ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

A VERSATILE ROUTE FOR THE SYNTHESIS OF FUNCTIONAL POLYCARBONATES HAVING *o*-NITROBENZYL AND ALLYL GROUPS

M.Sc. THESIS

Elif BAYSAK

Department of Polymer Science and Technology

Polymer Science and Technology Programme

Thesis Advisor: Prof. Dr. Gürkan HIZAL

JUNE 2013

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

A VERSATILE ROUTE FOR THE SYNTHESIS OF FUNCTIONAL POLYCARBONATES HAVING *o*-NITROBENZYL AND ALLYL GROUPS

M.Sc. THESIS

Elif BAYSAK
(515111039)

Department of Polymer Science and Technology

Polymer Science and Technology Programme

Thesis Advisor: Prof. Dr. Gürkan HIZAL

JUNE 2013

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

o-NİTROBENZİL VE ALLİL FONKSİYONEL GRUPLARINA SAHİP POLİKARBONAT SENTEZİ

YÜKSEK LİSANS TEZİ

Elif BAYSAK
(515111039)

Polimer Bilim ve Teknolojisi Anabilim Dalı

Polimer Bilim ve Teknolojisi Programı

Tez Danışmanı: Prof. Dr. Gürkan HIZAL

HAZİRAN 2013

Elif BAYSAK, a **M.Sc.** student of ITU **Graduate School of Science and Engineering and Technology** student ID **515111039**, successfully defended the **thesis** entitled **"A Versatile Route for the Synthesis of Functional Polycarbonates Having o-Nitrobenzyl and Allyl Groups''** which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. Gurkan HIZAL** Istanbul Technical University	.....
Jury Members :	**Prof. Dr. Gurkan HIZAL** Istanbul Technical University	.....
	Prof. Dr. Umıt TUNCA Istanbul Technical University	.....
	Assoc. Prof. Dr. Amitav SANYAL Bogazici University	.....

Date of Submission : 03 May 2013
Date of Defense : 05 June 2013

To my dearest family and friends,

FOREWORD

This master study has been carried out at Istanbul Technical University, Institute of Science and Technology.

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.

I would like to also extend my sincere Neşe Çakır, Ufuk Saim Günay, Deniz Kopan and İpek Ösken, Eren Elik and Macar group mates for their friendly assistance and for their friendship.

I would like to thank my family for assisting me all time along in my life. I know that nothing is important then a family. I will appreciate my parents and brother forever.

June 2013

Elif BAYSAK
(Chemist)

TABLE OF CONTENTS

Page

ABBREVIATIONS

^{1}H NMR	**:** Hydrogen Nuclear Magnetic Resonance Spectroscopy
GPC	**:** Gel Permeation Chromatography
$CDCl_3$	**:** Deuterated Chloroform
CH_2Cl_2	**:** Dichloromethane
DCC	**:** *N*,*N*'-dicyclohexylcarbodiimide
DMAP	**:** 4-methylaminopyridine
DMPA	**:** 2,2-Dimethoxy-2-phenylacetophenone
Et_3N	**:** Triethlamine
PC	**:** Polycarbonate
PDI	**:** Polydispersity Index
ROP	**:** Ring Opening Polymerization
THF	**:** Tetrahydrofuran
UV	**:** Ultra Violet
CL	**:** Caprolactone

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SYMBOLS

λ	**:** Wavelength
R·	**:** Radical
nm	**:** Nanometer
C	**:** Concentration
A	**:** Absorbance
k_{act}	**:** Activation rate constant
k_{deact}	**:** Deactivation rate constant
R_p	**:** Rate of polymerization
ppm	**:** Parts per million
^oC	**:** Celsius
M	**:** Molarity
T_g	**:** Glass-transition temperature
M_n	**:** The number average molecular weight
M_w	**:** The weight average molecular weight
M_w/M_n	**:** The molecular weight distribution

A VERSATILE ROUTE FOR THE SYNTHESIS OF FUNCTIONAL POLYCARBONATES HAVING *o*-NITROBENZYL AND ALLYL GROUPS

SUMMARY

Well-defined biodegradable and biocompatible polymers are becoming more and more important materials nowadays. Polycarbonates are ones these type of polymers that are used for a variety of biomedical applications such as devices for controlled drug release that the drug stays stabile until it reaches the right place where it is used for and also controlling the amount of the drug. Other examples are anti-cancer drugs, implants and bioresorbable prostheses etc.

Polycarbonates are considered as biodegradable, biocompatible and low toxic materials which may be mainly synthesized using three different methods, e.g. the polycondensation of diol compounds via phosgene or dialkylcarbonates, the copolymerization of oxiranes with carbondioxide and the ring opening polymerization (ROP) of cyclic carbonate monomers. Cyclic carbonate monomers are used for the synthesis of PCs in recent years with increasing attetion. The catalysts for ROP are generally metalic compounds such as $Sn(Oct)_2$. But in these systems metal impurities are possible in the polymer that the usage of the PCs can be limitted. Polycarbonates are generally used in human body that the metals in PCs can be dangerous to the human system. To prevent this, recently, metal-free catalysts such as several amines and phosphines have been extensively used for an efficient synthesis of aliphatic PCs.

Click reactions have bring a new sight to the green chemistry and also the reactions are not very difficult to make. By this way new functionally groups or polymer chains can be clicked to each other and give new topology. There is not much study on PCs with click reactions and it brings more attention into the academical area.

Amoung the click reactions, thiol-ene click raction is considered the most encouraging the green aspects. This metal-free reaction can be performed in the absence of solvents in some cases, and can be photochemically controlled (even in the absence of a photoinitiator). Some stuedies have showed that the thiol-ene click reaction is more efficient when initiated by light than by thermally.

In this study, we aimed to synthesised polycarbonates from the carbonate monomers which were 5-methyl-5-(2-nitro-benzoxycarbonyl)-1,3-dioxan-2-one which has o-nitrobenzyl functionallity and 5-methyl-5-allyloxycarbonyl-1,3-dioxan-2-one which has allyl functionallity in the structure. Firstly, homo polymers were synthesised after that copolymer was synthesised with using two monomers together. Polymerization is proceed by ROP which is an excellent process however ROP is sensitive to impurities and moisture. Benzyl alcohol was used as initiator, TU/DBU organic catalyst system and as solvent $CHCl_3$. Using the organic catalyst system have provide less temperature actually room temperature to proceed the ROP reaction although almost no possibility for low temperature ROP for metalic catalysted

systems. High reaction temperature causes high PDI, anyway. Further study was one of the click reactions, thiol-ene click on the copolymer that RSH was added under UV via the double bond. The copolymer backbone has also another functional group which is photolabile that under UV irritation photolabile o-nitrobenzyl group leaved the structure to give carboxylic acid functionallity while the RSH compound were adding. The composition and molecular weight of the polycarbonates were characterized by ^{1}H NMR and GPC.

o-NİTROBENZİL VE ALLİL FONKSİYONEL GRUPLARINA SAHİP POLİKARBONAT SENTEZİ

ÖZET

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.

Alifatik polikarbonatlar ilaç sistemlerinde kullanılabilecek en iyi malzemelerdendir. Çünkü bu polimerler düşük toksisiteye sahip olup aynı zamanda biyolojik olarak uyumlu ve biyobozunabilirlerdir. Ayrıca, kontrollü ilaç salınım sistemleri en önemli örneklerinden biri olup, kullanılan ilacın istenilen yerde ve istenilen zamanda etkin olabilmesi sağlanılmaktadır.

Polikarbonat sentezi genellikle üç farklı yolla yapılmaktadır. Bunlar diol bileşiklerinin fosgen varlığında polikondenzasyonu, okziranların karbondioksitle kopolimerizasyonu ve siklik karbonat monomerlerinin halka açılma polimerizasyonudur. Bunlardan en etkin olanı halka açılma polimerizasyonu olup çeşitli mekanizmalar üzerinden yürümektedir. En çok kullanılan mekanizmalar anyonik halka açılma polimerizasyonu ve koordinasyon ekleme halka açılma polimerizasyonudur. Ayrıca katyonik halka açılma polimerizasyonu da yapılabilinmektedir. Bu mekanizmaları kullanılan başlatıcılar ve katalizör sistemleri belirlemektedir. Hangi mekanizma üzerinden olursa olsun halka açılma polimerizasyonu neme, havayave safsızlıklara karşı oldukça hassastır. Bu yüzden, çalışılması dikkat ve önem gerektirmektedir. Kullanılan kimyasalların ve malzemelerin kuru ve temiz olması reaksiyonun ilerlemesini kolaylaştırarak sağlamaktadır.

Halka açılma polimerizasyonu ile iyi tanımlanmış polimer sentezi yapılmaktadır. Siklik yapıdaki monomerlerin açılması ile lineer yapıda polimer yapısı elde edilmektedir. Laktide ve laktonlar bu amaçla sıklıkla kullanılan monomerlerdir. Halka açılma polimerizasyonu ile aşı, dallanmış ve star gibi farklı topolojilere sahip polimerler sentezlenebilir. Ayrıca, bu polimerleşme tekniği ile herhangi bir yan ürün oluşumu gerçekleşmemektedir.

Halka açılma polimerizasyonu ile farklı fonksiyonelitelere sahip polimer sentezleyebilmek olasıdır. Bu amaçla kullanılılacak monomerlerin sentez ve seçimi akademik ve endüstri alanlarında araştırmalara açıktır.

Kullanılan başlatıcılar, katalizörler ve monomerler reaksiyonun süresini, verimini ve oluşan polimerin molekül ağırlığını etkilemektedir. Başlatıcının reaksiyonu başlatabilecek kadar etkin olması önemli bir parametredir. Kullanılan katalizör sistemleri polimerleşme süresi ve reaksiyon sıcaklığını etkileyebilmektedir. Genellikle kullanılan katalizörler $Sn(Oct)_2$ (Tin(II) 2-etilheksanoat) gibi metal katalizörleri olup yüksek sıcaklıklarda çalışmayı gerektirmektedir. Yüksek

sıcaklıklarda çalışmak dezavantajları da beraberinde getirmektedir. Yüksek sıcaklık, polimer zincirlerinin birbirleriyle etkileşmesini ve yan reaksiyonlara neden olup PDI değerini kötü etkileyebilmektedir. Son yıllarda kullanılan DBU ve TU organik katalizör sistemiyle daha ılımlı koşullarda polimerleşme gerçekleştirilmektedir. Ayrıca reaksiyon oda sıcaklığında bile olabilmektedir. Metal içeren katalizörleri kullanılmasının bir diğer dezvantajı ise oluşan polimerlerde metal safsızlıklarının bulunuyor olmasıdır. Bu polimerler biyolojik uygulamalarda kullanıldığında insan sağlığı için olumsuz şartlar oluşturmaktadır.

Kullanılan monomerlerin de reaksiyona girebilme eğilimleri polimerleşmeyi etkileyebilmektedir. Beş üyeli halka yapasında olan karbonat monomerlerinin polimerleşmesi yüksek kararlılıkları nedeniyle altı üyeli halkalarla karşılaştırıldıklarında polimerleşmeleri daha zordur.

Click kimyası 2001 yılında Sharpless tarafından tanımlanmıştır. Tek cümle ile click kimyasından bahsedecek olursak molekülleri birbirine kolayca bağlamak diyebiliriz. Click reaksiyonları yeşil kimyayı desteklemektedir ve de yüksek verimle ve az yan reaksiyonlarla moleküller birbirine bağlanılabilmektedir.

Thiol-en click reaksiyonları ile tiyol bileşikleri polimer zincirinde bulunan çifte bağ ile yapıya radikalik olarak bağlanılmaktadır. Thiol-ene click reaksiyonları termal yolla yapılabileceği gibi ışıkla da yapılabilmektedir. Işıkla gerçekleştirilen bu reaksiyonlarda ortama foto başlatıcılar konulmaktadır ve de mekanizma radikalik olarak yürümektedir. Işık altında gerçekleştirilen thiol-ene reaksiyonu, termale göre daha etkili olduğu çeşitli yayınlarda belirtilmiştir. Reaksiyon ortamında bulunan nem ya da hava reaksiyon üzerine pek olumsuz etki yapmazken; havanın oksijeni radikal oluşumunu artırıp reaksiyon verimini artırmaktadır. Herhangi bir metal bulunmaması bu reaksiyonunun yeşil kimyayı desteklemesini ortaya koymaktadır. Thiol-ene reaksiyonlarının bazı dezavantajları vardır. Bunlar; disülfit oluşumu ve coupling (radikallerin baş başa katılması) gibi yan reaksiyonlardır.

o-Nitrobenzil grubu UV bölgede ışık absorplanmasıyla polimer yapısından ayrılabilmektedir. Bu olay fotoliz olarak adlandırılıp, grubun ayrılmasıyla karboksilik asit fonksiyonelitesi yapıya kazandırılmaktadır. Bu işlem için çalışılan dalga boyu 260 nm den 400 nm ye kadar olabilmektedir. Ancak en iyi ayrılmanın gerçekleştiği dalga boyu yaklaşık olarak 350 nm dir. Bu dalga boyundaki ışık aynı zamanda gün ışığında da bulunmaktadır. Elde edilen polimerin yapısına göre UV ışığıyla muamelenin süresi değişebilmektedir. *o*-Nitrobenzil grubunun uç grup olması yada polimer zincirlerini birbirine bağlayan yapı olması gibi durumlar sonucu bu süre 5-10 dakika gibi bir süreden uzun saatlere kadar kayabilmektedir. Kullanılan ışığın gücü, lamba sayısı gibi etkenler de reaksiyon süresini etkileyen önemli parametrelerdir. Polimer yapısında bulunan grup ile ayrılan grup UV spektroskopisinde farklı dalga boylarında absorbans vermektedirler.

Bu çalışmada iki çeşit karbonat monomeri sentezlenmiş olup bunlardan biri allil grubu diğeri de *o*-nitro benzil grubu içermektedir. İlk olarak her bir monomerden yola çıkarak DBU, TU katalizör sistemini ve $CDCl_3$ solventi ile oda şartlarında halka açılma polimerizasyonu ile homopolimerler sentezlenmiştir. Daha sonra ise iki monomerin birlikte halka açılma polimerleşmesi yapılıp hem allil hem de *o*-nitrobenzil fonksiyonelitesine sahip kopolimer sentezlenmiştir. Sentezlenen kopolimerin allil fonksiyonelitisi ile UV altında thiol-ene click reaksiyonu yapılıp yapıya thiol bileşiği katılırken; *o*-nitrobenzil grubunda da aynı zamanda fotoliz reaksiyonu ile nitro grubunun yapıdan ayrılıp karboksilik asit fonksiyonelitesi

oluşturması sağlanmıştır. Karboksil grubu polimerin suda çözünürlüğünü artırmaktadır. Karakterizasyon işlemleri ^{1}H NMR ve GPC ile gerçekleştirilmiştir.

1. INTRODUCTION

Ring-opening polymerization (ROP) is a well defined and well-established polymerization process that a cyclic monomer is opened to give a linear polymer. Lactones and lactides are the most known carbonate monomers for this aim. The most remarkable aspect of ROP was theoretically explained by Flory for the first time. The advanteges of ROP in conjuction with a "living" method have facilitated the controlled synthesis of block, graft, and star polymers [1]. In a ROP reaction a hydroxyl group or an alcohol is generally used as the initiator for cyclic carbonate monomers [2]. ROP proceeds with different mechanisms depending on which monomer, initiator and catalytic system are used. Generally used catalyst is Tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) for the polymerisation for monomers such as ε-caprolatone (ε-CL) and lactide (LA). There are several different mechanisms have been hypothesised for ROP, in fact the most commonly accepted mechanism for the initiation is that $Sn(Oct)_2$ is converted into tin alkoxide, the actual initiator, by reaction with alcohols or other protic compounds/impurities. Effectively, by tuning the alcohol- to- monomer ratio, the molecular weight of the final polymer can be controlled [2-4].

Traditionally, mechanisms for ROP are cationic, anionic polymerization and coordination-insertion" mechanism that is proceed with metal involving catalyst. In cationic and anionic systems ROP proceed with the ionic charge of active side propagates species [5].

N-heterocyclic carbenes (NHCs) become a new class of highly active catalysts for ROP owing to their high nucleophility. Their important reactivity for transesterification reactions are manifested in their ability to catalyze ROP of lactones and carbonates [6]. For this good ability TU and DBU organic catalysts are used frequently.

"Click chemistry" is a chemical term defined in 2001 by Sharpless and describes chemistry tailored to generate substances quickly and reliably by joining small units

together [19]. Click chemistry can be summarized with only one sentence: ‘’Molecules that are easy to make. ‘’ Sharpless also introduced some criteria in order to fullfill the requirements as reactions that: are modular, wide in scope, high yielding, create only inoffensive by-products, are stereospecific, simple to perform and that require benign or easily removed solvent. Nowadays there are several processes have been identified under this term in order to meet these criterias such as nucleophilic ring opening reactions; non-aldol carbonyl chemistry; thiol additions to carbon–carbon multiple bonds (thiol-ene and thiol-yne); and cycloaddition reactions. Among these selected reactions, copper(I)-catalyzed azide-alkyne (CuAAC) and Diels-Alder (DA) cycloaddition reactions and thiol-ene reactions have gained much interest among the chemists not only the synthetic ones but also the polymer chemists.

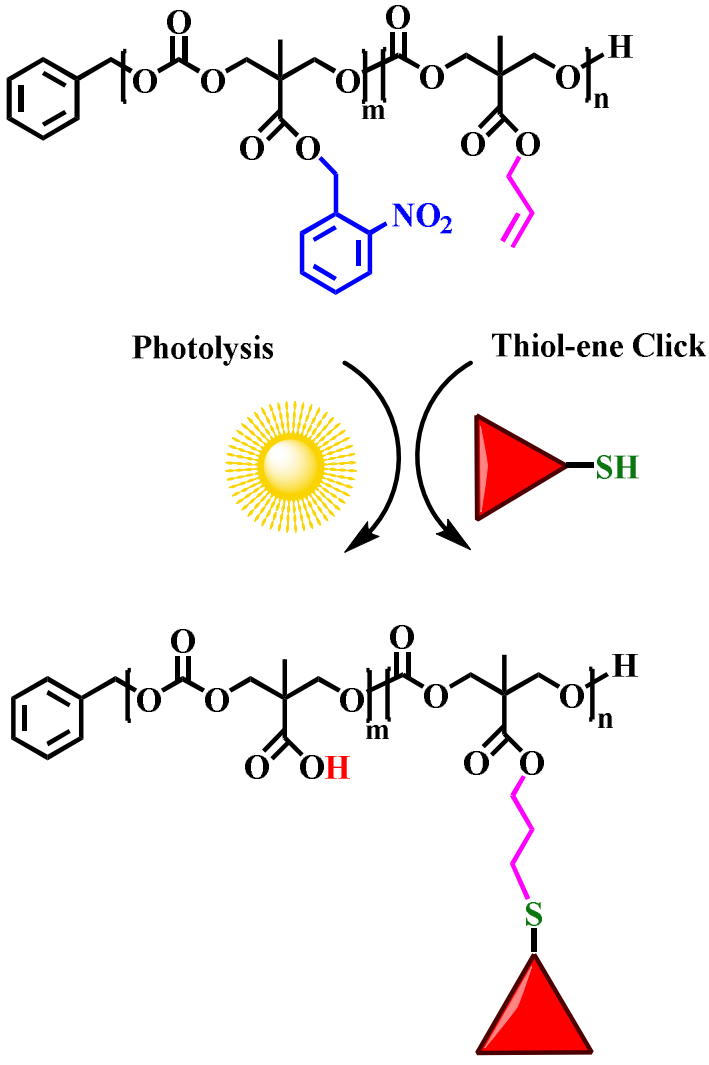


Figure 1.1 : Synthesis of copolymers via ROP and functionalization with UV photolysis and thiol-ene click reaction.

The thiol-ene click reaction has realized between a thiol and an alkene to form a thioether linkage. More specifically, the sulfur–carbon bond formation follows an anti-Markonikov process that can be promoted by UV light radiation or by radical initiators. Thiol-ene click reactions are discovered in chemistry at early times, but have been rather extensively studied over the last century.

By using thiol-ene click a new group can be added to the polymer backbone that changes the topology of the chain. In our study we added RSH compound to the polycarbonate backbone while the photolysis of the o-nitrobenzyl group happened at the same time under UV irritation at 350 nm. After photolysis reaction more water soluable chemical structure, carboxylic acid was obtained. On the other hand with adding RSH compound hydrophilicity increased.

2. THEORETICAL PART

2.1 Ring-Opening Polymerization (ROP)

Ring-opening polymerization (ROP) is a well defined and well-established polymerization process, that a cyclic monomer such as lactones and lactides are opened to give a linear polymer.

The most remarkable aspect of ROP was theoretically explained by Flory; the invariant number of propagating chains in the ROP results in the generation of polymerization. The advanteges of ROP in conjuction with a "living" method have facilitated the controlled synthesis of block, graft, and star polymers, which leads to a present consensus that living ROP is a powerful and versatile addition-polymerization method [1].

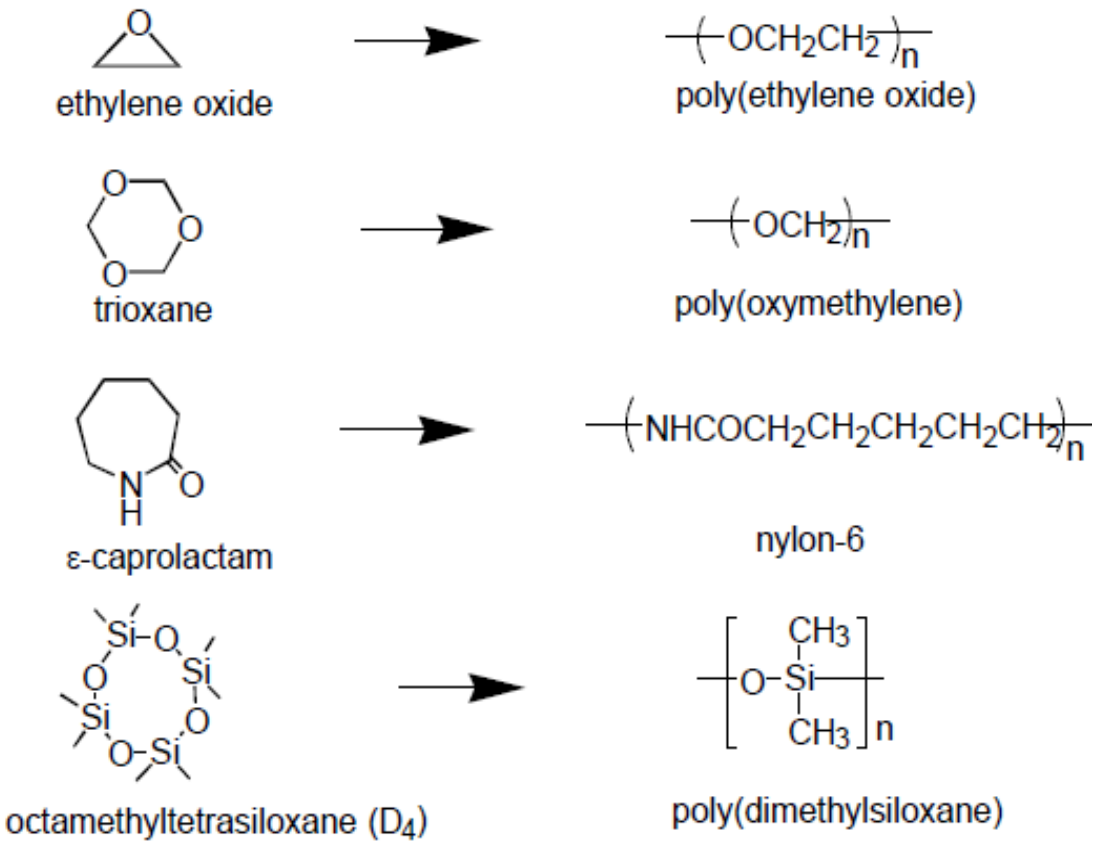


Figure 2.1 : Carbonate monomers and ROP of those monomers.

In a ROP reaction an alcohol or hydroxyl group is generally used as the initiator for cyclic carbonate monomers[2]. ROP proceeds through different mechanisms depending on which monomer, initiator and catalytic system that are used. Generally used catalyst is Tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) for the polymerization for monomers such as ε-caprolatone (ε-CL), lactide (LA) and p-dioxanone. There are several different mechanisms have been hypothesised for this system, in fact the most commonly accepted mechanism for the initiation is that $Sn(Oct)_2$ is converted into tin alkoxide, the actual initiator, by reaction with alcohols or other protic compounds/impurities. Effectively, by tuning the alcohol- to- monomer ratio, the molecular weight of the final polymer can be controlled [2-4].

ROP is fundamentally different from condensation polymerization because there is no small molecule by-product during the polymerization. A wide variety of functional groups containing polymers can be produced by ring-opening polymerizations. Preparation of cyclic monomers, studies of catalysis and mechanisms are active areas of research both in industry and academiacal areas [8-11].

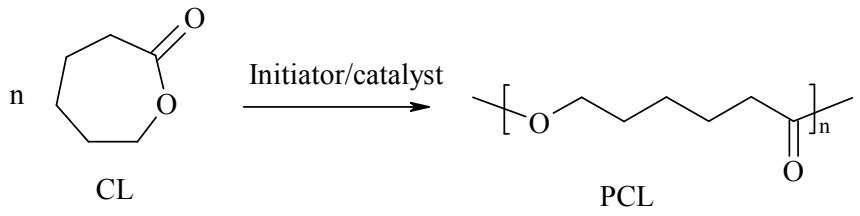


Figure 2.2 : Ring-opening polymerization of CL.

Technologies of polymers made by ROP are usually of much smaller scale. Their total production volume is much lower than that of vinyl or olefin polymers. Nevertheless, most of technical polymers made by ROP could hardly be replaced by any other synthetic or natural material. Poly(ethylene oxide) is one of the most hydrophilic polymers that finding hundreds of applications mostly in the biomedical area. And it is a good example of these type of polymers that based on ROP.

Tradationally, mechanisms for ROP are ‘’cationic, anionic polymerization and coordination-insertion’’ mechanism that is done with metal involving catalyst. In cationic and anionic systems happens and ionic charge of active side propagates

species [5]. So, anionic and cationis polymerization proceed by the charged species which resembles to each other.

2.1.1 Anionic Ring-Opening Polymerization

Anionic polymerization of ethylene oxide (EO) the best example ROP that has been extensively researced by a number of authors. In the mid-forties Flory observed that propagation may proceed without side reactions, such as irreversible transfer and termination in anionic polymerization of EO. [12,13].

The chain growth in EO polymerization, as well as other anionic ROPs, proceeds in agreement with the SN_2 mechanism. In this mechanism, nucleophilic bimolecular substitution at the carbon atom is happened. Despite an apparent simplicity of the anionic polymerization of EO, controlled synthesis of PEO, with regard to its molar mass (Mn) and end groups structure requires special precautions [14,15]. Ionic (e.g. alkoxide) active species can participate in a number of different physical forms: ions, ion pairs and ionic aggregates in the polymerization being in slower or faster interexchange.

2.1.1.1 Initiation in the Anionic ROP

Initiating systems are known for major cyclic ethers, sulfides, siloxanes, lactones and cyclic esters of phosphoric acid to initiate polymerization without any side reactions. These are carboxylic salts for β-lactones [16,17], alkoxide anions for higher lactones [18], thiolate anions for cyclic sulfides [19,20] and polysulfides [20,21], and silanolates for cyclic siloxanes [22]. Therefore, the pertinent discussion from the past and related to the side reactions in initiation with some other initiating systems do not have to be covered and even remembered. Indeed, lots of various compounds have unsuccessfully been used, although the acetates are known to initiate the anionic ROP of strained, four membered b-lactones but do not initiate polymerization of the less strained lactones with higher membered rings. Anions with high basicity and steric hindrance, low nucleophilicity (e.g. tert-butoxide) initiate polymerization mostly with proton transfer with irreversible [e.g. b-propiolactone (PL)] or reversible [e.g. ε-caprolactone (CL)] [23].

Alkoxides are much more nucleophilic than carboxylates so much efficient as initiators.

Initiation step must be fast to obtain good polydispersity indexes. If the initiation is slow, than the polymerization proceeds in slow way because of inefficient anionic centers.

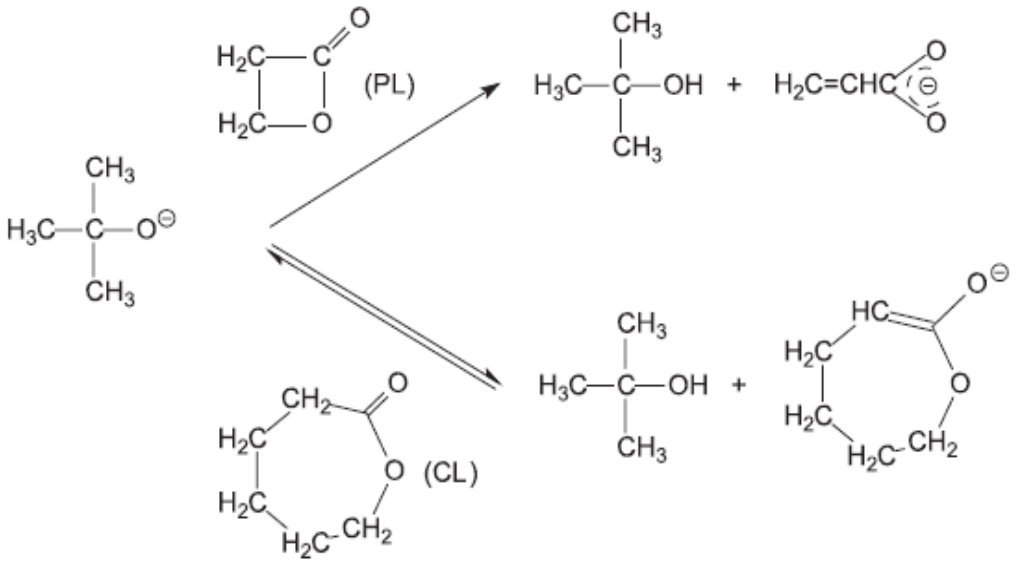


Figure 2.3 : Initiation of lactones polymerization with anions of high basicity.

2.1.1.2 Propagation in the Anionic ROP

Anionic ring polymerization of 1,2-propylene oxide (PO) is used for the preparation of oligomeric block copolymers with EO in industrial. High molar mass polymers cannot be obtained this way, because of an extensive chain transfer to PO. [29]

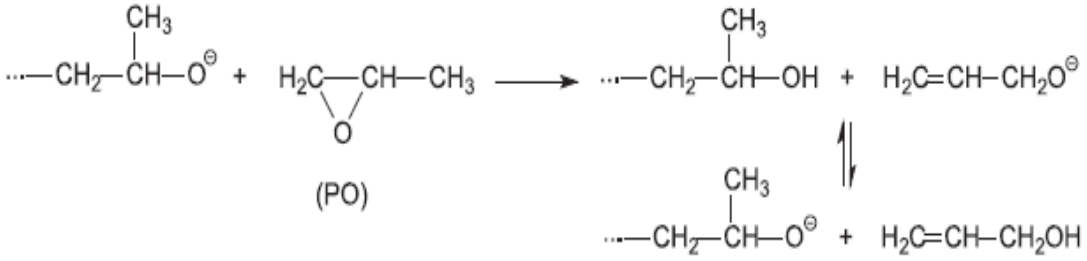


Figure 2.4 : Chain transfer to monomer in the anionic polymerization of 1,2-propylene oxide (PO).

2.1.1.3 Termination in the Anionic ROP

The polymerization can be terminated by a variety of nucleophilic reagents such as excess water, THF, alcohols(methanol, ethanol etc.) and salts.

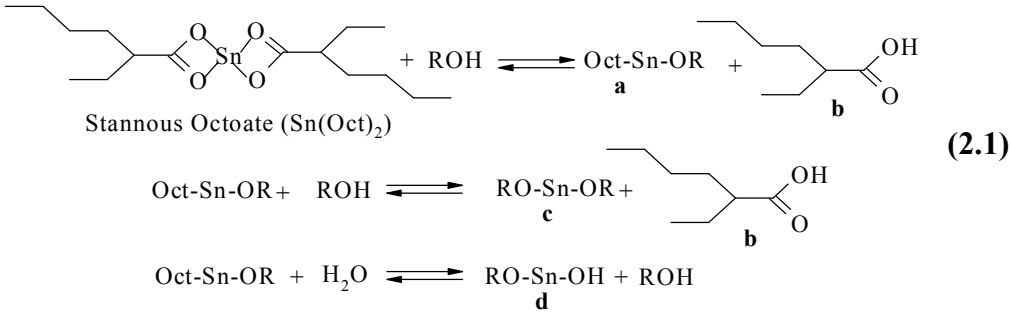
According to the desired specialty of the resulting polymer, many functionalities and end-groups can be introduced [30].

2.1.2 Cationic Ring-Opening Polymerization

For the ROP of a variety of cyclic heterocycles, cationic polymerization has been applied. The cationic ROP of lactones has been achieved using alkylating agents, acylating agents, Lewis acids, and protic acids. Early 1970s, it was reportted by Dittrich and Schultz that LA polymerization with cationic compounds were unsuccessfull. In 1986, Kricheldorf and co-workers screened a variety of acidic compounds, among which triflouromethanesulfonic acid (triflic acid, HOTf) and methyl triflate (MeOTf) proved to be useful initiators for cationic ROP of LA [1].

2.1.3 Coordination-Insertion ROP

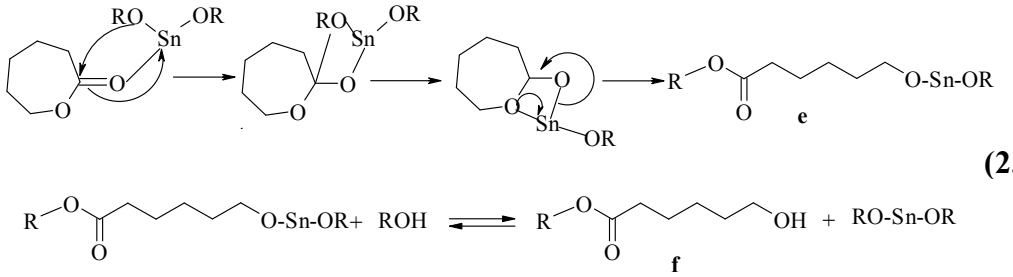
Covalent metal carboxylates, particularly tin(II) bis(2-ethylhexanoate) usually referred to as tin(II) octanoate, $Sn(Oct)_2$ belong to the most frequently used initiators for polymerization of cyclic esters due to its low cost and high efficiency. Although, there are several reports in the literature about the nature of $Sn(Oct)_2$ activity in the polymerization of lactones, two basic types of mechanism have been proposed. The first one is directly catalytic type where the catalyst serves to activate monomer through coordination with its carbonyl oxygen [31,32]. The second mechanism is the monomer insertion type mechanism where the catalyst acts as co-initiator along with either purposely added or adventitious hydroxyl impurities, and polymerization proceeds through an activated stannous alkoxide bond [33,34].



(2.1)

Kricheldorf and co-workers have recently illustrated how the structure of the alcohol initiator may influence the strength of the catalyst/alcohol interaction [32, 34]. According to these authors, this interaction, in the early stages of reaction, is responsible for formation of the "true" initiating species, subsequent ring opening, and formation of the active, propagating chain end. Prior to the beginning of

polymerization, adventitious hydroxyfunctional impurities (e.g. water) or purposely added alcohol first complex and subsequently react with $Sn(Oct)_2$ producing a stannous alkoxide species (a) and free 2-ethylhexanoic acid (b) as shown in (2.1). Further reaction with a second equivalent of alcohol produces the stannous dialkoxide initiator (c) and releases a second equivalent of 2-ethylhexanoic acid (b) as depicted (2.1) [33]. Adventitious water, meanwhile, serves mainly as a catalyst deactivator via a reversible reaction with a or c, thereby decreasing the concentration of active initiator and producing a stannous alcohol derivative (d), such as shown in (2.1), which is more thermodynamically stable than the stannous dialkoxide and is less efficient as an initiator [34].



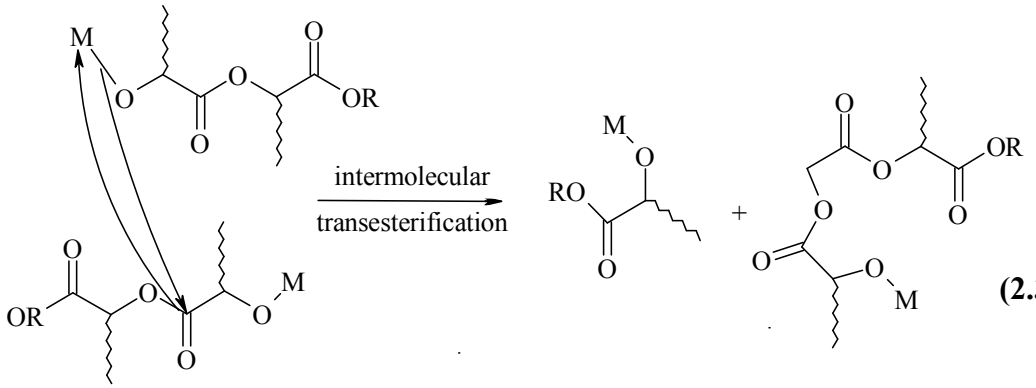
Reaction of c with monomer by means of coordination- insertion generates the first actively propagating chain end (e) consisting of not only the initiating alcohol fragment but also the active propagating center derived from the first monomer unit and stannous alkoxide. The e species may either propagate or undergo rapid intermolecular exchange of the stannous alkoxide moiety for a proton from either hydroxyl groups of initiator (if remaining) or another hydroxy chain end, either e or polymeric in nature. This rapid exchange of protons and stannous alkoxide moieties results in a dynamic equilibrium between activated and deactivated chain ends as depicted in (2.2), where R= unreacted alcohol initiator or hydroxy chain ends generated in situ. This process eventually consumes the remaining unreacted alcohol initiator not involved in the initial formation of c. ROP based on coordination-insertion mechanism has been thoroughly investigated since it may yield well-defined polyesters through living polymerization [35, 36].

In such coordination-insertion polymerizations the efficiency of the molecular-weight control depends from the ratio $k_{propagation}/k_{initiation}$ but also from the extent of transesterification side reactions. These transesterification reactions can occur both intramolecularly (backbiting leading to macrocyclic structures and shorter chains)

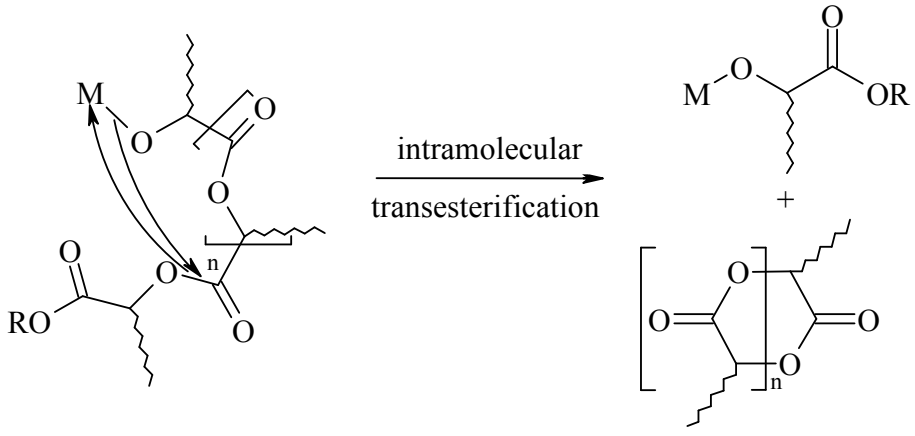
and intermolecularly (chain redistributions) (2.3) and (2.4) [37]. Intermolecular transesterification reactions modify the sequences of co-polylactones and prevent the formation of block co-polymers. Intramolecular transesterification reactions cause degradation of the polymer chain and the formation of cyclic oligomers. This oligomers causes bad PDIs.

The polymerization/depolymerization equilibrium should also be taken into account as a particular case of intramolecular transesterification reaction. All of these side reactions result in broader molecular-weight distributions, sometimes making the molecular weights of the resulting polymers irreproducible. The extent of these undesirable transesterification reactions was found to strongly depend on the metallic initiator [38]. Side reactions occur from the very beginning of the polymerization with $Sn(Oct)_2$, leading to rather broad MWD (PDI indexes around 2) but only at high or even complete conversion with $Al(O\textit{i}\text{-}Pr)_3$, yielding lower PDI indexes (less than 1.5) [39, 40].

Parameters that influence the number of transesterifications are temperature, reaction time, and type and concentration of catalyst or initiator. Depending on the metal used, the initiator is more or less active towards transesterification reactions [40].



(2.3)



(2.4)

The promising results obtained with $Sn(Oct)_2$, $Al(Oi\text{-}Pr)_3$, and $Zn(Lact)_2$ have given rise to a growing interest in metal-based initiators that would display higher catalytic activity and better control the extent of the undesirable transesterification reactions.

By using these type of catalyst system, metallic impurities can be in the polymer.

2.1.4 Controlled ROP of Cyclic Esters

The ring opening polymerization (ROP) of lactones and lactides to produce poly(ester)s provides versatile biocompatible and biodegradable polymers that possessing good mechanical properties. Because of these advantages aliphatic poly(ester)s have received increasing attention over the last few years [41].

Aliphatic poly(ester)s can be either synthesized by polycondensation of hydroxyl-carboxylic acids or by the ring-opening polymerization (ROP). The polycondensation technique yields low molecular weight polyesters (Mn<30.000) with poor control of specific end groups [42]. On the other hand, with ROP high molecular weight aliphatic polyesters can be obtained in short periods of time. There has been much research directed towards the controlled ROP of commercially available cyclic esters including glycolide, lactide and ε-caprolactone resulting in aliphatic poly(ester)s with high molecular weights [43].

In practice, the ROP of lactones and lactides requires an appropriate catalyst to proceed in reasonable conditions and to afford polymers with controlled properties. Since the pioneering work of Kleine et al. in the 1950s metal-based catalytic systems have been the focus of considerable attention for the polymerization of cyclic esters, and numerous studies have been carried out to elucidate the mechanism of such coordination polymerizations. Through variation in the nature of the metal center and of the surrounding ligands, a broad range of initiators have been prepared and evaluated [44, 45, 46, 47].

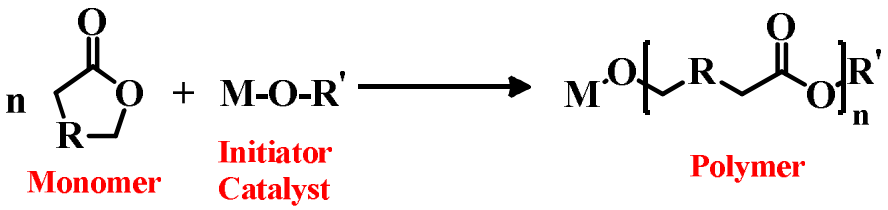


Figure 2.5 : Schematic reprensantation of the ROP of a cyclic ester R=$(CH_2)_{0\text{-}3}$ and/or (CHR').

Besides the coordination-insertion mechanism, alternative strategies based on anionic, nucleophilic, or cationic promoters have also been recently (re)evaluated, the preliminary results reported in these fields being rather promising [48, 49]. Among the mechanisms anionic ring opening polymerization is mostly used because of no metal impurities and can be applied in a good way.

2.1.5 Catalysts

A large number of organometallic compounds, such as metal alkoxides and metal carboxylates, has been studied as initiators or catalysts to achieve effective polymer synthesis [50]. The covalent metal alkoxides with free p or d orbitals react as coordination initiators and not as anionic or cationic initiators [51]. The most widely used complex for the industrial preparation of polylactones and polylactides is made by $Sn(Oct)_2$. It is easy to find in commercially, easy to handle with, and soluble in common organic solvents and in melt monomers. It is really active and allows for the preparation of high-molecular-weight polymers in the presence of an alcohol [52]. Aluminum alkoxides have also proved to be efficient catalysts for the ROP of cyclic esters. The common example, namely, aluminum (III) isopropoxide, $Al(Oi\text{-}Pr)_3$, has been extensively used for mechanistic studies. However, it has been released to be significantly less active than $Sn(Oct)_2$ [53]. Moreover, an induction period of a few minutes is systematically observed with $Al(Oi\text{-}Pr)_3$ attributed to aggregation phenomenon [54]. For all these reasons, $Al(Oi\text{-}Pr)_3$ is much less used for the preparation of biodegradable polyesters, and especially since aluminum ions do not belong to the human metabolism and are suspected of supporting Alzheimer's disease. Much interest has thus been devoted to zinc derivatives as potential nontoxic catalysts. Zinc powder itself is a relatively good polymerization catalyst that has been used industrially [55]. With reaction times of several days at 140 °C in bulk, it is roughly as active as $Al(Oi\text{-}Pr)_3$. Numerous zinc salts have also been investigated [56].

Polymerization of alifatic cyclic carbonetes has been reported by using organometallic catalysts such as $Sn(Oct)_2$ and $Al(Oi\text{-}Pr)_3$ and as well as enzymes. There are some metal-free catalysts for polymerizations of carbonetes and other cyclic monomers. In recent years these types ara more selective and researchers and academicians are working on these.

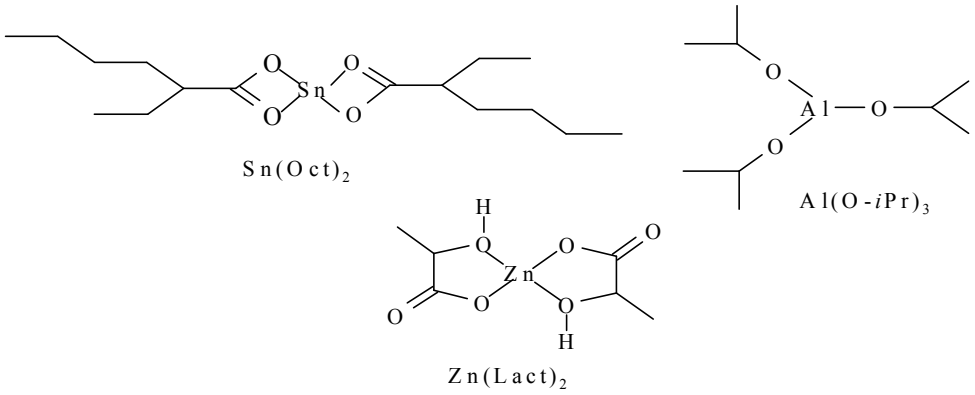


Figure 2.6 : Catalysts of Ring Opening Polymerization.

Simple organic molecules like 4-dimethylaminopyridine (DMAP), 4-pyrrolidinopyridine (PPY) and some phosphines have shown to support ROP of cyclic monomers in the presence of a proper nucleophilic initiator. Most of these catalysts have the advantages of being commercially available or readily synthesized [57,58].

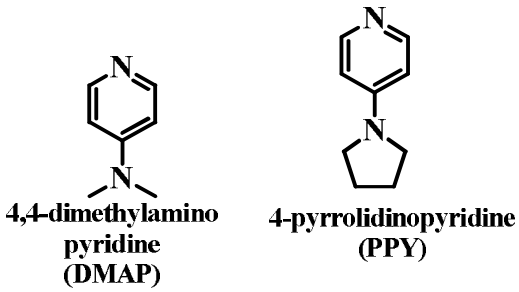


Figure 2.7 : Metal-free catalysts of Ring Opening Polymerization.

N-heterocyclic carbenes (NHCs) become a new class of highly active catalysts owing to their high nucleophility. Their important reactivity for transesterification reactions are manifested in their ability to catalyze ROP of lactones and carbonates [6].

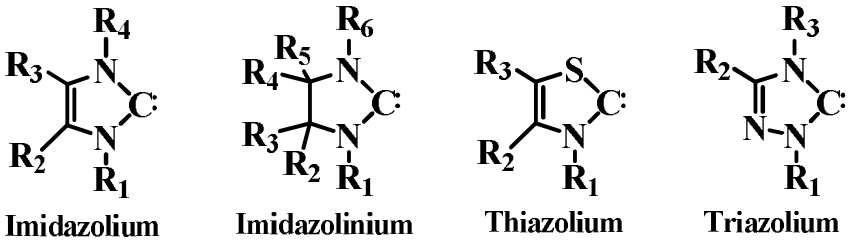
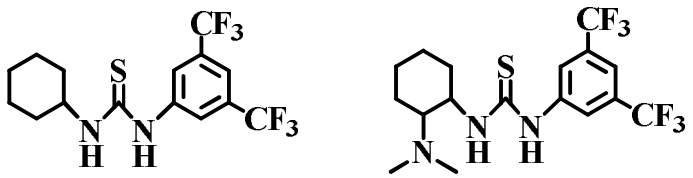


Figure 2.8 : N-heterocyclic Carbenes Catalysts for Ring Opening Polymerization

Other organic catalysts have been developed that supply electrophilic and nucleophilic activations. Amine substituted ureas and thioureas are approved to be

highly selective for the ROP of cyclic carbonetes to give predictable molecular weights, narrow polydispersity indexes along with end-group fidelty. DBU is a type of material that is commercially available and has high nucleophlicity and it increases the negativity in the media. By this way, aninonic initiation can be obtained in a good way.



bis(3,5-triflouromethyl) phenylcyclohexyl thiourea cocatalyst (TU)

Thiourea-amine

Figure 2.9 : Amine substituted ureas and thioureas catalysts for ROP.

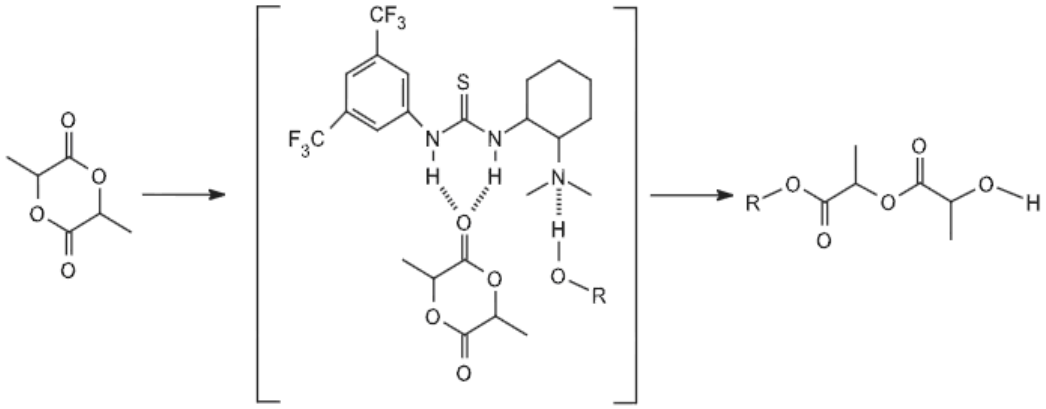


Figure 2.10 : ROP of lactide involving dual activation by a thiourea-tertiary amine catalyst.

Both using bis(3,5-triflouromethyl) phenylcyclohexyl thiourea cocatalyst (TU) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gives a quantitative monomer conversion in much shorter times while maintaining the excellent control over the polyester molecular parameters [5].

Polycarbonates [60] are especially attractive due to the easy synthesis of functional carbonate monomers [61,62] and the facility at which the six-membered carbonates undergo ring-opening polymerization [60, 63]. Organic catalysts such as thioureas and neutral bases are useful as they exhibit good activities at room temperature and at the same time high selectivities and functional group tolerance.[64,62−67]

The production of functionalized polyesters or polycarbonates by ring-opening polymerization technique requires the functional groups of the monomers and polymers are compatible with the polymerization conditions and the reactivity of the ester bond.[68] A particular advantage of thiourea catalysts that they exhibit a high selectivity for ring opening of carbonates and also a very low activity for transesterification [65−67]. This selectivity provides for facile ring-opening without redistribution or transesterification of the pendant functional groups.

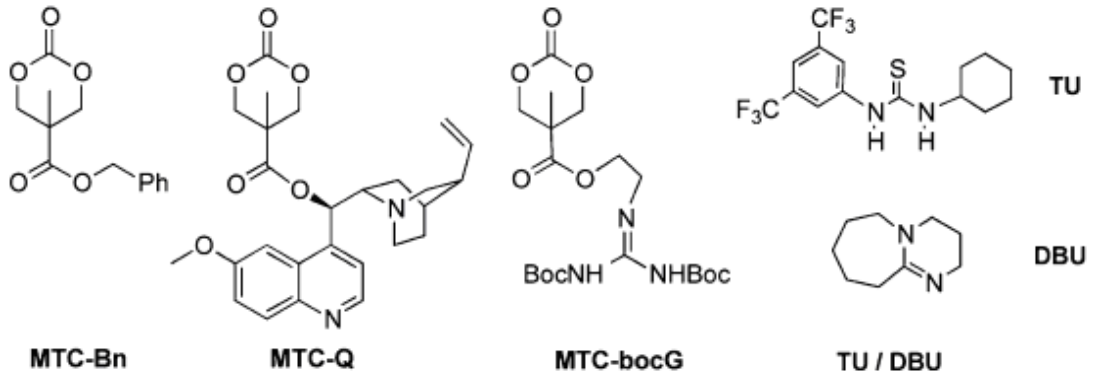


Figure 2.11 : Some Monomers and catalysts for ROP

2.2 Polycarbonates

Cyclic carbonates chemistry, which has been studied since the 1930s, has becoming an interesting area for researchers in the past 30 years [78]. Polymers that have carbonate groups, in the main or in the side chains, attracted much attention because of their application as biocompatible, optical, high dielectric, and/or adhesive materials [79, 80]. Cyclic carbonates gives both anionic and cationic ring-opening polymerizations. The polymerizability of the cyclic monomer depends on the ring-size. As seen in the literature six-membered cyclic carbonates result in the corresponding polycarbonates by anionic or cationic ring-opening polymerization [78,81–89]. On the other hand, five-membered cyclic carbonates are thermodynamically stable that they do not result in the corresponding polycarbonates; instead poly(ether carbonate)s are obtained by partial decarboxylation [90, 91]. Cyclic carbonates, even substituted five-membered cyclic carbonates, react with amines to afford the corresponding hydroxyl urethanes [92-96]. The reactivity of cyclic carbonates is dependent on the ring-size. Under the same reaction condition the rate constant (k) for the bimolecular reaction of six-membered

ring carbonates with amines is 29–62 times bigger than that of five-membered ring carbonates depending on the reaction temperature [94-96].

2.2.1 Cyclic Carbonate Monomers

Aliphatic polycarbonates are synthesized by ring-opening polymerization of cyclic carbonate monomers. Five and seven membered macro cyclic carbonate monomers have been used for this purpose but six-membered cyclic carbonates are the most widely studied type of cyclic carbonate monomers because of their stability and ease of synthesis as well as polymerization.[97]

2.2.2 Synthesis of 6-Membered Cyclic Carbonates

Six-membered cyclic carbonates can be synthesized by several different ways. Although, through organometallic catalysis, cyclic carbonates may be obtained by direct coupling of CO_2 with oxetanes at 60 °C and pressures up to 3.5 MPa (Figure 2.12),[98] more common procedures use 1,3-diols [99] as precursors to six-membered cyclic carbonates. Using a palladium catalyst, cyclic carbonates can be synthesized through direct oxidative carbonylation of 1,3-diols at 100 °C and a pressure of 20 atm (2 MPa), as illustrated in (Figure 2.13).[100]

Under less drastic conditions, cyclic carbonates may be obtained through transesterification with a dialkyl carbonate. In this two-step synthesis, oligomers are initially formed. As the temperature increases, depolymerization produces the cyclic monomer which may be distilled off under reduced pressure. Using elemental sodium as a basic catalyst for the transesterification, this was the method used for the original synthesis of trimethylene carbonate by Carothers and Van Natta. [101] More recent varieties employ organometallics such as stannous 2-ethylhexanoate (Sn(Oct)2) as transesterification and depolymerization catalysts. [102, 103] For smaller-scale preparation, it is typically more convenient to use a phosgene derivative as the carbonyl source. Suitable reagents include triphosgene, [104] di-tert-butyl dicarbonate,[105] di-2-pyridyl carbonate,[106] bis(pentafluorophenyl) carbonate [107] and 1,1'-carbonyldimidazole (CDI) [108]. A particularly popular method, introduced by Endo et al., [109] employs ethyl chloroformate as the ring-closing reagent in THF together with stoichiometric amounts of triethylamine as a catalyst (Figure 2.14).

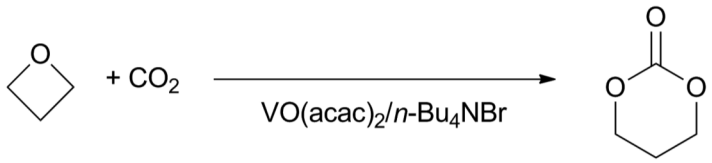


Figure 2.12 : Synthesis of TMC from oxetane by catalytic addition of CO_2.

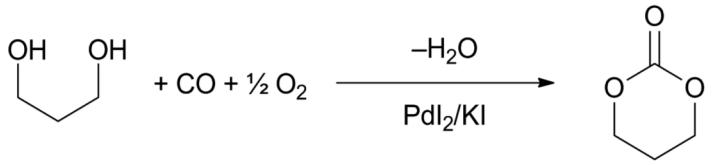


Figure 2.13 : Synthesis of TMC by catalytic direct oxidative carbonylation of 1,3-propanediol.

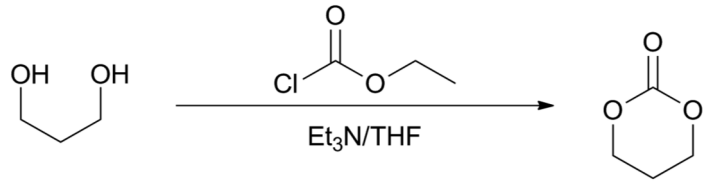


Figure 2.14 : Synthesis of TMC from 1,3-propanediol using ethyl chloroformate as aring-closing reagent.

In 2012, Tunca- Hizal group described for the first time the synthesis of well-defined PC-based block copolymers using the Diels-Alder click reaction of the PC_{30}-anthracene with a variety of the a-furan protected maleimide-terminated polymers. The polycarbonate which has benzyl alcohol functionality on the backbone and anthracene functional end group by click chemistry other polymer chains have clicked to the antracene group to obtain more functional polycarbonate (Figure 2.15) [110].

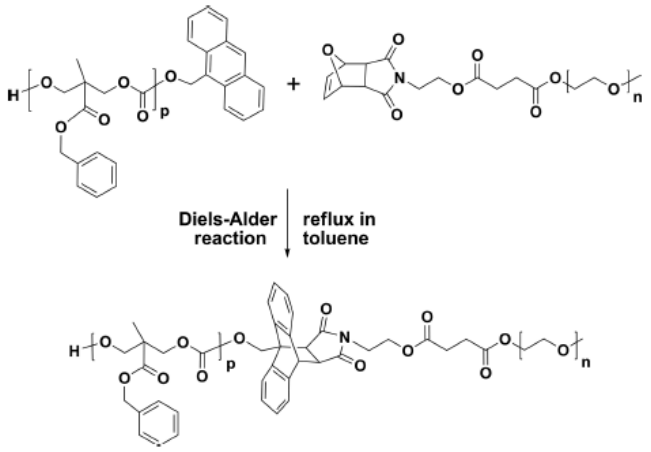


Figure 2.15 : Preparation of PC-b-PEG copolymer via Diels-Alder click reaction.

An other study based on well-defined polycarbonates is done by Dove group in 2010 whose study assembles to the research that we have done. In the study they have synthesized allyl group functionallity polycarbonate in presence of TU and spartein catalyst system. Then, they have made an thiol-ene reaction on the double bond of the polymer's allyl functionality (Figure 2.16) [111].

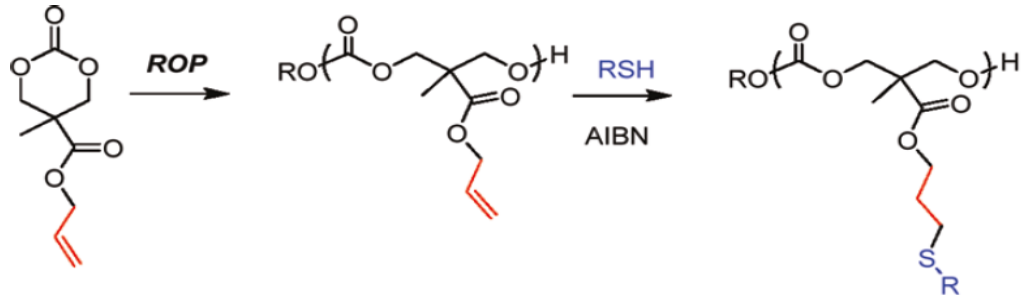


Figure 2.16 : ROP of ally functional carbonate monomer and functionalization with thiol-ene reaction.

And the other study on polycarbonates is experienced by Dove and Sanyal. They have described a strategy to synthesize and functionalize maleimide containing thiol reactive biodegradable polymers by the organocatalyzed (co)polymerization of a furan-protected maleimide-functional carbonate monomer (Figure 2.17) [112].

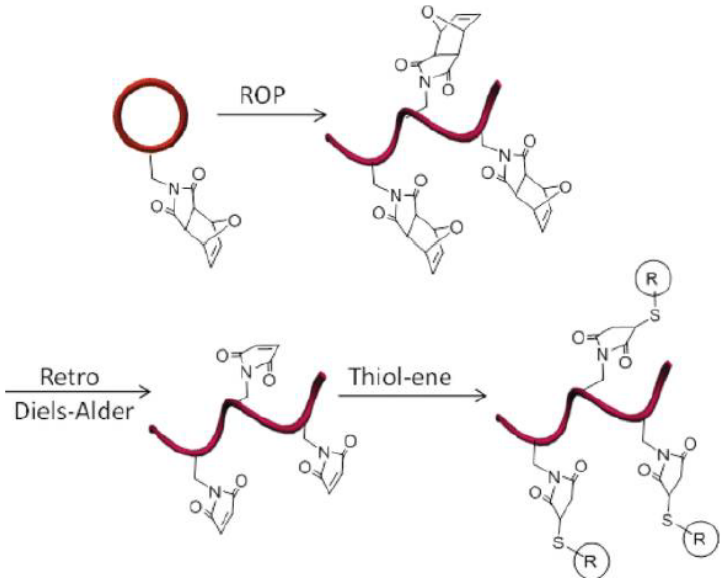


Figure 2.17 : ROP of maleimide containing carbonate monomer and functionalization with click reactions.

Xiabin Jing and co-workers have synthesised biodegradable poly(carbonate ester)s with photolabile protecting groups by ring-opening copolymerization of L-lactide (LA) with 5-methyl-5-(2-nitro-benzoxycarbonyl)-1,3-dioxan-2-one (MNC) with

diethyl zinc (Et_2Zn) as catalyst. The poly(L-lactide-*co*-5-methyl-5-carboxyl-1,3-dioxan-2-one) (P(LA-*co*-MCC)) was obtained by UV irradiation of poly(L-lactide acid-*co*-5-methyl-5-(2-nitro-benzoxycarbonyl)-1,3-dioxan-2-one) (P(LA-*co*-MNC)) to remove the protective 2-nitrobenzyl group. The free carboxyl groups on the copolymers P(LA-*co*-MCC) were reacted with paclitaxel, a common antitumor drug (Figure 2.18) [125].

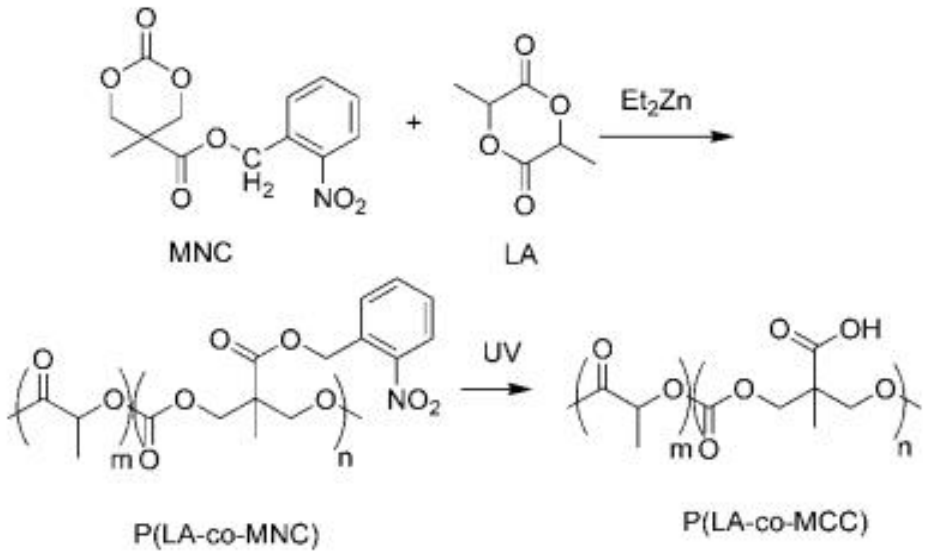


Figure 2.18 : Copolymer synthesis with LA and MNC monomers.

2.3 Click Chemistry

"Click chemistry" is a chemical term defined by Sharpless in 2001 and describes chemistry tailored to generate substances quickly and reliably by joining small units together [7]. Click chemistry can be summarized with only one sentence: ''Molecules that are easy to make. '' Sharpless also introduced some criteria in order to fullfill the requirements as reactions that: are modular, wide in scope, high yielding, create only inoffensive by-products, are stereospecific, simple to perform and that require benign or easily removed solvent. Nowadays there are several processes have been identified under this term in order to meet these criterias such as nucleophilic ring opening reactions; non-aldol carbonyl chemistry; thiol additions to carbon–carbon multiple bonds (thiol-ene and thiol-yne); and cycloaddition reactions. Among these selected reactions, copper(I)-catalyzed azide-alkyne (CuAAC) and Diels-Alder (DA) cycloaddition reactions and thiol-ene reactions have gained much interest.

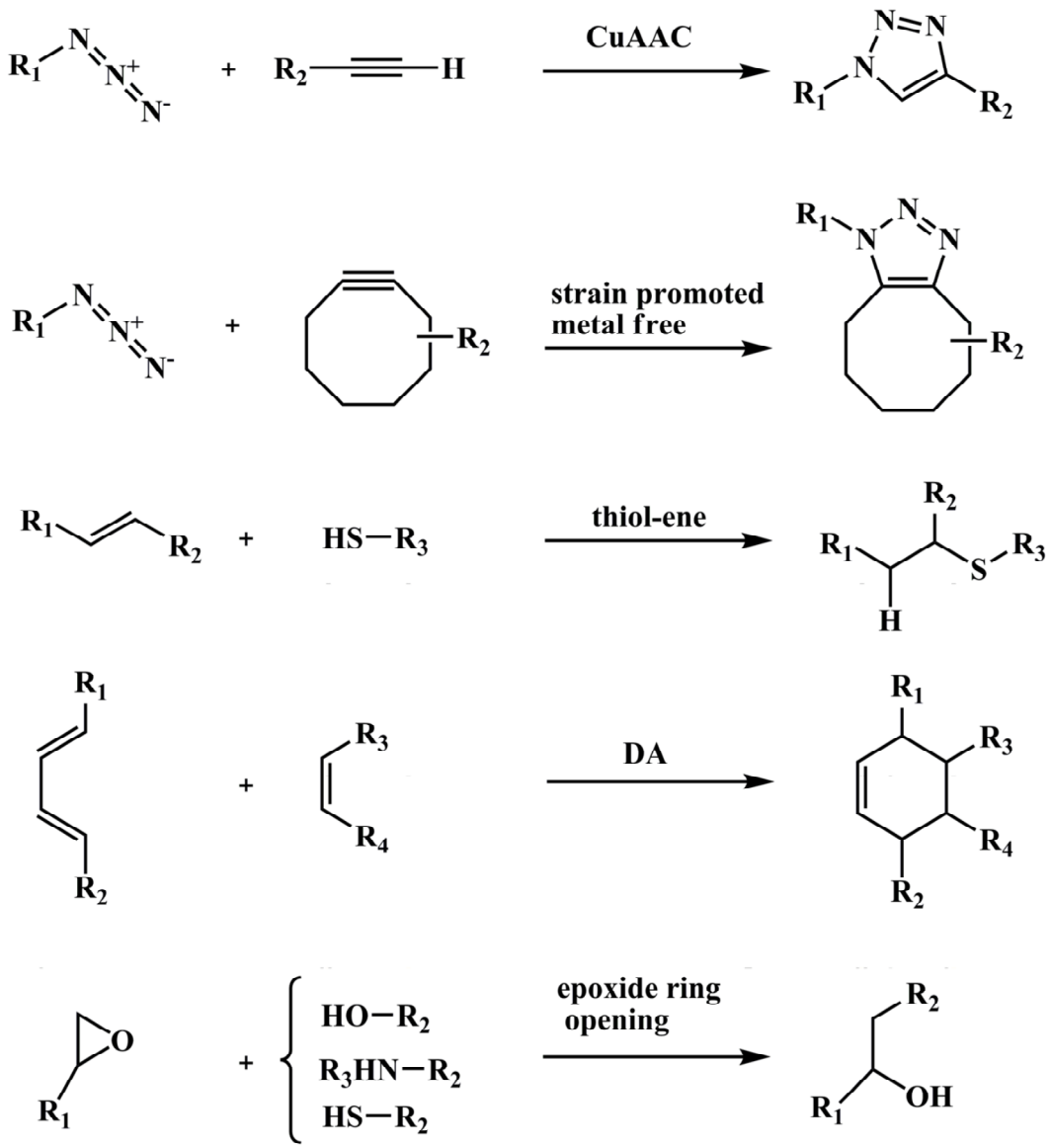


Figure 2.19 : General representation click reactions.

2.3.1 Thiol-ene Reaction

The thiol-ene click reaction has realized between a thiol and an alkene to form a thioether linkage. More specifically, the sulfur–carbon bond formation follows an anti-Markonikov process that can be promoted by UV light radiation or by radical initiators.

Thiol-ene click reactions are discovered in chemistry at early times, but have been rather extensively studied over the last century [69-71] Thiol-ene click reaxtions depicted in1926 by Braun and Murjahn [72]. During the time that thiol-ene polymerizations utilize for the formation of networks [73, 74] or for the purpose of controlling molecular weight in radical polymerizations, thiol-ene reaction is more

recently also referred to as a click reaction [75]. Among the ‘‘click’’ reactions, thiol-ene click is considered the most encouraging the green aspects of these reactions. Furthermore, this metal-free reaction can be performed in the absence of solvents in some cases, and can be photochemically controlled (even in the absence of a photoinitiator). Recent reports has showed that the thiol-ene click reaction is more efficient when initiated by light than by thermally [76]. The another advantage is that water- tolerant and oxygen makes it even more attractive.

Radicalic thiol-ene click proceeds by the same mechanism with chain transfer polymerization mechanism. Firstly, a thiyl radical is generated from a thiol-functionalized molecule by hydrogen abstraction from an initiator-derived radical, which subsequently reacts with carbon–carbon double bond. This is like propagation step. And then, the radical abstracts a proton from another thiol to form the reaction product and recover a thiyl radical (reaction 2.16). But unfortunately, thiol-ene chemistry has significant side reactions [77], the whole process may not be considered a click reaction, as this is a direct paradox to the click concept. Known side reactions are disulfide formation and another one is head-to-head coupling of the carbon centered radicals. These two reactions are arguably the most prominent reactions terminating the thiol-ene cycle. Thus, thiol-ene may only serve as an efficient conjugation tool if such reactions can be largely avoided.

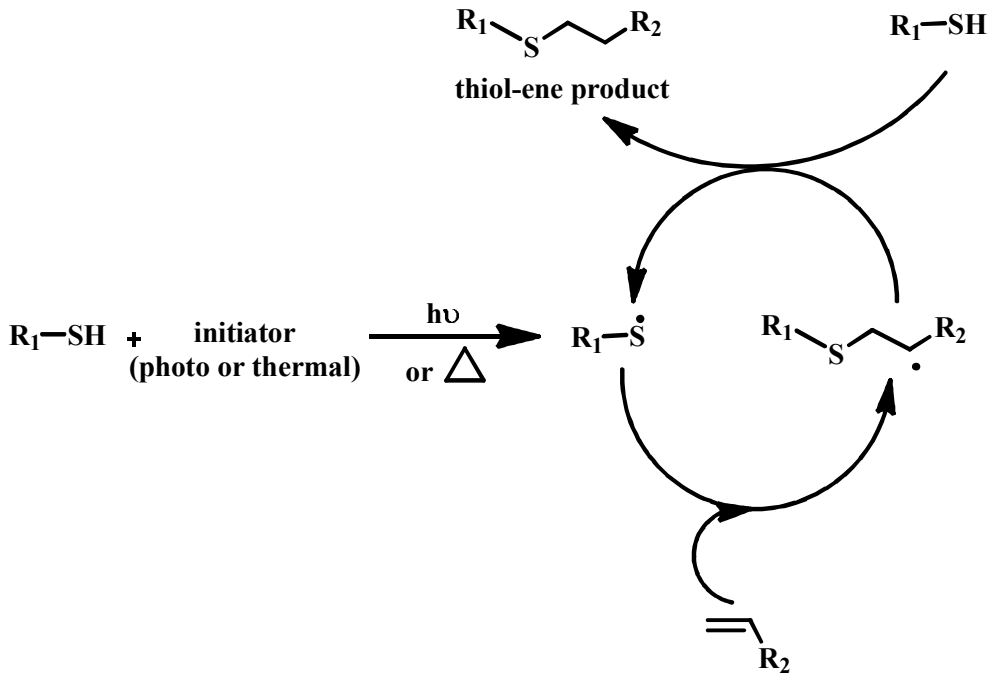


Figure 2.20 : Presentation of Thiol-ene Reaction.

2.4 Photolysis of o-Nitrobenzyl Group

o-Nitrobenzylic polymers have been used in various synthetic and biological applications especially for caged biomolecules.

o-Nitrobenzyl (oNB) and 1-(2-nitrophenyl)ethyl derivatives which carry a leaving group at the benzylic position release the protected substrate if any UV irradiation happens. The reaction proceeds by flash photolysis at $\lambda_{max} \approx 350$ nm.

o-Nitrobenzyl group can be leaved under UV. Earlier reports on their photochemistry [113] including the one on the photoisomerization of o-nitrobenzaldehyde into the corresponding nitrosobenzoic acid [114].

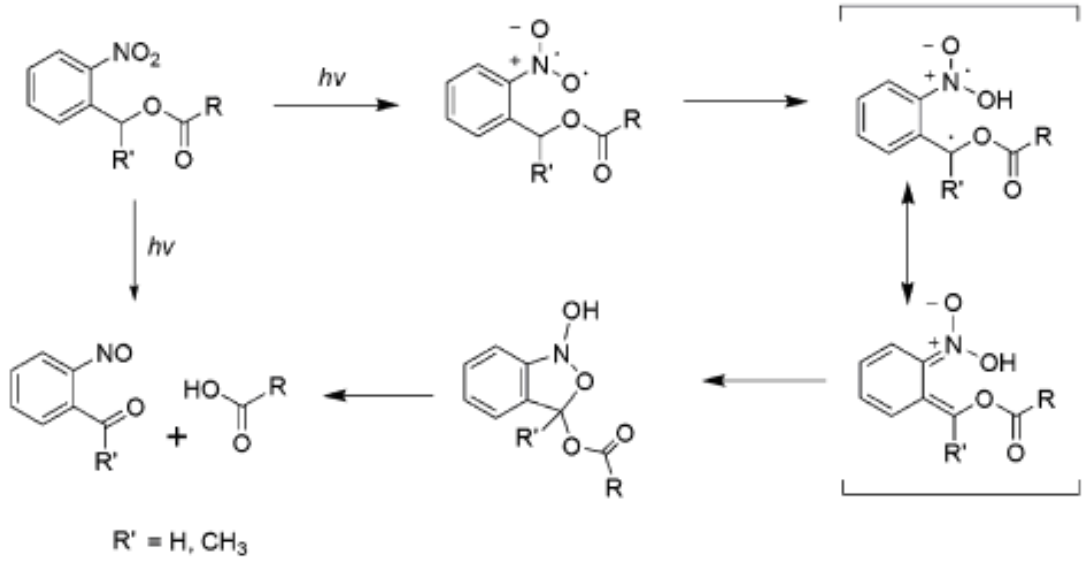


Figure 2.21 : Photoisomerization mechanism of o-nitrobenzyl alcohol into an o-nitrosobenzaldehyde, releasing a carboxylic acid [115,116,117]

Photolabile protecting groups have been used in applications in chemistry extensively [118-120]. The removal of this category of protecting groups is “clean”: in contrast to most other protecting strategies because the release of the protected (“caged”) substrate requires no added reagent, just with light. This feature makes them particularly favorable if access to the reaction site is difficult or if chemical reagents are of restricted use. We observe these cases with living organisms. In these systems, addressing biological issues often requires delivery of biologically active part of the drug at a given time and to a given location. This may be achieved by manipulating microsyringes. A noninvasive alternative involves adding to the biological medium caged compounds that reveal their biological activity only upon

illumination. A pulse of a focussed laser beam provides temporal and spatial control over the delivery of the material [121].

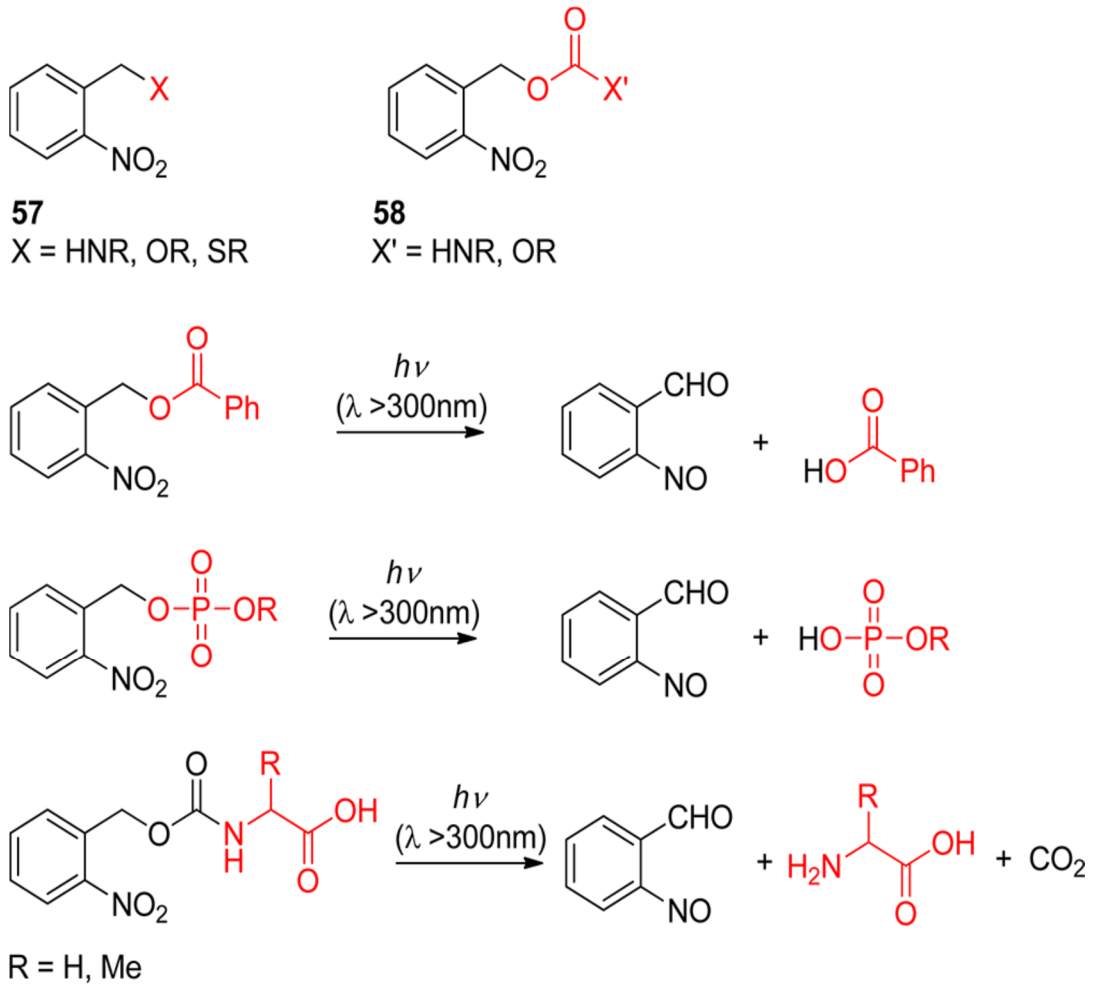


Figure 2.22 : Photolysis of Some o-Nitrobenzyl Derivatives.

Scott L. Diamond and his group have employed photo-decomposition reactions various photo-active compounds and various irradiation protocols for biochemical or chemical research. The photoreactions carried out in the body tend to use photosource with comparable long wavelength (k > 300 nm) to minimize damage to tissue. Therefore, we have chosen o-nitrobenzyl group which can be activated by photoirradiation of 365 nm.

Also they have showed decomposition and wave length relation. As seen in the graph maximum decomposition is at 300 nm but when we use this polymer as a drug this wave length can damage tissues [126]. This study also shows that decomposition is percentage is very high at wavelength 300 nm (Figure 2.23).

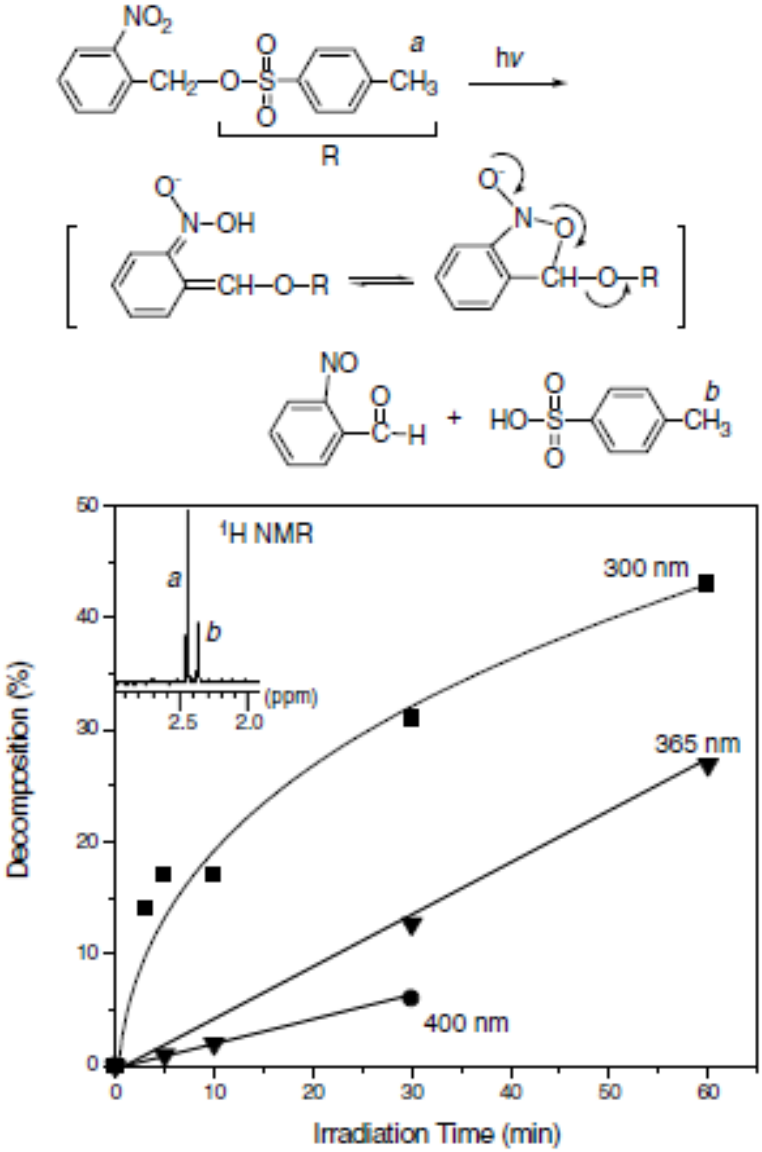


Figure 2.23 : Wavelenght effect on photolysis.

3. EXPERIMENTAL WORK

3.1 Materials

N,N'-Dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Acros), o-nitrobenzyl alcohol (97%, Aldrich), allyl alcohol (98.5%, Aldrich), Hydrochloric acid 37%), HPLC water (Aldrich), triethylamine (99.5%, Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 99%, Aldrich), ethyl chloroformate (97%, Aldrich), 1-octanethiol (98.5%, Aldrich), 2,2-Dimethoxy-2-phenylacetophenone (DMPA, 99%, Aldrich) were used as received. Dichloromethane (CH_2Cl_2, Aldrich) was used after distillation over P_2O_5. Tetrahydrofuran (THF; 99.8%, J.T. Baker) was dried and distilled over benzophenone-Na. Benzyl alcohol (99.8%, Aldrich) is used after vacuum distillation. Solvents unless specified here were purified by conventional procedures.

3.2 Instrument

^{1}H and ^{13}C NMR spectra were recorded on an Agilent VNMRS 500 (500 MHz for proton and 125 MHz for carbon) and on a Bruker AC-250 spectrometer (250 MHz for proton). 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

2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid **(1)** [123], (3,5 bis(triflоromethyl)phenyl)-3-cyclohexylthiourea) **(2)** [124], 2-nitrobenzyl 2,2,5 trimethyl-1,3-dioxane-5-carboxylate **(3)**, 2-nitrobenzyl 3-hydroxy-2(hydroxymethyl)-2-methylpropanoate **(4)**, 5-methyl-5-(2-nitro-benzoxycarbonyl)-1,3-dioxan-2-one **(5)**, allyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate **(6)**, allyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate **(7)**, 5-methyl-5-allyloxycarbonyl-1,3-dioxan 2-one **(8)**, were synthesised with the given procedures. **(1)** and **(2)** were synthesised according to the literature.

3.3.1 Synthesis of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid

The 2,2-bis(hydroxymethyl)propanoic acid (8 g, 59.6 mmol) along with *p*-TSA (0.45 g, 2.32 mmol), and 2,2-dimethoxypropane (11.2 mL, 89.4 mmol) dissolved in 40 mL of dry acetone, and stirred 2h at room temperature. In the vicinity of 2h, while stirring continued the reaction mixture was neutralized with 6 mL of totally NH_4OH (25%), and absolute ethanol (1:5), filtered off by-products and subsequent dilution with dichloromethane (100 mL), and once extracted with distilled water (40 mL). The organic phase dried with Na_2SO_4, concantrated to yield 7.4 g (71%) as white solid after evaporation of the solvent. ^{1}H NMR ($CDCl_3$, δ) ,4.18 (d, 2H, CC*H*$_2$O), 3.63 (d, 2H, CC*H*$_2$O), 1.38 (s, 3H, C*CH*$_3$) ,1.36 (s, 3H, C*CH*$_3$), 1.18 (s, 3H, C=OC(CH$_2$O)$_2$*CH*$_3$).

3.3.2 Synthesis of (3,5-bis(triflоromethyl)phenyl)-3-cyclohexylthiourea)

Cyclohexylamine (1.85 g, 18.5 mmol) was added dropwise at room temperature to a stirring solution of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (5.0 g, 19 mmol) in THF (20 mL). After the solution was stirred for 4 h, the solvent was evaporated. The white residue was recrystallized from hexane to give TU as a white powder. Yield: 5.90 g (86%).

3.3.3 Synthesis of o-Nitrobenzyl Functional Monomer

The synthesis of the monomer with o-nitrobenzyl functionality includes 3 steps.

3.3.3.1 Synthesis of 2-nitrobenzyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate

o-Nitrobenzyl alcohol (6.0 g, 39.2 mmol), (1) (8.18 g, 47.0 mmol) and DMAP (2.44 g, 20 mmol) was dissolved in 150 mL of CH_2Cl_2 were added to the reaction mixture in that order. After stirring 5 minutes at room temperature, DCC (9.70 g, 39.2 mmol) dissolved in 50 mL of CH_2Cl_2 was added. Reaction mixture was stirred overnight at room temperature and ammonium salt by-product was filtered. After that product was purified by column chromatography over silica gel eluting with ethyl acetate/hexane (1/4) that was further purified by crystallization from ethanol to give white-yellow solid (Yield =7.13 g; 59%). ^{1}H NMR ($CDCl_3$, δ) 8.10 (d, 1H, Ar*H* of o-nitrobenzyl), 7.70 and 7.63 (m, 2H, Ar*H* of o-nitrobenzyl), 7.47 (t, 1H, Ar*H* of o-nitrobenzyl), 5.59 (s, 2H, *CH_2*-o-nitrobenzyl), 4.26 (d, 2H, CC*H_2*O), 3.70 (d, 2H, CC*H_2*O), 1.44 (s, 3H, C*CH_3*), 1.38 (s, 3H, C*CH_3*), 1.17 (s, 3H, C=OC(CH_2O)$_2$*CH_3*).

3.3.3.2 Synthesis of 2-nitrobenzyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate

Previously obtained product **(3)** (7.13 g, 23.0 mmol) was dissolved in a mixture of 80 mL of THF and 80 mL of 1 M HCl. The reaction mixture was stirred for 2 h at room temperature. After 2 h, the reaction solvent was evaporated and product was extracted with 320 mL of CH_2Cl_2 and 80 mL of water. The combined organic phase was dried with Na_2SO_4 and concentrated. (Yield = 6.19 g, 100 %). ^{1}H NMR ($CDCl_3$, δ) 8.11 (d, 1H, Ar*H* of o-nitrobenzyl), 7.66 (m, 2H, Ar*H* of o-nitrobenzyl), 7.52 (t, 1H, Ar*H* of o-nitrobenzyl), 5.59 (s, 2H, *CH_2*-o-nitrobenzyl), 3.97 (d, 2H, CC*H_2*O), 3.77 (d, 2H, CC*H_2*O), 2.85 (br, 2H, OH), 1.11 (s, 3H, C*CH_3*).

3.3.3.3 Synthesis of 5-methyl-5-(2-nitro-benzoxycarbonyl)-1,3-dioxan-2-one

Previously obtained product **(4)** (6.19 g, 23.0 mmol) was added in a 250 mL of three-neck round bottom flask and dissolved in 100 mL of THF. The solution was cooled to 0 °C and a solution of ethyl chloroformate (4.36 mL, 46.0 mmol) in 30 mL of THF was added dropwise to the reaction mixture. Next a solution of triethylamine (9.57 mL, 69.0 mmol) in 30 mL of THF was added dropwise to the reaction mixture for 20 min. The white suspension was stirred at 0 °C for 2 h and subsequently at ambient temperature overnight. The ammonium salt was filtered off and the solvent was removed under reduced pressure. The remaining residue was further purified by crystallization from ethyl acetate/hexane (1/6) to give as a white-yellow powder and

finally dried at 40 ºC in vacuum oven for 24 h (Yield = 5.43 g 80%) ^{1}H NMR ($CDCl_3$, δ) 8.13 (d, 1H, Ar*H* of o-nitrobenzyl), 7.71 (m, 2H, Ar*H* of o-nitrobenzyl), 7.57 (t, 1H, Ar*H* of o-nitrobenzyl), 5.61 (s, 2H, *CH_2*-o-nitrobenzyl), 4.75 (d, 2H, CC*H_2*OC=O), 4.25 (d, 2H, CC*H_2*OC=O) ,1.37 (s, 3H, C=OC(CH_2O)$_2$*CH_3*).

3.3.4 Synthesis of Allyl Functional Monomer

The synthesis of the monomer with allyl functionality includes 3 steps.

3.3.4.1 Synthesis of allyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate

Allyl alcohol (3.5 mL, 52.0 mmol) , **(1)** (9.9 g, 57.0 mol) and DMAP (1.22 g, 10.0 mmol) was dissolved in 150 mL of CH_2Cl_2 were added to the reaction mixture in that order. After stirring 5 minutes at room temperature, DCC (11.8 g, 57.0 mmol) dissolved in 50 mL of CH_2Cl_2 was added. Reaction mixture was stirred overnight at room temperature and ammonium salt byproduct was filtered. Product was purified by column chromatography over silica gel eluting with hexane/ethyl acetate (9:1) to give white-yellow solid**.** (Yield = 6.68 g; 60%). ^{1}H NMR ($CDCl_3$, δ) 5.92 (m, 1H, CH_2=C*H*), 5.31-5.17 (m, 2H, C*H_2*=CH), 4.60 (d, 2H, vinylic H), 4.17 (d, 2H,C=OC(C*H_2*)(CH_3)), 3.62 (d, 2H,C=OC(C*H_2*)(CH_3)), 1.38 and 1.34 (s, 3H, COC(C*H_3*), s and 3H, COC(C*H_3*)), 1.17 (s, 3H, C=OC(CH_2)$_2$(C*H_3*)).

3.3.4.2 Synthesis of allyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate

Previously obtained product **(6)** (6.68 g, 31.0 mmol) was dissolved in a mixture of 70 mL of THF and 70 mL of 1.0 M HCl. The reaction mixture was stirred for 2 h at room temperature. After 2 h, the reaction solvent was evaporated and product was extracted with 280 mL of CH_2Cl_2 and 70 mL of water. The combined organic phase was dried with Na_2SO_4 and concentrated. (Yield = 5.39 g, 100%). ^{1}H NMR (250 MHz, $CDCl_3$, δ) 5.84 (m, 1H, CH_2=C*H*), 5.28-5.18 (m, 2H, C*H_2*=CH), 4.57 (d, 2H, vinylic H), 3.81 (d, 2H, C*H_2*OH), 3.77 (d, 2H, C*H_2*OH), 3.49 (s, 2H, CH_2O*H*), 1.04 (s, 3H, C=OC(CH_2)$_2$(C*H_3*)).

3.3.4.3 Synthesis of 5-methyl-5-allyloxycarbonyl-1,3-dioxan-2-one

Previously obtained product **(7)** (5.39 g, 31.0 mmol) was added in a 250 mL of three-neck round bottom flask and dissolved in 100 mL of THF. The solution was cooled to 0 °C and a solution of ethyl chloroformate (5.88 mL, 62.0 mmol) in 30 mL of

THF was added dropwise to the reaction mixture. Next a solution of triethylamine (12.90 mL, 93.0 mmol) in 60 mL of THF was added dropwise to the reaction mixture for 20 min. The white suspension was stirred at 0 °C for 2 h and subsequently at ambient temperature overnight. The ammonium salt was filtered off and the solvent was removed under reduced pressure. The remaining residue was further purified by crystallization from ethyl acetate/hexane (1/6) to give a white powder and finally dried at 40 ºC in vacuum oven for 24 h (Yield = 5.27 g 85%) ^{1}H NMR ($CDCl_3$, δ) 5.89 (m, 1H, CH_2=C*H*), 5.31 (m, 2H, C*H*$_2$=CH), 4.69 (d, 2H, CH_2=CHC*H*$_2$), 4.69 (d, 2H, CC*H*$_2$OC=O), 4.22 (d, 2H, CC*H*$_2$OC=O), 1.35 (s, 3H, C=OC(CH_2O)$_2$*CH*$_3$).

3.3.5 ROP of *o*-Nitrobenzyl Functional Carbonate Monomer

PC-nitrobenzyl was prepared by ROP of *o*-nitrobenzyl functionality contaning monomer (5-methyl-5-(2-nitro-benzoxycarbonyl)-1,3-dioxan-2-one) (1.0 g, 3.39 mmol) using DBU (0.026 mL, 0.17 mmol) and TU (0.06 g, 0.17 mmol) as catalyst and benzyl alcohol (0.017 mL, 0.017 mmol) as an initiator in $CHCl_3$ at room temperature for 4 h. The degassed monomer in $CHCl_3$ (1.0 mL), catalyst, and initiator were added to a 10 mL two-neck round bottom flask that had been flame-dried under vacuum and purged with argon. The tube was degassed with three freeze-pump-thaw (FPT) and left in vacuum. After the polymerization, the mixture was solved with a little THF and precipitated into an excess amount of methanol at ambient temperature. The recovered polymer was precipitated in ethanol for second time. The purified polymer was finally dried at 40 ºC in a vacuum oven for 24 h. (Yield: 0.8 g, 80%; $M_{n,theo}$= 4830 g/mol, $M_{n,NMR}$ = 6010 g/mol, $M_{n,GPC}$ = 2450 g/mol, M_w/M_n= 1.23, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.05 (d, 1H, Ar*H* of o-nitrobenzyl), 7.63 and 7.54 (m, 2H, Ar*H* of o-nitrobenzyl), 7.52 (t, 1H, Ar*H* of o-nitrobenzyl), 7.35 (s, 5H, Ar*H* of benzyl), 5.51 (s, 2H, *CH*$_2$-o-nitrobenzyl), 5.13 (s, 2H, C*H*$_2$-benzyl), 4.32 (s, 2H, CC*H*$_2$O), 3.70 (s, 2H, CC*H*$_2$O), 1.30 (s, 3H, C*CH*$_3$)

3.3.6 ROP of Allyl Functional Carbonate Monomer

PC-allyl was prepared by ROP of allyl functionality containing monomer (5-methyl-5-allyloxycarbonyl-1,3-dioxan-2-one) (1.0 g, 5.0 mmol) using DBU (0.037 mL, 0.25 mmol) and TU (0.09 g, 0.25 mmol) as catalyst and benzyl alcohol (0.026 mL, 0.025 mmol) as an initiator in $CHCl_3$ at room temperature for 4 h. The degassed monomer in $CHCl_3$ (1.0 mL), catalyst, and initiator were added to a 10 mL two-neck round

bottom flask that had been flame-dried under vacuum and purged with argon. The tube was degassed with three freeze-pump-thaw (FPT) and left in vacuum. After the polymerization, the mixture was solved with a little THF and precipitated into an excess amount of methanol at ambient temperature. The recovered polymer was precipitated in ethanol for second time. The purified polymer was finally dried at 40 ºC in a vacuum oven for 24 h. (Yield: 0.96 g, 96%; $M_{n,theo}$= 3950 g/mol, $M_{n,NMR}$ = 5710 g/mol, $M_{n,GPC}$ = 4140 g/mol, M_w/M_n= 1.28, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 5.92 (m, 1H, CH_2=C*H*), 5.31-5.17 (m, 2H, C*H*$_2$=CH), 4.60 (d, 2H, vinylic H), 4.17 (d, 2H,C=OC(C*H*$_2$)(CH_3)), 3.62 (d, 2H,C=OC(C*H*$_2$)(CH_3)), 1.38 and 1.34 (s, 3H, COC(C*H*$_3$), s and 3H, COC(C*H*$_3$)), 1.17 (s, 3H, C=OC(CH_2)$_2$(C*H*$_3$)).

3.3.7 Copolymer Synthesis with *o*-Nitrobenzyl and Allyl Functionallity by ROP

PC-nitrobenzyl-allyl was prepared by ROP of nitro monomer (1.0 g, 3.39 mmol) and allyl monomer together (0.68 g, 3.39 mmol) using DBU (0.049 mL, 0.34 mmol) and TU (0.12 g, 0.34 mmol) as catalyst and benzyl alcohol (0.035 mL, 0.34 mmol) as an initiator in $CHCl_3$ at room temperature for 6 h. The degassed monomer in CH_2Cl_2 (2.0 mL), catalyst, and initiator were added to a 10 mL two-neck round bottom flask that had been flame-dried under vacuum and purged with argon. The tube was degassed with three freeze-pump-thaw (FPT) and left in vacuum. After the polymerization, the mixture was solved with a little THF and precipitated into an excess amount of methanol at ambient temperature. The recovered polymer was precipitated in ethanol for second time. The purified polymer was finally dried at 40 ºC in a vacuum oven for 24 h. (Yield: 0.64 g, 76%; $M_{n,theo}$= 3280 g/mol, $M_{n,NMR}$ = 5060 g/mol, $M_{n,GPC}$ = 4283 g/mol, M_w/M_n= 1.02, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.06 (d, 1H, Ar*H* of o-nitrobenzyl), 7.62 and 7.53 (m, 2H, Ar*H* of o-nitrobenzyl), 7.48 (t, 1H, Ar*H* of o-nitrobenzyl), 7.33 (s, 5H, Ar*H* of benzyl), 5.84 (s, 1H, CH_2=C*H*), 5.51 (s, 2H, *CH*$_2$-o-nitrobenzyl), 5.28-5.20 (d, 2H, C*H*$_2$=CHCH_2O), 5.11 (s, 2H, C*H*$_2$-benzyl), 4.59 (s, 2H, CH_2=CHC*H*$_2$O), 4.30 (s, 4H, CC*H*$_2$O), 3.75 (s, 2H, CC*H*$_2$O), 2.24 (s, 1H, CCH_2O*H*), 1.30 (s, 3H, C*CH*$_3$)

3.3.8 Photo Thiolene Reaction and Photolysis of the *o*-Nitrobenzyl Group

In a 25 mL of Schlenk tube, copolymer **(11)** (0.6 g, 0.14 mmol, $M_{n,GPC}$= 4283 g/mol), 1-octanethiol (0.10 mL, 0.58 mmol), DMPA (0.06 g, 0.24 mmol) as photoinitiator and dry THF (10 mL) were added and the reaction mixture was degassed by three

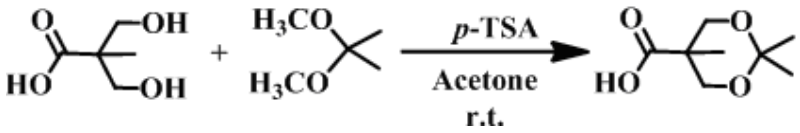
FPT cycles and left in vacuum. The tube was then placed in a photoreactor with 350 nm for 6 hours. After that, THF is evaporated and polymer is precipitated in cold methanol. The polymer was dried for 24 h in a vacuum oven at 40 ^{o}C. (Yield: 0.5 g, 83 %, $M_{n,theo}$= 4280 g/mol, $M_{n,NMR}$ = 4280 g/mol, $M_{n,GPC}$ = 4145 g/mol, M_w/M_n = 1.14, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ), 7.33 (s, 5H, Ar*H* of benzyl), 5.12 (s, 2H, C*H*$_2$-benzyl), 4.28 (br, 4H, CC*H*$_2$O), 4.28 (br, 2H, OC*H*$_2$CH$_2$CH$_2$S), 2.54 (m, 2H, OCH$_2$CH$_2$C*H*$_2$S), 2.50 (m, 2H, SC*H*$_2$(CH$_2$)$_6$CH$_3$), 1.90 (br, 2H, OCH$_2$C*H*$_2$CH$_2$S), 1.27 (m, C*CH*$_3$ and (C*H*$_2$)$_6$CH$_3$), 0.87 (s, 3H, (CH$_2$)$_6$C*H*$_3$).

4. RESULTS AND DISCUSSION

Herein we studied polycarbonates which were homo and copolymers that were obtained by ROP of the synthesized allyl and o-nitrobenzyl functionallity monomers. Following study for the copolymer was based on the thiol-ene reaction on the double bond with photo initiation and also photolysis of the *o*-nitrobenzyl group under UV irritation (λ= 350 nm) to give carboxylic acid functionallity.

4.1 Preparation of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid

2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid **(1)** was synthesized by the reaction between 2,2-bis (hydroxymethyl)-propanoic acid and 2,2-dimethoxy-propane with excess amount of dry acetone using *p*-toluene sulfonic acid as catalyst (4.1).



(4.1)

^{1}H NMR spectrum of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid, showing resonances corresponding to -COOH proton at 11.20 ppm, methylene groups at 4.18 and 3.63, the methyl protons adjacent to ketal group and adjacent to methylene groups at 1.38-1.36 ppm and 1.18 ppm respectively.

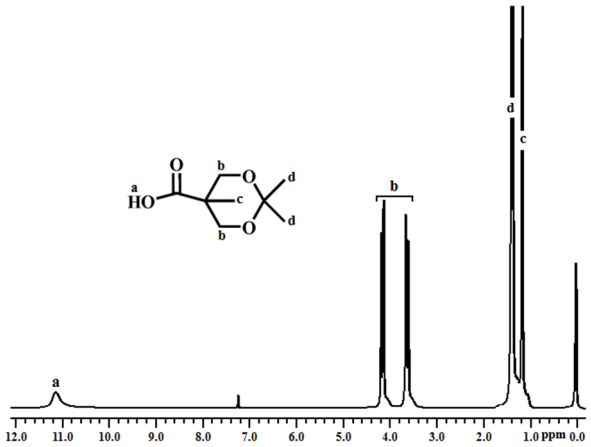
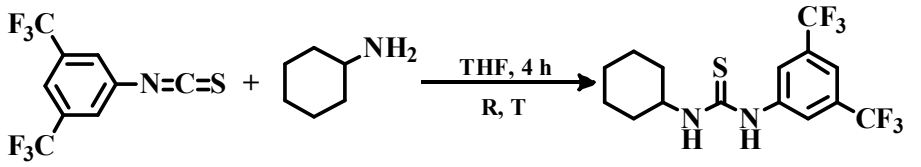


Figure 4.1: ^{1}H NMR spectrum of **(1)** in $CDCl_3$.

4.2 Preparation of 1-(3,5-bis(trifloromethyl)phenyl)-3-cyclohexylthiourea)

To synthesize 1-(3,5-bis(trifloromethyl)phenyl)-3-cyclohexylthiourea) is in other world co-catalyst (TU), cyclohexylamine and 3,5-bis(trifluoromethyl)phenyl isothiocyanate were reacted in THF at room temperature for 4h (equation 4.2). Finally, compound **(2)** was obtained as a white solid.



(4.2)

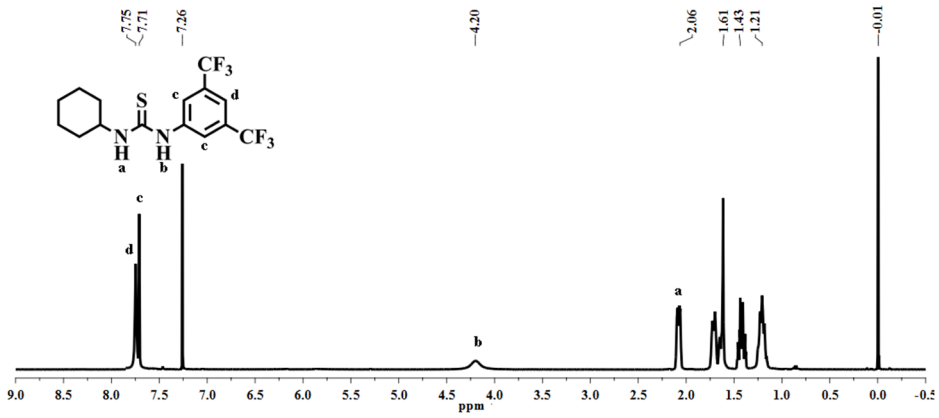
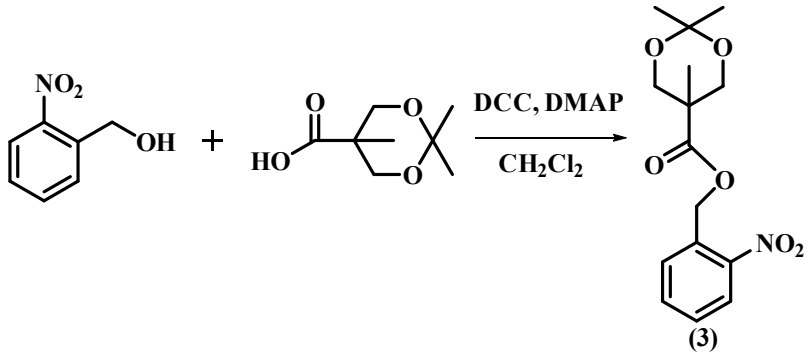


Figure 4.2: ^{1}H NMR spectrum of **(2)** in $CDCl_3$

4.3 Preparation of *o*-Nitrobenzyl Functional Monomer (5)

Carbonate monomer with *o*-nitrobenzyl functional was prepared in 3 steps. In the first step, *o*- nitrobenzyl alcohol was reacted with **(1)** in the presence of DMAP and DCC at room temperature for over night in CH_2Cl_2 intermedia to give **(3)**. At the same time ammonium salt occured in the reaction mixture as by-product that was removed after the reaction. Purification method was coloumn chromatography and then crystallizaiton of the ketal structure. Process is given below (4.3).



(4.3)

^{1}H NMR spectroscopy confirmed clearly the structure of **(3)** by appearance of characteristic signals of *o*-nitrobenzyl group 7.5-8.1 ppm and the signal of the CH_2 of o-nitrobenzyl group is at 5.59 ppm. It is obviously seen that the peak of methylene protons neighbouring to oxygen is between 4.26 and 3.68 ppm (Figure 4.3).

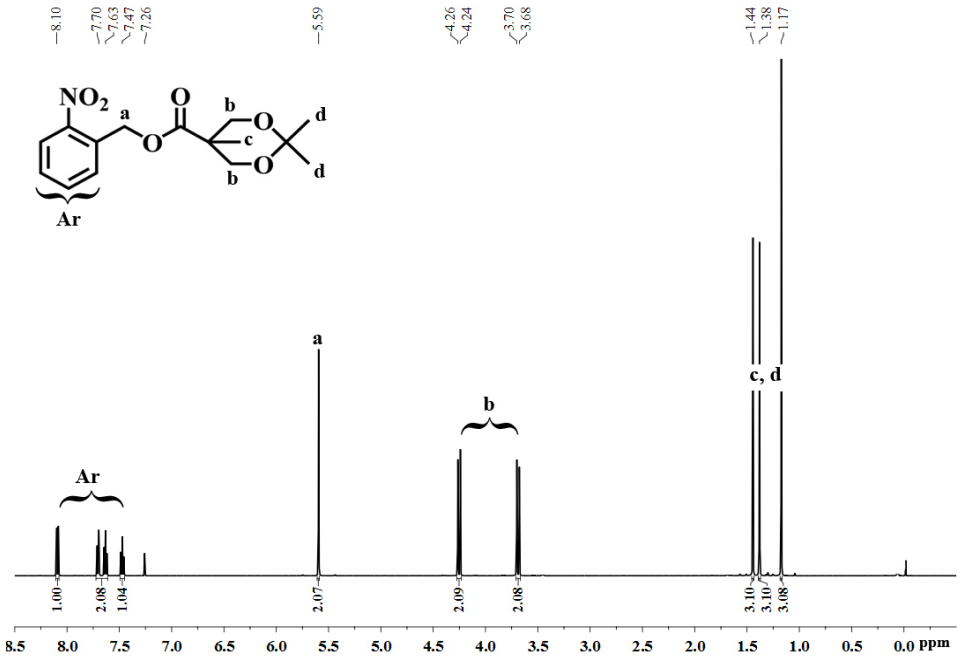
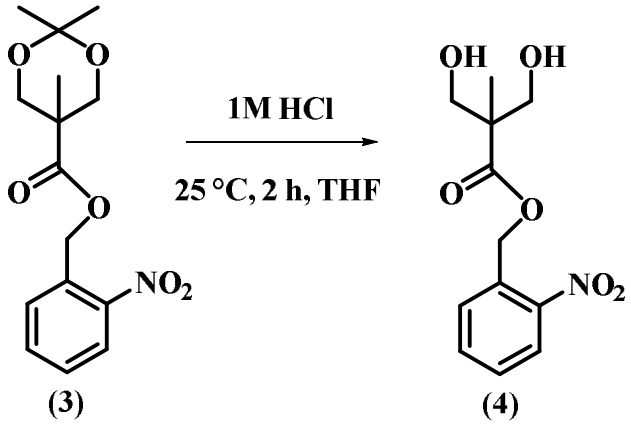


Figure 4.3: ^{1}H NMR spectrum of **(3)** in $CDCl_3$.

In the second step was hydrolysis of the **(3)** with 1M HCl solution in THF for 2 hours at room temperature to give dihydroxy funcitonal structure **(4)** (4.4).



(4.4)

In the ^{1}H NMR spectroscopy of the product **(4)**, the signal which is broad at 2.85 ppm is observed due to the hydroxy groups in the structure that differ from the previously product **(3)** (Figure 4.4).

This is a product that is obtained from the hydrolysis of the previous material.

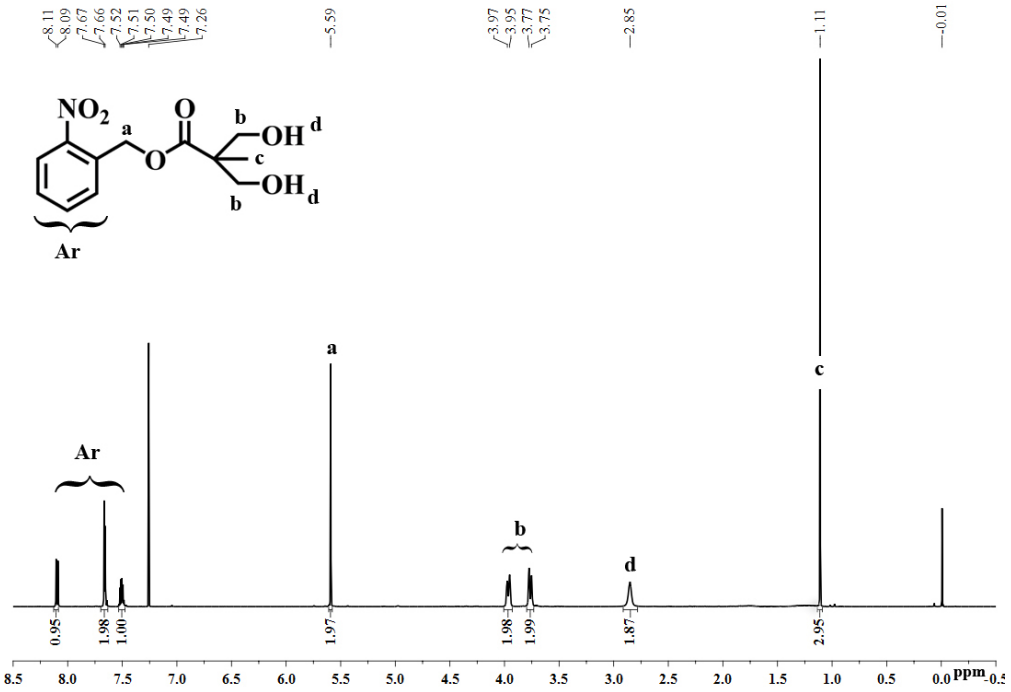
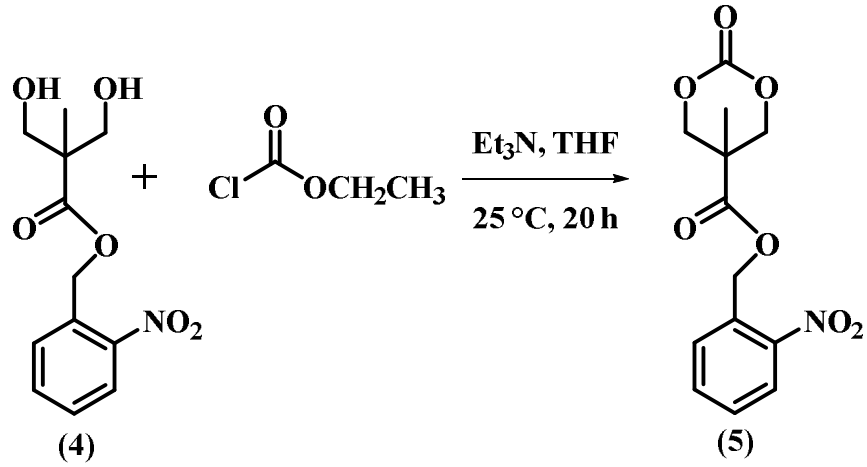


Figure 4.4: ^{1}H NMR spectrum of **(4)** in $CDCl_3$

In the last step, *o*-nitrobenzyl functional monomer 5-methyl-5-(2-nitro-benzoxycarbonyl)-1,3-dioxan-2-one **(5)** was synthesized with over night reaction. The cyclization was performed b ethyl chloroformate in dilute anhydrous THF solution via dropwise addition of triethylamine (4.5).



(4.5)

^{1}H NMR spectroscopy confirmed clearly the structure of **(5)** by disappearance of characteristic signals of hydroxyl groups at 2.85 when it compared with **(4)** (Figure 4.5).

The characteristic peak for the methyl group that is bonded is seen at 5.61 ppm.

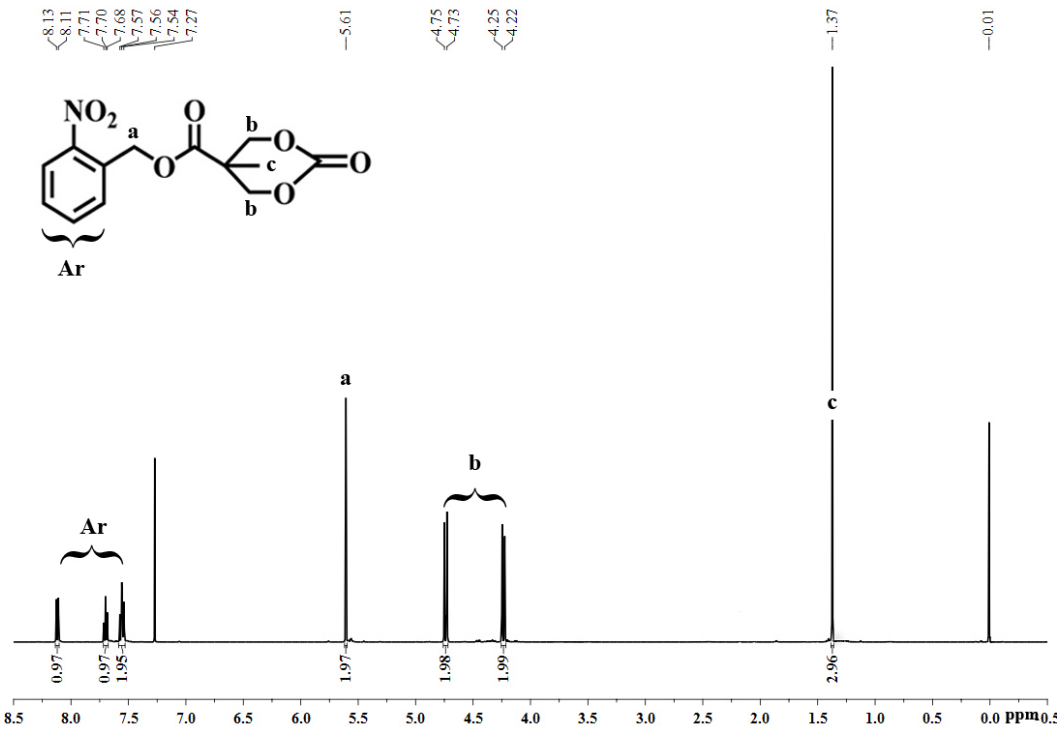
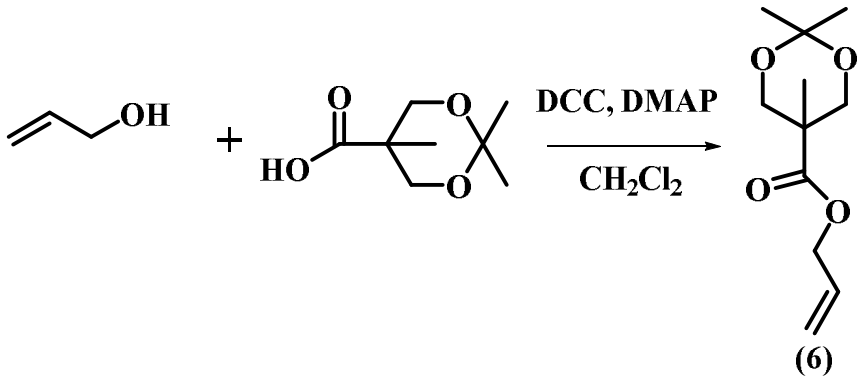


Figure 4.5: ^{1}H NMR spectrum of **(5)** in $CDCl_3$

4.4 Preparation of Allyl Functional Monomer (8)

Carbonate monomer with allyl functional was prepared in 3 steps. In first step allyl alcohol was reacted with **(1)** in the presence of DMAP and DCC at room temperature for over night, in CH_2Cl_2 intermedia to give **(6)**. At the same time ammonium salt occured in the reaction mixture as by-product that was removed after the reaction. Process is given below (4.6).



(4.6)

^{1}H NMR spectroscopy confirmed clearly the structure of **(3)** by appearance of characteristic signals of allyl group 5.90- 5.31- 4.62 ppm. It is obviously seen that the peak of methylene protons neighbouring to oxygen is between 4.17 and 3.62 ppm (Figure 4.6).

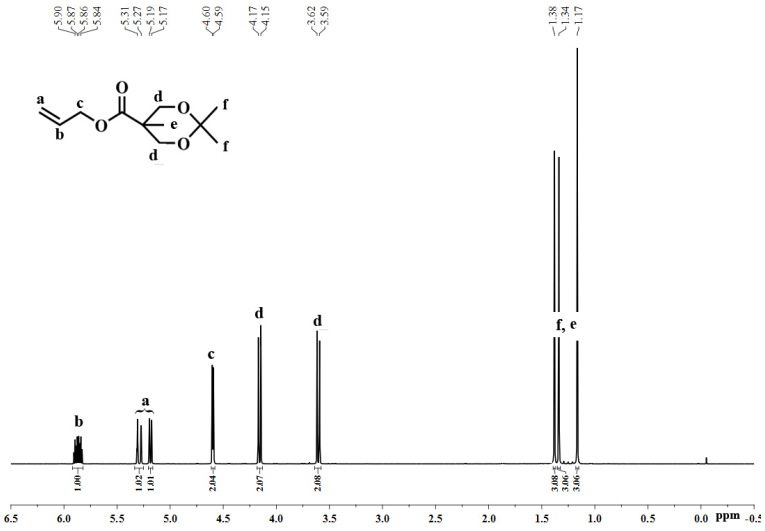
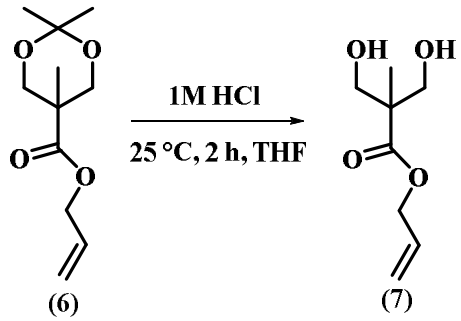


Figure 4.6: ^{1}H NMR spectrum of **(6)** in $CDCl_3$

The second step was hydrolysis of the **(6)** with 1M HCl solution in THF for 2 hours at room temperature to give dihydroxy functional structure **(4)** (4.7).



(4.7)

In the ^{1}H NMR spectroscopy of the product **(8)**, the signal at 3.49 ppm is observed due to the hydroxy groups in the structure that differ from the previously product **(7)** (Figure 4.7).

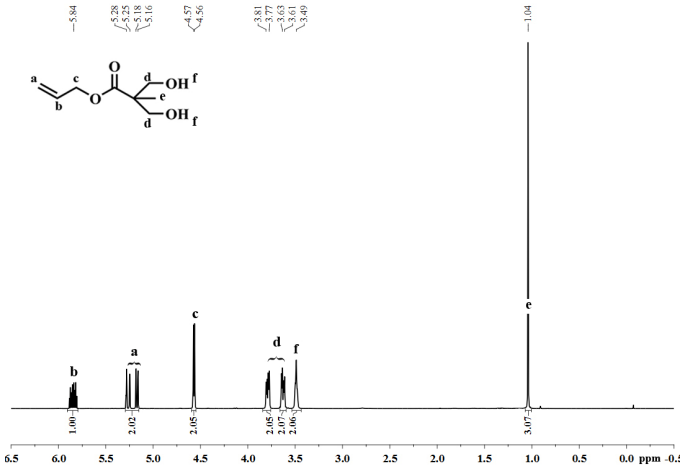
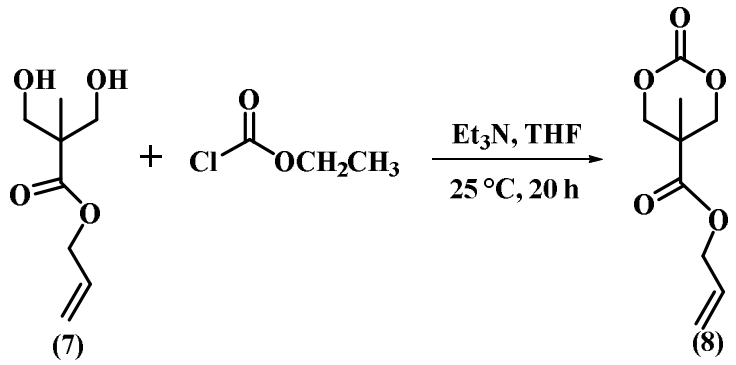


Figure 4.7: ^{1}H NMR spectrum of **(7)** in $CDCl_3$

In the last step, allly functional monomer 5-methyl-5-allyloxycarbonyl-1,3-dioxan-2-one **(8)** was synthesized. The cyclization was performed in the presence of ethyl chloroformate in dilute anhydrous THF solution via dropwise addition of triethylamine (4.8).



(4.8)

^{1}H NMR spectroscopy confirmed clearly the structure of **(8)** by disappearance of characteristic signal of hydroxyl groups at 3.49 (Figure 4.8).

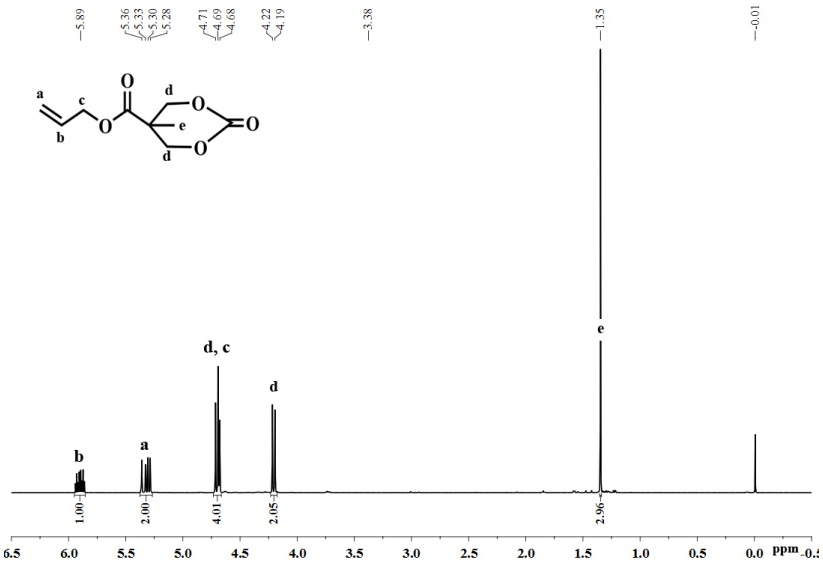


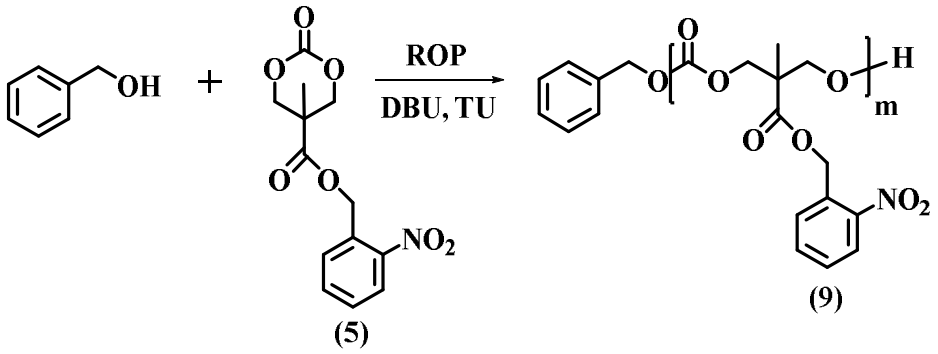
Figure 4.8: ^{1}H NMR spectrum of **(8)** in $CDCl_3$

4.5 Preparation of *o*-Nitrobenzyl Functional Polcarbonate (9)

The polycarbonate with o-nitrobenzyl functional was prepared from the ROP of (5-methyl-5-(2-nitro-benzoxycarbonyl)-1,3-dioxan-2-one (**5**) using benzyl alcohol as initiator and TU/DBU as catalyst in $CHCl_3$ intermedia at room temperature for 4 h. The structure of the **(9)** was confirmed by ^{1}H NMR (4.9).

From ^{1}H NMR spectroscopy, signals at 5.51 pmm corresponding to the CH_2 of o-nitrobenzyl group and the signal at 5.13 corresponds to the CH_2 of benzyl.

Characteristic signals of the o-nitrobenzyl are at 8.05 to 7.53 respectively (Figure 4.9).



(4.9)

The number-average molecular weight ($M_{n,NMR}$ = 20 (DP_n) X 295 g/mol + MW of end-groups (108 g/mol) = 6008 g/mol) of the o-nitrobenzyl functional PC could be calculated by comparing integrated signals of the main backbone CH_2(C=O)O protons (2H) at 5.13 ppm and the benzyl protons of the initiator (5H) at 7.35 ppm. Next, the $M_{n,theo}$ was determined according to the following equation, $M_{n,theo}$ = ($[M]_0/[I]_0$) X MW of **(5)** (295 g/mol) X conv. % + MW of end-groups (108 g/mol) = 4828 g/mol. The GPC analysis of **(9)** displayed a monomodal GPC trace with narrow polydispersity ($M_{n,GPC}$ = 2434 g/mol, M_w/M_n = 1.23 with respect to PS standards).

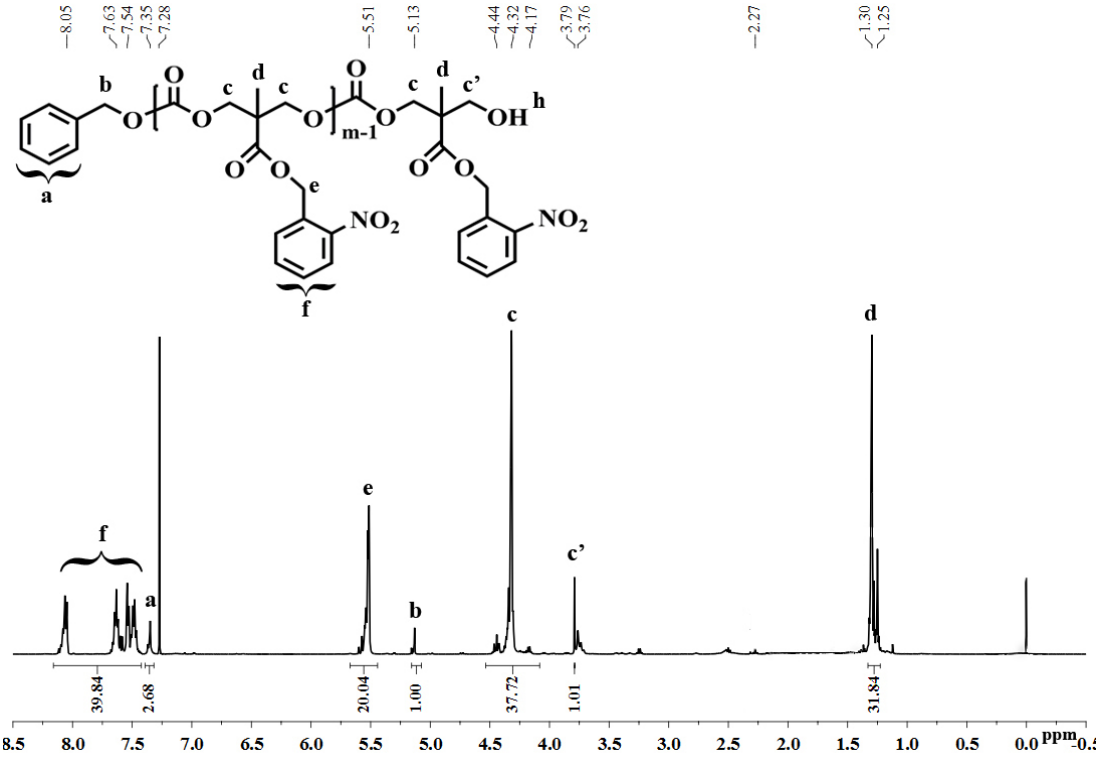
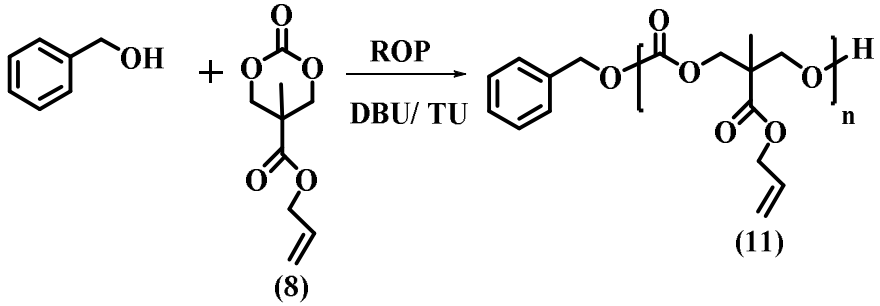


Figure 4.9: ^{1}H NMR spectrum of **(9)** in $CDCl_3$

4.6 Preparation of Allyl Functional Polycarbonate (10)

The polycarbonate with allyl functional was prepared from the ROP of 5-methyl-5-allyloxycarbonyl-1,3-dioxan-2-one **(8)** using benzyl alcohol as initiator and TU/DBU as catalyst in $CHCl_3$ at room temperature for 4 h. The structure for the PC was confirmed by ^{1}H-NMR (4.10).

From ^{1}H NMR spectroscopy, two signals (4.29 and 3.70 ppm) corresponding to the CH_2 in the backbone of (10). PC appeared in association with the characteristic signals of the CH_2 linked to the benzyl at 7.34 pmm that belongs to the initiator's hydrogens (Figure4.10).



(4.10)

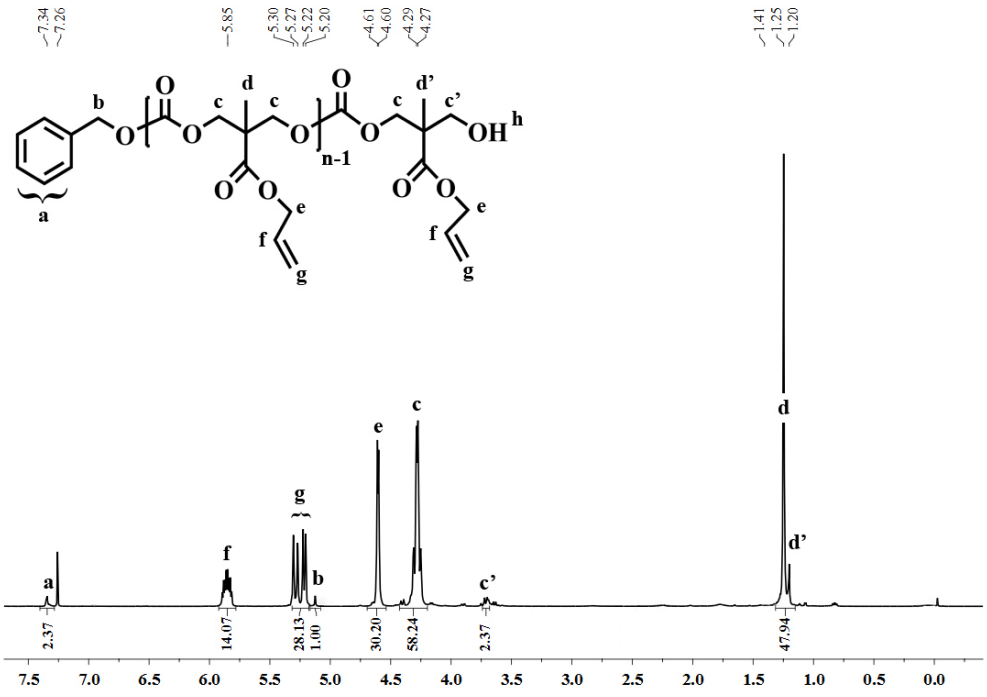


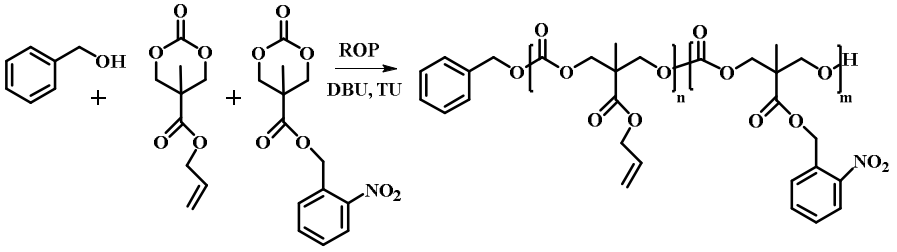
Figure 4.10: ^{1}H NMR spectrum of **(10)** in $CDCl_3$

The number-average molecular weight ($M_{n,NMR}$ = 20 (DP_n) X 200 g/mol + MW of end-groups (108 g/mol) = 4108 g/mol) of the allyl functional PC could be calculated

by comparing integrated signals of the main backbone CH_2(C=O)O protons (2H) at 5.13 ppm and the benzyl protons of the initiator (5H) at 7.35 ppm. Next, the $M_{n,theo}$ was determined according to the following equation, $M_{n,theo}$ = ([M]$_0$/[I]$_0$) X MW of **(8)** (200 g/mol) X conv. % + MW of end-groups (108 g/mol) = 3948 g/mol. The GPC analysis of **(10)** displayed a monomodal GPC trace with narrow polydispersity ($M_{n,GPC}$ = 4138 g/mol, M_w/M_n = 1.28 with respect to PS standards).

4.7 Preparation of the Copolymer with *o*-Nitrobenzyl and Ally Functionality (11)

Copolymerization was done with **(5)** and **(8)** using benzyl alcohol as initiator and TU/DBU as catalyst in $CHCl_3$ at room temperature for 6 h. The structure of the (MNC-co-MATMC) was confirmed by ^{1}H NMR (4.11).



(4.11)

From ^{1}H NMR spectroscopy, characteristic signals of the o-nitrobenzyl and CH_2 linked to the o-nitrobenzyl at 8.06-7.48 and 5.11 ppm, respectively. Vinyl group signals are at 5.84, 5.20 and 4.59 ppm that shows that copolymer is in the media (Figure 4.11).

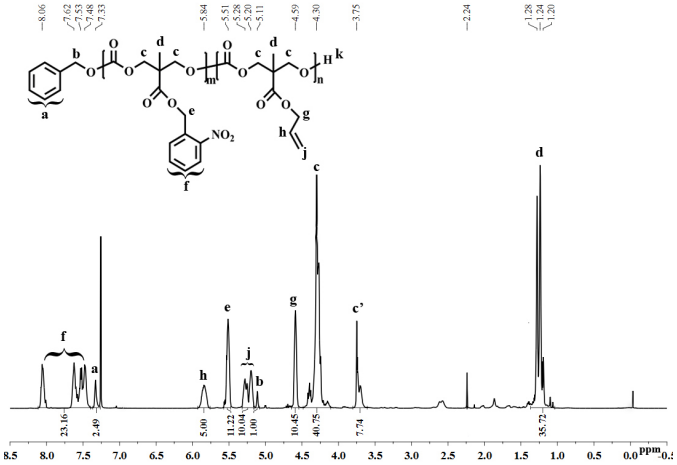
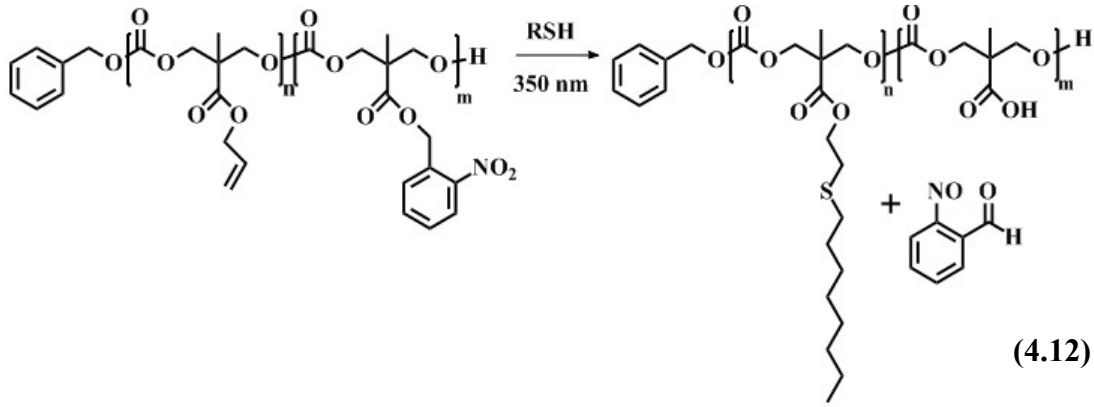


Figure 4.11: ^{1}H NMR spectrum of *o*-nitrobenzyl and allyl functional PC **(11)** in $CDCl_3$

The number-average molecular weight ($M_{n,NMR}$ = 10 (DP_n) X 200 g/mol + 10 (DP_n) X 295 g/mol + MW of end-groups (108 g/mol) = 5058 g/mol) of the copolymer (11) could be could be calculated by comparing integrated signals of the main backbone CH_2(C=O)O protons (2H) at 5.13 ppm and the benzyl protons of the initiator (5H) at 7.35 ppm. Next, the $M_{n,theo}$ was determined according to the following equation, $M_{n,theo}$ = ($[M]_0/[I]_0$) X MW of (8) (200 g/mol) X conv. % + MW of end-groups (108 g/mol) = 7632 g/mol. The GPC analysis of (11) displayed a monomodal GPC trace with narrow polydispersity ($M_{n,GPC}$ = 4283 g/mol, M_w/M_n = 1.09 with respect to PS standards).

4.8 Preparation of Copolymer with Carboxylic Acid and Thiol Functionality (12)

(11) (0.6 g, 0.14 mmol, $M_{n,GPC}$= 4283 g/mol), 1-octanethiol (0.10 mL, 0.58 mmol), DMPA (0.06 g, 0.24 mmol) as photo initiator and 10.0 mL dry THF were put into a Schlenk tube. The reaction mixture was degassed by three FPT cycles and left in vacuum. The mixture was irradiated by a photoreactor at 350 nm at room temperature. After 6 hours THF was evaporated and polymer dissolved little amount of THF then precipitated in methanol. This dissolution-precipitation procedure was repeated two times. The polymer was dried for 24 h in a vacuum oven at 40 ^oC. Yield = 0.5 g (83%).



(4.12)

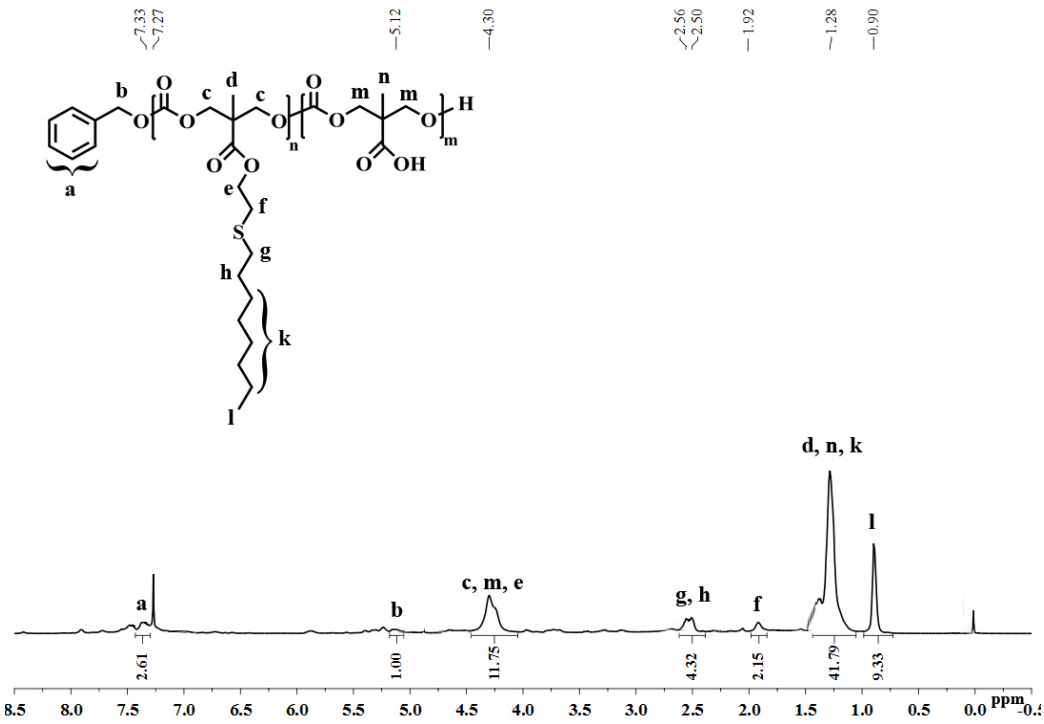


Figure 4.12 : ^{1}H NMR spectrum of structure **(12)** in $CDCl_3$.

In the 1H-NMR spectrum of the **(12)** it is clearly seen that the signals of the o-nitrobenzyl group is dissappered where the signal of the benzyl alcohol' 5H is still in the structure. But we are not able to see the signal of the carboxyl group hydrogen. The phenly-CH_2 signal is in the same place at 5.12 ppm. Aliphatic hydrogens are at 2.5 ppm to 0.90 ppm that we understand that RSH is bounded to the structre.

Table 4.1 : The characteristics of homo and copolymers.

Polymer	$M_{n,GPC}$[f] (g/mol)	M_w/M_n	$M_{n,theo}$[g] (g/mol)	$M_{n,NMR}$[i] (g/mol)
PC_{20}-*o*-NB[a]	2434	1.23	4830	6000
PC_{20}-allyl[b]	4140	1.28	3950	5700
PC(o-NB-*co*-allyl)[c]	4283	1.02	4455	5058
PC(COOH-*co*-SH)[d]	4145	1.14	3550	4280

[a] Synthesized by ROP of **(5)** in $CHCl_3$ using TU/DBU as catalysts and benzyl alcohol as an initiator at 25 °C. $[M]_0:[I]_0 = 20$

[b] Synthesized by ROP of **(8)** in $CHCl_3$ using TU/DBU as catalysts and benzyl alcohol as an initiator at 25 °C. $[M]_0:[I]_0 = 20$

[c] Synthesized by ROP of **(5)** and **(8)** in $CHCl_3$ using TU/DBU as catalysts and benzyl alcohol as an initiator at 25 °C. $[M]_0:[I]_0 = 10$ for each monomer

[d] Synthesized **(11)** in THF using and DMPA as an photo initiator at 25 °C. $[M]_0:[I]_0 = 0.6$ for each monomer

[f] Determined by using conventional GPC (RI detection) in THF at 30 ºC relative to PS standards except PMMA standards.

[g] $M_{n,theo} = ([M]_0/[I]_0)$ X conversion% X MW of monomer + MW of initiator.

[i] Determined by ^{1}H NMR.

In the experiment we synthesized the homo polymers with 20:1 monomer to initiator ratio and for the copolymer the ratio was 20:1 with the same equvalent of the monomers. Although *o*-Nitrobenzyl groups prevent polymerization due to the high resonance stability, in our study we have not observed this effect. We have obtained good PDI for four PCs. The number average moleculer weight differences between GPC and NMR is seen in the table. This is may be the due to the precipitation processes. PC(*o*-NB-*co*-allyl) after irritation with UV the moleculer weight supposed to decrease but with adding the thiol compound have not changed much because the molecular weight for the adding thiol compound and leaving o-nitro group close to each other.

5. CONCLUSION

Aliphatic polycarbonates are excellent candidate for pharmaceutical are that in our experiment, for the first time PC with both *o*-nitrobenzyl and allyl functional groups have been synthesized with good PDI and M_w values. The importance of the this synthesized copolymer is that it can give further functionalization reactions.

Thiol-ene reactions have been studied on the vinyl group by other research groups but no research group have studied thiol-ene click reaction and photolysis of a photolabile group in one pot with UV. After this reaction under UV, polymer gains a hydrophobicity with thiol chain while carboxylic acid provides hydrophilicity that makes the PC act like a micelle. The organic catalyst system is not toxic that it seems that the PC(*o*-NB-*co*-allyl) can be used in pharmaceutical area.

REFERENCES

[1] **Kreiser-Saunders, I., and Kricheldorf, H. R.** 1998. Polylactones, 39. Zn Lactate- Catalyzed Copolymerization of L-Lactide with Glycolide or ε-Caprolactone, *Macromol. Chem. Phys.,* **199(6)**, 1081-1087.

[2] **Jerome C, Lecomte P.** Recent advances in the synthesis of aliphatic polyesters by ring-opening polymerization. Adv Drug Deliv Rev 2008; 60(9):1056–76.

[3] **Dubois P, Coulembier O, Raquez J.-M**, editors. Handbook of Ring-Opening Polymerization, 2009.

[4] **Dechy-Cabaret O, Martin-Vaca B, Bourissou D**. Controlled ringopening polymerization of lactide and glycolide. Chem Rev (Washington, DC, United States) 2004;104(12):6147–76.

[5] **Kamber, N.E.; Jeong, W.; Waymouth, R.M. 2007,** Chem. *Rev.,* 107, 5813-5840

[6] **(a) Dove, A. P., Pratt, R. C., Lohmeijer, G.B.G., Culkin, D. A. Hagberg , E. C., Nyce, G. W., Waymouth, R. M., Hedrick, J. L.** 2006, Polyme*r* , 47, 4018; **(b) Suriano,F.; Coulembier, O.; Hedrick,J.L; Dubois P**. Polym. Chem., 2011, 2, 528–533

[7] **Kolb, H.C., Finn, M.G., and Sharpless, K.B.**, 2001, Click chemistry: Diverse chemical function from a few good reactions*, Angewandte Chemie-International Edition*, **40,** 2004-2021.

[8] **Ivin, K, J., and Saegusa, T,** eds. 1984. Ring-opening Polymerization,Vols.13, Elsevier, London.

[9] **Zhang, X.; Zhong, Z.; Zhuo, R.** Macromolecules 2011, 44, 1755-1759.

[10**] Xu, J.; Prifti, F.; Song, J.** *Macromolecules* **2011**, 44, 2660-2667.

[11] **Brunelle, D. J.,** Ed. 1993. Ring-opening Polymerization: Mechanisms, Catalysis, Structure, Utility,Carl Hanser Verlag, NY.

[12] **Flory PJ**. Molecular size distribution in ethylene oxide polymers. J Am Chem Soc 1940;62:1561–5.

[13] **Flory PJ**. Principles of polymer chemistry. Ithaca, NY: Cornell University Press; 1953. p. 336.

[14] **Wojtech B**. Zur darstellung hochmolekularer polyaethelenoxyde. Makromol Chem 1963;66:180–95.

[15] **Kazanskii KS, Lapienis G, Kuznetsova VI, Pakhomova LH, Evreinov VV**, Penczek S. Strictly monofunctional methyl ethers of poly(ethylene glycol) and the related methacrylate macromonomers. Vysokomol Soed Ser A 2000;42:915–26.

[21] **Hofman A, Slomkowski S, Penczek S.** Structure of active centers and mechanism of the anionic polymerization of lactones. Makromol Chem 1984;185:91–101.

[22] **Duda A.** Anionic polymerization of 4-methyl-2-oxetanone (b-butyrolactone). J Polym Sci Polym Chem Ed 1992;30: 21–9.

[23] **Sosnowski S, Slomkowski S, Penczek S**. Kinetics of anionic polymerization of e-caprolactone (eCL). Propagation on poly-eCL-K+ ion pairs. J Macromol Sci-Chem 1983;A20: 979–88.

[24] **Boileau S.** Use of cryptates in anionic polymerization of heterocyclic compounds. Am Chem Soc Symp Ser1981;166:283–305;[b] Sigwalt P, Spassky N. Cyclic compounds containing sulfur in the ring. In: Ref. [10], p. 603–714.

[25] **Duda A.** Anionic copolymerization of elemental sulfur. PhD thesis, Center of Molecular and Macromolecular Studies, Polish Academy of Sciences; Lodz, Poland, 1983.

[26] **Baran T, Duda A, Penczek S.** Anionic polymerization of norbornene trisulfide. J Polym Sci Polym Chem Ed 1984; 22:1085–95.

[27] **Mazurek M, Chojnowski J**. Cross-aggregation of active centers in a model anionic polymerization system. The kinetics of the reactions of silanolates with cyclic and linear polysiloxanes. Macromolecules 1978;11:347–56.

[28] **Dale J, Schwarz JE. Macrocyclic** lactones by oligomerization of simple lactones. Acta Chem Scand 1986;B40: 559–67.

[29] **Yu G-E, Heatley F, Booth C, Blease TG.** Anionic polymerization of propylene oxide; isomerisation of allyl ether to propenyl ether end groups. J Polym Sci Part A: Polym Chem 1994;32:1131–5.

[30] **Penczek S., Cypryk M., Duda A., Kubisa P., Slomkowski S**. ,2007, Prog. Polym. Sci. 32 (2007) 247–282

[31] **Schwach, G., Coudane, J., Engle, R., and Vert, M.,** 1997. More About the Polymerization of Lactides in the Presence of Stannous Octoate, *J. Polym. Chem., Part A: Polym. Chem.,* **35(16)**, 3431-3440.

[32] **Kricheldorf, H. R., Kreiser-Saunders, I., and Boettcher, C.,** 1995. Polylactones: 31. Sn(II)Octoate-Initiated Polymerization of L-Lactide: A Mechanistic Study, *Polymer,* **36(6)**, 1253-1259.

[33] **Kowalski, A., Duda, A., and Penczek, S.,** 2000. Mechanism of Cyclic Ester Polymerization Initiated with Tin(II) Octoate. 2. Macromolecules Fitted with Tin(II) Alkoxide Species Observed Directly in MALDI-TOF Spectra *Macromolecules,* **33(3)**, 689-695.

[34] **Kricheldorf, H. R., Kreiser-Saunders, I., and Stricker, A.,** 2000. Polylactones 48. $SnOct_2$-Initiated Polymerizations of Lactide: A Mechanistic Study, *Macromolecules*, **33(3)**, 702-709.

[35] **Mecerreyes, D., Jerome, R. and Dubois, P.,** 1999. Novel Macromolecular Architectures Based on Aliphatic Polyesters: Relevance of

the"Coordination-Insertion" Ring-Opening Polymerization, *Adv. Polym. Sci.,* **147**, 1-59.

[36] **Löfgren, A., Albertsson, A.C., Dubois, P. and Jerome, R.,** 1995. Recent Advances in Ring-Opening Polymerization of Lactones and Related-Compounds, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.,* **35(3)**, 379-418.

[37] **Kricheldorf, H. R., Kreiser, S. I.,** 1996. Polylactides - Synthesis, Characterization and Medical Application, *Macromol. Symp.,* **103**, 85-102.

[38] **Wang, J.S. and Matyjaszewski, K.**, 1995. Controlled Living Radical Polymerization - Halogen Atom-Transfer Radical Polymerization Promoted by a Cu(I)Cu(II) Redox Process*, Macromolecules*, **28**, 7901-7910.

[39] **Kricheldorf, H. R., Berl, M., and Scharnagl, N.,** 1988**.** Poly(Lactones). 9. Polymerization Mechanism of Metal Alkoxide Initiated Polymerizations of Lactide and Various Lactones, *Macromolecules,* **21(2)**, 286-293.

[40] **Dubois, P., Ropson, N., Jérôme, R. and Teyssie, P.,** 1996. Macromolecular Engineering of Polylactones and Polylactides. 19. Kinetics of Ring-Opening Polymerization of Epsilon-Caprolactone Initiated With Functional Aluminum Alkoxides, *Macromolecules,* **29(7)**, 1965-1975.

[41] **a) A. C. Albertsson and I. K. Varma,** 2003. *Biomacromolecules*, **4**, 1466-1486. **b) E. S. Place, J. H. George, C. K. Williams and M. M. Stevens,** 2009. *Chem.Soc. Rev*., **38**, 1139–1151.

[42] **A. C. Albertsson and I. K. Varma,** 2002. *Adv. Polym. Sci.*, **157**, 1-40.

[43] **O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou,** 2004. *Chem.Rev*., **104,** 6147-6176.

[44] **Kleine, J., and Kleine, H.-H.,** 1959. Über Hochmolekulare, İnsbesondere Optisch Aktive Polyester der Milchsäure, ein Beitrag zur Stereochemie Makromolekularer Verbindungen, *Makromol. Chem.,* **30(1),** 23-38.

[45] **Löfgren, A., Albertsson, A.C., Dubois, P. and Jerome, R.,** 1995. Recent Advances in Ring-Opening Polymerization of Lactones and Related-Compounds, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.,* **C35(3),** 379-418.

[46] **Duda, A., and Penczek, S.,** 2000. In *Polymers from Renewable Resources: Biopolyesters and Biocatalysis,* ACS Symposium Series 764, American Chemical Society, Washington, D.C., p 160.

[47] **O'Keefe, B., Hillmyer, M. A., and Tolman, W. B.,** 2001. Polymerization of Lactide and Related, Cyclic Esters by Discrete Metal Complexes, *J. Chem. Soc., Dalton Trans,* 2215-2220.

[48] **Penczek, S.,** 2000. Cationic Ring-Opening Polymerization (Crop) Major Mechanistic Phenomena, *J. Polym. Sci. Polym. Chem.,* **38(11),** 1919-1933.

[49] **Penczek, S. and Slomkowski, S.,** 1987. Progress In Anionic Ring-Opening Polymerization, in "*Recent Advances in Anionic Polymerization,* Chap **19**, 275, Eds. Hogen, E.T. and Smid, J., Elsevier, New York.

[50] **Duda, A., and Penczek, S.,** 2000. In *Polymers from Renewable Resources: Biopolyesters and Biocatalysis,* ACS Symposium Series 764, American Chemical Society, Washington, D.C., p 160.

[51] **Mecerreyes, D., Jerome, R. and Dubois, P.,** 1999. Novel Macromolecular Architectures Based on Aliphatic Polyesters: Relevance of the"Coordination-Insertion" Ring-Opening Polymerization, *Adv. Polym. Sci.,* **147**, 1-59.

[52] **Lundberg, R.D. and Cox, E.F.,** 1969. Lactones, in *Ring-Opening Polymerization,* Frish, K., Reegen, S., Eds, 2:247 Marcel Dekker, New York.

[53] **Kricheldorf, H. R., Berl, M., and Scharnagl, N.,** 1988**.** Poly(Lactones). 9. Polymerization Mechanism of Metal Alkoxide Initiated Polymerizations of Lactide and Various Lactones, *Macromolecules,* **21(2)**, 286-293.

[54] **Kowalski, A., Duda, A., and Penczek, S.,** 1998. Polymerization of L,L-Lactide Initiated by Aluminum Isopropoxide Trimer or Tetramer, *Macromolecules,* **31(7)**, 2114-2122.

[55] **Schwach, G.**, **Coudane, J., Engel, R., and Vert, M.,** 1998. Ring Opening Polymerization of D,L-Lactide in the Presence of Zinc Metal and Zinc Lactate, *Polym.* Initiated by Aluminum Isopropoxide Trimer or Tetramer, *Macromolecules, Int.* **46(3)**, 177-182.

[56] **Kreiser-Saunders, I., and Kricheldorf, H. R.** 1998. Polylactones, 39. Zn Lactate- Catalyzed Copolymerization of L-Lactide with Glycolide or ε-Caprolactone, *Macromol. Chem. Phys.,* **199(6)**, 1081-1087.

[57] **Myers, M.;Connor, E.F; Moller, M.; Glauser, T.; Hedrick, J.L**. 2001, *Angew. Chem*., Int. Ed., 40, 2712.

[58] **Biela,T.; Penczek, S.; Slomkowski, S.; Vogl,O.** 1983, *Makromol. Chem*., 184, 811.

[59] (a) **Dove, A. P., Pratt, R. C., Lohmeijer, G.B.G., Culkin, D. A. Hagberg , E. C., Nyce, G. W., Waymouth, R. M., Hedrick, J. L.** 2006, *Polymer*

[60] **Rokicki, G.** Prog. Polym. Sci. 2000, 25, 259−342.

[61] **Sanders, D. P.; Fukushima, K.; Coady, D. J.; Nelson, A.; Fujiwara, M.; Yasumoto, M.; Hedrick, J. L. J.** Am. Chem. Soc. 2010, 132, 14724−14726.

[62] **Pratt, R. C.; Nederberg, F.; Waymouth, R. M.; Hedrick, J. L. Chem**. Commun. 2008, 114−116.

[63] **Suriano, F.; Coulembier, O.; Hedrick, J. L.; Dubois**, P. Polym. Chem. 2011, 2, 528−533.

[64] **Cooley, C. B.; Trantow, B. M.; Nederberg, F.; Kiesewetter, M. K.; Hedrick, J. L.; Waymouth, R. M.; Wender, P. A. J.** Am. Chem. Soc. 2009, 131, 16401−16403.

[65] **Kiesewetter, M. K.; Shin, E. J.; Hedrick, J. L.; Waymouth, R. M.** Macromolecules 2010, 43, 2093−2107.

[66] **Lohmeijer, B. G. G.; Pratt, R. C.; Leibfarth, F.; Logan, J. W.; Long, D. A.; Dove, A. P.; Nederberg, F.; Choi, J.; Wade, C.; Waymouth, R. M.; Hedrick, J. L**. Macromolecules 2006, 39, 8574−8583.

[67] **Dove, A. P.; Pratt, R. C.; Lohmeijer, B. G. G.; Waymouth, R. M.; Hedrick, J. L. J. Am**. Chem. Soc. 2005, 127, 13798−13799.

[68] **Williams, C. K**. Chem. Soc. Rev. 2007, 36, 1573−1580.

[69] **Posner, T.**, 1905. Beiträge zur kenntniss der ungesättigten verbindungen. Ii. Ueber die addition von mercaptanen an ungesättigte kohlenwasserstoffe. *Berichte der deutschen chemischen Gesellschaft* 38, (1), 646-657.

[70] **Mayo, F. R.; Walling, C.**, 1940. The peroxide effect in the addition of reagents to unsaturated compounds and in rearrangement reactions. *Chemical Reviews* 27, (2), 351-412.

[71] **Griesbaum, K.**, 1970. Problems and possibilities of the free-radical addition of thiols to unsaturated compounds. *Angewandte Chemie International Edition in English* 9, (4), 273-287.

[72] **v. Braun, J.; Murjahn, R.**, 1926. Haftfestigkeit organischer reste (iv). *Berichte der deutschen chemischen Gesellschaft (A and B Series)* 59, (6), 1202-1209.

[73] **Cook, W. D.; Chen, F.; Pattison, D. W.; Hopson, P.; Beaujon, M.**, 2007. Thermal polymerization of thiol-ene network-forming systems. *Polymer International* 56, (12), 1572-1579.

[74] **Carioscia, J. A.; Stansbury, J. W.; Bowman, C. N.**, 2007. Evaluation and control of thiol-ene/thiol-epoxy hybrid networks. *Polymer* 48, (6), 1526-1532.

[75] **Dondoni, A.**, 2008. The emergence of thiol–ene coupling as a click process for materials and bioorganic chemistry. *Angewandte Chemie International Edition* 47, (47), 8995-8997.

[76] **Campos, L. M.; Killops, K. L.; Sakai, R.; Paulusse, J. M. J.; Damiron, D.; Drockenmuller, E.; Messmore, B. W.; Hawker, C. J.**, 2008. Development of thermal and photochemical strategies for thiol-ene click polymer functionalization. *Macromolecules* 41, (19), 7063-7070.

[77] **Chan, J. W.; Yu, B.; Hoyle, C. E.; Lowe, A. B.**, 2009. The nucleophilic, phosphine-catalyzed thiol-ene click reaction and convergent star synthesis with raft-prepared homopolymers. *Polymer* 50, (14), 3158-3168.

[78] **G. Rokicki,** Prog. Polym. Sci. 25 (2000) 259–342.

[79] **D.C. Webster**, Prog. Org. Coat. 47 (2003) 77–86.

[80] **B. Ochiai, T. Endo**, Prog. Polym. Sci. 30 (2005) 183–215.

[81] **S. Kuhling, H. Keul, H. Hocker, Die Makromol**. Chem. 193 (1992) 1207–1217.

[82] **S. Kuhling, H. Keul, H. Hocker**, Die Makromol. Chem. 191 (1990) 1611–1622.

[83] **H. Tomita, F. Sanda, T. Endo**, Macromolecules 34 (2001) 7601–7607.

[84] **J. Feng, X.L. Wang, F. He, R.X. Zhuo**, Macromol. Rapid Commun. 28 (2007) 754–758.

[85] **M. Kalbe, H. Keul, H. Hocker**, Macromol. Chem. Phys. 196 (1995) 3305–3321.

[86] **S. Kuehling, H. Keul, H. Hoecker, H.J. Buysch, N. Schoen, E. Leitz**, Macromolecules 24 (1991) 4229–4235.

[87] **H.R. Kricheldorf, B. Weegen-Schulz**, Macromolecules 26 (1993) 5991–5998.

[88] **H.R. Kricheldorf, B. Weegen-Schulz, Polymer 36** (1995) 4997–5003.

[89] **H. Keul, H. Hocker**, Cyclic carbonates, in: J.C. Salamone (Ed.), The Polymeric Materials Encyclopedia: Synthesis, Properties, and Applications, CRC Press, Boca Raton, 1996, p. 1647.

[90] **L. Vogdanis, W. Heitz**, Die Makromol. Chem., Rapid Commun. 7 (1986) 543–547.

[91] **L. Vogdanis, B. Martens, H. Uchtmann, F. Hensel, W. Heitz**, Die Makromol. Chem. 191 (1990) 465–472.

[92] **L. Ubaghs, N. Fricke, H. Keul, H. Hocker**, Macromolecules Rapid Commun. 25 (2004) 517–521.

[93] **L. Ubaghs, C. Novi, H. Keul, H. Hocker**, Macromolecules Chem. Phys. 205 (2004) 888– 896.

[94] **H. Tomita, F. Sanda, T. Endo**, J. Polym. Sci., Part A: Polymer Chemistry 39 (2001) 860– 867.

[95] **H. Tomita, F. Sanda, T. Endo**, J. Polym. Sci., Part A: Polymer Chemistry 39 (2001) 162– 168.

[96] **H. Tomita, F. Sanda, T. Endo**, J. Polym. Sci., Part A: Polymer Chemistry 39 (2001) 851– 859.

[97] **Rokicki, G**. *Prog. Polym. Sci.* **2000,** *25,* 259–342.

[84] **Darensbourg, D. J**.; **Horn, A**.; Moncada, A. I. *Green Chem.* **2010,** *12,* 1376–1379.

[85] **Gabriele, B.; Mancuso, R.; Salerno, G.; Ruffolo, G.; Costa, M.; Dibenedetto, A**. *Tetrahedron Lett.* **2009,** *50,* 7330–7332.

[86] **Carothers, W. H.; Van Natta, F. J**. *J. Am. Chem. Soc.* **1930,** *52,* 314–326.

[87] **Albertsson, A. C.; Sjöling,** M. *J. Macromol. Sci. Pure Appl. Chem.* **1992,** *29,* 43–54.

[88] **Löwenhielm, P.; Claesson, H.; Hult**, A. *Macromol. Chem. Phys.* **2004,** *205,*1489-1496.

[89] **Burk, R. M.; Roof, M. B**. *Tetrahedron Lett.* **1993,** *34,* 395–398.

[90] **Basel, Y.; Hassner, A**. *J. Org. Chem.* **2000,** *65,* 6368–6380.

[91] **Kim, S.; Ko, Y. K**. *Heterocycles* **1986,** *24,* 1625–1630.

[92] **Sanders, D. P.; Fukushima, K**.; Coady, D. J.; Nelson, A.; Fujiwara, M.; **Yasumoto, M.; Hedrick, J. L.** ***J****. Am. Chem. Soc.* **2010,** *132,* 14724–14726.

[93] **Kutney, J. P.; Ratcliffe, A. H**. *Synth. Commun.* **1975,** *5,* 47–52.

[94] **Ariga, T.; Takata, T.; Endo, T.** *J. Polym. Sci., Part A: Polym. Chem.* **1993,** *31,* 581–584.

[110] **Omurtag, P. S., Gunay, U. S., Dag, A., Durmaz, H., Hizal, G., Tunca U.,** Diels-Alder Click Reaction for the Preparation of Polycarbonate Block Copolymers, **2012**, Polymer Chemistry, 10.1002/pola.26608

[111] **Tempelaar, S., Mespouille, L., Dubois, P., Dove, A.P.,** Organocatalytic Synthesis and Postpolymerizaiton Funtionalization of Allyl-Functional Poly(carbonate)s, **2010**, *Macromolecules*

[112] **Onbulak, S., Tempelaar, S., Pounder, R.J., Gok O., Sanyal, R., Dove , A.P., Sanyal, A.,** Synthesis and Funtionalization of Thiol-Recative Biodegredable Polymers, **2011,** *Macromolecules*

[113] **Barltrop, J. A.; Plant, P. J.; Schofield, P. J. Chem. Soc., Chem. Commun**. 1966, 22, 822.

[114] **Ciamician, G.; Silber, P. Chem. Ber**. 1901, 34, 2040

[115] **Bochet, C. G. J. Chem. Soc., Perkin Trans**. 1 2002, 2, 125−142.

[116] **Gaplovsky, M.; Il'ichev, Y. V.; Kamdzhilov, Y.; Kombarova, S. V.; Mac, M.; Schworer, M. A.; Wirz, J**. Photochem. Photobiol. Sci. 2005, 4,33−42.

[117] **Corrie, J. E. T.; Barth, A.; Munasinghe, V. R. N.; Trentham, D. R.;** Hutter, M. C. J. Am. Chem. Soc. 2003, 125, 8546−8554.

[118] **V. N. R. Pillai**, Synthesis 1980,1 –26.

[119] **C. G. Bochet**, J. Chem. Soc. Perkin Trans. 1 2002,125 – 142.

[120] **A. P. Pelliccioli,J . Wirz**, Photochem. Photobiol. Sci. 2002, 1,441 – 458.

[121] **H. Ando,T . Furuta,R. Y. Tsien, H. Okamoto**, Nat. Genet. 2001, 28, 317 – 325.

[122] **Xie Z., Hu X., Chen X., Sun J., Shi Q., Jing X**., Biomacromolecules, 2008, 9, 376-380

[123] **Henrik Ihre and Anders Hult, Jean M. J. Fre´chet, Ivan Gitsov** (1998) Double-Stage Convergent Approach for the Synthesis of Functionalized Dendritic Aliphatic Polyesters Based on 2,2-Bis(hydroxymethyl)propionic Acid. Macromolecules 31, 4061-4068.

[124] R**. C. Pratt, B. G. G. Lohmeijer, D. A. Long, P. N. P. Lundberg, A. P. Dove, H. Li, C. G. Wade, R. M. Waymouth, J. L. Hedrick**, Macromolecules 2006, 39, 7863–7871.

[125] **Xie Z., Hu X., Chen X., J Sun J., Shi Q., (2010)** Synthesis and Characterization of Novel BiodegradablePoly(carbonate ester)s with Photolabile Protecting Groups, 2008, Biomacromolecules

[126] **Kim M.S., Diamond S.L., (2006),** Photocleavage of o-nitrobenzyl ether derivatives for rapid biomedical release applications, 2006, Bioorganic and medical chemistry

CURRICULUM VITAE

Name Surname: Elif BAYSAK

Place and Date of Birth: Izmir / 31.01.1989

Address: Konaklar Mah. Org. Izzettin Aksalur Cad. Deniz Sb. Lojmanlari Konuray Apt. Daire : 8 Besiktas/Istanbul

E-Mail: elifbaysak@itu.edu.tr

B.Sc.: Ege University

Presentation: Baysak E., Cakir N., Tunca U., Hizal G. 2013: A Versatile Route For The Synthesis Of Functional Polycarbonates Having *o*-Nitrobenzyl And Allyl Groups. *1. Uluslararası Plastik ve Kauçuk Teknolojileri Sempozyum ve Ürün Sergisi, ispart 2013*, 29-31 Mayıs, Ankara