty years (Figure 2.2). They are found in nature as well but their amount is really insufficient to be extracted in commercialy. Therefore, sugar acohols should be produced.

2.1.1 Mono- and Disaccharide Hydrogenolysis and Hydrogenation

Disaccharides and monosaccharides can be hydrogenated to produce sugar alcohols which also known poliol and polyhydric alcohol. Hydrogenation of sugars is evaluated by two main reaction types. 1-) Hydrogenation is defined as adding hydrogen to a ketone or an aldehyde (hemiacetal or hemiketal) to produce poliol with similar carbon chain. 2-) Hydrogenolysis directs the reaction producing shorter alcohols/poliols formation with hydrocracking of carbon chains. After this kind of reaction speacially glycerol or glycols obtain. Since these two reaction types are intertwined, it is difficult to interpret without one. Both steps can be carried out in separate reactors or in the same reactor by changing the reaction conditions. In the first step (hydrogenation) is performed at a neutral pH, low

temperature and pressure with a hydrogenation catalyst. As for the second step (hydrogenolysis), H_2 pressure and temprature is increased and using a base that is usually CaO[18].

According to many procedure, heterogeneous catalysts are used for sugar hydrogenation and hydrogenolysis reactions but hydrogenolysis part (hydrocracking of C-C bond) needs strong conditions. For this reason there are other metods with homogenous catalysts in literature to conduct an experiment in mild condition (Table 2.2).

Table 2.2 Heterogeneous and homogeneous catalysts for the hydrogenation and hydrogenolysis of mono- and disaccharides[18].

Heterogeneous Catalyst	Homogeneous Catalyst
Pt black, KOH	[H2Ru (PPh3)4]
CuO-Cr2O3	Ru complexes
Cu-Al2O3	Ru and Os phosphine
CuO-CeO2-SiO2	Ru-PPh3 complex
Cu/SiO2	Ru-TPPTS complex
CuO-ZnO	
NiCrO4	
Ni/SiO2	
Ru/C, Ru/Al2O3, Ru/SiO2	
Ni or Co powder	
Metallic Ni	
Ru on zeolites	

2.1.1.1 D-Mannitol Commercial Production

This hydrogenation reaction carries under high pressure with 1:1 ratio D-glucose/D-fructose mixtures and as catalyst Raney-Nickel is used. In this reaction D-fructose gives D-glucitol and D-mannitol upon hydrogenation (Figure 2.3).

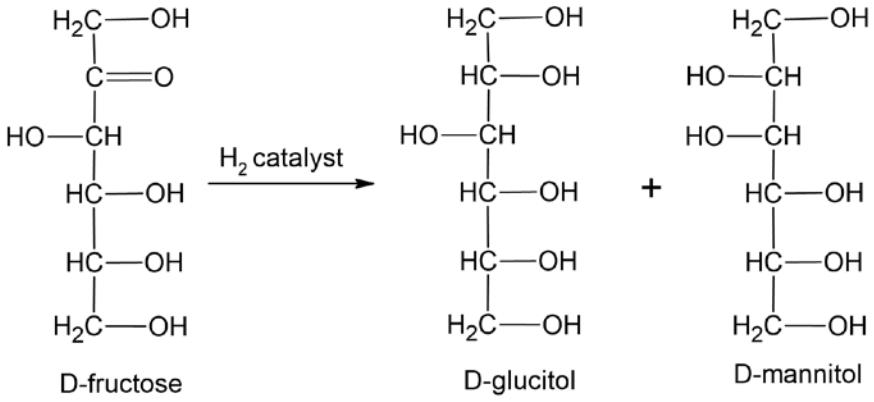


Figure 2.3 Hydrogenation of D-fructose[19]

The D-glucose portion of this mixture can convert to D-glucitol over time(Figure 2.4)[19].

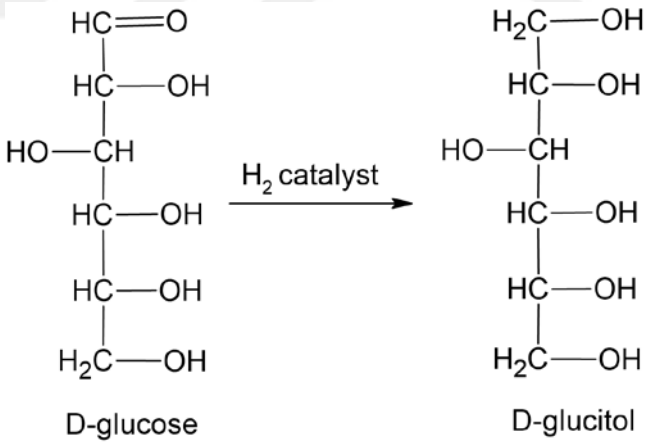


Figure 2.4 Hydrogenation of D-glucose[19]

In D-glucose/D- fructose procedures, different catalysts have different selectivity. Vlll metals Raney-Nickel and nickel-on-silica catalysts have similar selectivity with these kind of reactions. (40-50%). In addition, the use of copper catalysts has been shown to provide great selectivity (65-90%)[19].

2.1.1.2 Hydrogenation of D-mannose by NiO-TiO_2 Supported Ruthenium Catalyst

The slurry is prepared by dissolving D-mannose in deionized water and adding Ru / (NiO-TiO_2) catalyst solution. The reactor is deoxygenated with forcing H_2 gas into it when reaction is stirring in room temperature, then pressure is released and the reaction continues 120°C and 240 min. After finished hydrogenation reaction ,catalyst is precipitated with cooling the solution and then separated. When same procedure is followed with Ru/TiO2 catalyst in 320°C is shown that conversion is more efficient with Ru / (NiO-TiO_2) (Table 2.3).

Table 2.3 Activities of catalysts which used during hydrogenation[20]

Catalysts	Catalysts(g)	Conversiton(%)	Initial rate (m mol h^{-1} g_{ga}^{-1})[a]	TOF^B (h^{-1})
No catalyst	-	-	-	-
NiO(5.0%)-TiO_2	1.0	-	-	-
Ru(1.0%)/NiO(5.0%)-TiO_2	1.0	26.7	2958.3	298.9
Ru(1.0%)/TiO_2	1.0	18.4	2044.2	206.6

a: Mannose 10 (wt%), time= 60 min, pressure= 40 bar and temperature= 120°C.

b: TOF fort he given conversion.

The reduction reaction of D-mannose to D-mannitol is shown in (Figure 2.5).

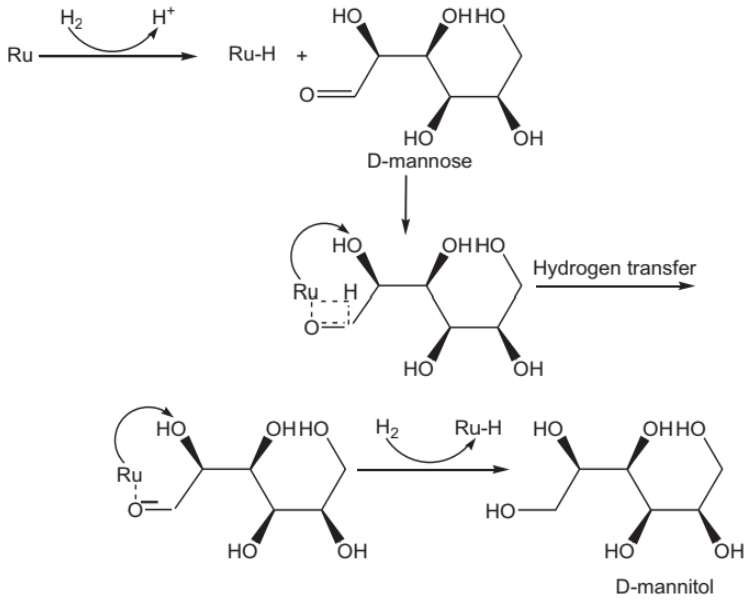


Figure 2.5 Reduction mechanism from D-mannose to D-mannitol[20]

2.1.1.3 Chemical Production Process of Xylitol

D-xylose is raw material to produce xylitol production. It is produced by reduction of D-xylose is based on hemicellulose hydrolysates of xylose rich materials[21]. Xylitol production reactions with starting xylans is shown in (Figure 2.6).



Figure 2.6 Xylitol production reactions from xylans

Hydrolysis reaction of corn cobs lasts adequate time at 100°C with 4% H_2S0_4 afterwards is purified by extraction with methanol. The produced D-xylose is crystallised by magnesium sulphate in methanol. D-xylitol is produced by apparatus which recycles of solvent and reagents. However after finishing reaction by-products are plenty and needed severe separation and purification to clear main product. Yield of xylitol after purification is around 50-60%[21].

2.1.1.4 Fermentation Method to Produce Xylitol

Production xylitol by using fungi, bacteria was studied less than yeast strains. A few bacteria such as Gluconobacter oxydans, Enterobacter liquefaciens, Corynebacteriurn sp. have been found for xylitol production. According to the general opinion, between the microorganisms yeast was seen as the best source for xylitol production and production with yeast was concentrated on. Candida guilliermondii and C. tropicalis are the best kind of yeast as reactant for xylitol. After fermentation with these yeasts 65–85% xylitol is obtained from D-xylose as theoretically[22].

Industrial applications and purification of fermentation reactions are time-consuming, therefore more chemical procedures are preferred.

2.1.1.5 Production of Erythritol

First method is that aldehyde starch converts into erythritol at the high temperature and with presence of nickel catalyst. However, this reaction cannot be applied industry because of low yield[22].

Industrial production of erythritol is obtained with the enzymatic hydrolysis of starch from corn to glucose. A method in another for producing erythritol is fermentation with yeast or some sort of fungus[23].

2.1.1.6 Commercial Production of Sorbitol

The process of producing sorbitol by catalytic hydrogenation occurs at high temperature and pressure with copper-chromium or nickel catalyst that is inexpensive in industry, but the purification step is expensive because extreme conditions are required. This process starts with hydrogenation step of glucose that carries out at 120–150°C for 2–4h (depending on the catalyst) in agitated autoclave. According to production 70 bar is applied for a batch process, 180 bar for a continuous process. After the reaction is completed pure product is obtained by applying appropriate purification and separation processes, firstly raw material is precipitated and filtreted, then it is decolorised with activated charcoal.Mixed-bed ion exchangers is used so as to remove the nickel ions and gluconate from raw sorbitol. Sorbitol solution (70%) which is desired by commercial way is

evaporated under vacuum condition and dehydrated. Water-free melt crystals obtained from these processes seed and then are removed from the surface as a final pure sorbitol particles[24].

Methods such as electronic reduction and biotechnological fermentation can also be used to obtain sorbitol[24].

2.2 Polymeric Polyols

Polymeric polyols are usually used to define polyether polyols and polyester polyols (Figure 2.7) and (Figure 2.8).

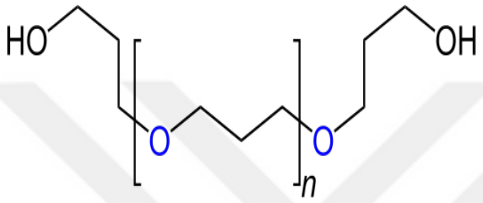


Figure 2.7 Polyether polyol

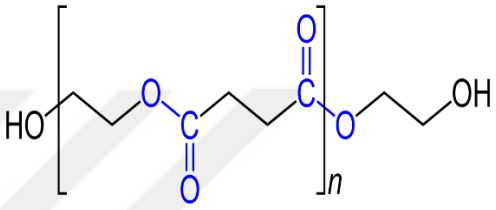


Figure 2.8 Polyester polyol

Polyether polyols are synthesized by using multifunctional initiator and various epoxides such as ethylene oxide or propylene oxide in a strong base condition which can be provided by a potassium hydroxide or a double metal cyanide catalyst[25]. Examples of polyether diols are (Figure 2.9) and (Figure 2.10).

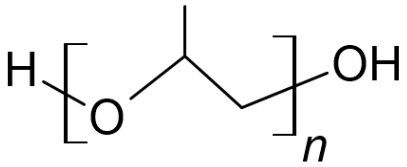


Figure 2.9 Polypropylene glycol

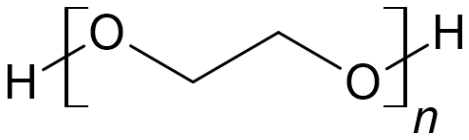


Figure 2.10 Polyethylene glycol

Another group of polymeric polyols are polyesters which have ester functional groups in the main chains and are obtained by condensation polymerization. In these reactions diols and types of dicarboxylic acids are used as reactants[25]. The most important commercial polyester synthesized in this way is polyethylene terephthalate (PET) (Figure 2.11).

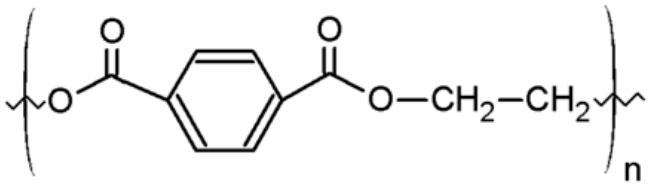


Figure 2.11 Polyethylene terephthalate (PET)

2.3 Polyurethane

Polyurethane was discovered in 1937 by Prof. Dr. Otto Bayer. At the beginning of the second world war and it was used instead of rubber substitute. First polyurethane production is shown in (Figure 2.12). The versatility of this new organic polymer and its ability to be used instead of scarce materials has enabled it to be used in many applications. Polyurethane coatings were used in the processes of obtaining a high gloss surface in aircraft, chemical and corrosion resistant metals, wood and wall decorations during the second world war. Towards the end of the war, polyurethane coatings were manufactured, started to be used on an industrial scale and formulated for specific applications[26].

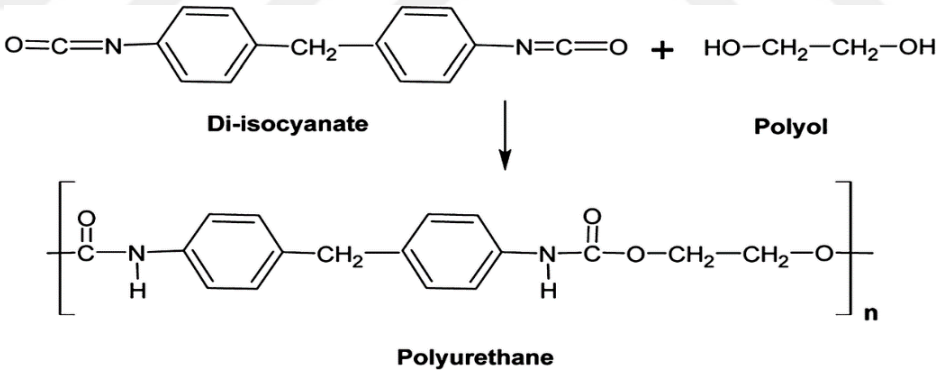


Figure 2.12 The first reaction of polyurethane production

First polyurethane were obtained by reaction of diisocyanate with ethanediol. If water exist in the the reaction medium, a part of the diisocyanate polymerizes with diol, while a small part reacts with water and gas (carbon dioxide) to form a porous polyurethane structure (foam or sponge structure). At the end of the maturation period (24-72 hours), a very solid polymer structure is obtained. Later, diols were replaced by polyols with higher molecular weight, polyether or

polyester structure. Polyurethane formed in this way creates a stronger and more flexible elastomer[27].

Isocyanates are essential for polyurethane synthesis and can be aromatic, aliphatic, cycloaliphatic or polycyclic and usually have a molecular weight less than 200g/mol. These contain two or more than two –NCO groups in each of molecules[28],[29]. In the (Figure 2.13) is shown some common examples of isocyanates which are important for industry.

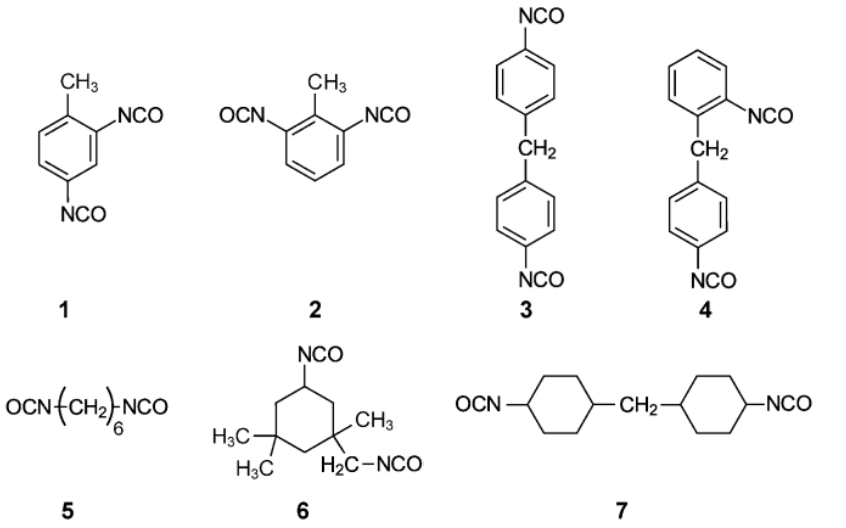


Figure 2.13 Important isocyanates in industry[29]

The most important isocyanate in industry is toluene diisocyanate (TDI). 2,4-TDI (1) and 2,6-TDI (2) are isomers. 4,4'-MDI (3) and 2,4'-MDI (4), HDI (5) is a aliphatic isocynates by full name hexamethylene diisocyanate. IPDI (6) is isophorone diisocyanate and H12MDI (7) is hyrdrogenated MDI (Figure 2.13).

Isocyanate carries successive double bonds as R-N=C=O. Isocyanate is directed by oxygen, carbon and nitrogen. Carbon positive character gives a possibility to be attack by nucleophiles. In the same way oxygen and nitrogen by attack electrophiles[30]. Isocyanate resonance structure is shown in (Figure 2.14).

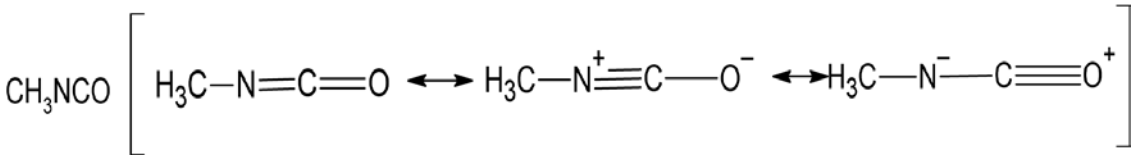


Figure 2.14 Resonance structure of isocyanate

If isocyanate-bonded substituent is an aromatic group, this increases the reactivity, because the negative charge on nitrogen is delocalized in aromatic substituent. In this case substrate character affects the reactivity of isocynate, electron withdrawing substrates (ortho or para director) increase the reactivity, electron donating gruops (meta director) decrease the reactivy[28].

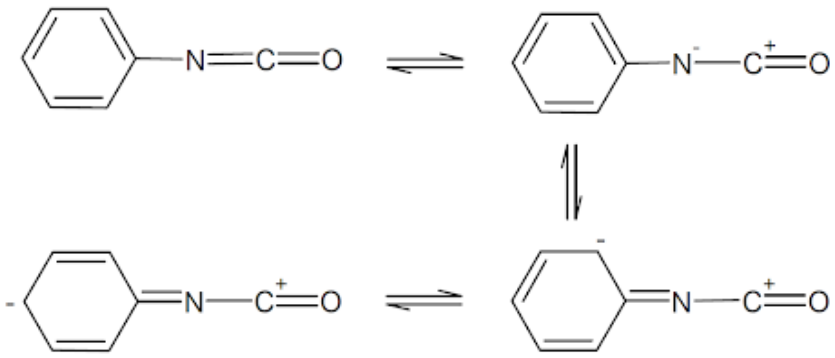


Figure 2.15 Resonance structure in aromatic isocyanate

The reactivities of the -NCO groups of isocyanate differ according to their position (Figure 2.15). For instance two different positions of -NCO groups in IPDI molecule (6) in (Figure 2.13)[28],[30].

Molecules with a large number of hydroxyl groups (more than two) are named polyols. These molecules might bear other functional groups other than the hydroxy group, such as ester, amide, ether, metal, acrylic. The five most important polyol types are polyether, polybutadiene, polyester, polycarbonate and polyacrylate polyols. The latter two are used on a much smaller scale because they are more expensive and are typically chosen where superior weathering and/or heat resistance is necessary[31]. Polyester polyol (PEP) which is widely used in polyurethane production consist of ester and hydroxylic groups by generally condensation reaction. The molecular weight and degree of crosslinking of the polyols which are used in PU forming reactions affect the polyurethane properties. Low molecular weight polyols are utilized to obtain rigid polyurethanes while high molecular weight polyols gives flexible PU. In the same way, rigid polyurethanes with high chemical and heat resistance properties are produced by high branched

polyols, while low branched polyols are used to produce flexible polyurethanes with less heat and mechanical resistance properties[28],[32].

Polyether polyols (PETP) are cheaper than PEP and obtained by the addition reaction of ethylene or propylene oxide in presence of alcohol or amine initiators with using acid or base catalyst. However, polyurethanes are developed by existing polyether polyol show low glass transition temperature (Tg) and high moisture permeability. Their usage is limited due to these properties in coatings and paints areas. Another example of polyol is acrylate polyol (ACP) is produced by free radical polymerization and PU obtained with ACP has thermal stability and characteristic properties which come from acrylics. This type of PU is used as coating materials. Polyols can also be modified by metal salts and produce metal containing polyols or hybrid polyols (MHP). MHP gives PU gloss, thermal stability and antimicrobial behavior[28].

There are three precursors for polyurethane synthesis polyol, isocyanate and chain-extender. Final product as polyurethanes are block polymers and consist of hard and soft segments in which polyols are responsible for soft segments and give rubbery character and chain-extenders and isocyanates are responsible for hard segments. Chain-extender as last precursors are usually short aliphatic or aromatic diols or having diamines between 2 to 6 carbon atoms. These enable the polyurethane to reach its final molecular weight[33].

2.3.1 Polyurethane Synthesis

Polyurethane block polymers are produced by two-step synthesis. In the first step prepolymer is obtained from polyether/polyester diols and excess diisocyanate. Isocyanates have unsaturated bonds and when they react with the hydroxyl group form the urethane bond (Figure 2.16).

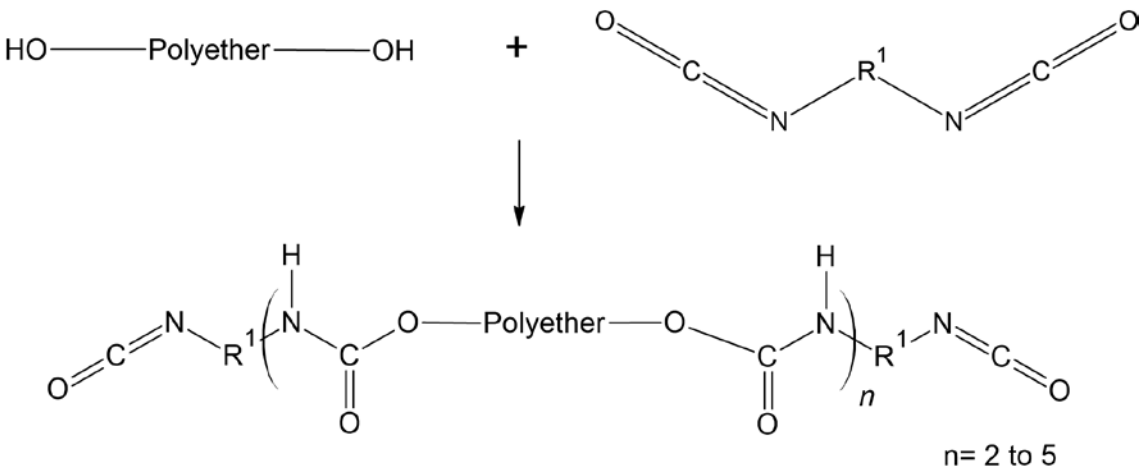


Figure 2.16 Preparation of prepolymers from polyether diols and excess diisocyanate[34]

In the second step, the prepolymer is reacted with chain extenders to obtain a high weight polymer (Figure 2.17).

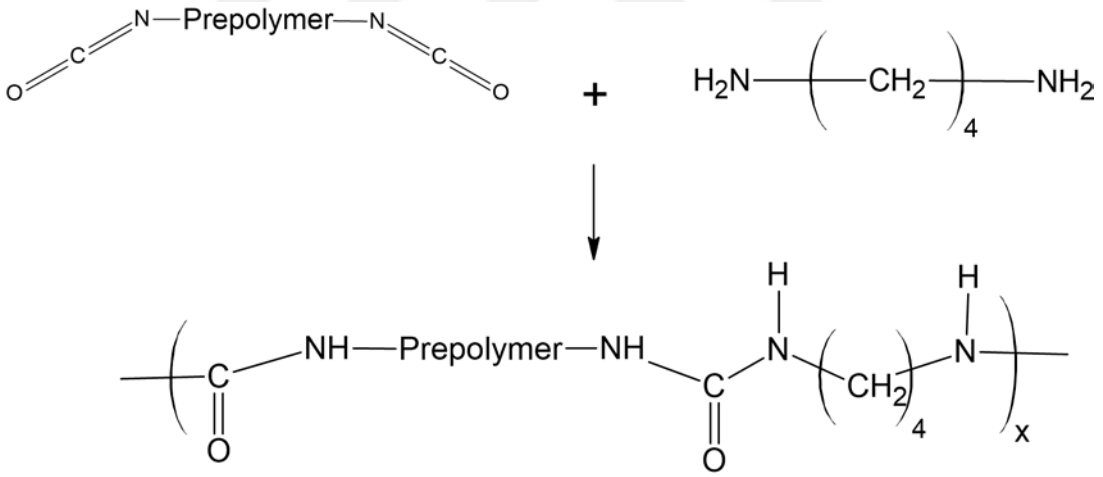


Figure 2.17 Reaction of prepolymer with chain-extender to obtain high molecular weight polyurethane[34].

2.3.2 Categories of Polyurethane

1. Hard polyurethane foams

Hard polyurethane foams are widely known as energy saving efficient insulation and all-purpose materials. Besides, energy-cost reducing and noise reduction

properties make them more efficient for the commercial and residential appliances. Rigid polyurethane foams can be made from gasoline-based polyols or bio-based polyols derived from vegetable oils and plant-based lignin. The qualities of the resulting polyurethane are determined by the hydroxyl group category found in polyols. For example, glycerin (a gasoline-based polyol) contains a main hydroxyl group, whereas castor oil, a bio-based oil, has a secondary hydroxyl group. Due to these two different sort of polyols final polyurethane structures display different mechanical and physical properties .Besides that, isocyanate and polyol(containing primary hydroxyl group) react faster than secondary hydroxyl groups polyol and isocyanate[35].

2. Elastic polyurethane foams

Elastic polyurethane foams include certain block copolymers in the structure and their flexibility due to the phase difference is between hard and soft segments. Therefore, polyurethane foams can be shaped by controlling the proportion of each ingredient of hard and soft segments[36].

The synthesis of flexible polyurethane typically consists of two major steps: blowing and gelling. The reaction of the hydroxyl groups of polyol and isocyanate produces urethane linkages in the blowing step; also, carbon dioxide and urea are formed during this reaction, which broaden and are absorbed by the reaction blend. The shape and microstructure of PUs foam are determined by a number of criteria, including the ratio of cross-linking following the reaction of the diisocyanate and polyol, the interaction between the polyol as well as urea, the segmental motion ability of the urea group, and so on[37]. Besides, there are some technical approaches to increase the flexibility of the materials for instance, keeping density of the cross-linking lower with the convenient NCO/OH ratio, forming the flexible chain by adding it to the main backbone with chain extender are efficient techniques to obtain the flexible PU[38].

3. Thermoplastic polyurethanes

Thermoplastic polyurethanes (TPUs) have a lot combination of physical properties and applications, are resistant to impact, weather and abrasion, can be colored by

fabrication techniques besides, they are flexible and elastic. The durability of many products can be improved by the inclusion of thermoplastic polyurethanes. Thermoplastic polyurethanes are processed and fabricated such as other thermoplastic elastomers, with using blow, extrusion, injection, molding, compression equipment and additionally they might be formed by vacuum and coated by solution which make them convenient wide scale production techniques and usage like footwear, construction, automotive industries[39]. Besides, thermoplastic polyurethane due to its high mechanical, water-insoluble, inert and non-ionic properties was modified successfully in the drug release systems and in medical tubing as polymer controllers[40].

4. Ion-containing polyurethane

Existence of an ionic group in the carbon skeleton of polyurethane gives it a few advantages owing to improving hydrophobicity, good thermal and mechanical properties. Specially, better dispersion in the polar solvents, biocompatible properties and shape memory are supplied to materials. Shape memory polyurethane has shape-memory feature (like thermo-responsive shape memory) so displays different mechanical effect when compared with the other polyurethanes. The polyurethane's permanent form is recalled by the hard section (managing the cooled period) and the soft segment (managing the reversible period). The permanent shape is restored by heating the material's temporary form to the transition temperature[41],[42].

The temporal deformation is shaped by the soft section and the glass transition temperature (T_g), whereas the permanent shape memory is caused by the solid section. The form memory of materials is affected by changes in the T_g and crystallization of hard section. Those characteristics can be modified by adding ionomers in PUs. This combination can be produced by employing ionic diols and maybe ionic groups carrying diisocyanate throughout the PU process. Poly(urethane-ureas) and segmented PU which have haemo-compatibility was examined and seen it has a better performance than former studies in the medical-grade PUs with utilization of these materials with efficiency give them a

variety medical application areas such as connector tubing for heart pacemakers, haemo dialysis tubes and artificial hearts[41].

5. Polyurethanes as Adhesives, Coatings, Elastomers and Sealants

Polyurethanes have a wide range of applications as sealants, coatings, adhesives, and elastomers due to their excellent chemical, physical, and mechanical qualities. For convenient coating application, PUs need to have good adhesive, excellent drying, adequate scratch resistivity, low temperature flexibility and high chemical resistivity properties. Although polyurethane coatings have the desired properties, it should be taken into consideration that their insufficiency to impact resistance and their tendency to UV degradation in exterior coatings may limit their use. Consequently, some advanced methods have been searched to overcome these shortcomings. For example, nanoparticles like titanium oxide and silicon dioxide can be applied in coating process to give the materials anti-corrosive qualities[37],[43].

Many adhesive formulations contain phenol formaldehyde and urea formaldehyde-based wood composites and sandwich materials. These are typically used as binders for inner and external components of solid wood and plywood, however it has been discovered over time that they cause considerable environmental damage due to the emission of organic solvents. Environmental, social and economic reasons led recent work has focused on the synthesis of adhesives and binders by using renewable energy sources for instance, oil-based gums might be converted into adhesives with renewable materials[44].

Another form of material that is useful is PU elastomers. They are versatile, have highly desirable stress recovery properties, are lighter than metals, and can withstand a wide range of environmental factors. Despite these, their stretch is restricted and they cannot achieve the desired maximum level. There are several methods to get around this problem such as the addition of graphene oxide into the polyurethane structure or adding hybrid fillers, like carbon nanotubes or/and titanium oxide. PU elastomers are another important kind of PU. They can be turned into fashioned materials as colors, design and shape thus, widely used such as household items, ski boots, shoe soles, surfboards and goggles[45].

6. Waterborne polyurethane dispersions

Coating and adhesives using water as a solvent are classified as waterborne polyurethane[46]. The use of solvent-based polyurethanes has been restricted owing to the leaking of volatile organic solvents and other pollutants into the environment. Therefore, the use of water-based polyurethanes has been increasing in commercial and industrial areas for several years[47]. Polyurethane dispersion's viscosity is independent of molecular weight of polymer so, water-based PUs with high solids content can only be manufactured through the drying process. The dispersion is a two-phase colloidal system composed of polyurethane molecules and water environment. Polyurethane dispersion properties are determined by the amount of isocyanate, polyol, ionomer and chain extender used[48].

Water-based polyurethanes cannot be synthesized by conventional ways like emulsion and suspension polymerization due to the intense reactivity of the isocyanate group towards water. For this reason, several ways have been developed for the synthesis of aqueous polyurethane dispersion, the most important of which is the acetone process which consists of a two-step procedure. In the first stage of this procedure, hydrophilic and potentially charged groups are combined into the polymer main backbone during polyurethane synthesis in acetone solution and in a second stage, water is added to the PU / acetone system. By adding hydrophilic groups to the polymerization process beforehand, the polyurethane precipitates and gives stable dispersion. Finally, acetone is removed from the product medium. Arranging convenient condition for the acetone process, stable dispersion are made by low-energy emulsification methods[47].

7. Binders

Polyurethane binders are applied to bind different sorts of materials and fibers. These binders supply permanent adhesion effect amongst organic materials and long-strand woods, straw panels, mild density fiber boards, particle boards, laminated veneer lumbers. To obtain a quality binder, the polyurethane should have a good soft/hard segment ratio and thermal stability, needed specific or medium acid number, PU dispersion with a low molecular weight and a narrow

particle size and weak crystallinity. PU, which is one of the organic solvent based binders, has usage areas such as foam, coating, panel, board, rocket propellants and polymer based explosives (PBX) due to its excellent sealing, adhesion and bonding abilities[49].

Some binder polymers go into permanent chemical reactions when exposed to heat, moisture and air, while others melt and undergo physical changes only[50]. Chemically changed polymers are called thermosets, which result from extensive cross-linking formation between polymer chains and this creates insoluble polymer network[51].

2.3.3 Polyurethane Usage Areas

Polyurethane is found thermoplastic and thermoset form in nature. The type of starting materials and additives used affect the properties of the final product (PU) and consequently the usage areas of these polymers. Polyurethanes(PU) are used inmultiple areas and diverse applications such as adhesives, flame retardants, automobiles industry, paints and coatings, insulation, textile industry, purification of waste water, biomedical applications, fuel binders, construction, electronics cast elastomers and so on[52].



Figure 2.18 Roof insulation with polyurethane foam

Polyurethane foam can be applied to almost all areas with its superior strength, high heat and sound insulation properties. Polyurethane foam is an insulation tool that can swell up to 40 times its volume and does not absorb water through its cells. It has a strong adhesion force in all areas and provides integrity with the structure it is applied to. Thermal insulation application with polyurethane foam has more advantageous aspects compared to other products (Figure 2.18). It is resistant to water, insects, rodents and mild acids, but not UV rays. It is capable of continuous coating[53].

Rigid polyurethane insulation foams assist to eco-design by reducing the energy necessary to keep refrigerators and freezers always cold. Rigid polyurethane foam is the most common insulating material used in refrigerators and freezers around the world. It is necessary for low-temperature processing, storage, and delivery of foods. Without polyurethane insulated cooling, approximately 50% of food products affecting human life in the world will be destroyed as a result of rotting. In the shoes industry, polyurethane shoes types have a wide application area (Figure 2.19). PU is used for shoes, slippers and boots and work safety shoes as well. It is suitable for manufacturing models that are light abrasion resistant and colorful, as well as having superior mechanical qualities[53] .



Figure 2.19 Applied to polyurethane shoes and freezer

Flexible foams can also be produced with viscoelastic properties. These foams are also called memory foams and when used, they support and memorize the body shape. These products are used in mattresses, medical chairs and body supports (Figure 2.20).



Figure 2.20 Viscoelastic flexible PU foam[54]

Another usage area of polyurethanes is medicine and medicine-related areas such as hospital bedding, surgical drapes, catheters (Figure 2.21), general purpose tubing, wound care and a variety of injectable tools. Polyurethane applications are not restricted to this; they are also utilized for a variety of other purposes, such as short-term implants, due to their excellent mechanical and physical qualities, availability, and biocompatibility. Sensitive and smart polyurethanes are also used in drug delivery systems. For instance, peculiar drug delivery systems, like vaginal suppositories and microbicides were suggested to control the transmission of sexually transmitted illnesses, including HIV-AIDS[55],[56].

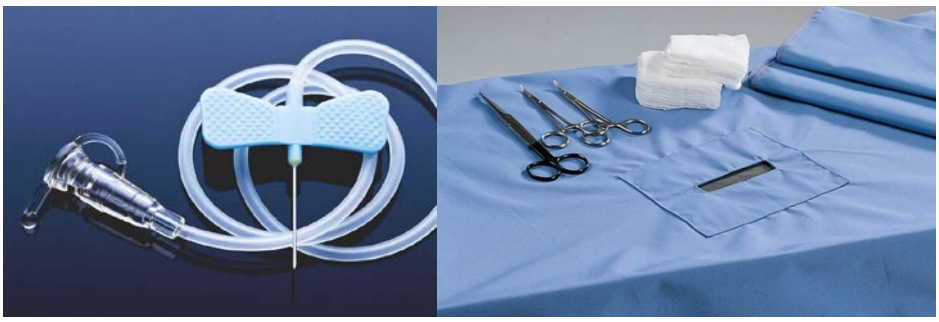


Figure 2.21 Surgical catheter and drapes

3
ADDITIVES IN THE PRODUCTION OF POLYURETHANE DERIVATIVES

Polyurethane has two-phase structure and its properties are basically determined by stoichiometric ratio between isocyanates and -OH(diols) but these features can be modified with many different techniques and additives such as cross-linkers, catalysts, blowing agents, foam stabilizer, antioxidants, binders, flame retardants and so on[29].

3.1 Ratio of Diol and Isocyanate

Polyurethane block polymers have hard and soft segment parts (Figure 3.1).

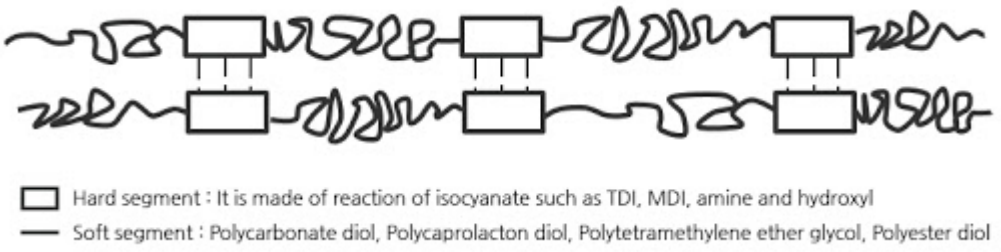


Figure 3.1 Showing hard segment and soft segment shape in a molecule

The density of these segments determine the properties of the polyurethane (Figure3.2). Hard segments offer high glass transition temperature (Tg), stability and tensile strength while soft segments offer elastic properties and lower glass transition temperature (Tg). For instance the soft foams are generally produced by a 2:1 reaction of long chain polyether polyols with TDI (toluene diisocyanate) and the rigid foams are produced by mixing MDI and polyols in a 2:1 ratio[54],[57].

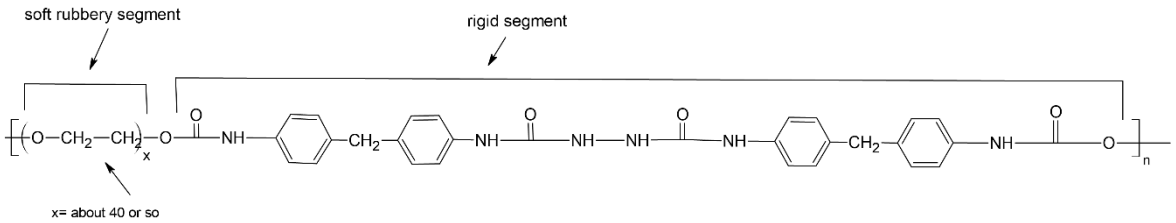


Figure3.2 Soft and hard segment in polyurethane molecule

3.2 Hydrogen Bond Effect in Polyurethane Structure

The interactions within the segments according to phase morphology affect the mechanical properties of the polymer. The hydrogen bond plays a role in determining the mechanical properties. Polyurethanes are resistant to cracking and abrasion. They have long-lasting thermal stability at various temperatures (80-240°C) and this stability is caused by the isocyanate type and hydrogen bonds. The hydrogen atoms in PU is partial positive and they bond with the oxygen of different groups, whereby PU can contain three different hydrogen bonds (Table 3.1).

- (Ester-urethane interaction: SSEs-HS)
- (Ether-urethane interaction: SSEt-HS)
- (Urethane-urethane interaction: HS-HS)

Table 3.1 Sorts of hydrogen bonds in polyurethane blocks[58]

Hydrogen bondings	Interaction
~~ $\overline{HS}$ – NH ····· O = C ⟨ O – $\overline{HS}$ ~~~~ / NH – $\overline{HS}$ ~~~~	Urethane-urethane HS < - > HS
~~ $\overline{HS}$ – NH ····· O ⟨ C – $\overline{SS_{Et}}$ ~~~~ / C – $\overline{SS_{Et}}$ ~~~~	Urethane-ether HS < - > SS_{Et}
~~ $\overline{HS}$ – NH ····· O = C ⟨ O – $\overline{SS_{Es}}$ ~~~~ / C – $\overline{SS_{Es}}$ ~~~~	Urethane-ester HS < - > SS_{Es}

The interactions within the rigid segment provide the properties which are desired in cohesion and stiffness levels, and these can be controlled by the hydrogen bonds density. When it comes to the coating performance depends not only on the rigid segment properties but also on its resistance and ability to remain associated at high temperatures. Therefore, besides hydrogen bonding, other additives and cross-linkers may be required [57].

3.3 Catalysts

In polyurethane formation reaction, catalysts are used due to decreasing the curing time and temperature, adjusting the chain growth rate, optimized characters of polymer, economically reasonable polymer production. Extending the reaction time with adding the catalyst in Isocyanate-use phase helps not only the polymer ratio to be formed, but also to affect the structure and properties of the finished product. In the stage in which isocyanate is present, mixed catalysts are generally used[58]. Examples of these catalysts are as follows:

- A few aromatic and aliphatic amines (eg, diaminobicyclooctane, DABCO, diazabicyclooctane), that immensely catalyzes the reaction of isocyanate groups with water (Table 3.2).

Table 3.2 Few Amine Catalysts[58][59]

Name	Main Compound
DABCO K-15	Potassium octavian in glycol
DABCO TMR	IV-Quaternary ammonium salt in glycol
POLYCAT 41	Tris(dimethylaminomethyl) triazine
POLYCAT 5	PMDETA

- Di- and tetravalent types (tin caprylates and laurates, and dibutyltin, diacetate, dilaurates) as organometallic compounds immensely catalyze the isocyanate's reaction with hydroxyl groups (Table 3.3).

- Alkali metal salts of phenols and carboxylic acids such as Bi, Fe, Sn, Co, Cd, Zn, Pb, Ti, and Sb ...

Table 3.3 Several organometallic catalysts

Name	**Application**
Sodium bicarbonate	Polyurethane foams
Potassium acetale	Cross-linked polyurethanes
Dibenzyltindichloride	Polyurethane foams, elastomers, cross-linked polyurethanes
Tin dicaprylate	Polyurethane foams, elastomers, cross-linked polyurethanes

Catalytic activity is related to basicity when considering tertiary amines. The efficiency of the catalyst increases with the basicity and decreases with it.

Metal catalysts are more useful than tertiary amines because they are less volatile and toxic. In addition, metals can form a complex formation with hydroxyl and isocyanate groups thus, they catalyse the isocyanate-hydroxyl reaction. The metal center has a positive charge density and attacks the oxygen of the isocyanate and the hydroxyl groups and forms an intermediate structure which results in urethane bonds with rearrangement[28].

3.4 Blowing Agents

The formation of polyurethane reaction is exothermic and occur between long polymeric chain which has hydroxyl functional groups and polymeric isocyanate .During these reaction additives are added to obtain the desired thermal and mechanical properties of the polymer and one of them is blowing agent is added to blow the polymer to foam[60]. The blowing agents produce a cellular structure by various materials and these are separated two groups as physical blowing agents and chemical blowing agents. For instance, chemical blowing agents are isocyanate and water for polyurethane production, sodium bicarbonate for thermoplastic foams production, azodicarbonamide for vinyl compound production, hydrazine

and other nitrogen-containing materials for thermoplastic and elastomeric foams production. As for the physical blowing agents are CFCs, HCFCs, hydrocarbons, carbon dioxide. Using CO_2 as blowing agent is the result of the reaction of isocyanate and water, it has additionally low cost. In addition, physical blowing agents also reduce the polyurethane foam density visibly[61],[62],[63].

The use of blowing agents such as CFCs (chemicals damaging the ozone layer and it is prohibited) and HCFCs (Using is limited in many procedures). The ozone depletion potential of some of them can be seen in (Table 3.4).

The use of saturated hydrocarbons is very common due to their wide boiling point ranges. They are also cheap, ODP rate is zero, chlorine-free, highly applicable. As for the Fluorohydrocarbons (HCF), there is no evidence that HCF is toxic for environment and damaging ozone layer due to not inclusion of chlorine. That is why use of HCF is not limited[58].

Table 3.4 Some blowing agents and their properties in polyurethane foam technology[22]

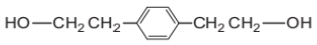
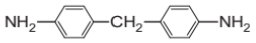
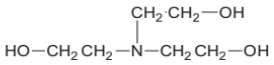
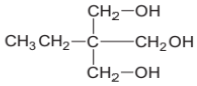
Name	Formula	Boiling Point [°C]	Ozone Depletion Potential
HCFC-141b	CH_3CCL_2F	32	0.11
HCFC-22	$CFCLF_2$	−40.8	0.06
HCF-142b	CH_3CCLF_2	−9.2	0.07
HCF 134a	CF_3CH_2F	−26.3	0
HCF 245 ca	$CF_2HCF_2CFH_2$	25.4	0
HCF245 fa	$CF_3CH_2CHF_2$	15.3	0
C-pentane	C_5H_{10}	49	0
N-pentane	C_5H_{10}	36	0
Carbon dioxide	CO_2	−87.8	0

3.5 Cross-linkers and Chain Extenders

Another additives that impact on the polymeric morphology of polyurethane is chain extenders (f=2) and cross-linkers (f=3 or more) despite their small mass fraction. If branched oligomerols are used in the PU synthesis reaction[37], PU's chains will be extended by low molecular weight difunctional compounds which have two groups with active hydrogen atoms such as diols and diamines. On the other hand, to synthesize branched polyurethanes, bifunctional oligomerols are

used as well as tri- or polyfunctional compounds which are called cross-linkers are used for chain extention. Chain extenders and cross-linkers commonly used in polyurethane synthesis (Table 3.5).

Table 3.5 Examples of Chain Extender and Cross-linkers Used in Polyurethane Synthesis[58]

Name	Formula	Application
1,4-Butanediol	$HO-CH_2CH_2CH_2CH_2-OH$	Extender
Diethylene glycol	$HO-CH_2CH_2-O-CH_2CH_2-OH$	Extender
1,4-Di(hydroksoetyleno)benzen		Extender
1,6-Hexamethylenediamine	$NH_2-CH_2CH_2CH_2CH_2CH_2CH_2-NH_2$	Extender
4 4'-Diaminodiphenylmethane		Extender
Glicerol		Cross-linking agent
Triethylenediamine		Cross-linking agent
1,1,1-Tris(hydroxymethyl)propane		Cross-linking agent

The elastomeric properties of polyurethane comes from copolymer interface which is resulted from rigid and soft domains different properties. These two phases which are rigid (high melting) part is made from from isocyanate and crosslinkers, soft (low melting and non-polar) part is made of polyols are immiscibility and incompatibility. Thus, the rigid domains are immobile and hard and soft domains are mobile and move easily[64].

Water and ethylene glycol can be used as chain extenders in the synthesis of biodegradable polyurethanes (Figure3.3). These glycols are advantageous in thermoplastic PU synthesis. They produce well separated phases and well organized hard segments and are easily processed in the molten form. The sole exception to this situation is ethylene glycol because it can cause undesirable degradation when the level of the rigid segment goes too high.

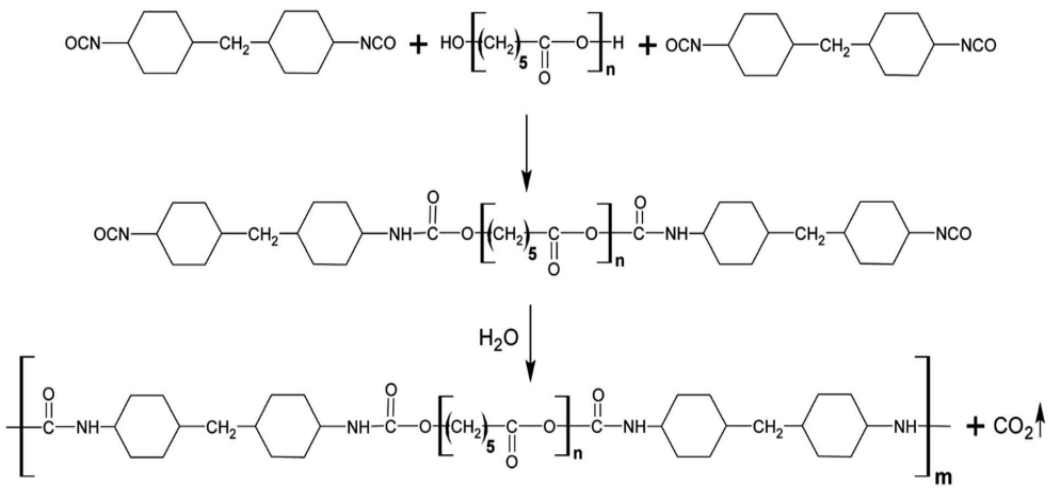


Figure 3.3 Biodegradable PU formation reaction with chain extender as ethylene glycol[37]

3.5.1 Synthesis and Reactions of Cross-Linking Polyurethanes

The final structure of thermoset polyurethanes macroscopic properties and their characteristics are created by cross-linking process. The crosslink density is characterized by the hydrogen bonds, physical cross-links and chemical cross-bonds in the structure, and thus, the effectiveness of the cross-linking PU is determined. This comes from presence of varied interactions by van der Waals forces. Cross-linking formation can perform during the reaction of PU or after obtaining already final polyurethane according to the sort of comonomers which used in polyurethane synthesis and reaction paramaters like temperature, type and amount of catalysts, ratio of the reactants. Choosing convenient cross-linking methods and cross-linkers are essential for producing PU with special properties which desired. There are few different processes to obtain cross-linking polyurethane[58]:

- Using chain extender that have functional groups more than two (cross-linker) in a hard segment.
- Using polyols which have functional groups more than two in a soft segment.

- Using multifunctional isocyanates in a hard segment.
- Using excess of isocyanates with the proper catalyst which produce the formation allophanate or biuret bonds that give cross-linking or branching in a polyurethane structure at a certain temperature.
- Using isocyanate dimerization or trimerization products with appropriate catalysts in the hard segment.
- By crosslinking unsaturated polyurethanes by radical polymerization or by sulfur curing(vulcanization) of unsaturated grindable polyurethane.

3.6 Surfactants

There are a wide variety of surfactants are used to improve polyurethane properties, can be applied on foam and non-foam PU polymers. In application involving foam PU polymer, they are used the aim of arranging the cell sizes, stabilization of cell structures, protection against polymer structure's collapse and removal of underlying voids. As for the applications of surfactants with non-foam PU polymer, they are often used as air release, anti-foaming and as wetting agents. Surfactants can also be used to eliminate flaws like pinholes and orange peel as well. Polyether-polysiloxane polymers, nonylphenol ethoxylates, silicone oil, and a few more chemical substances are examples of this group. In addition to these, numerous additional non-ionic and cationic surfactants are utilized in polyurethane applications. Nonionic surfactants improve surface activity while cationic surfactants are effective against corrosion resistance[65],[66].

3.7 Auxiliary Agents

Various additives can be used to improve the final product during polyurethane synthesis process. Thus, the properties of the final product are changed for use in different areas such as automotive, medicine, construction and coating. This group agents are organic pigments, flame retardants, reinforcing fibers, thixotropic compounds, fillers and polymer-processing aids[58].

- Flame Retardants

The substances in this group delay the combustion process by reducing the speed of pyrolysis or oxidation reactions of the polymer or plastics in contact with the flame (e.g. hexabromo phthalate, pentabromophenol, tetrabromodienes, polyols containing phosphorus or halides)[67].

- Organic Pigments

The dyes for polymer systems depend on their chromophoric systems that contain. The largest group are azo dyes (it gives red and yellow color), anthraquinone (mostly blue and purple), In addition to these, it is used in phthalocyanine, benzopyran, perylene based paints as well[58].

- Polymers-Processing Aids

The auxiliary substances in this group are effective in improving the rheological properties of the surface in the polymer formation process and are basically divided into the following groups[68]:

1. Lubricants
2. Fluidifying-Flow Modifiers or High-Temperature Plasticizers
3. Anti-Adhesives

- Fillers

Fillers are organic or inorganic additives that might be solids, sheets, spheres, or fibers. Fillers not only lower the cost of composites, but they also typically increase performance in ways that reinforcement and resin ingredients alone would not be able to do. They improve mechanical qualities such as fire and smoke performance by minimizing organic content in composite laminates. Water resistance, weathering, dimensional stability, surface smoothness, stiffness, and temperature resistance are all important attributes that can be improved by using the proper fillers[69].

4
BORON-BASED POLYMERS

In recent years, significant developments have occurred in boron-containing polymers. Since the 1990s, many boron-based polymers have been synthesized by using common monomer units such as borazine, phosphine borane, decarborane. As the research in this area progressed, many sorts of polymers were synthesized like organoborane, functionalized boronic ester polymers, conjugated boron hetero cyclic polymers, boron diketonate, boron quinolate, borane or carborane cluster containing polymers etc. Polymers with boron elements are named as organoboron polymers. These polymers are formed by including the organoboron complex or boron clusters in the main or internal chain. Additionally, boron-based polymer serves as the initiator for the production of various nanostructure materials[70].

Boron-based polymers give different advanced technological properties to the material with their unique structure and combinations. For instance, polymers containing boron nitride in their structure reduce the cost of production and this kind of polymers have high temperature flexibility, easy process ability and sustainability[70].

4.1 Boron-containing Organic Compounds

4.1.1 Boric Acid

Boric acid with other names; orthoboric acid, hydrogen borate or orthoboric acid is an inorganic compound as weak monobasic lewis acid of boron. It is found as solid crystals in room temperature and soluble in water. When it is shaped as a mineral, is called sassolite[71]. Boric acid is found in the structure of many natural minerals such as borax, colemanite, boracite, ulexite. It is also found in seawater, all fruits and some plants[72]. Its chemical formula is H_3BO_3 (or it is $B(OH)_3$) ,structure formula is shown (Figure 4.1).

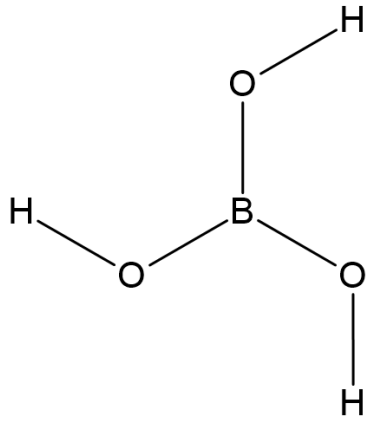


Figure 4.1 Structure of Boric acid

Wilhelm Homberg has obtained boric acid crystals for the first time in 1702. Boric acid is obtained by reacting a mineral acid (e.g. hydrochloric acid) and borax (sodium tetra borate decahydrate), like it is seen below[71].

$Na_2B_4O_7 \cdot 10H_2O + 2\ HCl \rightarrow 4\ B(OH)_3$ [or H_3BO_3] $+ 2\ NaCl + 5\ H_2O$

Boron trihalides and diborane hydrolysis gives the boric acid as a byproduct as well[71].

$B_2H_6 + 6\ H_2O \rightarrow 2\ B(OH)_3 + 6\ H_2$

$BX_3 + 3\ H_2O \rightarrow B(OH)_3 + 3\ HX$ (X = Cl, Br, I)

There are many other ways to obtain or use boric acid to form boron-based materials.

4.1.2 Boron Sulfide

The boron sulfide compound is synthesized in the form of an amorphous glass. It is quite difficult to purify it. Boron sulfide has normally transparent color but due to the impurities such as sulfur and oxygen in it might seem yellow color. Since amorphous compounds do not have a specific melting point, there is no definitive definition on this subject. It begins to sublimate at around 300°C. Boron sulfide gives reaction with many protonic compounds and with water, it reacts very strongly. Boric acid, boric esters can be produced via these reactions[73].

$B_2S_3 + 6H_2O \longrightarrow 2B(OH)_3 + 3H_2S$

$B_2S_3 + 6ROH \longrightarrow 2B(OR)_3 + 3H_2S$

$B_2S_3 + 6R_2NH \longrightarrow 2B(NR_2)_3 + 3H_2S$

4.1.3 Boron Trihalides

Boron trihalides are named trihaloboranes with trifluoride (BF_3), triiodide (BI_3),

Trichloride (BCI_3) and tribromide (BBr_3). These four boron halides are colorless, when tribromide and triiodide exposure the light they change their color. All these compounds have trigonal symmetry with X-B-X 120 ° angle. Boron trihalides chemistry is controlled by Lewis acid – base reactions, the acceptor strength changes as $BF_3 < BCl_3 < BBr_3 < BI_3$. All kind of boron halides goes exchange reaction of halides, but only BBr_2I and $BBrI_2$ can be isolated from the mixed halides kinds[73].

$BX_3 + 2BR_3 \longrightarrow 3BXR_2$

Boron halides but the boron trifluoride react with compounds which have active hydrogen bond such as alcohols, water, amines, thiols, arsines and phosphines **(1)**, **(2).** Halide replacement reaction of BF_3 occur lower rate than other boron halides due to the boron — fluorine bond strength and most of the BF_3 displacement reactions need high temperature and active nucleophile like grignard reagent[73]. Boron trihalides reactivity against the compound having active hydrogen bond increases with decreasing B-X bond energy;

$BF_3 < BCl_3 < BBr_3$

$BX_3 + 3H_2O \longrightarrow B(OH)_3 + 3HX$ **(1)**

$BX_3 + 3ROH \longrightarrow B(OR)_3 + 3HX$ **(2)**

4.1.4 Boric Acid Esters

The first boric acids ester represents the oldest examples of organoboron compounds and was synthesized in 1846 by the reaction of aliphatic alcohol and boron trichloride[73]. This kind of esters are synthesized by the stoichiometric condensation reaction of alcohols and

boric acid. Boric acid esters are generally divided into two groups such as orthoborates $B(OR)_3$ and metaborates $B_3O_3(OR)_3$, R might be alkyl or aryl groups[74].

Boric acid esters are colorless, their boiling and melting points vary according to the substituent alkyl and aryl group. Boric acid esters which have straight-chain alcohol or aryl groups are more resistant to high temperatures, increasing branching in the structure decreases resistance to heat. They are usually soluble in organic solvents, dissolved in water and hydrolyzed to the starting material boric acid or the corresponding phenol or alcohol. Boric acid ester's tendency to react with water and atmospheric humidity severely limits the use of these substances. Their tendency to react with water can be reduced by modifying the molecules by steric or electronic effects as known the molecules like tri-tert-amyl borate and triethanolamine borate which have hydrolytic stability. It is obtained in many ways, but the standard method is to obtain boric acid by reacting with alcohol. This equilibrium reaction can be shifted to the right by overuse of alcohol[73].

$$B(OH)_3 + 3ROH \rightleftharpoons B(OR)_3 + 3H_2O$$

4.1.5 Boronic Acid

Boronic acid [$RB(OH)_2$] has B-C bonds and two hydroxyl groups are attached to the boron atom. This compound refers to boric acid which has one of the three hydroxyl groups is modified by an alkyl or aryl group. Boronic acid has a slight Lewis acid property due to the boron atom's unoccupied molecular orbital. Its pKa is ~9, but it might form into tetrahedral boronate complexes with a pKa of 7.

In addition, it is widely used in organic chemistry as chemical building blocks and mainly as intermediates in reactions such as Suzuki coupling, Liebeskind-Srogl coupling[75],[76].

Boronic acid has many applications in chemistry, medicine, biology, and materials science. Boronic acid is eco-friendly and does not affect the environment or human health because, it decomposes to ortho boric acid. Its toxicity is really low[76].

The first oxidation product of boranes is borinic acid, the second oxidation product is boronic acid, and the third oxidation product is CO_2. Most boronic acid in white crystalline form is very stable at high temperature, but must be stored in an inert atmosphere to minimize oxidation. When boronic acid is exposed to water, it undergoes dehydration from the hydroxyl part (Figure 4.2). When dehydrated, boronic acids transform into cyclic or straight chain oligomeric anhydride structures[76].

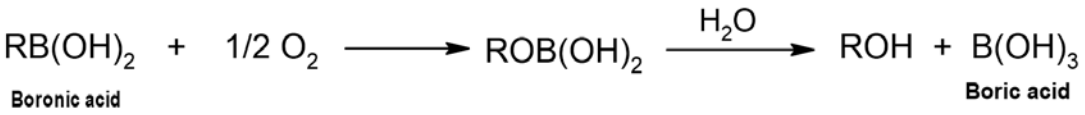


Figure 4.2 Formation of boric acid from the boronic acid

4.2 Examples of Boron-based Polymer Synthesis

4.2.1 Formation of Poly [4-bis (pentafluorophenyl) borylstyrene] via Cationic Polymerization

Cationic polymerization is a sort of chain growth reaction. It begins with a cationic initiator transferring its charge to a monomer, and then the active monomer forms the polymer form with chain growth. By displacing the side group or functional groups which are attached to the boron on the soluble boron polymer, the binding nature of the nucleophilic species of polymeric Lewis acids is obtained[70].

The polymeric Lewis acid is synthesized by the controlled free radical polymerization reaction of the silicon-bonded active monomer then is followed by the borylation reaction. In such a situation, the trimethylsilylated polystyrene which has low dispersion (1.15) and controlled molecular weight is formed by the 4-(trimethylsilyl) styrene with atom transfer radical polymerization reaction. The Silylated polymer formed reacts with BBr_3 via a borylation reaction and results in poly (4-dibromoborylstyrene) and then, this polymeric lewis acid helps in the synthesis of the new boron-based polymer by reacting with a nucleophile. Lewis acidic polymer is poly [4-bis (pentafluorophenyl) borylstyrene] as final product

(Figure 4.3). It has been found that this polymer is efficient for catalysis and materials science[70].

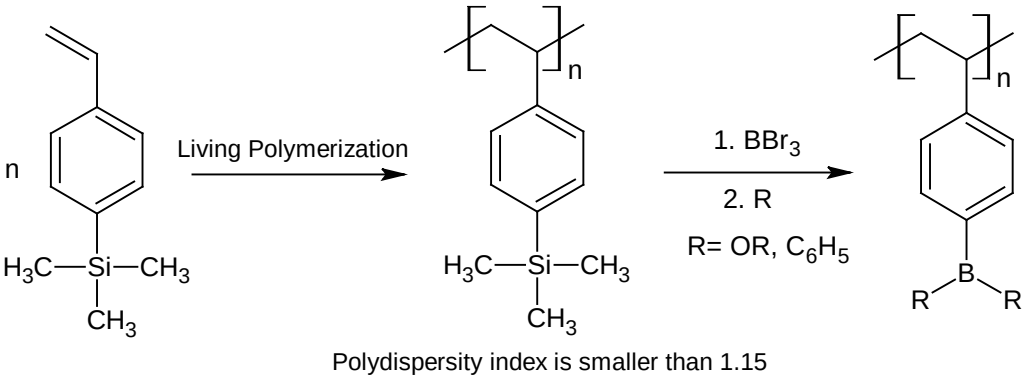


Figure 4.3 Formation reactions for Poly [4-bis (pentafluorophenyl) borylstyrene]

4.2.2 Preparation of Boron Nitride Fibers by the Polyborazine-derived Polymers

Boron nitride is a crucial and old commercial ceramic material for developed technological applications. Different polymorphic forms of BN, namely hexagonal (h-BN), rhomboedral (r-BN), cubic (c-BN), or würtzite (w-BN) boron nitride is able to prepared. Hexagonal polymorph consists of hexagonal layers which are alternatively placed boron and nitrogen atoms. All atoms are connected by covalent bonds within the layers (a-axis), while the next two layers are connected by Van derWaals-type bonds (c-axis)[77]. In particular, the anisotropic nature of H-BN provides unique optical, mechanical, thermal, electrical properties such as:

- Low thermal expansion coefficient
- Thermal resistance between 25°C and 2000°C (below nitrogen)
- Strong resistance
- Resistance to oxidation at 900°C
- High tensile strength

As a result, these materials features are dependent on the chemical purity, crystallinity and microstructural order of the samples and preparation methods. BN powders are able to prepare by the conventional high temperature with inexpensive reagents such as boric acid and urea. Most commercially available BN articles are obtained hot pressing of BN powders or chemical vapor deposition (CVD) technique. Among the BN materials, continuous thin fibers are specially, scientifically and technologically significant because of their potential applications as fibrous reinforcements in composite materials and high temperature usage in aggressive environments instead of carbon fibers. Among the molecular compounds containing boron and nitrogen, borazine, derivatives such as $H_3B_3N_3H_3$ and B-tri (alkylamino) borazines, $[(RR')\ N]_3\ B_3N_3R''_3$ are particularly interesting as polymer starting materials. One of the most promising methods in the preparation of BN fibers is the derivation of thermoplastic polyborazines derived from B-tri (alkylamino) borazines. B-tri (alkylamino) borazine has been re-investigated since 1998 and seen that it is suitable for BN fibers preparation[77].

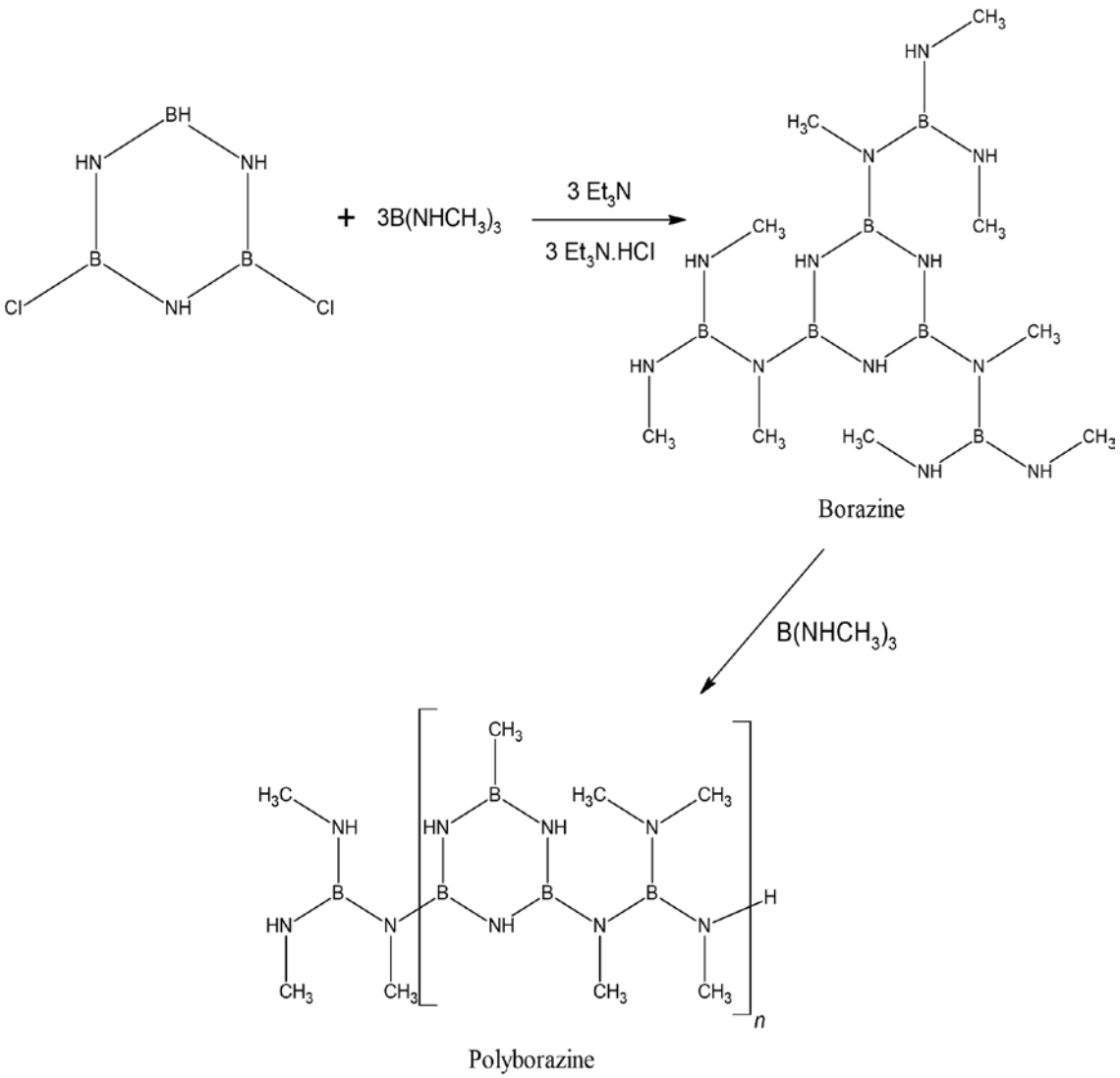


Figure 4.4 Formation of Polyborazine

BN matrices and oxidation protective coatings have been successfully synthesized using this polymer (Figure 4.4). Borylborazine was prepared from $B(NHCH_3)_3$ and then heated to 150°C under vacuum. Later, it was determined that polyborazine developed during the heating of borylborazine, and NMR investigations showed that the final product polyborazine contains primarily three atom bridges between the rings[77].

4.2.3 Improvement of Thermal and Mechanical Properties of Polyurethane Composites with Boron Nitride Modified on the Surface

The latest advances in electronics have enabled miniaturization of devices, allowing more components to be integrated into a single device, resulting in higher device performance in a smaller volume. However, the smaller volume causes a greater amount of heat to be generated, and the doubling of the temperature rise reduces the life of the device, resulting in power leakage and failure. This undesired heat increase must be prevented to ensure proper functioning of the device. Prevention of heat build-up is achieved by the product packaging material having a good thermal conductivity[78].

Among polymer resins, thermoplastic polyurethane elastomers which contain poly(tetramethylene glycol) (PTMG) as the soft segment and methyl diphenyl diisocyanate (MDI) as hard segment are widely used as reagents in many reactions because of its excellent properties (elasticity, flexibility, good adhesion). By modification the molecular chain structure of the soft and hard segments in TPU structure, the polymer properties can be adapted to the desired shape. Therefore, it can be expected that TPU can serve as an ideal matrix for polymeric materials but, due to their low thermal conductivity, TPU resins cannot effectively dissipate the heat generated in microelectronic devices. Besides, to enhance thermal conductivity, carbon-based materials such as graphene, carbon nanotubes and ceramic materials (boron nitride [BN], AlN and Al_2O_3) have arisen as cost-effective materials to improve their thermal conductivity. Especially BN is the most attractive among them due to its low weight, moderate cost, electrical insulation, high thermal conductivity and temperature resistance properties, and outstanding resistance to oxidation. As a result of these previous works, in this article[78] was produced PU grafted BN (PU-g-BN), which is expected to improve the thermal conductivity of the polyurethane and provide a good distribution. The reaction scheme is as shown below (Figure 4.5).

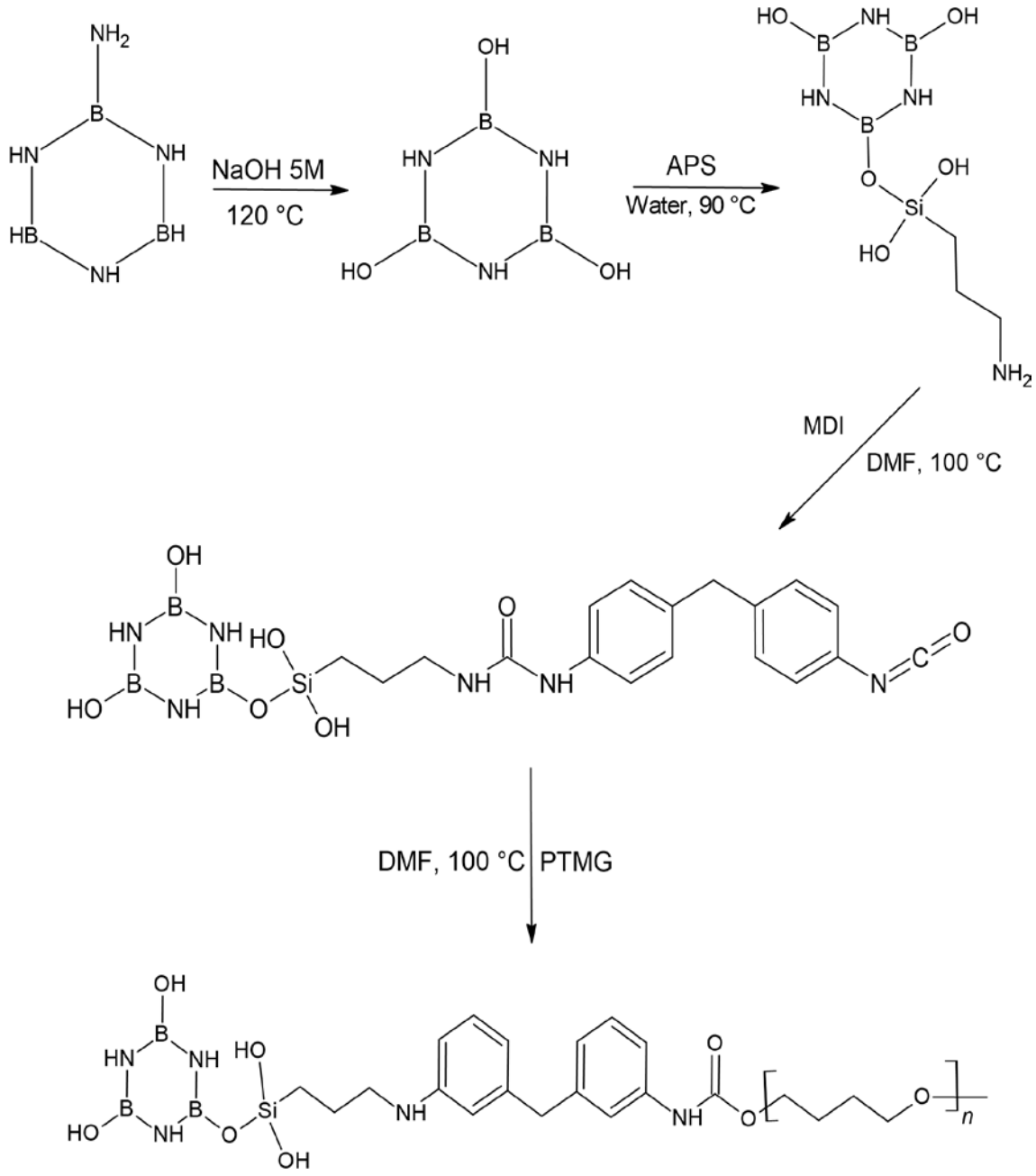


Figure 4.5 The formation of surface-modified BN particles (BN—NH_2 and PU - grafted BN)

4.2.4 Porous Diazaborol Bonded Polymers (DBLPs) Synthesis by Condensation Reactions

Porous organic polymers (POPs) have recently been studying considerably for their potential in gas storage and separation, catalysis, electronics, conductivity and chemical detection. While POPs are synthesized by variety synthetic ways, these polymers properties (chemical composition and textural features) can be modified for variety usages. During synthesis, the covalent nature of POPs makes them amorphous if the kinetic and thermodynamic parameters are not controlled as in covalent organic frameworks (COFs) forming microcrystalline materials, here the building units are linked by B-O, C-N and B-N bonds. Despite the increasing interest in this field, there are only very few examples of porous network preparation via B-N bond creation such as borazine-linked polymers (BLPs) and B, N-containing cross-linked polymers (PPs-BN). In this research, the first use of B-N bond structure to form highly porous diazaborol bonded polymers (DBLPs) was synthesized by condensation reactions. DBLPs are highly porous and indicate great H_2 and CO_2 uptake, high CO_2 selectivity over CH_4 and N_2, and high thermal stability and exhibit capability their use in small gas storage and separation[79].

A-) Synthesis of DBLP-3

1,4-Benzenediboronic acid (BDBA) and 2,3,6,7,14,15-hexaaminotriptycene (HATT) was ground in the mortar then placed in a schlenk tube with a 30 ml dry N-N-dimethylformamide (DMF) solution. The reaction was bubbled under nitrogen atmosphere for 10 minutes and then sonicated for 30 minutes. The reaction flask was placed in an oven and gradually heated to 130°C, at which temperature it remained for 3 days. The bottle was placed in a glovebox after that filtered over a medium glass frit, then washed with dry DMF and acetone. The product was left in dry acetone / DMF (50:50 v:v) for 12 hours, at this point the solvent was decanted and after that only dry acetone was added for 12 hours. It was decanted and treated again with fresh dry acetone for the last time. Afterwards, solid was filtrated and activated at 120°C under reduced pressure during 16 hours. Consequently, DBLP-3 polymer (65% yield) (Figure 4.6) was obtained as a greenish solid[79].

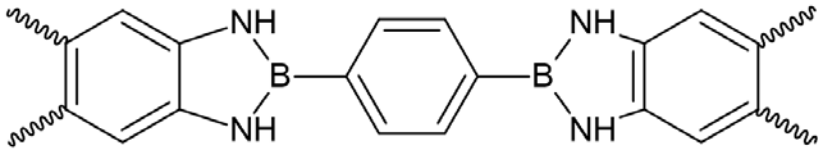


Figure 4.6 Synthesis of Diazaborole-linked Polymer ($DBLP_3$)

B-) Synthesis of DBLP-4

This polymer was synthesized with same method which is mentioned above by using DBLP-3 using 1,3,5-benzenetris (4-phenylboronic acid) (BTPA) and 2,3,6,7,14,15- hexaaminotriptycene (HATT) reagents. After the final drying step, the final product DBLP-4 polymer (Figure 4.7) was obtained in 66% yield as an off-white solid[79].

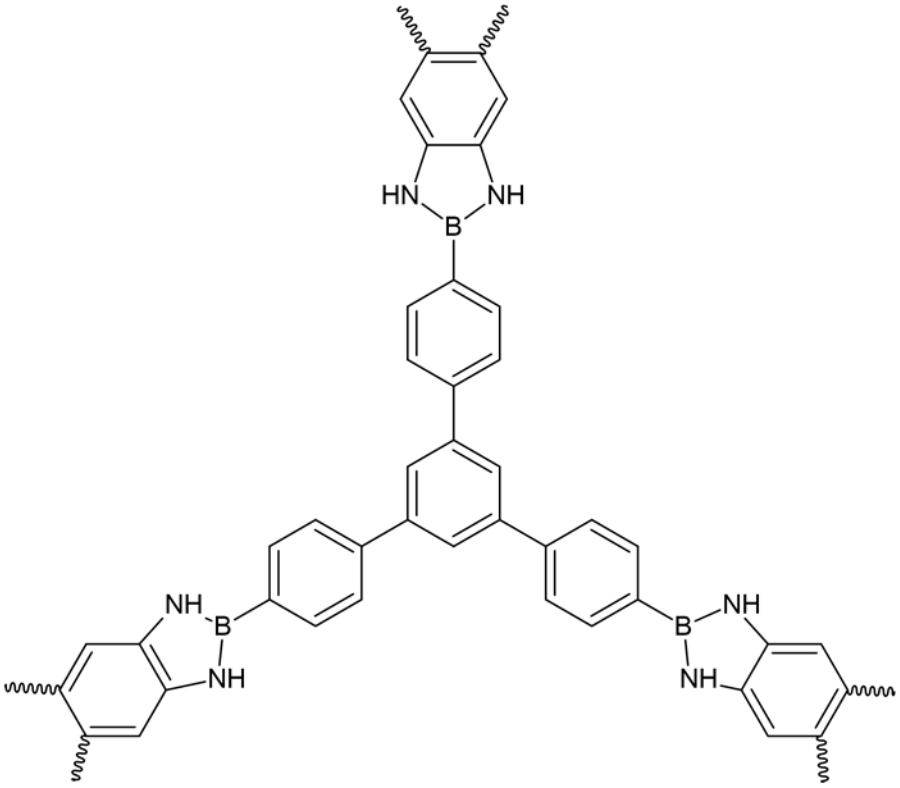


Figure 4.7 Synthesis of Diazaborole-linked polymer ($DBLP_4$)

4.2.5 The Effect of Some Boron-based Flame Retardants on the Effectiveness of Polyurethane Coatings

There are regulations that mandate the use of fire retardants in the production of flexible polyurethane foams, but commercially available flame retardants have some disadvantages such as toxicity, persistence, bioaccumulation issues. In this research, a flexible polyurethane foam has been synthesized by methylene diphenyl isocyanate and 1,3-propane diol and incorporated into the structure of boron -based flame retardants that can be useful to address this foam flammability. Various analysis methods have been used to measure the effect of flame retardants on polyurethane and the heat release potential of chemicals. The tested polymers were prepared in two different ways in this article[80]. In the first way, polyurethane is synthesized of in the presence of monomers and flame retardants. In the second way, polyurethane is first synthesized without flame retardant, and then, while this polyurethane is in solution, the flame retardant additive is added to the bottle and mixed for a while and the solvent is removed.

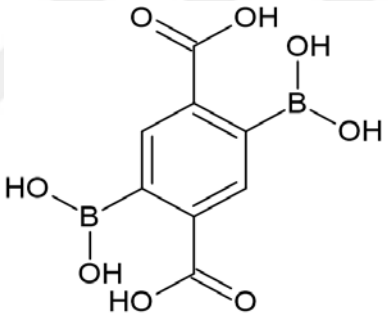


Figure 4.8 Structure of (DBA)

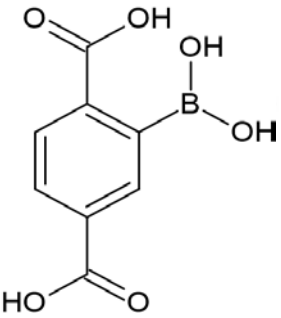


Figure 4.9 Structure of (MBA)

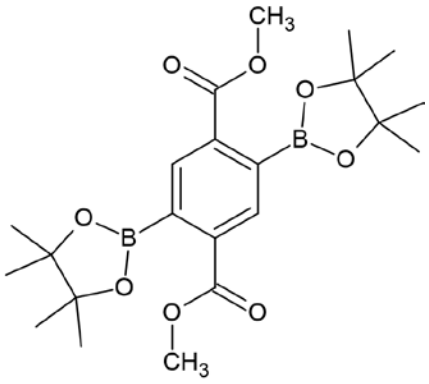


Figure 4.10 Structure of (DBB)

Boronoterephthalic acid (MBA) (Figure 4.9), diboronoterephthalic acid (DBA) (Figure 4.8) and dimethyl 2,5-bis (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) terephthalate (DBB) (Figure 4.10) were used as fire retardants. Research results showed that prep and blend form of PU with diboronotereftalik asit (DBA) samples show slight effect on the reduction of heat release but could not prevent the melting and flowing durig combustion. The monoboronoterephthalic acid (MBA) indicates the similar behavior to DBA. MBA is a little more effective at total heat release reduction. MBA-PU (Prep) is more influential than MBA-PU (Blend).

According to TGA results, thermal stability of PU +10%DBB blend and prep are examined and research showed that DBB flame retardant has a real impact on thermal stability. Additionally , in DTG results are shown that regardless of how DBB is incorporated into the polyurethane, both samples begin to degrade at 200°C[80].

5
EXPERIMENTAL METHODS

5.1 Experimental

5.1.1 Materials and Chemicals

Boric acid was used for the synthesis of borate ester and it was bought from Polex chemistry Sanayi ve Ticaret A.Ş. (Turkey). Adipic acid, tyzor tpt catalyst, diethylene glycol (DEG) and monoethylene glycol (MEG) were used in the polyol synthesis and procured by Polex chemistry Sanayi ve Ticaret A.Ş. (Turkey), H_2SO_4 dilute solution procured from Merck. Borate ester (starting material), polyol BT4 was prepared in this thesis, polyol BT5 was prepared in this thesis and polyol BT6 was prepared in this thesis as well. Expol, water, toluen, silicone, glycerin, TEGO amine MEG, quaternary DABCO as catalysts as well as prepolymer procured from Polex chemistry Sanayi ve Ticaret A.Ş. (Turkey), polymix was prepared in this thesis.

5.1.2 Instrumentation and Software

Oil bath: Oil bath is prepared by using silicon oil in a fan.

Magnetic stirrer: Magnetic stirrer supplied by Heidolph type MR 3001AC 230/240V, 625W, serial No. 100478499, made in Germany.

Rotary evaporator: Heidolph rotary evaporator, manufactured in Germany. Heating is controlled by a water tank, cooling is controlled by a Thermoset cooler, and vacuum is controlled by a motor (ILMVAC SL No 132805).

Dialysis Membrane: Dialysis membrane produced by Sterlitech Corporation. NADIR NP010 (item no 300789, MWCO 1000Da) and NADIR NP030 (item no 300786, MWCO 500Da) membrane have been used for ultrafiltration.

FT-IR spectrometer: The IR spectra (4000–400 cm−1, resolution were recorded with a Perkin Elmer Spectrum One (Serial No: C68739) in ATR.

NMR instrument: A Bruker 500 MHz spectrometer was used to record 1H and 13C NMR spectra, samples were dissolved in deuteromethanol.

848 Titrino plus: By Metrohm AG, titrator for volumetric titrations, Swiss made.

Viscometer: By AMETEK Brookfield from US.

915 KF Ti-Touch: The compact titrator for Karl Fischer titration from Metrohm. Volumetric system for the determination of water content above 0.1% and coulometric system for the determination of water levels down to 0.001%.

Tensile and Compression Test Device DVT BB5: By DEVOTRANS, operating voltage: 220V AC 50 Hz, electricity consumption: max. 1 KVA, test speed setting: 0.5-500 mm/min, sensitivity: ± 0.5%.

5.2 Synthesis of Borate Ester

The starting product was synthesized by modifying this method[81]. 25 g (0.40 mol) boric acid and 99.2 g (1.60 mol) excess monoethylene glycol (MEG) was taken into 250 mL round- bottom flask and stirred for a while to dissolve. In this experiment, no solvent was involved. The round-bottom flask was placed in the oil bath and 2 drops of sulfuric acid dropped into it as a catalyst, 6-7 hours later, the reaction was continued by adding organometallic catalyst (tyzor tpt). The reaction was continued at 170°C for 24 hours under reflux. The released water was collected by the dean-stark apparatus. In case there was still water and unreacted monoethylene glycol (MEG) in it, the reaction was taken into a rotary evaporator under vacuum effect and the remaining water and unreacted monoethylene glycol (MEG) was evaporated. Final Product was white solid. Percentage of yield is found 61.07.

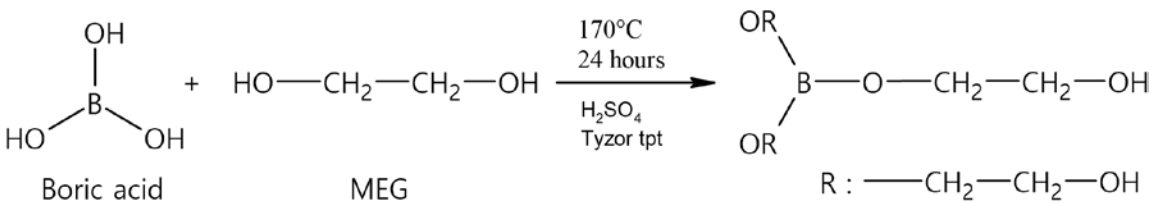


Figure 5.1 Boron crosslinker synthesis

5.3 BT4- Polyol Synthesis in the Presence of Monoethylene Glycol (MEG) and Diethylene Glycol (DEG)

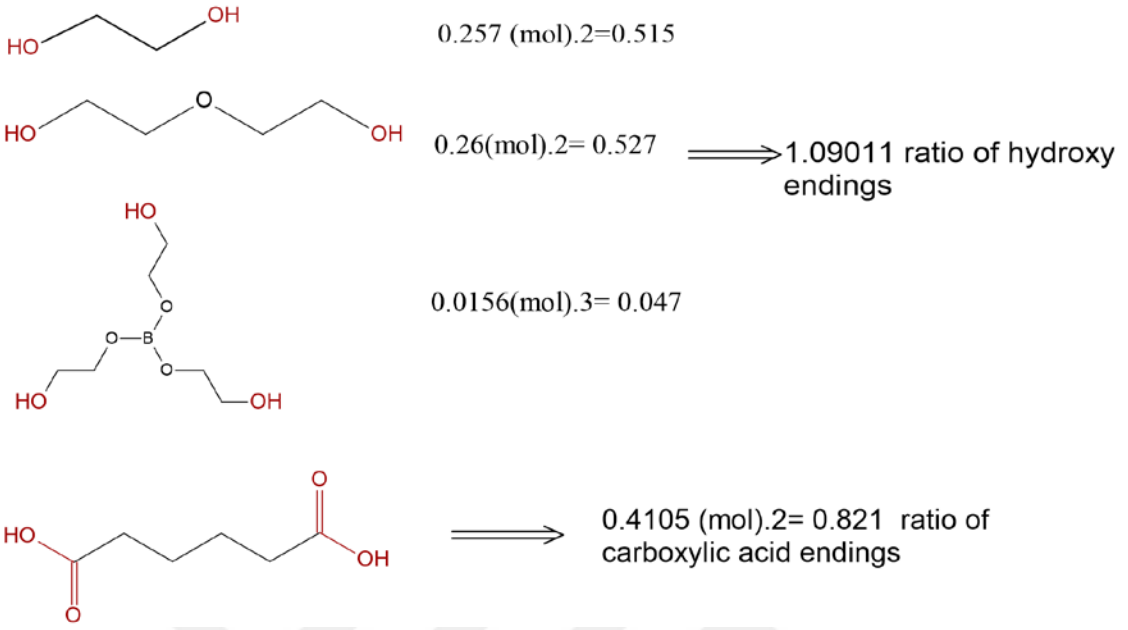


Figure 5.2 Ending group ratio of carboxylic acid and hydroxy substituted reactants

60 g adipic acid (0.41 mol), 16.657 g (0.26 mol) monoethylene glycol (MEG), 28.77 g (0.27 mol) diethylene glycol (DEG) and 2.54 g (0.015 mol) starting material were added into 250 mL round- bottom flask.

In order to obtain polyol to terminate with a hydroxy end, there must be a difference in the hydroxy and carboxylic acid end ratios as seen in (Figure 5.2). The hydroxy end ratio should be more than carboxylic acid end ratio, thus excess diols was used. Afterwards, reaction flask was put in the oil bath under reflux and 2 or 3 drops of sulfuric acid dropped into it as a catalyst, after the reaction continued for 6-7 hours, organometallic catalyst (tyzor tpt) was added into reaction. Under reflux, the reaction was held at 170°C for 30 hours. The Dean-Stark apparatus was used to capture the emitted water. In case there was already water in it, the reaction was taken into a rotary evaporator by vacuum effect time by time during the reaction. Following the completion of the reaction, the remaining MEG in the environment was evaporated in the oil bath using a rotary evaporator by vacuum effect, for the remaining diethylene Glycol (boiling point: 244°C) was evaporated

by simple distillation. The obtained polyol (final product) was purified by LPR technique. 1:3 water / ethyl alcohol was used as the solvent for purification part. The formation scheme of the reaction is shown in the (Figure 5.3) below[82].

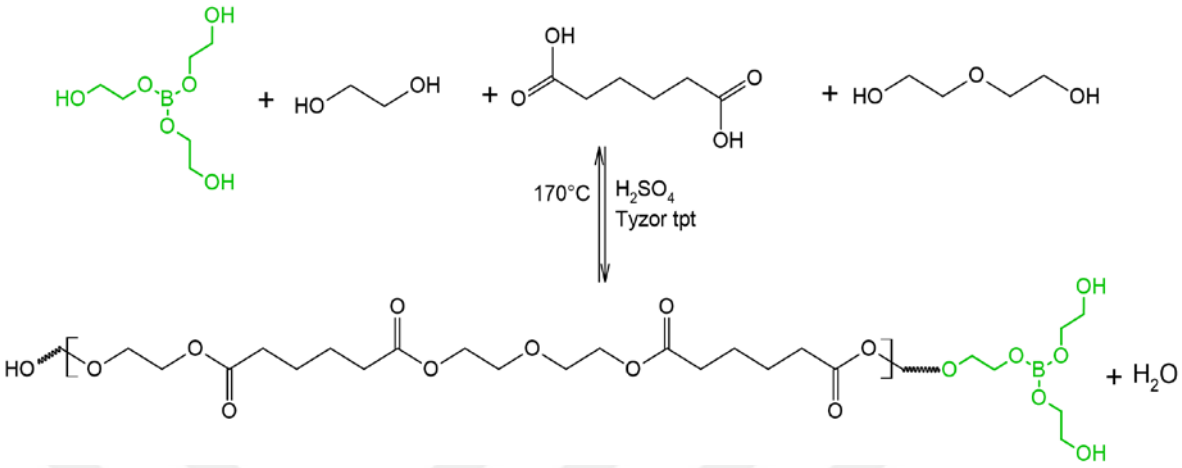


Figure 5.3 Polyol reaction in the presence of monoethylene glycol and diethylene glycol

5.4 BT5-Polyol Synthesis in the Presence of Diethylene Glycol (DEG)

60 g adipic acid (0.41 mol), 53.50 g (0.50 mol)excess diethylene glycol (DEG), and 2.36 g (0.012 mol)starting material were transferred to a 250 mL round-bottom flask, which was then placed in an oil bath under reflux and 2 or 3 drops of sulfuric acid were dropped into it as a catalyst. After the reaction progressed for 6-7 hours, an organometallic catalyst (tyzor tpt) was added to the reaction. The reaction was held at 170°C for 30 hours under reflux. The emitted water was captured using the Dean-Stark apparatus. In case there was already water in it, the reaction was taken into a rotary evaporator under vacuum effect time by time during the reaction. Following the completion of the reaction, the remaining diethylene Glycol (boiling point: 244°C) was evaporated by simple distillation. LPR was used to purify the obtained polyol (final product). The solvent for the purification part was 1:3 water / ethyl alcohol. The formation scheme of the reaction is shown in the (Figure 5.4) below.

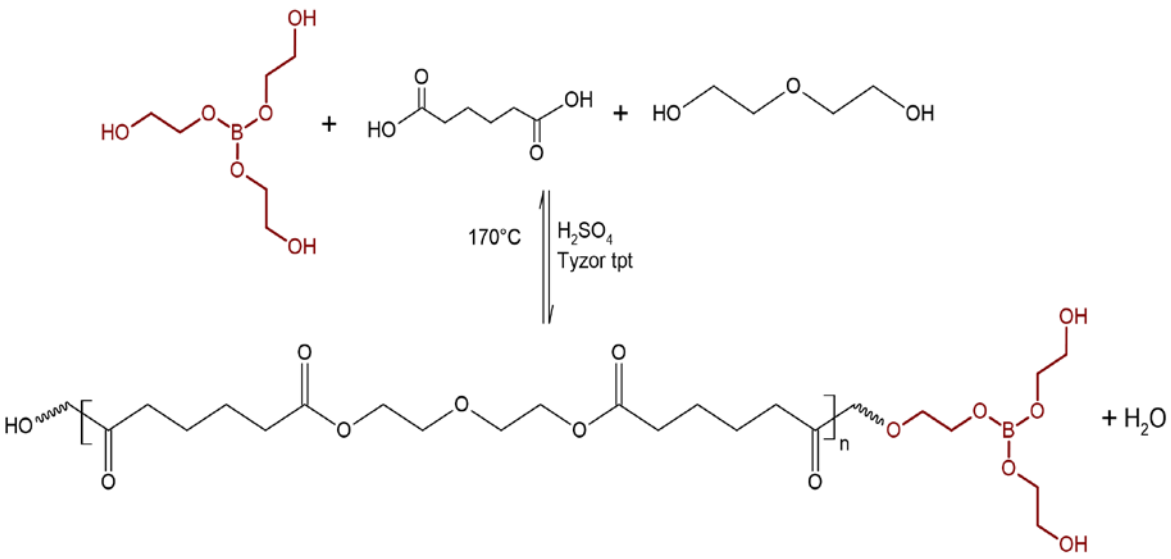


Figure 5.4 Polyol reaction in the presence of diethylene glycol

5.5 BT6-Polyol Synthesis in the Presence of Monoethylene Glycol (MEG)

60 g adipic acid (0.41 mol), 36.1793 g (0.58 mol) monoethylene glycol (MEG) and 2.68 g (0.017 mol) starting material were added into 250 mL round- bottom flask then was placed in the oil bath under reflux and 2 or 3 drops of sulfuric acid dropped into it as a catalyst, after the reaction continued for 6-7 hours, organometallic catalyst (tyzor tpt) was added into reaction. Under reflux, the reaction was held at 170°C for 30 hours. The Dean-Stark apparatus was used to capture the emitted water. In case there was already water in it, the reaction was taken into a rotary evaporator time by time during the reaction. Following the completion of the reaction, the remaining MEG in the environment was evaporated in the oil bath using a rotary evaporator by vacuum effect. The obtained polyol (final product) was purified by LPR technique. 1:3 water / ethyl alcohol was used as the solvent for purification part. The formation scheme of the reaction is shown in the (Figure 5.5) below.

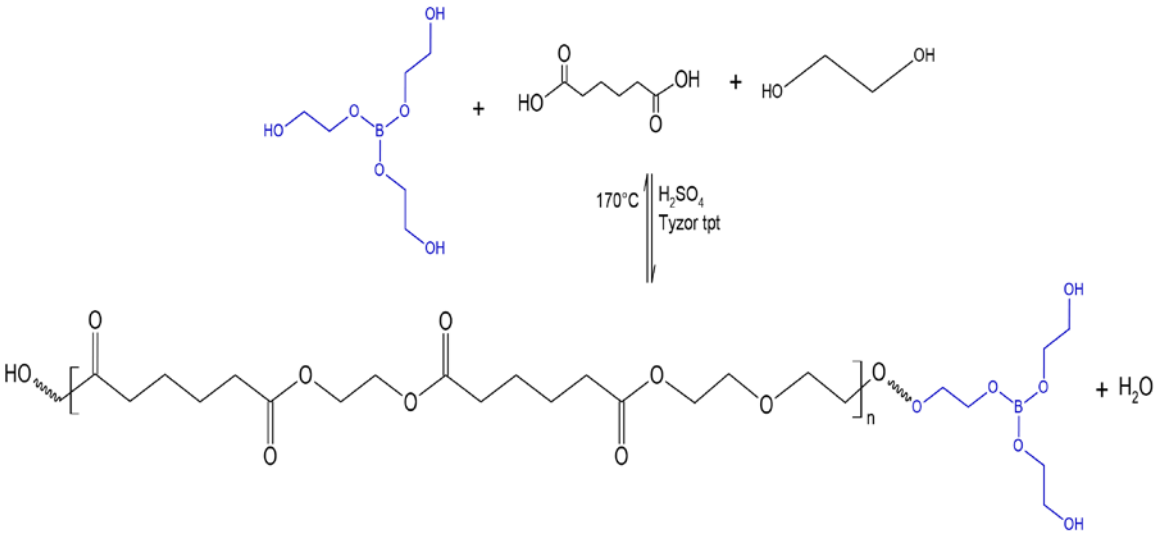


Figure 5.5 Polyol reaction in the presence of monoethylene glycol

5.6 Boron-based Cross-linked Polyurethane Synthesis

360 g of the previously synthesized BT4 coded polyol was added to a single glass, along with 64 g of MEG (monoethyleneglycol) as a chain extender, 18 g of styrene cross-linked resin (expol), and 8.88 g of TEGO Amine MEG and quaternary DABCO catalysts. The mixture was swirled at a speed of 150 revolutions per minute(rpm). This mixture, known as poly-mix, was stored at 40-45°C for reacting with the isocyanate (Figure 5.6).



Figure 5.6 Cup of Poli-mix

An isocyanate with additives(prepolymer) was used, when the isocyanate is used purely, the reaction proceeds quite aggressively, therefore it is softened with additives, and it is referred to prepolymer. The prepolymer to be used in polyurethane synthesis should be in the range of 35-40°C.

Trials were made to find out in what proportions polymix and prepolymer should be mixed. In the first trial, poly-mix and prepolymer at a ratio of 1:1.06 were taken into a separate pot and mixed at 150 rpm. In the following four trials, poly-mix/prepolymer ratios of 1:1.08, 1:1.10, 1:1.12, and 1:1.14 were utilized (Figure 5.7).

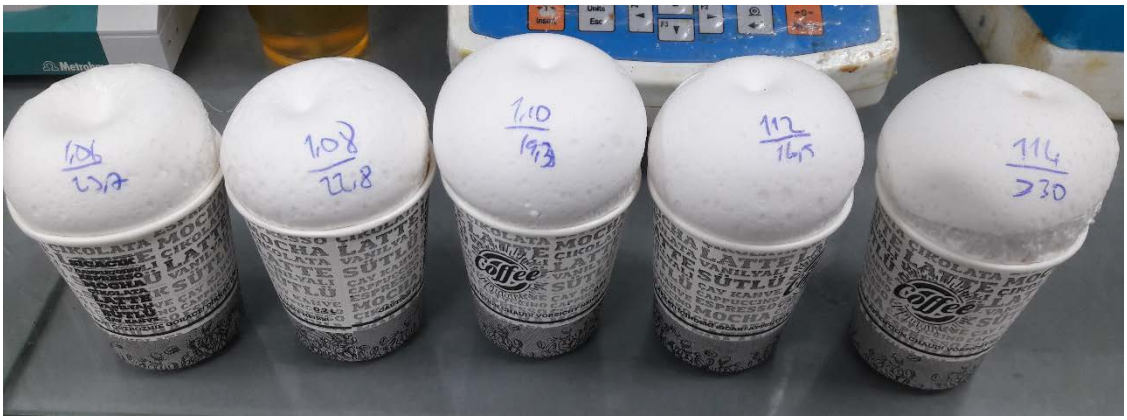


Figure 5.7 Syntheses with using different ratios of poly-mix/prepolymer

The best result was obtained with a ratio of 1:1.12 poly-mix/prepolymer. 25 g of poly-mix and 28 g of prepolymer were mixed in a single pot. The rising started at 9.5 seconds and a compression test was performed at 1.15 seconds, as a result it was seen that this trial was the most resistant to compression (Figure 5.8).



Figure 5.8 Compression test for polyurethane

A non-expol polymix was prepared for the second polyurethane synthesis. 360 g of the previously synthesized BT4 coded polyol was added to a single glass, along with 64 g of MEG as a chain extender, and 8.88 g of TEGO Amine MEG and quaternary DABCO catalysts. The mixture was swirled at a speed of 150 revolutions per minute(rpm). This poly-mix was stored at 40-45°C for reacting with the isocyanate. For polyurethane synthesis, the factory's standard prepolymer was used.

The best results were obtained with a poly-mix/prepolymer ratio of 1:1.08. In a single pot, 25 g of poly-mix and 27 g of prepolymer were mixed. The rising began at 8 seconds and a compression test was performed at 1.15 seconds; as a result, this experiment was found to be the most resistant to compression.

5.7 Polyurethane Mold Pressing

1:1.12 poly-mix (with expol)/prepolymer was produced on a large scale and poured into a 65°C mold. After waiting 3-5 minutes, the polyurethane (boron-based) layers were removed from the mold and submitted for mechanical testings.

1:1.08 poly-mix (without expol)/prepolymer was used to synthesis of PU (boron-based). It was produced on a large scale and poured into a 65°C mold. After waiting 3-5 minutes, the polyurethane(boron-based) layers were removed from the mold.

The standart polymix and prepolymer taken from the factory were mixed at the ratio of 1:1.09 and poured into the mold. The qualities of the ideal PU layer and the boron crosslinked PU layers with expol and non-expol were examined (Figure 5.9).



Figure 5.9 Polyurethane layers

The following (Table 5.1) are the standard values of the ideal prepolymer purchased from the factory and utilized in layer formation.

Table 5.1 Prepolymer standard values

%NCO value	23.36
35 °C viscosity	190
Color	Light yellow

5.8 The Findings of a Polyol Analysis Utilized in the Synthesis of Polyurethane

The boron-based polyol used in polyurethane trials is BT4. Characteristic features of it is seen at the (Table 5.2).

The acidity value of the polyester resin (boron-based polyol) was determined by acid-base titration. 5-6 grams of BT4 polyol was dissolved in a 1:1 solution of ethanol and toluene then, the dissolved product was mixed. 0.1 N KOH solution was prepared and poured into the burette after adding phenolphthalein as an indicator into the solution. The prepared polyol solution was titrated with the base and the turning point value is recorded, where the color changes from transparent to pink (Table 5.2).

calculation: (ml of KOH used*N of KOH*56.1) / (g sample)

Table 5.2 Characteristics of BT4 polyol

POLYOL	BT4
ACIDITY	0,50
OH	65.50
35°C Viscosity	3800
% HUMIDITY	0,020
COLOR	LIGHT CLEAR YELLOW

6
RESULTS AND CONCLUTION

6.1 Characterization of Borate Ester

6.1.1 FT-IR Spectra Result of Borate Ester

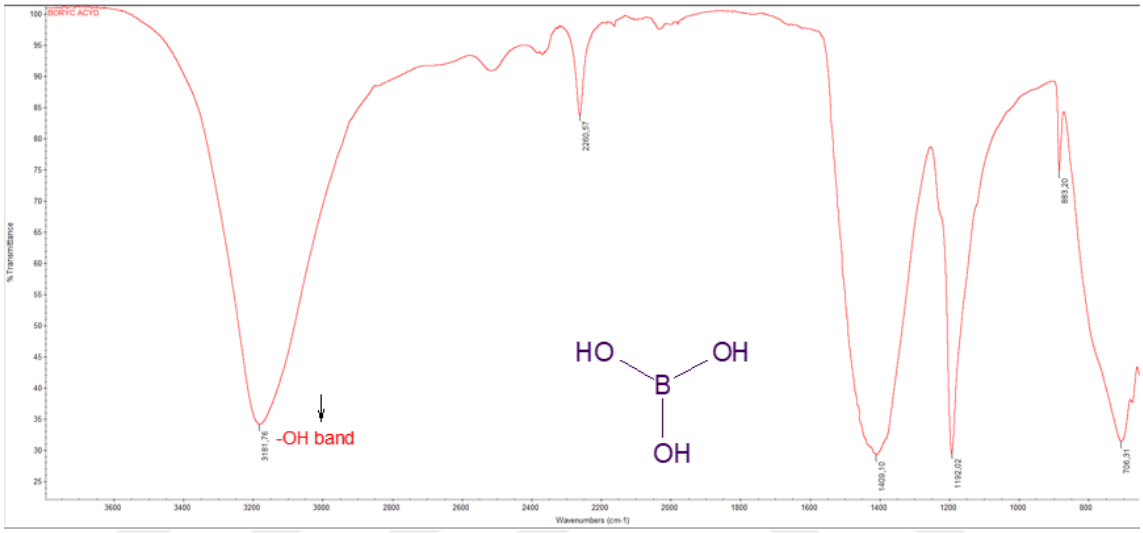


Figure 6.1 Boric acid FT-IR

When the FT-IR spectra of borate ester (Figure 6.2) and boric acid (Figure 6.1) are evaluated, the reduction of the wide -OH peak and the C-H aliphatic bonds peak below 3000 appears to be more pronounced in the FT-IR of borate ester. These alterations promote the production of borate ester. In addition, boric acid -OH is an acidic hydroxyl group whereas borate aster hydroxyl group is a basic hydroxyl group, because of it, their -OH peaks intense or location are different from each other.

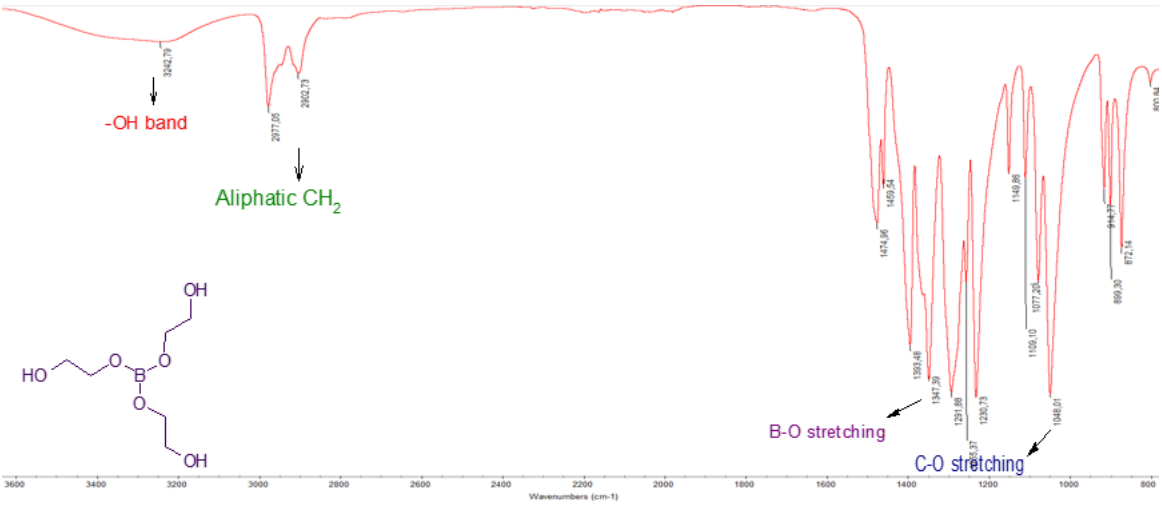


Figure 6.2 Borate ester FT-IR

B-O stretching band is shown 1347.39 cm-1, C-O stretching band is at 1048.01 cm-1, aliphatic C-H stretching, double band is at 2977.05 cm-1, O-H bending band is at 1291.88 cm-1. The peak at 3242.79 cm-1 shows O-H bond, the positive inductive effect of the aliphatic CH_2 chain may have made the -OH band appear weaker band and lower side than usual.

6.1.2 NMR Result of Borate Ester

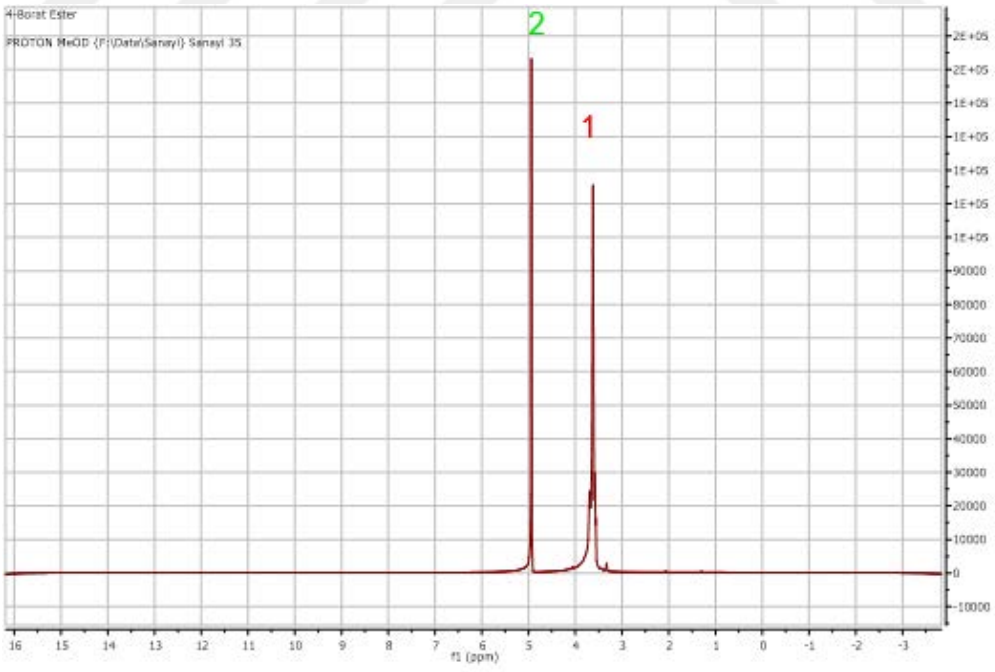


Figure 6.3 ^{1}H NMR spectrum of borate ester

Borate ester ^{1}H NMR result is shown at (Figure 6.3), the sample were dissolved in deuteromethanol and the peak at the 3.64 (1H, triplet) ppm refers aliphatic CH_2 protons **(1)** and left to it another intense peak at 5.00 (1H, singlet) ppm indicate OH protons **(2)** in the borate ester structure.

6.2 Characterization of BT4 Polyol

6.2.1 FT-IR Spectra Result of BT4 Polyol

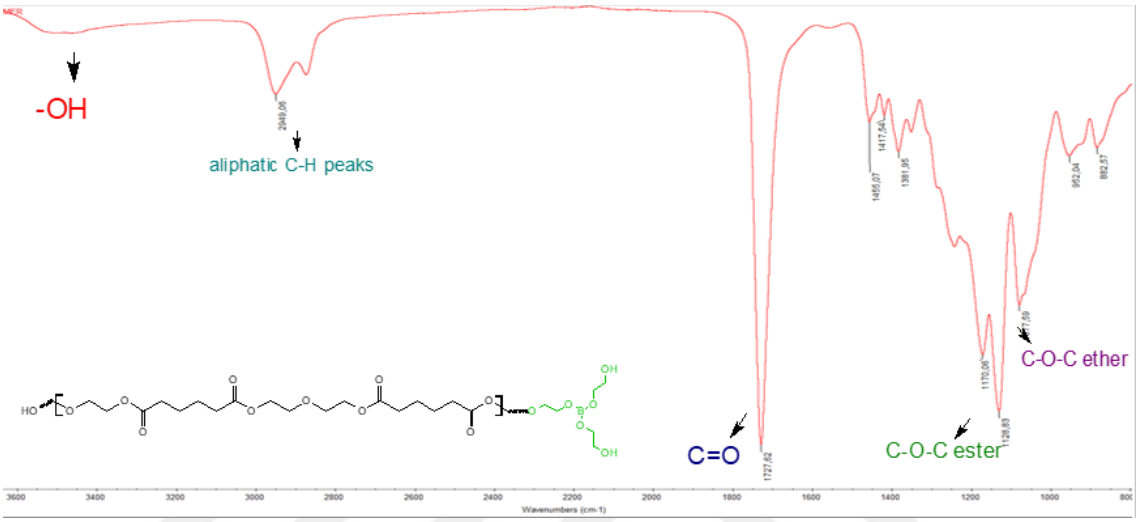


Figure 6.4 FT-IR spectrum of BT4 polyol

Infrared spectrum of BT4 polyol is seen at (Figure 6.4). The peak at 2949.06 cm^{-1} indicates aliphatic C-H bonds, -OH peak is displayed at 3436.00 cm^{-1}, at 1077.59 cm^{-1} peak indicates the C-O-C ether asymmetric stretching, The peak at 1128.83 cm^{-1} is C-O-C ester stretching peak seems as bright as the carbonyl peak. The location may vary depending on the ester type. Ester carbonyl peak (C=O) is shown at 1727.62 cm^{-1}, due to the mesomeric effect, oxygen next to the ester group shares electrons to the carbon atom as inductive effect, and the partial positivity of the carbonyl carbon decreases; hence, ester carbonyl has a lower frequency than carboxylic acid. The peak is seen for C-H in-plane asymmetric bending at 1455.07 cm^{-1}.

6.2.2 Gel Permeation Chromatography (GPC) Analysis of BT4 Polyol

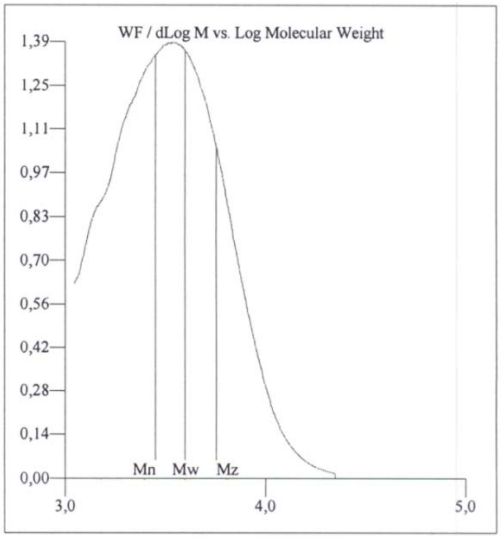


Figure 6.5 Molar weight distribution of BT4 polyol

The molecular weight averages define the polymer at various positions along the peak of the molecular weight distribution curve (Figure 6.5). Mn and Mw are the most significant averages.

HI= Mw/Mn describes the polydispersity index. The polydispersity value appears in the last column of (Table 6.1). As shown (Figure 6.5), the closer the polydispersity is to one, the narrower the molar weight distribution curve. When the figure and graph are compared, it is seen that the 1.4 PDI value creates a narrow curve. This ratio, known as polydispersity, approaches one as near-uniform oligomer chains occur. Furthermore, increasing the polydispersity value improves the material's flexibility. Depending on the application, an up or down polydispersity value may be desirable. For example, polydispersity higher than 1.2, is required for the polymers used in shoe soles.

Table 6.1 GPC results of BT4 polyol

Polyol	Targated Mn (g/mol)a	Solubility	Mw (g/mol)	Mn GPC (g/mol)c	PDI
BT4	**2000**	**THF**	**3972**	**2826**	**1.4**

The (table 6.1) shows the predicted and obtained number average molecular weight data. The values are close to each other, it gives the result that the desired polyol was obtained.

6.2.3 NMR İnterpretation of BT4 Polyol

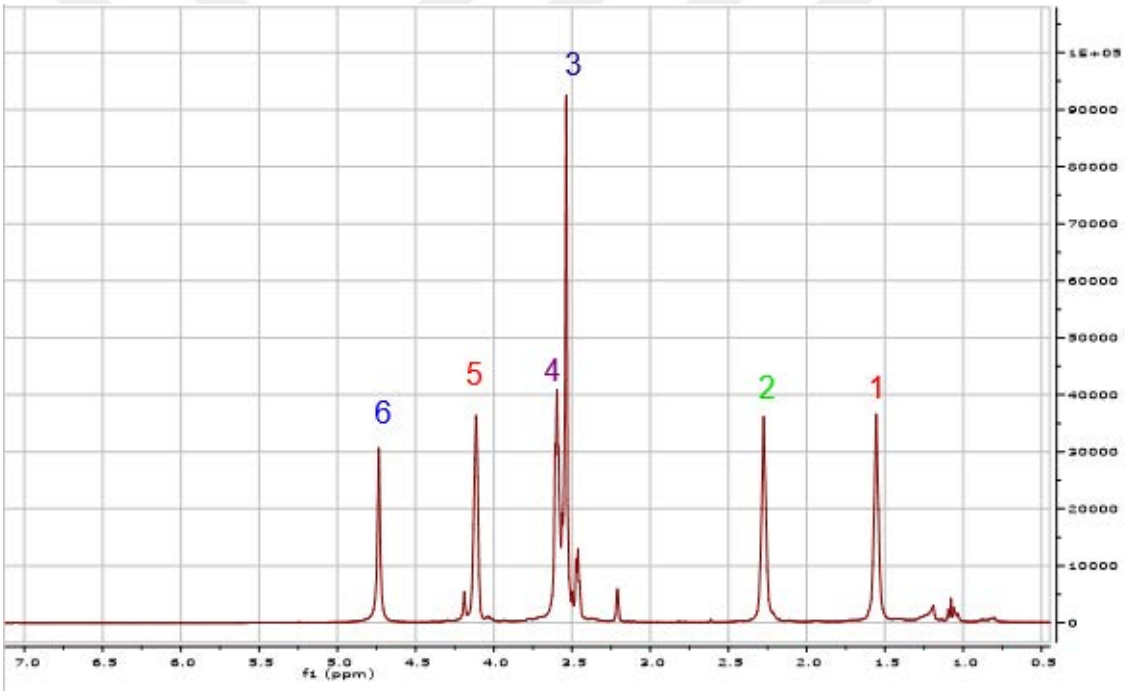


Figure 6.6 ^{1}H NMR Spectrum of BT4 Polyol

BT4 polyol NMR is shown at (Figure 6.6). The peak at the 2.25 (1H, triplet) ppm belongs the -CH2 which is next to the carbonyl**(2)**, the intense peak at 3.53 (1H, singlet) ppm indicates solvent peak (deutero methanol)**(3)**, 4.74 (1H, triplet) ppm refers -CH2 protons which adjacent to the ester group**(6)**, 3.69 (1H, singlet) ppm

belongs the -OH proton**(4)**, 4.09 (1H, triplet) ppm belongs the -CH2 adjacent to oxygen**(5)**, aliphatic -CH2 peaks appear at 1.57 ppm**(1)**.

6.3 Characterization of BT5 Polyol

6.3.1 FT-IR Spectra Result of BT5 Polyol

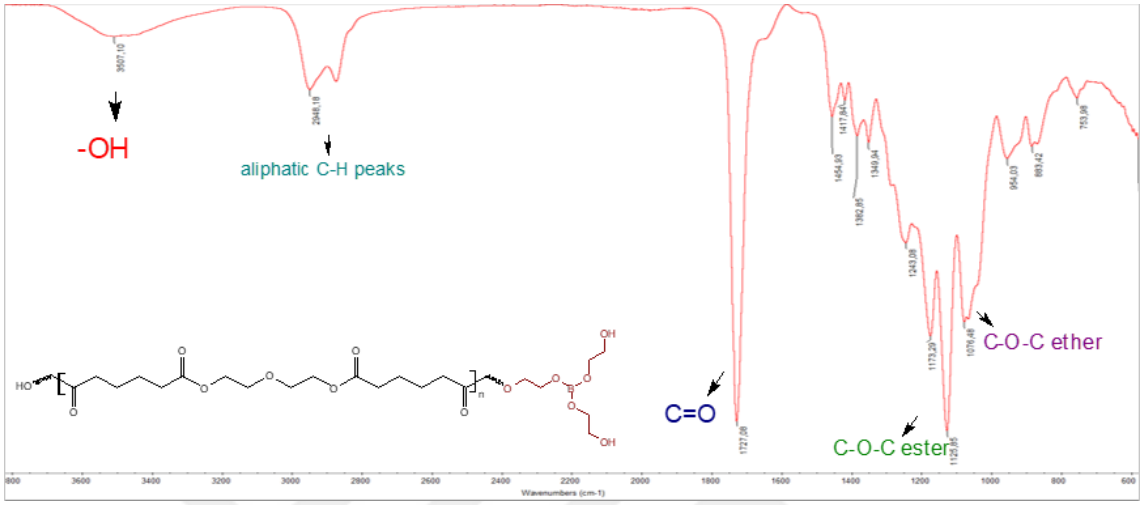


Figure 6.7 FT-IR spectrum of BT5 polyol

FT-IR of BT5 polyol is seen at (Figure 6.7). The peak at 2948.18 cm^{-1} shows aliphatic C-H bonds, -OH peak is shown 3507.10 $cm^{-1,}$ 1076.48 cm^{-1} indicate the C-O-C ether asymmetric stretching, The peak at 1125.85 cm^{-1} is C-O-C ester stretching peak appears more intense than the carbonyl peak. The location may vary depending on the ester type.

Ester carbonyl peak is shown at 1727.08 cm^{-1}, due to the mesomeric effect, oxygen next to the ester group gives electrons to the carbon atom, and the partial positivity of the carbonyl carbon decreases; hence, ester carbonyl has a lower frequency than carboxylic acid, C-O stretching peak is shown at 1076.48 cm^{-1}.

6.3.2 Gel Permeation Chromatography (GPC) Analysis of BT5 Polyol

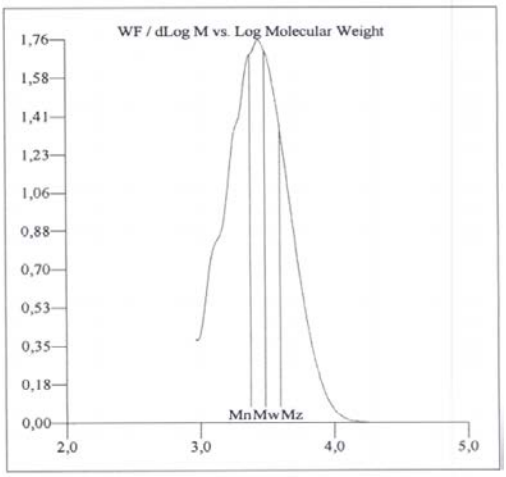


Figure 6.8 Molar weight distribution of BT5 polyol

The polydispersity value appears in the last column of (Table 6.2) and is shown (Figure 6.8), the near the polydispersity is to one, the narrower the molar weight distribution curve. When the figure and graph are compared, it is seen that the 1.28 PDI value creates a narrow curve. This ratio, known as polydispersity, approaches one as near-uniform polymer chains occur, indicating that the oligomer becomes ideal. Additionally, 1.28 PDI has flexibility, which makes the oligomer more favorable to the polymerization reaction of PU.

Table 6.2 GPC results of BT5 polyol

Polyol	Targated Mn (g/mol)a	Solubility	Mw (g/mol)	Mn GPC (g/mol)c	PDI
BT5	**2000**	**THF**	**3035**	**2362**	**1.28**

The (table 6.2) shows the predicted and obtained number average molecular weight data. The values are near to each other, As a result of this, the desired polyol was obtained.

6.3.3 NMR İnterpretation of BT5 Polyol

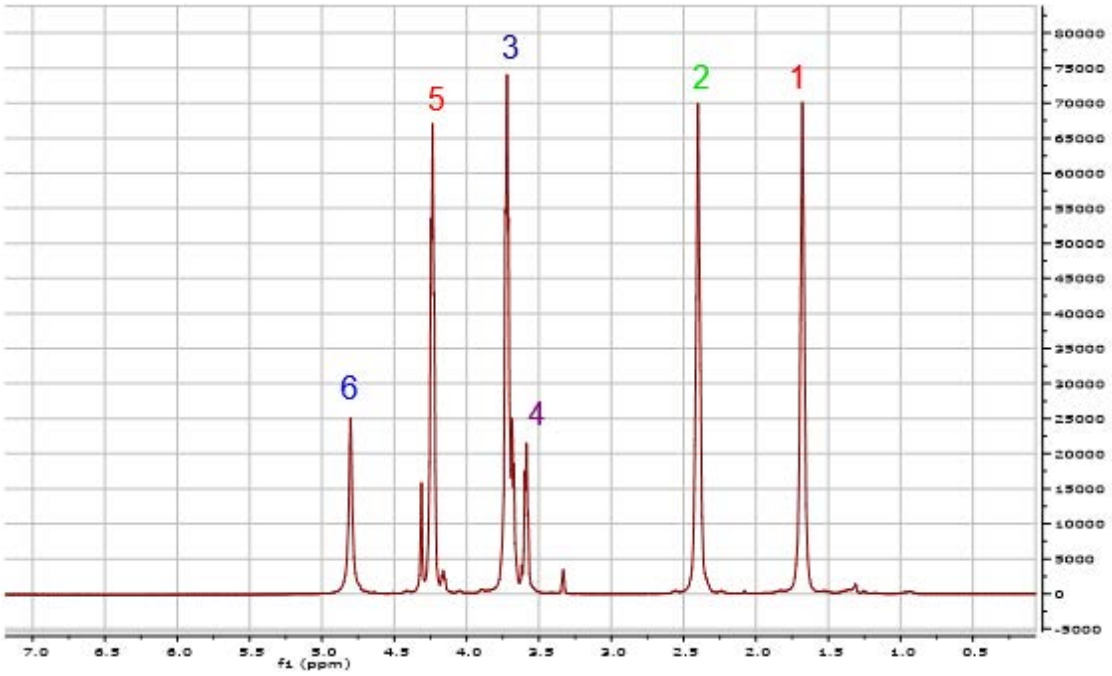


Figure 6.9 ^{1}H NMR Spectrum of BT5 Polyol

BT5 polyol NMR is shown at (Figure 6.9). The peak at the 2.37(1H, triplet) ppm belongs the-CH2 which is next to the carbonyl**(2)**, the intense peak at 3.66 (1H, singlet) ppm is a solvent peak (deutero methanol)**(3)**, 4.77 (1H, triplet) ppm refers -CH2 protons which adjacent to the ester group**(6)**, 3.58 (1H, singlet) ppm indicates OH proton**(4)**, at the 4.27 (1H, triplet) ppm the -CH2 adjacent to oxygen is appeared**(5)**, aliphatic -CH2 peaks appear at 1.68 ppm**(1)**.

6.4 Characterization of BT6 Polyol

6.4.1 FT-IR Spectra Result of BT6 Polyol

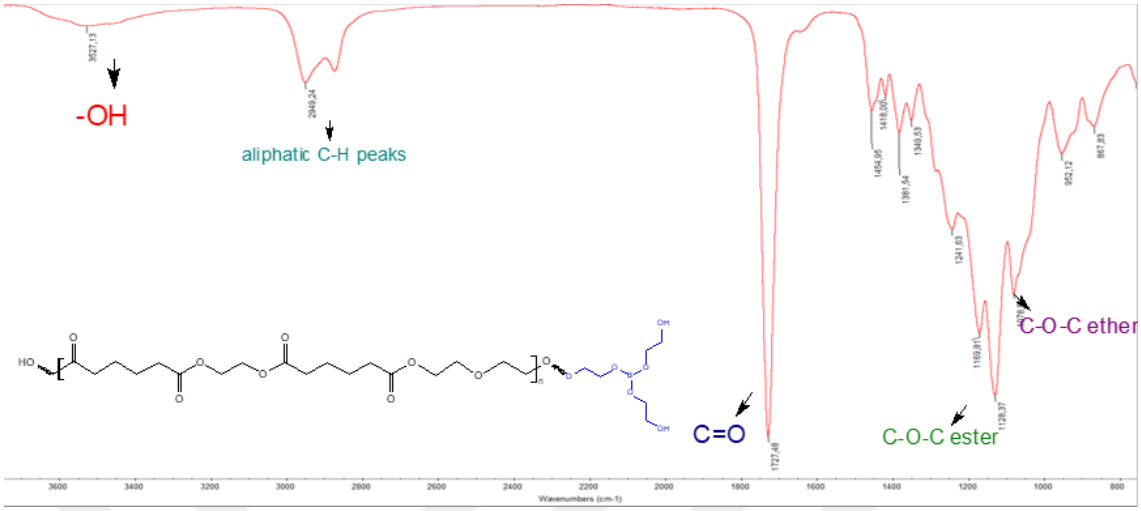


Figure 6.10 FT-IR spectrum of BT6 polyol

Infrared spectrum of BT6 polyol is shown above (Figure 6.10). The peak at 2949,24 cm^{-1} indicates the aliphatic C-H bonds in the structure, -OH bond is indicated at the peak of 3527.13 cm^{-1}. Ester carbonyl peak (C=O) is seen at 1727.48 cm^{-1}, due to the mesomeric effect, oxygen next to the ester group shares electrons to the carbon atom by inductive effeect, and the partial positivity of the carbonyl carbon decreases; therefore, the ester carbonyl has a lower frequency than carboxylic acid. The peak at 1128.37 cm^{-1} is C-O-C ester stretching peak appears intense like the carbonyl peak. The location may vary depending on the ester type. At the 1454.95 cm^{-1} peak indicates C-H in-plane bending and C-O stretching peak is shown at 1078.81 cm^{-1}.

6.4.2 Gel Permeation Chromatography (GPC) Analysis of BT6 Polyol

When the (Figure 6.11) and (Table 6.3) are compared, it is seen that the 1.28 PDI value creates a narrow curve. This ratio, known as polydispersity, approaches one as near-uniform polymer chains is obtained, indicating that the polyol becomes ideal to end-use application.

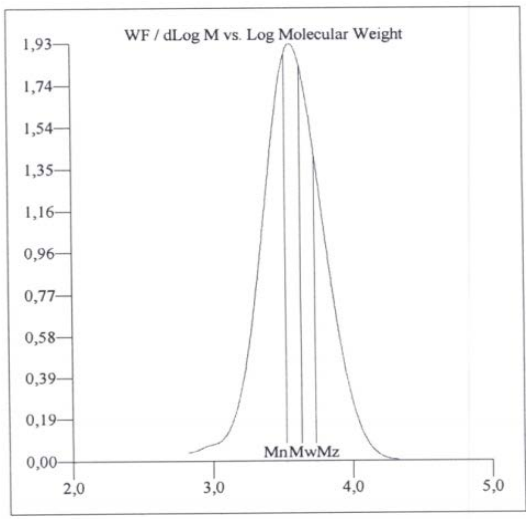


Figure 6.11 Molar weight distribution of BT6 polyol

The (Table 6.3) shows the targeted and in the fourth column, obtained number average molecular weight data. In comparison to other polyols, the results are not particularly close. The reason for this, the degree of polymerization may be longer or shorter than expected, it depends on the reaction conditions and the reactants which utilized. In our trial with only meg, the chain grew longer than expected.

Table 6.3 GPC results of BT6 polyol

Polyol	Targeted Mn (g/mol)a	Solubility	Mw (g/mol)	Mn GPC (g/mol)c	PDI
BT6	**2000**	**THF**	**4286**	**3345**	**1.28**

6.4.3 NMR İnterpretation of BT6 Polyol

BT6 polyol NMR is shown at (Figure 6.12). The peak at the 2.41 (1H, triplet) ppm belongs the -CH2 which is next to the carbonyl **(2)**, 4.82 (1H, triplet) ppm refers -CH2 protons which adjacent to the ester group **(6)**, 3.40 (1H, singlet) ppm refers OH proton **(4)**, at the 4.23 (1H, triplet) ppm the -CH2 adjacent to oxygen is appear

(5), aliphatic -CH2 peaks appear at 1.68 ppm **(1)** and the intense peak at 3.61 (1H, singlet) ppm is a solvent peak (deutero methanol) **(3)**.

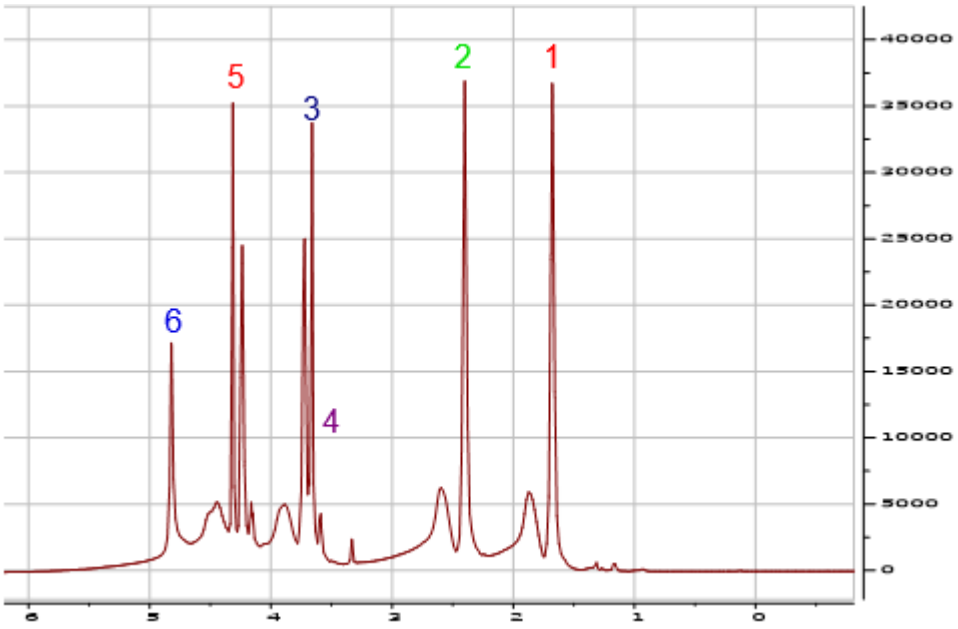


Figure 6.12 ^{1}H NMR Spectrum of BT6 Polyol

6.5 Boron-based Cross-linked Polyurethane Characterization

6.5.1 Tensile Break Test of Polyurethane Plates

According to (Table 6.4) data, polyurethanes with boron-based crosslinkers demonstrated good flexibility, regardless of the presence of expol in their structure. Based on these values, it can be interpreted that boron provides flexibility to the polymer structure. Comparison of the flexibility of polyurethanes is apparently seen in (Figure 6.13) below, the cross-linked PU without expol seems to perform best.

Table 6.4 Tensile break test results of PUs

POLYMER	THICKNESS (mm)	FLEXIBILITY (%)	BREAKING (N)	BREAKING(N/mm^2)
Boron-based Cross-linked PU (with expol)	9.18 mm	106%	195 N	2.26 N/mm^2
Boron-based Cross-linked PU (without expol)	8.63 mm	123%	181.5 N	2.22 N/mm^2
Standard PU	10.26 mm	106%	249 N	2.419 N/mm^2

Expol provides arrangement/stacking and surface smoothness to the polymer structure and the part that provides arrangement and stacking is styrene in expol structure. It has been observed that the structure of the boron-based polyurethane synthesized without expol is less stacked, therefore its stretching is greater, but besides, its resistance to rupture has decreased a little (Figure 6.14).

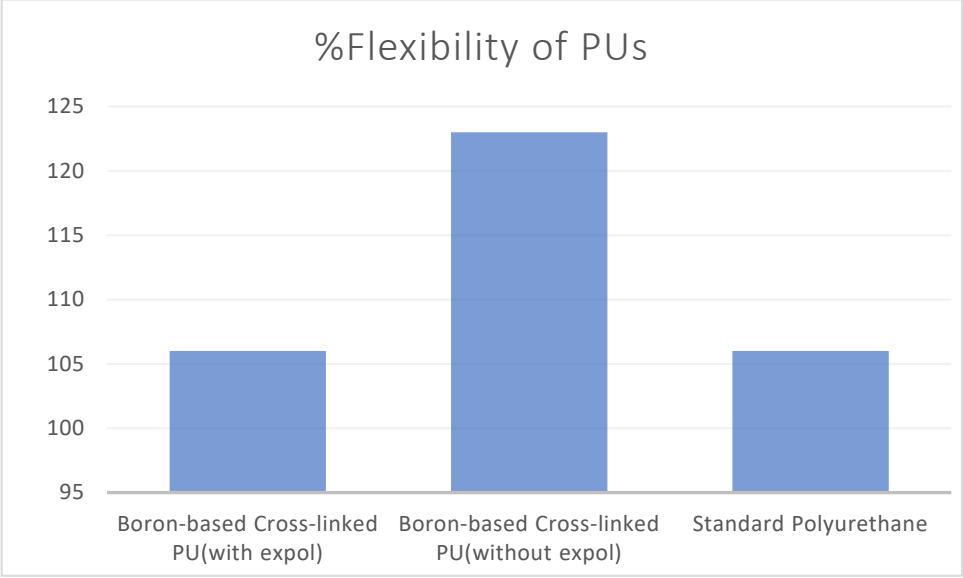


Figure 6.13 Comparison of the flexibility of polyurethanes

The standard polyurethane synthesized at the factory contains expol in its structure, but no boron or boron-based substance. This standard polymer has the same flexibility as boron-based polyurethane (with expol). According to these data, the main component that affects flexibility is the presence of expol in the polymer structure (Figure 6.13). Besides, it is seen that boron-based expol+ PU and standard polyurethane have comparable flexibility.

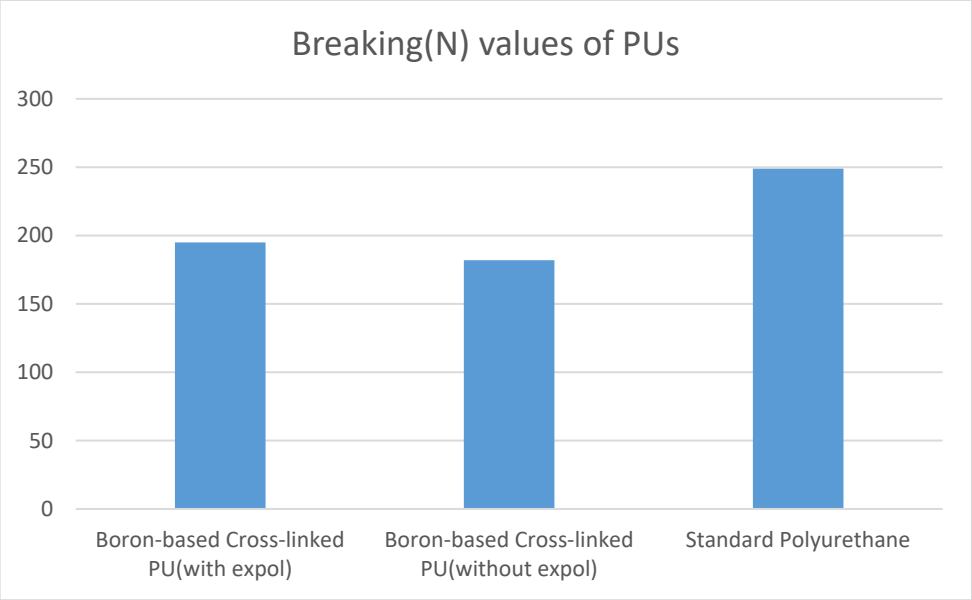


Figure 6.14 Comparison of the breaking values of polyurethanes

As the graph can be seen in (Figure 6.14), the rupture strength of boron-based PU is comparable to the standard polymer. The one with the worst resistance is PU which does not contain expol in its structure. While its flexibility is improved, its strength has decreased.

6.5.2 Compression Test of Polyurethane Plates

Compression testing is often performed on thick pads. This sort of test setup is commonly used to measure the compression modulus of foams and rubbers. Thus, adequate function in continuous usage for plastic objects such as carpet pads, shoe soles, knee and elbow protective gear can be predict[83].

The resultant PUs were compressed to 40% of their original height for a predetermined period of time at a room temperature and left for a specified period

of time then, their thickness at the end of compression was measured and the C_B value was calculated (Table 6.5). The following formula was used for this calculation.

$C_B = [(t_o - t_i) / (t_o - t_n)] * 100$

In formula, t_o original sample thickness, t_i sample thickness after testing, and t_n, spacer thickness during testing.

Table 6.5 Compression set

TYPES OF POLYURETHANES	ORIGINAL SPECIMEN THICKNESS (mm)	SPECIMEN THICKNESS DURING THE TEST (mm)	SPECIMEN THICKNESS AFTER TESTING (mm)	**C_B VALUES (%)**
STANDARD	**17.5**	**7**	**14.5**	**28.57**
EXPOL+	**17.5**	**7**	**14.5**	**28.57**
EXPOL -	**17.5**	**7**	**14**	**33.33**

After compression, the thickness of standard and expol+ polyurethanes is the same. Furthermore, it is seen that the thickness of the expol- is less than others (Table 6.6). This means that expol- PU has deformed easier than the other PU's trials.

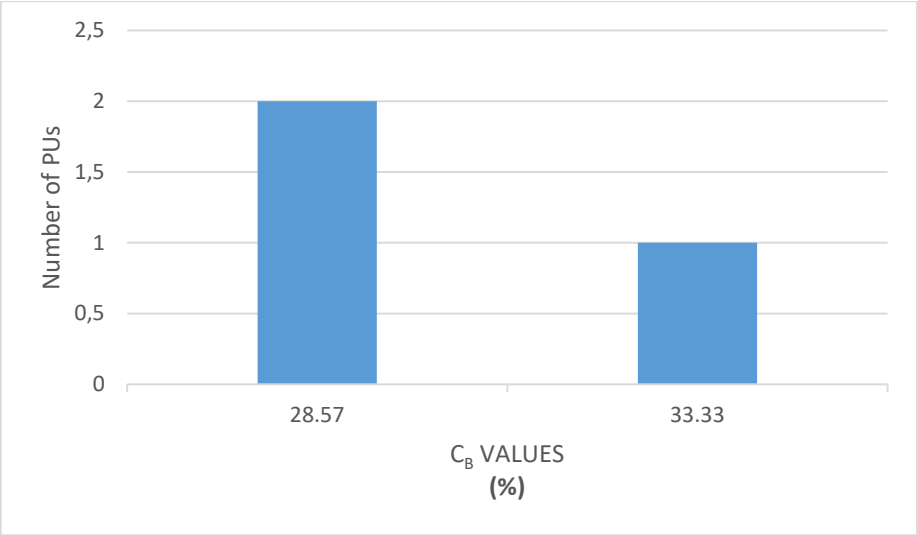


Figure 6.15 C_B values according to Pus

As a result of the test, the C_B values of expol+ and standard PU were the same. It is seen at the same point in the (Figure 6.15). Their resistance to pressure is greater than the expol- PU. As a result, the absence of expol in the PU structure lowered polymer strength.

6.5.3 Burning Test of Polyurethane Plates

Boron contributes long ignition delay and low combustion rates to the structure. Reference[84] suggests that these properties may be due to inhibition of the naturally occurring oxide layer on the particle surface. In order to see the fire retardant effect that boron gives to the PU structure, a comparative combustion test was carried out according to B2 combustion standards[85]. The plates were exposed to flame for 10 seconds with a flame gun to evaluate the fire behavior of building materials and elements. Burning test results are shown in (Figure 6.16), from left to right, the first and third plates are made of standard material that does not contain boron, the second plate is non-expol boron crosslinked, and the last plate is expol+ boron crosslinked PU plates.



Figure 6.16 Fire testing results of the building material

As a result, expol+ boron-based polymer demonstrated the best fire resistance in the test. There was no dripping or melting and no smoke, the flame was self-extinguishing. The boron-based non-expol PU plate produced the second best results. On the other hand, burning continued in the polyurethane structures without boron. Therefore, it has been confirmed that boron has a fire retardant effect on the structure.

7
CONCLUSIONS AND DISCUSSION

The purpose of this research is to prevent the weaknesses of polymeric materials, such as flammability and leaking from the structure at high temperatures, from limiting the usage area. A different way than conventional was utilized for this study, and the synthesized crosslinker was integrated into the polymer structure. Fort his purpose, borate ester was synthesized as a crosslinker.

Boron, one of Turkey's natural resources, was employed in the synthesis of the crosslinker, for the purpose of turning boron into a more valuable substance and to provide it new application areas.

The first synthesis attempt for borate ester was carried out using boric acid and monoethylene glycol (MEG) in the toluene solution. These reactants, 2.245 g boric acid, 10 g monoethylene glycol (MEG) and toluene (as solvent) were placed in a 100 mL round- bottom flask and stirred for a while to dissolve. The round-bottom flask was placed in an oil bath with dean-stark and reflux apparatus, and two drops of sulfuric acid were added as a catalyst. The reaction has continued at 170°C, but toluene, which was predicted to come out with water during the reaction, was not be released. There was no product produced. As a result, it was determined that the next experiment would be conducted without a solution. In the second attempt, no solvent was used and this reaction was successful.

The borate ester, which is an esterification reaction, was obtained with a yield close to 100% and the excess MEG was evaporated and purified. Since the reaction is an equilibrium reaction, effective water withdrawal enhances the reaction yield. IR and NMR results confirmed the construct.

The molecular weight range and polydispersity values of the polyols synthesized with the acquired crosslinker were within the desired ranges and different polyurethane trials were carried out utilizing one of the polyols.

The polyols and crosslinker were synthesized using two distinct catalysts. Since the organometallic catalyst is affected by water, firstly H_2SO_4 catalyst was employed and after removing the majority of the water from the reaction environment, Tyzor tpt catalyst was added for rest of the reaction. Thus, the yield was increased more.

In the mechanical test's results, non-expol boron-based PU demonstrated the best flexibility but it was also observed that its durability decreased at the same time. Besides, expol+ PU's tensile and strength performance is comparable to that of standard PU.

Furthermore, boron-based PUs showed better fire resistance than standart PU. When compared to expol- PU, the expol+ boron-based polymer displayed superior fire resistance.

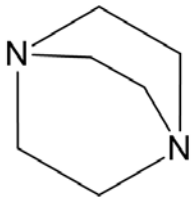
In the context of the combustion mechanism, according to the Glassman criteria[86], boron does not burn in the vapor phase. These characteristics are thought to contribute to the first low temperature boron oxidation being restricted to the passage of elemental boron or oxygen through the molten B_2O_3 shell. When the shell is volatilized and the clean surface of molten boron droplets heterogeneously interacts with the surrounding oxidizers at higher temperatures, further oxidation and full-fledged combustion occur. The boron ignition and combustion process presently describes these two steps.

The first step is completed when the oxide is fully eliminated. The diffusion of reactive species through the B_2O_3 shell limits the pace of the reaction during the first stage.In the second step, the rate is restricted by the kinetics of gas phase oxidizer contact with a clean boron surface. As a result, it is thought that the boron in the structure affects the combustion retardation in this way, he response processes, however, are not known in detail.

Two types of DABCO catalysts TEGO Amine MEG or with full name is 1,4-diazabicyclo [2.2.2] octane (Figure 7.1) and quaternary DABCO (Figure 7.2) were utilized in the polyurethane synthesis. TEGO Amine MEG, tertiary amine catalyst initiates the reaction at the beginning time and above 60-70°C, quaternary DABCO

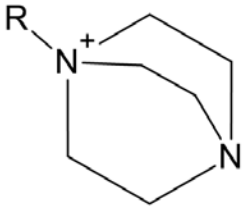
catalyst becomes active. The second catalyst is a quaternary ammonium salt and around 60-70°C hydrogen leaves the molecule and molecule becomes active that way.

The use of two catalysts in these polymerization reactions was done to prevent deformation during the molding process. Two step-by-step activated catalysts were used to extend the polyurethane rise time.



1,4-Diazabicyclo[2.2.2]octane

Figure 7.1 TEGO Amine MEG catalyst structure



Quaternary DABCO

Figure 7.2 Quaternary DABCO catalyst structure

An formation mechanism for the crosslinking borate ester is proposed in (Figure 7.3). The same steps continue until all 3 branches of boric acid are converted to esters.

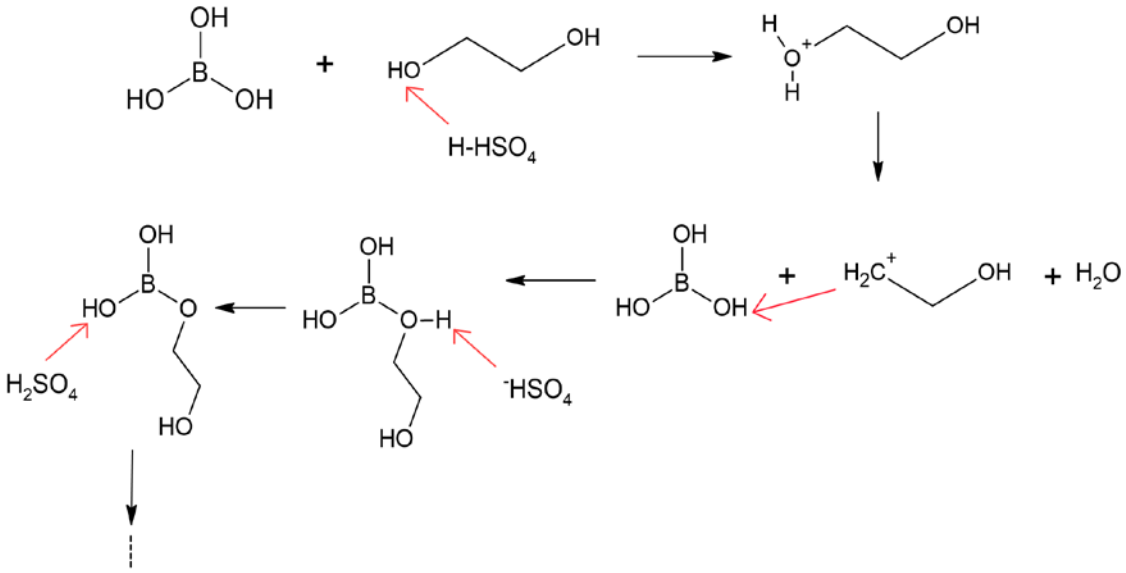


Figure 7.3 Proposal for a process for the production of borate ester

In (Figure 7.4), a structure is proposed for the way the boron crosslinker binds to the polyol structure[87].

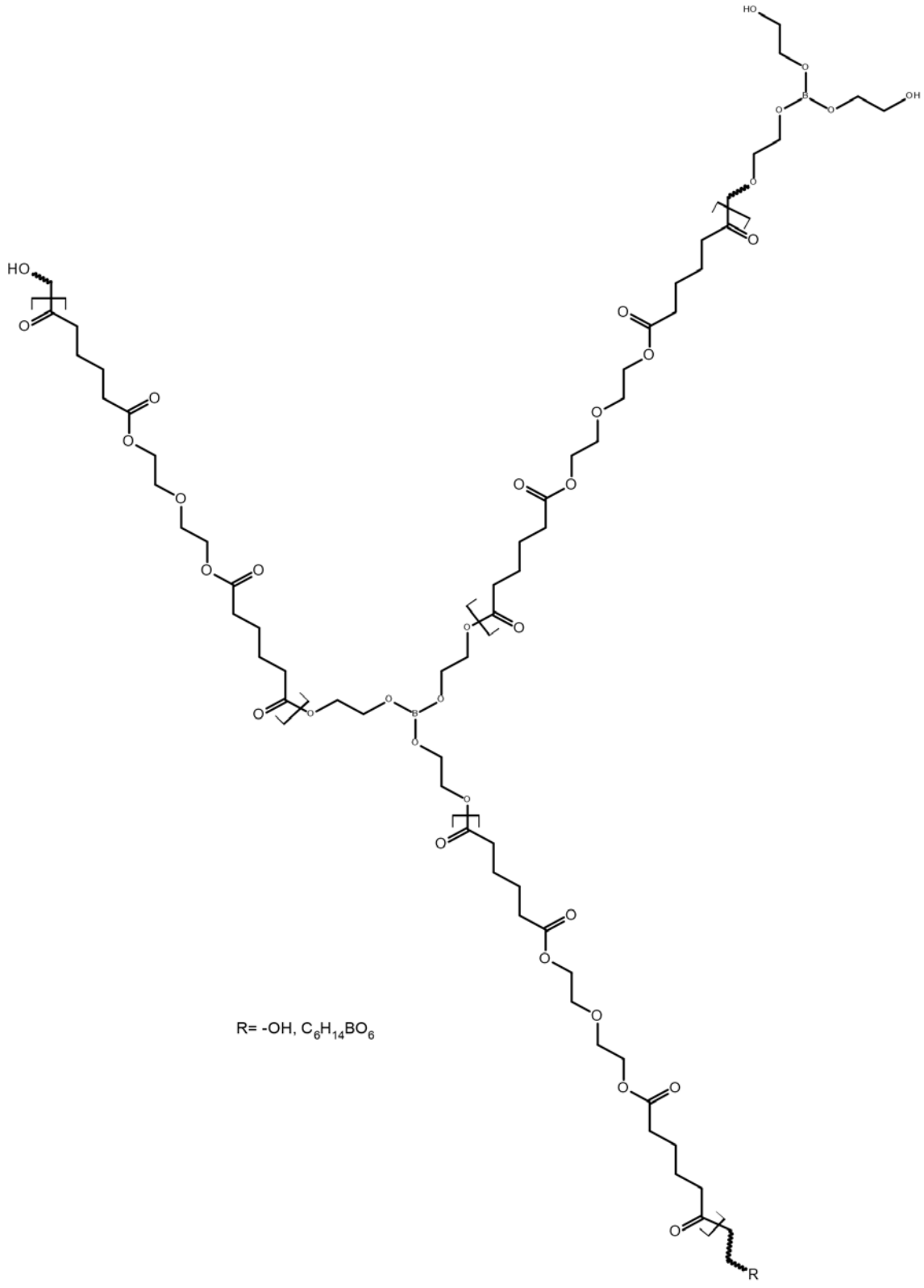


Figure 7.4 Suggestion for the crosslinker's presence in the polyol structure

In the (Figure 7.5) below, it is suggested for the position of the crosslinker in the polyurethane structure and the hydrogen bonds are shown in red color.

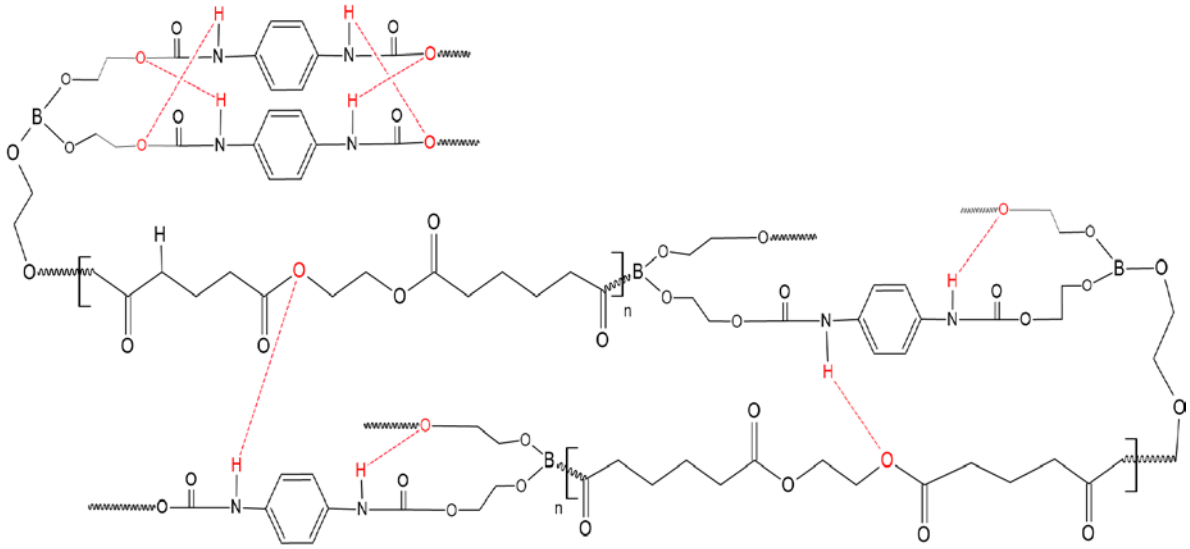


Figure 7.5 Suggestion for the crosslinker's presence in the polymer structure

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A
FT-IR SPECTRA

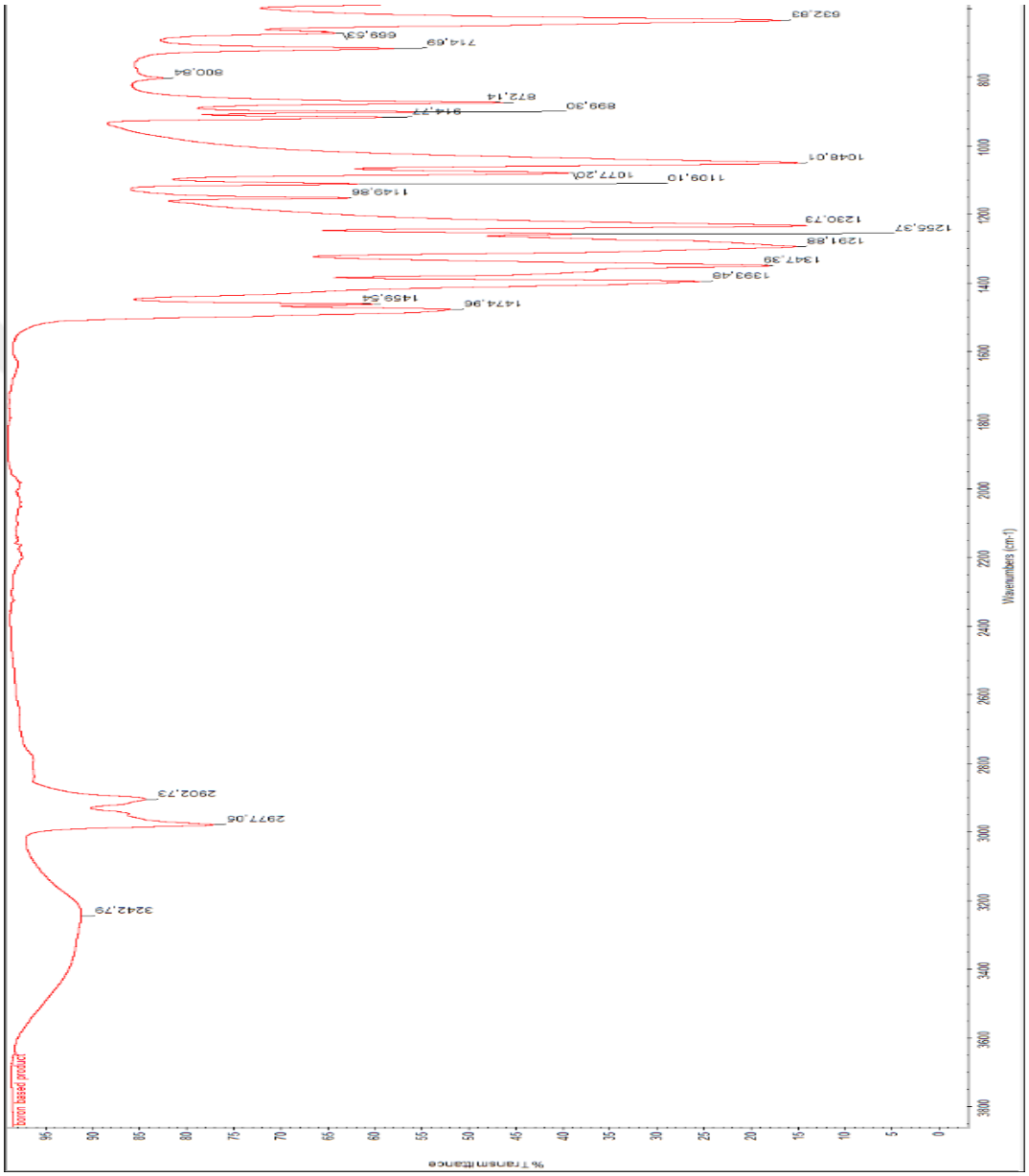


Figure A1 FT-IR of borate ester

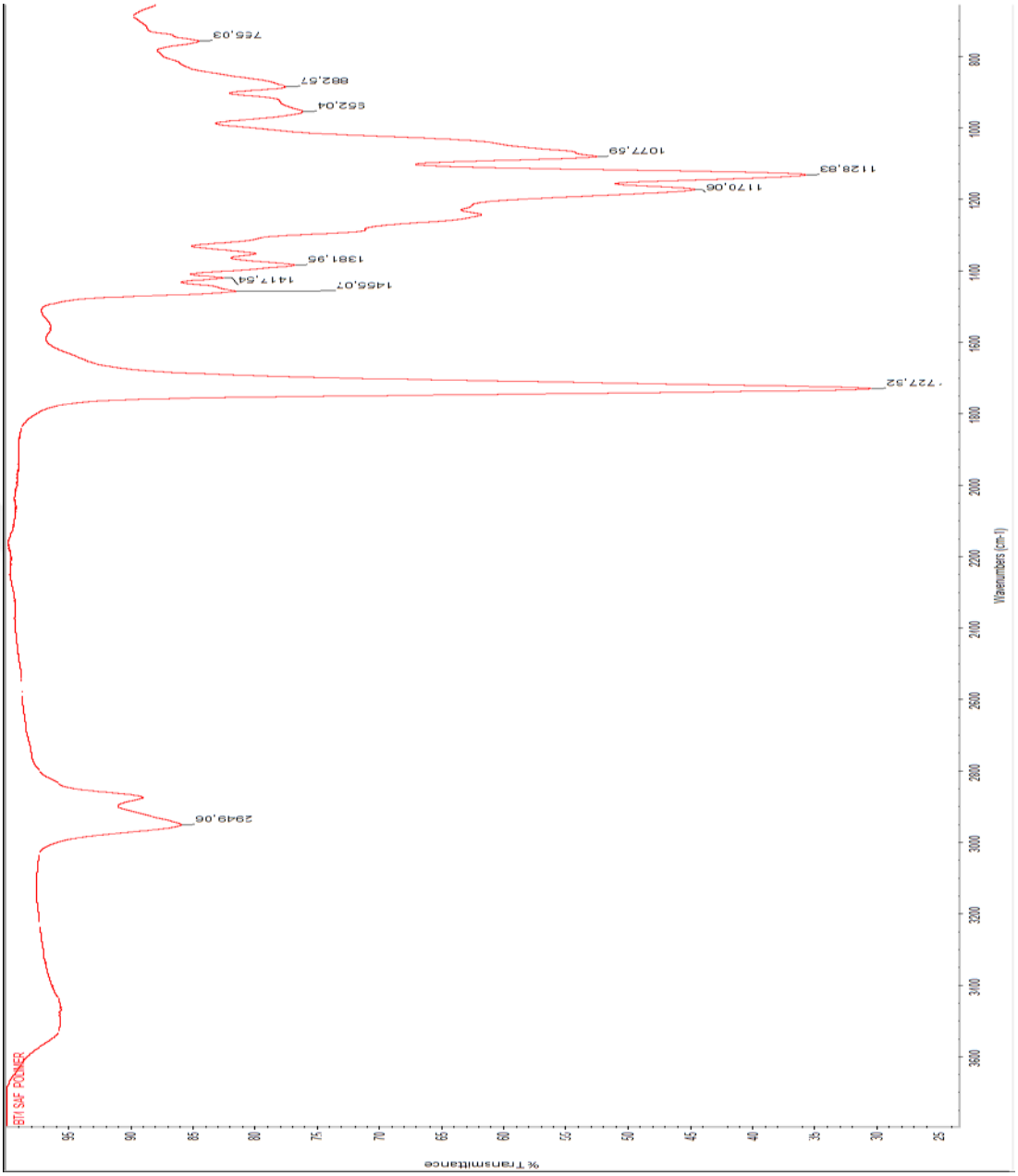


Figure A2 FT-IR of BT4 coded boron-based polyol

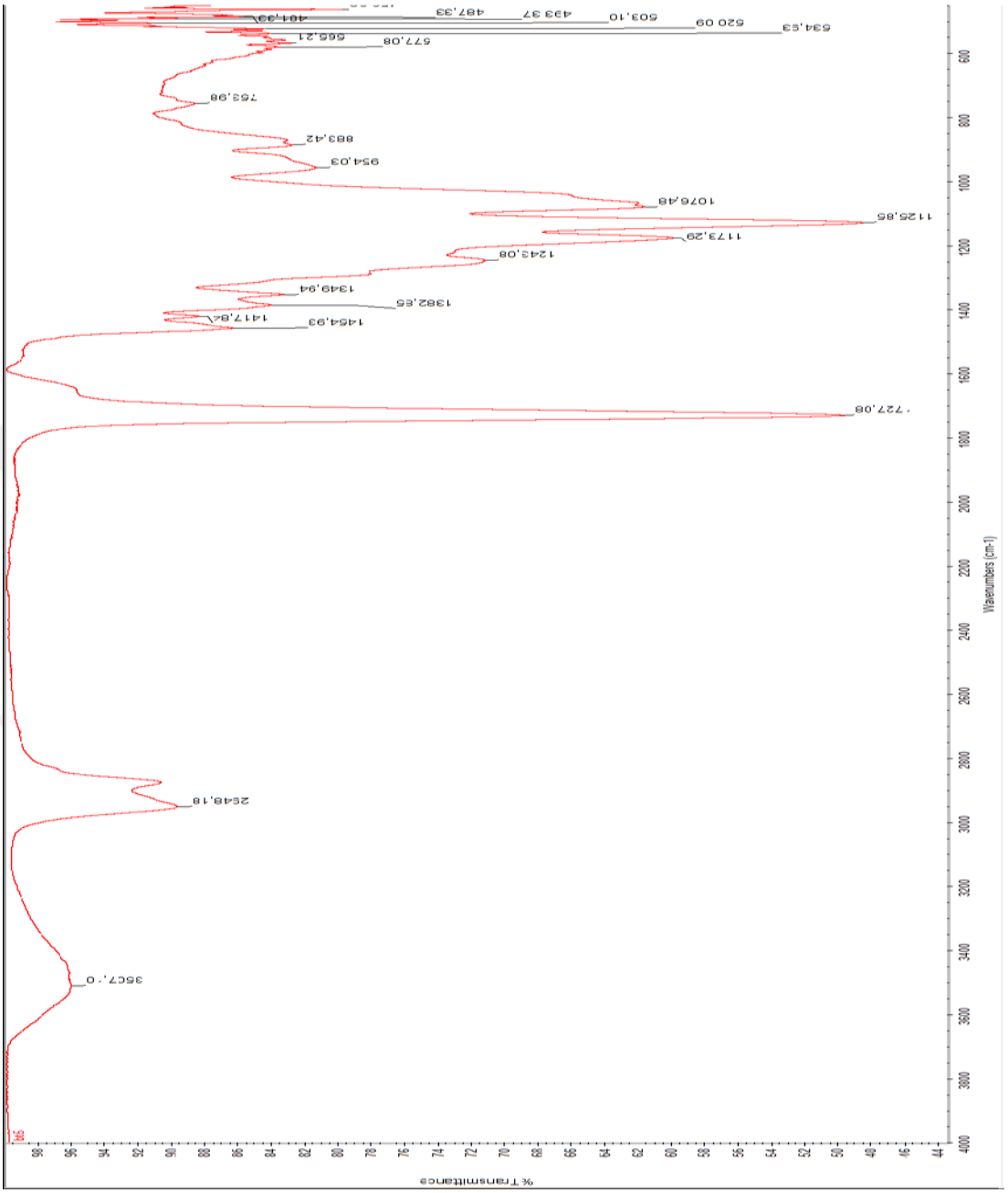


Figure A3 FT-IR of BT5 coded boron-based polyol

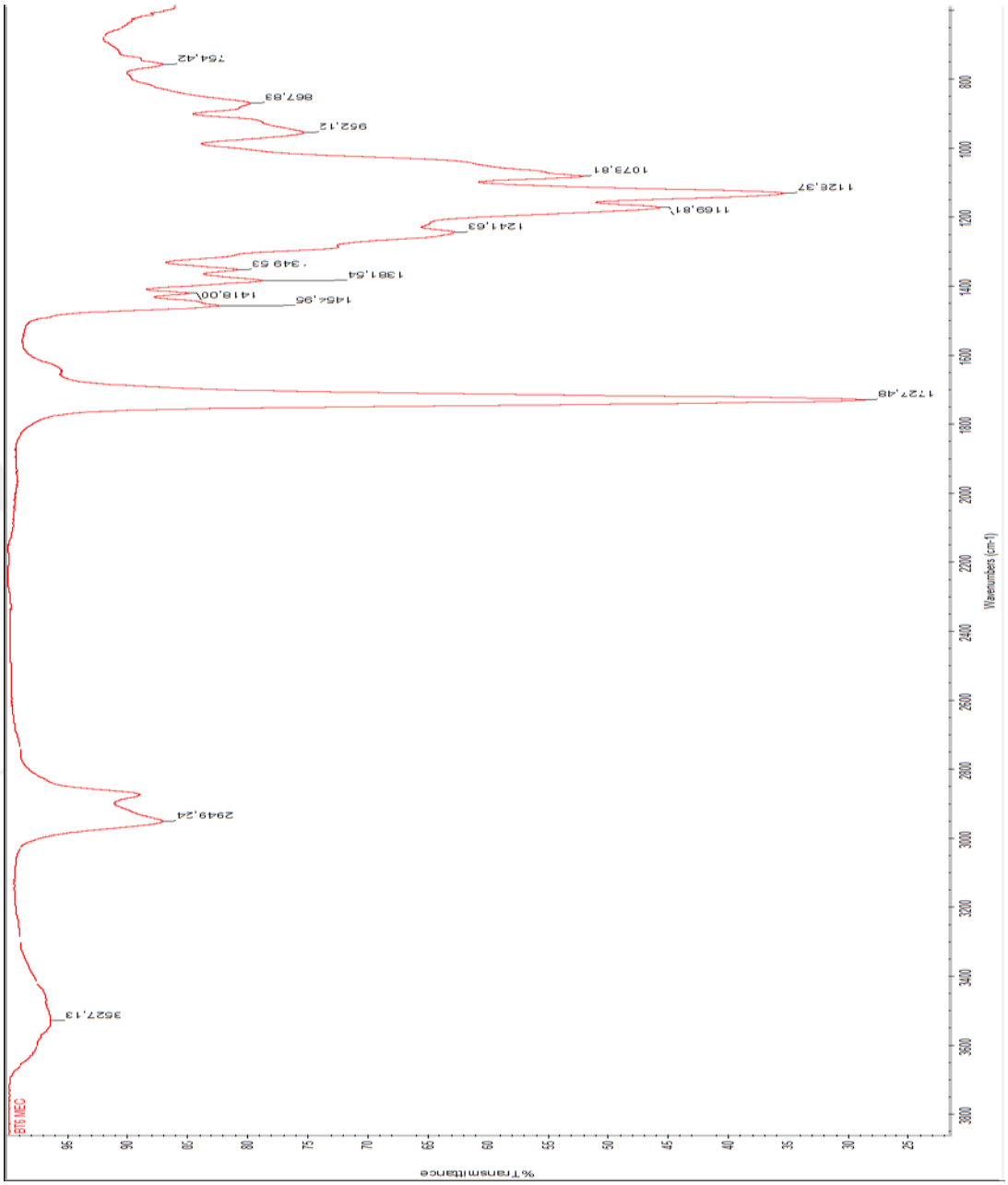


Figure A4 FT-IR of BT6 coded boron-based polyol

B
^{1}H NMR SPECTRA

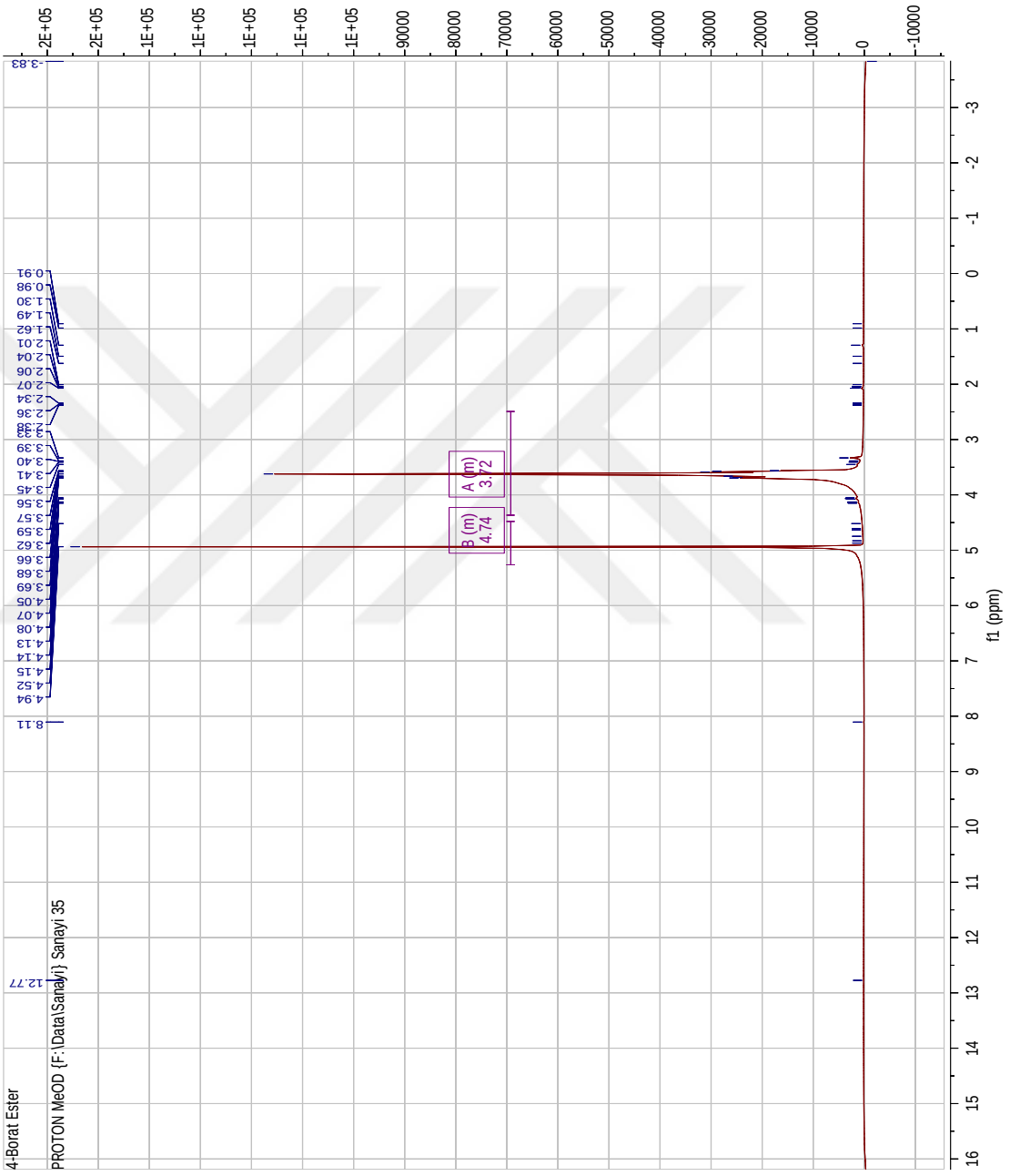


Figure B1 NMR of borate ester

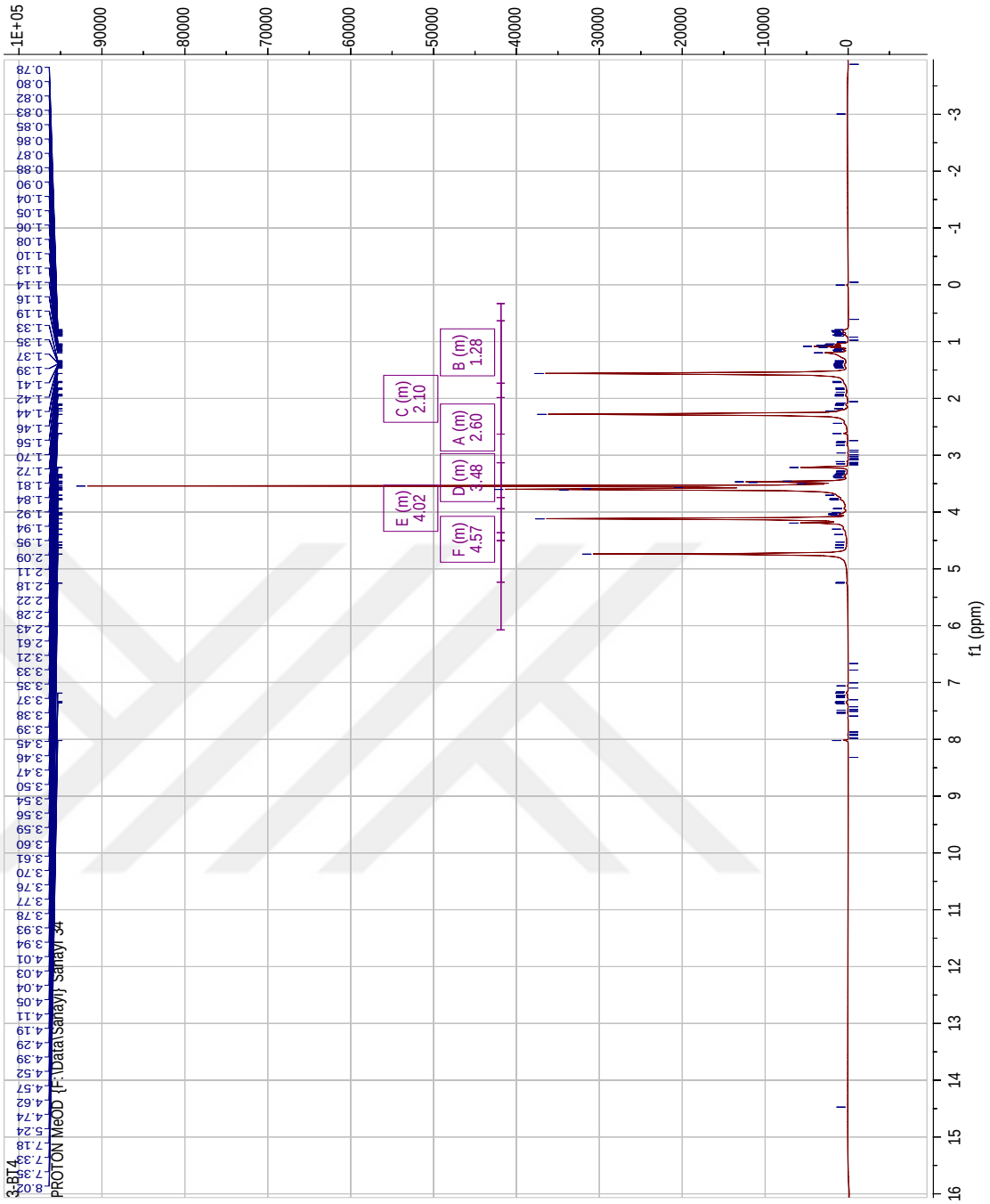


Figure B2 NMR of BT4 coded polyol

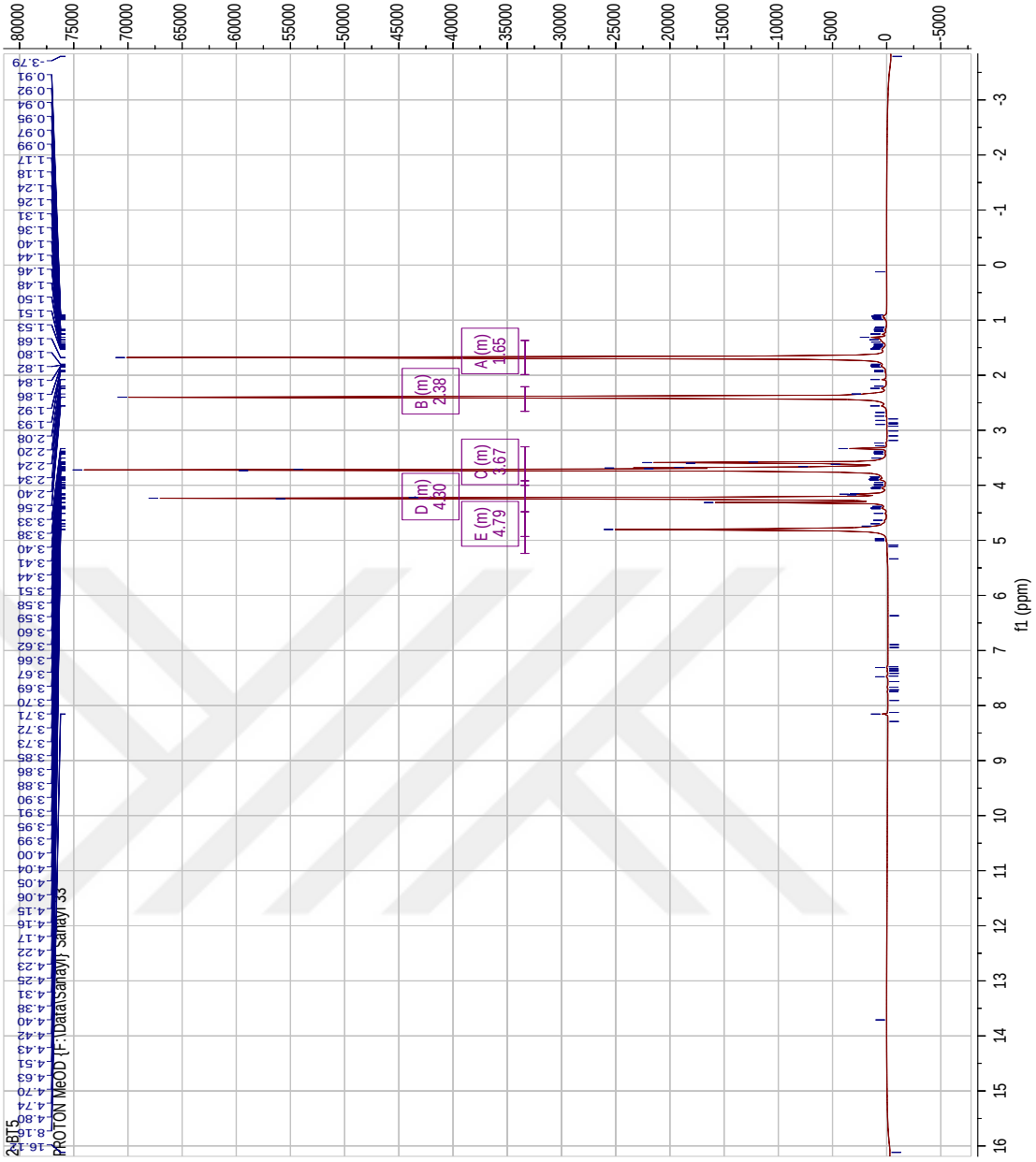


Figure B3 BT5 coded polyol

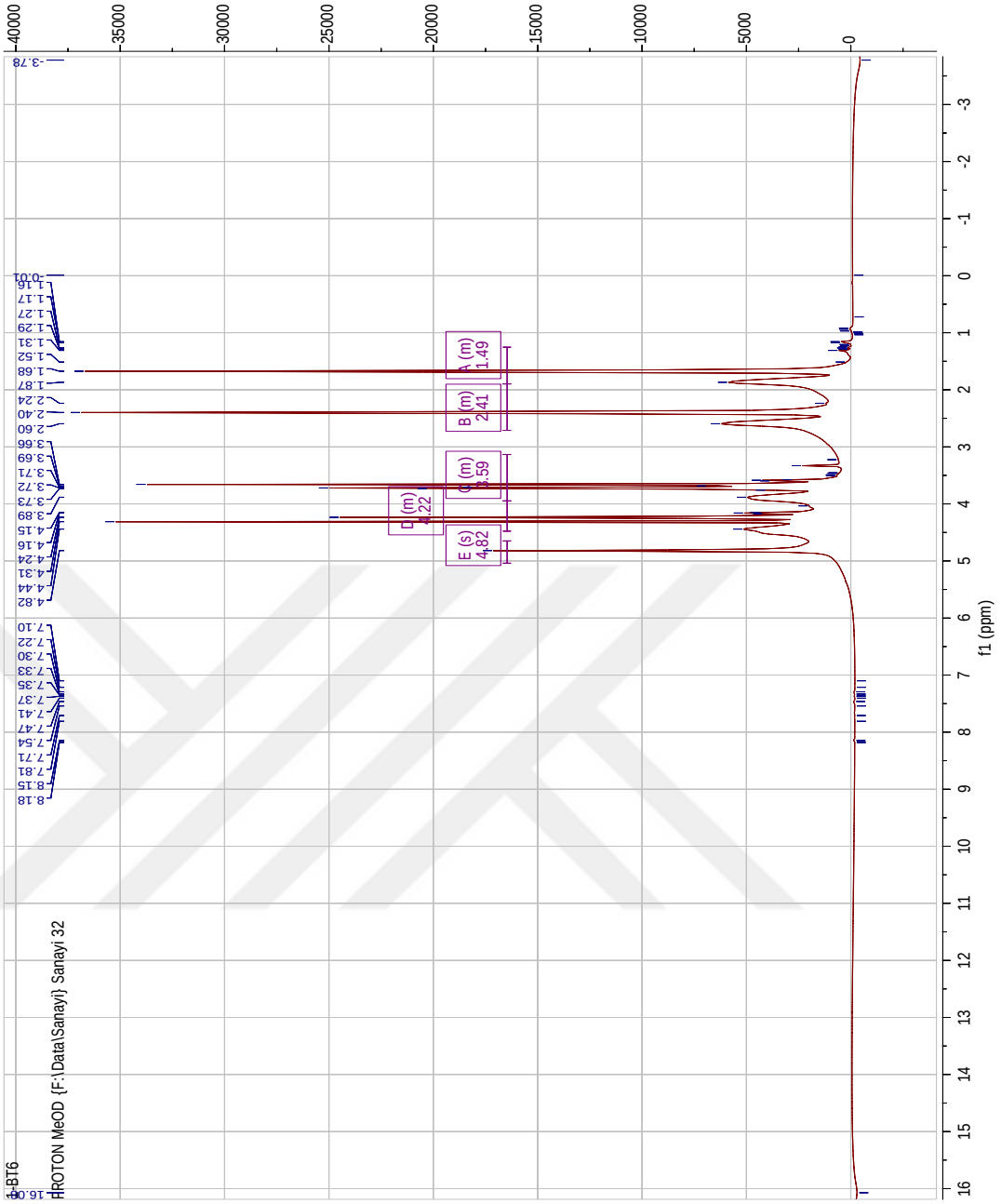


Figure B4 BT6 coded polyol

Publications from the thesis

Conference Papers

1. B. TAYLANLI and M. TULU, '' Spectroscopic and Rheological Analysis of Polyester Polyols'' IGSCONG'21, International Graduate Studies Congress, 17-20 June 2021, Turkey.