ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF TELECHELIC POLYTETRAHYDROFURAN

M.Sc. THESIS

Ecem TEMELKAYA

Department of Polymer Science and Technology

Polymer Science and Technology Programme

Thesis Advisor: Prof. Dr. Gürkan HIZAL

Anabilim Dalı : Herhangi Mühendislik, Bilim

Programı : Herhangi Program

JANUARY 2013

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Ecem Temelkaya, a **M.Sc.** student of ITU **Graduate School of Science, Engineering and Technology** 515111008, successfully defended the **dissertation** entitled "Synthesis and Characterization of Telechelic Polytetrahydrofuran", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my dearest family & friends,

FOREWORD

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ABBREVIATIONS

^{1}H NMR	**:** Hydrogen Nuclear Magnetic Resonance Spectroscopy
C/LRP	**:** Controlled/Living Radical Polymerization
CaH_2	**:** Calcium Hydride
$CDCl_3$	**:** Deuterated *Chloroform*
CH_2Cl_2	**:** Dichloromethane
CROP	**:** Cationic Ring-opening polymerization
CuAAC	**:** Copper Catalyzed Azide-Alkyne Cyclo-Addition
DA	**:** Diels-Alder
DIPEA	**:** *N*,*N*-diisopropylethylamine
DMF	**:** *N*,*N*-dimehthylformamide
Et_3N	**:** Triethylamine
EtOAc	**:** Ethyl Acetate
f	**:** Functionality
FPT	**:** Freeze-Pump-Thaw
FT-IR	**:** Fourier Transform Infrared Spectrophotometer
GC	**:** Gas Chromatography
GPC	**:** Gel Permeation Chromatography
HEBiB	**:** 2-hydroxyethyl 2-bromoisobutyrate
MeOTf	**:** Methyl Triflate
MWD	**:** Molecular Weight Distribution
NRC	**:** Nitroxide Radical Coupling
P_2O_5	**:** Phosphorus Pentoxide
PDI	**:** Polydispersity Index
PMDETA	**:** *N, N, N',N'', N''*-Pentamethyldiethylenetriamine
PMMA	**:** Poly(methyl metacrylate)
PS	**:** Polystyrene
PTHF	**:** Polytetrahydrofuran
ROMP	**:** Ring-Opening Metathesis Polymerization
SPAAC	**:** Strain-Promoted Azide-Alkyne Coupling
Tf_2O	**:** Triflic Anhydride
THF	**:** Tetrahydrofuran
UV	**:** Ultra Violet

LIST OF SYMBOLS

λ	**:** Wavelength
$R^{\cdot}$	**:** Radical
nm	**:** Nanometer
C	**:** Concentration
A	**:** Absorbance
ε	**:** Molar extinction coefficient
ppm	**:** Parts per million
^{o}C	**:** Celsius
$\boldsymbol{M_n}$	**:** The number average molecular weight
$\boldsymbol{M_w}$	**:** The weight average molecular weight
$\boldsymbol{M_w/M_n}$	**:** The molecular weight distribution

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SYNTHESIS AND CHARACTERIZATION OF TELECHELIC POLYTETRAHYDROFURAN

SUMMARY

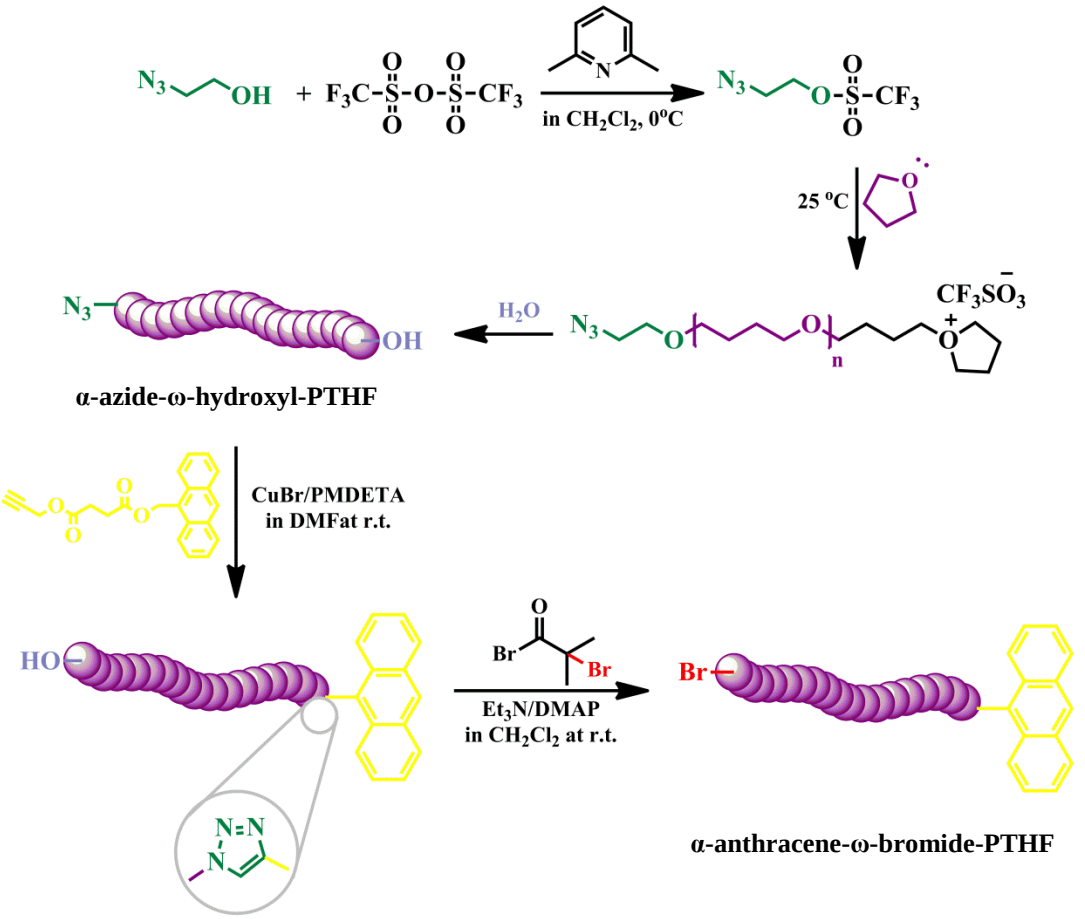
The synthesis of complex macromolecular structures with well-defined properties had been the main challenge for polymer chemists until the development of ionic polymerization methods. When Szwarc had discovered the *living* character of polymers with his study about anionic polymerization of styrene in the presence of sodium naphthalenide, he had introduced the polymer chemists to a new field of polymer science nowadays known as living polymerization. After Szwarc succeeded it with anions, the question "what about cations?" emerged and new studies have been begun in this field thereat. Meanwhile the living character of cationic ring-opening polymerization (CROP) of tetrahydrofuran (THF) initiated with triflate esters was discovered by Matyjaszewski, Penzcek et al.

Today in the light of all those studies and improvements in polymer science, macromolecules with different and complicated structures can be synthesized using many of those techniques or newly developed ones including click reactions, which provide so many conveniences in the synthesis of block, graft and star shaped polymers.

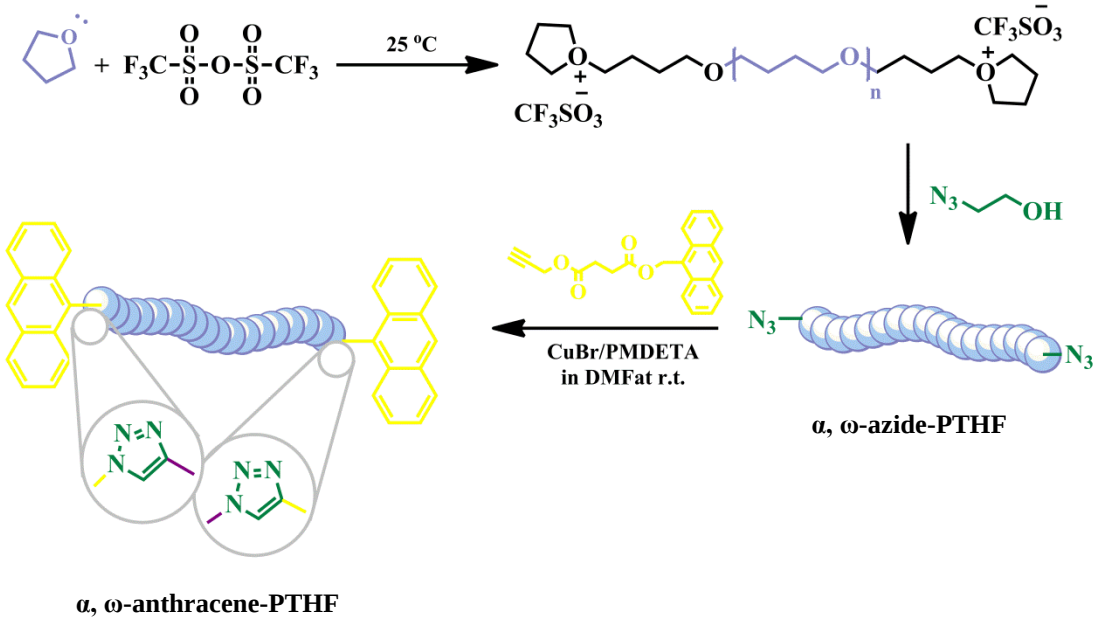
Nowadays with the increasing interest in the synthesis of polymers with different functional end groups, the term *telechelic polymers* has emerged and new studies have started with the inclusion of click chemistry.

The target of this dissertation was to obtain polymers having different functional end groups with the combination of living cationic ring-openig polymerization and click chemistry methods including Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reactions. In this sense, polytetrahydrofurans (PTHF) having various functionalities such as azide ($-N_3$), hydroxyl (-OH), bromo (-Br) and anthracene were obtained using *functionalization from initiator*, *functionalization from terminating agent* and *chain-end modification* methods including CuAAC click and esterification reactions. The resulting polymers are simply termed as telechelic polymers. Ideally, these polymers were synthesized in the expectation that they can go into further reactions resulting in block, graft and star shaped polymers depending on demand.

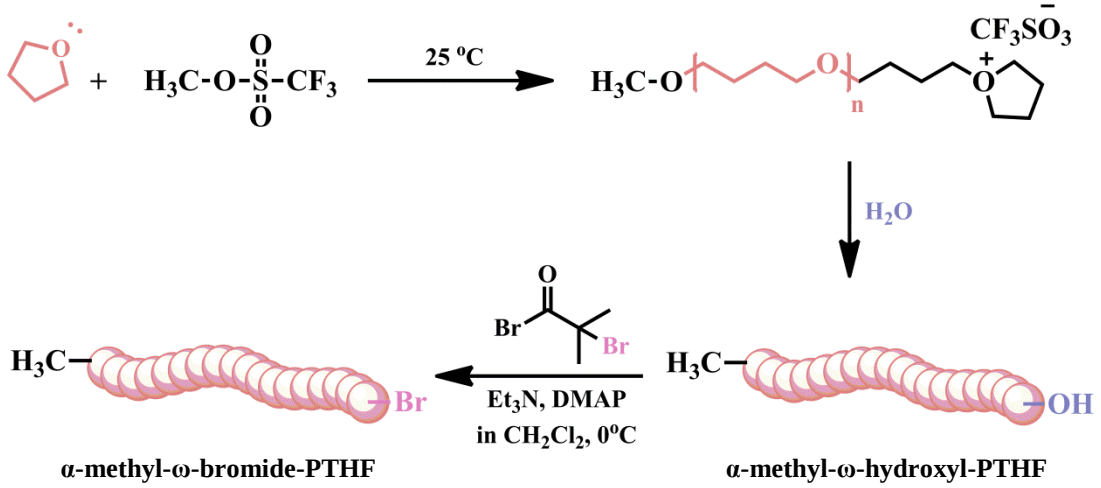
In the first study, CROP of THF was initiated by an azide functionalized triflate ester, which had been *in-situ* synthesized and terminated with excess of water resulting in α-azide-ω-hydroxyl-PTHF. Azide functionality at the α-end of the polymer was then converted to anthracene functionality via CuAAC click reaction. As a last step, a basic esterification reaction was carried out to convert the hydroxyl functionality to bromide functionality. Using *functionalization from initiator* and *chain-end modification* methods α, ω-telechelic PTHF has been synthesized and characterized by nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FT-IR).



In the second study, tetrahydrofuran was polymerized with triflic anhydride directly. Living chain ends were terminated with azide functionalized alcohol to obtain α, ω-azide-PTHF. Azide functionalities were then converted to anthracene functionalities via CuAAC click reaction resulting in α, ω-anthracene-PTHF.



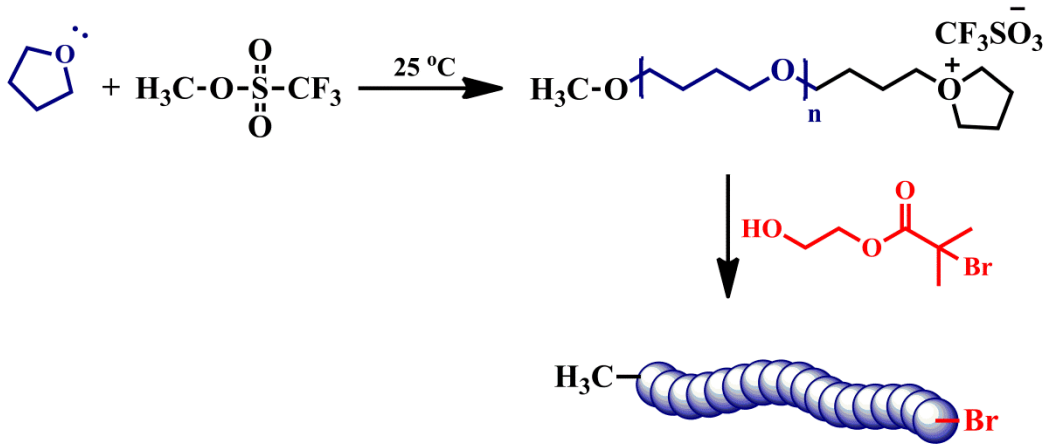
In the third study, methyl triflate was used as initiator in the CROP of THF and polymerization was terminated with excess of water resulting in α-methyl-ω-hydroxyl-PTHF. The hydroxyl functionality was then converted to bromide functionality via esterification. Resulting α-methyl-ω-bromide-PTHF was purified and characterized.



α-methyl-ω-bromide-PTHF

α-methyl-ω-hydroxyl-PTHF

In the last study, a reaction was designed as an alternative to third study to obtain α-methyl-ω-bromide-PTHF in one pot without post-modification reaction. For this purpose, a bromide functionalized alcohol was synthesized and used as terminating agent.



α-methyl-ω-hydroxyl-PTHF

FONKSİYONEL UÇ GRUBA SAHİP POLİTETRAHİDROFURANIN SENTEZİ VE KARAKTERİZASYONU

ÖZET

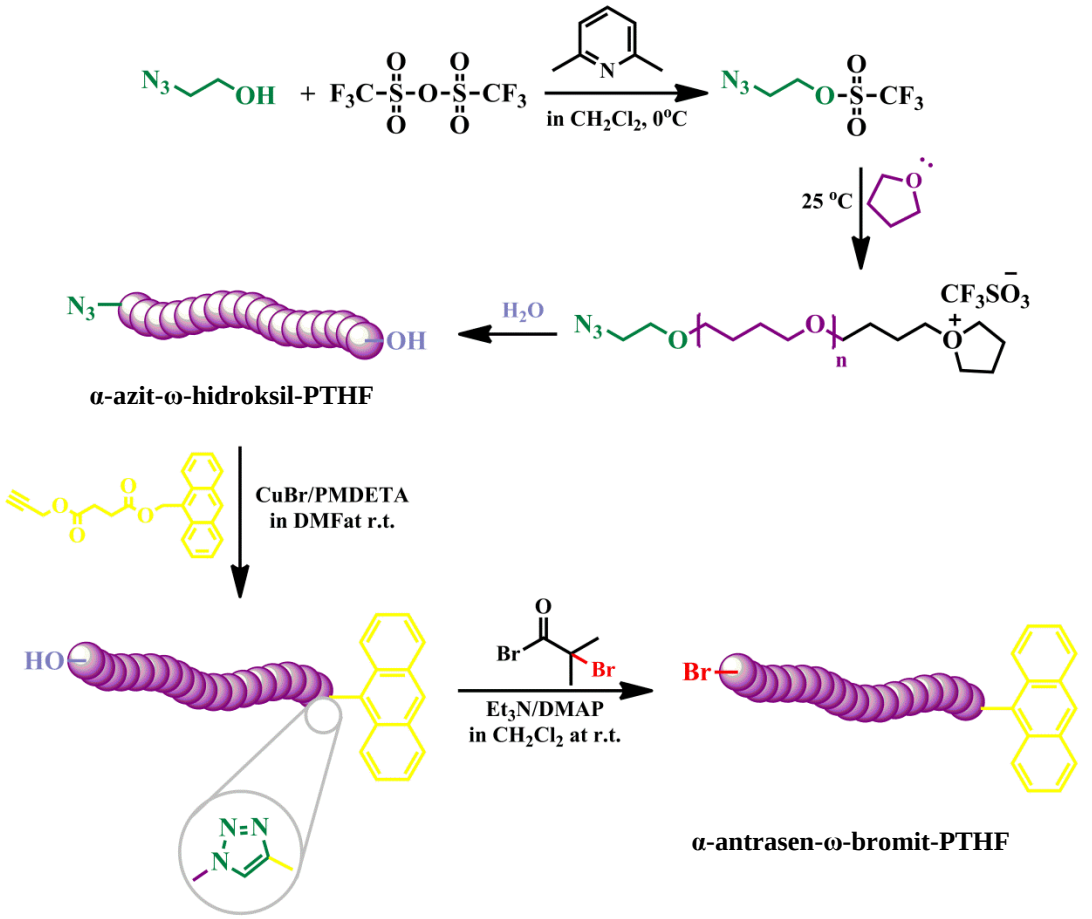
İyi tanımlanmış özelliklere sahip karmaşık makromoleküler yapıların sentezi, iyonik polimerizasyon metotları geliştirilene dek polimer kimyacıları için büyük sorun olmuştur. Szwarc, sodyum naftenat varlığında gerçekleştirdiği anyonik stiren polimerizasyonu çalışması ile polimerlerin *yaşayan* özelliğini keşfettiğinde; polimer kimyacılarını, polimer biliminin günümüzde yaşayan polimerizasyon olarak bilinen yeni bir alanı ile tanıştırmıştı. Szwarc bunu anyonlarla başardıktan sonra "ya katyonlar?" sorusu belirdi ve bu alanda yeni çalışmalar başlatıldı. Tetrahidrofuranın triflat esterleri ile başlatılan katyonik halka açılması polimerizasyonunun yaşayan özelliği de bu sırada Matyjaszewski, Penzcek ve arkadaşları tarafından keşfedildi.

Bugün polimer biliminde yapılmış tüm bu çalışmaların ve gelişmelerin ışığında, farklı ve karmaşık yapılara sahip makromoleküller, pek çok geleneksel tekniğin yanında blok, aşı ve yıldız polimerlerin sentezinde kolaylık sağlayan klik reaksiyonları gibi yeni geliştirilmiş olan teknikler ile sentezlenebilmektedir.

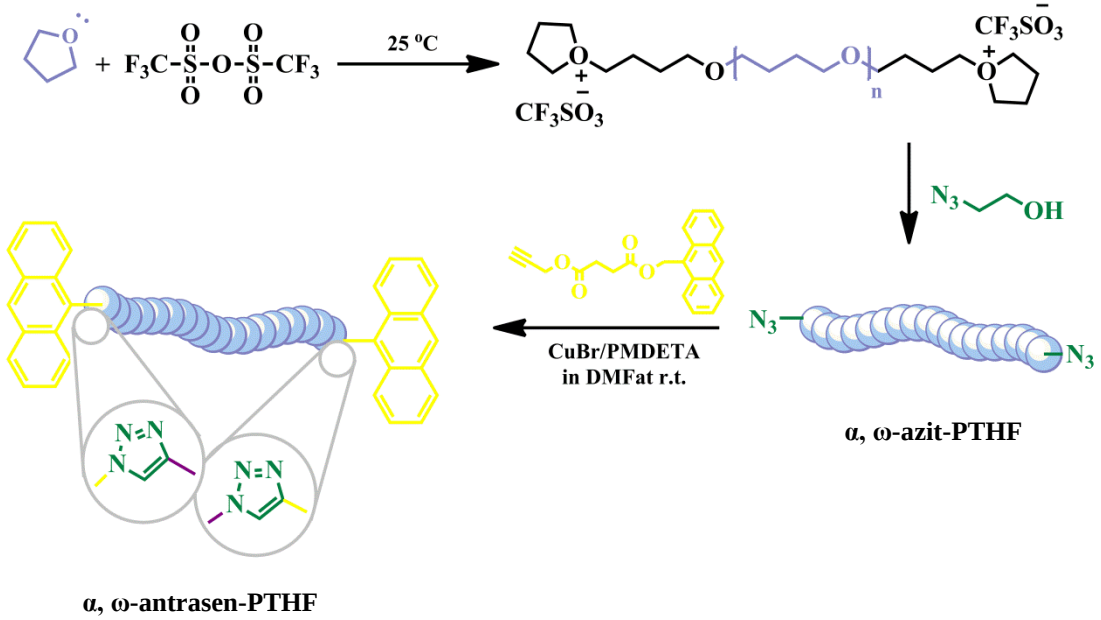
Günümüzde farklı uç gruplara sahip polimerlerin sentezine artan ilgi ile *telekelik polimerler* terimi gün ışığına çıkmış ve klik kimyasını da içeren yeni çalışmalar başlatılmıştır.

Bu tezin amacı; yaşayan katyonik halka açılması polimerizasyonu ve bakır(I) katalizli azit-alkin siklo katılma (CuAAC) reaksiyonlarını da içeren klik kimyası metotlarını birleştirerek farklı fonksiyonel uç gruplara sahip polimerler elde etmektir. Bu bağlamda, azit (-N_3), hidroksil (-OH), brom (-Br) ve antrasen fonksiyonlarına sahip çeşitli politetrahidrofuranlar, *başlatıcıdan fonksiyonlandırma*, *sonlandırma ajanı ile fonksiyonlandırma* ve CuAAC ve esterleşme reaksiyonlarını da içeren *zincir ucu modifikasyonu* teknikleri ile elde edilmiştir. Bu polimerler basitçe telekelik polimerler olarak isimlendirilirler. Bu polimerler ideal olarak blok, aşı ve yıldız polimerlerin sentezinde kullanılmak amacıyla sentezlendiler.

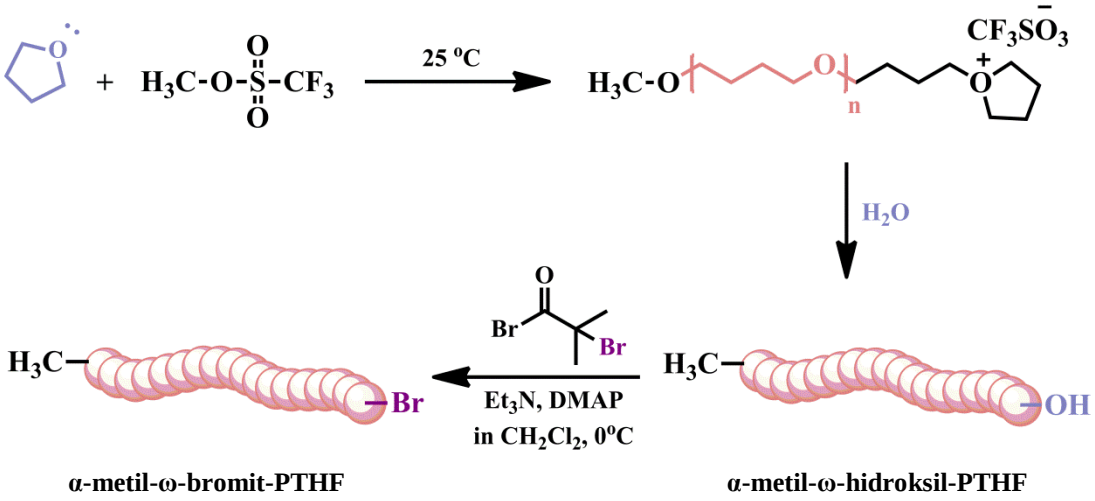
Ilk çalışmada, *in-situ* olarak sentezlenen azit fonksiyonlu triflate esteri tetrahidrofuranın katyonik halka açılması reaksiyonunu başlatmak üzere kullanıldı ve su ile sonlandırılarak α-azit-ω-hidroksil-PTHF elde edildi. Polimerin α-ucunda yer alan azit fonksiyonu CuAAC klik reaksiyonu ile antrasen fonksiyonuna dönüştürüldü. Son olarak bilindik bir esterleşme reaksiyonu gerçekleştirilerek hidroksil fonksiyonu bromit fonksiyonuna çevrildi. *Başlatıcıdan fonksiyonlandırma* ve *zincir ucu modifikasyonu* metotları ile α, ω-telekelik PTHF sentezlendi ve nükleer manyetik rezonans (NMR), jel geçirgenlik kromatografisi kullanılarak (GPC) ve Fourier dönüşümlü infrared spektroskopisi (FT-IR) karakterize edildi.



Ikinci çalışmada, tetrahydrofuran triflik anhidrit ile direkt olarak polimerleştirildi. Yaşayan zincir uçları azit fonksiyonlu alkol ile sonlanırılarak α, ω-azit-PTHF elde edildi. Azit fonksiyonları CuAAC klik reaksiyonu ile antrasen fonksiyonuna dönüştürülerek α, ω-antrasen-PTHF elde edildi.

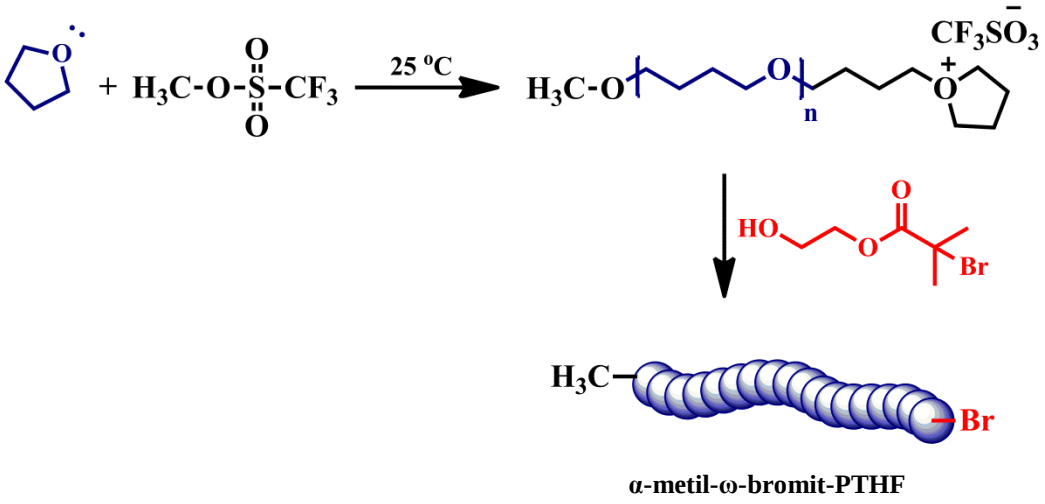


Üçüncü çalışmada, THF' in katyonik halka açılması polimerizasyonu için metil triflat başlatıcı olarak seçildi ve polimerizasyon su ile sonlandırılarak α-metil-ω-hidroksil-PTHF elde edildi. Hidroksil fonksiyonu esterleşme ile bromit fonksiyonuna dönüştürüldü ve elde edilen α-metil-ω-bromit-PTHF karakterize edildi.



α-metil-ω-bromit-PTHF **α-metil-ω-hidroksil-PTHF**

Son çalışma, α-metil-ω-bromit-PTHF' i post-modifikasyon olmaksızın tek seferde elde etmek için üçüncü çalışmaya bir alternatif olarak tasarlandı. Bu amaçla bromit fonksiyonlu bir alkol sentezlendi ve sonlandırma ajanı olarak kullanıldı.



α-metil-ω-bromit-PTHF

1. INTRODUCTION

Since the mid-1990s, the field of polymer chemistry has witnessed the explosive development of a number of procedures for conducting a controlled/living radical polymerization (C/LRP) [1,2]. CRP allows the synthesis of various types of functional polymeric materials and provides the capability of designing polymers with controlled molecular weight and molecular weight distribution (MWD), in addition to controlled chemical composition, chain-sequence distribution, site-specific functionality and predeterminable topology [3–5].

The term “living polymerization” was first defined in 1956 by Michael Szwarc as a chain polymerization from which chain transfer and chain termination are absent [6]. Thus, living polymerizations typically lead to very narrow molecular weight distributions and allow for the synthesis of block (co)polymers by sequential addition of monomers. However, a living polymerization does not necessarily allow for controlling the molecular weight or chain architectures of polymers. In 1987, the term “controlled polymerization” was introduced by Müller and Matyjaszewski to describe synthetic methods to prepare polymers with well-defined topology (e.g., linear, star-shaped, comb shaped, dendritic, and cyclic), terminal functionality, composition, and comonomer arrangement (e.g., statistical, gradient, block, and graft) [7].

Anionic polymerization was the first and only example of a living process for more than a decade after its realization, but other living techniques have since been discovered. In 1974, two types of active species were observed with spectroscopic techniques in the cationic ring-opening polymerization (CROP) of tetrahydrofuran initiated by triflate esters [8-11]. The activities and exchange dynamics among free ions, ion pairs, aggregates and significantly less active esters were quantitatively measured for growing oxonium cations and the dormant esters. Living CROP was subsequently extended to other heterocyclic monomers and eventually enabled the synthesis of many well-defined (co)polymers [12,13].

In 2001, Sharpless and co-workers [14] introduced “click” chemistry, a new approach in organic synthesis that involves a handful of almost perfect chemical reactions. Especially, the Cu(I)-catalyzed Huisgen 1,3-dipolar cyclo-addition reaction between azides and alkynes has been extensively used for post-modification reactions [15].

A major concern of polymer and material science is designing functional materials with physical features tuned to match the needs of expanding technology. In particular, end-functional polymers have an important economic position because of their possible applications as components in the synthesis of block (co)polymers, thermoplastic elastomers, polymer networks, surfactants, macromonomers, etc. [16]. According to the IUPAC, telechelic polymers are defined as polymeric molecules with reactive end groups that have the capacity to enter into further polymerization or other reactions. Reactive end-groups in telechelic polymers come from the initiator or the terminating or chain-transfer agents in chain polymerizations, but not from monomer(s) as in polycondensations and polyadditions [17]. Functionalization of polymer chain ends can also take place in post-polymerization reactions. Telechelic polymers can be used as cross-linkers, chain extenders, and pre-cursors for block and graft (co)polymers [18–20]. Moreover, star and hyper-branched or dendritic (or hyper-branched) are obtained by coupling reactions of monofunctional and multifunctional telechelics with appropriate reagents. The functionality of the end group is important. When such groups are bifunctional (e.g., vinyl groups) they can participate in polymerization reactions, yielding graft (co)polymers or networks; such telechelic polymers are called macromolecular monomers, macromonomers, or macromers [21].

In this dissertation, a set of approaches for the synthesis of various telechelic polymers with functional chain ends using living cationic ring-opening polymerization of tetrahydrofuran and click chemistry involving CuAAC click reactions were described. Resulting polymers were characterized and specified by NMR, GPC, FT-IR and UV spectroscopy. These functionalized polymers were intentionally synthesized to give further reactions for the synthesis of block, graft and star shaped polymers.

2. THEORETICAL PART

2.1 Living polymerization

Conventional free-radical polymerization (RP) is a very important commercial process for preparing high molecular weight polymers because it can be employed for polymerization of many vinyl monomers under mild reaction conditions, requiring the absence of oxygen, but tolerant to water, and can be conducted over a large temperature range (-80 to 250 ^{o}C) [22,23]. In addition, many monomers can easily copolymerize via a radical route, leading to an infinite number of (co)polymers with properties dependent on the proportion of the incorporated comonomers. The main limitation of RP is the poor control over some of the key elements of macromolecular structures such as molecular weight (M_w), polydispersity (PDI), end functionality, chain architecture, and composition. [24-26].

Well-defined polymers, with molecular weight, structural and compositional homogeneity, can only be synthesized by living ionic polymerizations or C/LRP methods. The way to living polymerization was opened in 1955 when the seminal work of Szwarc proved the livingness of macro-ions and the term "living" was coined.
[27-31].

The IUPAC Gold Book defines "living polymerization" as a chain polymerization from which chain transfer and chain termination are absent [32]. The elimination of transfer and termination reactions from chain growth polymerization formed the basis of Szwarc's discovery. These chain breaking processes were avoided with the development of special high vacuum techniques to minimize traces (< 1 ppm) of moisture and air in the anionic polymerization of non-polar vinyl monomers [6,24]. The techniques were first implemented in an academic setting but were quickly adapted on an industrial scale, which ultimately led to the mass production of several

commercial products, most notably well-defined block (co)polymers capable of performing as thermoplastic elastomers [34].

Anionic polymerization was the first and only example of a living process for more than a decade after its realization, but other living techniques have since been discovered. In 1974, two types of active species were observed with spectroscopic techniques in the cationic ring-opening polymerization of tetrahydrofuran initiated by triflate esters [8-11]. The activities and exchange dynamics among free ions, ion pairs, aggregates and significantly less active esters were quantitatively measured for growing oxonium cations and the "dormant" esters. Living CROP was subsequently extended to other heterocyclic monomers and eventually enabled the synthesis of many well-defined (co)polymers [12,13].

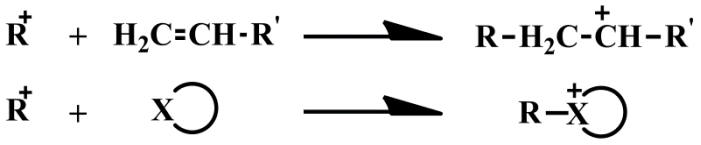
Because living polymerization has no chain transfer and chain termination, block (co)polymers by sequential addition of monomers can be obtained leading to very narrow molecular weight distributions. However, a living polymerization does not necessarily allow for controlling the molecular weight or chain architectures of polymers. To prepare polymers with well-defined topology "controlled polymerization" term was introduced to the polymer science.

2.2 Living cationic ring-opening polymerization

Most cationic polymerizations are chain polymerizations involving positively charged or electrophilic active centers at the growing chain end. Polymerization mechanisms are classified as either chain growth or step growth, with cationic polymerizations being one of the three major types of chain polymerizations. Both alkenes and heterocyclic monomers can be polymerized cationically. The two systems differ in that the active species in the polymerization of alkenes are carbenium-ions, whereas onium ions are the active species in the polymerization of heterocycles. Nevertheless, there are more similarities between the two systems than differences. These two areas of cationic polymerization are not completely separately fields. In spite of the differences, both processes proceed on electron-deficient active species: cations or species with a partial positive charge. Thus, propagation in both cases involves attack of the nucleophile (double bond or heteroatom) on electrophilic active centers [26].

To understand the main differences between vinyl and ring-opening cationic polymerization both mechanisms are formulated briefly. First of all, polymerization of vinyl monomers leads to polymers having all-carbon chains (although various heteroatoms may be incorporated in the side groups). Polymerization of heterocyclic monomers gives polymers containing heteroatom(s) within the main chain. Because there are several possible combinations within the cyclic monomer molecule, ring-opening polymerization allows the preparation of polymers with various sequences of carbon atoms and heteroatoms within the main chain. The typical example is the polyether series $[(CH_2)_nO]_m$, where polymers with n = 2,3,4,6 can be easily obtained [26].

The mechanistic consequence of this difference is the different structure of active species. Cationation of a vinyl monomer gives carbenium ion, whereas cationation of heterocyclic monomer results in onium ion (Equation 2.1) [26]:



(2.1)

Although the real situation may be more complex (at least in some systems), the vinyl polymerization is essentially carried out carbenium active species whereas ring-opening polymerization is carried out on onium active species [26].

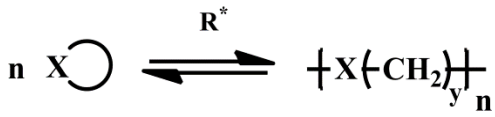
Due to the much lower reactivity (thus much higher stability) of onium ions, as compared with carbenium ions, various side reactions (i.e., leading to transfer and termination) are much easier to avoid in ring-opening polymerization and consequently conditions of living process can be approached in several systems in cationic ring-opening polymerization [26].

The other major difference stems from the fact that the nucleophilic site of vinyl monomer i.e., double bond, is consumed in the propagation step, whereas the nucleophilic site of the heterocyclic monomer, i.e., heteroatom, is still present in the formed chain. Thus, the saturated all-carbon chain becomes a neutral component of the polymerizing system, while the heteroatom containing chain may still participate in the reaction. Thus, the chain transfer to polymer is a general phenomenon in cationic ring-opening polymerization [26].

Finally, the polymerization of vinyl monomers usually proceeds as a practically irreversible reaction. Exceptions are heavily substituted monomers like α-methylstyrene for which propagation is clearly reversible. In the ring-opening polymerization, the driving force for polymerization comes from chain strain, thus it varies greatly for different monomers.

Highly strained 3- and 4-membered rings polymerize practically irreversibly but polymerization of 5-, 6-, 7-, and higher member rings, important from both a basic and practical point of view, is highly reversible.

Ring-opening polymerization provides a synthetic method for introducing functional groups typical of condensation polymers into a polymer backbone, separated by varying lengths of methylenic units as shown in the Equation 2.2. Typical functional groups include ethers, sulfides, esters, amides, double bonds, etc.

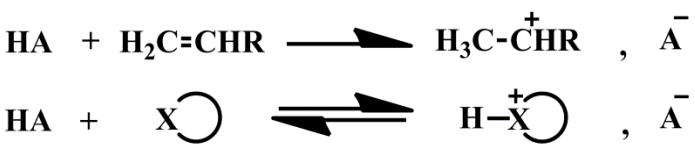


(2.2)

In addition to the ability to obtain polymers with controlled molecular weights and narrow molecular weight distributions, it's also possible to control the polymer architecture and chain end functionality. For example, diblock, triblock, and multiblock (co)polymers are prepared routinely by living ring-opening polymerizations, as are, star, comb and telechelic polymers which are going to be discussed in the next sections.

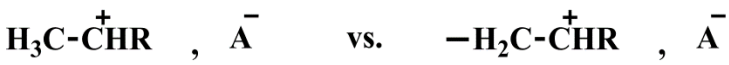
2.2.1 Initiation

Initiation is the reaction in which active species are generated through interaction of initiator and monomer molecules. In cationic ring-opening polymerization this process does not necessarily have to proceed in one step. Comparison of the polymerization of vinyl and heterocyclic monomers initiated by protonic acid illustrates the difference as seen in Equation 2.3.



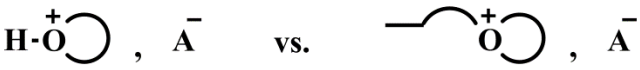
(2.3)

Protonation of vinyl monomers directly produces species with a structure similar to the structure of propagating species (Equation 2.4):



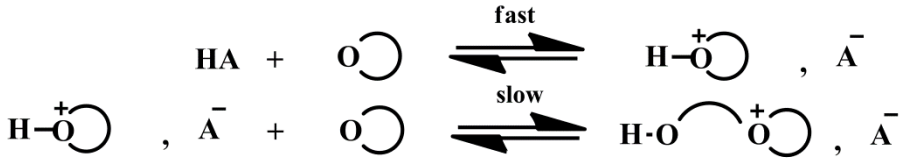
(2.4)

while in the case of heterocyclic monomers, for example, cyclic ethers, protonation produces secondary oxonium ions whereas propagation proceeds on tertiary oxonium ions (Equation 2.5):



(2.5)

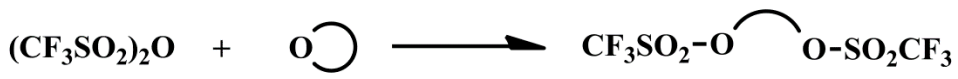
The reactivity of both species may be quite different. Because the protonation, at least when it involves proton exchange, is fast, the rate determining step in initiation may be the reaction of protonated monomer with the next monomer molecule to form tertiary oxonium ionas shown in Equation 2.6.



(2.6)

Formally similar scheme also operate for other initiating systems. In the polymerization of heterocycles, species originally formed by interaction of initiator with monomer, may differ significantly (both in structure and reactivity) from the propagating active species. Initiation may involve the sequence of at least two reactions and the second one may be the slow, thus rate-determining step in initiation.

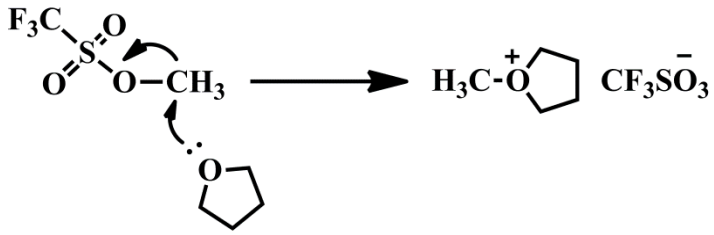
Covalent compounds, which are strong alkylating or acylating agents, may initiate the cationic polymerization of heterocycles. Esters of very strong protonic acids (trifluoromethanesulfonic, fluorosulfonic, perchloric) however, are sufficiently strong alkylating agents to initiate the polymerization of even weakly nucleophilic monomers (cyclic ethers, acetals) [12,13,35-37]. Also their anhydrides (e.g., triflic anhydride) are efficient initiators as indicated in Equation 2.7.



(2.7)

These compounds are excellent initiators for the living polymerization of THF. Triflic anhydride as a bifunctional initiator leads to PTHF capable of growing on

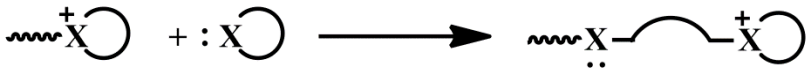
both ends, whereas methyl triflate produces PTHF, growing at one end only as shown in Equation 2.8 below.



(2.8)

2.2.2 Propagation

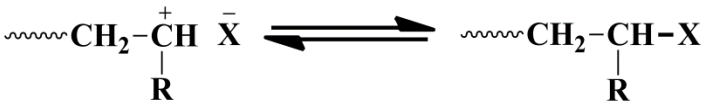
Cationic polymerization is known as chain polymerization in which propagating chains, namely active species are positively charged carbon centered ions or onium ions in vinyl polymerization or ring-opening polymerization, respectively. Various types of the initiation processes have been described in the previous section. The initiation is followed by propagation in which a nucleophilic attack of the monomer onto the active growing centers paired with non-nucleophilic counterions occurs. Nucleophilicity of counterion of the cationic growing species is crucial to achieve the living character of the polymerization. Therefore, counterions differ with respect to type of the monomer (vinyl ethers, styrenic monomers, substituted alkenes, and cyclic monomers) and mode of the polymerization (conventional or living cationic polymerization) (Equation 2.9) [21].



(2.9)

In any cationic polymerization, the counterion of the active species plays an important role for the determination of the living character of the polymerization. If this counterion is too nucleophilic, it will combine with the carbenium ion to form a covalently bonded species, which in principle does not propagate. If this happens, the propagating chain end is destroyed and this reaction is a termination. It is important that initiating systems are chosen in such a way that the corresponding counterions are less nucleophilic than the monomer. However, if the nucleophilicity of the counterion is properly tuned, there may exist an equilibrium between the active cationic species and the covalent non-active species which is then called a *dormant* species (Equation 2.10).

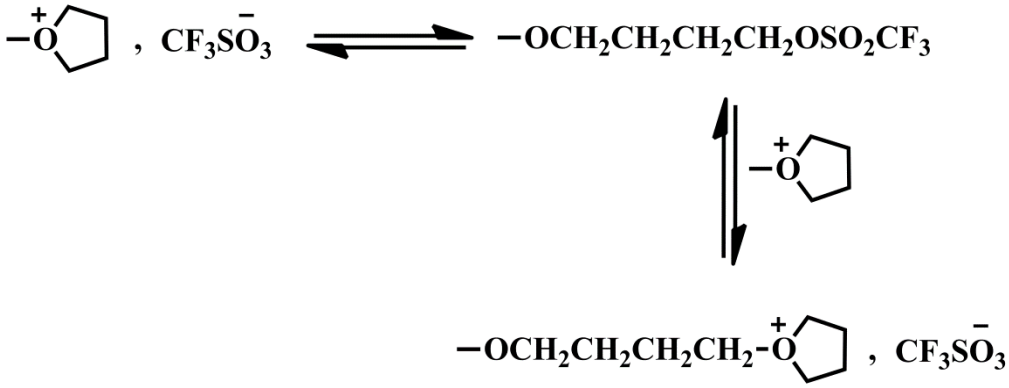
(2.10)



(2.10)

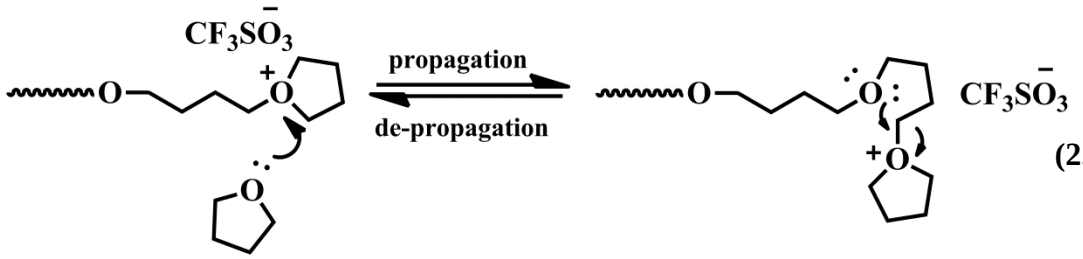
The control of this kind of equilibrium by the proper choice of the initiating system and reaction conditions or by performing the polymerization in the presence of specific (usually weak) nucleophiles, was one of the key factors which have made it possible to perform cationic polymerizations in a living/controlled way. [34] In some cases the non-ionic dormant species are also able to propagate and in that case, this kind of propagation is not a cationic one. If the propagation occurs by these non-ionic species exclusively, the polymerizations have been termed as 'electrophilic' polymerizations, which mean the active species is a neutral electrophilic function [38].

In cationic ring-opening polymerization, reaction between the ionic active species (onium ions) and counterions is reversible, giving covalent species, capable of reacting with monomer. The, best studied system, which both ionic and covalent species participate in propagation, is the cationic polymerization of THF with $CF_3SO_3^-$ counter ion [12,13,34-37,39-41] as indicated in Equation 2.11:



(2.11)

The propagating species in THF polymerization is an oxonium ion, and it associates with a negatively charged species. Because the ring strain of THF is lower than that of three and four membered rings, polymerization is highly reversible and propagation and de-propagation reactions take place [42-44] as shown in Equation 2.12.



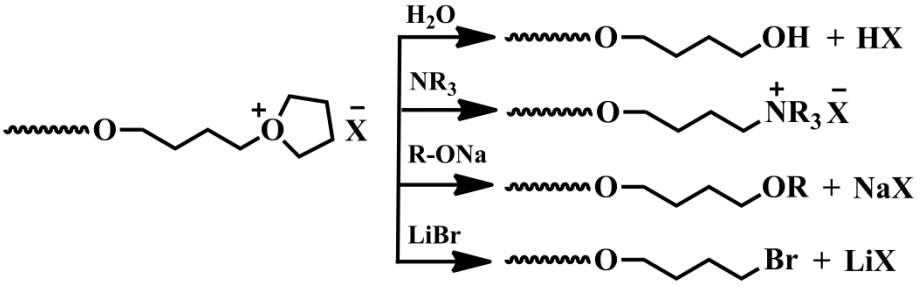
(2.12)

In this type of polymerization, the concentration of growing centers is equal or close to the initial initiator concentration. Polymers with low polydispersity can be obtained, only at low conversions and short times.

2.2.3 Termination

Cationic ring-opening polymerizations have been classified into three categories [45]: (1) living or almost living polymerizations (no or slow termination); (2) polymerizations showing a reversible termination; (3) polymerizations showing irreversible termination. These polymerizations of the first category allow optimal control of polymer structure, such as the incorporation of functional end groups by end-capping reactions, which is also one of the basic methods to prepare macromonomers [46].

The polymerization can be terminated by a variety of nucleophilic reagents such as excess water, tertiary amines, alcohols and lithium bromide. According to the desired specialty of the resulting polymer, many functionalities and end-groups can be introduced as seen in Equation 2.13.



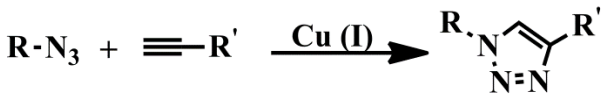
(2.13)

2.3 Click chemistry

Most of the major scientific challenges of the 21st century require nanomaterials with a high degree of structural order and defined properties. To meet this demanding level of complexity often necessitates the design of novel organic or inorganic molecules using sophisticated multistep experimental procedures [15].

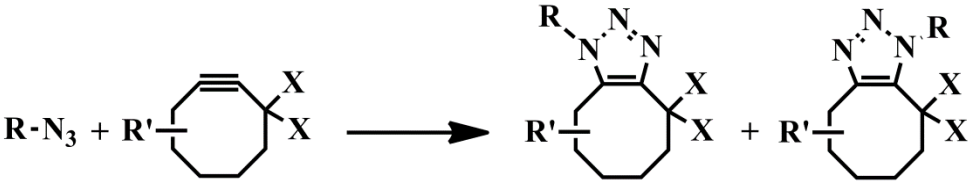
More tools than ever are readily available to engineer well-defined macromolecules with increasing complexity and functionality. Recent advances in living/controlled polymerization techniques have facilitated access to (co)polymers with controlled molecular weights, complex architectures, and precisely positioned functional groups. However, even the most robust polymerization methods are not sufficient for the synthesis of many interesting macromolecules. Post-polymerization modification is still an essential method of incorporating functionality not compatible with polymerization, characterization, or processing conditions [47]. Living polymerization techniques such as anionic, cationic and ring-opening metathesis (ROMP), and controlled radical polymerizations may provide polymers with the above mentioned well-defined properties to a certain extent [48-51]. The combination of the living and the controlled radical polymerization techniques with highly efficient 'click' chemistry based conjugation methodologies expands the toolbox of polymer chemists to realize various complex macromolecular architectures [52].

In 2002, the groups of Meldal and Sharpless independently reported the use of a copper(I) catalyst to allow azide/alkyne cyclo-additions to be conducted at low temperatures with high rates, efficiency, and (regio) specificity (Equation 2.14) [53,54].



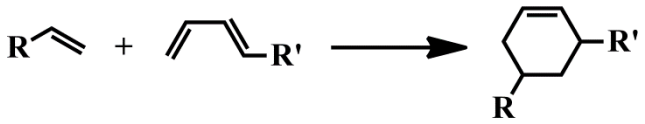
(2.14)

This coupling process reaches near quantitative conversion in both aqueous and organic media with little or no side reactions being observed. Additional cyclo-addition reactions such as strain-promoted azide-alkyne coupling (SPAAC) and Diels-Alder reactions have allowed many new polymers to be efficiently prepared or functionalized (Equation 2.15) [55,56].

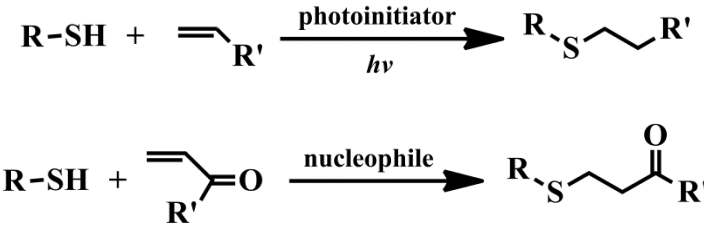


X= H or F

(2.15)



Thiol-ene reactions (radical- or nucleophile-mediated) have proven particularly useful for polymer synthesis under extremely mild conditions, often with no solvent and little-to-no product cleanup (Equation 2.16) [57] .



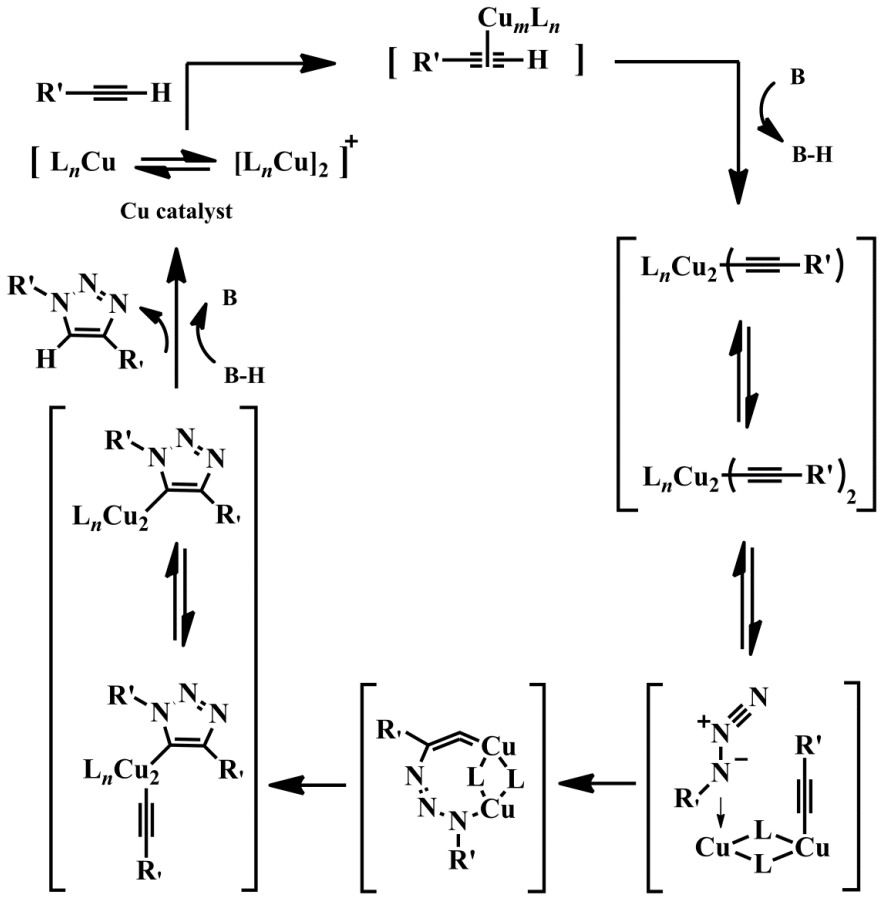
(2.16)

2.3.1 Copper (I)-catalyzed azide/alkyne click reaction (CuAAC)

Copper(I)-catalyzed azide/alkyne click reaction is a variation of the Huisgen 1,3-dipolar cyclo-addition reaction between terminal acetylenes and azides. CuAAC click reactions fulfill many requirements for the affixation of ligands onto polymers by post-modification processes. The purely thermal 1,3-dipolar cyclo-addition reaction between aryl/alkyl azides and strongly activated alkynes was proposed by Sharpless and co-workers in 2001 [14,48,59] as a click-type reaction, Meldal and co-workers published a paper in 2002 [53] that describes the acceleration of this process by Cu(I) salts, which leads to a reaction at 25 ^{o}C in quantitative yields, first mentioning the higher regioselectivity with respect to the purely thermal process. Later, Sharpless and co-workers published a paper in 2002 [54] where the formation of 1,2,3-triazoles by the Cu(I)-catalyzed Huisgen reaction between non-activated alkynes and alkyl/aryl azides was described.

A variety of catalytic systems have been used to effect the 1,3-dipolar cyclo-addition process. In case of the azide/acetylene process, mostly Cu(I) catalysts (but recently also Ru, Ni, Pd, and Fe salts) have been used and require about 0.25–2 mol % of the catalysts. Most methods use Cu(I) salts directly, other methods generate the Cu(I) species by reduction of Cu(II) salts using sodium ascorbate or metallic copper (Equation 2.17). Besides the copper catalyst, 1-5 equivalents of base are added, mechanistically to promote the formation of the copper(I)-acetylide. The mostly used bases are triethylamine (Et_3N), 2,6-lutidine, and *N*,*N*-diisopropylethylamine

(DIPEA), as well as *N,N,N′,N′,N″*-pentamethylethylenetetramine (PMDETA) or 2,2'-bipyridine [60].



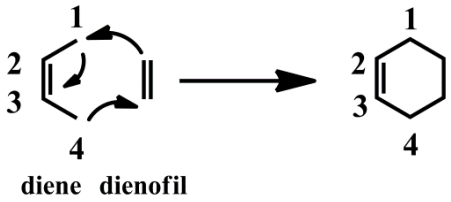
(2.17)

In the absence of an appropriate catalyst, in most cases, the reaction is generally slow and not regioselective [61], but in the presence of Cu(I), which binds to terminal alkynes to form intermediate copper acetylides, this cyclo-addition reaction is dramatically accelerated, regioselective and highly efficient. Cu(I) directly catalysis the reaction to form the 1,4-regioisomer exclusively and increases the reaction rate up to 10^7 times [62], eliminating the need for elevated temperature.

Although CuAAC click reaction was initially postulated as a general concept for organic synthesis, this strategy also has an enormous potential in polymer science. The important application of CuAAC in polymer chemistry is not only the synthesis of functional polymers (either end-functionalized or side functionalized) but also the construction of well-defined architectures.

2.3.2 Diels-Alder reaction

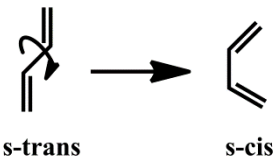
The Diels-Alder (DA) reaction is a concerted [4π+2π] cyclo-addition reaction of a conjugated diene and a dienophile. This reaction is one of the most powerful tools used in the synthesis of important organic molecules. The three double bonds in the two starting materials are converted into two new single bonds and one new double bond to afford cyclohexenes and related compounds (Equation 2.18). This reaction is named for Otto Diels and Kurt Alder, who received the 1950 Nobel prize for discovering this useful transformation [63-65].



(2.18)

Typically, the DA reaction works best when either the diene is substituted with electron donating groups (like -OR, $-NR_2$, etc) or when the dienophile is substituted with electron-withdrawing groups (like $-NO_2$, -CN, -COR, etc).

The basic requirement is that the conjugated dienes must have *cisoid* conformation in order to participate in the Diels-Alder reaction Equation 2.19. Even though rigid *trans*oid structures of dienes that are more stable due to steric reasons are unreactive in the Diels-Alder reactions [66]. Additionally, cyclic conjugated dienes, which are locked into the rigid *cisoid* form, are particularly more reactive.

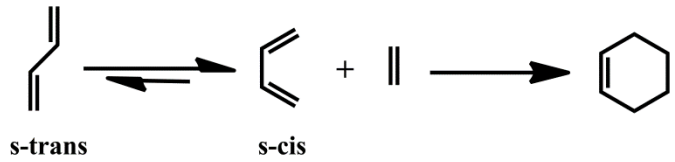


(2.19)

When diene and/or dienophile have a heteroatom, the cyclo-addition is called a hetero-Diels Alder reaction. The Diels-Alder reaction can be intermolecular or intramolecular and can be carried out under a variety of experimental conditions.

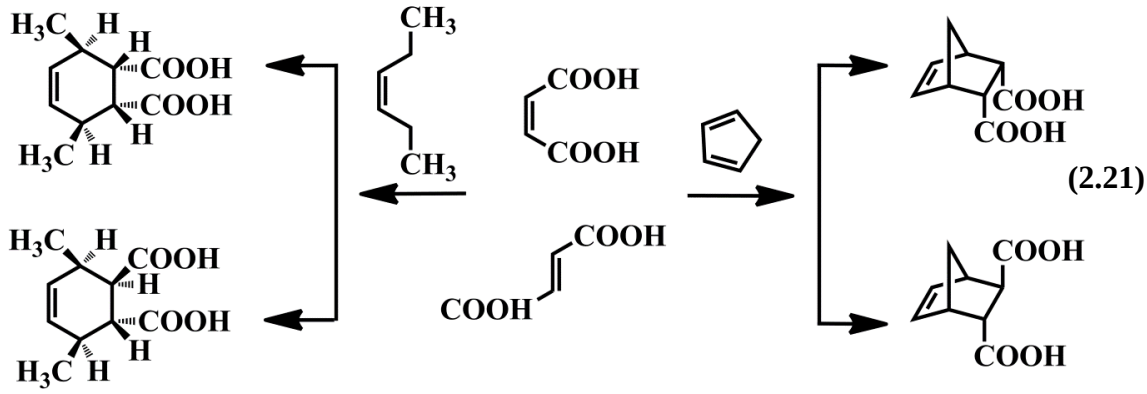
2.3.2.1 Stereochemistry of Diels-Alder reaction

There are stereochemical and electronic requirements for the DA reaction to occur smoothly. First, the diene must be in an s-*cis* conformation instead of an s-*trans* conformation to allow maximum overlap of the orbitals participating in the reaction (Equation 2.20).



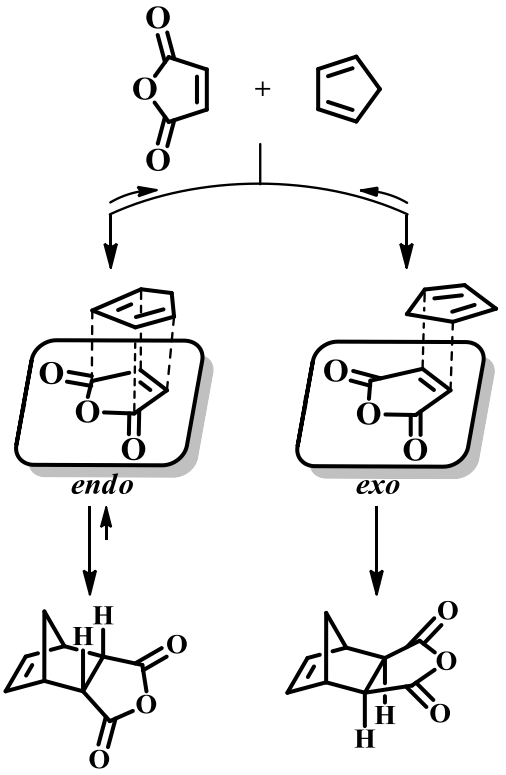
(2.20)

Since the Diels-Alder reaction is suprafacial reaction (sigma bonds are formed or broken on the same face of the π system) relative stereochemistry of the substituents in the 1,4-position of the diene and 1,2-positions of the dienophile is retained in the product. Thus, a *cis* dienophile gives cis substutients in the product, and a *trans* dienophile gives *trans* substutients in the product [67]. Similarly, *trans,trans*-1,4 disubstituted dienes give rise to adducts in which the 1,4-substituents are *cis* relative to each other. The *cis, trans* isomer of the dienes give products in which the 1,4-substituents are *trans* (Equation 2.21) [68-70].



(2.21)

If the diene is cyclic, the substituent on the dienophile can be either endo or exo in the product, based on the orientation of the diene and dienophile with respect to each other in the transition state. However, Diels-Alder reaction is known as highly selective reaction and quite often gives the *endo* product. This is the "*endo* rule", first proposed by Alder [67]. According to the endo mode of attack the substituent on the dienophile is underneath the diene framework (*endo* approach), while in the exo mode of addition the substituent on the dienophile is away from the diene framework (*exo* approach) (Equation 2.22).



(2.22)

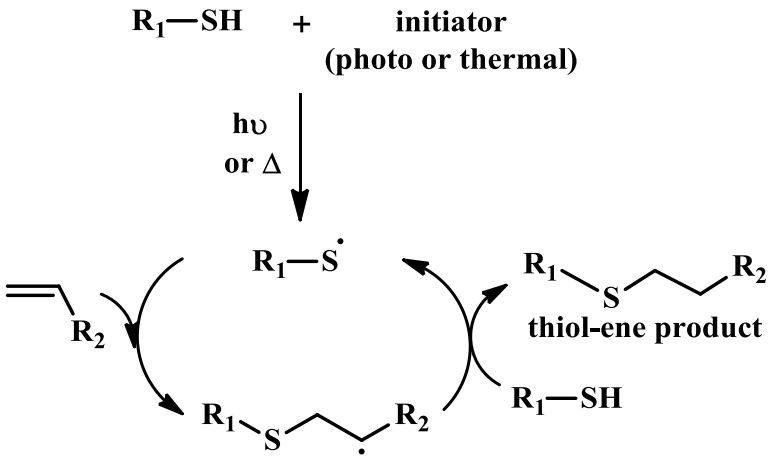
Considering that the Diels-Alder reaction is reversible at elevated temperatures, the *endo*/*exo* ratio depends on the reaction temperature. Therefore use of high temperature and extended periods of time can results in the formation of the thermodynamically more favorable exo product at the expence of the *endo* product.

2.3.3 Thiol-ene rection

The thiol-ene reaction is an emerging synthetic tool that is considered to be a "click" reaction because the reaction has many of the attributes of the click reaction, for example, quantitative yields, rapid reaction rates, mild reaction conditions, and tolerant of various solvents and functional groups.

The thiol-ene chemistry, which involves the hydrothiolation of a C=C bond, can be induced photochemically or thermally at ambient temperature to mainly give an anti-Markownik-type product. Generally, the thiol-ene reaction follows a radical-mediated process, with initiation, propagation and termination steps. Initiation involves the treatment of a thiol with an initiator, under irradiation or heat, subsequently generating a thiyl radical, $RS^{\cdot}$, via hydrogen abstraction, plus other byproducts (Equation 2.23). Propagation then occurs in two step which involves first the direct addition of the thiyl radical to the C=C bond producing an intermediate

thioether carbon radical followed by chain transfer to a second molecule of thiol to give the thiol-ene addition product with the concomitant generation of a new thiyl radical. Termination is believed to ocur through the radical-radical recombination of the thioether carbon and/or thiyl radicals.



(2.23)

Although thiol–ene click reaction has mainly been focused on a radical-mediated version to non-activated alkenes, this reaction can also proceed via Michael addition, especially when the vinyl group is alpha to an electron withdrawing moiety. The Michael addition applies to α, β-unsaturated carbonyl compounds such as acrylate, maleimido, etc., and an intermediate thioanion is usually generated owing to the usage of a base or nucleophilic catalysis such as Et_3N, primary/secondary amines or certain phosphines for the reaction.

The thiol-ene ‘‘click’’ reactions, through either a radical or nucleophilic mechanism, provide efficient hydrothiolation routes across virtually any double bond [71-75].

Over the years, the thiol-ene click reaction has been extensively exploited in polymer chemistry since it can be conducted under various conditions without any metal catalyst. The UV-induced crosslinking of unsaturated polymers (photocuring) by reaction with multifunctional thiols is currently employed in surface coating owing to a number of advantages over other curing methods. Biomaterials for application in medicine, especially dentistry, have been prepared by using this process. Only recently, however, has the click aspect of the thiol-ene ‘‘click’’ reaction been fully appreciated in the field of polymer science. The use of thio-Michael addition as a click reaction was recently reported by Lowe et al. for the synthesis of star polymers [76]. The great potential of thiol–ene chemistry was exploited by Hawker and co-

workers in the synthesis of poly(thioether) dendrimers [77]. Consequently, numerous examples are available in the literature for polymer end group and backbone modification [78-80], many of which are covered in various excellent reviews [72,81,82].

2.4 Telechelic polymers

Telechelic polymers are defined as polymeric molecules with reactive end groups that have the capacity to enter into further polymerization or other reactions. Reactive end-groups in telechelic polymers come from the initiator or the terminating or chain-transfer agents in chain polymerizations, but not from monomer(s) as in polycondensations and polyadditions [17].

A polymer can be considered to be telechelic if it contains end groups that react selectively to give a bond with another molecule. Depending on the functionality, which must be distinguished from the functionality of the end group itself, telechelics can be classified as mono-, di-, tri-, and multifunctional telechelics (poly-telechelics). The functionality is defined as Equation 2.24 [83]:

$$f = \frac{\text{Number of functional groups}}{\text{Number of polymer chains}} \qquad \textbf{(2.24)}$$

The functionality of the end group itself is important. When such groups are bifunctional (e.g., vinyl groups) they can participate in polymerization reactions, yielding graft (co)polymers or networks; such telechelic polymers are called macromolecular monomers, macromonomers, or macromers [21].

Controlled and living radical polymerization methods are great tools for the synthesis of well-defined polymeric materials and also excellent way to introduce functional moieties at one or both termini of polymer chains. Like the other polymerization methods, living mode of cationic polymerization also provides to introduce functional groups at polymer chain termini. The method involves the use of a functional initiator or a termination agent. Moreover, transformation of the primary end-capping groups to any other functional groups is an alternative method to obtain functional polymers [21].

The synthesis of telechelics by cationic ring-opening polymerization has the greatest practical interest due to the commercial value of the resulting compounds, such as

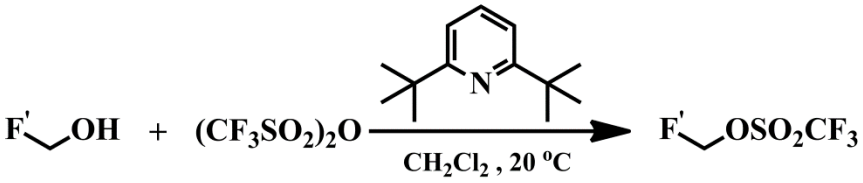
polyether, polyols and so on. Although a wide variety of heterocyclic monomers can be polymerized by cationic mechanisms, only tetrahydrofuran (THF), oxazolines, N-substituted aziridines, and cyclic sulfides are shown to polymerize under controlled or living conditions [84].

Telechelic polymers can be used as cross-linkers, chain extenders, and precursors for block and graft (co)polymers. Moreover, star and hyper-branched or dendric polymers are obtained by coupling reactions of monofunctional and multifunctional telechelics with appropriate reagents. Various macromolecular architectures can be obtained by the reactions of telechelics [21].

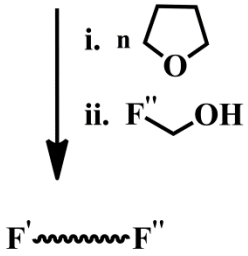
2.4.1 Functionalization by using functional initiator

This method involves the use of functional initiators with a protected or unprotected functional group. When the functional group is unreactive under the polymerization conditions, protection is not necessary [85]. Using functional initiators in cationic polymerization is a great tool to synthesize α-end-functionalized polymers with well-defined properties. Several different functional groups including carboxylic acid, [86] hydroxyl, [87] halogen etc. can be introduced to α-end-polymers [21].

Living polymerization of THF can be initiated from either commercially available methyl triflate or *in-situ* formed triflates by the reaction of alcohols with triflic anhydride in the presence of a sterically hindered amine as proton trap (Equation 2.25) [88]. A functional alcohol with triflic anhydride can be used as a functional initiator which is capable to introduce functional group on the polymer chain end. Addition of various kinds of alcohols with triflic anhydride into THF polymerization leads to halide, allyl, alkenyl, acrylate, and methacrylate telechelics with a high living character.



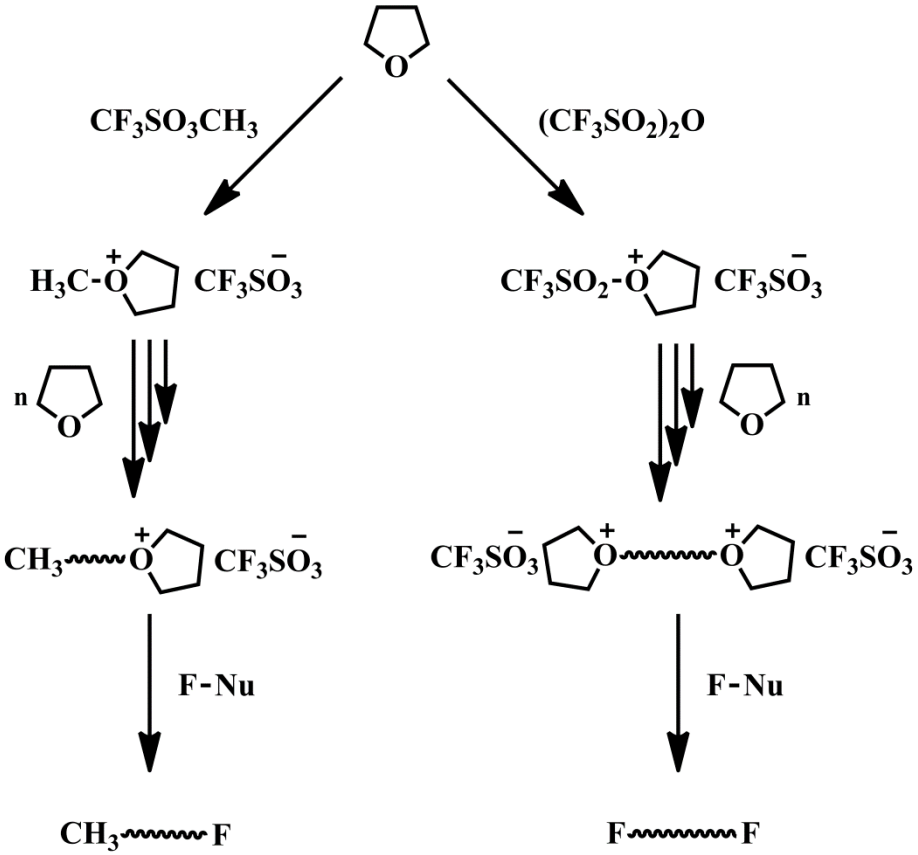
(2.25)



(2.26)

2.4.2 Functionalization by using terminating agent

This method involves end quenching of living polymers with appropriate nucleophiles in the cationic polymerization of cyclic monomers (Equation 2.26) [85]. Semitelechelic PTHF can be obtained after end-capping of the living polymers produced with a monofunctional initiator such as methyl triflate. Anhydrides of super acids such as trifluoromethane sulfonic acid or fluorosulfonic acid yield two reactive ends [88,89,90].



By the addition of a convenient nucleophile into the solution of living polymer, telechelic polymers with various functionalities can be easily obtained [91]. End-capping reagents and the resulting end groups are shown in the Table 2.1.

Proton-initiated polymerization of THF in the presence of carboxylic anhydrides as chain transfer agent gives ester terminated end groups [92-94].

The pyridinium salt end-functionalized PTHFs can be used as polymeric initiators for photo-induced reactions. Upon photolysis the pyridinium moiety decomposes and polymeric radicals are formed. Depending on the additives present in the system, hydroxy telechelics [95] or block (co)polymers [96] are thus formed. Interesting variation of end-capping reaction with N-phenylpyrrolidine can be used to prepare mono-, bi-, and tri-functional star-shaped, telechelic PTHF having N-phenylpyrrolidinium salt groups.

Another class of telechelic PTHFs has been also prepared, in which functional groups were located not only at the chain ends but also at the interior desired position. In this case, the tert-butyldimethylsilyl-protecting group was removed during the precipitation to yield α, ω-kentro-telechelic polymers [97].

Table 2.1 End-capping reagents and end groups of PTHF.

Reagents	Functionality
Ammonia	-NH_2 [88, 91]
Hydrogen sulfide	-SH [88, 91]
Succinic acid	-COOH [91]
Lithium bromide	-Br [88, 91]
N,N'-diethyl dithiocarbamic acid sodium salt	-dithiocarbamate [99]
4-Hydroxy butyl bromoisobutyrate	-bromoisobutyrate [100, 101, 102]
Allyl alcohol	-allyl [103, 104]
Propargyl alcohol	-propargyl [105]
Sodium methacrylate or methacrylic anhydride or methacrylic acid	-methacrylate [106-110]

2.4.3 Chain-end modification

In this method, the polymerizable function is incorporated by chemical modification of the α- or ω-end group after isolation of the polymer. Although a wide variety of polymerizable groups can be incorporated this way, previously reported methods are generally cumbersome as they involve several steps [98,111-113].

End-functionalized polymers obtained by cationic polymerization are transformed further to functional polymers by typical organic reactions including nucleophilic substitution, addition and esterification reactions [114,115].

3. EXPERIMENTAL WORK

3.1 Materials

Tetrahydrofuran (THF, 99.8%, J.T. Baker) was dried over sodium wire in the presence of traces of benzophenone until a purple color persisted, distilled under nitrogen atmosphere and was used directly after distillation. Trifluoromethanesulfonic anhydride (Tf_2O, 99%, Aldrich), methyl trifluoromethanesulfonate (MeOTf, 98%, Aldrich) and *N*, *N*, *N*', *N*'', *N*''-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) were purified by vacuum distillation prior to use. Dichloromethane (CH_2Cl_2, 99%, J. T. Baker) was distilled over P_2O_5 and stored on molecular sieves ($4A^o$) under argon atmosphere. 2-Bromoethanol (95%, Aldrich), 2,6-Lutidine (99%, Aldrich), ethylene glycol (99%, Aldrich), succinic anhydride (97%, Aldrich), 9-anthracenemethanol (97%, Aldrich), α-bromoisobutyryl bromide (98%, Aldrich), triethylamine (Et_3N, 99.5%, Aldrich), propargyl alcohol (99%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Aldrich), and CuBr (99.9%, Aldrich) were used as received. *N*,*N*-dimethylformamide (DMF, 99.8%, Aldrich) was dried and distilled under vacuum over CaH_2. Dichloromethane (CH_2Cl_2, 99%, J. T. Baker) was dried and distilled over P_2O_5. Diethyl ether (99.7%, Aldrich), 1.4-dioxane (99.8%, Aldrich), toluene (99.8%, Aldrich), methanol (99.8%, Aldrich) were used without further purification. Ethyl acetate (EtOAc) and hexane were in technical grade and distilled prior to use.

3.2 Instrumentation

Nuclear magnetic resonance spectroscopy (NMR)

^1H NMR measurements were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using an Agilent VNMRS 500 MHz instrument.

Infrared spectrophotometer (FT-IR)

FT-IR spectra were recorded on a Thermo Nicolet 6700 FT-IR spectrometer.

UV-visible spectrophotometer (UV-vis)

UV-visible spectra were recorded on a Shimadzu UV-1601 UV-visible spectrophotometer.

Gel permeation chromatography (GPC)

The conventional Gel Permeation Chromatography (GPC) measurements were conducted in THF at 30 °C using an Agilent instrument (Model 1100) consisting of a pump (0.3 mL/min) and four Waters Styragel columns (guard, HR 5E, HR 4E, HR 3, HR 2), (4.6 mm internal diameter, 300 mm length, packed with 5 μm particles) in series with two detection systems: a refractive index and UV detectors). Toluene was used as an internal standard. The determination of apparent molecular weights for the polymers was based on linear PS standards (Polymer Laboratories), whereas linear PMMA standards (Polymer Laboratories) were only used for the molecular weight determination of the PMMA homopolymer using PL Caliber Software from Polymer Laboratories.

Gas chromatography (GC)

Gas chromatography measurements were performed on the Agilent 6890N gas chromatograph, equipped with an FID detector using a wide-bore capillary column (HP5, 30 m x 0.32 mm x 0.25μm, J&W Scientific). Injector and detector were kept constant at 280 and 285 ºC, respectively. The chromatographic conditions: Injector and detector were kept constant at 280 °C and 285 ºC, respectively. Initial column temperature is 40 ºC, finally reaching up to 120 ºC at a heating rate of 40 ºC/min.

Mass spectroscopy (MS)

Mass spectroscopy was performed on Thermo LCQ-Deca ion trap mass instrument.

3.3 Synthesis methods

2-azido ethanol (**1**) [116], succinic acid mono-anthracen-9-ylmethyl-ester (**2)** [117] and 2-hydroxyethyl 2-bromoisobutyrate (**4**) [118] were synthesized according to the published procedures.

3.3.1 Synthesis of 2-azido ethanol (1)

To a 100 mL of round bottom flask was added 2-bromo ethanol (5 g, 0.04 mol) in 50 mL of water/acetone (1/4, v/v). NaN_3 (4 g, 0.06 mol) was added in one portion to the reaction and the mixture was stirred at 60 ^oC for overnight. After acetone was removed, remaining liquid was dissolved in CH_2Cl_2 and extracted with water. The aqueous layer was extracted with CH_2Cl_2 (50 mL) and combined organic layers were dried over Na_2SO_4. Solvent was removed under vacuum and **1** was obtained as pale yellow oil. Yield=95%. ^{1}H NMR ($CDCl_3$, δ) 3.75 (t, 2H, C*H*$_2$O), 3.44 (t, 2H, C*H*$_2$N$_3$).

3.3.2 Synthesis of succinic acid mono-anthracen-9-ylmethyl-ester (2)

9-Anthryl methanol (4.16 g, 20 mmol) was dissolved in 150 mL of CH_2Cl_2. To the reaction mixture were added Et_3N (14 ml, 100 mmol) and DMAP (2.44 g, 20 mmol), and succinic anhydride (8 g, 80 mmol) in that order. The mixture was stirred for overnight at room temperature. The reaction solution was poured into ice-cold water (150 ml) and stirred for 30 mins at room temperature. The organic phase was extracted with 1M HCl (150 ml). The aqueous phase extracted with CH_2Cl_2. Combined organic phase were dried over Na_2SO_4 and concentrated to give **2** as a green solid. Yield=95%. M.p. = 130-131 ºC (DSC). ^{1}H NMR **(**$CDCl_3$, δ**)** 8.51 (s, 1H, Ar*H* of anthracene), 8.31 (d, *J* = 8.8 Hz, 2H, Ar*H* of anthracene), 8.03 (d, *J* = 8.3 Hz, 2H, Ar*H* of anthracene), 7.60-7.45 (m, 4H, Ar*H* of anthracene), 6.16 (s, 2H, C*H*$_2$-anthracene), 2.69-2.62 (s, 4H, C=OC*H*$_2$C*H*$_2$C=OOH). ^{13}C NMR ($CDCl_3$, δ) 177.72, 172.46, 131.57, 131.35, 129.29, 129.07, 127.01, 126.05, 125.41, 124.04, 59.39, 29.01. Mass spectrometry (+EI) *m*/*z* (%): 308 [MH+] (65), 307 (92), 290 (30), 277 (47), 207 (58), 191 (100), 179 (25).

3.3.3 Synthesis of succinic acid anthracen-9-ylmethyl ester prop-2-ynyl ester (3)

Propargyl alcohol (0.545 g, 9.74 mmol, 1.5 equiv), DMAP (0.396 g, 3.25 mmol, 0.5 equiv) and **2** (2.00 g, 6.49 mmol, 1 equiv) were dissolved in 30 mL of dry CH_2Cl_2. After stirring 5 mins at room temperature, DCC (2.00 g, 9.74 mmol, 1.5 equiv) dissolved in 15 mL of CH_2Cl_2 was added to the reaction mixture. The reaction mixture was stirred overnight at room temperature. After filtering off the urea byproduct, the solvent was removed and the remaining product was extracted with CH_2Cl_2 and water. The aqueous phase was again extracted with CH_2Cl_2 and combined organic phase was dried with Na_2SO_4. The solution was concentrated and the crude product was purified by column chromatography over silica gel eluting with EtOAc/hexane (1:2) to give **3** as a yellow solid. Yield=85%. M.p. = 77-78 °C. ^{1}H NMR ($CDCl_3$, δ) 8.51 (s, 1H, Ar*H* of anthracene); 8.31 (d, *J* = 8.8 Hz, 2H, Ar*H* of anthracene); 8.03 (d, *J* = 8.3 Hz, 2H, Ar*H* of anthracene); 7.60-7.45 (m, 4H, Ar*H* of anthracene); 6.16 (s, 2H, C*H*$_2$-anthracene); 4.61 (d, *J* = 2.4 Hz, 2H, CH≡CC*H*$_2$O); 2.67 (s, 4H, C=OC*H*$_2$C*H*$_2$C=O); 2.44 (t, *J* = 2.4 Hz, 1H, C*H*≡CCH$_2$O). ^{13}C NMR ($CDCl_3$, δ) 172.39, 171.65, 131.44, 131.11, 129.21, 129.07, 126.65, 126.05, 125.08, 123.92, 75.16, 59.27, 52.54, 29.11, 29.01. Mass spectrometry (+EI) *m*/*z* (%): 346 [MH+] (10), 293 (30), 279 (20), 251 (10), 225 (100), 221 (20), 207 (75).

3.3.4 Synthesis of 2-hydroxyethyl 2-bromoisobutyrate (HEBiB) (4)

Ethylene glycol (2 g, 0.032 mol) and Et_3N (0.7 mL, 0.048 mol) were added into a dry flask in 55 mL of CH_2Cl_2 followed by adding 2-bromoisobutyryl bromide (4 mL, 0.032 mol) in 25 mL of CH_2Cl_2 dropwise over 30 mins at 0 °C under nitrogen atmosphere. The reaction mixture was kept at room temperature overnight, followed by adding distilled water and extracting with CH_2Cl_2, and saturated aqueous $NaHCO_3$. The water phase again extracted with CH_2Cl_2 and collected organic layer was dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography over silica gel eluting with EtOAc/hexane (1/9) gradually increased to ethyl acetate to give the product to give **4** as a yellowish liquid. Yield=85%. ^{1}H NMR ($CDCl_3$) δ: 3.85 (t, 2H, HOC*H*$_2$CH$_2$); 4.28 (t, 2H, HOCH$_2$C*H*$_2$); 1.93 (s, 6H, C(C*H*$_3$)$_2$-Br).

3.3.5 Synthesis of α-azide-ω-hydroxyl-PTHF

A 100 mL three-necked flask was evacuated and purged with pure argon three times, 2-Azido ethanol (0.106 g, 1.22 mmol) in 6 mL of CH_2Cl_2, 2,6-Lutidine (0.282 mL, 2.44 mmol) and Tf_2O (0.207 mL, 1.23 mmol) were placed at 0 ^oC under argon atmosphere and the mixture was stirred for 1 h. at 0 ^oC. The solution containing the initiator was warmed to 25 ^oC, after which THF (100 mL, 1.22 mol) was added to initiate the polymerization. The polymerization was carried out at 25 ^oC for the prescribed reaction time and terminated by adding 0.5 mL of distilled water. The polymer product was recovered by precipitation into water under cooling with liquid nitrogen, and dried in vacuum oven at 40 ^oC. ^1H NMR ($CDCl_3$) δ: 3.5 (t, 2H, N_3CH_2); 3.61 (t, 2H, CH_2O); 3.64 (t, 2H, CH_2OH); 3.4 (br, 4H, -$OCH_2CH_2CH_2CH_2$, repeating unit of PTHF); 1.6 (br, 4H, -$OCH_2CH_2CH_2CH_2$, aliphatic protons of PTHF).

3.3.6 Synthesis of α-anthracene-ω-hydroxyl-PTHF via CuAAC Click Reaction

α-azide-ω-hydroxyl-PTHF (0.47 g, 0.138 mmol, based on $M_{n,\,GPC}$), **3** (0.143 g, 0.414 mmol), PMDETA (0.080 mL, 0.414 mmol), CuBr (0.059 g, 0.414 mmol) and DMF (3 mL) were added into a 10 mL of schlenk tube. The reaction mixture was degassed by three FPT cycles, left in vacuum and stirred for 24 h at room temperature. After that time, solution was diluted with THF, and then filtered through a column filled with neutral alumina to remove the copper complex and precipitated into methanol. After two dissolution-filtration-precipitation procedure, polymer was dried in a vacuum oven at 40 °C for 24 h. Yield=85%. ^1H NMR ($CDCl_3$, δ) 8.5 (s, 1H, Ar*H* of anthracene); 8.3 (d, 2H, Ar*H* of anthracene); 8.0 (s, 2H, Ar*H* of anthracene); 7.5 (m, 4H, Ar*H* of anthracene); 6.1 (m, 2H, CH_2-anthracene); 7.6 (s, 1H, C*H* of triazole); 5.1 (s, 2H, OC=O-CH_2-triazole); 4.4 and 3.7 (t, 2H, triazole-CH_2CH_2O- and triazole-CH_2CH_2O-); 3.6 (t, 2H, CH_2OH); 3.4 (br, 4H, -$OCH_2CH_2CH_2CH_2$, repeating unit of PTHF); 1.6 (br, 4H, -$OCH_2CH_2CH_2CH_2$, aliphatic protons of PTHF).

3.3.7 Synthesis of α-anthracene-ω-bromide-PTHF

α-anthracene-ω-hydroxyl-PTHF (0.33 g, 0.097 mmol, based on $M_{n,\,GPC}$) and DMAP (0.011 g, 0.097 mmol) were dissolved in 50 mL of CH_2Cl_2, and Et_3N (0.135 mL, 0.97 mmol) was added. The reaction mixture was then cooled to 0 ^oC and α-bromoisobutyryl bromide (0.120 mL, 0.97 mmol) in 25 mL of CH_2Cl_2 was added

dropwise within 30 minutes to this solution under nitrogen atmosphere. The reaction mixture was stirred for 15 mins at 0 ^{o}C then for overnight at room temperature. The ammonium salt was filtered off and the solvent was evaporated under reduced pressure. The remaining residue was extracted with CH_2Cl_2, and saturated aqueous $NaHCO_3$. The aqueous phase again extracted with CH_2Cl_2, and combined organic phases dried over Na_2SO_4. Finally, bromo-functionalized polymer was dried in the vacuum oven at 40 ºC. Yield=80%. ^{1}H NMR ($CDCl_3$, δ) 8.5 (s, 1H, Ar*H* of anthracene); 8.3 (d, 2H, Ar*H* of anthracene); 8.0 (s, 2H, Ar*H* of anthracene); 7.5 (m, 4H, Ar*H* of anthracene); 6.1 (m, 2H, C*H*$_2$-anthracene); 7.6 (s, 1H, C*H* of triazole); 5.1 (s, 2H, OC=O-C*H*$_2$-triazole); 4.4 and 3.7 (t, 2H, triazole-C*H*$_2$CH$_2$O- and triazole-CH$_2$C*H*$_2$O-); 4.19 (t, 2H, C*H*$_2$OC=O); 1.93 (s, 6H, C(C*H*$_3$)$_2$-Br); 3.41 (br, 4H, -OC*H*$_2$CH$_2$CH$_2$C*H*$_2$, repeating unit of PTHF); 1.61 (br, 4H, -OCH$_2$C*H*$_2$C*H*$_2$CH$_2$, aliphatic protons of PTHF).

3.3.8 Synthesis of α, ω-azide-PTHF

A 100 mL three-necked flask was evacuated and purged with pure argon three times, THF (100 mL, 1.22 mol) and Tf_2O (0.205 mL, 1.22 mmol) were placed at 25 ^{o}C under argon atmosphere and the mixture was stirred for prescribed polymerization time. The solution containing living chain ends was terminated by adding **1** (10.62 g, 12.2 mmol) and was stirred for 15 mins to provide an effective termination. The polymer product was recovered by precipitation into water under cooling with liquid nitrogen, and dried in vacuum oven at 40 ^{o}C. ^{1}H NMR ($CDCl_3$) δ: 3.50 (t, 2H, N$_3$C*H*$_2$); 3.61 (t, 2H, C*H*$_2$O); 3.41 (br, 4H, -OC*H*$_2$CH$_2$CH$_2$C*H*$_2$, repeating unit of PTHF); 1.61 (br, 4H, -OCH$_2$C*H*$_2$C*H*$_2$CH$_2$, aliphatic protons of PTHF).

3.3.9 Synthesis of α, ω-anthracene-PTHF via CuAAC Click Rection

N_3-PTHF-N_3 (0.3 g, 0.073 mmol, based on $M_{n,\ GPC}$), **3** (0.126 g, 0.365 mmol), PMDETA (0.061 mL, 0.292 mmol), CuBr (0.042 g, 0.292 mmol) and DMF (3 mL) were added into a 10 mL of schlenk tube. The reaction mixture was degassed by three FPT cycles, left in vacuum and stirred for 24 h at room temperature. After that time, solution was diluted with THF, and then filtered through a column filled with neutral alumina to remove the copper complex and precipitated into methanol. After two dissolution-filtration-precipitation procedure, polymer was dried in a vacuum oven at 40 °C for 24 h. Yield=80%. ^{1}H NMR ($CDCl_3$, δ) 8.5 (s, 1H, Ar*H* of

anthracene); 8.3 (d, 2H, Ar*H* of anthracene); 8.0 (s, 2H, Ar*H* of anthracene); 7.5 (m, 4H, Ar*H* of anthracene); 6.1 (m, 2H, CH_2-anthracene); 7.6 (s, 1H, C*H* of triazole); 5.1 (s, 2H, OC=O-CH_2-triazole); 4.4 and 3.7 (t, 2H, triazole-CH_2CH$_2$O- and triazole-CH$_2$CH_2O-); 3.41 (br, 4H, -OCH_2CH$_2$CH$_2$CH_2, repeating unit of PTHF); 1.61 (br, 4H, -OCH$_2$CH_2CH_2CH$_2$, aliphatic protons of PTHF).

3.3.10 Synthesis of α-methyl-ω-hydroxyl-PTHF

A 100 mL three-necked flask was evacuated and purged with pure argon three times, THF (100 mL, 1.22 mol) and MeOTf (0.133 mL, 1.22 mmol) were placed under argon atmosphere and the mixture was stirred for the prescribed reaction time at 20 ^oC. The polymerization was terminated by adding 0.5 mL of distilled water. The polymer product was recovered by precipitation into water under cooling with liquid nitrogen, and dried in vacuum oven at 40 ^oC. ^1H NMR ($CDCl_3$) δ: 3.33 (s, 3H, CH_3O); 3.64 (t, 2H, CH_2OH); 3.41 (br, 4H, -OCH_2CH$_2$CH$_2$CH_2, repeating unit of PTHF); 1.61 (br, 4H, -OCH$_2$CH_2CH_2CH$_2$, aliphatic protons of PTHF).

3.3.11 Synthesis of α-methyl-ω-bromide-PTHF

α-methyl-ω-hydroxyl-PTHF (0.5 g, 0.217 mmol, based on $M_{n,\ GPC}$) and DMAP (0.0265 g., 0.217 mmol) were dissolved in 120 mL of CH_2Cl_2, and Et_3N (0.301 mL, 2.17 mmol) was added. The reaction mixture was then cooled to 0 ^oC and α-bromoisobutyryl bromide (0.227 mL, 2.17 mmol) was added dropwise within 30 mins to this solution under nitrogen atmosphere. The reaction mixture was stirred for 15 mins at 0 ^oC then for overnight at room temperature. The ammonium salt was filtered off and the solvent was evaporated under reduced pressure. The remaining residue was extracted with CH_2Cl_2, and saturated aqueous $NaHCO_3$. The aqueous phase again extracted with CH_2Cl_2, and combined organic phases dried over Na_2SO_4. Finally, bromo-functionalized polymer was dried in the vacuum oven at 40 ºC. Yield=80%. ^1H NMR ($CDCl_3$) δ: 3.33 (s, 3H, CH_3O); 4.19 (t, 2H, CH_2OC=O); 1.93 (s, 6H, C(CH_3)$_2$-Br); 3.41 (br, 4H, -OCH_2CH$_2$CH$_2$CH_2, repeating unit of PTHF); 1.61 (br, 4H, -OCH$_2$CH_2CH_2CH$_2$, aliphatic protons of PTHF).

3.3.12 Synthesis of α-methyl-ω-bromide-PTHF

1. A 100 mL three-necked flask was evacuated and purged with pure argon three times, THF (100 mL, 1.22 mol) and MeOTf (0.133 mL, 1.22 mmol) were placed at

30 ^{o}C under argon atmosphere and the mixture was stirred for the prescribed reaction time at 20 ^{o}C and the polymerization was terminated by adding 25.74 g of **4** (0.122 mol).The polymer product was recovered by precipitation into water under cooling with liquid nitrogen. To remove the excess of **4** resulting polymer was extracted after adding distilled water with CH_2Cl_2 and saturated aqueous $NaHCO_3$. The water again extracted with CH_2Cl_2 and collected organic layer was dried over anhydrous Na_2SO_4. The product was purified by column chromatography over silica gel eluting with EtOAc/hexane (1/4) gradually increased to ethyl acetate to give the polymer product. ^{1}H NMR ($CDCl_3$) δ: 3.33 (s, 3H, C*H*$_3$O); 4.19 (t, 2H, C*H*$_2$OC=O); 1.93 (s, 6H, C(C*H*$_3$)$_2$-Br); 3.41 (br, 4H, -OC*H*$_2$CH$_2$CH$_2$C*H*$_2$, repeating unit of PTHF); 1.61 (br, 4H, -OCH$_2$C*H*$_2$C*H*$_2$CH$_2$, aliphatic protons of PTHF).

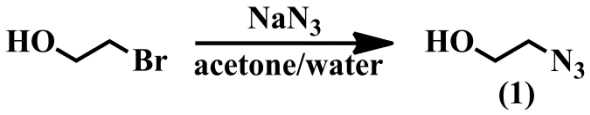
4. RESULTS AND DISCUSSION

As a general perspective, in this study the living cationic ring-opening polymerization of tetrahydrofuran with different functional end-groups was described. Tetrahydrofuran was polymerized by using different initiators. Other functionalities are then introduced by end-capping reactions and post-modification methods with esterification and click reaction involving CuAAC.

In fact, it is often advantageous to employ a combination of click chemistry with cationic ring-opening methods enabling macromolecular structures with various end functionalities.

4.1 Synthesis of the α-anthracene-ω-bromide-PTHF

2-azidoethanol **1** which was used as an initiator in the cationic ring-opening polymerization of tetrahydrofuran was obtained quantitatively via nucleophilic substitution reaction using 2-bromoethanol and NaN_3 in the presence of acetone/water mixture as seen in Equation 4.1.



(4.1)

It was observed from ^1H NMR spectrum of **1**, a signal related to methylene protons next to Br atom at 4.52 ppm completely disappeared and a new peak linked to $-N_3$ unit was observed at 3.44 ppm as seen in Figure 4.1. Additionally, FT-IR spectrum of **1** revealed the presence of absorbance peak at 2100 cm^{-1}, which is characteristic of the terminal azide group.

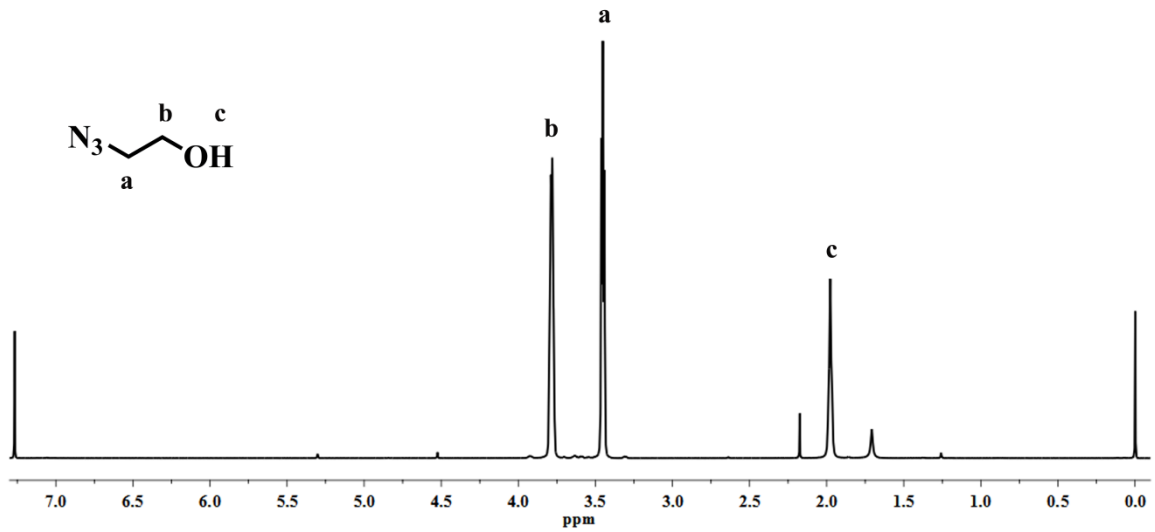
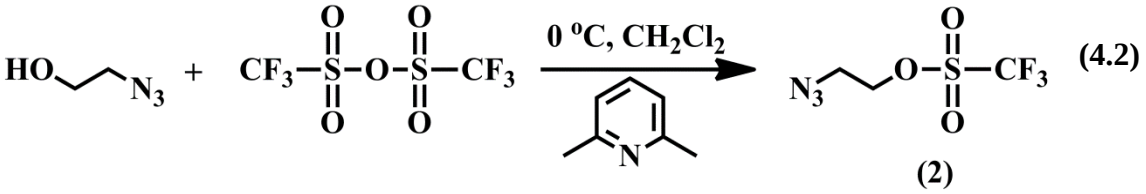


Figure 4.1: ^{1}H NMR spectra of 2-azido ethanol in $CDCl_3$.

Then, **1** and triflic anhydride were introduced into the three-necked flask where the polymerization was carried out and via *in-situ* esterification reaction between **1** and Tf_2O, the initiator **2** was synthesized in the presence of CH_2Cl_2 and 2,6-lutidine as proton trap as shown in Equation 4.2.



(4.2)

To investigate the formation of the structure, **2** was isolated from the reaction media and ^{1}H NMR measurements were obtained. From the ^{1}H NMR spectrum**,** it was observed from that methylene protons adjacent to azide unit ($N_3CH_2CH_2OH$) and methylene protons next to ($N_3CH_2CH_2OH$) hydroxyl unit of **1** were shifted from 3.45 ppm and 3.78 ppm to 3.67 ppm and 4.59 ppm respectively with the formation of **2** as seen in Figure 4.2. The peaks at 7.85 ppm, 7.25 ppm and 2.70 ppm were related to 2,6-Lutidine. This spectrum indicated that the *in-situ* formation of the initiator was totally successful.

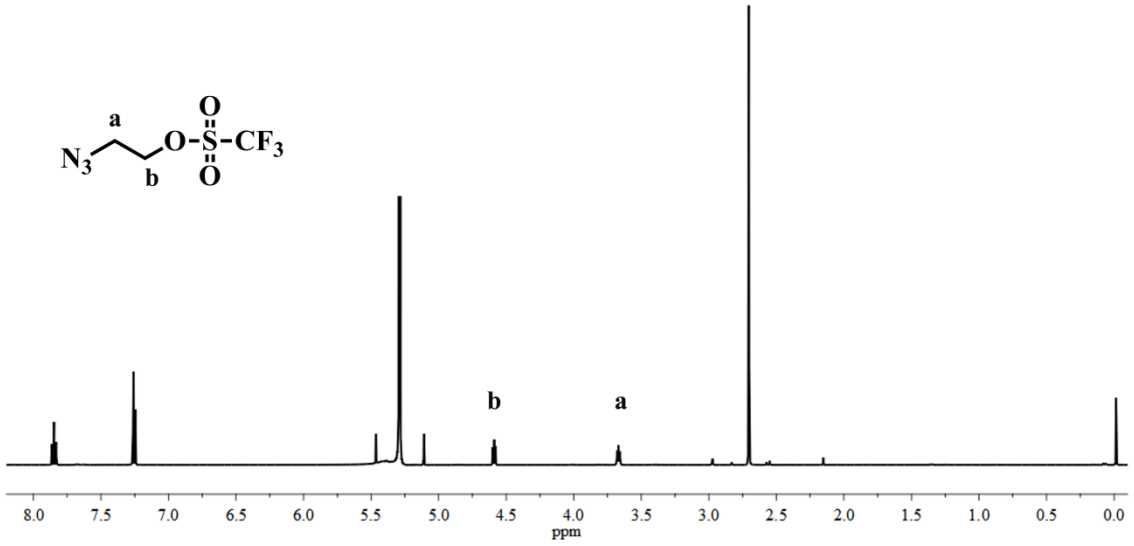
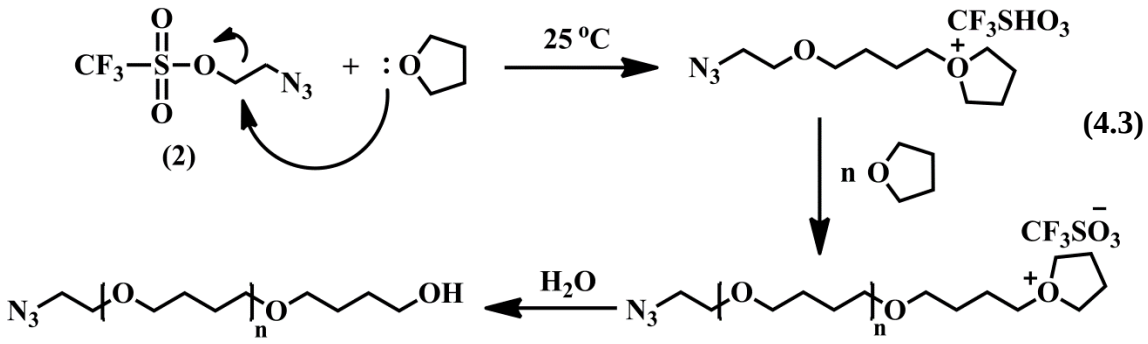


Figure 4.2: ^{1}H NMR spectra of **2** in $CDCl_3$.

After 1 hour's esterification period, tetrahydrofuran was added to the flask in which the initiator **2** had been synthesized, and the cationic ring-opening polymerization of THF was initiated. After the prescribed reaction time, polymerization was quenched with the addition of water to obtain hydroxyl terminated polytetrahydrofuran as seen in Equation 4.3.



From ^{1}H NMR spectrum of α-azide-ω-hydroxyl-PTHF, methylene protons next to the azide unit ($N_3CH_2CH_2O$) and methylene protons adjacent to the oxygen ($N_3CH_2CH_2O$) were appeared at 3.50 ppm and 3.61 ppm respectively. Methylene protons linked to the oxygen in the repeating unit ($CH_2CH_2CH_2CH_2O$) were detected at 3.41 ppm whereas methylene protons between them ($CH_2CH_2CH_2CH_2O$) were appeared at 1.61 ppm. Methylene protons adjacent to the hydroxyl unit at the ω-end were detected at 3.64 ppm as shown in Figure 4.3.

The NMR number-average molecular weight ($M_{n,NMR}$ = 2873 g/mol) was calculated from a ratio of the integrated values of four protons ($CH_2CH_2CH_2CH_2O$) in the repeating unit of PTHF to that of a signal at 3.50 ppm assignable to two protons linked to azide unit (N_3CH_2), while being included the molecular weight of initiator (219.14 g/mol) (Figure 4.3).

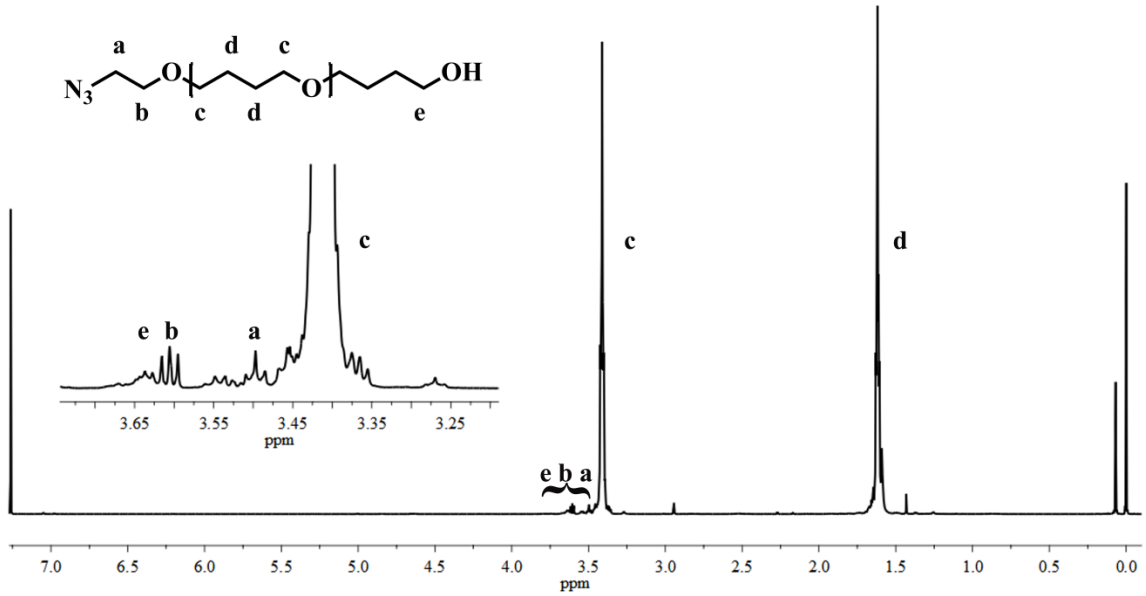
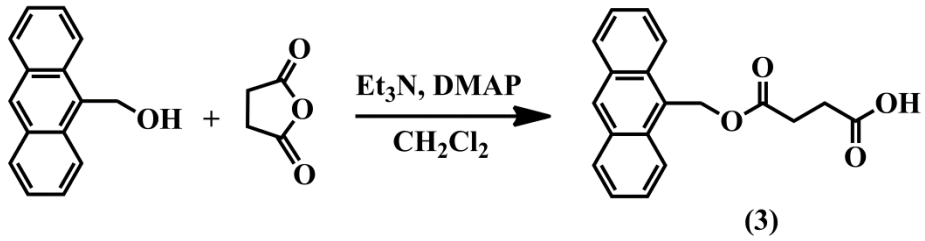


Figure 4.3: ^{1}H NMR spectra of α-azide-ω-hydroxyl-PTHF (N_3-PTHF-OH) in $CDCl_3$.

The number-average molecular weight obtained by GPC ($M_{n,GPC}$ = 6094 g/mol, relative to linear PS standards which was converted to PTHF standards by multiplying with 0.556 and found out as $M_{n,GPC}$ = 3336 g/mol.) is a consistent agreement with $M_{n,NMR}$, thus indicating that the quantitative azide end-group functionalization of PTHF was tolerably successful. Moreover, M_w/M_n = 1.3 calculated from GPC displays relatively narrow molecular weight distribution.

For the post-modification reactions, succinic acid anthracen-9-ylmethyl ester prop-2-ynyl ester **4** was synthesized in two steps. Firstly, the hydroxyl functionality of 9-anthryl methanol was converted to carboxylic acid via a reaction with succinic anhydride in the presence of Et_3N/DMAP catalyst system and CH_2Cl_2 as solvent to give **3** as shown in Equation 4.4.



(4.4)

(3)

The structure was confirmed by ^{1}H NMR spectrum (Figure 4.4, (a)). A shift from 5.6 ppm to 6.18 ppm of methylene protons linked to anthracene ring due to esterification reaction and multiplet peaks around 2.71 - 2.65 ppm assigned to C=OCH_2CH_2C=O clearly indicated that **3** was achieved. As a second step, **4** was synthesized through an esterification reaction between **3** and propargyl alcohol as seen in Equation 4.5.

(4.5)

(3) **(4)**

^{1}H NMR spectrum of **4** indicated the successful reaction (Figure 4.4, (b)). The methylene protons of propargyl (CH≡CCH_2OC=O) adjacent to ester unit were detected as doublet at 4.61 ppm and alkyne proton at 2.43 ppm confirmed that the reaction was successfully carried out.

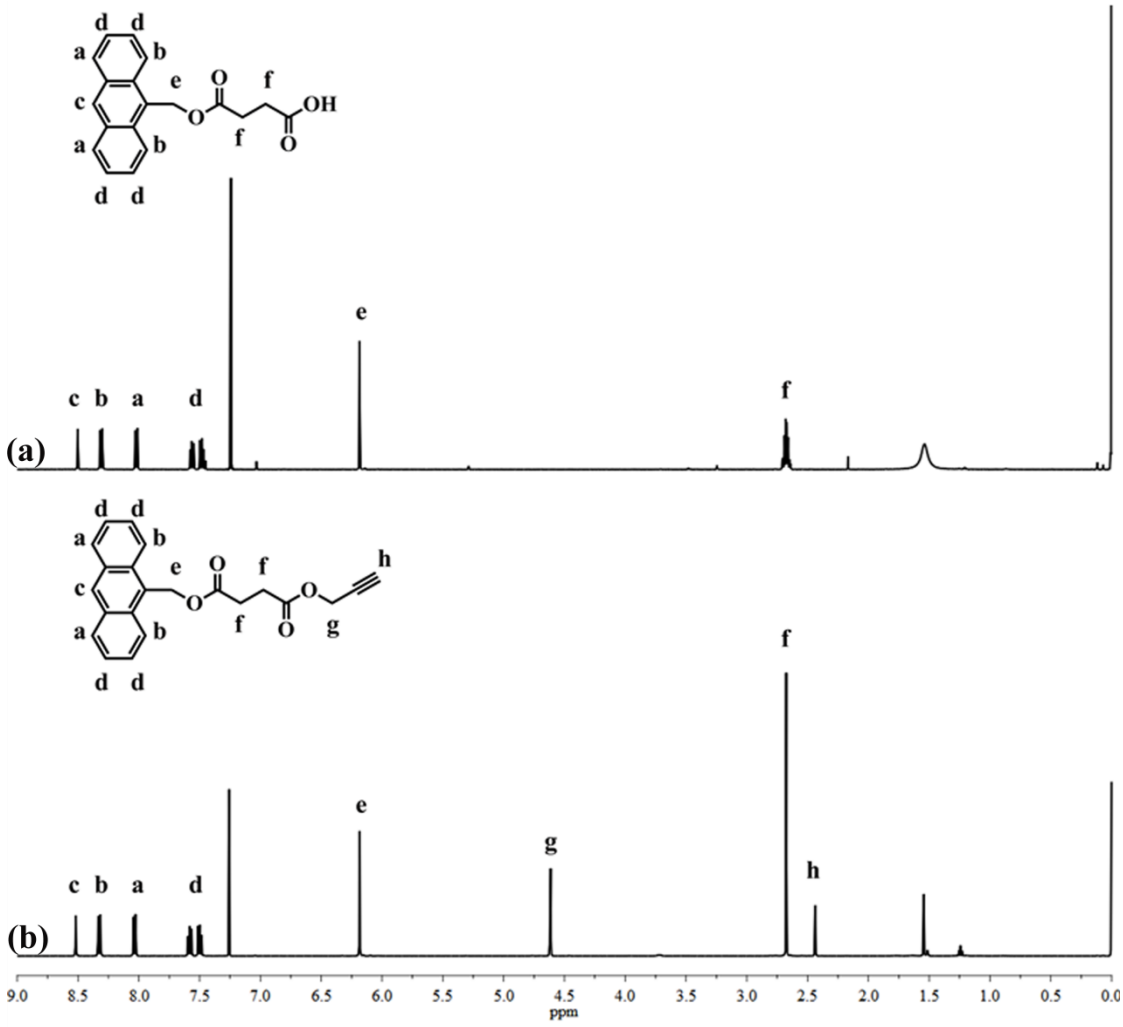
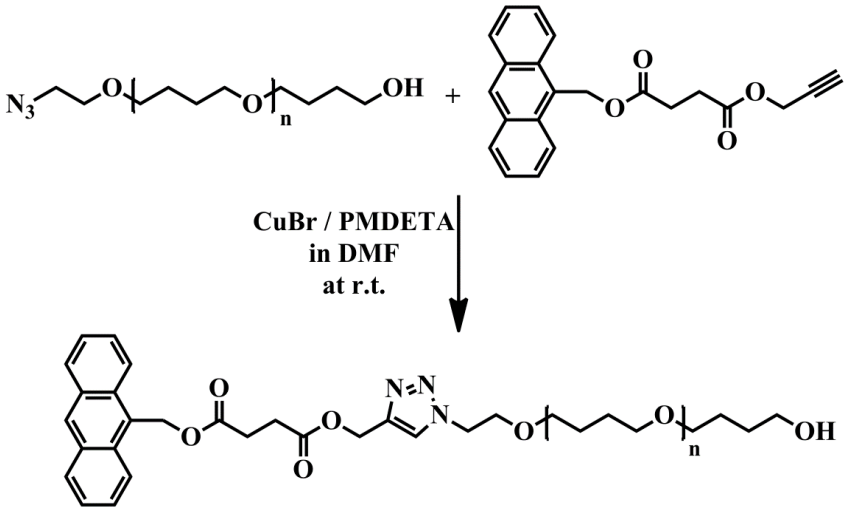


Figure 4.4: ^{1}H NMR spectra of: **a)** succinic acid mono-anthracen-9-ylmethyl-ester **(3) b)** succinic acid anthracen-9-ylmethyl ester prop-2-ynyl ester **(4)** in $CDCl_3$.

To introduce the anthracene functionality to the polymer, CuAAC click reaction was accomplished between α-azide end of PTHF and alkyne end-functional group of **4** catalyzed by CuBr/PMDETA in DMF at room temperature (Equation 4.6).



(4.6)

An evidence for the formation of triazole ring of the resulting polymer was obtained from ^{1}H NMR spectroscopy. The characteristic peaks for methylene protons adjacent to azide ($N_3CH_2CH_2O$) and methylene protons next to oxygen ($N_3CH_2CH_2O$) were shifted from 3.50 ppm and 3.61 ppm to 4.48 ppm and 3.75 ppm respectively. CH_2 protons between the triazole ring and ester unit were shifted from 4.61 ppm to 5.17 ppm because of [3+2] cyclo-addition, and a new signal corresponding to a (C*H*) proton of triazole ring was appeared at 7.63 ppm as indicated in Figure 4.5.

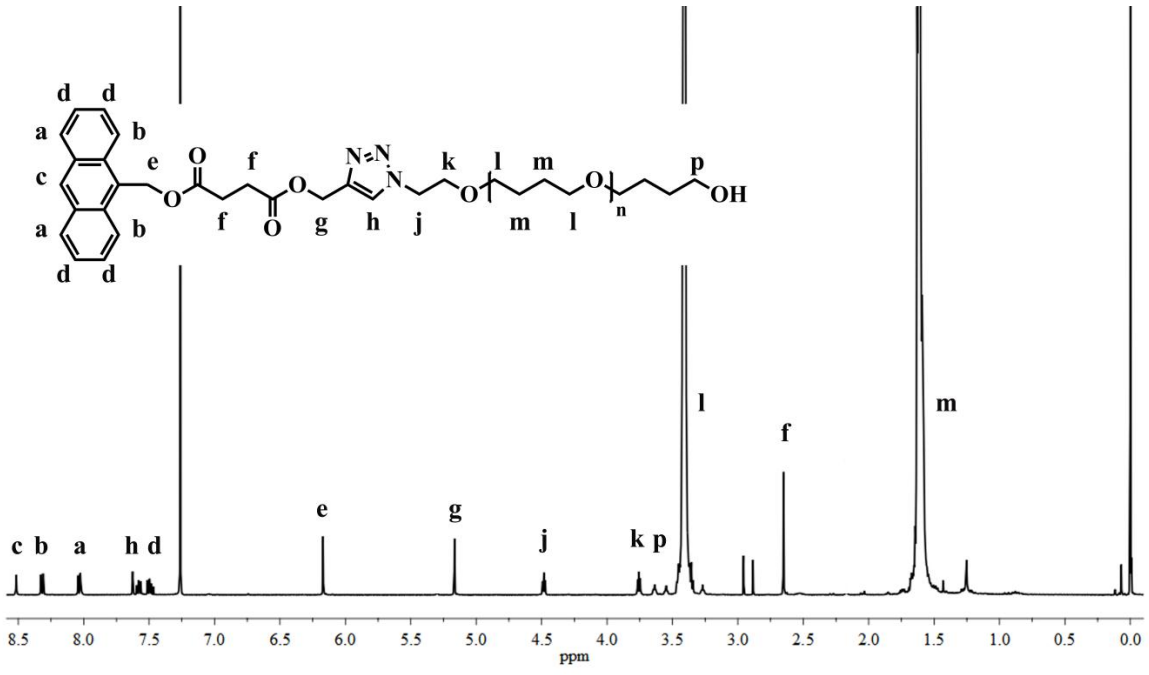


Figure 4.5: ^{1}H NMR spectra of α-anthracene-ω-hydroxyl-PTHF (Anth-PTHF-OH) in $CDCl_3$.

The ^{1}H NMR spectra of the resulting polymer displayed characteristic signals of both PTHF and **4** together, thus proving the click reaction (Figure 4.5).

In FT-IR spectrum of α-anthracene-ω-hydroxyl-PTHF, the absence of absorbance peak at 2100 cm^{-1}, which is characteristic of the terminal azide unit, revealed that the click reaction was carried out through all azide ends displaying high efficiency in fact. However, the reason of having low efficiency seen in ^{1}H NMR spectra is that the all polymer chains didn't undergo azide functionalization at the beginning of the polymerization in consequence of the esterification reaction during the synthesis of the initiator proceeds in a medial-efficiency fashion. Another issue is that the moisture in ppm order in the system causes hydroxyl functionalized polymers at both ends, which do not respond to CuAAC click reactions reducing the yield. These undesired α, ω-hydroxyl end functionalized polymers unfortunately could not be allocated from the required polymer.

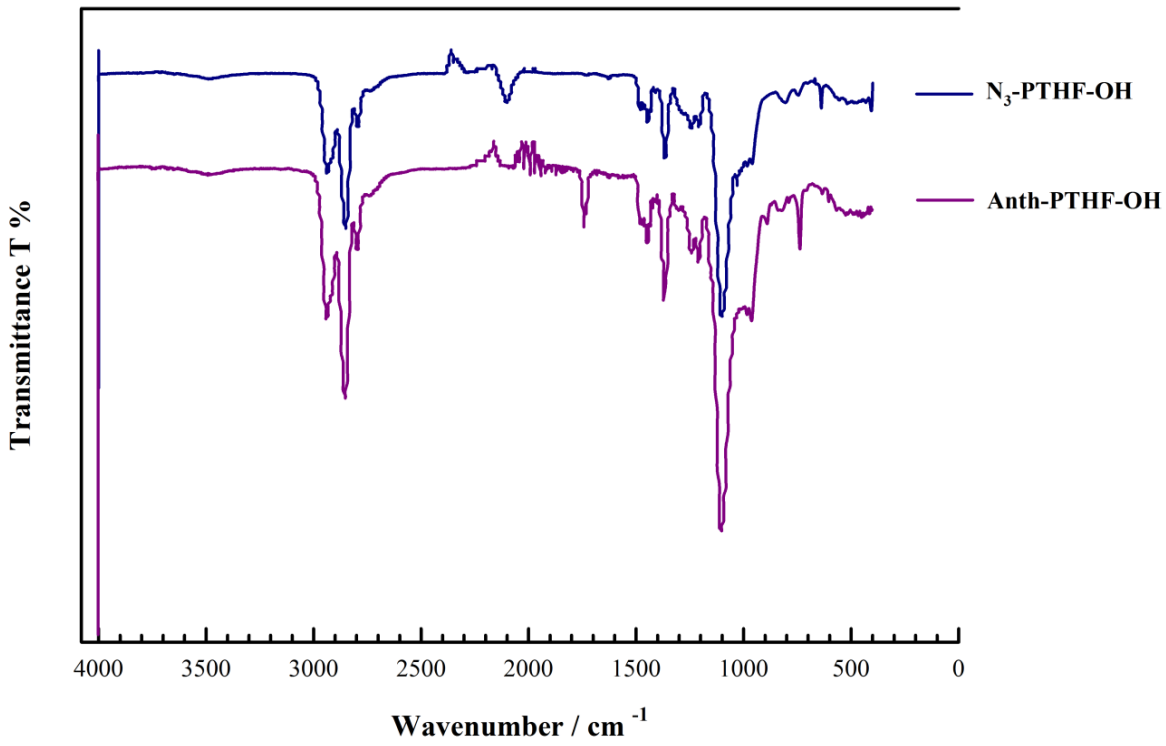
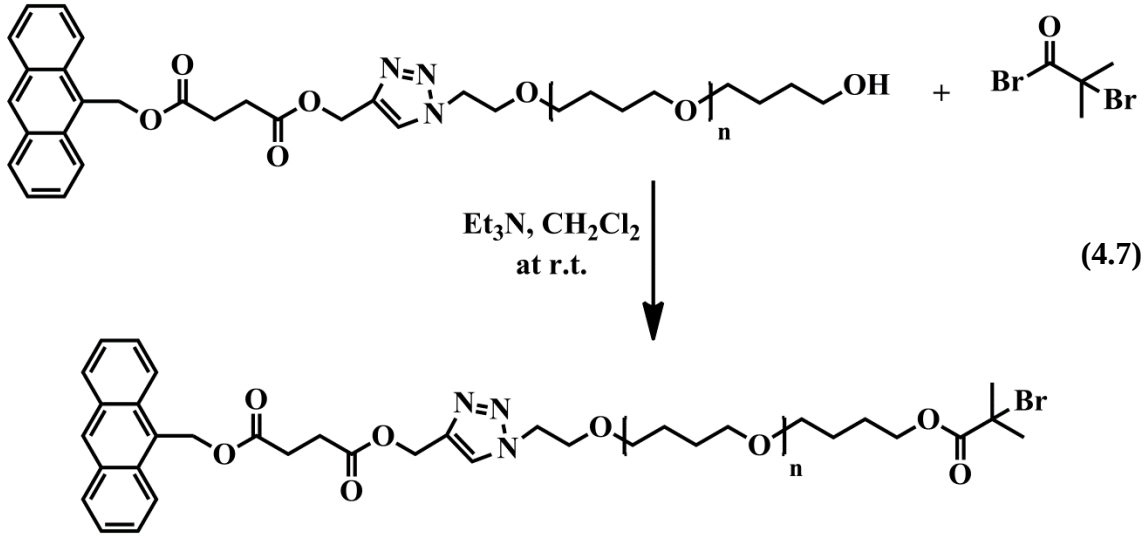


Figure 4.6: FT-IR spectra of α-azide-ω-hydroxyl-PTHF and α-anthracene-ω-hydroxyl-PTHF.

α-anthracene-ω-hydroxyl-PTHF was then reacted with α-bromoisobutyryl bromide in CH_2Cl_2 to introduce the bromo functionality to the polymer which can be used in the synthesis of macromolecules with various structures (Equation 4.7).



(4.7)

After estericification reaction with α-bromoisobutyryl bromide, ^{1}H NMR spectrum of the resulting polymer indicated that methylene protons adjacent to ω-hydroxyl end of PTHF appeared at 3.64 ppm were shifted to 4.19 ppm and methyl protons next to bromo were detected at 1.93 ppm. These results confirmed that the post-modification of PTHF was successfully achieved as seen in Figure 4.7.

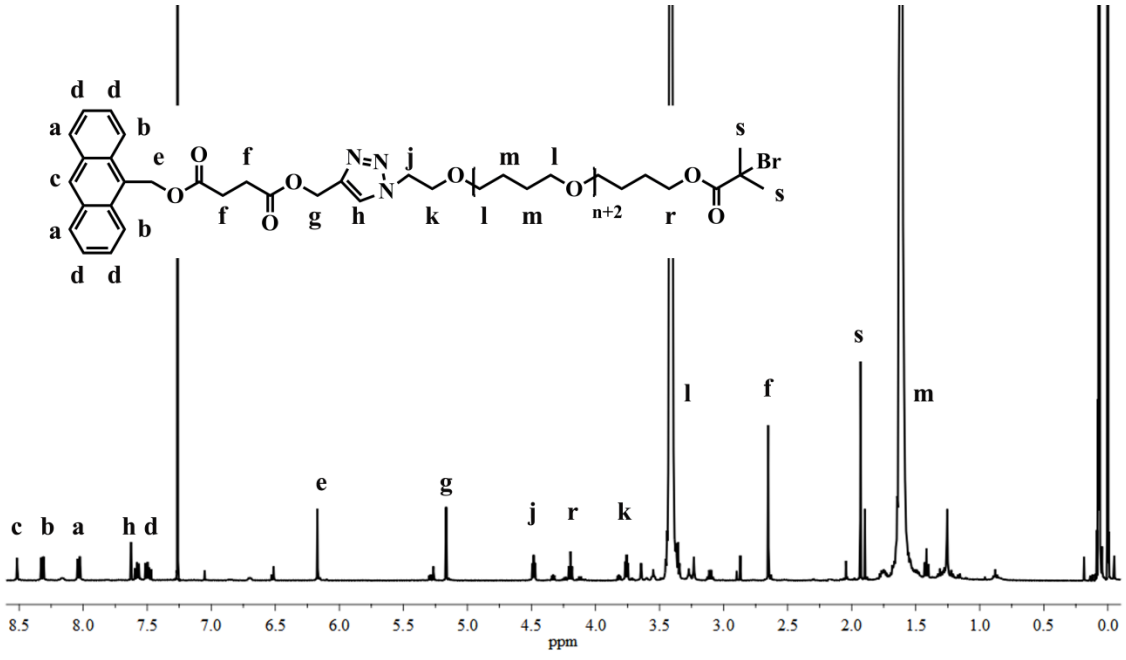


Figure 4.7: ^{1}H NMR spectra of α-anthracene-ω-bromide-PTHF (Anth-PTHF-Br) in $CDCl_3$.

The efficiency of esterification with α-bromoisobutyryl bromide was calculated from ^{1}H NMR spectrum. The integrated area of methyl protons linked to bromo was proportioned to the integrated area of methylene protons ($CH_2CH_2CH_2CH_2O$) in the repeating unit of PTHF and the result was found as 70% as indicated in Table 4.1.

Table 4.1: Molecular weights and functionalities of telechelic PTHF.

Functionalization Type	Polymer	M_n[a]	M_w/M_n[a]	Functionality[b] (%)		
				-N_3	-Anth	-Br
From initiator	**N_3-PTHF-OH**	3336	1.3	86	-	-
Through CuAAC click reaction	**Anth-PTHF-OH**	5598	1.2	-	87	-
Through esterification reaction	**Anth-PTHF-Br**	6277	1.6	-	-	70

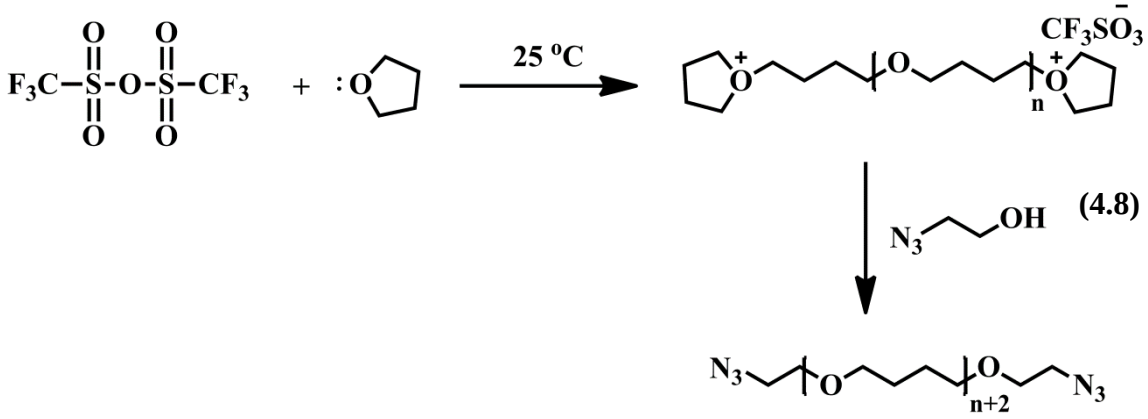
[a] Determined by GPC.

[b] Determined by ^{1}H NMR (see text).

4.2 Synthesis of the α, ω-anthracene-PTHF

Commercially available triflic anhydride was used as initiator for the living ring-opening polymerization of tetrahydrofuran. Polymerization was carried out at 25 ^oC for the prescribed reaction time and quenched with approximately 100 times excess of **2** as seen in Equation 4.8.

When tetrahydrofuran polymerization is initiated with triflic anhydride, two ends of the growing polymer chain are in the living character meaning that polymerization can be carried out until terminated by an appropriate nucleophile. Here almost all of the nucleophiles can be employed to functionalize the polymer as mentioned in the previous sections in order to use in the synthesis of desired macromolecules with various purposes.



In the ^{1}H NMR spectrum of α, ω-azide-PTHF, methylene protons next to the azide unit ($N_3CH_2CH_2O$) and methylene protons adjacent to the oxygen ($N_3CH_2CH_2O$) were appeared at 3.49 ppm and 3.60 ppm respectively. Methylene protons linked to the oxygen in the repeating unit ($CH_2CH_2CH_2CH_2O$) were detected at 3.41 ppm whereas methylene protons between them ($CH_2CH_2CH_2CH_2O$) were appeared at 1.61 ppm as shown in Figure 4.8. The ^{1}H NMR results verified that the end-functionalization with 2-azidoethanol was quite successful.

The NMR number-average molecular weight ($M_{n,NMR}$ = 6800 g/mol) was calculated from a ratio of the integrated values of CH_2CH_2 of PTHF to that of a signal at 3.49 ppm assignable to four protons linked to azide unit $N_3CH_2CH_2$, while being included the molecular weight of initiator (87.08 g/mol) (Figure 4.8).

The number-average molecular weight obtained by GPC ($M_{n,GPC}$ = 9469 g/mol, relative to linear PS standards which was converted to PTHF standards by multiplying with 0.556 and found out as $M_{n,GPC}$ = 5265 g/mol.) is a consistent agreement with $M_{n,NMR}$, thus indicating that the quantitative azide end-group functionalization of PTHF was successful. Moreover, M_w/M_n = 1.1 calculated from GPC displays excellent narrow molecular weight distribution.

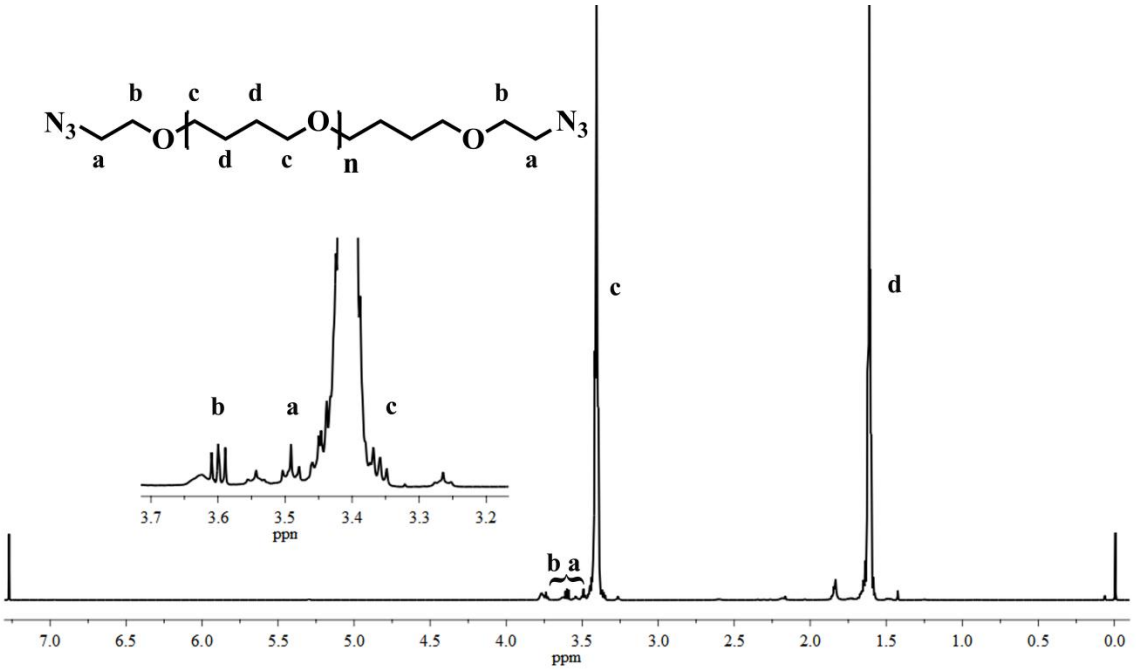
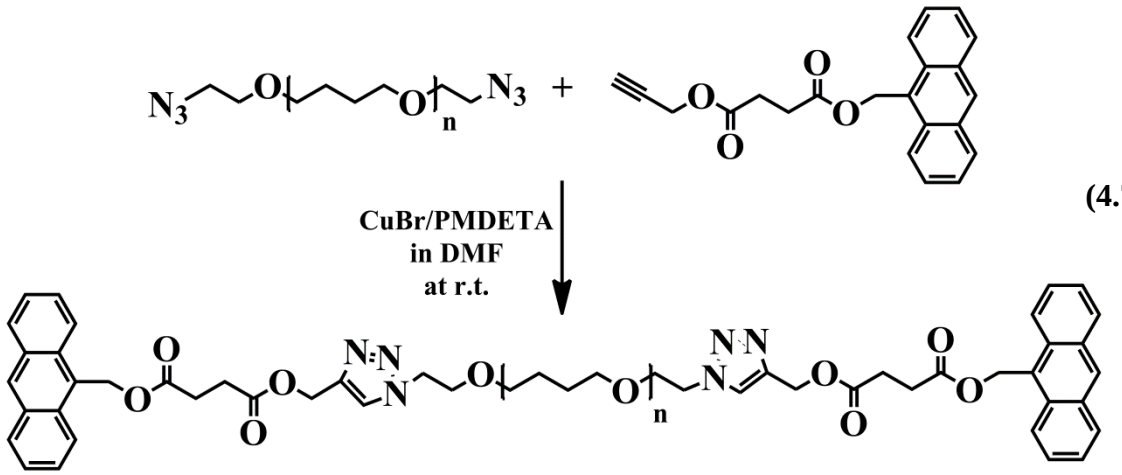


Figure 4.8: ^{1}H NMR spectra of α, ω-azide-PTHF (N_3-PTHF-N_3) in $CDCl_3$.

Then α, ω-azide-PTHF and **4** were reacted with each other via CuAAC click reaction in the presence CuBr/PMDETA in DMF at room temperature for 24 h as seen in Equation 4.9 and α, ω-anthracene-PTHF (Anth-PTHF-Anth) was obtained after passed through basic alumina column and precipitated in methanol.



(4.7)

The proof for the formation of triazole ring was obtained from ^{1}H NMR spectroscopy (Figure 4.9). The characteristic peaks for methylene protons adjacent to azide ($N_3CH_2CH_2O$) and oxygen ($N_3CH_2CH_2O$) were shifted from 3.49 ppm and 3.60 ppm to 3.76 ppm and 4.48 ppm respectively. CH_2 protons between the triazole ring and ester unit were shifted from 4.61 ppm to 5.17 ppm because of cyclo-addition, and a

new signal corresponding to a (C*H*) proton of triazole ring was appeared at 7.63 ppm.

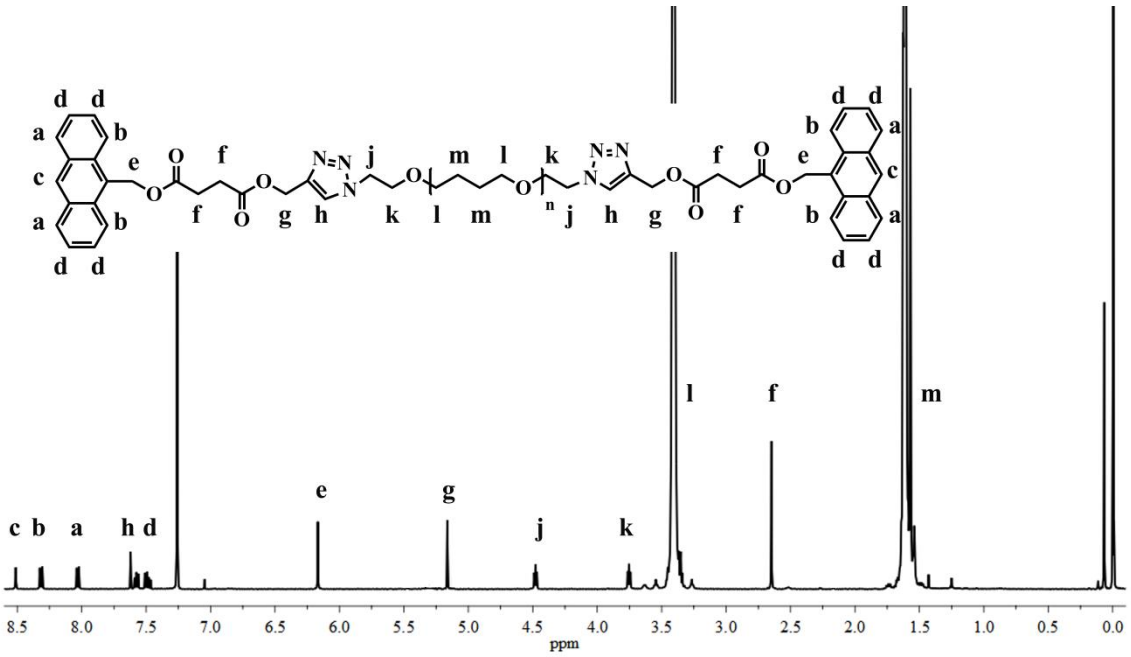


Figure 4.9: ^{1}H NMR spectra of α, ω-anthracene-PTHF (Anth-PTHF-Anth) in $CDCl_3$.

The ^{1}H NMR spectra of the resulting polymer displayed characteristic signals of both PTHF and **4** together, thus proving successful click reaction (Figure 4.9).

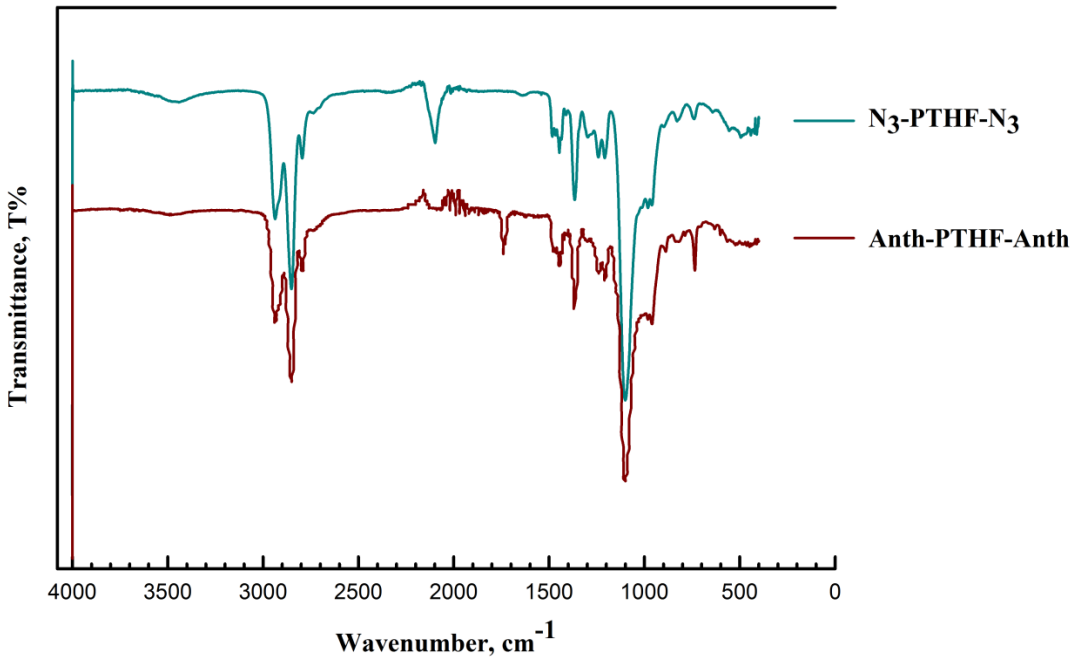


Figure 4.10: FT-IR spectra of α, ω-azide-PTHF and α, ω-anthracene-PTHF

In FT-IR spectrum of α, ω-azide-PTHF, the absence of absorbance peak at 2100 cm^{-1} proved that the click reaction was carried out through all azide ends displaying high efficiency in fact. However, the reason of having lower efficiency seen in ^1H NMR spectra is that the all polymer chains didn't undergo azide functionalization at the beginning of the polymerization in consequence of the esterification reaction during the synthesis of the initiator proceeds in a medial-efficiency fashion. The ration of $M_{n,\ GPC}$ / $M_{n,\ NMR}$ showed that the azide functionalization was yielded in 78% efficiency (Table 4.2) meaning that there are hydroxyl functionalized PTHFs, which do not respond to CuAAC click reactions.

Table 4.2: Molecular weights and functionalities of telechelic PTHF

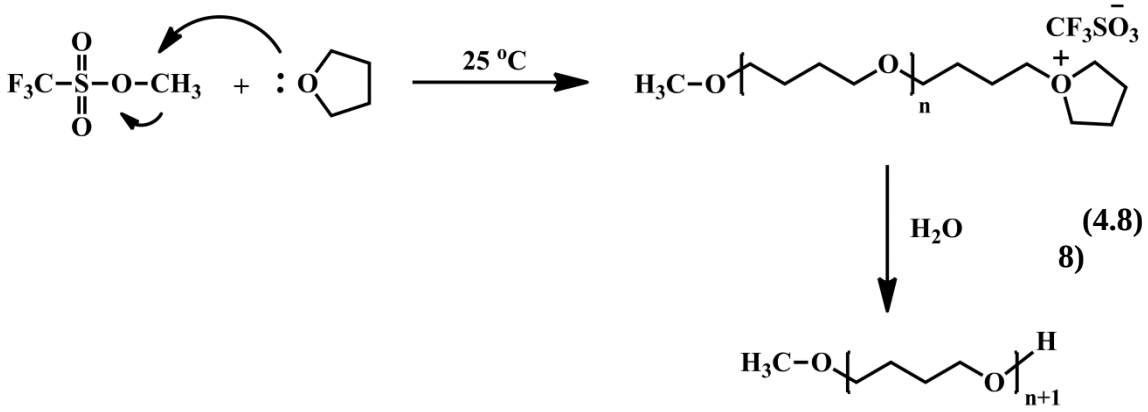
Functionalization Type	**Polymer**	M_n [a]	M_w/M_n [a]	**Functionality[b] (%)**	
				-N_3	**-Anth**
From terminating agent	**N_3-PTHF- N_3**	5265	1.1	78	-
Through CuAAC Click Reaction	**Anth-PTHF-Anth**	6130	1.2	-	85

[a] Determined by GPC.

[b] Determined by ^1H NMR (see text).

4.3 Synthesis of the α-methyl-ω-bromide-PTHF

Commercially available methyl triflate was used as initiator. Under the pre-mentioned reaction conditions, cationic ring-opening polymerization of tetrahydrofuran was carried out as shown in Equation 4.8 mechanistically. Polymerization was quenched with excess of water and precipitated in cold water.



From ^{1}HNMR spectrum of α-methyl-ω-hydroxyl-PTHF, methyl protons linked to the oxygen (OC*H*$_3$) at the α-end of the polymer were detected at 3.33 ppm. Methylene protons linked to the oxygen in the repeating unit (C*H*$_2$CH$_2$CH$_2$C*H*$_2$O) were detected at 3.41 ppm whereas methylene protons between them (CH$_2$C*H*$_2$C*H*$_2$CH$_2$O) were appeared at 1.61 ppm. Methylene protons adjacent to the hydroxyl unit at the ω-end were detected at 3.64 ppm as shown in Figure 4.11.

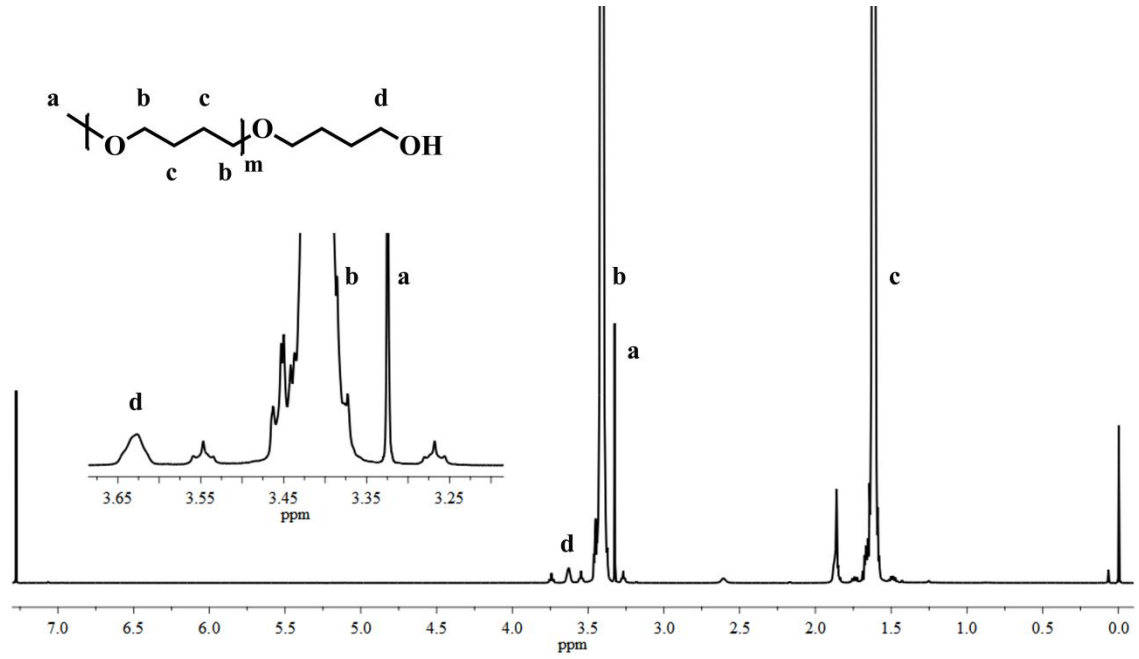
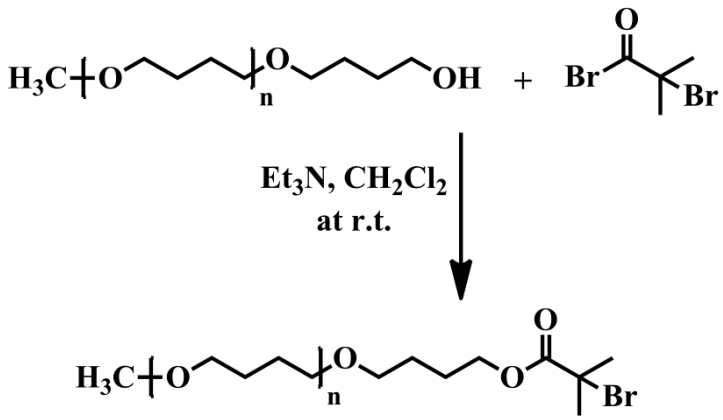


Figure 4.11: ^{1}H NMR spectra of α-methyl-ω-hydroxyl-PTHF (CH$_3$-PTHF-OH) in CDCl$_3$.

α-methyl-ω-bromide-PTHF was carried out through an esterification reaction with α-bromoisobutyryl bromide to introduce the bromo functionality to the polymer (Equation 4.9).



As seen in the ^{1}HNMR spectra of α-methyl-ω-hydroxyl-PTHF, after estericification reaction methylene protons adjacent to ω-hydroxyl end appeared at 3.64 ppm were shifted to 4.19 ppm and methyl protons next to bromo were detected at 1.93 ppm. These results confirmed that the post-modification of PTHF was successfully achieved as indicated in Figure 4.12.

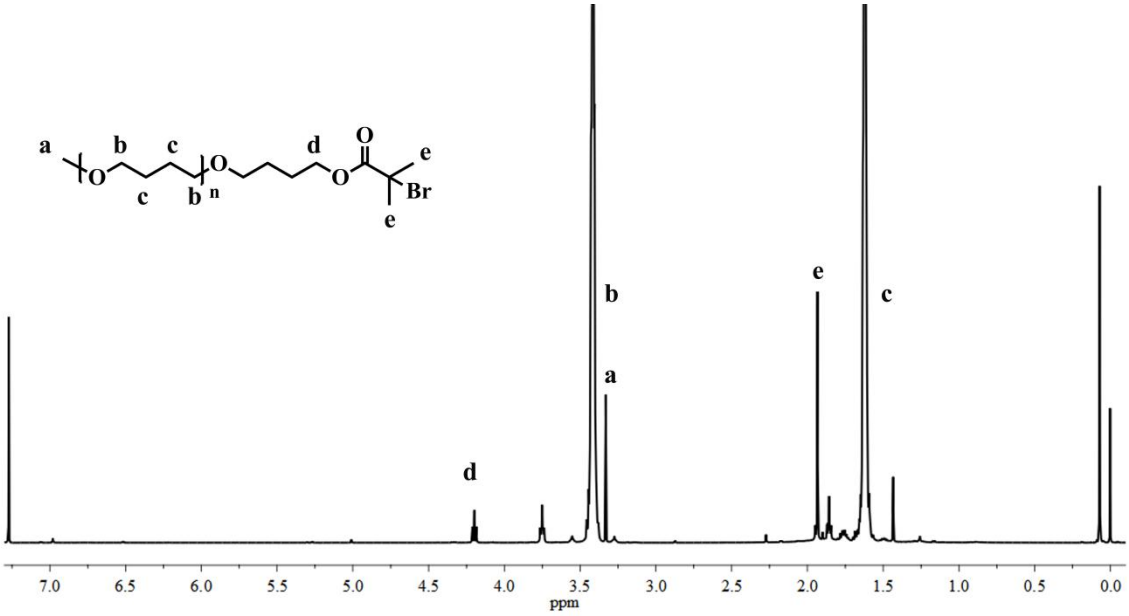


Figure 4.11: ^{1}H NMR spectra of α-methyl-ω-bromide-PTHF (CH_3-PTHF-Br) in $CDCl_3$.

The efficiency of esterification reaction was calculated from ^{1}H NMR spectrum. The integrated area of methyl protons adjacent to the bromo atom were proportioned to that of methylene protons ($CH_2CH_2CH_2CH_2O$) in the repeating unit of PTHF resulting 71% efficiency as indicated in Table 4.3. These results validated that the functionalization of PTHF through post-modification with esterification was quite successful.

Table 4.3: Molecular weights and functionalities of telechelic PTHF

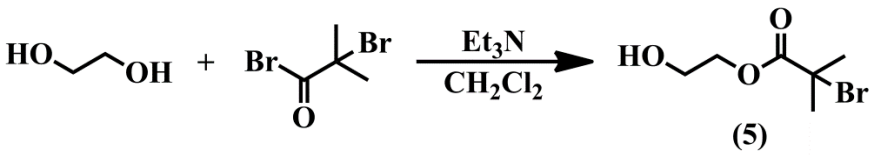
Functionalization Type	Polymer	M_n[a]	M_w/M_n[a]	Functionality[b] (%)
				-Br
From terminating agent	CH_3-PTHF- OH	3408	1.2	-
Through CuAAC click reaction	CH_3-PTHF-Br	3545	1.2	71

[a] Determined by GPC.

[b] Determined by ^{1}H NMR (see text).

4.4 Another pathway for the synthesis of α-methyl-ω-bromide-PTHF

2-hydroxyethyl 2-bromoisobutyrate (HEBiB) which was used as terminating agent was synthesized quantitatively via basic esterification reaction using α-bromoisobutyryl bromide in the presence of Et_3N as shown in Equation 4.10.



(5) **(4.10)**

From ^{1}H NMR spectrum of **5**, methylene protons adjacent to ester unit and methylene protons next to hydroxyl unit were detected at 4.28 ppm and 3.85 ppm respectively. A signal related to methyl protons next to Br atom at 1.93 ppm as seen in Figure 4.12.

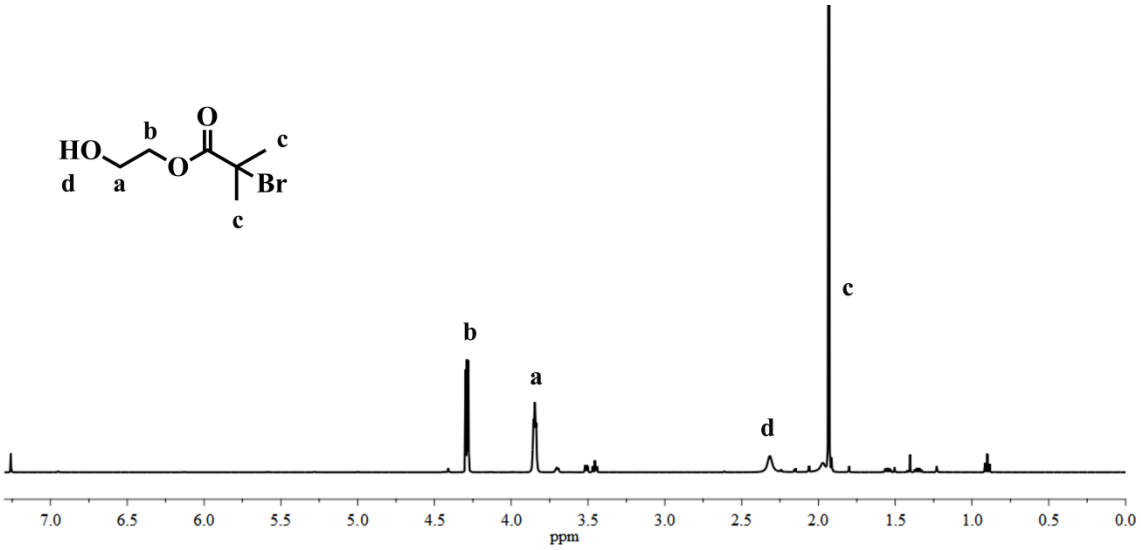
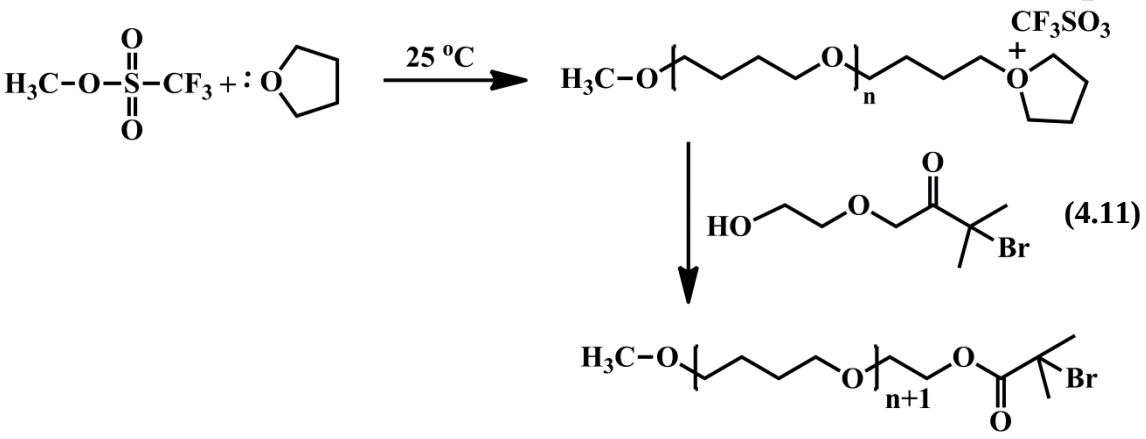


Figure 4.12: ^{1}H NMR spectra of 2-hydroxyethyl 2-bromoisobutyrate in $CDCl_3$.

Cationic ring-opening polymerization of tetrahydrofuran was initiated with methyl triflate. After the prescribed reaction time, polymerization was quenched with approximately 100 times excess of synthesized **5** as seen in Equation 4.11.



In the ^{1}H NMR spectra of α-methyl-ω-hydroxyl-PTHF, methyl protons linked to the oxygen (O*CH*$_3$) at the α-end of the polymer were detected at 3.33 ppm. Methylene protons linked to the oxygen in the repeating unit (C*H*$_2$CH$_2$CH$_2$C*H*$_2$O) were detected at 3.41 ppm whereas methylene protons between them (CH$_2$C*H*$_2$C*H*$_2$CH$_2$O) were appeared at 1.61 ppm. Methyl protons adjacent to Br atom were detected at 1.93 ppm as shown in Figure 4.13.

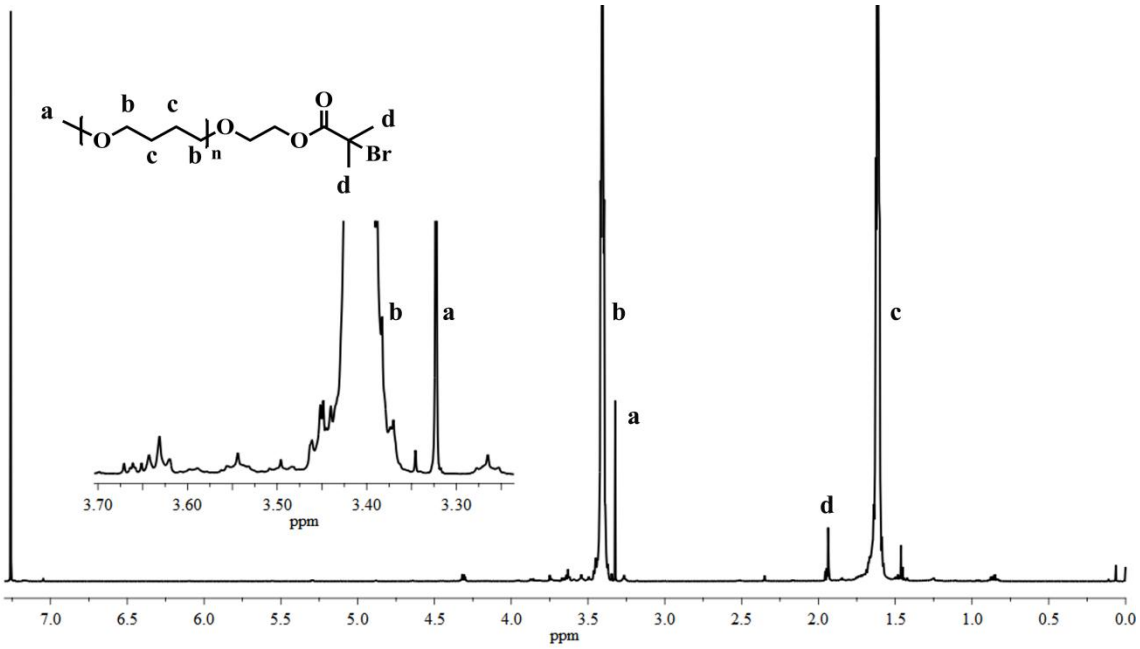


Figure 4.13: ^{1}H NMR spectra of α-methyl-ω-bromide-PTHF (CH_3-PTHF-Br)in $CDCl_3$.

As seen in the ^{1}H NMR spectra of α-methyl-ω-hydroxyl-PTHF, the peak assigned to methylene protons adjacent to hydroxyl unit at 3.63 ppm wasn't disappeared meaning that the terminating activity of **5** was unsatisfactory. Besides the integrated area of the methyl protons next to Br atom was lower than expected, stating that the terminating efficiency of **5** was certainly insufficient.

Table 4.4 : Molecular weight and functionality of telechelic PTHF

Functionalization Type	**Polymer**	M_n [a]	M_w/M_n [a]	**Functionality[b] (%)**
				-Br
From terminating agent	**CH_3-PTHF- Br**	3995	1.2	30

[a] Determined by GPC.

[b] Determined by ^{1}H NMR (see text).

5. CONCLUSION

The intention of this M.Sc. dissertation was to synthesize well-defined α, ω-homo and -hetero telechelic PTHFs with different end functionalities which provide further reactions for the synthesis of block, graft and star shaped polymers.

- In the first study, PTHF was functionalized from both functional initiator and terminating agent providing azide and hydroxyl unit. Well-defined azide functionalized PTHF was firstly introduced to the literature and characterized. Functionalities were then converted to anthracene and bromide via CuAAC click reaction and esterification respectively. In this study, three types of α, ω-hetero telechelic PTHF were synthesized and characterized. α-anthracene-ω-bromide-PTHF can be used in the synthesis of various triblock terpolymers with the combination of atom transfer radical polymerization (ATRP) and DA click reaction. In another concept, α-azide-ω-hydroxyl-PTHF can be carried out through an esterification reaction with 2-Bromopropionyl bromide resulting in α-azide-ω-bromide(secondary)-PTHF, which can be used in the synthesis of various triblock terpolymers with the combination of atom transfer nitroxide radical coupling (NRC) and CuAAC clck reaction. α-anthracene-ω-bromide-PTHF can also be used as macroinitiator in the synthesis of star shaped polymers with divinylbenzen (DVB). The end polymer can then be carried out through DA click reaction, resulting in star polymer, which each arm has two polymer sequences.
- In the second study, PTHF was functionalized from terminating agent resulting in α, ω-azide-PTHF, which was firstly synthesized and characterized. α, ω-azide-PTHF can be a favorable alternating method for the synthesis of commercially used PCL-PTHF-PCL or PU-PTHF-PU block (co)polymers. N_3-PTHF-N_3 and alkyne functionalized PCL can be carried out through CuAAC click reaction yielding in high efficiencies. In the synthesis

of PU-PTHF-PU, CuAAC click reactions can be alternatively used instead of esterification reactions, yielding higher efficiencies than that of esterification.

- With the aid of CuAAC and DA click reactions, functionalities such as amine can be introduced to the telechelic PTHFs.
- In the last two studies, it was aimed to synthesize a telechelic polymer at a time without post-modification. However studies indicated that the results were unsatisfying with the chosen terminating agent. More studies are required to improve the terminating efficiency of the chosen agent or build up a new compound for this purpose.

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