ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS OF POLY-(5,6-ISOPROPYLIDENE-L-ASCORBIC ACID) THROUGH ADMET POLYMERIZATION

M.Sc. THESIS

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ADMET POLİMERİZASYONU YÖNTEMİ KULLANARAK POLİ-(5,6-IZOPROPİLİDEN-L-ASKORBİK ASİT) SENTEZİ

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Meir ABUAF, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID 515121014, successfully defended the **thesis** entitled "**SYNTHESIS OF POLY-(5,6-ISOPROPYLIDENE-L-ASCORBIC ACID) THROUGH ADMET POLYMERIZATION**", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 15 December 2014
Date of Defense : 21 January 2015

To my family and friends,

FOREWORD

This master study has been carried out at Istanbul Technical University, Chemistry Department of Science & Letter Faculty.
I would like to express my gratitude to my thesis supervisor, Prof. Dr. Gürkan HIZAL and co-supervisor Prof. Dr. Ümit TUNCA for offering invaluable help in all possible ways, continuos encouragement and helpful critisms throughout this research.
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December 2014

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ABBREVIATIONS

^{1}H NMR	**:**Hydrogen Nuclear Magnetic Resonance Spectroscopy
AcCl	:Acetyl chloride
ADMET	**:**Acyclic Diene Methathesis
CH_2Cl_2	**:**Dichloro methane
$CHCl_3$	**:**Chloroform
$CDCl_3$	**:**Deuterated chloroform
CM	:Cross methathesis
d-DMSO	: Deuterated Dimethyl sulfoxide
DCM	**:**Dichloromethane
DMAP	**:**4-dimethylaminopyridine
DSC	**:**Differantial scanning calorimetry
G-1	:Grubbs 1st generation catalyst
GH-2	**:**Grubbs 2nd generation catalyst
GPC	**:**Gel Permeation Chromatography
ODCB	**:**Ortho- Dicholorobenzene
PC	**:**Polycarbonate
RCM	**:**Ring closing methathesis
ROCM	**:**Ring opening cross methathesis
ROMP	**:**Ring opening methathesis polymerization
THF	**:**Tetrahydrofuran

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SYNTHESIS OF POLY-(5,6-ISOPROPYLIDENE-L-ASCORBIC ACID) THROUGH ADMET POLYMERIZATION

SUMMARY

Ascorbic acid is a naturally occurring organic compound with antioxidant properties. It is a white solid, but impure samples can appear yellowish. It dissolves well in water to give mildly acidic solutions. The overwhelming majority of species of animals (but not humans or guinea pigs) and plants synthesize their own vitamin C. Therefore, some animal products can be used as sources of dietary vitamin C.

Vitamin C is most present in the liver and least present in the muscle. Since muscle provides the majority of meat consumed in the western human diet, animal products are not a reliable source of the vitamin.

There are three main types of biological activity distinctive to L-ascorbic acid in plants and animals. These are (1) its function as an enzyme co-factor; (2) as a direct physiological radical scavenger and finally; (3) as a donor/acceptor in electron transport in both plasma membrane and chloroplasts

1) Function as an enzyme co-factor

L-ascorbic acid is involved in the modulation of a number of important enzymatic reactions such as in the metabolism of several amino acids which lead to the formation of hydroxyproline, hydroxylysine, norepinephrine, serotonin, carnitine and homogenistic acid. It has also been found to be essential for the normal functioning of the osteoblasts,fibroblasts, adrenal hormones and carnitine biosynthesis.

2) Function as a direct radical scavenger

Since oxygen is required for cell viability in both plant and animal systems, it is essential that a mechanism be available to control the reactive oxygen species (ROS) generated during cellular metabolism and from exogenous sources and environmental chemicals. L-ascorbic acid interacts enzymatically and non-enzymatically with ROS and their derivatives to neutralize their cellular damaging effects

3) Function as a donor/acceptor in electron transport

The biochemical and physiological functions of L-ascorbic acid primarily depend on its reducing properties and its role as an electron carrier.35, 115 L-ascorbic acid and its single-electron oxidized product, semidehydro-L-ascorbate functions as a cycling redox couple in various electron transport reactions and changes the activities of cytochromes, the electron membrane-protein carriers.

In addition, simple derivatives of L-ascorbic acid have been shown to possess important pharmacological properties. For example 5,6-Omodified ascorbic acid derivatives have been found to be effective anti-tumor agents for various human cancers, and induce apoptosis in tumor cells and C2 alkylated derivatives have been shown to have immuno-stimulant activity. Recently, the chemistry of ascorbic acid has also been exploited to develop strategies for central nervous system drug delivery.

Because of using in drug industries lots of scientists are interested in L-Ascorbic Acid. However there are huge studies in L- Ascorbic Acid area, there is no investigation about polymerization of the structure. Because of having antioxidant and redox properties which are closely associated with the electron rich 2, 3-enediol moiety of the molecule, free radical polymerization can not be used. We thought that polymerization type should be one of the step-growth polymerization.

Acyclic diene metathesis is considered to be a step-growth polycondensation-type polymerization reaction, which makes strictly linear chains from unconjugated dienes.10-14 As such, ADMET requires very high monomer conversion rates to produce polymer chains of considerable size. Therefore, the more active 2nd generation catalysts such as 2 and 3 are usually better suited for ADMET than bisphosphine ones. Since the loss of ethylene is the main driving force behind the cross metathesis of terminal olefins, the efficient removal of this volatile gas from the reaction vessel is also crucial. Consequently, although olefin metathesis with ruthenium catalysts is, in general, very mild and does not require stringent air removal, ADMET greatly benefits from conditions which promote the diffusion and expulsion of ethylene (i.e., higher reaction temperatures, application of vacuum, and rigorous stirring). In addition, the use of concentrated or even neat solutions of monomers is usually helpful to polycondensation reactions but, in the case of ADMET, a very viscous solution might be detrimental to efficient stirring and ethylene removal. Furthermore, as a consequence of the poor molecular weight control of stepgrowth reactions, the polydispersity index (PDI) of polymers obtained by this method is usually quite large. However, an important advantage of ADMET is that it allows a large variety of monomers to be polymerized since terminal olefins are quite easy to install. Many functional groups and moieties of interest can be incorporated into such polymers directly through monomer design, due to the excellent tolerance of ruthenium catalysts.

In this study Polyvitamine is synthesised from L-Ascorbic acid backbone monomer via ADMET method using both bulk and solution polimerization.

In bulk polimerization monomer was reacted with each catalysts G-1 and GH-2. For mixing reactants DCM was used then evaporated from reaction mixture. Both two catalysts were reacted three different temperatures at 40^{o}C, 60^{o}C ve 80^{o}C to see temperature effects.

Also in solution polymerization monomer was reacted with each catalysts G-1 and GH-2. O-DCB was used asa solvent. These reactions were happened at just 60^{o}C.

The composition and molecular weight of the polyvitamines were characterized by ^{1}H NMR and GPC.

ADMET POLİMERİZASYONU YÖNTEMİ KULLANILARAK POLİ-(5,6-IZOPROPİLEN-L-ASKORBİK ASİT) SENTEZİ

ÖZET

Askorbik asit olarak da bilinen C Vitamini, suda eriyebilen ve birçok görevi olan bir vitamindir. Asetonda çok zor çözünen vitamin C eter, petrol eteri, benzen, kloroform ve yağlarda çözünmez. Yapıca glikoza benzeyen ir monosakkarit türevidir. Fiziksel özellikleri renksiz, beyaz ve dikdörtgen kristal klindedir. Hafif özel bir kokusu olup ekşi tatta ve asidiktir.

C vitamini omurilik, akciğer ve göz gibi pek çok hayvansal dokunun sulu bölümlerinde oldukça yüksek yoğunlukta (milimolar ve üstü) bulunur. Bazı meyveler yüzde 1'den fazla (~6 mM) içerebilir. İnsan kanı plazmasında normal olarak 0,1 mM düzeyinde bulunur. Birçok hayvan ve bitkiler, kendi C vitaminlerini glukozdan üretebilirler. İnsanlar, bazı meyve yarasaları, hint domuzu ve insan benzeri primatlar C vitamini üretemediklerinden bunu besinlerden almak zorundadırlar.

L-Askorbic Asit'in kimyasal yapısı incelendiğinde oldukça reaktif bir yapıya sahip olduğu gözlenmektedir. 2-3 endiol yapısının C1 karbonil grubuna bağlı olmasından dolayı C3'te bulunan hidrojende güçlü bir asidite bulunmaktadır (pKa: 4.25). C3'teki hidrojen kadar olmasa da C2'deki hidrojende de aynı sebeplerden dolayı asidite bulunmaktadır. Molekülün asitliği bu iki hidrojenin asitliğinden kaynaklanmaktadır. Aynı zamanda 2,3-endiol yapısı L-Askorbik Asit'e bir veya iki electronunu sunma olanağını sağlamaktadır. Bu da yapıyı semidehydro-L-Ascorbic Acid'e ve son olarak da dehydro-L-Ascorbic Acid'e çevirir. L-Askorbik Asit bu yapılarından dolayı metabolizmalarda oldukça önemli bir yere sahiptir.

Yapıdaki C5 ve C6'daki hidroksil grupları moleküle alkol fonksiyonu katmaktadır. Bundan dolayıdır ki ayrı ayrı aldehit ve ketonlarla reaksiyona girerek siklik asetal ve ketal yapılarını oluşturabilir. Bunların dışında L-Askorbik Asit'in canlıların yapısında önemi oldukça fazladır.

L-Askorbic Asit'in biyolojik fonksiyonları üç ana grupta incelenmektedir. Birincisi enzim kofaktör olarak, ikincisi radikal tutucu olarak ve üçüncüsü hücrenin elektron transferinde yardımcı olarak.

Birinci biyolojik fonksiyonu enzim kofaktörü olarak görev almasıdır. Birçok önemli enzimatik reaksiyonların gerçekleşmesinde büyük rol oynamaktadır. Örnek olarak hidroksipirolin, hidroksilisin, norepinefrin, serotinin, karnitin ve homogenistik asit eldesi için gerekli amino asitlerin sentezlenmesinde kullanılmaktadır. Aynı zamanda osteoblast, fibroblastların, andrenalin hormonlarının ve karnitin biosenthezinin düzgün çalışmasında görev almaktadır.

İkinci biyolojik fonksiyonu ise radical tutucu olarak görev almasıdır. Hem bitkilerde hem de hayvanlarda hücre yaşamı için oksijene ihtiyaç duyulmaktadır. Hücre metabolismasından dolayı kendi ürettiği veya çevresel etkilerden dolayı kendiliğinden oluşan reaktif oksijen taneciklerini (ROT) kontrol altına alabilecek bir

mekanizmanın olması temel ihtiyaçlar arasındadır. L-askorbik asit antioksidant özelliği sayesinde ROT'lar ile reaksiyon vererek, ortamı nötralleştirip hücreye radikalik zarar gelmesini engellemektedir.

Son olarak üçüncü biyolojik fonksiyonu ise hem plazma membranında hem de kloroplastlarda elektron transferini donör/ekseptör gibi davranarak gerçekleştirmesidir. L-Askorbik Asit'in biyokimyasal fonksiyonları ağırlıklı olarak indirgeyici ve elektron taşıyıcı özelliklerinden kaynaklanmaktadır. L-ascorbic acid ve okside olmuş yapısı (L-Askorbat) redoks döngüsü gerçekleştirerek çeşitli elektron transfer reaksiyonlarında ve elektron membran protein taşıyıcı olarak da bilinen sitokromların aktivitesini değiştirmesinde görev alır.

Son yıllarda biyobozunur ve biyouyumlu polimerler, biyomedikal uygulamalarda ve malzeme bilimi alanlarında giderek artan önem kazanmışlardır. Biyobozunur polimerler, biyolojik moleküllerle fonksiyonlandırılarak ilaç salınım sistemlerinde ve doku mühendisliğinde kullanılmaktadır.

L- askorbik asit antioksidant ve radikal tutucu özelliklerinden dolayı ilaç sanayisinde kullanılan önemi büyük bir kimyasaldır. L askorbik asidin modifikasyonları kanser, tümör ve aids gibi ciddi hastalıklarda tedavi amaçlı kullanılmaktadır. Bu kullanım alanlarından dolayı bilim adamlarının dikkatini fazlaca çekmiştir. Yapılan araştırmalar doğrultusunda çok sayıda L- askorbik asit adına çalışmalar görülse de polimerizasyonu hakkında hiçbir bilgiye rastlanılmamıştır. Yapısı ve özellikleri gereği serbest radikal polimerizasyonuna uygun olmadığından dolayı acyclic diene metathesis (ADMET) polimerizasyonu uygun görülmüştür.

ADMET polimerizasyonu eşlenmemiş ikili olefin yapısından lineer bir zincir yapar. ADMET ile elde edilen polimerin uzun zincirlere sahip olabilmesi için, reaksiyona giren monomerlerin yüksek verimle dönüşme oranına sahipolması gerekmektedir. Bundan dolayı ADMET polimerizasyonlarında Grubbs katalizlerinden daha reaktif olan Hoveyda-Grubbs Catalyst 2^{nd} Generation tercih edilmektedir. ADMET polimerizasyonunda, verimli sonuçlar elde edebilmek için reaksiyondan etilen gazını uzaklaştırmak kritik rol oynar. Daha yüksek reaksiyon sıcaklıklarında çalışarak, reaksiyona vakum vererek veya reaksiyonu şiddetli karıştırarak etilen gazının ortamdan uzaklaştırılmasında uygulanabilecek yöntemlerdir. Bunun dışında konsantre çözücülerin polikondenzasyon reaksiyonlarına yardımı büyük olsa da ADMET'de vizkoz çözelti, reaksiyonun şiddetli karışmasını ve reaksiyondan etilen gazının uzaklaştırılmasını engeller. Aynı zamanda ADMET yöntemi ile elde edilen düşük molekül ağırlıklı polimerlerin polidispersiteleri de yüksek çıkmaktadır. Buna rağmen alken uçlu çok fazla çeşitteki monomerlerin polimerleşmesi için basit bir yöntemdir.

Bu çalışmada, ADMET yöntemi kullanılarak ana zincirinde C vitaminini bulunduran monomer polimerleştirilmiştir. Öncelikle alken uç fonksiyonu bulundurmayan C vitaminine alken uç takılıp, ADMET yöntemlerinden hem bulk polimerizasyonu hem de solution polimerizasyonu uygulanmıştır.

Bulk polimerizasyonu sırasında monomer, G-1 ve GH-2 katalizleri ile ayrı ayrı reaksiyona sokulmuştur. Reaktanların birbirine karışabilmesi için çözücü olarak DCM kullanılıp ardından reaksiyon ortamından uzaklaştırılarak bulk polimerizasyonu için uygun koşullar sağlanmıştır. Her iki katalizin etkisi 40^oC, 60^oC ve 80^oC olmak üzere üç ayrı ortamda bir hafta boyunca incelenmiştir.

Solution polimerizasyonunda da monomer, G-1 ve GH-2 katalizleri ile ayrı ayrı reaksiyona sokulmuştur. Çözücü olarak O-DCB kullanılmıştır. Solution polimerizasyonu için ortam sıcaklığı 60^oC olarak belirlenmiştir. Karakterizasyon işlemleri ^1H NMR ve GPC ile gerçekleştirilmiştir.

ADMET'de vizkoz çözelti, reaksiyonun şiddetli karışmasını ve reaksiyondan etilen gazının uzaklaştırılmasını engeller. Aynı zamanda ADMET yöntemi ile elde edilen düşük molekül ağırlıklı polimerlerin polidispersiteleri de yüksek çıkmaktadır. Buna rağmen alken uçlu çok fazla çeşitteki monomerlerin polimerleşmesi için basit bir yöntemdir.

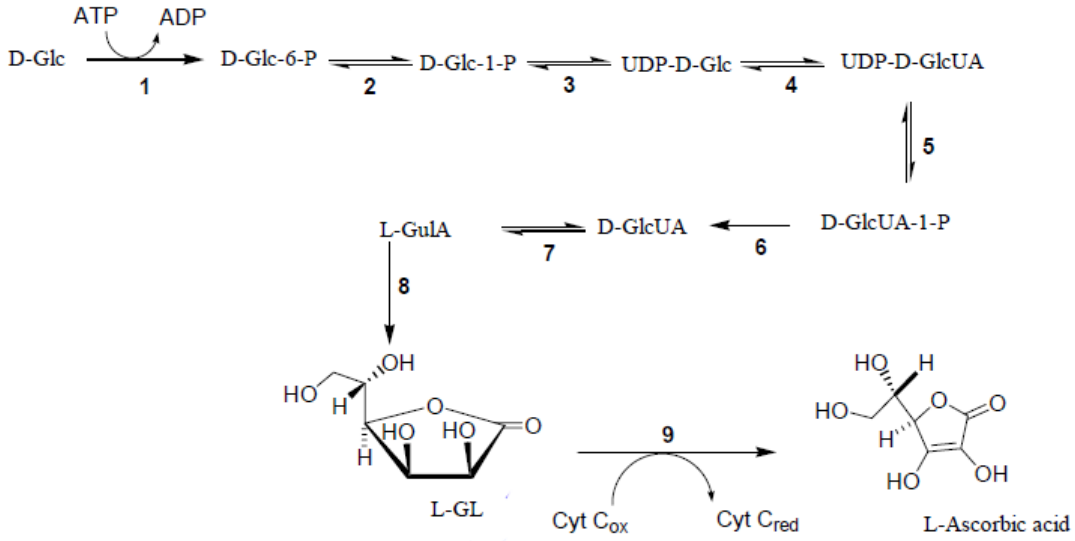
1. INTRODUCTION

Ascorbic acid is a versatile water soluble radical scavenger widely distributed in aerobic organisms that plays a central role in the protection of cellular components against oxidative damage by free radicals and oxidants that are involved in the development and exacerbation of a multitude of chronic diseases such as cancer, heart disease, brain dysfunction, aging, rheumatism, inflammation, stroke, emphysema, and AIDS[1-5]. It also plays a critical role as a physiological reductant for key enzymatic transformations in catecholamine neurotransmitter, amidated-peptide hormone, and collagen biosynthetic pathways. In addition, simple derivatives of L-ascorbic acid have been shown to possess important pharmacological properties. For example, 5,6-Omodified ascorbic acid derivatives have been found to be effective anti-tumor agents for various human cancers, and induce apoptosis in tumor cells [6-10]. C2 alkylated derivatives have been shown to have immuno-stimulant activity C2-O and C3-O alkylated derivatives are known to protect against peroxidation of lipids of the biomembrane. Recently, the chemistry of ascorbic acid has also been exploited to develop strategies for central nervous system drug delivery[11].

The main sources of L-ascorbic acid for humans are from plants and animals with indigenous biosynthetic capabilities of producing L-ascorbic acid. The biquitousness of L-ascorbic acid throughout the human body emphasizes its daily requirement and vitality as a nutrient for healthy maintenance. Its biological half-life in humans is 14-40 days after normal intake and a vitamin-C-free diet in a human develops scurvy in about 3-4 months.[12]

The vast majority of species of animals and plants are known to synthesize their own vitamin C. A majority of vertebrates such as amphibians, reptiles, birds, and mammals are able to synthesize L-ascorbic acid. Molecules similar to ascorbic acid are made by some fungi but not by bacteria.

The biosynthesis of L-ascorbic acid in animals (Figure: 1) is integrated with the glucuronic acid metabolic pathway. This metabolic pathway is involved in the metabolism of sugars under both normal and disease states and is regulated by the body's physiological functions.



Catalytic Step	Enzyme	Substrate
1	Hexokinase	D-Glucose
2	Phosphoglucomutase	D-Glucose-6-phosphate
3	UDP-D-Glucose pyrophosphorylase	D-Glucose-1-phosphate
4	UDP-D-Glucose dehydrogenase (EC 1.1.1.22)	UDP-D-Glucose
5	D-Glucuronate-1-phosphate uridylytransferase (EC 2.7.7.44)	UDP-D-Glucuronic acid
6	D-Glucurono kinase (Hydrolase)	UDP-D-Glucuronic acid-1-phosphate
7	D-Glucuronate reductase (EC 1.1.1.19)	D-Glucuronic acid
8	Aldonolactonase (EC 3.1.1.17)	L-Galacturonic acid
9	L-Gulono-1,4-lactone dehydrogenase (EC 1.1.3.8)	L-Gulono-1,4-lactone

Figure 1.1 : The biosynthesis of L-ascorbic acid in animals

The biosynthesis of L-ascorbic acid in plants has not been clearly and easily established when compared to its biosynthesis in animals. However, recent advances

in the understanding of L-ascorbic acid biosynthesis in plants have helped to resolve many of the contradictions of the past decades. There is now a general consensus that the biosynthetic pathway, which proceeds *via* GDP-D-mannose and GDP-L galactose[13-15]. As proposed by the Smirnoff group,120 represents the major L-ascorbic biosynthetic pathway in plants (Scheme 2).

Antioxidant as well as redox and pharmacological benefits of L-ascorbic acid and its derivatives are closely associated with the electron rich C2,C3-enediol moiety of its five-membered lactone ring.35 Therefore, the selective modification of its C2- and C3-OH groups is essential for detailed structure-activity studies of L-ascorbic acid. Reactions are shown in Figure: 3 and Figure: 4.

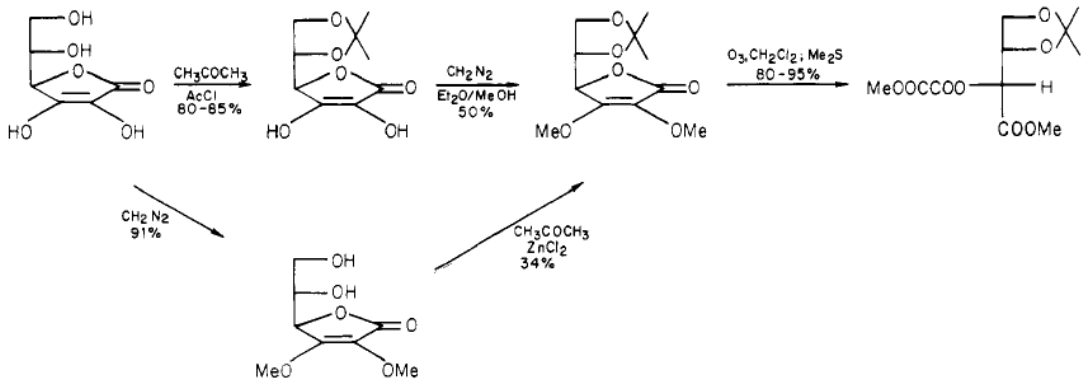


Figure 1.2 : Example reaction of L-ascrobic acid

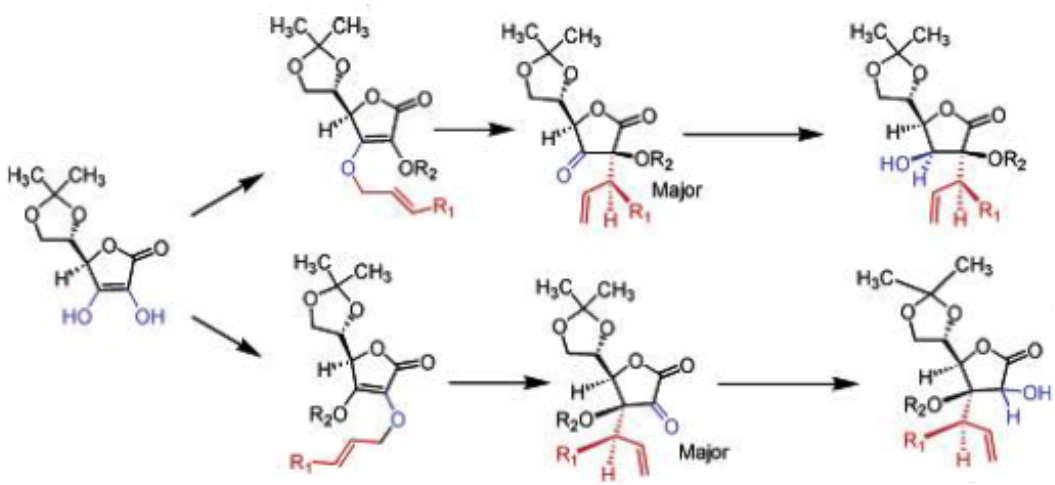
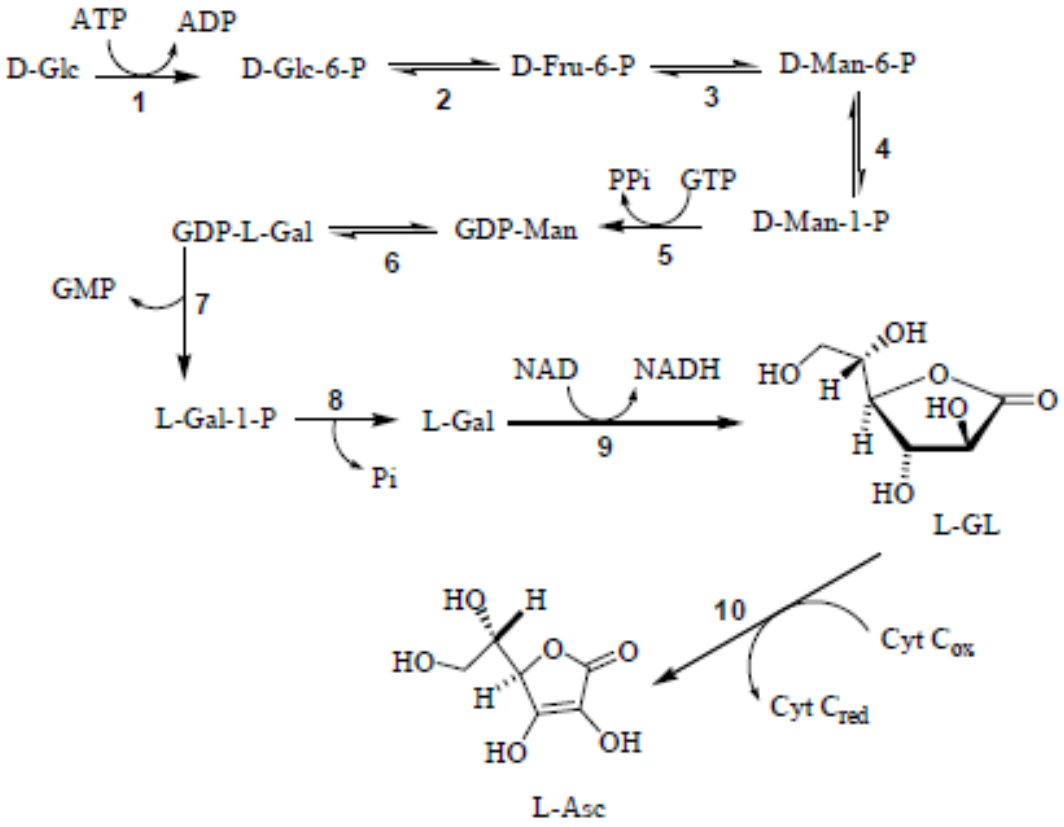


Figure 1.3 : Example reactions of protected L-ascorbic acid



Catalytic Step	Enzyme	Substrate
1	Hexokinase (E.C. 2.7.1.1)	D-Glucose
2	Phosphoglucose isomerase (E.C. 5.3.1.9)	D-Glucose-6-phosphate
3	Phosphomannose isomerase (E.C. 5.3.1.8)	D-Fructose-6-phosphate
4	Phosphomannose mutase (E.C. 5.4.2.8)	D-Mannose-6-phosphate
5	GDP-Mannose pyrophoshorylase (E.C. 2.7.7.22)	D-Mannose-1-phosphate
6	GDP-Mannose-3,5-epimerase (E.C. 5.1.3.18)	GDP-D-Mannose
7	GDP-L-Galactose pyrophosphatase	GDP-L-Galactose
8	L-Galactose-1-phosphate phosphatase	L-Galactose-1-phosphate
9	L-Galactose dehydrogenase	L-Galactose
10	L-Galactono-1,4-lactone dehydrogenase (E.C. 1.3.2.3)	L-Galactono-1,4-lactone

Figure 1.4 : L-ascorbic biosynthetic pathway in plants

2. THEORETICAL PART

2.1 Step-Growth Polymerization

Chain-growth polymerization is one in which each polymer chain, after being started by a free radical initiator, a cationic catalyst or an anionic catalyst, grows rapidly, producing a high molecular weight polymer. Once the propagation reaction within a given polymer chain is stopped either by a termination or chain-transfer step, usually no further chain growth occurs. The initiation, propagation, and termination steps are distinctly different .

In a step-growth polymerization, the molecular weight of the polymer chain builds up slowly and there is only one reaction mechanism for the formation of polymer. The distinct initiation, propagation, and termination steps of chain-growth polymerization are meaningless in step-growth polymerization. A difunctional monomer or equal molar amounts of two different difunctional monomers are necessary at least to form a linear high molecular weight polymer. The polymerization reaction proceeds by individual reactions of the functional groups on the monomers. Thus, two monomers react to form a dimer. The dimer may now react with another dimer to produce a tetramer, or the dimer may react with more monomer to form a trimer. This process continues, each reaction of the functional groups proceeding essentially at the same reaction rate until over a relatively long period of time a high molecular weight polymer is obtained. In Figure 2.1 Differences between Step-Growth polymerization and Chain-Growth polymerization are shown.

Requirements For High Molecular Weight: There are three critical requirements for the step-growthpolymerization to yield a high molecular weight linear polymer.First, a perfect stoichiometric balance of the two difunctional monomers must be introduced, or alternately a self-balancing reaction is necessary. Of course, when a

single difunctional monomer can generate polymer, such as is the case of ε-aminocaproic acid, an internal balance (within the monomer) is provided

Step-Growth versus Chain-Growth Polymerization

	Step-Growth	Chain-Growth
• Reactions	One reaction is responsible for polymer formation.	Initiation, propagation, and termination reactions have different rates and mechanisms.
• Polymer Growth	Any two molecular species present can react; slow, random growth takes place.	The growth reaction takes place by the addition of one unit at a time to the active end of the polymer chain.
• Polymer Molecular Weight	Molecular weight rises steadily throughout the reaction. High conversion is required for high molecular weight polymer.	High molecular weight polymer is formed immediately.
• Monomer Concentration During Polymerization	Monomer disappears in the early stages of the polymerization. At an average degree of polymerization of 10, less than 1 weight percent of the monomer remains.	Monomer concentration decreases steadily throughout the reaction.
• Composition of the Polymerization Reaction	A relatively broad, calculable distribution of molecular species are present throughout the course of the polymerization.	Mixture contains only monomer, high molecular weight polymer and only about 10^{-8} part of growing chains. This is true shortly after initiation and at the end of the polymerization (except for the growing chain concentration) since 100% conversion of monomer usually is not achieved.

Figure 2.1 : Compraison of Step-Growth and Chain-Growth polymerization

Second, a high degree monomer purity is necessary. It is evident that in the case of ε -aminocaproic acid, if the decarboxylation product, n-pentylamine, is present, then internal balance is no longer achieved. Likewise, the presence of a trace of monocarboxyric acid iq adipic will lead to a stoichiometric imbalance. Furthermore, these monofunctional monomers act as caps to the polymer chain. Once the monocarboxylic acid has underagone amide formation, no further reaction is possible at the end of the chain.

Third, the reaction responsible for the polymerization must be a very high yield reaction with the absence of side reactions. Of the large number of reactions known to organic chemists today, only four are utilized in the synthesis of step-growth polymers in large amounts.[16]

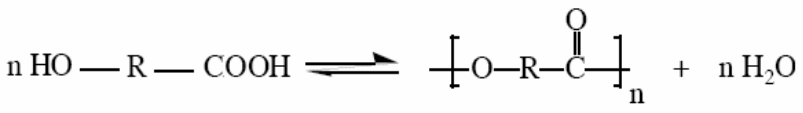
These four polymers meet the requirements of high yield reactions and cost feasibility. Polyesters, polyamides, polycarbonates and polyethers..

2.1.1 Polyesters

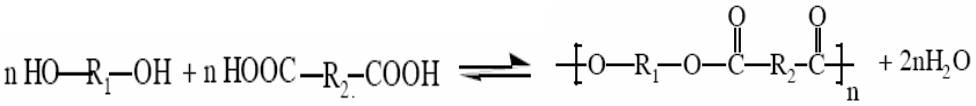
Polyesters are one of the most versatile synthetic copolymers. Polyesters are produced in high volume that exceeds 30 billion pounds a year worldwide.[17-19] They are widely used commercially as fibres, plastics, composites and for coatings

applications too. They are heterochain macromolecules that possess carboxylate ester groups as an integral component of their polymer backbones.

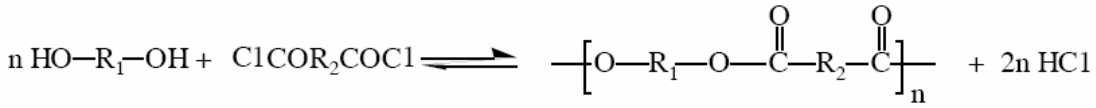
- Esterification of hydroxy acid



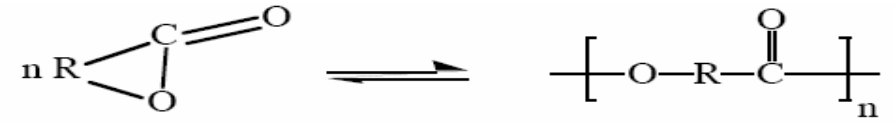
- Esterification of diol and diacid



- Esterification of diol and diacid chloride



- Lactone polymerization



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2.1.2 Polyamides

Polyamides are polymers which contain repeating amide, -CO-NH-, linkages. Proteins are examples of naturally occurring polyamides.

The best known manufactured polyamides are often called nylons (the trade name given by the manufacturer, DuPont) and these are aliphatic polyamides. However, other manufactured polyamides are also important and these include an aromatic polyamide, Kevlar© and plastics produced from carbamide (urea). The nomenclature for describing the linear, aliphatic polyamides (the nylons) is based on the number of carbon atoms in the repeating unit.

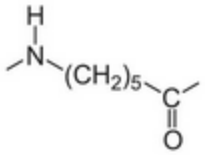
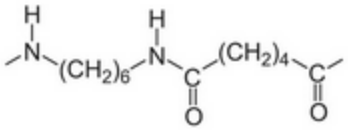
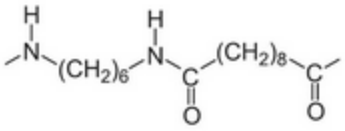
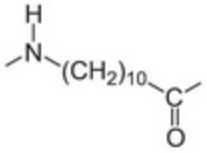
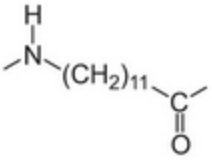
Polyamide (nylon)	Repeating unit
6	
6,6	
6,10	
11	
12	

Figure 2.2 : Examples of polyamide structures

2.1.3 Polycarbonates

Polycarbonates (PC), known by the trademarked names Lexan, Makrolon, Makroclear, arcoPlus® and others, are a particular group of thermoplastic polymers. They are easily worked, molded, and thermoformed. Because of these properties, polycarbonates find many applications. Polycarbonates do not have a unique resin identification code and are identified as Other, 7. Items made from polycarbonate can contain the precursor monomer bisphenol A (BPA).

Polycarbonates received their name because they are polymers containing carbonate groups (–O–(C=O)–O–). Most polycarbonates of commercial interest are derived from rigid monomers. A balance of useful features including temperature resistance, impact resistance and optical properties position polycarbonates between commodity plastics and engineering plastics.

The main polycarbonate material is produced by the reaction of bisphenol A (BPA) and phosgene COCl

The overall reaction can be written as follows:

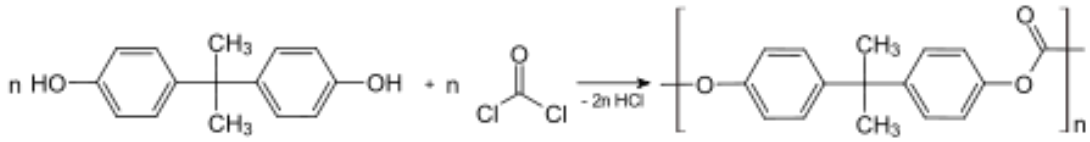


Figure 2.3 : Example of polycarbonate produce

2.1.4 Polyethers

Polyethers are compounds with more than one ether group. The crown ethers are examples of low-molecular weight polyethers. Some toxins produced by dinoflagellates such as brevetoxin and ciguatoxin are in a class known as cyclic or ladder polyethers. Polyether generally refers to polymers which contain the ether functional group in their main chain. The term glycol is reserved for low to medium range molar mass polymer when the nature of the end-group, which is usually a hydroxyl group, still matters. The term "oxide" or other terms are used for high molar mass polymer when end-groups no longer affect polymer properties.

2.2 Olefin Methathesise

Olefin metathesis is a metal-catalyzed transformation, which acts on carboncarbon double bonds and rearranges them via cleavage and reassembly.[20-23] While the reaction itself was discovered in the mid-1950s, its now generally accepted mechanism was not proposed until 1971[24]. According to this mechanism, first introduced by Chauvin, the coordination of an olefin to a metal carbene catalytic species leads to the reversible formation of a metallacyclobutane (Scheme 1.1). This intermediate then proceeds by cycloreversion via either of the two possible paths: 1) non-productive—resulting in the re-formation of the starting materials or 2) product-forming—yielding an olefin that has exchanged a carbon with the catalyst's alkylidene. Since all of these processes are fully reversible (Figure 1.1), only statistical mixtures of starting materials as well as all of possible rearrangement [i]products are produced in the absence of thermodynamic driving forces.

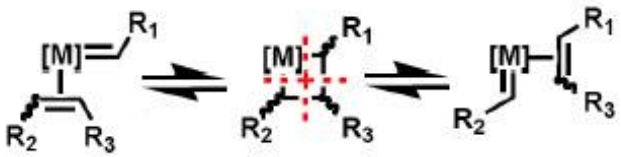


Figure 2.4 : General mechanism of olefin metathesis.

Fortunately for the organic and polymer chemistry communities, the olefin metathesis reaction's thermodynamic equilibrium can be easily influenced. There are two major approaches that are commonly employed to drive the reaction towards the desired products. One tactic is to rely on Le Chatelier's principle by continuously removing one of the products from the reaction system in order to shift the equilibrium in favor of the other product. This method is especially effective in the case of cross metathesis (CM)[25] reactions involving terminal olefins, ring-closing metathesis (RCM)[26-27] and acyclic diene metathesis polymerization (ADMET) [28-32], because the volatile ethylene gas by-product formed in these processes can be easily removed (Scheme 1.2). The other approach capitalizes on the ring strain of cyclic olefins such as cyclooctenes and norbornenes. The energy released during the ring-opening of these compounds is sufficient to drive forward reactions such as ring-opening cross metathesis (ROCM) [33-34] and ring-opening metathesis polymerization (ROMP)[35-36] (Scheme 1.2). In addition, in some instances, substrate concentration (which often distinguishes ADMET from RCM) or the catalysts' sensitivity to olefin substitution can also be taken advantage of to influence product selectivity. All of these methods are currently successfully employed in the synthesis of a large variety of small, medium, and polymeric molecules, as well as novel materials[37-41]

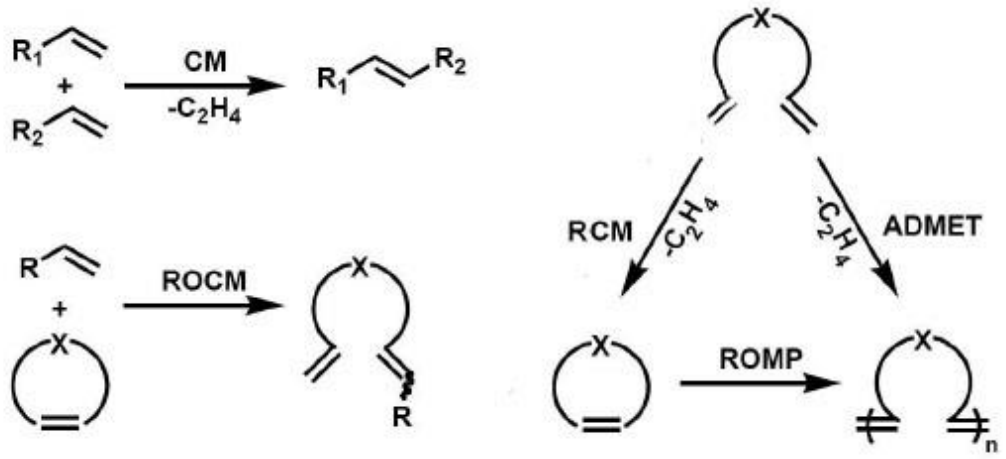


Figure 2.5 : Types of olefin metathesis reactions.

Once an olefin metathesis mechanism consistent with the experimental evidence was established, rational catalyst design became possible. Consequently, several welldefined, single-species catalysts based on different transition metals such as titanium[42], tungsten[43-44], molybdenum[45], rhenium,[46] osmium[47], and ruthenium[48-49] evolved from the original metathesis-active but ill-defined multi-component mixtures. However, eventoday, the early transition metal catalysts, although very active, are also sensitive to many functional groups found in organic molecules, as well as moisture and air—a drawback that significantly limits their synthetic applications. For example, as demonstrated in Table 1.1, a metathesis catalyst with a tungsten center will preferentially react with olefins in the presence of esters and amides, but it will ignore all of these functionalities in favor of ketones, aldehydes, alcohols, acids or water.4 On the other hand, the late transition metal, ruthenium-based catalysts proved to be very tolerant towards polar functional groups and water, albeit at the expense of activity, early in olefin metathesis research[50]. Overall, both Mo and Ru metathesis catalysts gained the most prominence and popularity due to their versatility, as they provided a good balance between activity and functional group tolerance (Figure 2.6)

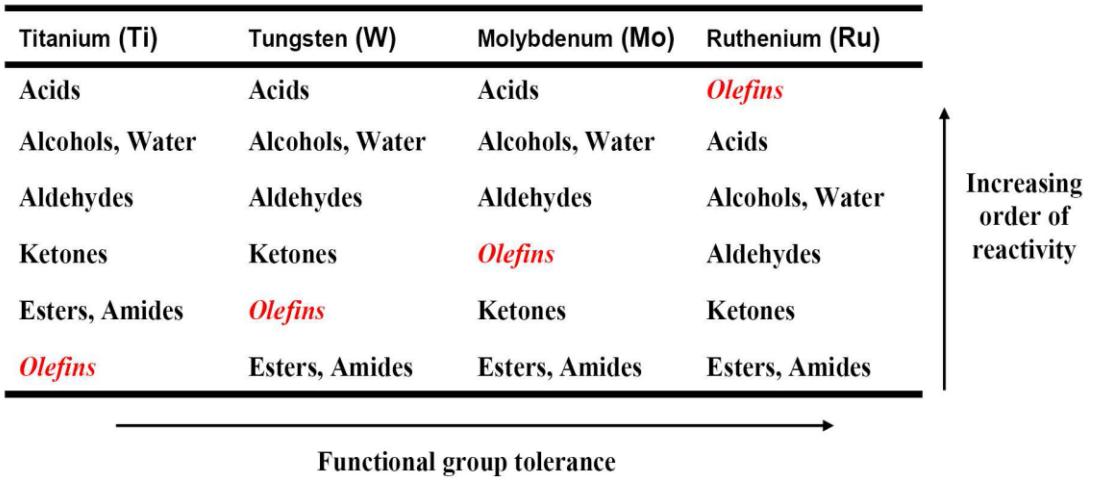


Figure 2.6 : Functional group tolerance of olefin metathesis catalysts.

The exceptional selectivity of ruthenium for C–C double bonds secured continuous interest for this line of catalysts despite the low activity of the early versions, relative to the molybdenum catalysts of the time. For example, the activity of bistriphenylphosphine (PPh3) predecessors of catalyst 1 (Figure 1.1) was limited to ROMP of strained monomers, yet the catalyst performed remarkably well in polar media such as alcohols.32 However, the subsequent replacement of the PPh3 ligands with tricyclohexyl phosphines (PCy3) produced a much more active catalyst 1 ("the 1st generation Grubbs catalyst"), which is capable of cross metathesis of acyclic olefins, while maintaining the stability and high functional group tolerance of earlier ruthenium catalysts [51].Furthermore, the substitution of one of the phosphine ligands for an even more electrondonating N-heterocyclic carbene (NHC) resulted in a series of 2nd generation catalysts, such as 230 and the phosphine-free[52] which now rival Mo catalysts in activity (Figure 1.1). While both 2 and 3 maintain the excellent selectivity for olefins typical of ruthenium catalysts, they have somewhat slower rates of initiation than the first generation catalysts, limiting their application in polymer synthesis. Alternatively, NHCcatalyst[53] which bears a bispyridine ligand in place of a phosphine (Figure1.1), has a sufficiently rapid initiation rate to promote ROMP of norbornenes with all of the attributes of a living polymerization. Moreover, the continuing emergence of new catalysts serves to further improve the metathesis reaction to be applicable to asymmetric,[54] sterically demanding,[55] or aqueous[56-57]transformations.

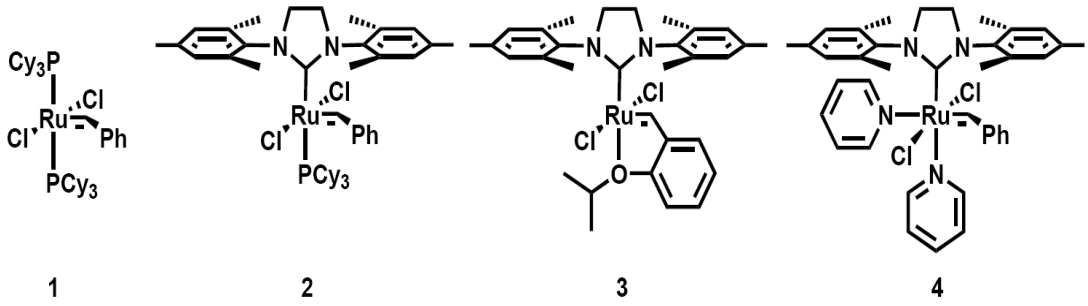


Figure 2.7 : Ruthenium-based olefin metathesis catalysts

One specific example of the improved reactivity of 2nd generation ruthenium catalysts, such as 2 and 3, is their ability to react with electron-deficient B,C-unsaturated carbonyls, which are inert to 1. As a result, excellent cross metathesis selectivity can be achieved in the reactions with such substrates[58-59]. While both types of catalysts will successfully homodimerize "easy," electron-rich, unsubstituted olefins, such as terminal aliphatic alkenes, even the active NHC-catalysts have very limited ability, if any, to cross a pair of "difficult," electron-deficient olefins, such as acrylates. Nevertheless, unlike 1, NHC-catalysts will promote selective cross metathesis between an "easy" and a "difficult" olefin. Therefore, a mixture of compounds, each functionalized with either a terminal alkene or an acrylate, will produce homodimers of the "easy" alkenes exclusively when exposed to 1, and mixed "easy"-"difficult" cross products when exposed to 2 or 3 (Scheme1.3). Importantly, although homodimerization of "easy" olefins occurs in the presence of

either 2 or 3, the disubstituted, electron-rich product of this cross is still qualified as "easy" and can proceed through secondary metathesis with acrylates and the NHC-catalyst to form a thermodynamically more stable cross product. In fact, this cross metathesis selectivity of 2nd generation ruthenium catalysts has already been creatively exploited in the synthesis of small molecules[60], macrocycles[61], and alternating A,B polymers[62].

2.2.1 ADMET

Acyclic diene metathesis (ADMET) polymerizations follow a step growth mechanism to produce strictly linear polymers with unsaturated polyethylene backbones.[63] As with all other olefin-metathesis reactions, ADMET proceeds through the exchange of substituents of two reacting olefins

in an equilibrium reaction, a transalkylidenation. In the case of ADMET polymerizations, this exchange results in the release of ethylene, which can be removed from the equilibrium reactionmby the application of vacuum or a constant flowof an inert gas to obtain high conversions and high-molecular-weight polymers[63]. This loss of ethylene during ADMET polymerizations

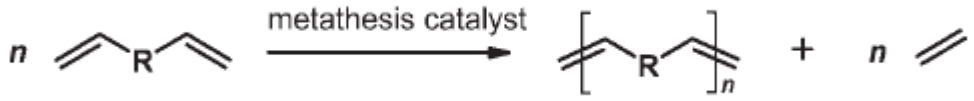


Figure 2.8 : ADMET polymerization

might be considered as unsustainable as it isnot atom economic, but it should be possible to collect the produced ethylene in large-scale operations to use it as feedstock for other processes und thus circumvent this problem. In particular, the introduction of ruthenium-based metathesis initiators in the 1990s allowed an unmatched functional group tolerance[64] and led to the development of the first-generation catalyst from Grubbs[65-66]. The observation that the introduction

of a N-heterocyclic carbene (NHC) to the catalyst leads to metathesis initiators with improved activity[67-69] as well as stability led to the development of the second-generation catalysts from Grubbs[70-71] and Hoveyda[72] that are widely applied

today in organic synthesis as well as polymer chemistry[63, 73-76].Therefore, the ADMET polymerization technique has not only led to the preparation of well-defined, branched polyolefins (from branched monomers) that would not be accessible by other methods[77-78] but has also opened ways to prepare polyolefins

with a number of different functional groups[79-82]. Even if the preparation of a large variety of different polymers is possible through ADMET polymerization as discussed above, relatively little is known about the use of ADMET polymerizations

for the preparation of telechelics or even block copolymers. As for any other step growth polymerisations, this is, however, possible. For instance, methoxydimethylsilane- and chlorodimethylsilane-terminated telechelic

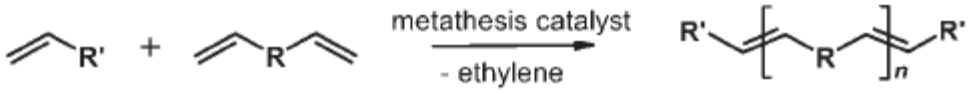


Figure 2.9 : ADMET polymerization with chain stoppers.

polyoctoenomer oligomers were prepared using ruthenium as well as molybdenum metathesis catalysts, and it was observed that the number-averaged molecular weight (Mn) values of the prepared telechelics was dictated by the initial ratio of the monomer to the chain stopper.[83]

2.3 Vitamins

Vitamins are essential nutrients found in foods. They perform specific and vital functions in a variety of body systems, and are crucial for maintaining optimal health. The two different types of vitamins are fat-soluble vitamins and water-soluble vitamins. Fat-soluble vitamins — vitamins A, D, E and K — dissolve in fat before they are absorbed in the bloodstream to carry out their functions. Excesses of these vitamins are stored in the liver, and are not needed every day in the diet. For more information on fat-soluble vitamins, see fact sheet 9.315 Fat-Soluble Vitamins: A, D, E, and K. In contrast, water-soluble vitamins dissolve in water and are not stored by the body. Since they are eliminated in urine, we require a continuous daily supply in our diet. The water-soluble vitamins include the vitamin B-complex group and vitamin C. Water-soluble vitamins are easily destroyed or washed out during food storage or preparation. Proper storage and preparation of food can minimize vitamin loss. To reduce vitamin loss, always refrigerate fresh produce, keep milk and grains away from strong light, and use cooking water from vegetables to prepare soups.

2.3.1 Vitamin C

The body needs vitamin C, also known as ascorbic acid or ascorbate, to remain in proper working condition. Vitamin C benefits the body by holding cells together through collagen synthesis; collagen is a connective tissue that holds muscles, bones, and other tissues together. Vitamin C also aids in wound healing, bone and tooth formation, strengthening blood vessel walls, improving immune system function, increasing absorption and utilization of iron, and acting as an antioxidant. Since our

bodies cannot produce or store vitamin C, an adequate daily intake of this nutrient is essential for optimum health. Vitamin C works with vitamin E as an antioxidant, and plays a crucial role in neutralizing free radicals throughout the body. An antioxidant can be a vitamin, mineral, or a carotenoid, present in foods, that slows the oxidation process and acts to repair damage to cells of the body. Studies suggest that vitamin C may reduce the risk of certain cancers, heart disease, and cataracts. Research continues to document the degree of these effects. Food Sources for Vitamin C. Consuming vitamin C-rich foods is the best method to ensure an adequate intake of this vitamin. While many common plant foods contain vitamin C, the best sources are citrus fruits. For example, one orange, a kiwi fruit, 6 oz. of grapefruit juice or 1/3 cup of chopped sweet red pepper each supply enough vitamin C for one day.

How much Vitamin C. The Recommended Dietary Allowance (RDA) for Vitamin C is 90 mg/day for adult males and 75 mg/day for adult females. For those who smoke cigarettes, the RDA for vitamin C increases by 35 mg/day, in order to counteract the oxidative effects of nicotine. Vitamin C Deficiency. Although rare in the United States, severe vitamin C deficiency may result in the disease known as scurvy, causing a loss of collagen strength throughout the body. Loss of collagen results in loose teeth, bleeding and swollen gums, and improper wound healing. More commonly, vitamin C deficiency presents as a secondary deficiency in alcoholics, the elderly, and in smokers. The following conditions have been shown to increase vitamin C requirements

- Environmental stress, such as air and noise pollution
- Use of certain drugs, such as oral contraceptives
- Tissue healing of wounds
- Growth (children from 0- 12 months, and pregnant women)
- Fever and infection
- Smoking.

Too Much Vitamin C. Despite being a water-soluble vitamin that the body excretes when in excess, vitamin C overdoses have been shown to cause kidney stones, gout, diarrhea, and rebound scurvy.

3. EXPERIMENTAL PART

3.1 Materials

L-Ascorbic acid, Acetyl chloride, 5,6-Isopropylidene-L-ascorbic acid (98%, Aldrich), 5-Bromo-1-pentene (95%, Aldrich). 1,2-Dichlorobenzene, anhydrous (99% Aldrich), Grubbs Catalyst, 1st Generation (97% Aldrich), Hoveyda-Grubbs Catalyst 2nd Generation (97% Aldrich), Butyl vinyl ether (contains 0.01% potassium hydroxide as stabilizer, 98%), Acetone, Dichloromethane (99.9%, Sigma-Aldrich), Dimethyl sulfoxyde (99% MERCK), Potasium Carbonate Anhydrous (K2CO3, 99%, J.T. Baker) Tetrahydrofuran (THF; 99.8%, J.T. Baker).

3.2 Instruments

^{1}H and ^{13}C NMR spectra were recorded on an Agilent VNMRS 500 (500 MHz for proton and 125 MHz for carbon). The conventional gel permeation chromatography (GPC) measurements were carried out with an Agilent instrument (Model 1100) consisting of a pump, refractive index (RI) detector and four Waters Styragel columns (guard, HR 5E, HR 4E, HR 3, and HR 2), (4.6 mm internal diameter, 300 mm length, packed with 5 μm particles). The effective molecular weight ranges are 2000-4,000,000, 50-100,000, 500-30,000, and 500-20,000 g/mol, respectively. THF and toluene were used as eluent at a flow rate of 0.3 mL/min at 30 °C and as an internal standard, respectively. The apparent molecular weights ($M_{n,GPC}$ and $M_{w,GPC}$) and polydispersities (M_w/M_n) were determined with a calibration based on linear PS standards using PL Caliber Software from Polymer Laboratories.

3.3 Synthetic Procedures

Synthesis of 5,6-Isopropylidene-L-ascorbic acid (1) Synthesis of 4-(but-3-en-1-yloxy)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3-(pent-4-en-1-yloxy)furan-2(5H)-one (2), Synthesis of Poly- 4-(but-3-en-1-yloxy)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3-(pent-4-en-1-yloxy)furan-2(5H)-one (3).

3.3.1 Synthesis of 5,6-Isopropylidene-L-ascorbic acid (1)

L-Ascorbic acid (10 g, 0.055 mol) was weighed into a 125- mL Erlen-meyer flask. Acetone (40 mL, 0.55 mol) and acetyl chloride (1 mL, 0.015 mol) were added and a calcium sulfate drying tube was placed on the flask and the slurry stirred at room temperature 2-3 h. The flask was then stoppered and stored in the refrigerator (7 ^{o}C) for 4-8 h. The solid was then filtered off and washed with a small amount of cold acetone. After being dried for a short period of time, 9.63 g (81%) of ascorbic acid acetonide was present.

^{1}H NMR (500 MHZ, $CDCL_3$, δ) 7.27 (1H,OCH2C*H*CH), 4.69 (1H,OCH2CHC*H*), 4.24 (1H, OC*H*HCHCH) 4.09 (1H, OCH*H*CHCH) 3.88 (4H, -O*H*) 3.36 (6H, OCC*HHH*) 1.25

3.3.2 Synthesis of 4-(but-3-en-1-yloxy)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3-(pent-4-en-1-yloxy)furan-2(5H)-one (2)

This compound was synthesized by reaction of 1.0 equiv of 5,6-Isopropylidene-L-ascorbic acid (2.00 g, 9.0 mmol) with 2.5 equiv of K_2CO_3 (3.18 g, 23.0 mmol) in DMSO/THF (9:8) solution. Reaction mixture was stirred for 20 min at room temperature. Then 2.5 equiv of 1-Bromo penten (2.74 mL, 23.0 mmol) in the same solvent was added dropwise and the mixture was vigorously stirred for 4-6 h at room temperature. The reaction mixture extracted with ethyl acetate. The organic layer was thoroughly washed with water and dried over anhydrous Na_2SO_4 and the solvents were removed under reduced pressure. The product was purified by conventional silica gel column chromatography using 4:1 n-hexane:ethyl acetate to give 91% yield as a viscous oil.

^{1}H NMR (500 MHZ, $CDCL_3$, δ) 7.27 (1H, C*H*=CH_2), 5.79 (2H, C=C*HH*) 5.03 (1H,OCH2C*H*CH) 4.49 (2H, OC*HH*CHCH) 4.42 (1H,OCH2CHC*H*) 4.26 (2H, OC*HH*CH2) 4.12, (2H, OC*HH*CH2) 4.03 (4H, C*HH*CH=CH_2) 2.15 (4H, OCH2C*HH*) 1.79 (3H, OCC*HHH*) 1.37 (3H, OCC*HHH*) 1.34

3.3.3 Synthesis of poly- 4-(but-3-en-1-yloxy)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3-(pent-4-en-1-yloxy)furan-2(5H)-one (3)

3.3.3.1 Via bulk polymerization

This polymer was synthesised by reaction of 1.0 equiv of 5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3,4-bis(pent-4-en-1-yloxy)furan-2(5H)-one (0.5 g, 1.4 mmol) with singly Hoveyda Grubbs catalysts; 0.01 equiv of GH-2 (9 mg, 0.014 mmol) and 0.01 equiv of GH-1 (5.8 mg, 0.007 mmol). DCM is used for mixing monomer and catalyst, then evaporated from reaction mixture by giving inert gas N_2. Then vacuum was given to reactions for remove consisted ethilene gas. This procedure was applied at each three temperatures; 40^{o}C, 60^{o}C and 80^{o}C. Polymerizations were terminated a week later with 3 mL Butyl Vinyl Ether/DCM (1:2) solution. The reaction mixture which involves GH-1 catalyst precipitated into an excess amount of diethylether, GH-2 catalyst inclusive reaction mixture precipitated into an excess amount of hegzan. The recovered polymer was dissolved in CH_2Cl_2 and finally dried under reduced pressure

^{1}H NMR (500 MHZ, $CDCL_3$, δ) 7.27 (1H, C*H*=CH_2), 5.46 (2H, C=C*HH*) 5.03 (1H,OCH2C*H*CH) 4.52 (2H, OC*HH*CHCH) 4.42 (1H,OCH2CHC*H*) 4.28 (2H, OC*HH*CH2) 4.14, (2H, OC*HH*CH2) 4.05 (4H, C*HH*CH=CH_2) 2.12 (4H, OCH2C*HH*) 1.78 (3H, OCC*HHH*) 1.40 (3H, OCC*HHH*) 1.36

3.3.3.2 Via solution polymerization

This polymer was synthesised by reaction of 1.0 equiv of 5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3,4-bis(pent-4-en-1-yloxy)furan-2(5H)-one (0.5 g, 1.4 mmol) with singly Hoveyda Grubbs catalysts; 0.01 equiv of GH-1 (5.8 mg, 0.007 mmol) and 0.01 equiv of GH-2 (9 mg, 0.014 mmol) by using 2 mL ODCB as a solvent. Then vacuum was given to reactions for remove consisted ethilene gas. This procedure was applied at 60^{o}C. Polymerizations were terminated a week later with 3 mL Butyl Vinyl Ether/DCM (1:2) solution. Two reaction mixture precipitated into an excess amount of hegzan. The recovered polymer was dissolved in CH_2Cl_2 and finally dried under reduced pressure Same ^{1}H NMR (500 MHZ) results with bulk polymerization ^{1}H NMR (500 MHZ) results.

4. RESULTS AND DISCUSSION

In this work, ADMET polymerization was applied on a monomer which has an alkene functional vitamine backbone structure. Grubbs Catalyst 1st Generation and Hoveyda Grubbs Catalyst 2nd Generation were used in order to different temperatures. Reactions were monitored by ^{1}H-NMR and GPC, DSC.

4.1 Synthesis of 5,6-Isopropylidene-L-ascorbic acid

5,6-Isopropylidene-L-ascorbic acid (1) was synthesized by the reaction of L-Ascorbic acid and Acetone and acetyl chloride. Reaction was purified by using washing technique.

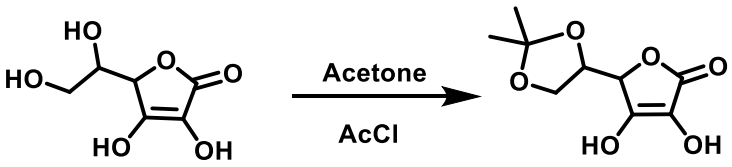


Figure 4.1 : Synthesis of 5,6-Isopropylidene-L-ascorbic acid

On the NMR spectrum of resultant 5,6-Isopropylidene-L-ascorbic acid (Figure 4.2), (Figure: 4.3) integration values corrected the structure of the compound. Peaks between 3.80-4.30 ppm were specific to vitamine backbone monomer.

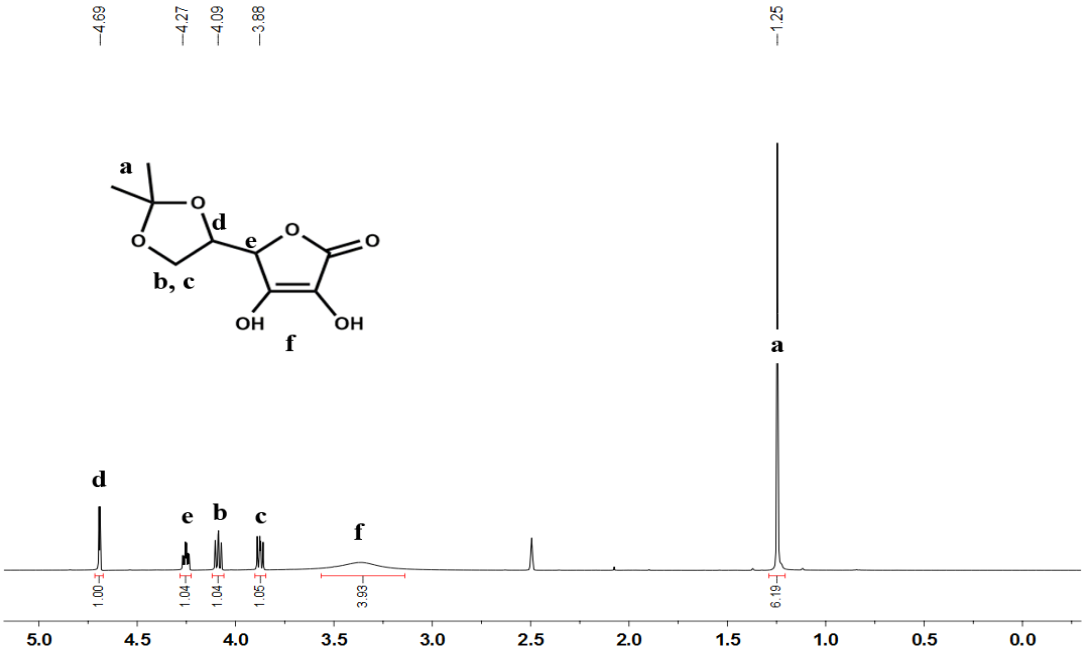


Figure 4.2 : 1H-NMR spectrum of 5,6-Isopropylidene-L-ascorbic acid in D-DMSO (500 MHz).

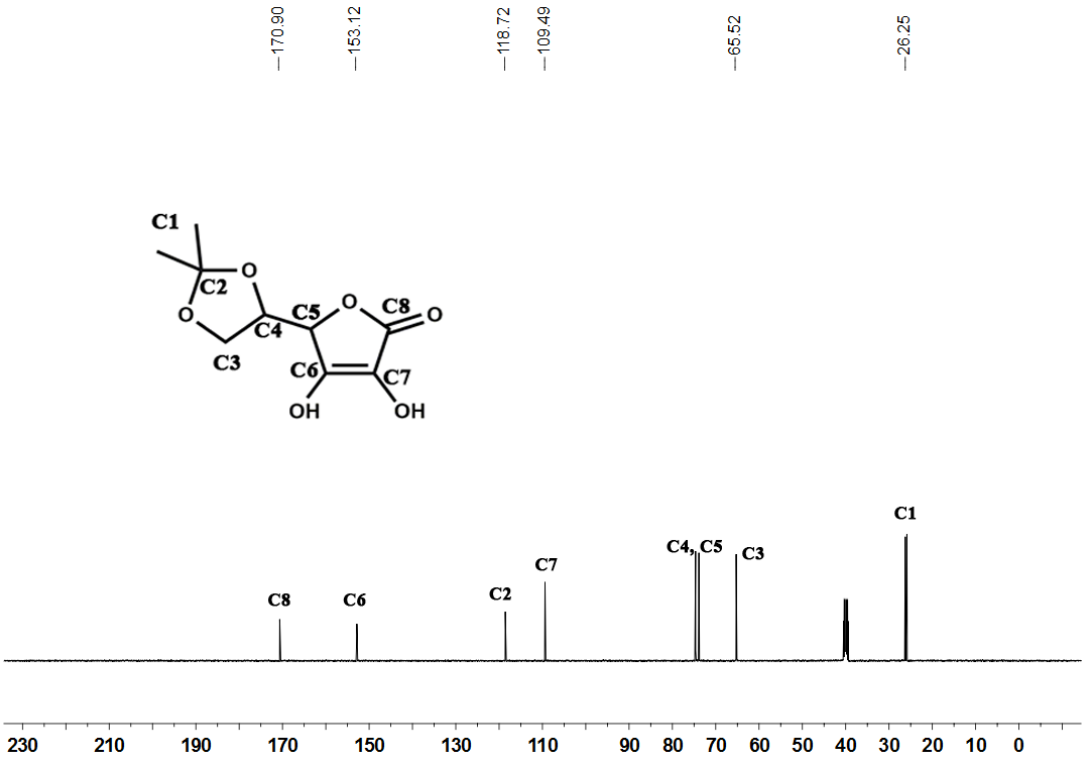


Figure 4.3 : 13C-NMR spectrum of 5,6-Isopropylidene-L-ascorbic acid in D-DMSO (500 MHz).

4.2 Synthesise of Alkene Functional Vitamine Backbone Monomer

5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3,4-bis(pent-4-en-1-yloxy)furan-2(5H)-one (1) was synthesized by the reaction of 5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3,4-dihydroxyfuran-2(5H)-one with 5-bromopent-1-ene with same amount of potassiumcarbonate and solvent mixture was DMSO/THF.

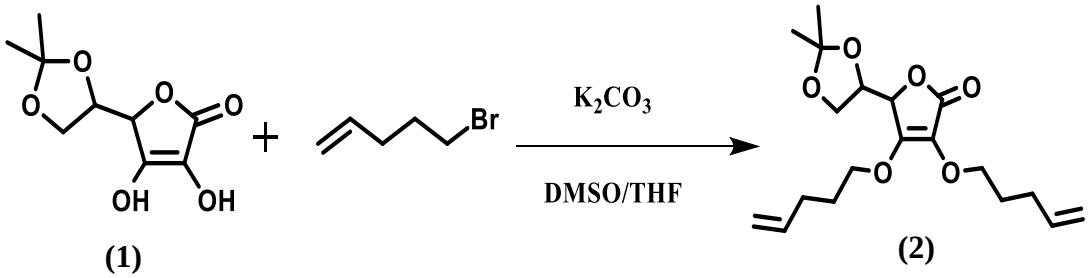


Figure 4.4 : Synthesis of vitamine backbone monomer

On the NMR spectrum of resultant vitamine backbone monomer (Figure 4.5), (Figure 4.6) integration values corrected the structure of the compound. Peaks between 4.20-4.50 ppm were specific to vitamine backbone monomer.

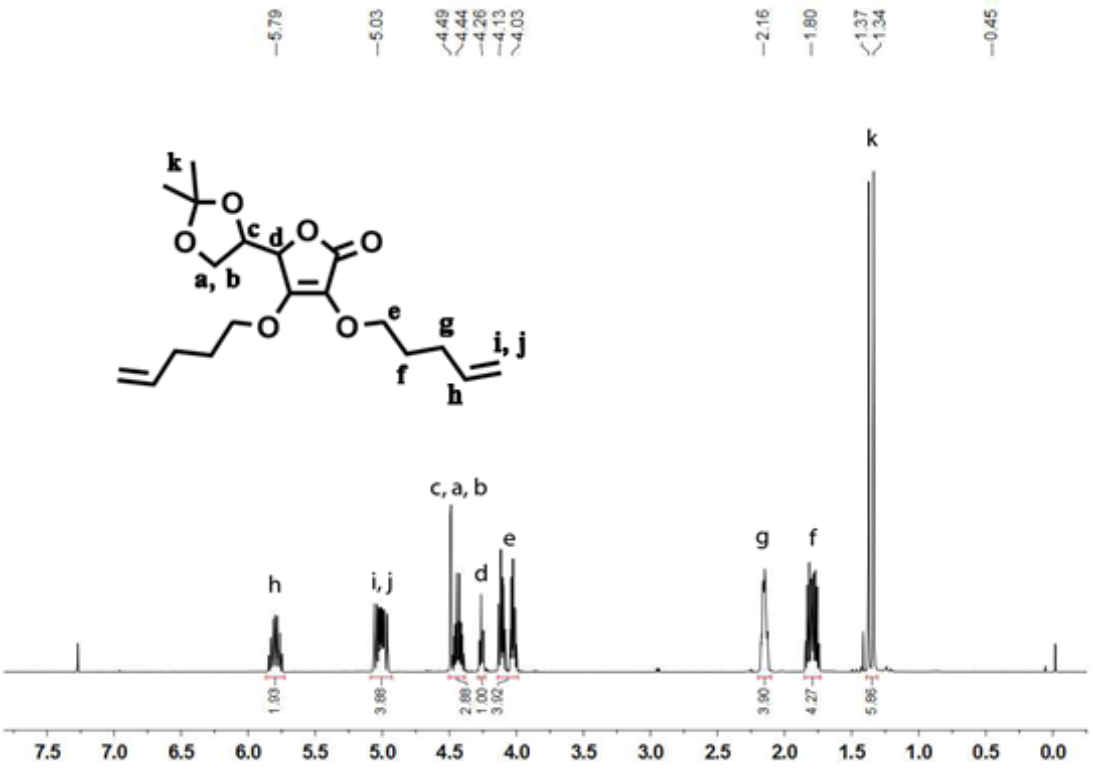


Figure 4.5 : 1H-NMR spectrum of 5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3,4-bis(pent-4-en-1-yloxy)furan-2(5H)-one in CDCl3 (500 MHz).

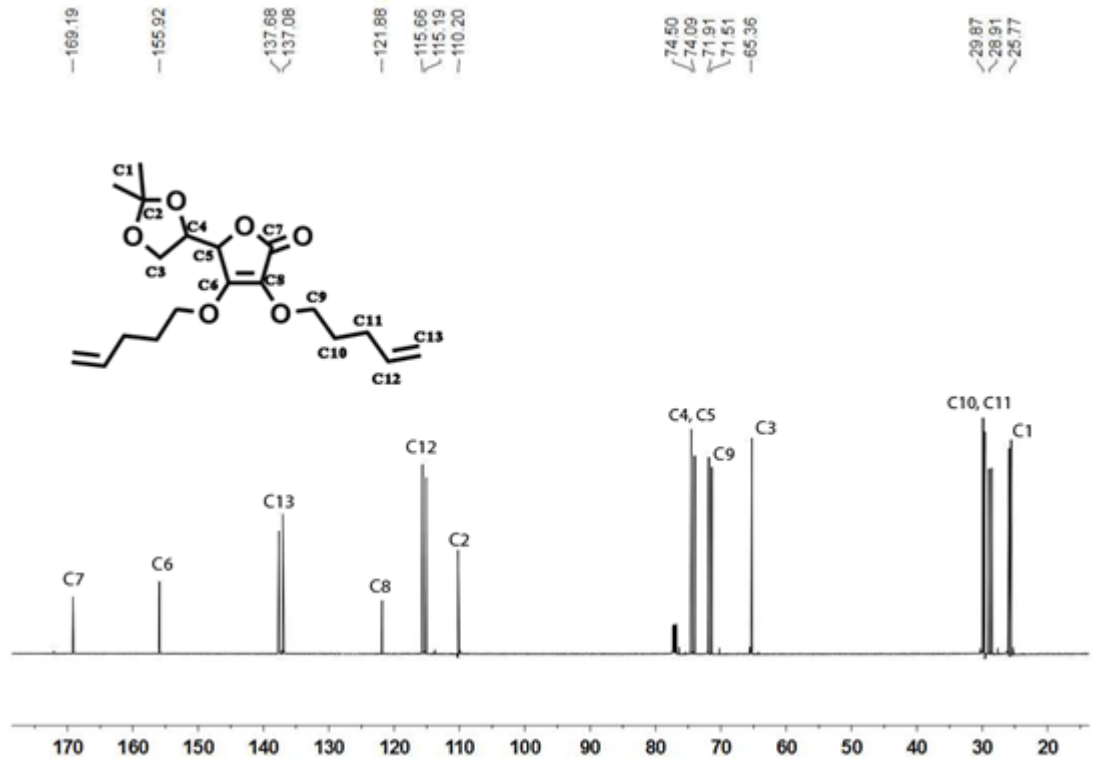
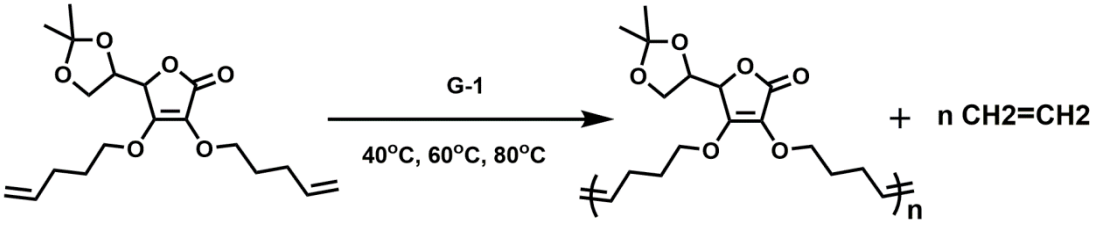


Figure 4.6 : 13C-NMR spectrum of 5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3,4-bis(pent-4-en-1-yloxy)furan-2(5H)-one in CDCl3 (500 MHz)

4.3 Synthesise of Alkene Functional Vitamine Backbone Polymer

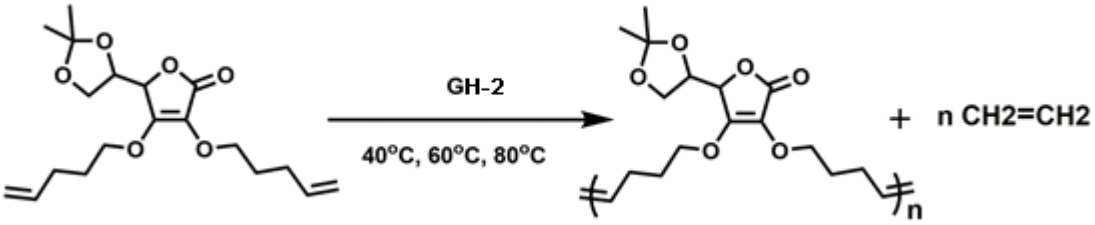
4.3.1 Via bulk polymerization

This polymer was synthesised by reaction of 5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3,4-bis(pent-4-en-1-yloxy)furan-2(5H)-one (2) with each GH-1 and GH-2 catalysts. Polymer characterized with ^{1}H-NMR (Figure 4.3), GPC (Figure 4.4).



(2) **(3)**

Figure 4.7 : Synthesis of vitamin backbone polymer via catalyst G-1 at 40, 60 and 80^{o}C in bulk polymerization



(2) **(3)**

Figure 4.8 : Synthesis of vitamin backbone polymer via catalyst GH-2 at 40, 60 and 80^{o}C in bulk polymerization

On the NMR spectrum of resultant alkene functional vitamine backbone polymer (Figure 4.7), (Figure 4.8) integration values corrected the structure of the compound. Peaks between 4.20-4.50 ppm were specific to alkene functional vitamine backbone polymer.

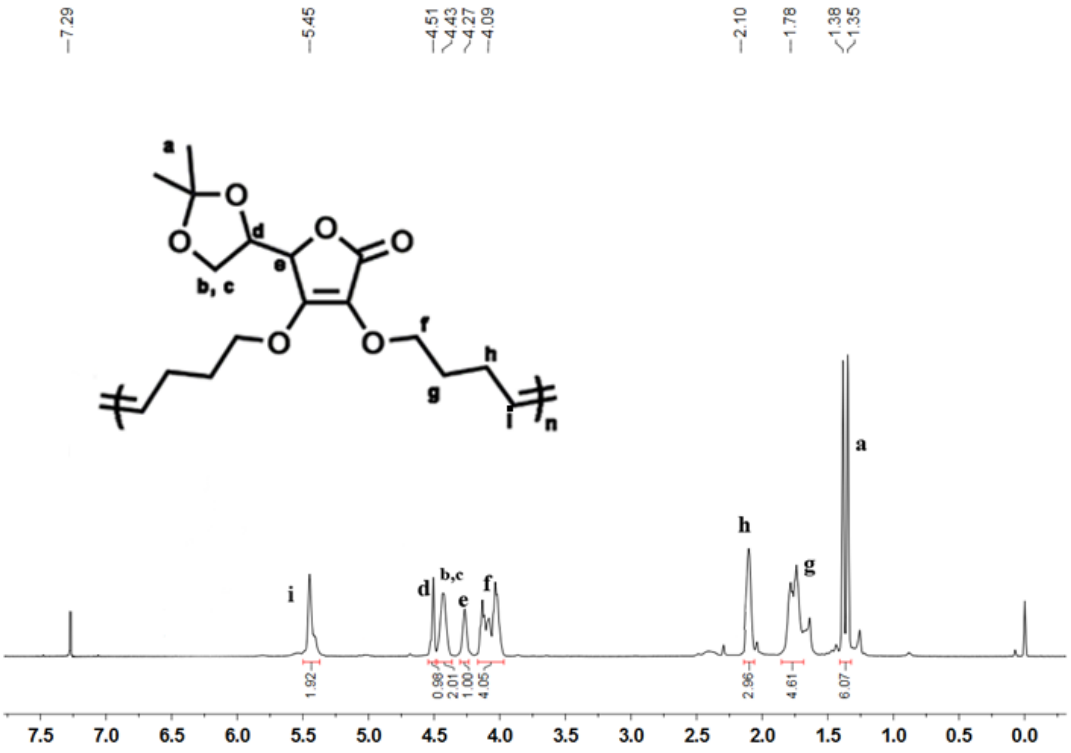


Figure 4.9 : 1H-NMR spectrum of Poly- 5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3,4-bis(pent-4-en-1-yloxy)furan-2(5H)-one in $CDCl_3$ (500 MHz)

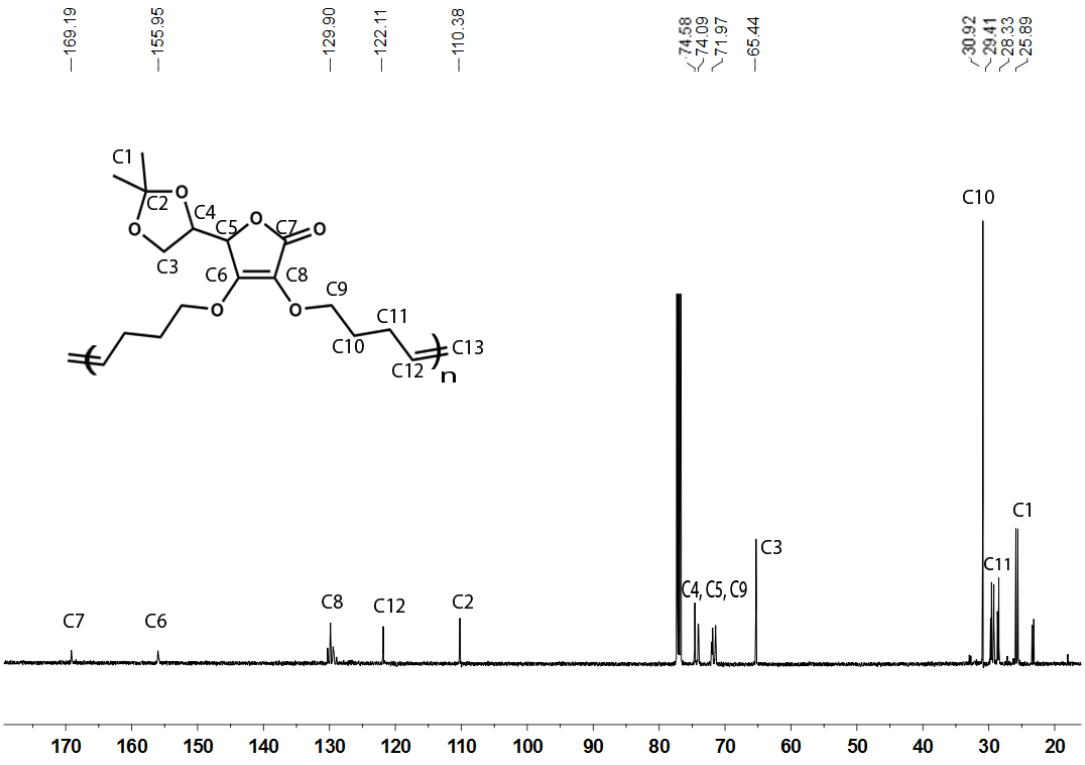


Figure 4.10 : 13C-NMR spectrum of Poly- 5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3,4-bis(pent-4-en-1-yloxy)furan-2(5H)-one in CDCl3 (500 MHz)

From GPC measurement (Figure 4.9) applying bulk polymerization in catalyst G-1 system, with increasing reaction temperature higher molecular weight polyvitamins were obtained determined relative to PS standards in THF.

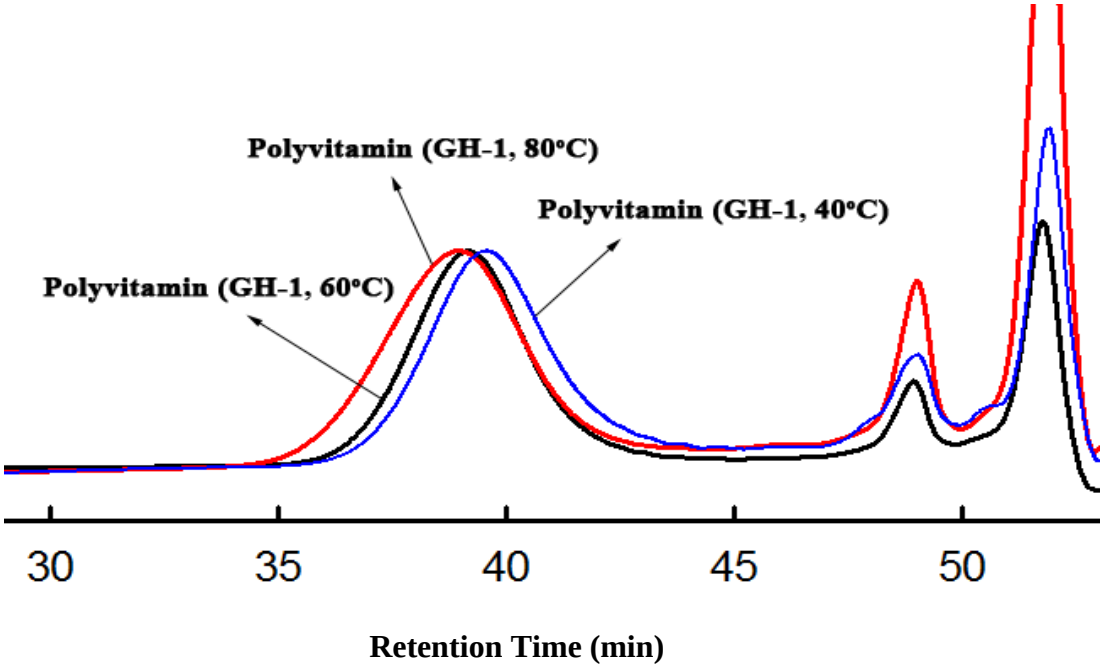


Figure 4.11 : GPC overlay of synthesised Polyvitamin at three different temperatures 40°C, 60°C and 80°C by using catalyst G-1

From GPC measurement (Figure 4.10) applying solution polymerization in catalyst GH-2 system, with increasing reaction temperature again higher molecular weight polyvitamins were obtained determined relative to PS standards in THF.

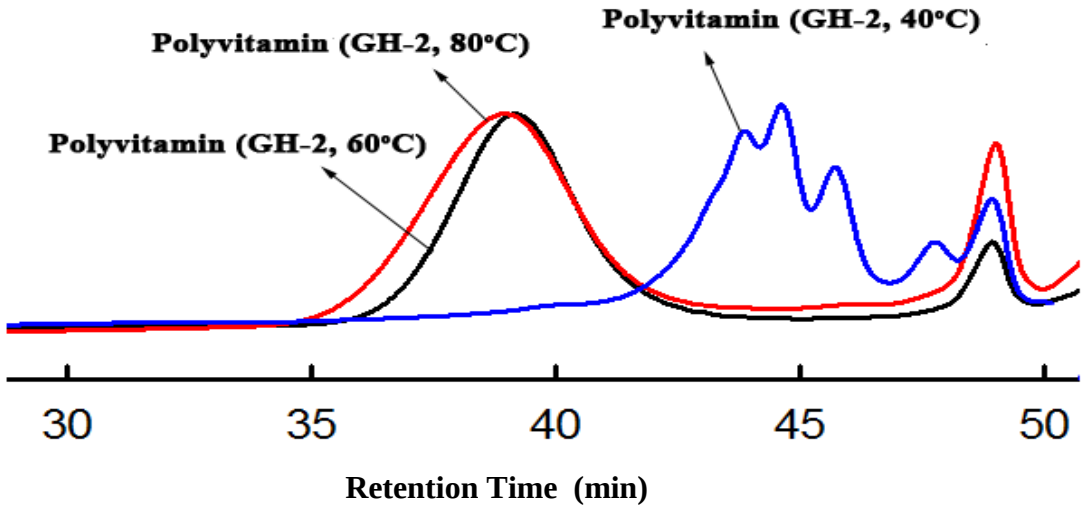
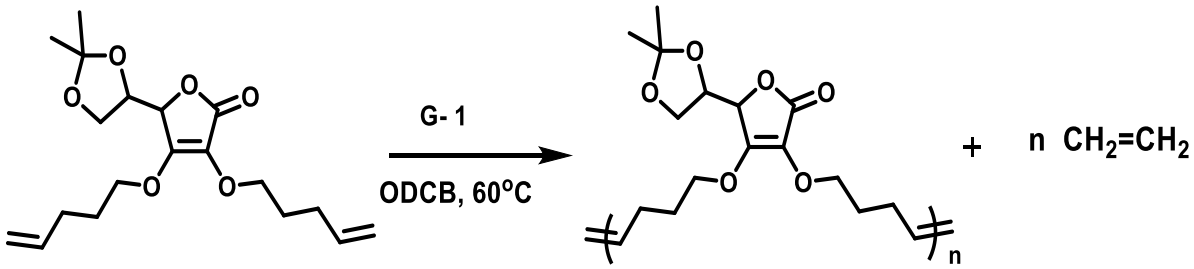


Figure 4.12 : GPC overlay of synthesised Polyvitamin at three different temperatures 40°C, 60°C and 80°C by using Grubbs catalyst 2nd Generation

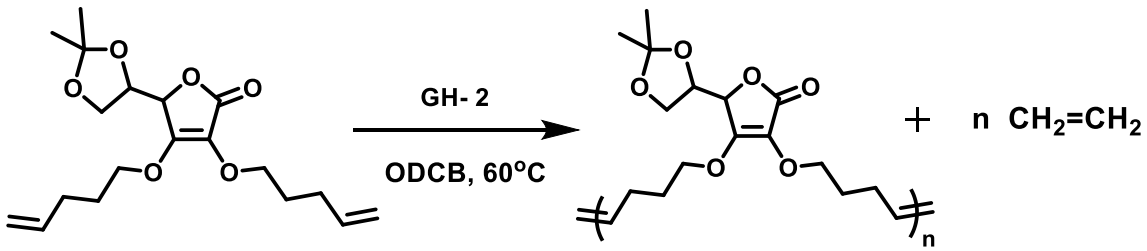
4.3.2 Via solution polymerization

This polymer was synthesised by reaction of 5-(2,2-dimethyl-1,3-dioxolan-4-yl)-3,4-bis(pent-4-en-1-yloxy)furan-2(5H)-one (1) with each Grubbs catalysts in 60^{o}C temperatur by using ODCB as solvent. Polymer characterized with ^{1}H-NMR (Figure 4.3), GPC (Figure 4.4).



(2) **(3)**

Figure 4.13 : Synthesis of vitamin backbone polymer via catalyst G-1 at 60^{o}C in solution polymerization



(2) **(3)**

Figure 4.14 : Synthesis of vitamin backbone polymer via catalyst GH-2 at 60^{o}C in solution polymerization

On the NMR spectrum of resultant alkene functional vitamine backbone polymer (Figure 4.11) integration values corrected the structure of the compound. Peaks between 4.20-4.50 ppm were specific to alkene functional vitamine backbone polymer. From GPC measurement (Figure 4.12) catalyst G-1 system gave us higher molecular weight polyvitamins rather than catalyst GH-2 system in solution polymerization at 60^{o}C determined relative to PS standards in THF. From DSC measurement (Figure 4.13) because of having higher T_g value higher moleculer weight polymer synthesised by catalyst G-1 rather than synthesised by catalyst GH-2 at same temperature 80^{o}C via bulk polymerization.

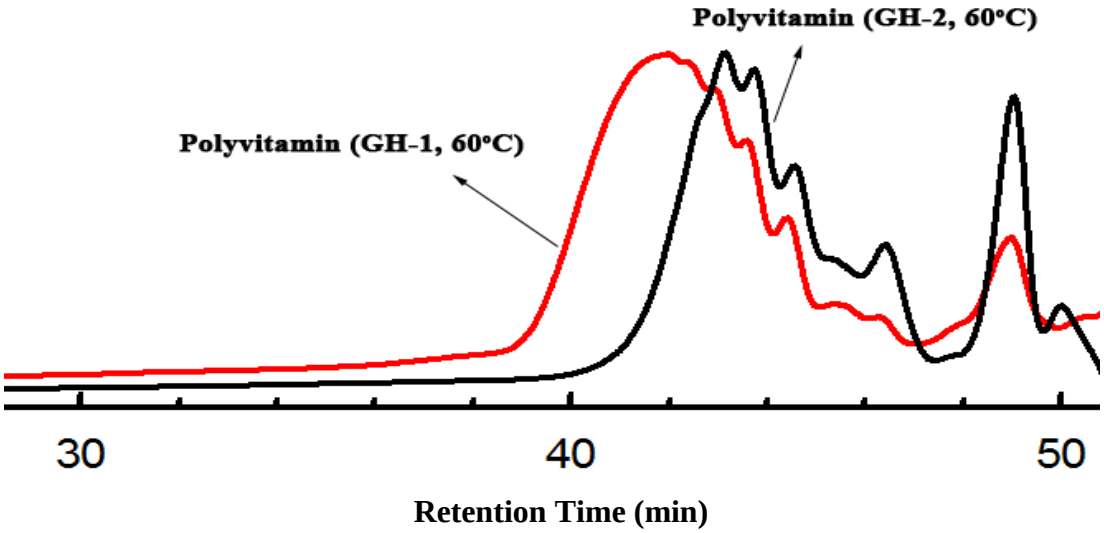


Figure 4.15 : GPC overlay of synthesised Polyvitamin with each catalysts G-1 and GH-2 at 60^{o}C

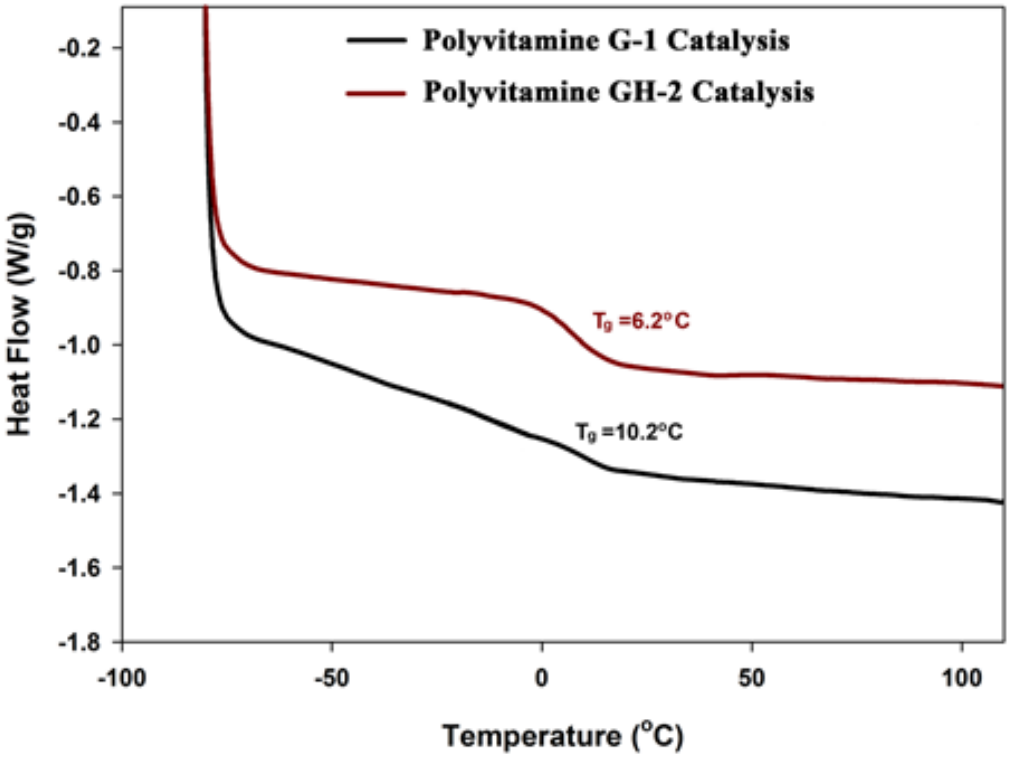


Figure 4.16 : DSC comprasion of Polyvitamins synthesised with G-1 and GH-2 catalysises via bulk polymerization at 80^{0}C

All synthesised polymers $M_{n,GPC}$, $M_{w,GPC}$ and M_w/M_n values are shown in Table 4.1 categorized by reaction's Polymerization type, Catalyst type and Temperature.

Table 4.1 : Characteristics of all synthesised Polyvitamine

Polymerization Type	Catalyst Type	Temperature (^{o}C)	Time (day)	$M_{n,GPC}$ (g/mol)	$M_{w,GPC}$ (g/mol)	M_w/M_n
Bulk Polymerization	G-1	40	3	5033	6060	1.20
	G-1	60	3	5693	6687	1.17
	G-1	80	3	6593	7825	1.18
	GH-2	40	7	931	1136	1.22
	GH-2	60	7	2577	3592	1.39
	GH-2	80	7	4494	5412	1.20
Solution Polymerization	G-1	60	7	2316	2850	1.23
	GH-2	60	7	1107	1552	1.40

5. CONCLUSION

In this study, we synthesised polymer from vitamine C backbone monomer. Because of its properties like being antioxidant and using as a radical scavenger ADMET polymerization was applied via both bulk polymerization and solution polymerization. We obtained higher moleculer weight and lower polydispersity with using bulk polymerization. According to our researchs, we had aspected better results when we used Hoveyda Grubbs Catalyst 2^{nd} Generation. However using Grubbs Catalyst 1^{st} Generation supplied us finer results. Optimum reaction temperature was determined as 80^0C in both catalysts. To conclude, applying bulk polymerization according to method of ADMET to alkene functional vitamine C backbone monomer gives us to best results while using G-1 at 80^0C.

Our future study will include hydrolised polyvitamin. Physical properties, chemical properties and also how does it effect in human body will be investigated.

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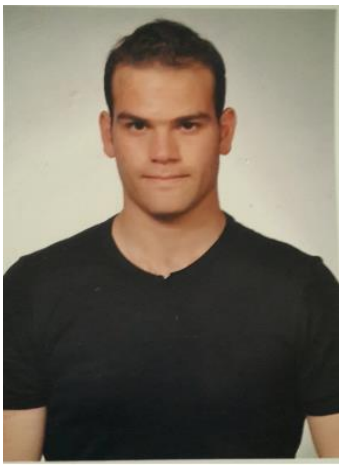

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