

**SYNTHESIS OF HETEROGRAFT COPOLYMERS
VIA TRIPLE CLICK REACTIONS**

M.Sc. THESIS

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JUNE 2012

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

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KOPOLİMERLERİ SENTEZİ**

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To my father and mother,

FOREWORD

This master study has been carried out at İstanbul Technical University, Chemistry Department of Science & Letter Faculty.

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ABBREVIATIONS

1,3-DPCA	: 1,3-Dipolar Cycloaddition
¹H NMR	: Hydrogen Nuclear Magnetic Resonance Spectroscopy
ATRP	: Atom Transfer Radical Polymerization
ATNRC	: Atom Transfer Nitroxide Coupling Reaction
CDCl₃	: Deuterated Chloroform
CH₂Cl₂	: Dichloromethane
CuAAC	: Copper Catalyzed Azide-Alkyne Cycloaddition
DA	: Diels-Alder
DCC	: <i>N,N'</i> -dicyclohexylcarbodiimide
DMF	: <i>N,N</i> -dimethylformamide
DSC	: Differential Scanning Calorimetry
EtOAc	: Ethyl acetate
FT-IR	: Fourier Transform Infrared Spectrophotometer
GPC	: Gel Permeation Chromatography
MMA	: Methyl Methacrylate
MWD	: Molecular Weight Distribution
NBE	: Norbornene
NMP	: Nitroxide Mediated Polymerization
PDI	: Polydispersity Index
PEG	: Poly(ethylene glycol)
PMDETA	: <i>N, N, N', N'', N'''</i> -Pentamethyldiethylenetriamine
PMMA	: Poly(methyl methacrylate)
ε-CL	: ε-caprolactone
PCL	: Poly(ε-caprolactone)
RAFT	: Reversible Addition Fragmentation Chain Transfer
r-DA	: retro-Diels-Alder
ROMP	: Ring Opening Metathesis Polymerization
TD-GPC	: Triple Detector-Gel Permeation Chromatography
TEA	: Triethylamine
TEMPO	: 2,2,6,6-Tetramethylpiperidine- <i>N</i> -oxyl
THF	: Tetrahydrofuran
UV	: Ultraviolet

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LIST OF SYMBOLS

λ	: Wavelength
$R\cdot$	: Radical
f	: Number of arm
nm	: Nanometer
$[\eta]$	: Intrinsic viscosity
R_h	: Hydrodynamic radius
C	: Concentration
A	: Absorbance
ϵ	: Molar extinction coefficient
k_{act}	: Activation rate constant
k_{deact}	: Deactivation rate constant
R_p	: Rate of polymerization
dn/dc	: Refractive index increment
K	: Mark-Houwink-Sakurada constant
ppm	: Parts per million
$^{\circ}\text{C}$	: Celsius
M	: Molarity
T_g	: Glass-transition temperature
M_n	: The number average molecular weight
M_w	: The weight average molecular weight
M_w/M_n	: The molecular weight distribution

SYNTHESIS OF HETEROGRAFT COPOLYMERS VIA TRIPLE CLICK REACTIONS

SUMMARY

Much effort has been paid to the synthesis of advanced polymeric materials with improved properties. Since they display much developed physical and mechanical properties block copolymers and graft polymers are the most demanded advanced materials. Despite their broad applications, the synthesis of block copolymers and graft polymers with well-defined structure remains a challenge.

Graft polymers have a considerable interest because of having nonlinear architecture with different composition and topology. Because of their branched structure they generally have also lower melt viscosities, which is advantageous for processing. Also, graft polymers have a better physical and chemical properties than their linear polymers. Graft copolymers can be obtained with three general methods: (i) grafting onto, in which side chains are preformed, and then attached to the backbone; (ii) grafting-from, in which the monomer is grafted from the backbone; and (iii) grafting through, in which the macromonomers are copolymerized.

Until last decade, living ionic polymerizations (cationic or anionic) were the only methods for the synthesis of block and star polymers in a controlled way. However, the harsh experimental conditions have limited the applicability of the ionic polymerizations. The polymer community has then witnessed the rapid growth of controlled/living radical polymerization (C/LRP) methods not only for the synthesis of block and star polymers but for also the polymers from linear to complex structures. In recent years, the use of controlled/living radical polymerization techniques in the synthesis of complex macromolecules (star and graft polymers) has quickly increased because of the variety of applicable monomers and greater tolerance to experimental conditions in comparison with living ionic polymerization routes. Nitroxide mediated radical polymerization (NMP) based on the use of stable nitroxide free radicals and Mtn(Metat)/ligand catalyst-mediated living radical polymerization, which is often called atom transfer radical polymerization (ATRP) are versatile methods among living radical polymerizations.

The most widely used methods for C/LRP include atom transfer radical polymerization (ATRP), nitroxide mediated radical polymerization (NMP), and reversible addition-fragmentation chain transfer polymerization (RAFT). In recent years, CRP techniques have developed rapidly for facile preparation of a variety of polymeric materials with predetermined M_n , low PDI, and high degrees of chain-end functionalization. Especially, ATRP and NMP have proved useful in the synthesis of triblock copolymers. In addition, controlled ring-opening polymerization (ROP) has found wide applications in the polymerization of lactones and lactides. Ring-opening polymerization (ROP) is a unique polymerization process, in which a cyclic monomer is opened to generate a linear polymer.

The Ring Opening Metathesis Polymerization (ROMP) has found wide applications in the polymerization of cyclic olefins (norbornene, oxanorbornene, norbornadiene, dicyclopentadiene, etc.). ROMP of cyclic olefins by using metal alkylidene initiators (e.g., molybdenum and ruthenium complex catalysis) has led to a number of well defined architectures including block, graft, star, and cyclic polymers which has controlled molecular weight and controlled end group. Nowadays, alternative routes such as Diels-Alder (DA) and the copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC) reactions which can be classified under the term “click chemistry” have emerged as a powerful tool for the preparation of graft polymers. In addition, nitroxide radical coupling reactions (NRC) reaction is considered as a potential click reaction due to its high efficiency and orthogonality in the synthesis of well-defined polymers with different topologies.

Diels-Alder reaction, a [4+2] system, is a cycloaddition between a conjugated diene and a dienophile. Diels-Alder reaction has attracted much attention based on the macromolecular chemistry, particularly in providing new materials.

Recently, Sharpless and coworkers used Cu(I) as a catalyst in conjunction with a base in Huisgen’s 1,3-dipolar cycloadditions ([3+2] systems) between azides and alkynes or nitriles and termed them click reactions. (CuAAC) Later, click chemistry strategy was successfully applied to macromolecular chemistry, affording polymeric materials varying from block copolymers to complex macromolecular structures. Click reactions permit C–C (or C–N) bond formation in a quantitative yield without side reactions or requirements for additional purification steps. Click chemistry has been used extensively due to its quantitative yields, high tolerance of functional groups, and insensitivity of the reaction to solvents. Nowadays, click reactions have already been widely used in polymeric science and material, such as the synthesis of linear, dendritic, cyclic, and star polymers.

Recently, Huang and co-workers reported a new coupling reaction called atom transfer nitroxide radical coupling (ATNRC) chemistry, which was realized by mixing a TEMPO-containing polymer with another Br-containing polymer in the presence of CuBr/PMDETA catalytic system. The coupling efficiency of ATNRC was as high as 90%, which is similar to that of click chemistry. Thus, ATNRC can serve as a relatively convenient and safe way with “click-like” efficiency to synthesize the graft copolymers with certain structures using the grafting-onto strategy. This methodology has been used to synthesize degradable and reversibly coupled linear multiblock copolymers, block and graft copolymers in the presence of a 10-fold molar excess of copper species per halide end group. It should be noted that the NRC reaction is considered as a potential click reaction due to its high efficiency and orthogonality in the synthesis of well-defined polymers with different topologies. From this point of view, in this thesis, we describe the synthesis of heterograft copolymers using subsequently ROMP, DA and NRC, CuAAC reactions.

In this study; anthracene-functionalized oxanorbornene monomer and oxanorbornenyl bromide and tosyl functionalized oxanorbornenyl monomer were first polymerized via ring opening metathesis polymerization (ROMP) using the first generation Grubbs’ catalyst in dichloromethane at room temperature to form random block copolymer and then clicked with maleimide end-functionalized polymer PMMA-MI in a Diels-Alder reaction in toluene, dioxan at 110 °C to create corresponding graft copolymers, poly(ONB-g-PMMA)-*b*-poly(ONB-bromide)-*b*-poly(ONB-OTs).

Diels-Alder click reaction efficiency for graft copolymerization was monitored by UV-Vis spectroscopy. This new graft copolymer reacted with Peg-Tempo in dimethylformamide at room temperature to create poly(ONB-g-PMMA)-*b*-poly(ONB-g-PEG)-*b*-poly(ONB-OTs) by using Atom Transfer Nitroxide Radical Coupling reaction and then this new graft copolymer reacted with pcl-alkyne in dimethylformamide at 40 °C to form heterograft copolymer, poly(ONB-g-PMMA)-*b*-poly(ONB-g-PEG)-*b*-poly(ONB-g-PCL) by using In-situ Azidation and Click reaction.

The dn/dc values of graft and graft block copolymers were experimentally obtained using a triple detection GPC (TD-GPC) and subsequently introduced to the software so as to give molecular weights, intrinsic viscosity ($[\eta]$) and hydrodynamic radius (R_h) values.

Thus, heterograft copolymers were characterized by using Gel permeation Chromatography (GPC), ^1H NMR, UV, DSC spectral measurements.

ÜÇLÜ CLICK REAKSIYONLARI İLE FARKLI KOLLU AŞI KOPOLİMERLERİ SENTEZİ

ÖZET

Üstün özellikler gösteren ileri polimer malzemelerin sentezi konusunda yoğun çaba harcanmaktadır. Daha gelişmiş mekanik ve fiziksel özellikleri birarada bulundurmalarından dolayı blok kopolimerler ve yıldız polimerler en çok rağbet edilen ileri malzemelerdir. Çok geniş uygulama alanlarına rağmen, blok kopolimerlerin ve yıldız polimerlerin iyi-tanımlı olarak sentezlenmesi halen bir meseledir.

Aşı polimerler sahip olduğu lineer olmayan yapısı, farklı bileşimi ve topolojisi nedeniyle önemli bir ilgiye sahiptir. Dallı yapılarından dolayı genellikle düşük vizkozite değerlerine sahiptir ve bu durumda polimerin işlenme koşullarını kolaylaştırır. Ayrıca, aşı polimerler lineer polimerlere kıyasla daha iyi fiziksel ve kimyasal özelliklere sahiptir.

Aşı polimerler genel olarak 3 farklı yöntemle elde edilirler: (i) önce yan zincirler düzenlenir ve ana zincire bağlanır; (ii) monomer ana zincirden aşılır; (iii) makromonomerlerin kopolimerizasyonu ile elde edilir.

On yıl öncesine kadar, blok ve yıldız polimerlerin kontrollü olarak sentezinde yaşayan iyonik polimerleşme (anyonik ve katyonik) metotları mevcut tek yöntemlerdi. Öte yandan, zorlu deney koşulları iyonik polimerleşme yöntemlerinin kullanımlarını sınırlamıştır. Daha sonra, polimer toplumunun yalnızca blok ve yıldız polimerlerin değil aynı zamanda düz zincirli polimerlerden daha karmaşık yapılara kadar olan polimerlerin sentezinde de kullanılan kontrollü/yaşayan radikal polimerleşme (C/LRP) yöntemlerinin hızlı büyümesine tanıklık ettiğini görmekteyiz. Son yıllarda, kompleks makromoleküllerin sentezinde kontrollü/yaşayan polimerizasyon tekniklerinin kullanılması, yaşayan iyonik polimerizasyon yöntemiyle mukayese edildiğinde deneysel koşullara daha fazla toleranslı olması ve çok çeşitli monomerlere uygulanabilir olması nedeniyle hızlı bir şekilde arttı. Kararlı nitroksit serbest radikallerin kullanımına dayanan Nitroksit Ortamlı Radikal Polimerizasyonu ve genellikle Atom Transfer Radical Polimerizasyonu (ATRP) olarak bilinen Mtn(Metat)/ligand kataliz ortamlı radikal polimerizasyonu yaşayan radikal polimerizasyon yöntemleri arasında çok yönlü metotlardır.

Atom transfer radikal polimerleşmesi (ATRP), nitroksit ortamlı radikal polimerleşmesi (NMP), ve tersinir eklenme-ayırılma zincir transfer polimerleşmesi (RAFT) en yaygın kullanım alanı olan C/LRP yöntemleridir. Son yıllarda, çeşitli polimerlerin hazırlanmasında düşük molekül ağırlığı, düşük PDI, yüksek değerde zincir fonksiyonallitesi ile CRP tekniği geliştirildi. Özellikle, üçlü block kopolimer sentezi için ATRP ve NMP geliştirildi. Öte yandan, kontrollü halka açılma polimerizasyonu, lakton ve laktidlerin polimerizasyonunda geniş uygulama alanı

bulmuştur. Halka açılma polimerizasyonu (ROP) siklik monomerin lineer polimer oluşturmak üzere açıldığı tek polimerizasyon yöntemidir.

ROMP, metal alkilidin başlatıcılar (molibdenyum ve rutenyum kompleks katalizi gibi) kullanılarak elde edilen halkalı olefinlerin (norbornen, oksanorbornen, norbornadien, ve disiklopentadien vs.) yaşayan polimerizasyonu için çok yönlü ve etkili bir sentez yöntemidir. Metal alkilidin kullanarak siklik olefinlerin Halka Açılma Metatez Polimerizasyonu (ROMP) ile blok, aşı, yıldız ve siklik polimerler gibi uç grup kontrolü, moleküler ağırlık kontrolü gibi özelliklere sahip birçok iyi tanımlı yapılar elde edilebilir. Günümüzde, “click kimyası” terimi altında sınıflandırılan Diels-Alder (DA) ve bakır katalizli azid-alkin siklokatılma (CuAAC) tepkimeleri blok ve yıldız polimerlerin eldelerinde güçlü bir alternatif yöntem olarak ortaya çıkmıştır. Buna ek olarak, nitroksit radikal birleşme reaksiyonları (NRC) farklı topolojileri iyi tanımlanmış polimerlerin sentezi, yüksek verimlilik nedeniyle potansiyel bir click reaksiyonu olarak kabul edilir.

Diels-Alder reaksiyonları ise konjuge bir dien ile dienofil bileşiğinin siklo katılması olarak bilinir ve makromoleküllerin sentezinde önemli bir yere sahiptir.

Son yıllarda, Sharpless ve arkadaşları azidler ve alkin/nitriller arasındaki Huisgen 1,3-dipolar siklokatılmalarda ($[3 + 2]$ sistemi) Cu(I)'i baz ile birleştirip kataliz olarak kullandılar ve bu reaksiyonu click reaksiyonu olarak adlandırdılar. Daha sonra click kimyası blok kopolimerlerden karmaşık makromoleküler yapılara kadar değişen birçok polimerik malzemenin sentezinde başarılı bir şekilde uygulandı. Click reaksiyonları, yan reaksiyonlara neden olmadan ve ilave saflaştırma işlemlerine gerek duyulmadan kantitatif verimle C-C (veya C-N) bağ oluşumuna izin vermektedir. Click kimyası kantitatif verim, yüksek toleranslı, solventlere karşı dirençli olduğundan yaygın olarak kullanılır. Bugüne kadar, click reaksiyonları polimer bilim ve malzemelerinde olduğu gibi lineer, dendritic, cyclic, star polimerlerinin sentezinde yaygın olarak kullanılır.

Son zamanlarda, Haung ve arkadaşları yeni birleşme reaksiyonu, ATNRC, Tempo içeren polimer ile Br içeren polimer karıştırarak CuBr/PMDETA varlığında katalizli sistemde, reaksiyonu gerçekleştirmiştir. ATNRC ile ürün verimliliği % 90, verim click kimyası ile orantılıdır. ATNRC, click reaksiyonuna benzer uygun ve güvenli bir yol, grafting-onto stratejisi ile aşı kopolimer sentezinde etkilidir. Bu metot bakır-halojen varlığında tersinir ve bozunabilir lineer block kopolimer, block, aşı kopolimerlerinin sentezinde kullanılır. NRC reaksiyonu click reaksiyonu gibi düşünülür, yüksek verimli, farklı topolojide polimer sentezinde kullanılır. Bu noktadan hareketle bu tezde ROMP, DA, NRC, CuAAC reaksiyonlarının birlikte kullanılmasıyla farklı kollu aşı blok kopolimerlerinin sentezi tanımlanmıştır.

Bu çalışmada, ilk olarak antrasen fonksiyonlu okzanorbornen monomeri ve okzanorbornenil brom ve tosil fonksiyonlu okzanorbornenil oda sıcaklığında diklorometan içerisinde birinci jenerasyon Grubbs katalizörü kullanılarak rastgele block kopolimer oluşturmak için halka açılma metatez polimerizasyonu ile sentezlendi. Oluşan ürün 110 °C 'de toluen, dioxan karışımı içerisinde Diels-Alder reaksiyonu ile maleimide uç fonksiyonlu polimer, PMMA-MI, poly(ONB-g-PMMA)-*b*-poly(ONB-bromide)-*b*-poly(ONB-OTs) aşı kopolimeri eldesi için sentezlendi. Aşı kopolimerizasyonun Diels-Alder click reaksiyonu etkinliği UV-Vis spektroskopisi ile gözlemlendi. Bu yeni kopolimer oda sıcaklığında dimetilformamid varlığında Peg-Tempo ile atom transfer nitroxide radikal reaksiyonu ile poly(ONB-

g-PMMA)-*b*-poly(ONB-*g*-PEG)-*b*-poly(ONB-OTs) aşı kopolimerinin sentezi için gerçekleştirildi. Oluşan yeni block kopolimer 40 °C de dimetilformamid varlığında PCl-Alkin ile azidasyon ve click reaksiyonu ile poly(ONB-*g*-PMMA)-*b*-poly(ONB-*g*-PEG)-*b*-poly(ONB-*g*-PCL) aşı kopolimerinin sentezi için gerçekleştirildi.

Aşı kopolimerleri ve aşı blok kopolimerlerinin dn/dc değerleri üçlü dedektör GPC (TD-GPC) kullanılarak elde edildi ve bu değerler cihaza tanıtılarak molekül ağırlıkları, intrinsik viskozite ($[\eta]$) and hidrodinamik yarıçapı (R_h) değerleri elde edildi. Oluşan hetero-aşı kopolimeri ^1H NMR, UV, GPC ve DSC ölçümleri ile karakterize edilmiştir.

1. INTRODUCTION

Recent developments in C/LRP methods provide the possibility to synthesize polymers such as block, graft, star and functional polymers with well-defined structures [1-4]. The most widely used methods for C/LRP include atom transfer radical polymerization (ATRP), nitroxide mediated radical polymerization (NMP), and reversible addition-fragmentation chain transfer polymerization (RAFT) [1, 2, 4-9].

Graft copolymers with a large number of side chains chemically attached onto a linear backbone are endowed with unusual properties thanks to their confined and compact structures, including wormlike conformation, compact molecular dimensions and notable chain end effects [10].

Graft copolymers can be obtained with three general methods: (i) grafting-onto, in which side chains are preformed, and then attached to the backbone; (ii) grafting-from, in which the monomer is grafted from the backbone; and (iii) grafting-through, in which the macromonomers are copolymerized [11, 12].

Among living polymerization methods, ring opening metathesis polymerization (ROMP) is a versatile and an efficient synthetic strategy for the polymerization of cyclic olefins (such as norbornene norbornadiene, and dicyclopentadiene etc.) by using metal alkylidene initiators (e.g. molybdenum and ruthenium complex catalysis) [12-31]. Ring-opening polymerization (ROP) is a unique polymerization process, in which a cyclic monomer is opened to generate a linear polymer. Polymers with a wide variety of functional groups can be produced by ring-opening polymerizations. Preparation of cyclic monomers, studies of catalysis and mechanisms are active areas of research both in academia and industry [32-35].

Click chemistry has been used extensively due to its quantitative yields, high tolerance of functional groups, and insensitivity of the reaction to solvents [36]. The reaction between a terminal alkyne and an azide groups to form a triazole group is the most popular one, which was first studied by Huisgen [37]. Nowadays, click

reactions have already been widely used in polymeric science and material, such as the synthesis of linear, dendritic, cyclic, and star polymers [38,39].

Recently, Huang and co-workers reported a new coupling reaction called atom transfer nitroxide radical coupling (ATNRC) chemistry, [40-44] which was realized by mixing a TEMPO-containing polymer with another Br-containing polymer in the presence of CuBr/PMDETA catalytic system. The coupling efficiency of ATNRC which is similar to that of click chemistry. Thus, ATNRC can serve as a relatively convenient and safe way with “click-like” efficiency to synthesize multiarm star polymer, the graft copolymers with certain structures using the grafting-onto strategy. Thus, under the ATNRC conditions (such as the Cu(0)/CuBr/PMDETA system), the graft, the star-shaped, and the linear copolymer were prepared successfully with high efficiency [45-47].

In this thesis we synthesised of well-defined graft copolymers generated from a combination of ROMP, Diels-Alder NRC reaction and click reaction. The ROMP technique is specially chosen for the construction of a well-defined main backbone. anthracene-functionalized oxanorbornene monomer and oxanorbornenyl bromide and tosyl functionalized oxanorbornenyl monomer were first polymerized via ring opening metathesis polymerization (ROMP) using the first generation Grubbs' catalyst in dichloromethane at room temperature to form random block copolymer and then clicked with maleimide end-functionalized polymer PMMA-MI in a Diels-Alder reaction in toluene, dioxan at 110 °C to create corresponding graft copolymers, poly(ONB-g-PMMA)-*b*-poly(ONB-bromide)-*b*-poly(ONB-OTs).

Diels-Alder click reaction efficiency for graft copolymerization was monitored by UV-Vis spectroscopy. This new graft copolymer reacted with Peg-Tempo in dimethylformamide at room temperature to create poly(ONB-g-PMMA)-*b*-poly(ONB-g-PEG)-*b*-poly(ONB-OTs) by using Atom Transfer Nitroxide Radical Coupling reaction and then this new graft copolymer reacted with pcl-alkyne in dimethylformamide at 40 °C to form heterograft copolymer, poly(ONB-g-PMMA)-*b*-poly(ONB-g-PEG)-*b*-poly(ONB-g-PCL) by using In-situ Azidation and Click reaction (figure 1.1) .

2. THEORETICAL PART

2.1 Living Polymerization

Living polymerizations are characterized by chain growth that matures linearly with time. Inherent in this definition are two characteristics of ionic polymerizations that both liken and distinguish ionic routes from the aforementioned free radical route. In order to grow linearly with time, ionic polymerizations must proceed by a chain mechanism in which subsequent monomer molecules add to a single active site; furthermore, addition must occur without interruption throughout the life of the active site. Thus, the chain transfer mechanisms described above must be absent. Living polymerizations may include slow initiation, reversible formation of species with various activities and lifetimes, reversible formation of inactive (dormant) species, and/or reversible transfer [48]. Living polymerizations must not include irreversible deactivation and irreversible transfer. Classical living polymerizations occur by the formation of active ionic sites prior to any significant degree of polymerization. A well-suited initiator will completely and instantaneously dissociate into the initiating ions. Dependent on the solvent, polymerization may then proceed via solvent pairs or free ions once a maximum number of chain centers are formed. Solvents of high dielectric constants favor free ions; solvents of low dielectric constants favor ionic pairs. Termination by coupling will not occur in ionic routes due to unfavorable electrostatic interactions between two like charges. Furthermore, chain transfer routes are not available to living polymerizations, provided the system is free of impurities. Polymerization will progress until all of the monomer is consumed or until a terminating agent of some sort is added. On the flip side, ionic polymerizations are experimentally difficult to perform: a system free of moisture as well as oxygen, and void of impurities is needed. Moreover, there is not a general mechanism of polymerization on which to base one's experiment: initiation may occur in some systems before complete dissociation of initiator. Knowledge of the initiating mechanism must be determined a priori to ensure a successful reaction. Despite the advantage of molecular control of living systems, the experimental rigor

involved in ionic polymerization is often too costly for industrial use and free radical routes are preferred.

2.1.1 Controlled/Living radical polymerization (C/LRP)

Living polymerization was first defined by Szwarc as a chain growth process without chain breaking reactions (transfer and termination) [49]. Such a polymerization provides end-group control and enables the synthesis of block copolymers by sequential monomer addition. However, it does not necessarily provide polymers with molecular weight (MW) control and narrow molecular weight distribution (MWD). Additional prerequisites to achieve these goals include that the initiator should be consumed at early stages of polymerization and that the exchange between species of various reactivities should be at least as fast as propagation [50-52]. It has been suggested to use a term controlled polymerization if these additional criteria are met [53]. This term was proposed for systems, which provide control of MW and MWD but in which chain breaking reactions continue to occur as in RP. However, the term controlled does not specify which features are controlled and which are not controlled. Another option would be to use the term “living” polymerization (with quotation marks) or “apparently living,” which could indicate a process of preparing well-defined polymers under conditions in which chain breaking reactions undoubtedly occur, as in radical polymerization [54, 55].

Conventional free radical polymerization techniques are inherently limited in their ability to synthesize resins with well-defined architectural and structural parameters. Free radical processes have been recently developed which allow for both control over molar masses and for complex architectures. Such processes combine both radical techniques with living supports, permitting reversible termination of propagating radicals. In particular, three controlled free radical polymerizations have been well investigated. Each of these techniques is briefly presented below and all are based upon early work involving the use of initiator-transfer-agent-terminators to control irreversible chain termination of classical free radical process.

Living polymerization is defined as a polymerization that undergoes neither termination nor transfer. A plot of molecular weight vs. conversion is therefore linear, as seen in Figure 2.1, and the polymer chains all grow at the same rate, decreasing the polydispersity. The propagating center at 100 % conversion still exists

and can be further reacted, which can allow novel block, graft, star, or hyperbranched copolymers to be synthesized. Living polymerizations have been realized in anionic processes where transfer and termination are easy to suppress. Due to the favorable coupling of two radical propagating centers and various radical chain transfer reactions, the design and control of a living radical processes is inherently a much more challenging task. The living process of radical polymerization involves the equilibration of growing free radicals and various types of dormant species. By tying up a great deal of the reactive centers as dormant species, the concentration of free radicals decreases substantially and therefore suppresses the transfer and termination steps. These reactions are also denoted as controlled /living polymerizations rather than as true living polymerizations because transfer and termination are decreased but not eliminated. Three processes, NMP, ATRP, and RAFT, will now be introduced [56].

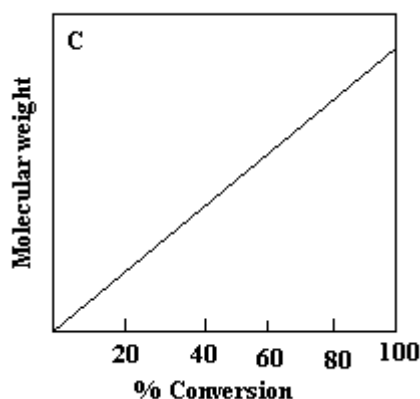


Figure 2.1: Molecular weight vs. conversion graph of a typical living polymerization

Living free radical polymerizations, although only about a decade old, have attained a tremendous following in polymer chemistry. The development of this process has been a long-standing goal because of the desire to combine the undemanding and industrial friendly nature of radical polymerizations with the power to control polydispersities, architectures, and molecular weights that living processes afford. A great deal of effort has been made to develop and understand different living free radical polymerization (LFRP) methods. The methods at the forefront fall into one of three categories: nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition fragmentation chain transfer (RAFT) [57].

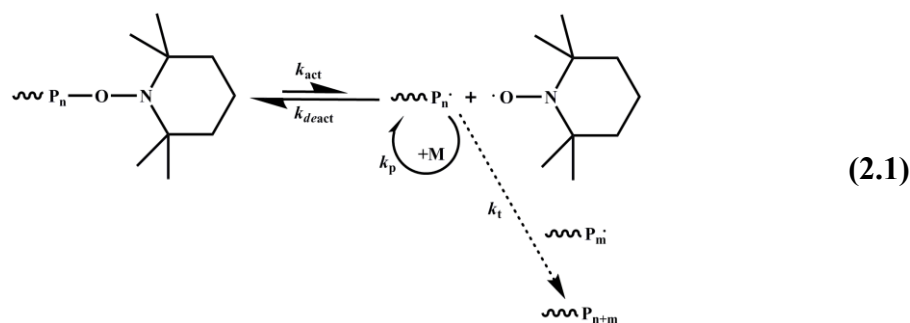
2.1.1.1 Nitroxide mediated radical polymerization (NMP)

Cyclic nitroxide radicals such as 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) have been extensively studied. SFRP with nitroxides is called nitroxide mediated polymerization (NMP). Polymerization is carried out by two methods that parallel those used in ATRP [58-61]. One method involves the thermal decomposition of an alkoxyamine such as 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine into a reactive radical and a stable radical. The other method involves a mixture of a conventional radical initiator such as AIBN or benzoyl peroxide and the nitroxide radical. Nitroxide radicals are sufficiently stable (due to steric hindrance) that they can be stored at ambient temperatures without change and some are available for purchase from chemical vendors. NMP with TEMPO generally requires higher temperatures (125–145 °C) and longer reaction times (1–3 days) compared to ATRP, and only styrene and 4-vinylpyridine polymerizations proceed with good control of molecular weight and polydispersity. Narrow molecular weight distributions with PDI below 1.1–1.2 are difficult to achieve with other monomers.

In this type of process, the propagating species ($P_n^\bullet$) reacts with a stable radical ($X^\bullet$) as seen in equation 2.1. The resulting dormant species (P_n-X) can then reversibly cleave to regenerate the free radicals once again. Once $P_n^\bullet$ forms it can then react with a monomer, M, and propagate further. The most commonly used stable radicals have been nitroxides, especially 2,2,6,6-tetramethylpiperidinoxyl (TEMPO). The 2,2',6,6'-tetramethylpiperidine-1-oxyl radical (TEMPO) was used as the nitroxide component in these initial studies. The alkoxyamine is formed in situ during the polymerization process. Shortly thereafter, it was shown that low molecular weight alkoxyamines such as styryl-TEMPO can be used as initiators/regulators for the controlled living radical polymerization of styrene [62]. NMP has some advantages and disadvantages compared to ATRP. A wide range of initiators (organic halides) are readily available for ATRP. Relatively few initiators for NMP, either nitroxides or alkoxyamines, are commercially available. The initiators need to be synthesized.

K is generally larger for ATRP compared to NMP and is more easily adjusted by changing the initiator, transition metal, and ligands. Larger K values mean faster polymerization and milder reaction conditions. On the other hand, ATRP requires a relatively large amount of metal (0.1–1% of the reaction mixture) that needs to be removed from the final polymer product. In both NMP and ATRP, control of the

reaction through establishment of a steady-state concentration of radicals is achieved by the balance between activation and deactivation. Conventional radical polymerization involves a balance between the rates of initiation and termination.



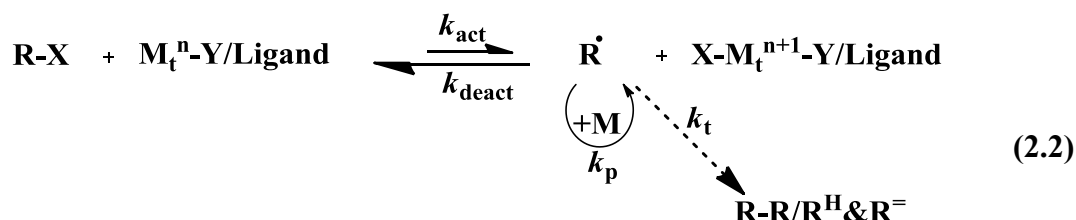
The chain end functionalization of polymers synthesized by NMP is a significant problem because dormant chains containing alkoxyamines can regenerate terminal radicals which can depolymerize at high temperatures. A very interesting chain end functionalization process has also been discovered by Hawker which involves the controlled monoaddition of maleic anhydride or maleimide derivatives to the alkoxyamine chain end. The alkoxyamine can then be easily eliminated and other functional groups can be introduced. This process relies on the resistance of maleic anhydride or maleimide derivatives to homopolymerize and the ability of the precursor to reform the olefin by elimination of the hydroxylamine [63].

2.1.1.2 Atom transfer radical polymerization (ATRP)

The Transition-metal mediated controlled/“living” radical polymerization, reported independently by Matyjaszewski [64], Sawamoto [65] and Percec [66] in 1995, is one of the most powerful techniques to obtain polymers with high control over compositions, architectures, and functionalities. The polymerization, which is mechanistically similar to atom transfer radical addition (ATRA), therefore, is often termed as atom transfer radical polymerization (ATRP).

A general mechanism for ATRP is shown in Scheme 2.2. ATRP is based on the reversible homolytic cleavage of carbon-halogen bond by a redox reaction. Homolytic cleavage of the alkyl (pseudo)halogen bond (RX) by a transition metal complex (activator, $M_t^n - Y$ / ligand, where Y may be another ligand or a counterion) in the lower oxidation state generates an alkyl radical ($R^\bullet$) and a transition metal

complex (deactivator, $X-M_t^{n+1} / \text{ligand}$) in the higher oxidation state. The formed radicals can initiate the polymerization by adding across the double bond of a vinyl monomer, propagate, terminate by either coupling or disproportionation, or be reversibly deactivated by the transition metal complex in the higher oxidation state to reform the dormant species and the activator.



This process occurs with a rate constant of activation, k_{act} , and deactivation k_{deact} , respectively. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation, k_p . Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. Other side reactions may additionally limit the achievable molecular weights.

This process generates oxidized metal complexes, the deactivators, which behave as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination at later stages. A successful ATRP will have not only small contribution of terminated chains but also uniform growth of all the chains; this is accomplished through fast initiation and rapid reversible deactivation.

The ATRP equilibrium ($K_{\text{eq}} = k_{\text{act}}/k_{\text{deact}}$) essentially mediates the rate of polymerization (R_p), defined by eq 2.1, by ensuring steady and concurrent growth of all polymer chains, resulting in well-defined polymers with narrow molecular weight distributions. K_{eq} must be low to maintain a low stationary concentration of radicals; thus, the termination reaction is suppressed.

$$R_p = k_p \cdot K_{\text{eq}} \frac{[\text{R-X}][\text{M}_t^n]}{[\text{M}_t^{n+1}]} \cdot [\text{M}] \quad (\text{Eq. 2.1})$$

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_p[R-X]}{k_{deact}[M_t^{n+1}]} \right) \left(\frac{2}{p} - 1 \right) = 1 + \frac{2}{k_{act}[M_t^n]t} \quad (\text{Eq. 2.2})$$

The rate of ATRP, R_p , has been shown to be the first order with respect to the monomer $[M]$ and initiator $[R-X]$. The rate of polymerization is also influenced by the ratio of concentrations of the activator to the deactivator, although this may change during polymerization.

Equation 2.2, which shows how the polydispersity index in ATRP (in the absence of chain termination and transfer) relates to the concentrations of initiator (RX) and deactivator (M_t^{n+1}), the rate constants of propagation (k_p), deactivation (k_{deact}), and monomer conversion (p). Lower polydispersities are obtained at higher conversion, higher k_{deact} relative to k_p , higher concentration of deactivator, and higher monomer to initiator ratio, $[M]_0/[I]_0$ [67, 68, 69].

An ATRP system consists of the monomer, an initiator, and a catalyst composed of a transition metal species complexed with any suitable ligand. A detailed discussion of the basic components of ATRP is elucidated extensively in the following sections.

Monomers

A variety of monomers, including styrene, acrylonitrile, (meth) acrylates, (meth) acrylamides, 1,3-dienes, and 4-vinylpyridine, undergo ATRP. The less reactive monomers, such as ethylene, vinyl chloride, and vinyl acetate, have not been polymerized by ATRP. Some other monomers may be difficult to polymerize since they exhibit side reactions. An example of such a monomer is 4-vinyl pyridine (4-VP), which can undergo quaternization by the (alkyl halide) initiator [70]. The most common monomers in the order of their decreasing ATRP reactivity are methacrylates, acrylonitrile, styrenes, acrylates, (meth)acrylamides [71].

Initiators

Generally, initiators used in ATRP are alkyl halides (RX) (or pseudohalides,) with α -phenyl, vinyl, carbonyl, cyano groups and multiple halogen atoms as well as any compound with a weak halogen-heteroatom bond, such as sulfonyl halides. The primary role of the initiator is to determine the number of dormant chains and to provide the end groups of the polymer chains.

To obtain well-defined polymers with narrow molecular weight distributions, the (pseudo)halide group, X, must rapidly and selectively migrate between the growing chain and the transition metal complex. Thus far, bromine and chlorine are the halogens that afford the best molecular weight control. Iodine works well for acrylate polymerizations; however, in styrene polymerizations the heterolytic elimination of hydrogen iodide is too fast at high temperatures. Fluorine is not used because the carbon–fluorine bond is too strong to undergo homolytic cleavage. As for other X groups, some pseudohalogens, specifically thiocyanates, have been used successfully in polymerization of acrylates and styrenes [72-74].

Initiator efficiency is of prime importance for successful ATRP. Generally, alkyl halides RX with resonance stabilizing substituents are efficient initiators for ATRP. Often, the structure of the initiator is analogous to the structure of the halogenated polymer chain end to obtain similar reactivity of the carbon-halogen bond. For example, styrene polymerizations often incorporate 1-phenylethyl chlorides or bromides as the initiators [75]. However, this guideline does not always hold as demonstrated in the polymerization. The use of sulfonyl chlorides as universal initiator in ATRP of styrene and methacrylates was reported [76].

The initiator can not only be a small molecule, but also a polyfunctional small molecule, or a macromolecule, which would produce end-functional polymers, star polymers, and graft copolymers, respectively.

Catalysts

Catalyst is the most important component of ATRP. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst. An efficient catalyst should be able to expand its coordination sphere and oxidation number upon halogen abstraction from an initiator (alkyl halide) or dormant polymer chains. The metal center should have reasonable affinity toward a halogen. Additionally, the catalyst should not participate in any side reactions which would lower its activity or change the radical nature of the ATRP process.

Various transition metals, such as Re [77], Ru [78], Rh [79], Fe [80-85], Ni [86,87], Pd [88] and Cu [89,90] have been successfully used as catalysts for ATRP. Among them,

Cu seems to be the most efficient metal as determined by the successful application of its complexes as catalysts in the ATRP of a broad range of monomers in diverse media [91].

Ligands

Ligands solubilize the transition metal salt in organic media and adjust the redox potential of the metal center for appropriate activity. For copper catalysts, bidentate and multidentate, but not monodentate, nitrogen ligands work best. Bridged and cyclic ligands as well as branched aliphatic polyamines yield more active catalysts than do simple linear ligands. 4,4-Dialkyl-2,20-bipyridines and tris-(2-dimethylaminoethyl)amine are examples of active ligands [92,93].

Ligands for ATRP systems include multidentate alkyl amines, pyridines, pyridineimines, phosphines, ethers or half-metallocene species. Copper complexes with various multidentate N-containing ligands are most often used as ATRP catalysts such as PMDETA, and tris[2-(dimethylamino) ethyl]amine (Me6-TREN). [93] The ATRP catalytic activity of Cu(I) complexes increases in the order bipyridine (bpy) < 1, 1, 4, 7, 10, 10- hexamethyltriethylene tetramine (HMTETA) < PMDETA < tris(2-pyridylmethyl)amine (TPMA) < Me6-TREN < dimethyl cross-bridge cyclam (DMCBCy). The most active complex known to date is derived from the cross-bridged cyclam ligand DMCBCy [67].

While nitrogen ligands are typically used for copper-based ATRP, phosphorus-based ligands are used for most other transition metals in ATRP.

Solvents

ATRP has been carried out in bulk, solution, suspension, and aqueous emulsion. A range of solvents have been used for solution polymerization, including toluene, ethyl acetate, alcohols, water, ethylene carbonate, DMF, and supercritical carbon dioxide. Apart from the usual considerations, one needs to consider if a solvent interacts with and affects the catalyst system, such as by displacement of ligands. Some polymer end groups (e.g., polystyryl halide) can undergo substitution or elimination in polar solvents at polymerization temperatures.

ATRP can be carried out in aqueous heterogeneous systems (suspension and emulsion) with proper choice of the components of the reaction system (initiator, activator, deactivator). The components need to be chosen so that they are stable in

the presence of water and soluble in the organic phase with minimal solubility in the aqueous phase [92,93].

2.1.1.3 Reversible addition–fragmentation chain transfer process (RAFT)

The most recent report of a controlled/“living” free radical polymerization has been reported by Haddleton and co-workers as well as Thang et al. Reversible addition-fragmentation chain transfer (RAFT) is achieved by performing a free radical polymerization in the presence of dithio compounds, which act as efficient reversible addition-fragmentation chain transfer agents. Much like the first two routes, the rapid switching mechanism between dormant and active chain ends affords living polymerization character [94].

Reversible addition-fragmentation chain transfer (RAFT) incorporates compounds, usually dithio derivatives, within the living polymerization that react with the propagating center to form a dormant intermediate. The dithio compound can release the alkyl group attached to the opposite sulfur atom which can then propagate with the monomer. The greatest advantage to RAFT is the incredible range of polymerizable monomers. As long as the monomer can undergo radical polymerization, the process will most likely be compatible with RAFT. However, there are many major drawback that arise when using this process. The dithio end groups left on the polymer give rise to toxicity, color, and odor and their removal or displacement requires radical chemistry. Also, the RAFT agents are expensive and not commercially available. Another drawback is that the process requires an initiator, which can cause undesired end groups and produce too many new chains which can lead to increased termination rates [56].

2.1.2 Ring-Opening Polymerization (ROP)

Ring-opening polymerization (ROP) is a unique polymerization process, in which a cyclic monomer is opened to generate a linear polymer. It is fundamentally different from a condensation polymerization in that there is no small molecule byproduct during the polymerization. Polymers with a wide variety of functional groups can be produced by ring-opening polymerizations. Preparation of cyclic monomers, studies of catalysis and mechanisms are active areas of research both in academia and industry [32-35].

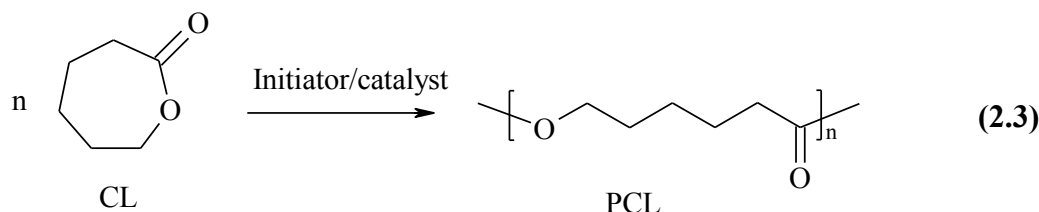
Nowadays, increasing attention is paid to degradable and biodegradable biocompatible polymers for applications in the biomedical and pharmaceutical fields, primarily because after use they can be eliminated from the body via natural pathways and also they can be a solution to problems concerning the global environment and the solid waste management. Aliphatic polyesters are among the most promising materials as biodegradable polymers.

2.1.2.1 Controlled Ring-Opening Polymerization of cyclic esters

The ring opening polymerization (ROP) of lactones and lactides to produce poly(ester)s provides versatile biocompatible and biodegradable polymers possessing good mechanical properties. These advantages have seen aliphatic poly(ester)s receive increasing attention over the last few years driven by their application as biodegradable substitutes for conventional commodity thermoplastics and applications in the biomedical field [95].

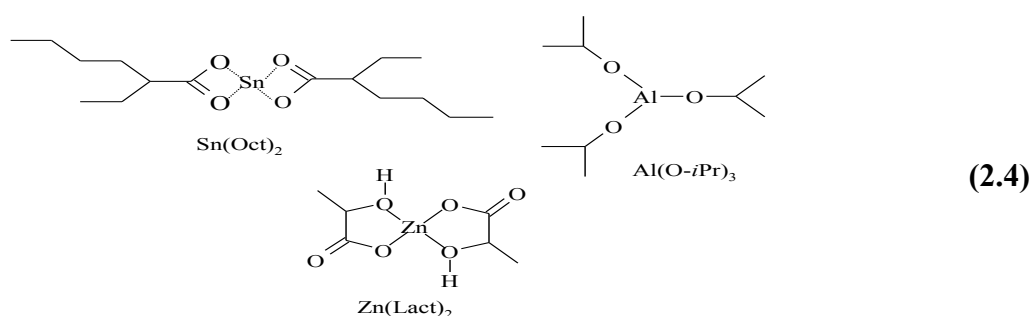
Aliphatic poly(ester)s can be either synthesized by polycondensation of hydroxyl-carboxylic acids or by the ring-opening polymerization (ROP) of cyclic esters. The polycondensation technique yields low molecular weight polyesters ($M_n < 30,000$) with poor control of specific end groups [96]. In contrast, high molecular weight aliphatic polyesters can be prepared in short periods of time by ROP. There has been much research directed towards the controlled ROP of commercially available cyclic esters including glycolide, lactide and ϵ -caprolactone resulting in aliphatic poly(ester)s with high molecular weights [97].

In practice, the ROP of lactones and lactides requires an appropriate catalyst to proceed in reasonable conditions and to afford polymers with controlled properties (2.3). Since the pioneering work of Kleine et al. in the 1950s metal-based catalytic systems have been the focus of considerable attention for the polymerization of cyclic esters, and numerous studies have been carried out to elucidate the mechanism of such coordination polymerizations. Through variation in the nature of the metal center and of the surrounding ligands, a broad range of initiators have been prepared and evaluated [98, 99, 100]. Besides the coordination-insertion mechanism, alternative strategies based on anionic, nucleophilic, or cationic promoters have also been recently (re)evaluated, the preliminary results reported in these fields being rather promising [101, 102].



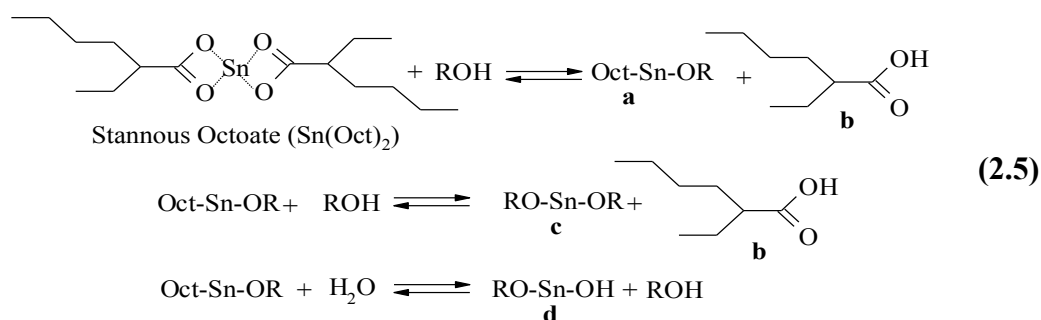
2.1.2.2 Catalysts

A large variety of organometallic compounds, such as metal alkoxides and metal carboxylates, has been studied as initiators or catalysts in order to achieve effective polymer synthesis [99]. The covalent metal alkoxides with free p or d orbitals react as coordination initiators and not as anionic or cationic initiators [103]. The most widely used complex for the industrial preparation of polylactones and polylactides is undoubtedly $\text{Sn}(\text{Oct})_2$. It is commercially available, easy to handle, and soluble in common organic solvents and in melt monomers. It is highly active and allows for the preparation of high-molecular-weight polymers in the presence of an alcohol [104]. Aluminum alkoxides have also proved to be efficient catalysts for the ROP of cyclic esters. The common example, namely, aluminum (III) isopropoxide, $\text{Al}(\text{Oi-Pr})_3$, has been largely used for mechanistic studies. However, it has been revealed to be significantly less active than $\text{Sn}(\text{Oct})_2$ [105]. Moreover, an induction period of a few minutes is systematically observed with $\text{Al}(\text{Oi-Pr})_3$ attributed to aggregation phenomenon [106]. For all these reasons, $\text{Al}(\text{Oi-Pr})_3$ is much less used for the preparation of biodegradable polyesters, and especially since aluminum ions do not belong to the human metabolism and are suspected of supporting Alzheimer's disease. Much interest has thus been devoted to zinc derivatives as potential nontoxic catalysts. Zinc powder itself is a relatively good polymerization catalyst that is used industrially [107]. With reaction times of several days at 140 °C in bulk, it is roughly as active as $\text{Al}(\text{Oi-Pr})_3$. Numerous zinc salts have also been investigated [108].



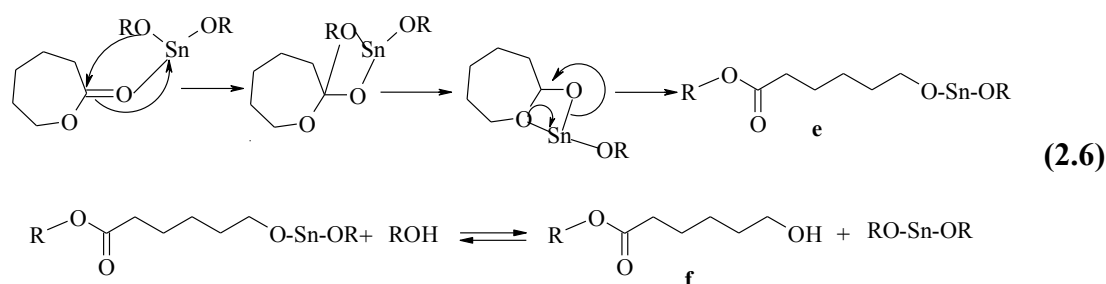
2.1.2.3 Coordination-Insertion ROP

Covalent metal carboxylates, particularly tin(II) bis(2-ethylhexanoate) usually referred to as tin(II) octanoate, $\text{Sn}(\text{Oct})_2$ belong to the most frequently used initiators for polymerization of cyclic esters due to its low cost, low toxicity, and high efficiency. Although, there are controversial reports in the literature about the nature of $\text{Sn}(\text{Oct})_2$ activity in the polymerization of lactones, two basic types of mechanism have been proposed. The first one is directly catalytic type where the catalyst serves to activate monomer through coordination with its carbonyl oxygen [109, 110]. The second mechanism is the monomer insertion type mechanism where the catalyst acts as co-initiator along with either purposely added or adventitious hydroxyl impurities, and polymerization proceeds through an activated stannous alkoxide bond [111, 112].



Kricheldorf and co-workers have recently illustrated how the structure of the alcohol initiator may influence the strength of the catalyst/alcohol interaction [110, 112]. According to these authors, this interaction, in the early stages of reaction, is responsible for formation of the “true” initiating species, subsequent ring opening, and formation of the active, propagating chain end. Prior to the beginning of polymerization, adventitious hydroxyfunctional impurities (e.g., water) or purposely added alcohol first complex and subsequently react with $\text{Sn}(\text{Oct})_2$ producing a stannous alkoxide species (a) and free 2-ethylhexanoic acid (b) as shown in 2.5. Further reaction with a second equivalent of alcohol produces the stannous dialkoxide initiator (c) and releases a second equivalent of 2-ethylhexanoic acid (b) as depicted in 2.5 [111]. Adventitious water, meanwhile, serves mainly as a catalyst deactivator via a reversible reaction with a or c, thereby decreasing the concentration of active initiator and producing a stannous alcohol derivative (d), such as shown in

2.5, which is more thermodynamically stable than the stannous dialkoxide and is less efficient as an initiator [112].



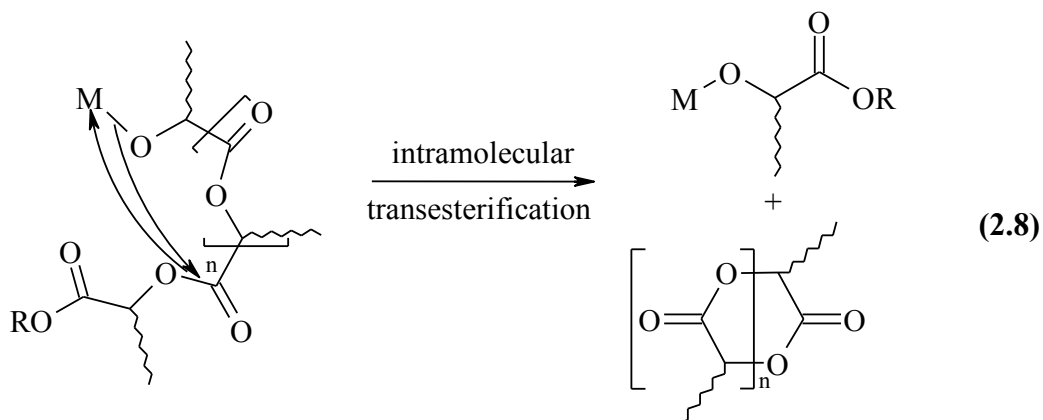
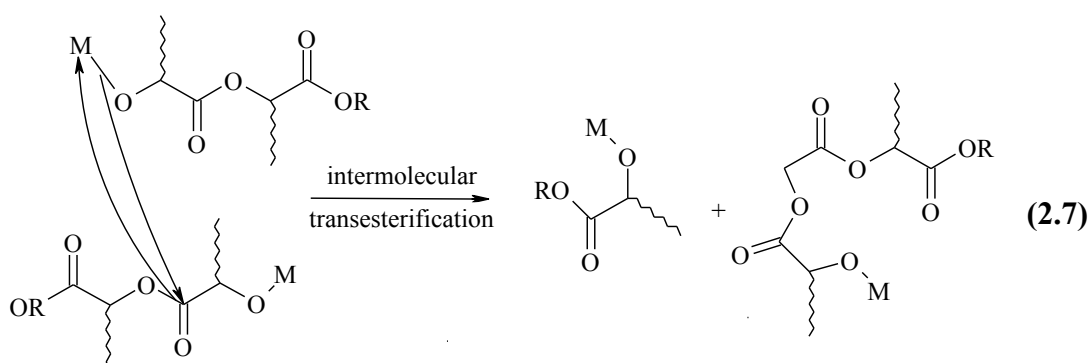
Reaction of **c** with monomer by means of coordination- insertion generates the first actively propagating chain end (**e**) consisting of not only the initiating alcohol fragment but also the active propagating center derived from the first monomer unit and stannous alkoxide. The **e** species may either propagate or undergo rapid intermolecular exchange of the stannous alkoxide moiety for a proton from either hydroxyl groups of initiator (if remaining) or another hydroxy chain end, either **e** or polymeric in nature. This rapid exchange of protons and stannous alkoxide moieties results in a dynamic equilibrium between activated and deactivated chain ends as depicted in 2.6, where R= unreacted alcohol initiator or hydroxy chain ends generated in situ. This process eventually consumes the remaining unreacted alcohol initiator not involved in the initial formation of **c**. ROP based on coordination-insertion mechanism has been thoroughly investigated since it may yield well-defined polyesters through living polymerization [103, 114].

In such coordination-insertion polymerizations the efficiency of the molecular-weight control depends from the ratio $k_{\text{propagation}}/k_{\text{initiation}}$ but also from the extent of transesterification side reactions. These transesterification reactions can occur both intramolecularly (backbiting leading to macrocyclic structures and shorter chains) and intermolecularly (chain redistributions) (2.7-2.8) [115]. Intermolecular transesterification reactions modify the sequences of copoly lactones and prevent the formation of block co-polymers. Intramolecular transesterification reactions cause degradation of the polymer chain and the formation of cyclic oligomers.

The polymerization/depolymerization equilibrium should also be taken into account as a particular case of intramolecular transesterification reaction. All of these side reactions result in broader molecular-weight distributions, sometimes making the

molecular weights of the resulting polymers irreproducible. The extent of these undesirable transesterification reactions was found to strongly depend on the metallic initiator [64]. Side reactions occur from the very beginning of the polymerization with $\text{Sn}(\text{Oct})_2$, leading to rather broad MWD (PDI indexes around 2) but only at high or even complete conversion with $\text{Al}(\text{Oi-Pr})_3$, yielding lower PDI indexes (less than 1.5) [105,116].

Parameters that influence the number of transesterifications are temperature, reaction time, and type and concentration of catalyst or initiator. Depending on the metal used, the initiator is more or less active towards transesterification reactions [116].



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

2.1.2.4 Poly(ϵ -caprolactone)

Poly(ϵ -caprolactone) (PCL) is a semicrystalline polymer which represents one of several aliphatic polyesters that undergo degradation and absorption in vivo [117,118]. The repeating molecular structure of PCL homopolymer consists of five non-polar methylene groups and a single relatively polar ester group. Although not produced from renewable raw materials, PCL is a fully biodegradable thermoplastic polymer due to the presence of the hydrolytically unstable aliphatic-ester linkage. PCL has good water, oil, solvent and chlorine resistance.

PCL has some unusual properties, including a low T_g (~ -60 °C) and T_m (~ 60 °C) and a high thermal stability. These properties are related to PCL's chain of carbons, as longer chains give rise to less mobility and lower T_m 's and T_g 's. PCL is also highly permeable, which results from its low T_g and subsequent rubbery state at room temperature.

PCL is one of biodegradable polymers which have been used to prepare functional materials [119]. Copolymers containing poly(ϵ -caprolactone) (PCL) are especially interesting because they are miscible with a wide range of polymers, and they have features like crystallizability, lack of toxicity, ability to disperse pigments, low-temperature adhesiveness, and printability [120].

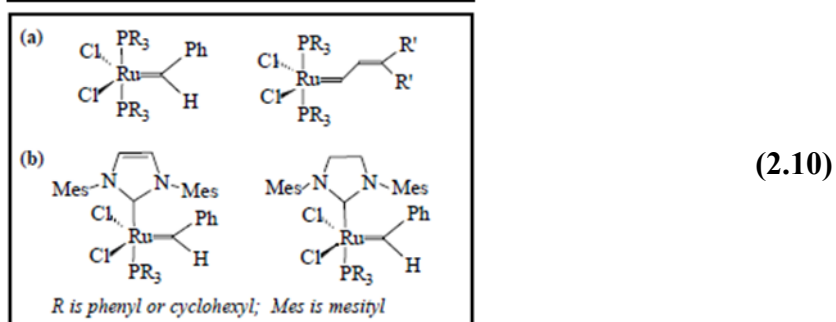
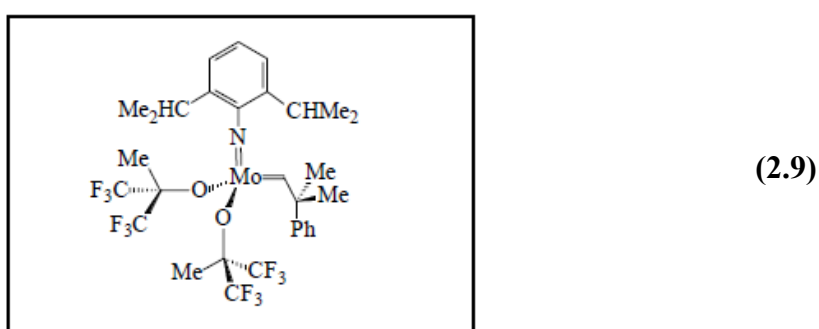
PCL has been increasingly studied in the scientific community and applied for drug delivery and tissue engineering [121]. Owing to its high crystallinity and strong hydrophobicity of polymer backbone, PCL homopolymer usually shows slow biodegradation and drug-release rate [122].

2.1.3 Ring-opening metathesis polymerization (ROMP)

Although a relatively new player on the field of polymer chemistry, ring-opening metathesis polymerization (ROMP) has emerged as a powerful and broadly applicable method for synthesizing macromolecular materials. The origins of ROMP can be traced to the mid-1950s when various metals and reagents were combined to uncover new transformations and reactivities involving olefins. However, the rapid rise in popularity and utility of this polymerization technique is the result of extensive work on the identification and isolation of key intermediates involved in the general olefin metathesis reaction. This led to the development of well-defined

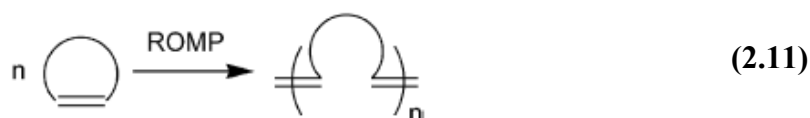
ROMP catalysts and ultimately enabled the synthesis of a wide range of polymers with complex architectures and useful functions [12].

It was only in 1971 that a metal-carbene intermediate was proposed by Y. Chauvin, to explain – satisfactorily for the first time – the mechanism. This extraordinary mechanistic proposal, rationalising Chauvin’s astonishing new observations, was immediately embraced by the metathesis community and prompted studies on metal-carbene initiators culminating in the creation of the molybdenum-alkylidene catalysts by R. R. Schrock (**2.9**), and the 1st and 2nd generation of ruthenium-alkylidene catalysts, by R. H. Grubbs (**2.10**) [123].



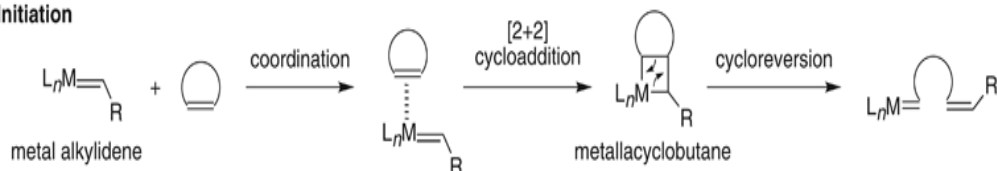
2.1.3.1 ROMP essentials: mechanism and thermodynamics

The word metathesis comes from the Greek *meta* (change) and *tithemi* (place). In olefin chemistry, it refers to the pair-wise exchange of substituents on a carbon-carbon double bond [124]. Ring-opening metathesis polymerization (ROMP) is a chain growth polymerization process where a mixture of cyclic olefins is converted to a polymeric material (**2.11**). The mechanism of the polymerization is based on olefin metathesis, a unique metal-mediated carbon-carbon double bond exchange process. As a result, any unsaturation associated with the monomer is conserved as it is converted to polymer. This is an important feature that distinguishes ROMP from typical olefin addition polymerizations (e.g. ethylene → polyethylene).



Chauvin proposed a general mechanism for ROMP in 1971 [16]. Initiation begins with coordination of a transition metal alkylidene complex to a cyclic olefin (2.12)

Initiation



Propagation



Termination



After formation of the metal-carbene complex, subsequent [2+2] cycloaddition forms a highly strained metallacyclobutane intermediate. The ring in the intermediate opens to give a new metal alkylidene. The chain growth process proceeds during the propagation stage until all monomer is consumed. Then living ROMP reaction is terminated by adding specialized reagent.

There are three important features regarding metal-mediated ROMP reactions. First, it is important to note that the propagating metal centers on the growing polymer chains may exist in either the metallacyclobutane or metal alkylidene form. This difference depends on the transition metal and its associated ligands, as well as the reaction conditions. Second, like most olefin metathesis reactions, ROMP reactions are generally reversible. Third, although most ROMP reactions are reversible, they are equilibrium-controlled and the position of the equilibrium (monomer vs. polymer) can be predicted by considering the thermodynamics of the polymerization. As with other ring-opening polymerizations, the reaction is driven from monomer to polymer by the release of strain associated with the cyclic olefin (so-called “ring strain”) balanced by entropic penalties. The most common monomers used in ROMP

are cyclic olefins which possess a considerable degree of strain (45 kcal/mol) such as cyclobutene, cyclopentene, cis-cyclooctene, and norbornene.

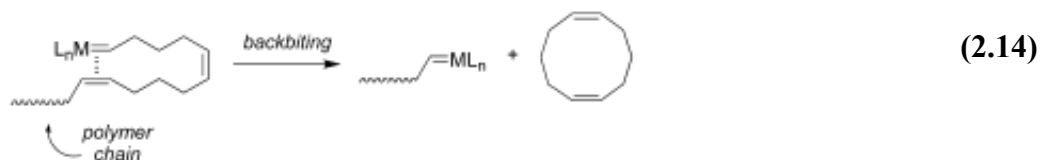
Generally, the most favorable conditions for a successful ROMP reaction is to use the highest monomer concentration at the lowest temperature possible, due to enthalpic contribution from the relief of ring strain [12].

In addition to the general ROMP mechanism illustrated in equation 2.12 (and its related depolymerization mechanism), the equilibria noted above can be established via other metathetical pathways, including intermolecular chain-transfer and intramolecular chain-transfer (so-called “backbiting”) reactions. Examples of these types of secondary metathesis reactions are shown in equations 2.13 and 2.14. In an intermolecular chain-transfer reaction, one polymer chain containing an active metal alkylidene on its terminus can react with any olefin along the backbone of a different polymer chain in the same reaction vessel. Although the total number of polymer chains remains the same, the molecular weights of the individual polymers will increase or decrease accordingly. In a backbiting reaction, the active terminus of a polymer chain reacts with itself to release a cyclic species and a polymer chain of reduced molecular weight. Collectively, these chaintransfer reactions effectively broaden molecular weight distribution (or polydispersity) of the system.

Intermolecular Chain Transfer:



Intramolecular Chain Transfer:

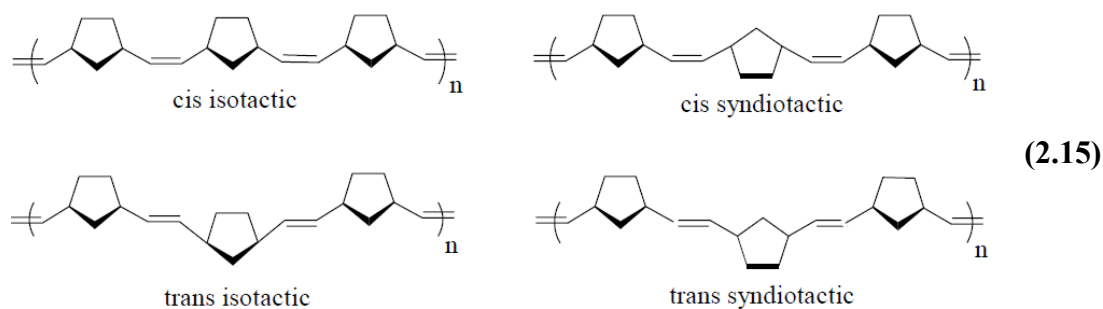


Another implication of equilibrium controlled polymerizations such as ROMP is the propensity to form cyclic oligomers. According to the Jacobson–Stockmayer theory of ring–chain equilibria, the formation of cyclic oligomers will always accompany the formation of high molecular weight polymer. The total amount of cyclic species present will depend on factors such as solvent, cis/trans ratio of the polymer

backbone, rigidity of the monomer, reaction time, and concentration. Formation of cyclic species is favored at higher temperatures and lower concentrations with a critical value dependent on the factors noted above. While these side reactions challenge the realization of living polymerizations based on ROMP, they can be advantageous. For example, cyclic oligomers can be synthesized in high yields by simply conducting the ROMP reaction under relatively dilute conditions.

A “living polymerization” was defined by Swarc as a reaction proceeding without chain transfer or termination. Besides Swarc’s original concept of the living polymerization, a ROMP reaction requires three more features for its living and controlled reaction. First, the initiation should be fast and complete. Second, there should be a linear relationship between polymer formation and monomer consumption. Third, polymers should be narrowly polydispersed with PDIs < 1.5 [12].

ROMP polymers can display a very rich microstructure. Depending on the monomer, three main characteristics can be observed: *cis/trans* isomerism, tacticity, and head-to-tail bias. *Cis/trans* isomerism is present in all ROMP polymers and relatively easy to quantify using spectroscopic techniques. Analysis of tacticity has only been successful with polymers made from prochiral monomers (2.15). Head-to-tail bias can be observed with non-symmetrical monomers.



The *cis/trans* isomerism is hard to predict as it results from the specific interaction between the metal complex and the monomer, and therefore can depend on the geometry of the metal center, the bulkiness of the metal substituents, and also the properties of the cyclic monomer (sterics and electronics). The reactions conditions (temperature, solvent) are also important as they can affect the organization of the ligands around the metal center. All these factors will influence the relative ease of formation of the intermediate *cis* and *trans* metallacyclobutanes. The use of well-defined metal carbene catalysts provided a better understanding of the factors

influencing the cis/trans isomerism and stereoselective polymerizations have been achieved in some particular cases [124].

2.1.3.2 Well-Defined Catalysts for ROMP

The studies of two groups deserve particular attention – as recognized by the award of the 2005 Nobel Prize for chemistry to R.H. Grubbs and R.R. Schrock. The award was shared with Y. Chauvin, who was honored for his fundamental studies on metathesis. The investigations of Grubbs and Schrock led to the development of well-defined transition metal alkylidenes that rapidly outrivaled any other initiator or initiation system, particularly those consisting of an often serendipitous mixture of transition metal salts, alcohols and tin alkyls [125].

Schrock-type initiators

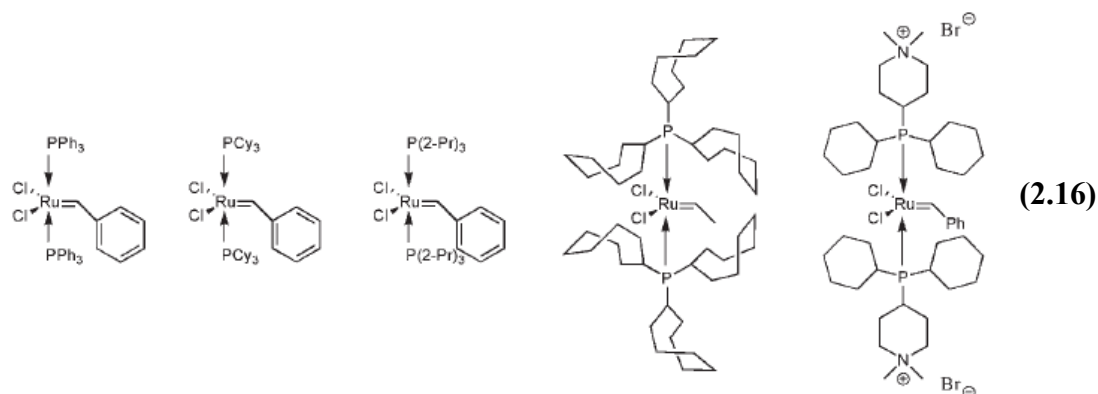
The synthesis of well-defined, high-oxidation state molybdenum alkylidenes was first reported by Schrock and coworkers in 1990. These, and the analogous tungsten systems, are now commonly named ‘Schrock-catalysts’. The systems possess the general formula $M(NAr')(OR')_2(CHR).L$, where $M = Mo, W$; $Ar' =$ phenyl or a substituted phenyl group; $R =$ ethyl, phenyl, trimethylsilyl, CMe_2Ph or t -butyl; $R' = CMe_3, CMe_2CF_3, CMe(CF_3)_2, C(CF_3)_2$, aryl, and so on, while $L =$ quinuclidine, trialkylphosphane and tetrahydrofuran (THF) [125].

The Schrock type catalysts are very active and somewhat tolerant with functional groups during ring open metathesis polymerization [126]. In 1993, first chiral molybdenum carbene catalyst was introduced. Then, Schrock and Hoveyda developed more active chiral molybdenum carbene catalyst system, they are so-called the Schrock-Hoveyda catalysts [127].

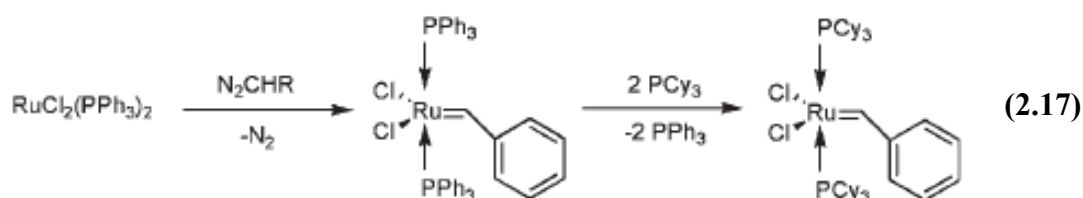
Grubbs-type initiators

In 1992, Grubbs described the synthesis of the first well-defined ruthenium alkylidene. Thus, the reaction of $RuCl_2(PPh_3)_3$ and $RuCl_2(PPh_3)_4$, respectively, with 2,2-diphenylcyclopropene in benzene or methylene chloride yielded the desired ruthenium carbene complex $RuCl_2(PPh_3)_2(CH=CH=CPh_2)$. As is the case of Schrock-type catalysts, the alkylidene proton in $RuCl_2(PPh_3)_2(CH=CH=CPh_2)$ experiences an agostic interaction with the metal, resulting in downfield NMR shifts for H_α and C_α to $\delta = 17.94$ and 288.9 ppm, respectively (both in C_6D_6). Despite a ratio

of $k_i/k_p < 1$ (k_p = rate constant of polymerization, k_i = rate constant of initiation), the compound was found to be a quite efficient initiator for the polymerization of norbornene (NBE) and substituted NBEs. The comparably low activity of the bis(triphenylphosphane)-derivative for other cyclic olefins than NBE such as bicyclo [3.2.0]hept-6-ene or trans-cyclo-octene was successfully enhanced by phosphane exchange with more basic analogues, for example tricyclohexylphosphane and tri-(2-propyl) phosphane (2.16) [125].



An alternative route to ruthenium alkylidenes that avoided the preparation of 2,2-diphenylcyclopropene was elaborated by Schwab and Grubbs. The synthetic protocol entailed the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with an diazoalkane (2.17) [125].



Via this route, the resulting compounds of the general formula $\text{RuCl}_2(\text{PR}_3)_2(\text{CHPh})$, ($\text{R}=\text{Ph}, \text{Cy}_3$)— which today are well known as the first-generation Grubbs catalyst—are accessible in high yields [125].

The Ru-based catalysts have exceptional functional group tolerances compared to other transition metal-based catalysts, especially toward polar functionalities. The first homogeneous well-defined Ru complex for ROMP was $(\text{PPh}_3)_2\text{Cl}_2\text{Ru}=\text{CH}-\text{CH}=\text{CPh}_2$ [128]. Although this catalyst has a broad range of functional group tolerance and mediates living ROMP reaction with norbornene and cyclobutene monomers, the catalytic activities for other olefins are reduced. To increase the catalytic activities, the bulky and electron-rich phosphine ligands were substituted.

Table 2.1 : Functional group tolerance of early and late transition metal-based ROMP catalysts

Reactivity	Ti/Ta	W	Mo	Ru
	acids	asids	asids	olefins
	alcohols	alcohols	alcohols	asids
	aldehydes	aldehydes	aldehydes	alcohols
	ketones	ketones	olefins	aldehydes
	esters/amides	olefins	ketons	ketons
	olefins	esters/amides	esters/amides	esters/amides

The catalysts containing phosphine are tolerant to a broader range of functional groups, such as water and alcohols. However, ROMP reactions of norbornene with the catalyst containing phosphine are not controlled. Because of the different reaction rates between initiation and propagation, the catalyst is not able to provide the desired polymers. Besides, chain transfer reactions occur to yield broadly polydispersed polymers ($PDI > 2$) [28].

2.1.3.3 Norbornene: the traditional ROMP monomer

Most common ROMP polymers are derived from norbornene-type monomers. The norbornene structure has recently been used extensively to introduce a variety of functional groups into polymers [129].

Interesting properties are associated with the polynorbornene backbone itself: high glass transition temperature and good thermal stability for example. One disadvantage could be its tendency to easily oxidize in air, but the unsaturation can be removed by hydrogenation.

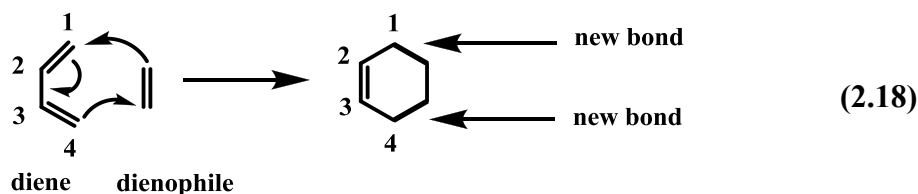
Also, as compared to other commercial polymerization techniques such as free radical polymerizations, the current ROMP-norbornene system is very attractive. One major problem of radical polymerization is molecular weight control because of chain transfer and termination processes. Controlled/"living" free radical polymerization can be obtained by nitroxyl radical-mediated polymerization and atom transfer radical polymerization (ATRP) [130]. But, those living polymerizations usually require long reaction time for completion. Molecular weight control can also be achieved with living ionic polymerizations but the stringent conditions limit their utility to non-functionalized monomers.

2.2 Click Chemistry

“Click chemistry” is a chemical term introduced by Sharpless in 2001 and describes chemistry tailored to generate substances quickly and reliably by joining small units together [36]. Click chemistry can be summarized only one sentence: “Molecules that are easy to make”. Sharpless also introduced some criteria in order to fulfill the requirements as reactions that: are modular, wide in scope, high yielding, create only inoffensive by-products, are stereospecific, simple to perform and that require benign or easily removed solvent. Nowadays there are several processes have been identified under this term in order to meet these criterias such as nucleophilic ring opening reactions; non-aldol carbonyl chemistry; thiol additions to carbon–carbon multiple bonds (thiol-ene and thiol-yne); and cycloaddition reactions. Among these selected reactions, copper(I)-catalyzed azide-alkyne (CuAAC), atom transfer nitroxide reaction coupling (ATNRC) and Diels-Alder (DA) cycloaddition reactions have gained much interest among the chemists not only the synthetic ones but also the polymer chemists. From this point view, these reactions will shortly be summarized.

2.2.1 Diels-Alder reaction

The Diels-Alder (DA) reaction is a concerted $[4\pi+2\pi]$ cycloaddition 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 (**2.18**). This reaction is named for Otto Diels and Kurt Alder, who received the 1950 Nobel prize for discovering this useful transformation [131-133].

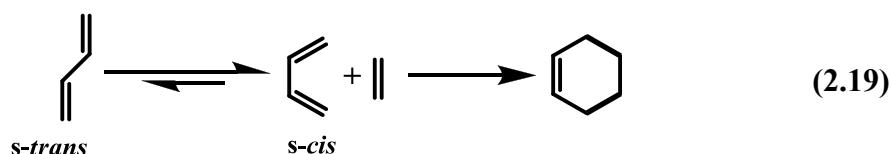


Typically, the DA reaction works best when either the diene is substituted with electron donating groups (like -OR, -NR₂, etc) or when the dienophile is substituted with electron-withdrawing groups (like -NO₂, -CN, -COR, etc). Many different versions of the DA reaction were elaborated, including intramolecular $[4+2]$

cycloadditions, hetero-Diels-Alder (HDA) reactions, pressure-accelerated DA reactions, and Lewis acid accelerated DA reactions [134].

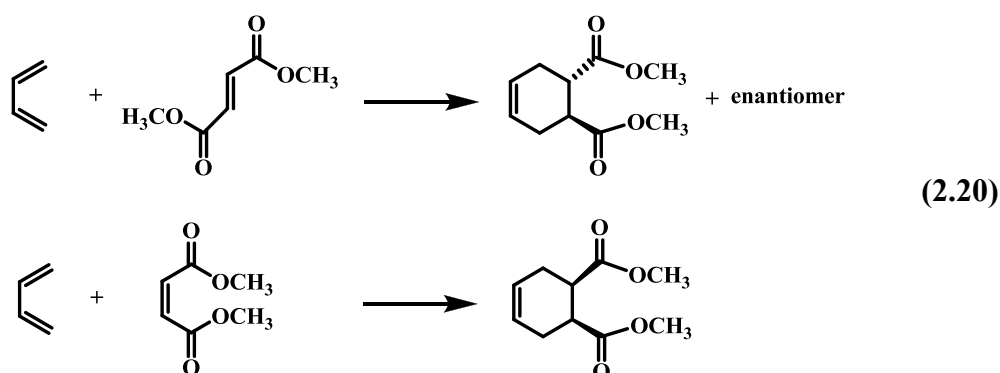
2.2.1.1 Stereochemistry of Diels-Alder reaction

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 (2.19).



The “s” in *s-cis* and *s-trans* refers to “sigma”, and these labels describe the arrangement of the double bonds around the central sigma bond of a diene. Dienes exist primarily in the lower energy *s-trans* conformation, but the two conformations are in equilibrium with each other. The *s-cis* conformation is able to react in the DA reaction and the equilibrium position shifts towards the *s-cis* conformer to replenish it. Over time, all the *s-trans* conformer is converted to the *s-cis* conformer as the reaction proceeds. Dienes such as cyclopentadiene that are permanently “locked” in the *s-cis* conformation are more reactive than those that are not.

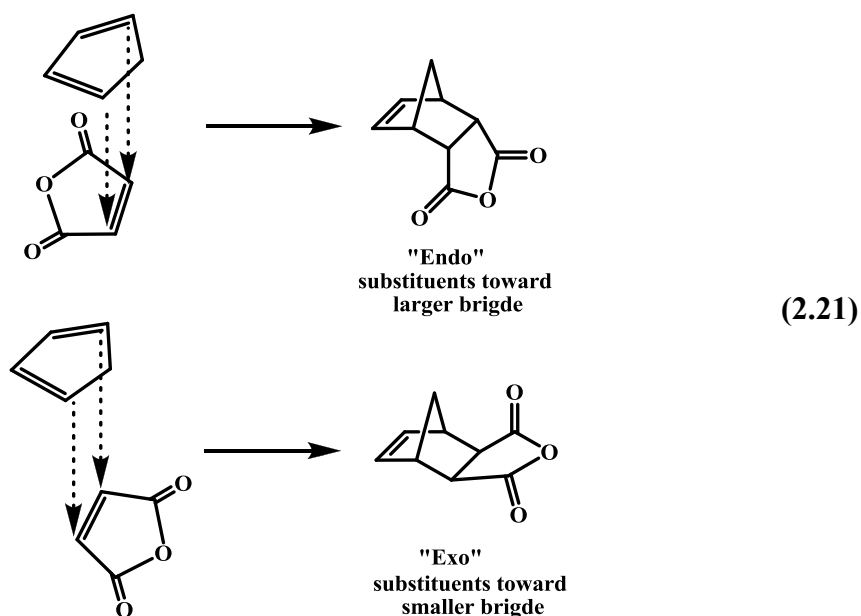
Since the reaction proceeds in a concerted fashion (*i.e.*, bonds are being formed and broken at the same time), substituents that are *cis* on the dienophile will also be *cis* in the product, and substituents that are *trans* on the dienophile will be *trans* in the product (2.20) [134-138].



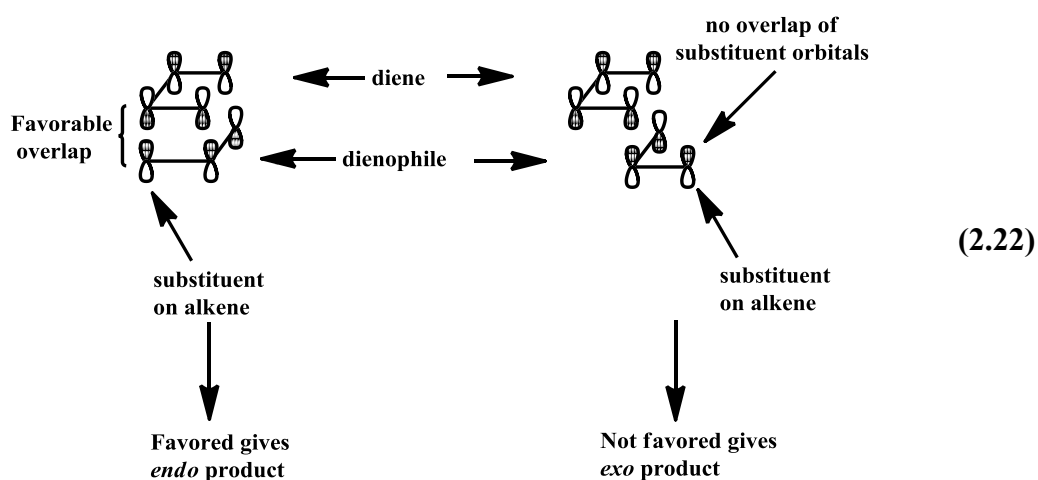
A unique type of stereoselectivity is observed in DA reactions when the diene is cyclic. In the reaction of maleic anhydride with cyclopentadiene, for example, the *endo* isomer is formed (the substituents from the dienophile point to the larger

bridge) rather than the *exo* isomer (the substituents from the dienophile point away from the larger bridge) (2.21).

The preference for *endo*-stereochemistry is "observed" in most DA reactions. The fact that the more hindered *endo* product is formed puzzled scientists until Woodward, Hoffmann, and Fukui used molecular orbital theory to explain that overlap of the *p* orbitals on the substituents on the dienophile with *p* orbitals on the diene is favorable, helping to bring the two molecules together [136,137].



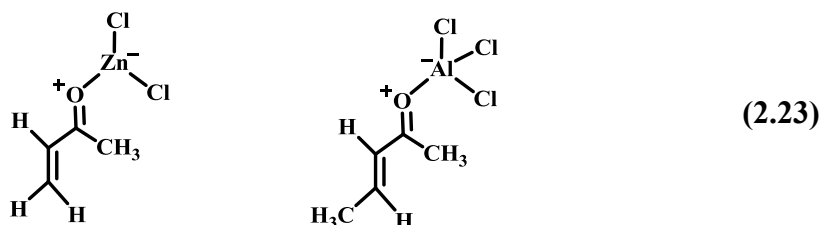
Hoffmann and Fukui shared the 1981 Nobel Prize in chemistry for their molecular orbital explanation of this and other organic reactions. In the illustration below, notice the favorable overlap (matching light or dark lobes) of the diene and the substituent on the dienophile in the formation of the *endo* product (2.22):



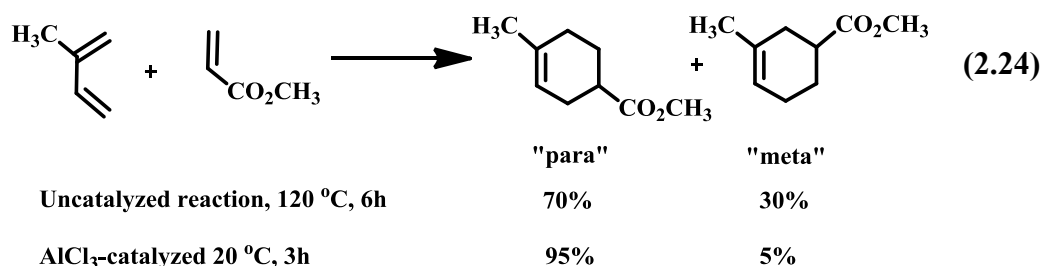
Oftentimes, even though the *endo* product is formed initially, an *exo* isomer will be isolated from a DA reaction. This occurs because the *exo* isomer, having less steric strain than the *endo*, is more stable, and because the DA reaction is often reversible under the reaction conditions. In a reversible reaction, the product is formed, reverts to starting material, and forms again many times before being isolated. The more stable the product, the less likely it will be to revert to the starting material. The isolation of an *exo* product from a DA reaction is an example of an important concept: thermodynamic vs kinetic control of product composition. The first formed product in a reaction is called the kinetic product. If the reaction is not reversible under the conditions used, the kinetic product will be isolated. However, if the first formed product is not the most stable product and the reaction is reversible under the conditions used, then the most stable product will often be isolated.

2.2.1.2 Catalysis of Diels-Alder reactions by Lewis acids

The DA reactions are catalyzed by many Lewis acids, including SnCl_4 , ZnCl_2 , AlCl_3 , and derivatives of AlCl_3 [134]. A variety of other Lewis acids is effective catalysts. The types of dienophiles that are subject to catalysis are typically those with carbonyl substituents. Lewis acids form complexes at the carbonyl oxygen and this increases the electron-withdrawing capacity of the carbonyl group (2.23) [139].



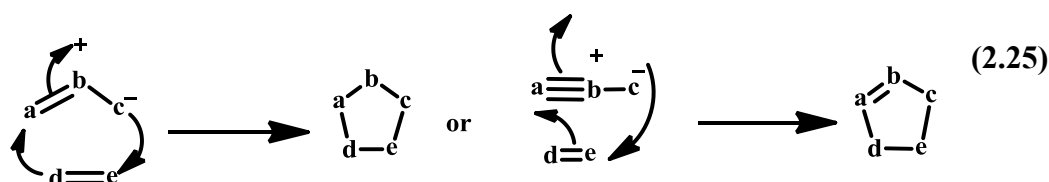
This complexation accentuates both the energy and orbital distortion effects of the substituent and enhances both the reactivity and selectivity of the dienophile relative to the uncomplexed compound [140]. Usually, both regioselectivity and *exo*, *endo* stereoselectivity increases. Part of this may be due to the lower reaction temperature. The catalysts also shift the reaction toward a higher degree of charge transfer by making the electron-withdrawing substituent more electrophilic (2.24).



The solvent also has an important effect on the rate of DA reactions. The traditional solvents were nonpolar organic solvents such as aromatic hydrocarbons. However, water and other polar solvents, such as ethylene glycol and formamide, accelerate a number of DA reactions [141-144]. The accelerating effect of water is attributed to “enforced hydrophobic interactions” [142]. That is, the strong hydrogenbonding network in water tends to exclude nonpolar solutes and forces them together, resulting in higher effective concentrations.

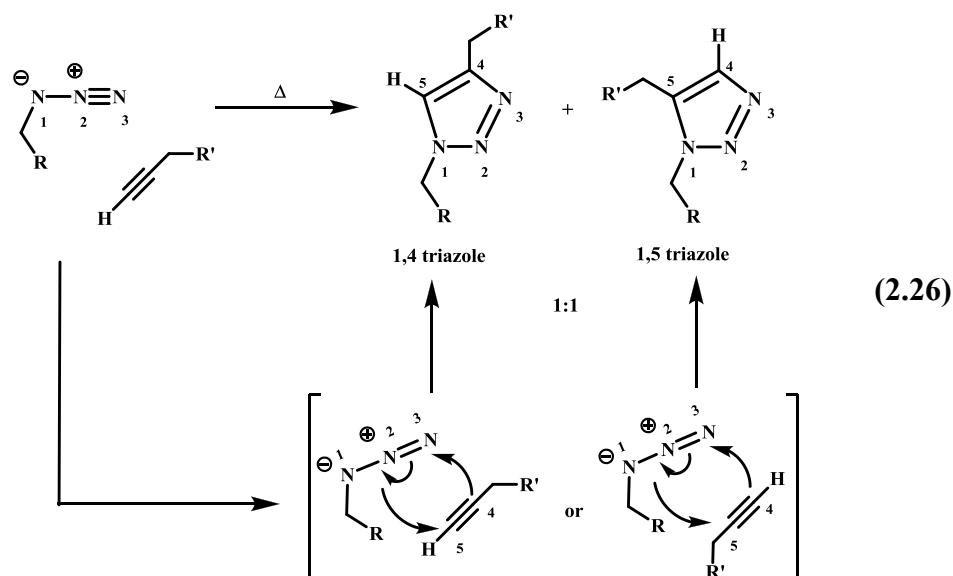
2.2.2 Copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC)

There is a large class of reactions known as 1,3-dipolar cycloaddition reactions (1,3-DPCA) that are analogous to the Diels-Alder reaction in that they are concerted $[4\pi+2\pi]$ cycloadditions [145,146]. 1,3-DPCA reactions can be represented as shown in the following diagram. The entity a-b-c is called the *1,3-dipole* and d-e is the *dipolarophile* (2.25).



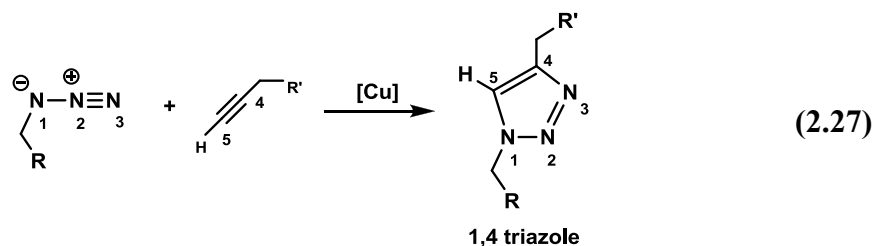
The 1,3-dipoles have a π -electron system consisting of two filled and one empty orbital and are analogous with the allyl or propargyl anion. Each 1,3-dipole has at least one charge-separated resonance structure with opposite charges in a 1,3-relationship. It is this structural feature that leads to the name 1,3-dipole for this class of reactants. The dipolarophiles are typically substituted alkenes or alkynes but all that is essential is a π bond, and other multiply bonded functional groups such as carbonyl, imine, azo, and nitroso can also act as dipolarophiles. The reactivity of dipolarophiles depends both on the substituents present on the π bond and on the nature of the 1,3-dipole involved in the reaction. Owing to the wide range of

structures that can serve either as a 1,3-dipole or as a dipolarophile, the 1,3-DPCA is a very useful reaction for the construction of five-membered heterocyclic rings. At this point, a particular interest must be given to Ralf Huisgen for his pionering works on this field (Huisgen 1,3-DPCA) [147]. In his studies, various five-membered heterocyclic rings such as triazole, triazoline, isoxazole, 4-isoxazoline etc. were described. The triazole ring, formed via Huisgen 1,3-DPCA reaction between an azide and an alkyne have gained much interest due to its chemically inert character e. g. oxidation, reduction and hydrolysis. The reason behind this fact lies in the inert character of the two components (azide and alkyne) to biological and organic conditions. Elevated temperatures and long reaction times are important requirements for the triazole formation as stated by Huisgen. Good regioselectivity in the uncatalyzed Huisgen type cycloaddition is observed for coupling reactions involving highly electron-deficient terminal alkynes, but reactions with other alkynes usually afford mixtures of the 1,4- and 1,5-regioisomers (**2.26**) [148].

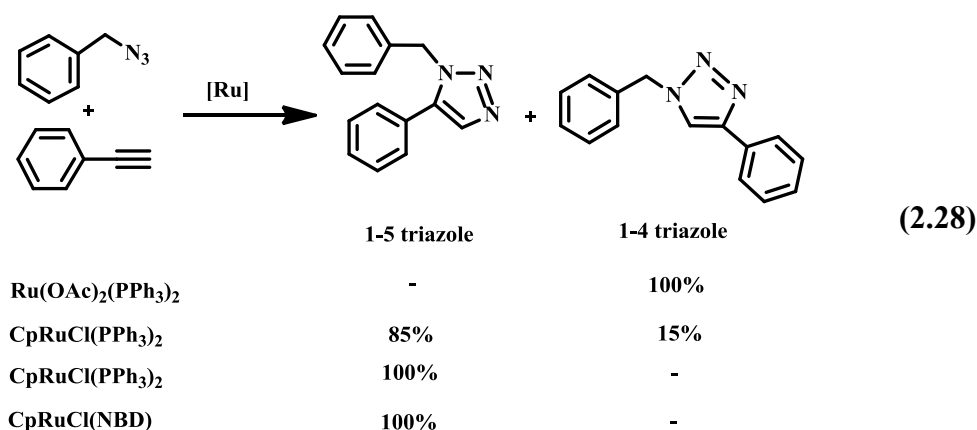


Thus, only following the recent discovery of the advantages of Cu(I)-catalyzed alkyne–azide coupling, reported independently by the Sharpless and Meldal groups, did the main benefits of this cycloaddition become clear [148, 149]. Cu(I) catalysis dramatically improves regioselectivity to afford the 1,4-regioisomer exclusively (**2.27**) and increases the reaction rate up to 10^7 times eliminating the need for elevated temperatures [151]. This excellent reaction tolerates a variety of functional groups and affords the 1,2,3-triazole product with minimal work-up and purification, an ideal click reaction [149,150]. Stepwise cycloaddition catalyzed by a monomeric Cu(I) species lowers the activation barrier relative to the uncatalyzed process by as

much as 11 kcal/mol, which is sufficient to explain the incredible rate enhancement observed under Cu(I) catalysis.



In fact, the discovery of Cu(I) efficiently and regiospecifically unites terminal alkynes and azides, providing 1,4-disubstituted 1,2,3-triazoles under mild conditions, was of great importance. On the other hand, Fokin and Sharpless proved that only 1,5-disubstituted 1,2,3-triazole was obtained from terminal alkynes when the catalyst switched from Cu(I) to ruthenium(II) [152]. In their experiments, one point has to be stressed, all reactions require higher temperatures with respect to Cu(I) catalyst systems, performed at room temperature **(2.28)**.



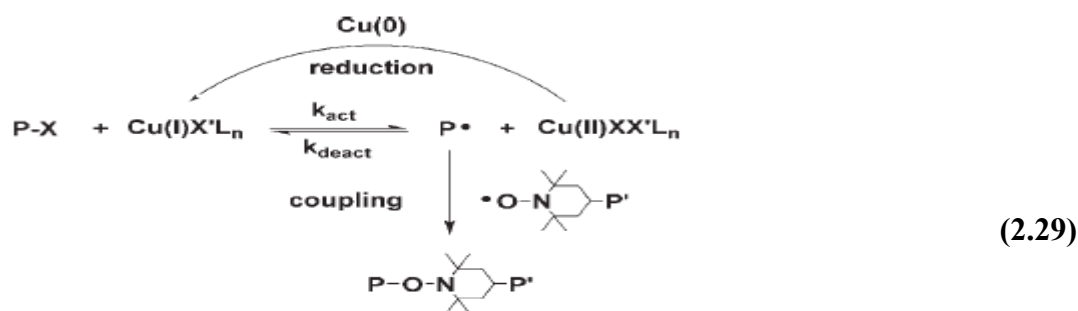
2.2.3 Atom Transfer Nitroxide Radical Coupling Reaction (ATNRC)

Recently, Huang and co-workers reported a new coupling reaction called atom transfer nitroxide radical coupling (ATNRC) chemistry, [40-44] which was realized by mixing a TEMPO-containing polymer with another Br-containing polymer in the presence of CuBr/PMDETA catalytic system. The coupling efficiency of ATNRC was as high as 90%, 48,49 which is similar to that of click chemistry. Thus, ATNRC can serve as a relatively convenient and safe way with “click-like” efficiency to synthesize multiarm star polymer, the graft copolymers with certain structures using

the grafting-onto strategy. When compared with azide group, TEMPO group is less sensitive to light, shock, and thermal changes, which makes the polymer materials stable. In ATNRC reaction, CuBr participated in the reaction was served as reactant and its action was quite different from the ATRP. If some Cu(0) was added, the Cu(0) would react with the formed Cu^{+2} and the Cu^{+1} was regenerated, which promoted the reaction completely. Thus, under the ATNRC conditions (such as the Cu(0)/CuBr/PMDETA system), the graft, the star-shaped, and the linear copolymer were prepared successfully with high efficiency [45-47].

A new reversible coupling strategy termed atom transfer nitroxide radical coupling (ATNRC) [153-160] has the attributes of a “click” reaction. This reaction involves formation of a carbon centered radical by an atom transfer reaction with Cu(I)Br and trapping of this radical with a persistent nitroxide radical at close to diffusion-controlled rates. The unique aspect of this reaction is its reversibility, in which the product alkoxyamine can readily be converted to the starting incipient radical and parent nitroxide at elevated temperatures ($>100\text{ }^{\circ}\text{C}$ when TEMPO-type nitroxides are used) [161-163]. This methodology has been used to synthesize degradable and reversibly coupled linear multiblock copolymers, block and graft copolymers in the presence of a 10-fold molar excess of copper species per halide end group [159]. The rate determining step in the coupling reaction is the speed (k_{act}) at which the halide end groups on the polymer chains convert (or are activated) to the carbon-centered radical via atom transfer reactions with Cu(I) species.

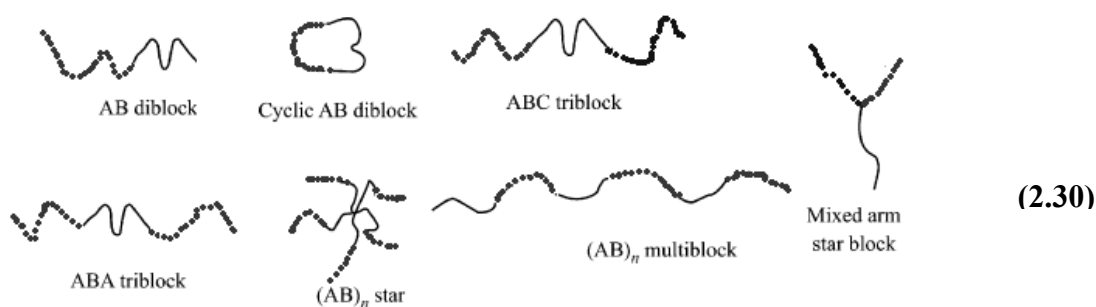
Recently, our group reported a new coupling reaction: “atom transfer nitroxide radical coupling” (ATNRC) reaction.[164] In which the bromine end-functional group of one polymer served as oxidant is reduced to bromine anion and carbon radical is formed. The Cu^{1+} is oxidized to Cu^{2+} in the presence of CuBr/ ligand. Then polymeric radical is immediately captured by another 2,2,6,6-tetramethyl-piperidinyl-1-oxy (TEMPO) end-functional polymer, and alkoxyamine is formed between the two polymers [165]. (2.29). Since the bromine and TEMPO are the typical groups for ATRP and nitroxide-mediated polymerization (NMP), ATNRC reaction can be widely used in synthesis of polymers with various structure.



2.3 Topology

2.3.1 Block Copolymers

Block copolymers, or more general segmented copolymers, are a fascinating class of polymeric materials made by covalent bonding of two or more chemically different polymeric chains that, in most cases, are thermodynamically incompatible giving rise to a rich variety of microstructures in bulk and in solution. In this way, versatile properties can be combined, leading to the possibility of using block copolymers as compatibilizers, impact modifiers, surface modifiers, coating materials, antistatic agents, adhesives, for drug delivery and information storage [166-167]. Their properties, including their mechanical, thermal, and solubility behavior, can be controlled through their composition. Another well-known application field is their use as thermoplastic elastomers in which soft and rigid segments are covalently combined. Block copolymers can be synthesized by various ways such as sequential addition of monomers to a living polymerization system, transformation approach, the use of dual or heterofunctional initiator and coupling reactions.



2.3.2. Graft copolymers

Graft copolymers consist of a main polymer chain, the backbone, with one or more side chains attached to it through covalent bonds, the branches. Graft copolymers are comb-shaped polymers where the chemical nature of the backbone and the branches differs. The chemical nature and composition of the backbone and the branches differ in most cases. Branches are usually distributed randomly along the backbone, although recently advances in synthetic methods allowed the synthesis of better defined structures [168, 169]. Randomly branched graft copolymers can be prepared by three general synthetic methods: the “grafting from”, “grafting through” or macromonomer and the the “grafting onto”.

2.3.2.1 “Grafting from” method

In the “grafting from” method, the backbone is chemically modified in order to introduce active sites capable of initiating the polymerization of a second monomer as seen in Figure 2.2. The number of grafted chains can be controlled by the number of active sites generated along the backbone assuming that each one participates in the formation of one branch [170].

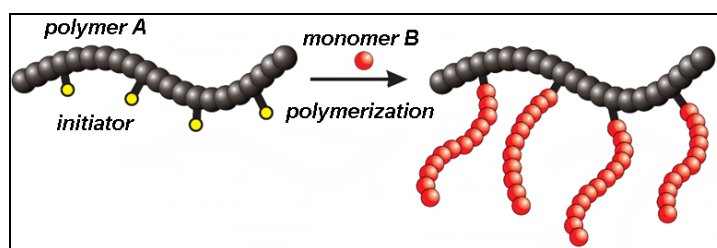


Figure 2.2 : Illustration of the synthesis of graft copolymers by “grafting-from” method.

2.3.2.2. “Grafting through” method

In the grafting through method, preformed macromonomers are copolymerized with another monomer in order to produce the graft copolymer as seen in Figure 2.3. Macromonomers are oligomeric or polymeric chains that have a polymerizable end group. In this case, the macromonomer comprises the branch of the copolymer and the backbone is formed in situ. The number of branches per backbone can be

generally controlled by the ratio of the molar concentrations of the macromonomer and the comonomer [171].

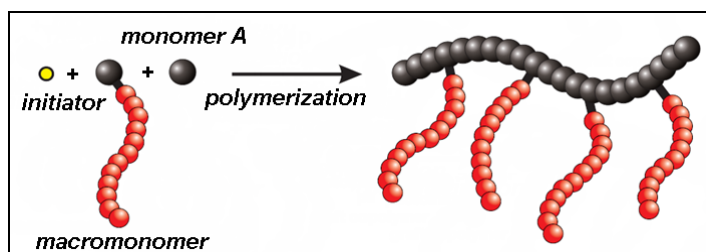


Figure 2.3: Illustration of the synthesis of graft copolymers by “grafting-through” method.

2.3.2.3 “Grafting onto” method

One of the methods widely used for the synthesis of graft copolymers is the “grafting onto” method, i.e. reaction of preformed polymeric chains bearing functional groups with other polymeric chains bearing active chain ends as seen in Figure 2.4. In most cases, the incorporation of functional groups is performed by chemical modification of the backbone. Characterization of the backbone and the preformed side chains can be performed separately from the graft copolymer, thus allowing for the detailed characterization of the final structure.

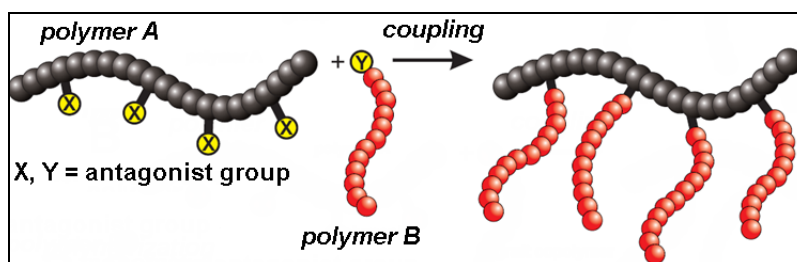


Figure 2.4: Illustration of the synthesis of graft copolymers by “grafting-onto” method.

2.3.2.4 Synthesis of graft and heterograft copolymers

Grafting reaction, which can offer the possibility of varying the physical and chemical properties of polymers. The interest in heterograft copolymer comes from the unique properties relating to their variety of compositions, such as the combination of a crystallizable and an amorphous side chain, or a hydrophobic and a hydrophilic side

chain [172].

ROMP has been considered to be an efficient way to synthesize polymacromonomer with complete conversion as well as with a uniform molecular weight distribution since the ring strain and a larger space of ring functional group provide a favorable environment for polymerization. Grubbs et al. firstly prepared a variety of polymers including PS, PMMA, and PtBA, via ATRP [173].

The “click”-type reactions, mainly exemplified by Huisgen 1,3-dipolar azide-alkyne, $[3 + 2]$, or Diels–Alder cycloadditions, $[4 + 2]$, have attracted much attention due to their important features including high yields, high tolerance of functional groups, and selectivity [174].

Nitroxide radical coupling reaction is considered as a potential click reaction due to its high efficiency and orthogonality in the synthesis of well-defined polymers with different topologies. The NRC click reaction proceeds between a halide- and a 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-terminated polymers in the presence of CuBr and ligand under mild reaction temperature based on the ATRP mechanism [175].

The past few years have witnessed the rapid growth of synthesis of graft copolymers using click type reactions. In here, we investigated the some of the publication which was published recently.

Well-defined poly(GTEMPO-co-EO)-g-PS/PtBA heterograft copolymers were prepared in one-pot by ATNRC reaction via “graft onto.” The density of GTEMPOs on precursor copolymer poly (GTEMPO-co-EO), the structure of macroradicals, molecular weights of side chains PS-Br and PtBA-Br can exert great effect on the coupling efficiency. The PS radicals are more reactive than that of PtBA in the coupling reaction. This approach can afford a useful strategy for synthesis of heterograft copolymers with various compositions and well-defined structures [172].

The combination of ATRP with ROMP has been shown to have some utility in designing block copolymers, graft copolymers, liquid crystals, and other systems where it is desirable to combine the elements of “polymerizing from” a specific point (ATRP), and “polymerizing through” (ROMP). Weck and co-workers exploited this discreet mechanistic difference by creating a ROMP backbone that contained ATRP initiators, and subsequently polymerizing from this backbone to create a graft copolymer [176].

3. EXPERIMENTAL

3.1 Materials

Methyl methacrylate (MMA, 99%, Aldrich) was passed through basic alumina column to remove inhibitor and then distilled over CaH_2 in vacuum prior to use. ϵ -Caprolactone (ϵ -CL, 99 %, Aldrich) was distilled from CaH_2 in vacuum. Poly(ethylene glycol monomethyl ether) (Me-PEG-OH) ($M_n = 550$, Acros) was dried over anhydrous toluene by azeotropic distillation. N,N,N',N'',N'' -pentamethyldiethylenetriamine (PMDETA, 99 %, Aldrich) was distilled over NaOH prior to use. 4-Hydroxy-TEMPO (97%, Aldrich), N,N' -dicyclohexylcarbodiimide (DCC, 99 %, Aldrich), 4-dimethylaminopyridine (DMAP, 99 %, Acros), CuCl (99.9 %, Aldrich), and CuBr (99.9 %, Aldrich) were used as received. *p*-Toluene sulfonyl chloride (99 %, Aldrich), sodium azide (99 %, Acros) and 2-bromopropanoyl bromide (98 %, Aldrich) were used as received. Dichloromethane (CH_2Cl_2 , 99.9 %, Aldrich) was used after distillation over P_2O_5 . Tetrahydrofuran (THF, 99.8 %, J.T. Baker) was dried and distilled over benzophenone-metallic Na. N,N -Dimethylformamide (DMF, 99.8 %, Aldrich) was dried and distilled under vacuum over CaH_2 . Solvents unless specified here were purified by conventional procedures. All other reagents were purchased from Aldrich and used as received without further purification.

3.2 Instrumentation

^1H NMR spectra were recorded on Bruker AC250 spectrometer. The conventional gel permeation chromatography (GPC) measurements were carried out with an Agilent instrument (Model 1100) consisting of a pump, refractive index (RI), and ultraviolet (UV) detectors and four Waters Styragel columns (guard, HR 5E, HR 4E, HR 3, and HR 2), (4.6 mm internal diameter, 300 mm length, packed with 5 μm particles). The effective molecular weight ranges are 2000-4,000,000, 50-100,000,

500-30,000, and 500-20,000, respectively. THF and toluene were used as eluent at a flow rate of 0.3 mL/min at 30 °C and as an internal standard, respectively. The apparent molecular weights ($M_{n, GPC}$ and $M_{w, GPC}$) and polydispersities (M_w/M_n) were determined with a calibration based on linear PS standards using PL Caliber Software from Polymer Laboratories. The three detection GPC (TD-GPC) set-up with an Agilent 1200 model isocratic pump, four Waters Styragel columns (guard, HR 5E, HR 4, HR 3, and HR 2), and a Viscotek TDA 302 triple detector including RI, dual laser light scattering (DLLS) ($\lambda = 670$ nm, 90° and 7°) and a differential pressure viscometer was conducted to measure the absolute molecular weights ($M_{w, TDGPC}$) in THF with a flow rate of 0.5 mL/min at 35 °C. Three detectors were calibrated with a PS standard having narrow molecular weight distribution ($M_n = 115,000$, $M_w/M_n = 1.02$, $[\eta] = 0.519$ dL/g at 35°C in THF, $dn/dc = 0.185$ mL/g) provided by Viscotek company. UV spectra were recorded on a Shimadzu UV-1601 spectrophotometer in CH_2Cl_2 .

3.3 Syntheses of ROMP Monomers and Initiators

(4-(2-hydroxyethyl)-10-oxa-4-aza tricyclo[5.2.1.0^{2,6}]dec-8- ene-3,5-dione) (**1**) , oxanorbornenyl bromide (ONB-bromide) (2-bromo-propionic acid 2-(3,5-dioxo-10-oxa-azatricyclo [5.2.1.0^{2,6}] dec-8-en-4-yl)-ethyl ester) (**3**), 2-bromo-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl)-ethyl ester (**4**), succinic acid anthracen-9-yl methyl ester prop-2-ynyl ester (**5**) and Oxanorbornenyl Anthracene (**7**), were prepared according to published procedures [177-181].

3.3.1 Synthesis of 4,10-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (**1**)

Maleic anhydride (60.0 g, 0.6 mol) was suspended in 150 mL of toluene and the mixture warmed to 80 °C. Furan (66.8 mL, 0.9 mol) was added via syringe and the turbid solution was stirred for 6 h. The mixture was then cooled to ambient temperature white solids formed during standing were collected by filtration and washed with 2×30 mL of petroleum ether and once with diethyl ether (50 mL) afforded **1** as white needles. Yield: 80.2 g (80%). ^1H NMR ($CDCl_3$, δ) 6.57 (s, 2H, $CH=CH$, bridge protons), 5.45 (s, 2H, $-CHO$, bridge-head protons), 3.17 (s, 2H, $CH-CH$, bridge protons).

3.3.2 Synthesis of 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (2)

1 (10.0 g, 60.0 mmol) was suspended in methanol (150 mL) and the mixture cooled to 0 °C. A solution of ethanolamine (3.6 mL, 60 mmol) in 30 mL of methanol was added dropwise (10 min) to the reaction mixture, and the resulting solution was stirred for 5 min at 0 °C, then 30 min at ambient temperature, and finally refluxed for 6 h. After cooling the mixture to ambient temperature, solvent was removed under reduced pressure, and residue was dissolved in 150 mL of CH₂Cl₂ and washed with 3 × 100 mL of water. The organic layer was separated, dried over Na₂SO₄ and filtered. Removal of the solvent under reduced pressure gave white-off solid which was further purified by flash chromatography eluting with ethylacetate (EtOAc) to give the product as a white solid. Yield: 4.9 g (40%). ¹H NMR (CDCl₃, δ) 6.51 (s, 2H, CH=CH, bridge protons), 5.26 (s, 2H, -CHO, bridge-head protons), 3.74-3.68 (m, 4H, NCH₂CH₂OH), 2.88 (s, 2H, CH-CH, bridge protons).

3.3.3 Synthesis of 2-bromo-2-methyl-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl) ethyl ester (3)

In a 250 mL of round bottom flask were added **2** (2.0 g, 9.55 mmol) and Et₃N (1.44 mL, 10.54 mmol) in 100 mL of THF. The mixture was cooled to 0 °C, and a solution of 2-bromo isobutyryl bromide (2.34 g, 10.0 mmol) in 25 mL of THF was added dropwise (30 min) to the reaction mixture. The white suspension was stirred for 3 h at 0 °C and subsequently at ambient temperature for overnight. The ammonium salt was filtered off and the solvent was removed under reduced pressure to give a pale-yellow residue that was further purified by column chromatography over silica gel eluting with EtOAc /hexane (1:4) to give **3** as a white solid. Yield: 1.86 g (55%). ¹H NMR (CDCl₃, δ) 6.49 (s, 2H, CH=CH, bridge protons), 5.24 (s, 2H, -CHO, bridge-head protons), 4.31 (t, *J* = 5.2 Hz, 2H, NCH₂CH₂OC=O), 3.79 (t, *J* = 5.2 Hz, 2H, NCH₂CH₂OC=O), 2.85 (s, 2H, CH-CH, bridge protons), 1.87 (s, 6H, C(CH₃)₂-Br).

3.3.4 Synthesis of 2-bromo-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl)-ethyl ester (4)

In a 250 mL of round bottom flask were added **2** (2.0 g, 9.55 mmol) and Et₃N (1.44 mL, 10.54 mmol) in 100 mL of THF. The mixture was cooled to 0 °C, and a solution of 2-bromo propanol bromide (2.34 g, 10.0 mmol) in 25 mL of THF was added

dropwise (30 min) to the reaction mixture. The white suspension was stirred for 3 h at 0 °C and subsequently at ambient temperature for overnight. The ammonium salt was filtered off and the solvent was removed under reduced pressure to give a pale-yellow residue that was further purified by column chromatography over silica gel eluting with EtOAc /hexane (1:4) to give **4** as a white solid. Yield: 1.84 g (53%). ¹H NMR (CDCl₃, δ) 6.49 (s, 2H, CH=CH, bridge protons), 5.24 (s, 2H, -CHO, bridge-head protons), 4.30 (t, *J* = 5.2 Hz, 2H, NCH₂CH₂OC=O), 3.79 (t, *J* = 5.2 Hz, 2H, NCH₂CH₂OC=O), 2.85 (s, 2H, CH-CH, bridge protons), 1.85 (s, 3H, CH(CH₃)-Br), 1.60 (s, 3H, CH(CH₃)-Br).

3.3.5 Synthesis of succinic acid mono-anthracen-9-ylmethyl-ester, (**5**)

9-Anthracene methanol (4.16 g, 20 mmol) was dissolved in 150 mL of CH₂Cl₂. To the reaction mixture were added Et₃N (14 ml, 100 mmol), 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. After that time, the reaction solution was poured into ice-cold water (150 mL), stirred for 30 min. at room temperature before taking into separating funnel. The organic phase was extracted with 1M HCl (150 mL). The aqueous phase extracted with CH₂Cl₂ and combined organic phases dried over Na₂SO₄ and concentrated to give **5** as a green solid. Yield: 5.85 g (95%). ¹H NMR (CDCl₃, δ) 8.50 (s, 1H, ArH of anthracene), 8.32 (d, *J* = 8.8 Hz, 2H, ArH of anthracene), 8.02 (d, *J* = 8.2 Hz, 2H, ArH of anthracene), 7.60-7.45 (m, 4H, ArH of anthracene), 6.18 (s, 2H, CH₂-anthracene), 2.69-2.62 (m, 4H, C=OCH₂CH₂C=OOH).

3.3.6 Synthesis of Oxanorbornenyl Tosyl (ONB-OTs), (**6**)

2 (1.0 g, 4.78 mmol) and DMAP (0.12 g, 0.96 mmol) were dissolved in 50 mL of CH₂Cl₂ and Et₃N (1.3 mL, 9.56 mmol) was added. The reaction mixture was then cooled to 0 °C. *p*-toluene-sulfonyl chloride (1.37 g, 7.18 mmol) was dissolved in 10 mL of CH₂Cl₂ and added dropwise within 30 min. to this solution under nitrogen. The reaction mixture was stirred for 15 min. at 0 °C then for overnight at room temperature. After that time, the mixture extracted with cold 1 M HCl then with distilled water. The aqueous layers were again extracted with CH₂Cl₂, and combined organic layers were dried over Na₂SO₄. The organic phase was evaporated under reduced pressure and the remaining product was crystallized from ethanol gave the product as white crystals. It was isolated by filtration and dried at 40 °C in a vacuum

oven for 24 h. Yield: 1.5 g (86%). Mp: 138–139 °C (DSC). ¹H NMR (CDCl₃, δ): 7.7 (d, 2H, ArH), 7.3 (d, 2H, ArH), 6.5 (s, 2H, CHCH=CHCH, vinyl protons), 5.2 (s, 2H, CHCH=CHCH, bridge-head protons), 4.2 (t, 2H, NCH₂CH₂OS=O), 3.7 (t, 2H, NCH₂CH₂OS=O), 2.8 (s, 2H, CH-CH, bridge protons), 2.4 (s, 3H, Ar-CH₃). ¹³C NMR (CDCl₃, δ): 175.7, 145.0, 136.5, 129.9, 128.0, 80.8, 65.3, 47.5, 37.7, 21.6.

3.3.7 Synthesis of Oxanorbornenyl Anthracene, (7)

Compounds **2** (1.63 g, 7.80 mmol, 1.2 equiv), **5** (2.00 g, 6.50 mmol, 1 equiv), and DMAP (0.400 g, 3.25 mmol, 0.5 equiv) were dissolved in 50 mL of dry CH₂Cl₂. After stirring 5 min at room temperature, DCC (1.6 g, 7.8 mmol, 1.2 equiv) dissolved in 25 mL of CH₂Cl₂ was added to the reaction mixture. The reaction mixture was stirred overnight at room temperature. After filtration, the solvent was removed and the remaining product was extracted with CH₂Cl₂/water. The aqueous phase was again extracted with CH₂Cl₂ and the combined organic phases were dried with Na₂SO₄, and concentrated to dryness. The crude product was purified by column chromatography over silica gel eluting with CH₂Cl₂ to give **7** as a yellow solid (Yield = 2.6 g; 80%). ¹H NMR (CDCl₃, δ): 8.5 (s, 1H, ArH of anthracene), 8.3 (d, 2H, ArH of anthracene), 8.0 (d, 2H, ArH of anthracene), 7.5 (m, 4H, ArH of anthracene), 6.4 (s, 2H, vinyl protons), 6.1 (s, 2H, CH₂-anthracene), 5.2 (s, 2H, CHCH=CHCH, bridge-head protons), 4.2 (t, 2H, NCH₂CH₂OC=O), 3.7 (t, 2H, NCH₂CH₂OC=O), 2.8 (s, 2H, CH-CH, bridge protons), 2.6 (s, 4H, C=OCH₂CH₂C=O).

3.3.8 Synthesis of succinic acid anthracen-9-ylmethyl ester prop-2-ynyl ester, (8)

Propargyl alcohol (0.545 g, 9.74 mmol, 1.5 equiv), DMAP (0.396 g, 3.25 mmol, 0.5 equiv) and **5** (2.00 g, 6.49 mmol, 1 equiv) were dissolved in 30 mL of dry CH₂Cl₂. After stirring 5 min at room temperature, DCC (2.00 g, 9.74 mmol, 1.5 equiv) dissolved in 15 mL of CH₂Cl₂ 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 CH₂Cl₂ and water. The aqueous phase was again extracted with CH₂Cl₂ and combined organic phase was dried with Na₂SO₄. The solution was concentrated and the crude product was purified by column chromatography over silica gel eluting with EtOAc/hexane (1:2) to give as a yellow solid. Yield: 1.9 g (85%). Mp = 77-78 °C. ¹H NMR (CDCl₃, δ) 8.51 (s, 1H, ArH of anthracene), 8.31 (d, *J* = 8.8 Hz, 2H,

ArH of anthracene), 8.03 (d, $J = 8.3$ Hz, 2H, ArH of anthracene), 7.60-7.45 (m, 4H, ArH of anthracene), 6.16 (s, 2H, CH_2 -anthracene), 4.61 (d, $J = 2.4$ Hz, 2H, $\text{CH}\equiv\text{CCH}_2\text{O}$), 2.67 (s, 4H, $\text{C}=\text{OCH}_2\text{CH}_2\text{C}=\text{O}$), 2.44 (t, $J = 2.4$ Hz, 1H, $\text{CH}\equiv\text{CCH}_2\text{O}$).

3.3.9 General procedure for the synthesis of furan protected maleimide end-functionalized PMMA (MI-PMMA)

In a 25 mL of Schlenk tube, MMA (5.00 mL, 56.1 mmol), PMDETA (0.234 mL, 1.12 mmol), CuCl (0.11 g, 1.12 mmol), toluene (5 mL), and **3** (0.40 g, 1.12 mmol) were added, and the reaction mixture was degassed by FPT cycles, and left in argon. The tube was then placed in a thermostated oil bath at 40 °C for predetermined times. Tributyltinhydride (3.01 mL, 11.2 mmol) which terminated agent added about later 30 min. The polymerization reaction is completed later 10 min. The polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated into hexane. The polymer was dried for 24 h in a vacuum oven at 40 °C. ($[\text{M}]_0/[\text{I}]_0 = 50$, $[\text{I}]:[\text{CuCl}]:[\text{PMDETA}] = 1:1:1$, conv. (%) = 36 $M_{n,\text{theo}} = 2150$, $M_{n,\text{NMR}} = 3850$, $M_{n,\text{GPC}} = 3700$, $M_w/M_n = 1.29$, RI detector, relative to PMMA standards). $^1\text{H-NMR}$ (CDCl_3 , δ): 6.5 (s, 2H, vinyl protons), 5.3 (s, 2H, $\text{CHCH}=\text{CHCH}$, bridge-head protons), 4.1 (m, 2H, $\text{NCH}_2\text{CH}_2\text{OC}=\text{O}$), 4.0–3.2 (m, OCH_3 of PMMA and $\text{NCH}_2\text{CH}_2\text{OC}=\text{O}$), 2.9 (s, 2H, $\text{CH}_2\text{NC}=\text{OCH-CH}$, bridge protons), 2.5–0.5 (m, CH_2 and CH_3 protons of PMMA).

3.3.10 Synthesis of alkyne end-functionalized PCL (Alkyne-PCL)

Alkyne-PCL was prepared by ROP of ϵ -CL (5.0 mL, 0.047 mol) in bulk using tin(II)-2-ethylhexanoate as a catalyst and propargyl alcohol (0.056 mL, 0.94 mmol) as an initiator at 110 °C for 28 h. The degassed monomer, catalyst, and initiator were added to a previously flamed schlenk tube equipped with a magnetic stirring bar in the order mentioned. The tube was degassed with three FPT, left in argon, and placed in a thermostated oil bath. After the polymerization, the mixture was diluted with THF, and precipitated into an excess amount of cold methanol. It was isolated by filtration and dried at room temperature in a vacuum oven for 24 h. $[\text{M}]_0/[\text{I}]_0 = 30$; conversion = 90%; $M_{n,\text{theo}} = 3150$; $M_{n,\text{NMR}} = 3000$; $M_{n,\text{GPC}} = 6170$ (relative to linear PS, $M_{n,\text{PCL}} = 3000$ g/mol = $0.259 \times M_{n,\text{GPC}}^{1.073}$); $M_w/M_n = 1.08$. $^1\text{H NMR}$ (CDCl_3 , δ) 4.65 (s, 2H, $\text{CH}\equiv\text{C-CH}_2\text{O}$), 4.0 (t, 2H, $\text{CH}_2\text{OC}=\text{O}$ of PCL), 3.62 (t, 2H,

CH_2OH , end-group of PCL), 2.45 (t, 1H, $\text{CH}\equiv\text{C}-\text{CH}_2\text{O}$), 2.3 (t, 2H, $\text{C}=\text{OCH}_2$ of PCL), 1.2-1.8 (m, 6H, CH_2 of PCL).

3.3.11 Synthesis of carboxylic acid end-functionalized PEG (PEG-COOH)

PEG-OH (5 g, 8 mmol, $M_n = 550$) was dissolved in 150 mL of CH_2Cl_2 . Succinic anhydride (3.13 g, 32.0 mmol), triethylamine (Et_3N) (5.6 mL, 40 mmol) and DMAP (1.46 g, 12.0 mmol) were added to the reaction mixture. After stirring overnight at room temperature, solution was poured into ice-cold water (150 mL) and extracted with CH_2Cl_2 . The organic layer was washed with 1 M HCl (150 mL) and then with distilled water. Finally, organic phase was dried with anhydrous Na_2SO_4 and the solvent was removed in vacuum to give mono carboxylic acid end-functionalized PEG (PEG-COOH) as colorless oil (Yield = 5 g, 95%; $M_{n,\text{theo}} = 650$, $M_{n,\text{NMR}} = 615$, $M_{n,\text{GPC}} = 450$, $M_w/M_n = 1.1$, relative to PS standards). ^1H NMR (CDCl_3 , δ) 4.2 (d, 4H, $\text{C}=\text{OOCH}_2$), 3.65-3.5 (m, $-\text{OCH}_2\text{CH}_2\text{O}-$, PEG backbone), 3.35 (s, 3H, OCH_3), 2.6 (bs, 4H, $\text{C}=\text{OCH}_2\text{CH}_2\text{C}=\text{O}$).

3.3.12 Synthesis of TEMPO end-functionalized PEG (TEMPO-PEG)

PEG₅₅₀-COOH (1.01g, 1.5 mmol), 4-Hydroxy-TEMPO (1.06 g, 6.2 mmol) and DMAP (0.19 g, 1.5 mmol) were dissolved in 25 mL of dry CH_2Cl_2 . After stirring 5 min at room temperature, DCC (1.27 g, 6.2 mmol,) dissolved in 25 mL of CH_2Cl_2 was added to the reaction mixture. The reaction mixture was stirred overnight at room temperature. After filtration off the salt, the solution was concentrated and the viscous brown color product was purified by column chromatography over silica gel eluting with $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ mixture (1:1, v/v) and then with $\text{CH}_2\text{Cl}_2/\text{methanol}$ (1:1, v/v) to obtain PEG-Tempo as viscous brown oil. (Yield: 1.05 g 85% $M_{n,\text{theo}} = 800$ g/mol; $M_{n,\text{GPC}} = 650$ g/mol; $M_{n,\text{NMR}} = 750$; $M_w/M_n = 1.06$, relative to linear PS.)

3.3.13 Model ROMP Reaction of Oxanorbornenyl Tosyl (ONB-OTs)

The first generation Grubbs' catalyst (PCy_3)₂(Cl)₂-RuCHPh (0.034 g, 0.041 mmol) was placed in a Schlenk tube and dissolved in 2 mL of anhydrous CH_2Cl_2 in a glove box. Oxanorbornenyl Tosyl (ONB-OTs) (0.3 g, 0.83 mmol) in 4 mL of anhydrous CH_2Cl_2 was added to the catalyst solution via syringe. The flask was capped with a septum and removed from glove box. The polymerization was allowed to stir at room temperature for 30 min. The polymerization was then terminated by the addition of

butyl vinyl ether (0.5 mL) and stirred for additional 30 min. at room temperature. Finally, the polymer solution was precipitated in methanol and the obtained polymer was dried for 24 h in a vacuum oven at 40°C. (monomer/catalyst =20; conv. (%) =100; $M_{n, GPC}$ =5200, $M_{n, theo}$ =7300; M_w/M_n =1.17, RI detector, relative to linear PS). ^1H NMR ($CDCl_3$, δ): 7.7 (bs, ArH), 7.3 (bs, ArH), 6.0 (bs, CH=CH, trans), 5.8 (br, CH=CH, cis), 4.9 (br, =CH-CH-O, cis), 4.5 (bs, =CH-CH-O, trans), 4.2 (bs, NCH₂CH₂OS=O), 3.7 (bs, NCH₂CH₂OS=O), 3.3 (bs, CH-CH, bridge protons), 2.4 (bs, Ar-CH₃).

3.3.14 Synthesis of Random Poly(ONB-anthracene)₁₀-*b*-Poly(ONB-bromide)₁₀-*b*-Poly(ONB-OTs)₁₀ Block Copolymer via ROMP

The first generation Grubbs' catalyst (PCy₃)₂(Cl)₂-RuCHPh (0.041 g, 0.05 mmol) was placed in a Schlenk tube and dissolved in 2 mL of anhydrous CH₂Cl₂ in a glove box. The ROMP monomers **7** (0.25 g, 0.5 mmol), **4** (0.17 g, 0.5 mmol) and **6** (0.18 g, 0.5 mmol) in 10 mL of anhydrous CH₂Cl₂ was added to the catalyst solution via syringe. The flask was capped with a septum and removed from glove box. The polymerization was allowed to stir at room temperature for 4 h. The polymerization was then terminated by the addition of butyl vinyl ether (0.5 mL) and stirred for additional 30 min. at room temperature. Finally, the polymer solution was precipitated in methanol and the obtained polymer was dried for 24 h in a vacuum oven at 40°C. (monomers/catalyst =10 for each; conv. (%) =100; $M_{n, GPC}$ =8050; M_w/M_n =1.12, RI detector, relative to linear PS).

^1H NMR ($CDCl_3$, δ): 8.5 (bs, ArH of anthracene), 8.3 (bs, ArH of anthracene), 7.9 (bs, ArH of anthracene), 7.7 (bs, ArH), 7.5–7.4 (bs, ArH of anthracene), 7.3 (bs, ArH), 6.1 (br, CH₂-anthracene and CH=CH, trans), 5.7 (bs, CH=CH, cis), 4.9 (bs, 2H, =CH-CH-O, cis), 4.4-4.1 (br, =CH-CH-O, trans, CH(Br)CH₃, CH₂C=OOCH₂CH₂N, CH₃CH(Br)C=OOCH₂CH₂N, S=OOCH₂CH₂N), 3.7 (bs, C=OOCH₂CH₂N), 3.3 (bs, CH-CH), 2.5 (bs, C=OCH₂CH₂C=O), 2.4 (bs, Ar-CH₃), 1.7 (bs, CH(Br)CH₃).

3.3.15 Preparation of Poly(ONB-*g*-PMMA)₁₀-*b*-Poly(ONB-bromide)₁₀-*b*-Poly(ONB-OTs)₁₀ via Diels-Alder Click Reaction of Poly(ONB-anthracene)₁₀-*b*-Poly(ONB-bromide)₁₀-*b*-Poly(ONB-OTs)₁₀ with PMMA-MI

A solution of PMMA-MI (0.96 g, 0.25 mmol, $M_{n,NMR} = 3850$, 12 eq.) in 25 mL of toluene was added to a 25 mL dioxane solution of poly(ONB-anthracene)₁₀-*b*-poly(ONB-bromide)₁₀-*b*-poly(ONB-OTs)₁₀ (0.25 g, 0.0208 mmol, $M_{n,theo} = 12000$). The mixture was bubbled with nitrogen for 30 min. and refluxed for 48 h at 110°C in the dark. After that time, the solution was evaporated to dryness, and the residual solid was dissolved in THF, and subsequently precipitated in methanol/diethyl ether (1/1). Recovered polymer was dissolved in THF and precipitated in methanol. This dissolution-precipitation (THF-MeOH) procedure was repeated two times. The obtained product was dried in a vacuum oven at 40°C for 24 h ($M_{n, GPC} = 23500$; $M_w/M_n = 1.27$, relative to linear PS).

¹H NMR (CDCl₃, δ): 7.7 (bs, ArH), 7.3–7.1 (br, ArH), 6.0 (bs, 2H, CH=CH, trans), 5.8 (bs, CH=CH, cis), 5.4 (bs, CH₂-adduct), 5.0 (bs, =CH-CH-O, cis), 4.7 (bs, CH, bridge-head proton), 4.5–4.2 (bs, =CH-CH-O, trans, CH(Br)CH₃, C=OOCH₂CH₂N, S=OOCH₂CH₂N), 3.7–3.30 (m, OCH₃ of PMMA, C=OOCH₂CH₂N, S=OOCH₂CH₂N and CH-CH), 2.7 (bs, C=OCH₂CH₂C=O), 2.4 (bs, Ar-CH₃), 2.0–1.0 (m, CH₂ and CH₃ of PMMA).

3.3.16 Preparation of Poly(ONB-*g*-PMMA)₁₀-*b*-Poly(ONB-*g*-PEG)₁₀-*b*-Poly(ONB-OTs)₁₀ via ATNRC Reaction of Poly(ONB-*g*-PMMA)₁₀-*b*-Poly(ONB-bromide)₁₀-*b*-Poly(ONB-OTs)₁₀ with PEG-TEMPO

Poly(ONB-*g*-PMMA)₁₀-*b*-Poly(ONB-bromide)₁₀-*b*-Poly(ONB-OTs)₁₀ (0.20 g, 0.004 mmol, $M_{n, theo} = 49000$ g/mol,) was dissolved in DMF (10 mL) in a 25 mL of Schlenk tube. PEG-TEMPO (0.1 g, 0.12 mmol, $M_{n, theo} = 800$ g/mol, 30 equiv) was added to this solution, and the mixture was stirred at room temperature for 10 min. Next, Cu(0) (0.013 g, 0.2 mmol, 50 equiv), CuBr (0.006 g, 0.04 mmol, 10 equiv), and PMDETA (0.085 mL, 0.04 mmol, 10 equiv) were immediately added to the Schlenk tube. The reaction mixture was degassed by three FPT cycles, left in vacuum, and stirred for 24 h at room temperature. The mixture was diluted with THF, filtered through a column filled with neutral alumina to remove the copper

complex, and precipitated in methanol. The crude product was purified by a two times dissolution–precipitation cycle in THF-MeOH. The polymer was dried at 40°C in a vacuum oven for 24 h. ($M_{n, \text{GPC}} = 15500$ g/mol; $M_w / M_n = 1.14$, relative to linear PS).

^1H NMR (CDCl_3 , δ): 7.7 (br, ArH), 7.3–7.0 (m, ArH), 6.0 (bs, CH=CH, trans), 5.8 (br, CH=CH, cis), 5.5 (br, CH₂-adduct), 5.0 (br, =CH-CH-O, cis and CHOC=O), 4.7 (bs, CH, bridge-head proton), 4.5–4.2 (br, =CH-CH-O, trans, C=OOCH₂CH₂N, S=OOCH₂CH₂N, C=OCH(CH₃), PEG-CH₂OC=O), 3.8–3.2 (m, -OCH₂CH₂O-, PEG backbone, OCH₃ of PMMA, C=OOCH₂CH₂N, S=OOCH₂CH₂N and CH-CH, OCH₃ of PEG), 2.6–2.4 (br, C=OCH₂CH₂C=O), 2.4 (bs, Ar-CH₃), 2.0–1.0 (m, CH₂ and CH₃ of PMMA).

3.3.17 Model Azidation Reaction of Poly(ONB-OTs)

Poly(ONB)₂₀ (0.30 g, 0.042 mmol, $M_{n, \text{theo}} = 7300$) and NaN₃ (0.5 g, 8.2 mmol, 200 equiv) were dissolved in nitrogen purged DMF (5 ml). The reaction mixture was stirred overnight at room temperature. The same reaction condition was applied under at 40 °C. Polymer was precipitated in methanol. For at room temperature ^1H NMR (CDCl_3 , δ): 7.7 (bs, ArH), 7.3 (bs, ArH), 6.0 (bs, CH=CH, trans), 5.8 (br, CH=CH, cis), 4.9 (br, =CH-CH-O, cis), 4.5 (bs, =CH-CH-O, trans), 4.2 (bs, NCH₂CH₂OS=O), 3.7 (bs, NCH₂CH₂OS=O), 3.5 (bs, NCH₂CH₂N₃), 3.3 (bs, CH-CH, bridge protons), 2.4 (bs, Ar-CH₃).

For at 40 °C temperature ^1H NMR (CDCl_3 , δ): 6.0 (bs, CH=CH, trans), 5.8 (br, CH=CH, cis), 4.9 (br, =CH-CH-O, cis), 4.5 (bs, =CH-CH-O, trans), 3.7 (bs, NCH₂CH₂N₃), 3.5 (bs, NCH₂CH₂N₃), 3.3 (bs, CH-CH, bridge protons).

3.3.18 Model In-situ Azidation and Click Reaction of Poly(ONB-OTs) with PCL-Alkyne

Poly(ONB)₂₀ (0.10 g, 0.014 mmol, $M_{n, \text{theo}} = 7300$) and PCL-alkyne (1.02 g, 0.342 mmol, based on $M_{n, \text{NMR}} = 3000$, 25 equiv) were dissolved in nitrogen purged DMF (15 mL) in a Schlenk tube equipped with magnetic stirring bar. NaN₃ (0.18 g, 2.76 mmol, 200 equiv), CuBr (0.040 g, 0.276 mmol, 20 equiv) and PMDETA (0.057 mL, 0.276 mmol, 20 equiv) were added and the reaction mixture was degassed by three freeze-pump-thaw (FPT) cycles and left in vacuum and stirred 40°C for 24 h.

Reaction mixture was passed through alumina column to remove copper salt and precipitated into methanol/diethyl ether (1/1) and recovered polymer was dissolved in THF, precipitated in methanol. This dissolution-precipitation (THF-MeOH) procedure was repeated two times. The obtained polymer was dried overnight in a vacuum oven at 40 °C ($M_{n, GPC}$ = 23000; M_w/M_n = 1.26, relative to linear PS). ^1H NMR ($CDCl_3$, δ): 7.7 (br, CH of triazole), 6.1- 5.8 (br, $CH=CH$, trans and $CH=CH$, cis), 5.2 (bs, $=CH-CH-O$, cis and triazole- CH_2O), 4.4-4.2 (br, $=CH-CH-O$, trans and NCH_2CH_2 -triazole), 4.0 (br, CH_2O of PCL), 3.8-3.4 (br, $CH-CH$ and NCH_2CH_2 -triazole and CH_2OH , end-group of PCL), 2.28 (br, $C=OCH_2$ of PCL), 1.8-1.2 (m, CH_2 of PCL).

3.3.19 Model In-situ Azidation and Click Reaction of Poly(ONB-OTs) with 8

Poly(ONB)₂₀ (0.15 g, 0.020 mmol, $M_{n, theo}$ = 7300) and 8 (0.22 g, 0.60 mmol, 30 equiv) were dissolved in nitrogen purged DMF (5 mL) in a Schlenk tube equipped with magnetic stirring bar. NaN_3 (0.26 g, 4.0 mmol, 200 equiv), CuBr (0.060 g, 0.40 mmol, 20 equiv) and PMDETA (0.086 mL, 0.40 mmol, 20 equiv) were added and the reaction mixture was degassed by three FPT cycles and left in vacuum and stirred 40°C for 24 h. Reaction mixture was passed through alumina column to remove copper salt and precipitated in methanol. This dissolution-precipitation (THF-MeOH) procedure was repeated two times. The obtained polymer was dried overnight in a vacuum oven at 40 °C ($M_{n, GPC}$ = 4350 M_w/M_n = 1.17, relative to linear PS). ^1H NMR ($CDCl_3$, δ): 8.4 (bs, ArH of anthracene), 8.2 (bs, ArH of anthracene), 7.9 (bs, ArH of anthracene), 7.5–7.4 (bs, ArH of anthracene), 6.2-5.4 (br, CH_2 -anthracene, $CH=CH$, trans and $CH=CH$, cis), 5.2-4.6 (br, $=CH-CH-O$, cis and triazole- CH_2O), 4.4 (br, 2H, $=CH-CH-O$, trans and NCH_2CH_2 -triazole), 3.6-3.1 (br, $CH-CH$ and NCH_2CH_2 -triazole), 2.6 (bs, $C=OCH_2CH_2C=O$).

3.3.20 Preparation of Poly(ONB-g-PMMA)₁₀-b-Poly(ONB-g-PEG)₁₀-b-Poly(ONB-g-PCL)₁₀ via In-situ Azidation and Click Reaction of Poly(ONB-g-PMMA)₁₀-b-Poly(ONB-g-PEG)₁₀-b-Poly(ONB-OTs)₁₀ with PCL-Alkyne

Poly(ONB-g-PMMA)₁₀-b-Poly(ONB-g-PEG)₁₀-b-Poly(ONB-OTs)₁₀ (0.40 g, 0.007 mmol, $M_{n, theo}$ = 57000) and PCL-alkyne (0.32 g, 0.105 mmol, based on $M_{n, NMR}$ = 3000, 15 equiv) were dissolved in nitrogen purged DMF (5 mL) in a Schlenk tube equipped with magnetic stirring bar. NaN_3 (0.050 g, 0.7 mmol), CuBr (0.010 g,

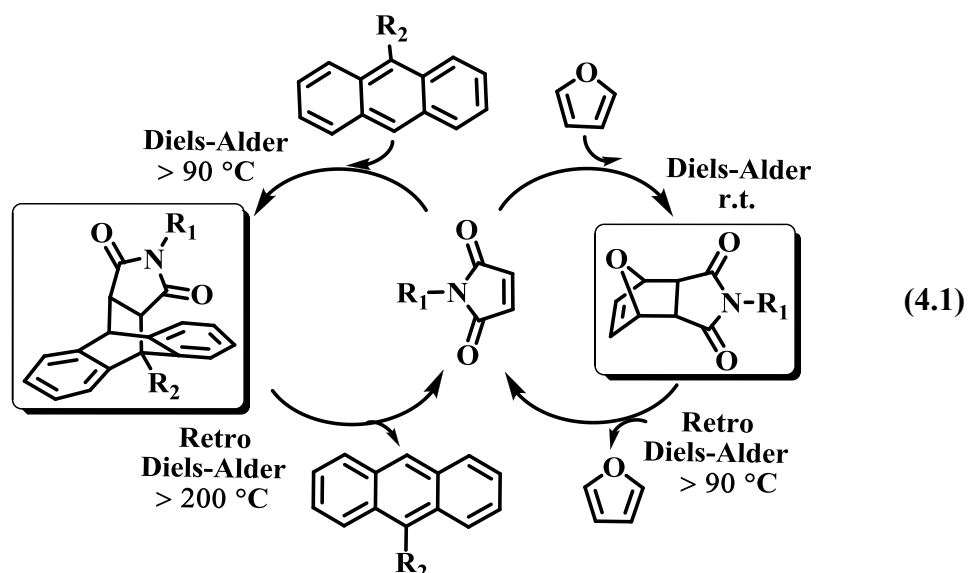
0.07mmol) and PMDETA (0.014 mL, 0.07 mmol) were added and the reaction mixture was degassed by three FPT cycles and left in vacuum and stirred 40°C for 24 h. Reaction mixture was passed through alumina column to remove copper salt and precipitated into methanol/diethyl ether (2/1) and recovered polymer was dissolved in THF and precipitated in methanol. Finally the polymer was dried for 24 h in a vacuum oven at 40°C ($M_{n, GPC}$ =23000; M_w/M_n =1.26, relative to linear PS).

^1H NMR (CDCl_3 , δ): 7.6 (br, CH of triazole), 7.24 (m, ArH), 6.0 (br, $\text{CH}=\text{CH}$, trans), 5.8 (br, $\text{CH}=\text{CH}$, cis), 5.4 (br, CH_2 -adduct), 5.2 (br, triazole- CH_2O), 4.9 (br, $=\text{CH}-\text{CH}-\text{O}$, cis and $\text{CHOC}=\text{O}$), 4.7 (br, CH , bridge-head proton), 4.5 (br, $=\text{CH}-\text{CH}-\text{O}$, trans and NCH_2CH_2 -triazole), 4.2-4.0 (m, $-\text{OCH}_2\text{CH}_2\text{O}-$, $\text{C}=\text{OOCH}_2\text{CH}_2\text{N}$ and $\text{C}=\text{OCH}(\text{CH}_3)$), 4.0 (br, CH_2O of PCL), 3.8-3.2 (m, $-\text{OCH}_2\text{CH}_2\text{O}-$, PEG backbone, OCH_3 of PMMA, $\text{C}=\text{OOCH}_2\text{CH}_2\text{N}$, $\text{S}=\text{OOCH}_2\text{CH}_2\text{N}$ and $\text{CH}-\text{CH}$, OCH_3 of PEG), 2.6 (bs, $\text{C}=\text{OCH}_2\text{CH}_2\text{C}=\text{O}$), 2.3 (br, $\text{C}=\text{OCH}_2$ of PCL), 1.8-0.5 (m, CH_2 of PCL and CH_2 and CH_3 of PMMA).

4. RESULTS AND DISCUSSION

Using a combination of ROMP-Diels-Alder click and sequential double click reaction strategies enabled us to prepare graft and graft block copolymers, respectively. In particular, ROMP-double click reaction strategy affords the synthesis of graft block copolymers that cannot be attained by employing a combination of ROMP-azide-alkyne click reaction alone. Nevertheless, Diels-Alder click reaction combining with ROMP has not been utilized in the synthesis of graft copolymers. Therefore, it was tested whether Diels-Alder click reaction was sufficient to form graft copolymers and the same concept was further applied to create graft block copolymers using an azide-alkyne cycloaddition, followed by Diels-Alder reaction.

The strategy that we followed during this thesis is based on a DA reaction between anthracene and maleimide end-functionalized polymers. The whole synthetic pathways during this thesis can be summarized as the following equation (4.1).

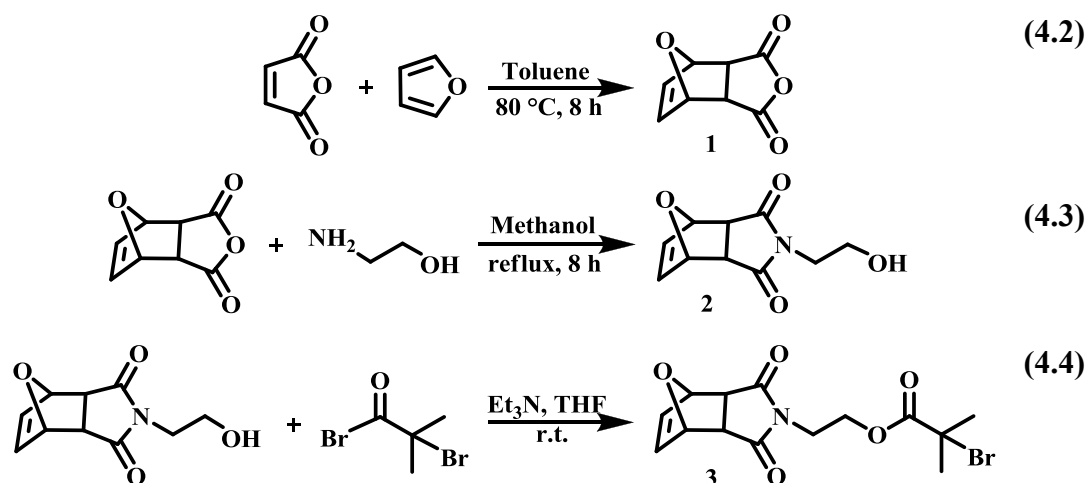


First, furan protected maleimide and anthracene end-functionalized polymers are prepared by ATRP. Then protected maleimide end-functionalized prepolymers are deprotected by retro Diels-Alder (r-DA) by heating at 110 °C in toluene. The

recovered maleimide groups are added irreversibly to anthryl functional polymers *in situ* to undergo the DA reaction in order to obtain anthracene-maleimide adduct.

4.1 Synthesis of Precursor Monomers and Polymers

The initiators with proper functionalities for DA reaction were first prepared. 2-bromo-2-methyl-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl) ethyl ester (**3**) was first synthesized within three steps. Furan and maleic anhydride were reacted in toluene at 80 °C, then the formed adduct (**1**) (**4.2**), was utilized for the synthesis of **2** by adding the solution 2-amino ethanol in methanol into dispersion of **1** in methanol (**4.3**). Finally, **3**, was obtained via an esterification reaction between **2** and 2-bromoisobutryl bromide in THF at room temperature (**4.4**).



From overlay ^1H NMR spectra of **3** as seen in Figure 4.1, it was clearly seen that the methyl protons next to Br were detected at 1.87 ppm and the methylene protons next to the ester unit at 4.31 ppm. Moreover, the characteristic protons of the adduct were also detected at 6.49 ppm (bridge vinyl protons), 5.24 ppm (bridge-head protons) and 2.85 ppm (bridge protons) respectively. These results confirmed that the synthesis of **3** was achieved.

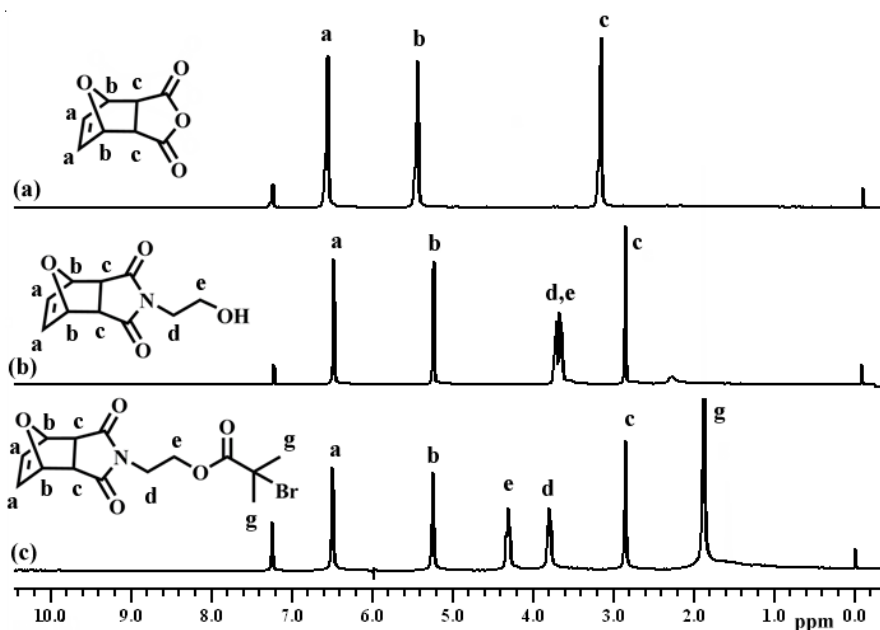
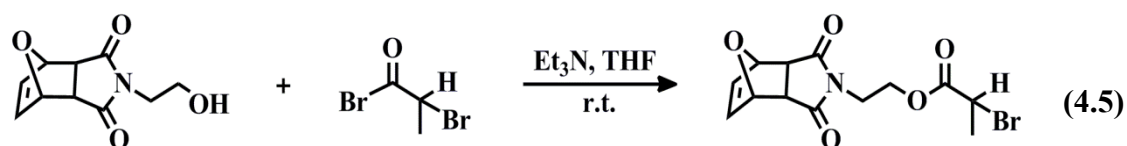


Figure 4.1: ^1H NMR spectra of: a) 3-acetyl-N-(2-hydroxyethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid (**1**); b) 3-acetyl-N-(2-hydroxyethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxamide (**2**); c) 2-bromo-2-methyl-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl) ethyl ester (**3**) (c) in CDCl_3 .

As the synthesis tertiary structure (**3**), secondary bromide structure (**4**) can be synthesized by using similar condition as seen that reaction 4.5.



By using ^1H NMR spectra of **4**, $\text{CH}_3\text{-Br}$ were detected at 1.60 ppm and 1.85 ppm of CHCH_3 . The other adduct protons are the same.

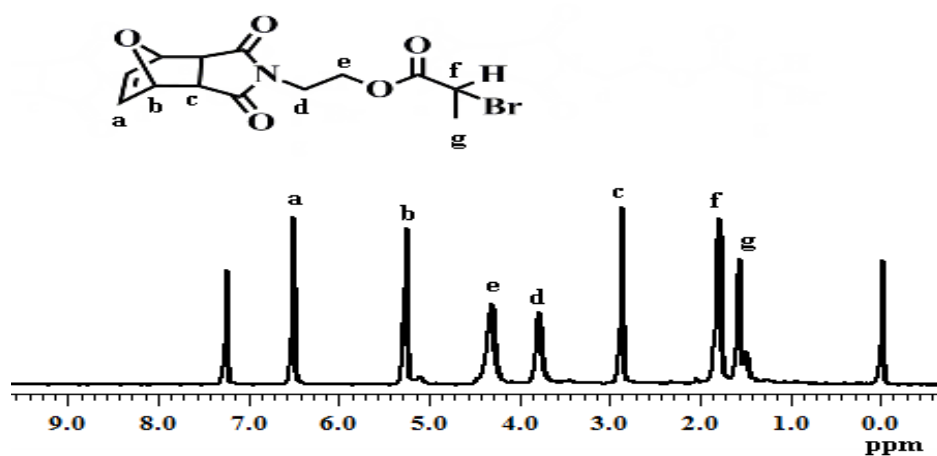
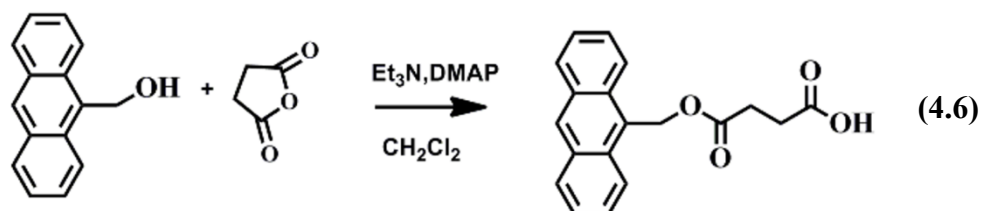


Figure 4.2: 2-bromo-2-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.0.2,6]dec-8-en-4-yl) ethyl ester

The hydroxyl functionality of anthracene 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 in order to give **5**.



Again, the structure was confirmed by ^1H NMR spectrum as seen in Figure 4.3. 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 2.69-2.62 ppm assigned to $\text{C}=\text{OCH}_2\text{CH}_2\text{OC}=\text{O}$ clearly indicated that **5** was achieved.

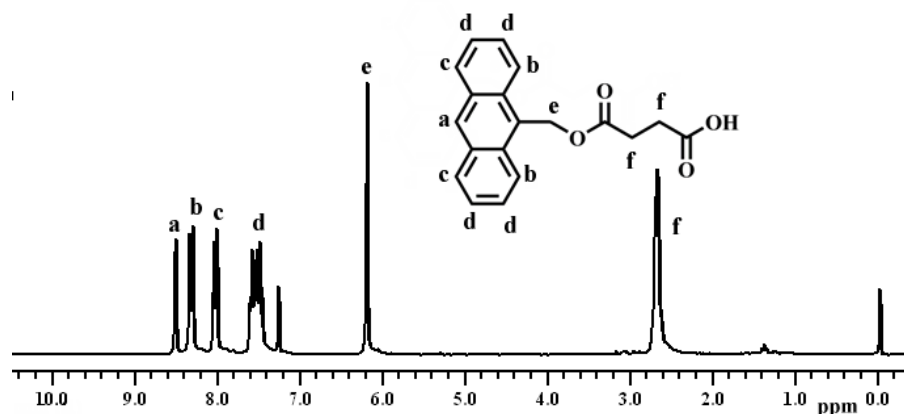
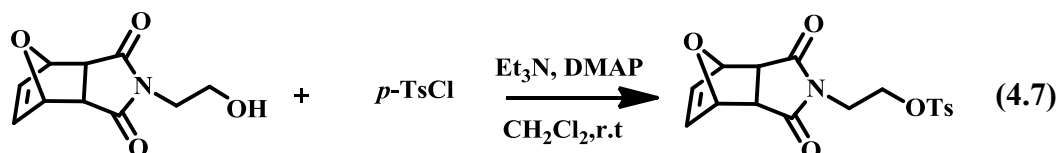


Figure 4.3 : ^1H NMR spectrum of succinic acid mono-anthracen-9-ylmethyl-ester (5) in CDCl_3 .

The reaction of 2 and *p*-toluene-sulfonyl chloride to give (6) Oxanorbornenyl Tosyl (ONB-OTs) in the presence of Et_3N and CH_2Cl_2 as a solvent as seen in reaction 4.7.



From ^1H NMR spectrum as seen in Figure 4.4 of 6, 7.75 ppm of phenyl protons and both 4.17 and 3.73 ppm of *p*-toluene-sulfonyl group protons (t, 2H, $\text{NCH}_2\text{CH}_2\text{OS}=\text{O}$) are detected by using NMR spectrum.

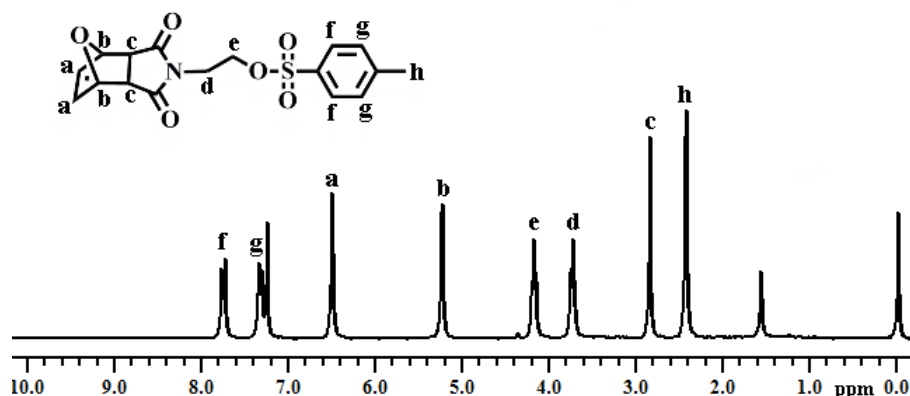


Figure 4.4 : ^1H NMR spectrum of Oxanorbornenyl Tosyl (ONB-OTs) in CDCl_3 .

The thermal analyses of the oxanorbornenyl tosyl was carried out using DSC measurements. DSC thermogram of the ONB-OTs reveals a $T_g = 138\text{-}139^\circ\text{C}$.

As showed Figure 4.5.

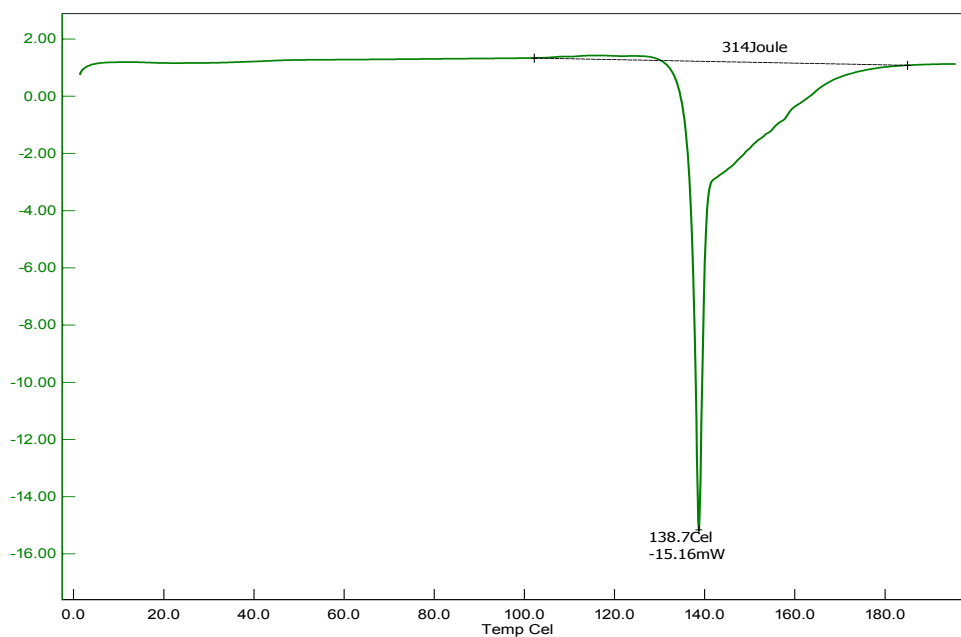
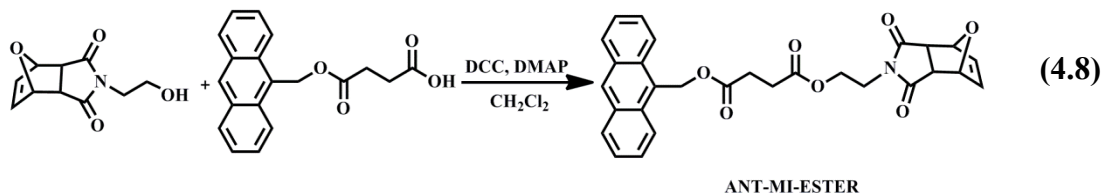


Figure 4.5: DSC measurements of Oxanorbornenyl Tosyl (ONB-OTs).

Anthracene-end functionalized oxanorbornene (ONB-Anth) monomer **7** was synthesized via esterification reaction of **2** and **5** catalyzed by DCC and DMAP in CH_2Cl_2 at room temperature overnight as seen in reaction 4.8.



^1H NMR spectroscopy as can be seen that figure 4.6 confirmed clearly the structure of **7** by appearance of characteristic signals of anthracene (δ 8.5-7.5) and vinyl protons (δ 6.4).

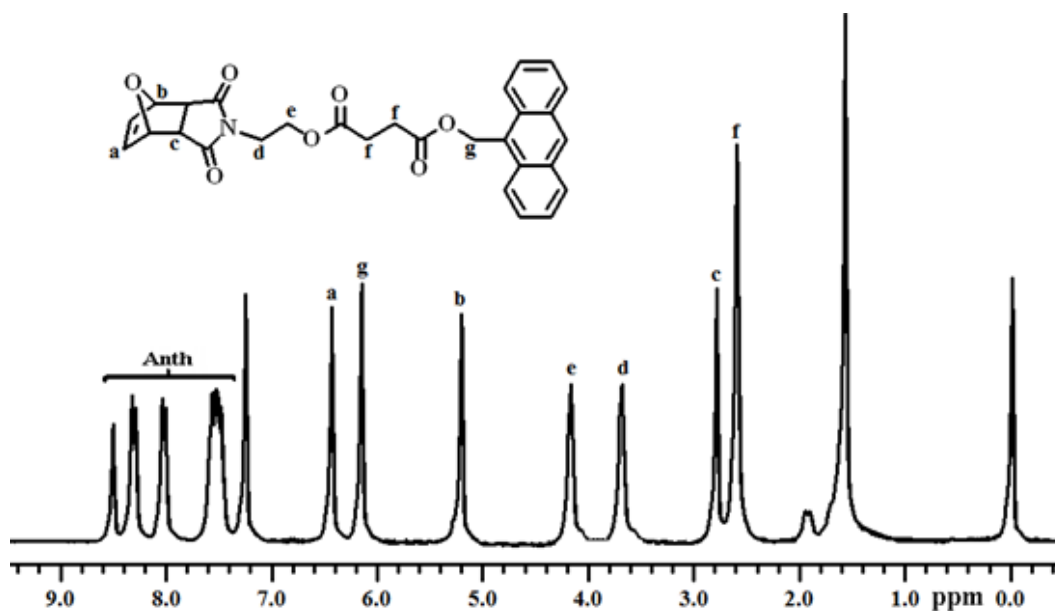
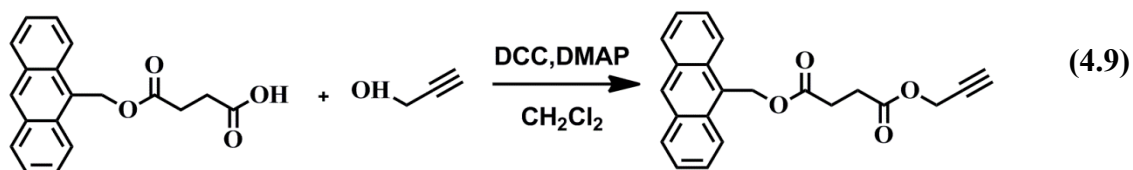


Figure 4.6: ^1H NMR spectrum of Oxanorbornenyl Anthracene in CDCl_3 .

8 comprising both alkyne and anthracene unit was synthesized through an esterification reaction between 5 and propargyl alcohol (reaction 4.9).



^1H NMR spectrum of 8 as seen Figure 4.7 indicated the successful reaction. The methylene protons of propargyl ($\text{CH}\equiv\text{CCH}_2\text{OC}=\text{O}$) adjacent to ester were detected as doublet at 4.61 ppm and alkyne proton at 2.44 ppm confirmed that the reaction was successfully carried out.

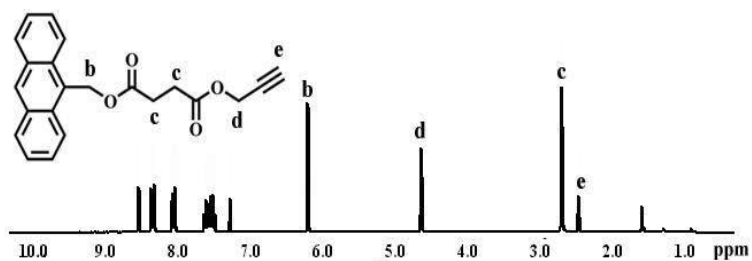
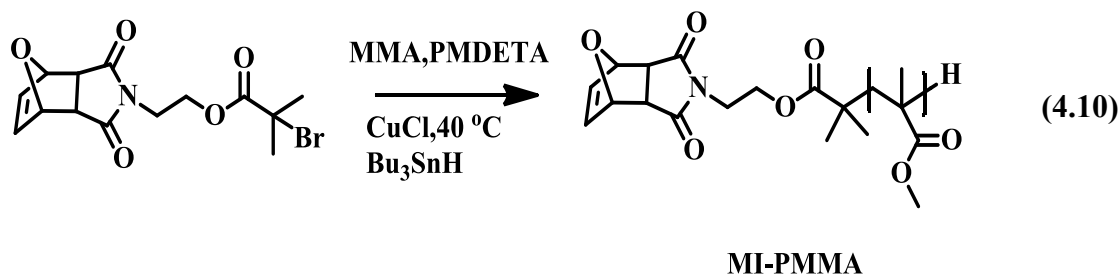


Figure 4.7 : ^1H NMR spectrum of succinic acid anthracen-9-ylmethyl ester prop-2-ynyl ester (8) in CDCl_3 .

Next, MI-PMMA (reaction 4.10), was obtained by ATRP of MMA, using **3** as initiators. Since furan protection was easily deprotected at elevated temperatures, the polymerization temperature for *t*BA and MMA were purposely kept low in order to prevent possible copolymerization of maleimide and monomers during polymerization. Number-average molecular weight calculated by GPC ($M_{n, \text{GPC}}$) of MI-PMMA was in fairly good agreement with the theoretical one ($M_{n, \text{theo}}$) indicating that the initiations were not quantitative under these polymerization conditions.



From ^1H NMR spectrum as seen in Figure 4.8, 4.0 ppm of OCH_3 proton of PMMA and 3.2 ppm of $\text{NCH}_2\text{CH}_2\text{OC}=\text{O}$ protons are showed succesfully synthesis of PMMA. The $M_{n, \text{NMR}}$ of MI-PMMA was determined from a ratio of integrated peaks at 3.58 ppm (OCH_3 protons of MMA) to 6.5 ppm (vinyl end protons).

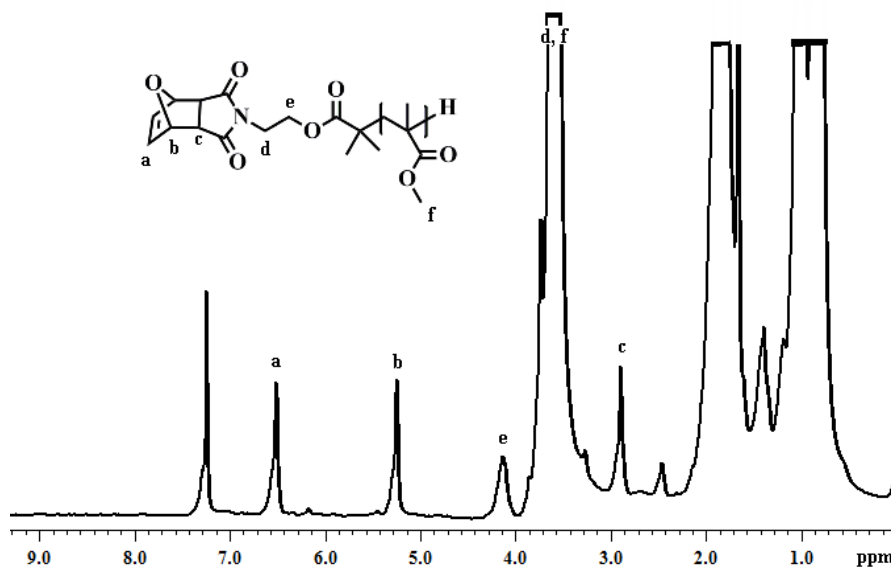
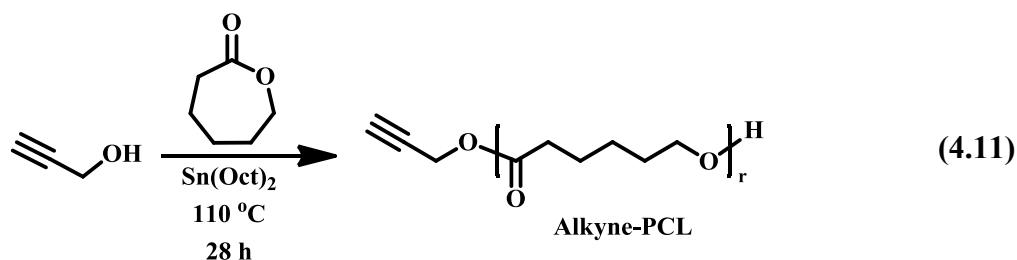


Figure 4.8 : ^1H NMR spectrum of furan protected maleimide end-functionalized PMMA (MI-PMMA) in CDCl_3 .

Alkyne-PCL was prepared by ROP of ϵ -CL in bulk using $\text{Sn}(\text{Oct})_2$ as a catalyst and propargyl alcohol as an initiator at $110\text{ }^\circ\text{C}$ as seen in reaction 4.11.



Alkyne end-functionality was confirmed by the observation of a signal at 4.65 (CH≡CCH₂OC=O) in the ¹H NMR spectrum (Figure 4.9). *M*_{n,NMR} = 3000 of the polymer was determined accordingly from the integration of the peaks at 4.03 and 4.65 ppm related to PCL repeating unit and CH≡CCH₂OC=O end-group protons, respectively.

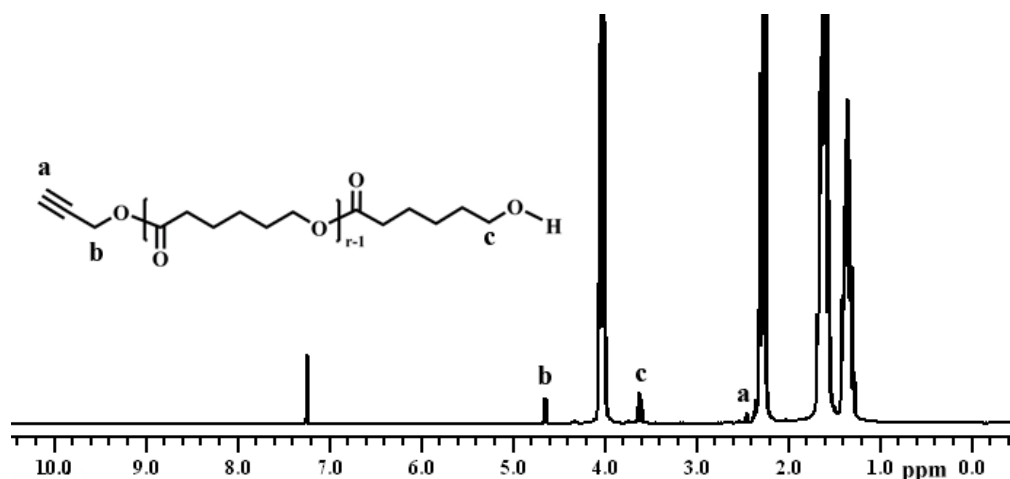


Figure 4.9: ¹H NMR spectrum of Alkyne-PCL in CDCl₃.

Mono carboxylic acid functional PEG (PEG-COOH) was synthesized with a reaction of PEG-OH in the presence of succinic anhydride. When DMAP, Et₃N and CH₂Cl₂ were used as the catalysts and the solvent respectively, the reaction proceeded efficiently, and PEG-COOH were obtained in high yield (Yield = 5 g, 95%). Figure 4.10 depicts the ¹H NMR spectrum of PEG with a COOH end group. The methylene proton of PEG is assigned as 4.25 ppm because of the introduction of succinic anhydride. The methylene proton formed by the ring opening of succinic anhydride is assigned as 2.65 ppm.


$$\text{TEMPO-OH} + \text{HOOC-PEG-OH} \xrightarrow[\text{CH}_2\text{Cl}_2, \text{r.t.}]{\text{DCC, DMAP}} \text{TEMPO-PEG} \quad (4.12)$$

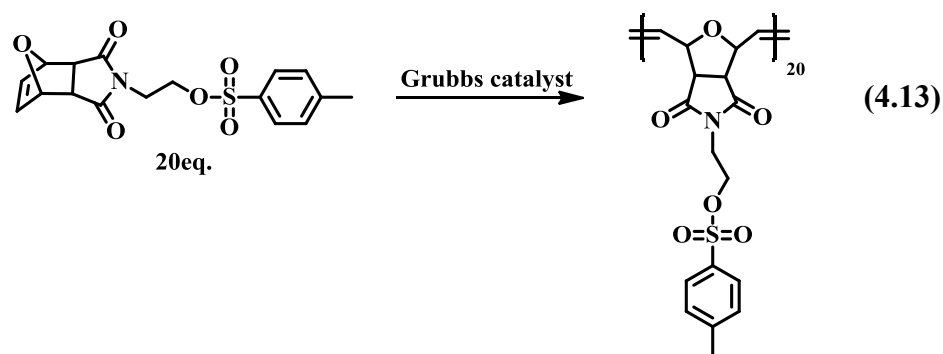
Table 4.1: The conditions and the results of linear polymers used in the synthesis of block and graft copolymer via DA, NRC, click reactions.

Polymer	Conv ^d (%)	M _{n,theo} (g/mol)	M _{n,GPC} (g/mol)	M _w /M _n
Alkyne-PCL ^a	90	3150 ^e	6170	1.08
MI-PMMA ^b	36	2150 ^e	3700	1.29
TEMPO-PEG ^c	85	800 ^e	650	1.06

$$^e M_{n, \text{theo}} = ([M]_0/[I]_0) \times \text{conversion \%} \times M_W \text{ of monomer} + M_W \text{ of initiator}.$$

4.2 Preparation of Heterograft Copolymers via Combination of ROMP and Diels- Alder Click Reaction

Poly (ONB-OTs) was obtained via ROMP of **6** using the first generation Grubbs' catalyst $(\text{PCy}_3)_2(\text{Cl})_2\text{-RuCHPh}$ in CH_2Cl_2 at room temperature for 30 min, followed by a reaction with butyl vinyl ether as a terminating agent for additional 30 min as seen in reaction 4.13. Polymer was precipitated in methanol.



^1H NMR spectroscopy confirmed that poly(oxanorbornenyl tosyl) was appropriately prepared with controlled molecular weight, low polydispersity index (PDI). In the NMR spectrum, the shift of the vinyl protons (6.0 to 4.5 ppm) to the 6.0 ($\text{CH}=\text{CH}$, trans) and 5.8 ppm ($\text{CH}=\text{CH}$, cis) was observed upon the ROMP of **6**, which revealed that poly(oxanorbornenyl tosyl) had occurred as seen in Figure 4.11.

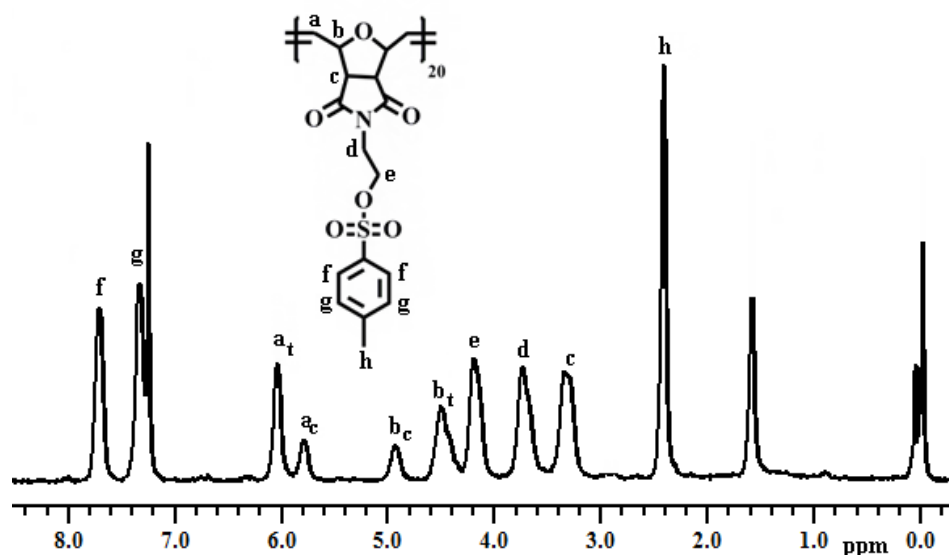
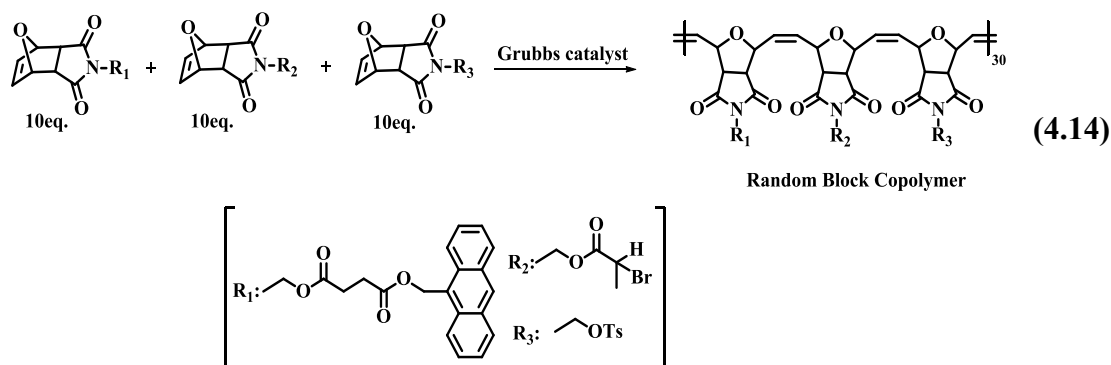


Figure 4.11: ^1H NMR spectrum of poly(ONB-OTs) in CDCl_3 .

Random Poly(ONB-anthracene) $_{10}$ -*b*-Poly(ONB-bromide) $_{10}$ -*b*-Poly(ONB-OTs) $_{10}$
 Block Copolymer was prepared via ROMP of **4**, **6**, **7** using the first generation

Grubbs' catalyst $(\text{PCy}_3)_2(\text{Cl})_2\text{-RuCHPh}$ in CH_2Cl_2 at room temperature for 4 hour, followed by a reaction with butyl vinyl ether as a terminating agent for additional 30 min (4.14).



^1H NMR spectrum of this structure have been completely accomplished as seen Figure 4.12.

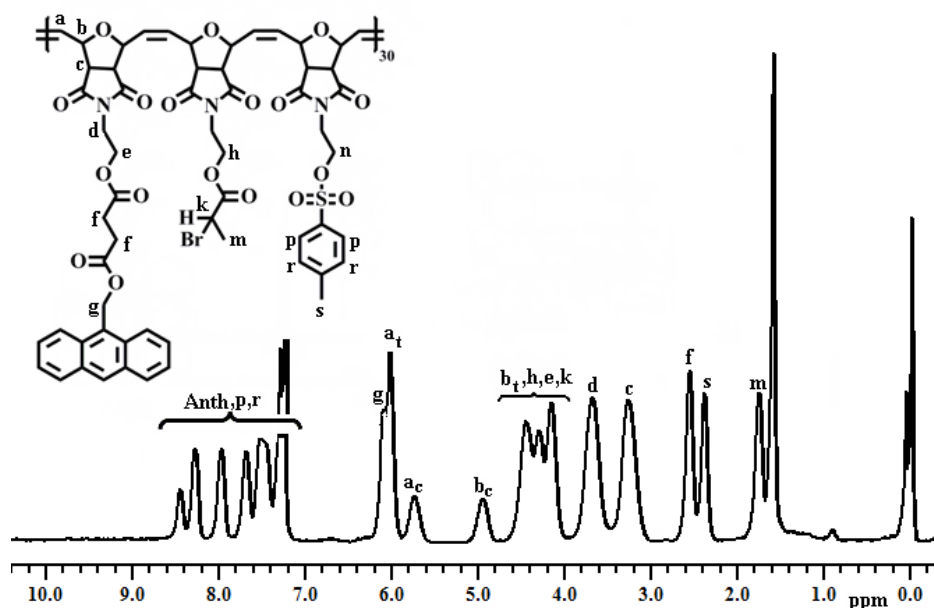


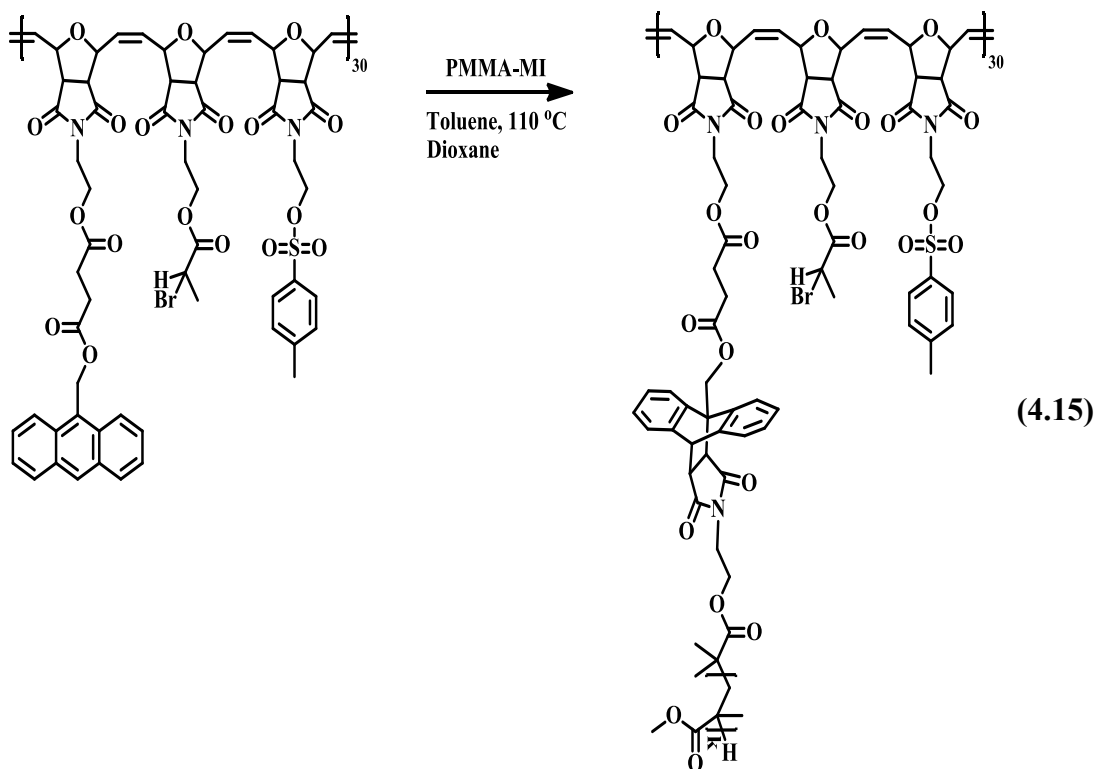
Figure 4.12: ^1H NMR spectrum of Poly(ONB-anthracene) $_{10}$ -b-Poly(ONB-bromide) $_{10}$ -b-Poly(ONB-OTs) $_{10}$ Block Copolymer in CDCl_3 .

In the NMR spectrum, anthracene protons from 8.5 to 7.3 ppm, 7.3 and 7.7 ppm of phenyl protons of tosyl group, the 6.1 ($\text{CH}=\text{CH}$, trans) and 5.7 ppm ($\text{CH}=\text{CH}$, cis) was observed upon the ROMP of 4, 6, 7. Although ^1H NMR spectrum of PolyONB(Anth-*co*-Br-*co*-OTs) is not informative, the monomodal GPC trace displays a clear shift to lower retention time as compared to its macromonomer precursor, thus confirming a successful ROMP of PolyONB(Anth-*co*-Br-*co*-OTs).

Moreover, when the $dn/dc = 0.162 \text{ mL/g}$ was introduced into the software of TD-GPC, $M_{n,TDGPC}=12500$ ($M_w/M_n = 1.12$) is obtained for PolyONB(Anth-*co*-Br-*co*-OTs), which is close to a $M_{n,theo} = 12000$ (Table 4.2).

Next, poly(ONB-anthracene)₁₀-*b*-Poly(ONB-bromide)₁₀-*b*-Poly(ONB-OTs)₁₀ was clicked PMMA-MI via Diels-Alder reaction to yield Poly(ONB-*g*-PMMA)₁₀-*b*-Poly(ONB-bromide)₁₀-*b*-Poly(ONB-OTs)₁₀ respectively (4.15). Polymer precipitated in methanol/diethyl ether (1/1).

Unreacted PMMA precursors were easily removed from the reaction mixture by dissolution-precipitation. ¹H NMR analysis of Poly(ONB-*g*-PMMA)₁₀-*b*-Poly(ONB-bromide)₁₀-*b*-Poly(ONB-OTs)₁₀ indicated that the PMMA was readily incorporated into the poly(oxanorbornenyl anthracene) by appearance of the characteristic peaks of both segments and as well as disappearance of anthracene peaks.



TD-GPC measurement was performed by introducing a $dn/dc = 0.097 \text{ mL/g}$ derived from Diels-Alder click efficiency into the instrument and subsequent the $M_{w,TDGPC}$ value was calculated as 72500 (Table 4.2). ¹H NMR spectrum of the graft copolymer Poly(ONB-*g*-PMMA)₁₀-*b*-Poly(ONB-bromide)₁₀-*b*-Poly(ONB-OTs)₁₀ confirmed the grafting of PMMA segment into the poly(oxanorbornenyl anthracene)

displaying the signals corresponding to the both segments as seen in Figure 4.13.

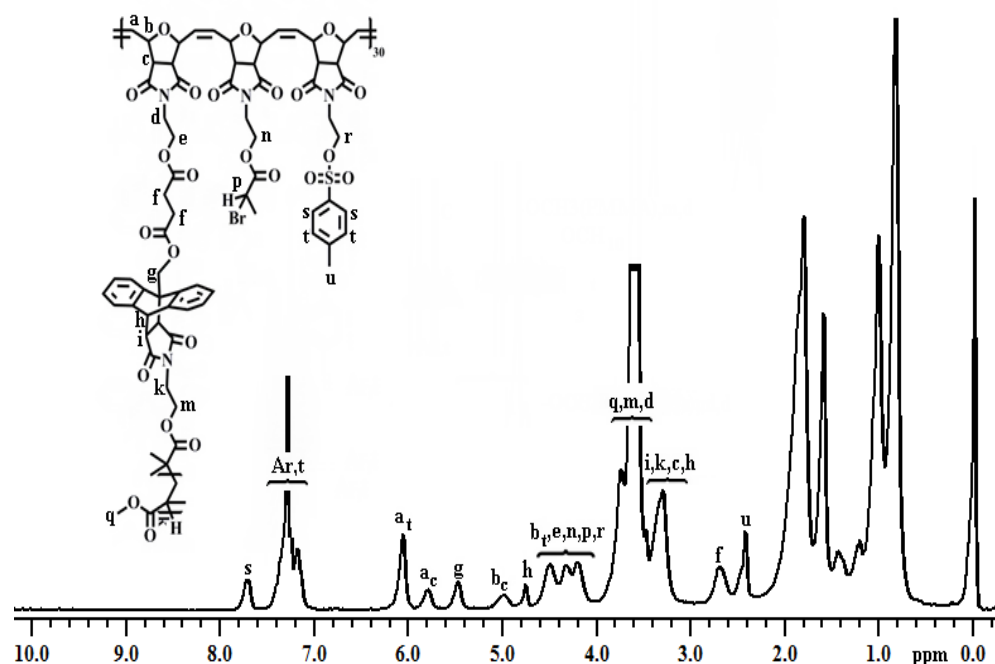


Figure 4.13: ^1H NMR spectrum of PolyONB-*g*-(PMMA-*co*-Br-*co*-OTs) in CDCl_3 .

Diels-Alder click reaction efficiency was also monitored by UV spectroscopy after the decrease in absorbance of anthracene between 300 and 400 nm in the reaction medium as seen in Figures 4.14. Diels-Alder efficiency was calculated by following anthracene Conv. % = $(1 - A_t / A_0)$, where A_0 and A_t are initial and final absorbance values of anthracene Diels-Alder click reaction efficiencies were calculated by monitoring the disappearance of the signals corresponding to the anthracene group and found to be 97 %, respectively.

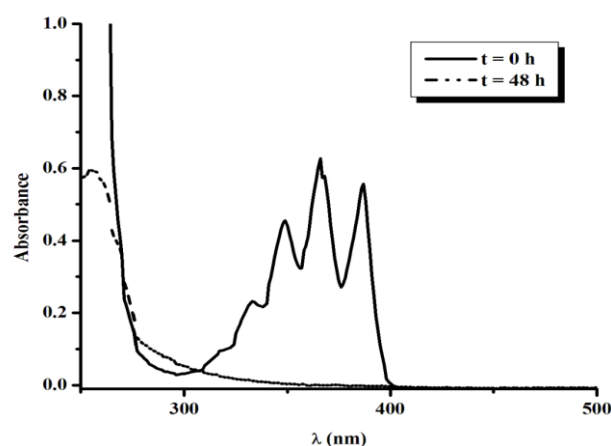
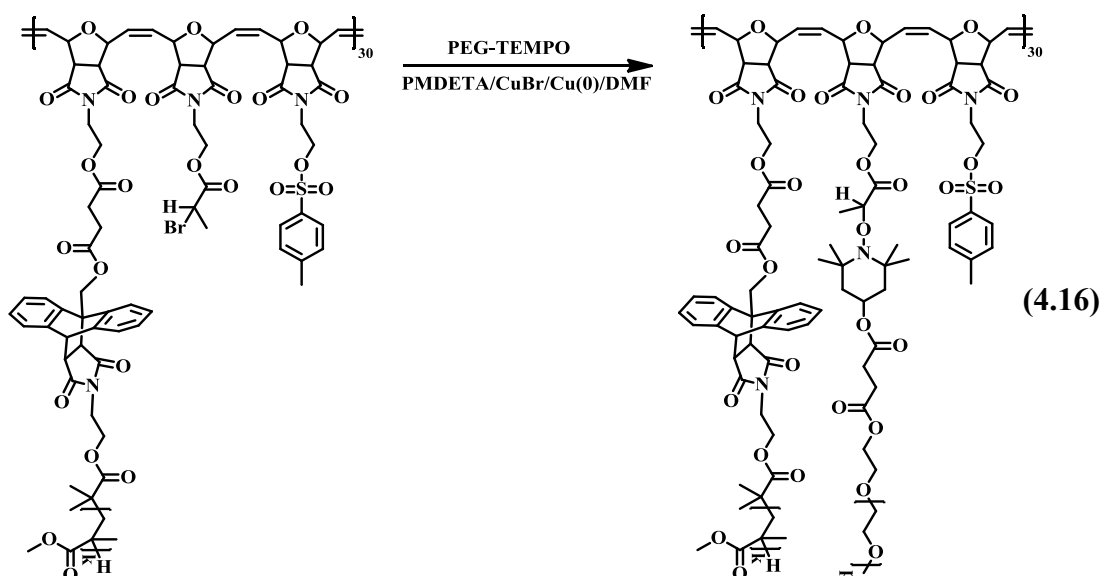


Figure 4.14: UV spectra to monitor the efficiency of Diels-Alder reaction of PolyONB(Anth-*co*-Br-*co*-OTs) with PMMA-MI after 0 h and 48 h in CH_2Cl_2 .

4.3 Preparation of Heterograft Copolymers via Combination of ROMP and Diels-Alder ATNRC Reaction

Heterograft block copolymers, PolyONB-*g*-(PMMA-*co*-PEG-*co*-OTs) was simply obtained via a grafting-onto technique, in which PolyONB-*g*-(PMMA-*co*-Br-*co*-OTs) main chain was clicked with a TEMPO-PEG graft in a NRC reaction to yield related heterograft block copolymers in the presence of Cu(0) and Cu(I)/PMDETA in DMF at room temperature for 24 h (4.16). The crude product was purified by a two times dissolution–precipitation cycle in THF-MeOH.



The $dn/dc = 0.093$ mL/g for PolyONB-*g*-(PMMA-*co*-PEG-*co*-OTs) was determined by experimentally and introduced into the OmniSec software to yield molecular weights, intrinsic viscosity ($[\eta]$) and hydrodynamic radius (R_h). The $M_{n,theo} = 57000$ was calculated by following equation.

$$M_{n,theo} = 10 \times (M_W \text{ of } 4 + M_W \text{ of } 6 + M_W \text{ of } 7) \times \text{conv. \%} + (\text{Diels-Alder efficiency} = 97\%) \times 10 \times M_{n,NMR} \text{ of PMMA-MI} + 10 \times M_{n,theo} \text{ of PEG-Tempo) and were close to } M_{n,TDGPC} = 60500.$$

In the NMR spectrum confirmed the incorporation of PEG into the block copolymer by appearance of the characteristic signals of the PEG segment at 4.5-4.2, 3.8-3.2 ppm (Figure 4.15).

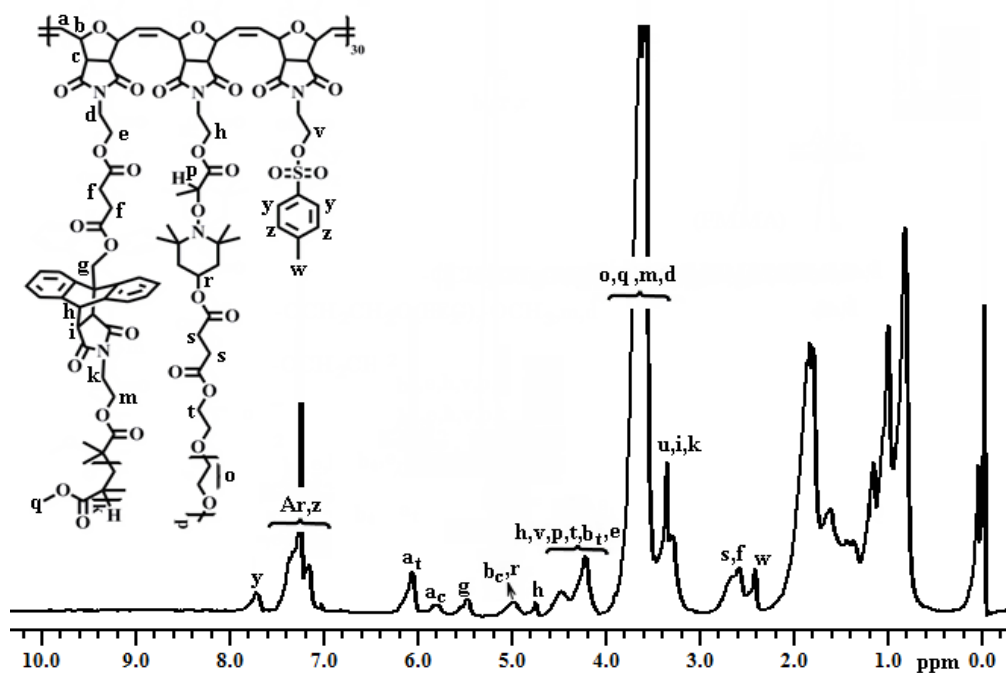
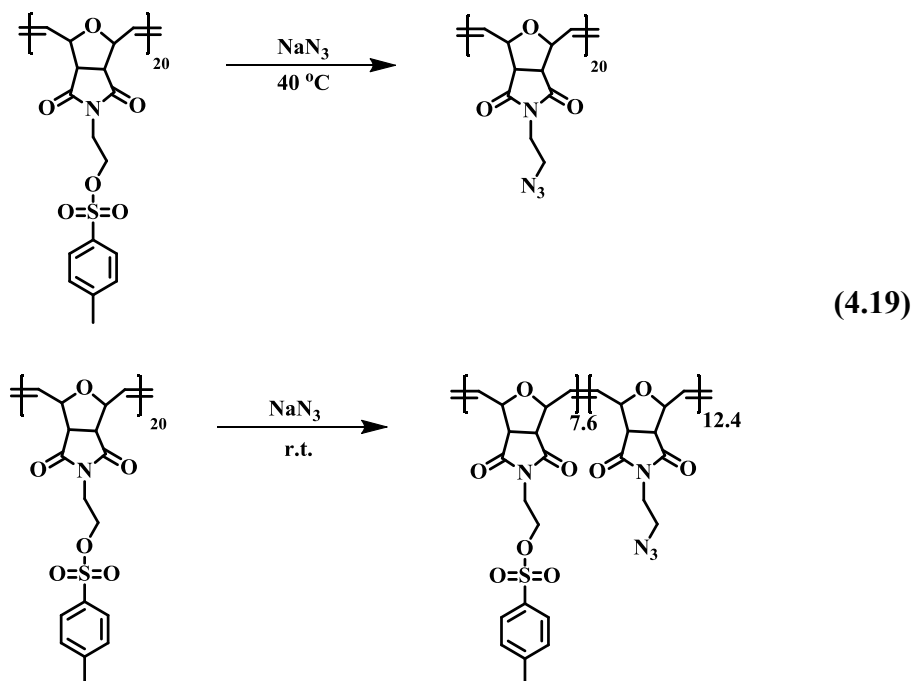


Figure 4.15: ^1H NMR spectrum of PolyONB-*g*-(PMMA-*co*-PEG-*co*-OTs) in CDCl_3 .

4.4 Preparation of Heterograft Copolymers via Combination of ROMP and Diels-Alder ATNRC In situ-Azidation Click Reaction

Azidation reaction of Poly(ONB-OTs) is carry out in presence of NaN_3 both at 0°C and at 40°C . This reaction at 40°C is succesfully accomlished by using NMR spectrum .These reaction was showed below (4.19).



In the NMR spectrum confirmed by disappearance of the characteristic signals of the phenyl of tosyl segment at 7.6-7.8, methyl of tosyl segment 2.4-2.6 ppm (Figure 4.16).

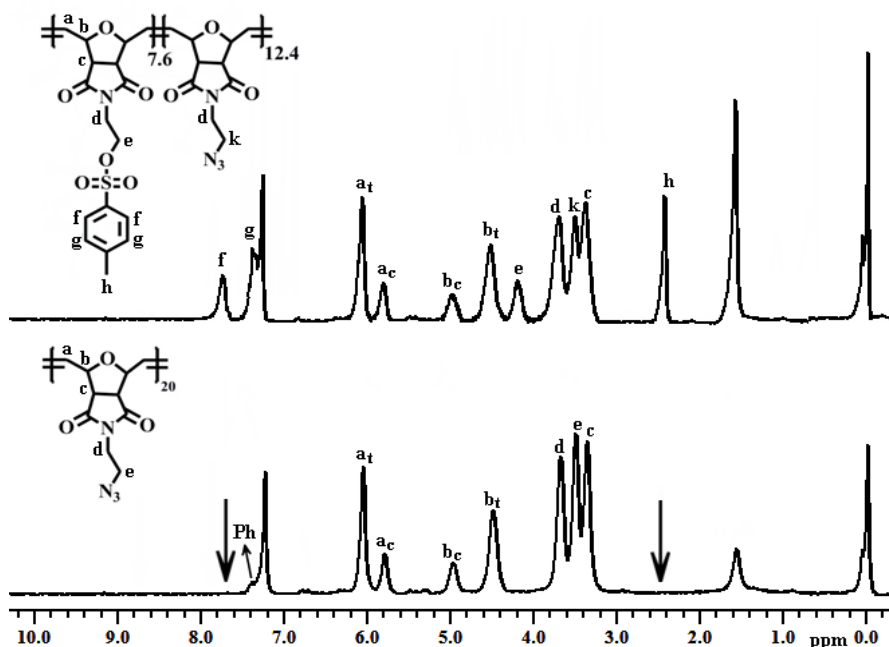
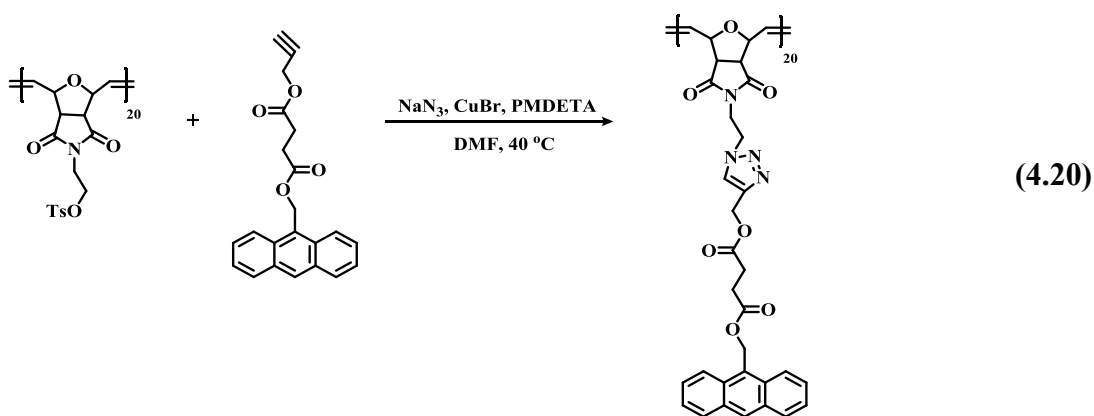


Figure 4.16: ^1H NMR spectrum of In-situ Azidation Reaction of Poly(ONB-OTs)

Poly(ONB-OTs) is reacted with anthracene-alkyne (8) to form clicked structure in the presence of Cu(I), NaN_3 and PMDETA in DMF at 40°C temperature for 24 h (4.20). Polymer was precipitated in methanol. This dissolution-precipitation (THF-MeOH) procedure was repeated two times.



^1H NMR spectrum of model structure as seen Figure 4.17 indicated the successful reaction. The protons of anthracene were detected at 8.4, 8.2, 7.4-7.5 ppm and

proton of anthracene at 6.2-5.4 ppm (br, CH_2 -anthracene, $\text{CH}=\text{CH}$, trans and $\text{CH}=\text{CH}$, cis) confirmed that the reaction was successfully carried out.

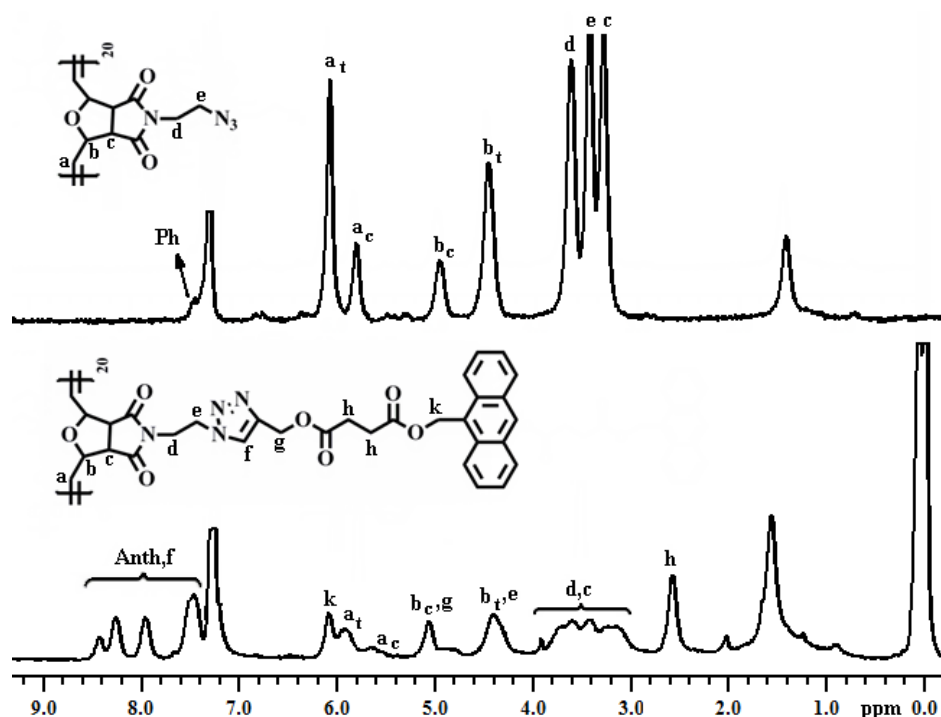
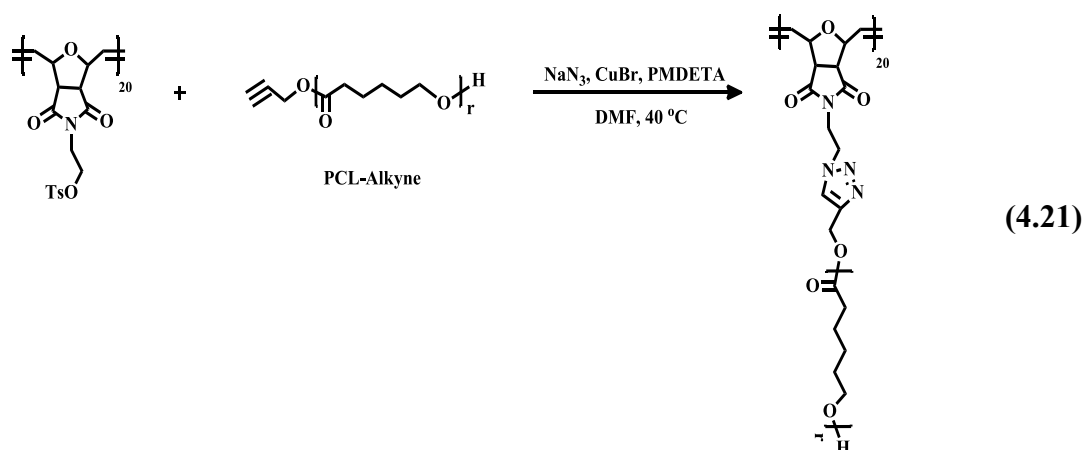


Figure 4.17: ^1H NMR spectrum of Poly(ONB-Anth)

Poly(ONB-OTs) is reacted with PCL-alkyne to form clicked structure in the presence of Cu(I) , NaN_3 and PMDETA in DMF at 40°C temperature for 24 h (4.21). Polymer was precipitated into methanol/diethyl ether (1/1) and recovered polymer was dissolved in THF, precipitated in methanol.



^1H NMR spectrum of model structure as seen Figure 4.18 indicated the successful reaction. The protons of triazole were detected at 7.7 ppm, 6.1- 5.8 ppm (br,

$CH=CH$, trans and $CH=CH$, cis), 5.2 (bs, $=CH-CH-O$, cis and triazole- CH_2O) and proton of PCL 4.0 ppm confirmed that the reaction was successfully carried out.

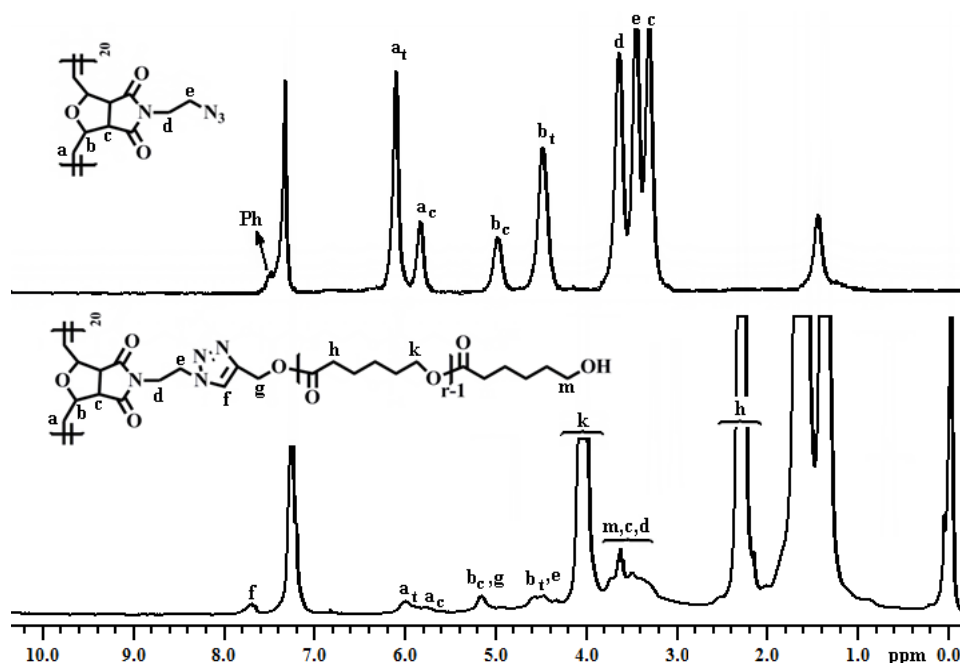
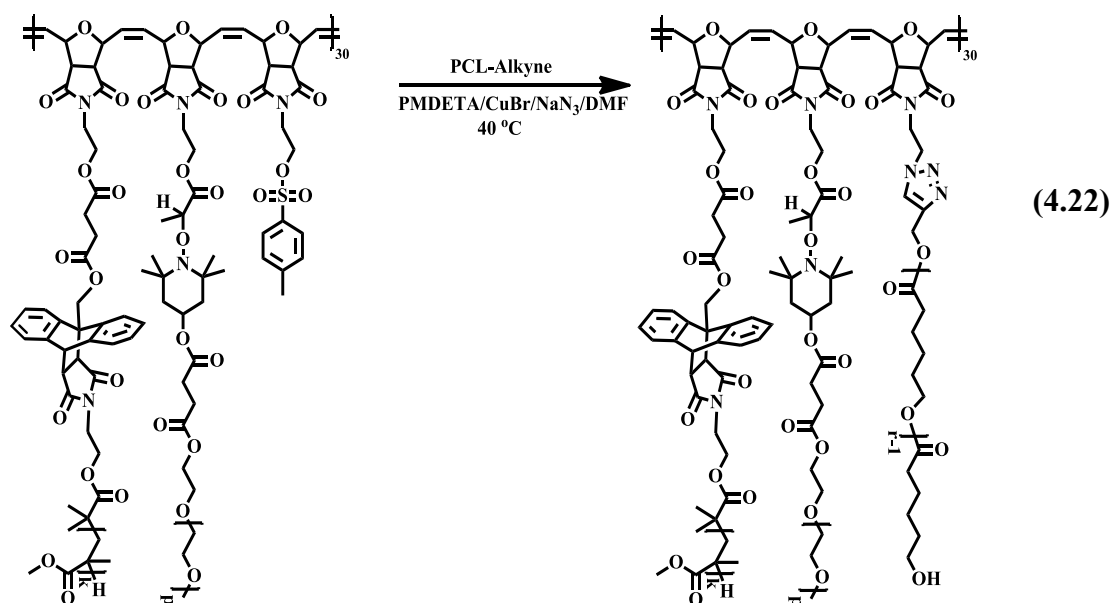


Figure 4.18: ^1H NMR spectrum of Poly(ONB-PCL)

Next, the In-situ azidation and click reaction strategy was applied to the preparation of the final heterograft block copolymers PolyONB-*g*-(PMMA-*co*-PEG-*co*-PCL). PolyONB-*g*-(PMMA-*co*-PEG-*co*-PCL) was obtained by using the reaction between Poly(ONB-*g*-PMMA)₁₀-*b*-Poly(ONB-*g*-PEG)₁₀-*b*-Poly(ONB-OTs)₁₀ with PCL-Alkyne via In-situ azidation and click procedure in the presence of Cu(I), NaN₃ and PMDETA in DMF at 40 °C temperature for 24 h (4.22).



Polymer was precipitated into methanol/diethyl ether (2/1) and recovered polymer was dissolved in THF and precipitated in methanol.

^1H NMR spectra displayed that an incorporation of the PCL graft onto the polyONB-*g*-(PMMA-*co*-PEG-*co*-OTs) main backbone by appearance of the characteristic signals of the PCL (δ 2.3) and protons of Peg 3.2-3.8 ppm , pehnyl group of proton 7.24 ppm and triazole-CH₂ segment were detected at 5.2 ppm (Figure 4.19)

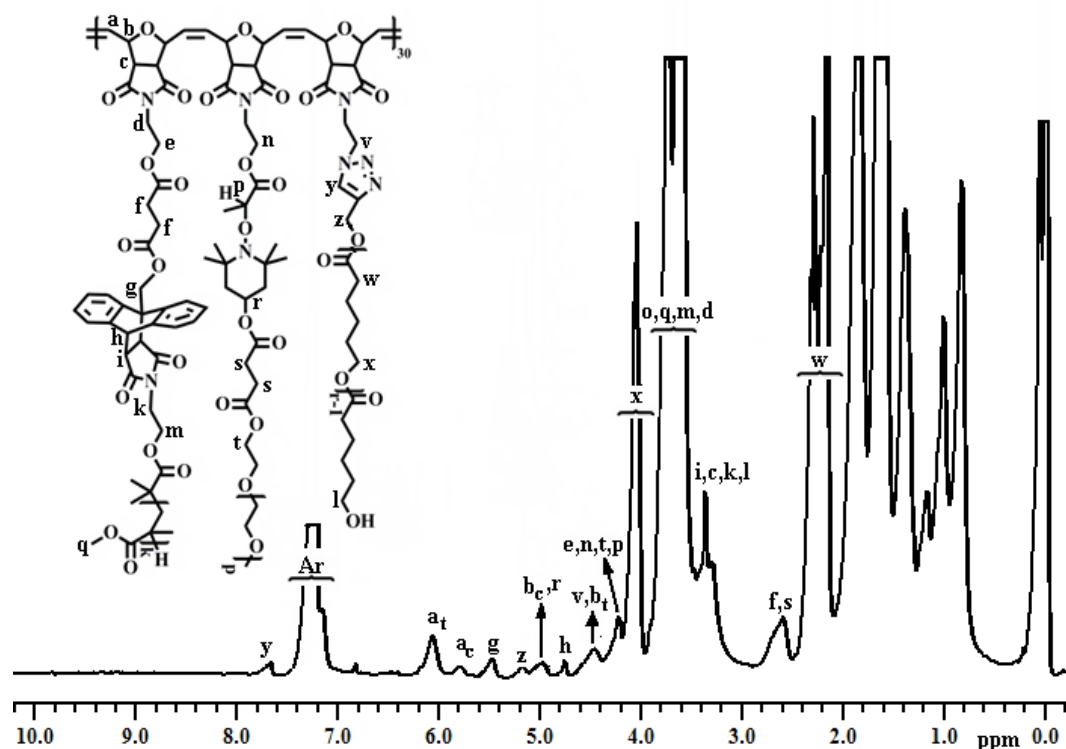


Figure 4.19: ^1H NMR spectrum of Poly(ONB-*g*-PMMA)₁₀-*b*-Poly(ONB-*g*-PEG)₁₀-*b*-Poly(ONB-*g*-PCL)₁₀

The $dn/dc = 0.084 \text{ mL/g}$ for PolyONB-*g*-(PMMA-*co*-PEG-*co*-PCL) was determined by experimentally and introduced into the OmniSec software to yield molecular weights, intrinsic viscosity ($[\eta]$) and hydrodynamic radius (R_h). The $M_{n, \text{theo}} = 87000$ was calculated by following equation

$$M_{n, \text{theo}} = (10 \times (M_W \text{ of } \mathbf{4} + M_W \text{ of } \mathbf{6} + M_W \text{ of } \mathbf{7}) \times \text{conv. \%}) + (\text{Diels-Alder efficiency} = 97 \%) \times 10 \times M_{n, \text{NMR}} \text{ of PMMA-MI} + 10 \times M_{n, \text{theo}} \text{ of PEG-Tempo} + 10 \times M_{n, \text{NMR}} \text{ of PCL-Alkyne}$$

and were close to $M_{n, \text{TGPGC}} = 95000$ (Table 4.2).

The dn/dc values of heterograft block copolymers were determined from a slope of RI area-concentration linear plot containing at least four different polymer concentrations, assuming that truly size-exclusion mechanism was operative in the

columns of TD-GPC. These experimental dn/dc values are subsequently introduced to the OmniSec software of the TD-GPC to yield $M_{w,TDGPC}$, $[\eta]$ and R_h of the analyzed heterograft block copolymers (Table 4.2).

It should be noted that the obtained molecular weights ($M_{n,TDGPC}$) are close to $M_{n,theo}$ values, thus displaying target well-defined heterograft block copolymers.

Monomodal GPC traces with narrow polydispersity display a clear shift to a lower retention time as compared to those of starting precursor, thus proving the synthesis of graft block copolymer as seen in Figures 4.20. GPC analysis of polyONB-*g*-(PMMA-*co*-PEG-*co*-OTs) heterograft block copolymer showed a monomodal peak, however, which shifted to higher retention time with respect to that of polyONB-*g*-(PMMA-*co*-Br-*co*-OTs) graft block copolymer (Figure 4.20).

This may be due to that adsorption of the PEG segment on the stationary phase caused a shift to lower molecular weight region. Moreover, from Table 2, it is deduced that hydrodynamic radius (R_h) of heterograft block copolymer is slightly higher than that of, polyONB-*g*-(PMMA-*co*-Br-*co*-OTs) graft block copolymer indicating that GPC trace shift is not the result of a decrease in the hydrodynamic volume.

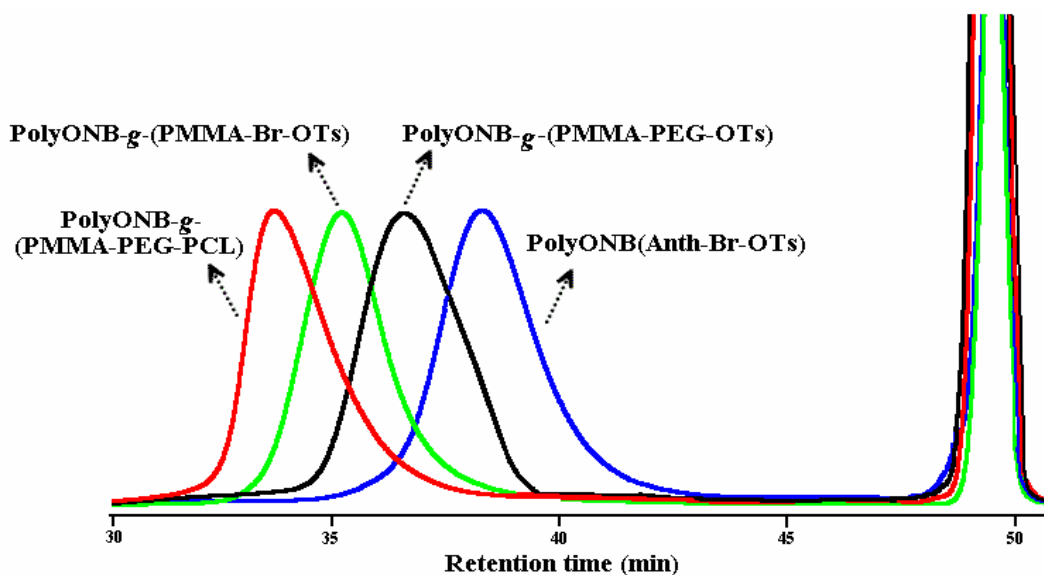


Figure 4.20: Evolution of GPC traces: PolyONB(Anth-*co*-Br-*co*-OTs), PolyONB(*g*-(PMMA-*co*-Br-*co*-OTs), PolyONB-*g*-(PMMA-*co*-PEG-*co*-OTs), PolyONB-*g*-(PMMA-*co*-PEG-*co*-PCL).

Table 4.2. The Characterization of Heterograft Copolymers.

Entry	Polymers	GPC ^a			TD-GPC ^b				
		M_n (g/mol)	M_w/M_n	$M_{n,theo}$ (g/mol)	M_n (g/mol)	M_w (g/mol)	$[\eta]$ (dL/g)	R_h (nm)	dn/dc^g (mL/g)
1	PolyONB(Anth- <i>co</i> -Br- <i>co</i> -OTs)	8050	1.12	12000 ^c	12500	17000	0.067	2.56	0.162
2	PolyONB-g-(PMMA- <i>co</i> -Br- <i>co</i> -OTs)	23600	1.27	49000 ^d	51000	72500	0.088	4.53	0.097
3	PolyONB-g-(PMMA- <i>co</i> -PEG- <i>co</i> -OTs)	15500	1.14	57000 ^e	60500	73000	0.109	4.94	0.093
4	PolyONB-g-(PMMA- <i>co</i> -PEG- <i>co</i> -PCL)	23300	1.26	87000 ^f	95000	118000	0.188	6.84	0.084

^aDetermined by conventional GPC calibrated relative to linear PS standards in THF at 30 °C.

^bCalculated from triple detection GPC (TD-GPC) in THF at 35°C.

^c $M_{n,theo} = 10 \times (M_w \text{ of } \mathbf{4} + M_w \text{ of } \mathbf{6} + M_w \text{ of } \mathbf{7}) \times \text{conv. \%}$.

^d $M_{n,theo} = 12000 \times (\text{Diels-Alder efficiency \%}) \times 10 \times M_{n,NMR} \text{ of PMMA-MI}$.

^e $M_{n,theo} = 49000 \times 10 \times M_{n,theo} \text{ of PEG-Tempo}$.

^f $M_{n,theo} = 57000 \times 10 \times M_{n,NMR} \text{ of PCL-Alkyne}$.

^gDetermined from a slope of RI area concentration linear plot containing at least four different polymer concentrations assuming that truly size-exclusion mechanism was operative through the columns of TD-GPC.

5.CONCLUSIONS

As a conclusion, we here described that heterograft block copolymers were successfully prepared via first time combining ROMP , Diels-Alder , ATNRC and In-situ azidation click strategy. Grafting efficiency for all polymeric samples was monitored by using UV-Vis spectroscopy and found to be over the range of 90-98%. GPC traces of heterograft block copolymers showed a clear shift when compared to their linear precursors, proving that graft reactions were carried out. However, polyONB-*g*-(PMMA-*co*-PEG-*co*-OTs) sample displayed a different behavior, probably due to its adsorption on the column stationary phase. The heterograft block copolymers were successfully prepared and polydispersities 1.12-1.26. It should be noted that $M_{n,theo}$ values are closed $M_{n,TDGPC}$.

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1. Merve YAVUZARSLAN, Neşe ÇAKIR, Gürkan HIZAL, Ümit TUNCA
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