İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

GRAFT COPOLYMERS VIA ROMP AND DIELS-ALDER CLICK REACTION STRATEGY

M.Sc. Thesis by
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Department : Polymer Science and Technology

Programme : Polymer Science and Technology

JANUARY 2011

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Date of submission : 20 December 2010
Date of defence examination: 24 January 2011

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JANUARY 2011

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

HALKA AÇILIMI METATEZ POLİMERİZASYONU VE DİELS-ALDER CLICK REAKSİYONLARI İLE AŞI KOPOLİMERLERİ ELDESİ

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Tezin Enstitüye Verildiği Tarih : 20 Aralık 2010
Tezin Savunulduğu Tarih : 24 Ocak 2011

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OCAK 2011

To my father,

FOREWORD

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

I would like to express my gratitude to my thesis supervisor, Prof. Dr. Ümit TUNCA and co-supervisor Prof. Dr. Gürkan HIZAL for offering invaluable help in all possible ways, continuous encouragement and helpful critics throughout this research.

I wish to express my special thanks to my friend and co-worker Hakan DURMAZ for his friendship, helpful and understanding attitudes during my laboratory and thesis study in ITU. It has been a pleasure to work with him.

I would like to also extend my sincere gratitude Aydan DAĞ for her friendly and helpful attitudes and unbelievable sensibility during my laboratory works. In addition, I would like to thank my friends Eda GÜNGÖR, Neşe ÇAKIR, Hatice ŞAHİN for her support and sincerity during my laboratory study.

I also acknowledge to my family for their encouragement and support throughout my education.

Finally, I would like to dedicate this thesis my fiance Mustafa Gökhun YAYLA for his patience, understanding moral support during all stages involved in the preparation of this research.

January 2011

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ABBREVIATIONS

1,3-DPCA : 1,3-dipolar cycloaddition
^{1}H NMR : Hydrogen Nuclear Magnetic Resonance Spectroscopy
ATRP : Atom Transfer Radical Polymerization
$CDCl_3$: Deuterated chloroform
CH_2Cl_2 : Dichloromethane
CuAAC : Copper catalyzed azide-alkyne cycloaddition
DA : Diels-Alder
DMF : *N*,*N*-dimehthylformamide
DSC : Differential Scanning Calorimetry
DVB : Divinyl benzene
EtOAc : Ethyl acetate
FT-IR : Fourier Transform Infrared Spectrophotometer
GC : Gas Chromatography
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 : *N, N, N',N'', N''*-Pentamethyldiethylenetriamine
PMMA : Poly(methyl metacrylate)
PS : Poly(styrene)
P*t*BA : Poly(*tert*-butyl acrylate)
RAFT : Reversible Addition Fragmentation Chain Transfer
r-DA : retro-Diels-Alder
ROMP : Ring Opening Metathesis Polymerization
St : Styrene
***t*BA** : *tert*-Butylacrylate
TD-GPC : Triple Detector-Gel Permeation Chromatography
TEA : Triethylamine
TEMPO : 2,2,6,6-Tetramethylpiperidine-*N*-oxyl
THF : Tetrahydrofuran
UV : Ultra Violet

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LIST OF SYMBOLS

λ	**:** Wavelength
R·	**:** Radical
f	**:** Number of arm
nm	**:** Nanometer
[η]	**:** 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
d*n*/d*c*	**:** Refractive index increment
K	**:** Mark-Houwink-Sakurada constant
ppm	**:** Parts per million
^oC	**:** Celsius
M	**:** Molarity
T_g	**:** Glass-transition temperature
M_n	**:** The number average molecular weight
M_w	**:** The weight average molecular weight
M_w/M_n	**:** The molecular weight distribution

GRAFT COPOLYMERS VIA ROMP AND DIELS-ALDER CLICK REACTION STRATEGY

SUMMARY

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.

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.

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. 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. 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.

In this study; anthracene-functionalized oxanorbornene monomer and oxanorbornenyl PS with ω-anthracene end-functionalized macromonomer were first polymerized via ring opening metathesis polymerization (ROMP) using the first generation Grubbs' catalyst in dichloromethane at room temperature and then clicked with maleimide end-functionalized polymers, PEG-MI, PMMA-MI, and P*t*BA-MI in a Diels-Alder reaction in toluene at 120 ^{o}C to create corresponding graft copolymers, poly(oxanorbornene)-*g*-PEG, poly(oxanorbornene)-*g*-PMMA, and graft block copolymers, poly(oxanorbornene)-*g*-(PS-*b*-PEG), poly(oxanorbornene)-*g*-(PS-*b*-PMMA), and poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA), respectively. Diels-Alder click reaction efficiency for graft copolymerization was monitored by UV-Vis spectroscopy. The d*n*/d*c* 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 ([η]) and hydrodynamic radius (Rh) values.

HALKA AÇILIMI METATEZ POLİMERİZASYONU VE DIELS ALDER-CLICK REAKSİYONLARI İLE GRAFT KOPOLİMERLERİ ELDESİ

ÖZET

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 aşılanır; (iii) makromonomerlerin kopolimerizasyonu ile elde edilir.

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.

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

Bu çalışmada, ilk olarak antrasen fonksiyonlu okzanorbornen monomeri ve *ω*-antrasen uç-fonksiyonlandırılmış okzanorbornenil PS makromonomeri oda sıcaklığında diklorometan içerisinde birinci jenerasyon Grubbs katalizörü kullanılarak halka açılma metatez polimerizasyonu ile sentezlendi. Sonra 120 ^{o}C' de toluende Diels-Alder reaksiyonu ile maleimid uç-fonksiyonlu polimerler, PEG-MI, PMMA-MI ve P*t*BA-MI sırasıyla poly(oxanorbornen)-*g*-PEG, poly(oxanorbornen)-*g*-PMMA aşı kopolimerleri ve poly(oxanorbornen)-*g*-(PS-*b*-PEG), poly(oxanorbornen)-*g*-(PS-*b*-PMMA), ve poly(oxanorbornen)-*g*-(PS-*b*-P*t*BA) aşı blok kopolimerleri eldesi için sentezlendi. Aşı kopolimerizasyonun Diels-Alder click reaksiyonu etkinliği UV-Vis spektroskopisi ile gözlemlendi. Aşı kopolimerleri ve aşı blok kopolimerlerinin d*n*/d*c* değerleri üçlü dedektör GPC (TD-GPC) kullanılarak elde edildi ve bu değerler cihaza tanıtılarak molekül ağırlıkları, intrinsik viskozite ([η]) and hidrodinamik yarıçapı (Rh) değerleri elde edildi.

1. INTRODUCTION

A combination of living polymerization methods and their compatible partner click reactions allows increasingly the synthesis of the complex macromolecular structures, such as star, cyclic, hyperbranched polymers, dendrimers, and graft copolymers, with well-defined molecular weight, composition, topology and functional groups [1-13]. It is well known that complex architectures display different properties both in bulk and solution, i.e. morphology and assembly in solution and in bulk, and the solution and the melt viscosity, while compared to their linear counterparts.

Graft copolymers can be obtained with three general methods: (i) grafting-onto, in which side chains are preformed, and then attached to the main polymer backbone; (ii) grafting-from, in which the monomer is grafted from the main backbone; and (iii) grafting-through, in which the macromonomers are copolymerized in order to give the resultant graft copolymer [14, 15].

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) [16-34]. Although there have been many published studies on the synthesis of graft copolymers by using a combination of ROMP and other living polymerization techniques ; such as ROMP-ROMP , ROMP-atom transfer radical polymerization (ATRP) , ROMP-reversible addition fragmentation chain transfer polymerization (RAFT) , ROMP-living anionic polymerization , and ROMP-ring opening polymerization (ROP) combinations , relatively few publications have emerged in the literature based on combining ROMP and click reactions [35-52]. Grubbs first time employed a ROMP-click combination for the synthesis of graft copolymers using grafting-through method [53]. Various macromonomers were efficiently synthesized through azide-alkyne click reaction of a norbornene-alkyne with azido terminal group of polystyrene (PS), poly(methyl methacrylate (PMMA) and

poly(*tert*-butyl acrylate) (P*t*BA). ROMP of these macromonomers were carried out using the ruthenium catalyst, $(H_2IMes)(pyr)_2(Cl)_2RuCHPh$ in tetrahydrofuran (THF) at room temperature in order to give graft copolymers with narrow polydispersity and high molecular weights. Later, Fontaine *et al.* used same strategy by reacting alkyne-functionalized oxanorbornene with azido-terminated pol(ethylene glycol) (PEG) so as to give *ω*-oxanorbornenyl PEG macromonomers [54]. Subsequent ROMP of these macromonomers gave poly(oxanorbornene)-*g*-PEG with narrow polydispersity and moderate molecular weights employing third generation Grubbs' catalyst in dichloromethane at room temperature via grafting-through method.

Recently, our group has reported the synthesis of well-defined graft and heterograft copolymers via combination of living radical polymerization techniques with click reactions: Diels-Alder and copper catalyzed azide-alkyne cycloaddition reaction [55, 56]. More recently, our group has demonstrated the synthesis of various types of star polymers by a ROMP-azide alkyne click reaction combination [57, 58].

In this thesis, we first time applied the ROMP-Diels-Alder click reaction combination to the synthesis of well-defined graft copolymers via grafting-onto and grafting-through methods. Anthracene-functionalized oxanorbornene monomer and oxanorbornenyl PS with *ω*-anthracene end-functionalized macromonomer were first polymerized via ROMP using the first generation Grubbs' catalyst and then clicked with maleimide end-functionalized polymers, PEG-MI, PMMA-MI, and P*t*BA-MI, in a Diels-Alder reaction to produce corresponding graft copolymers, poly(oxanorbornene)-*g*-PEG, poly(oxanorbornene)-*g*-PMMA, and graft block copolymers, poly(oxanorbornene)-*g*-(PS-*b*-PEG), poly(oxanorbornene)-*g*-(PS-*b*-PMMA), and poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA), respectively. Representative structures are shown in Figure 1.1.

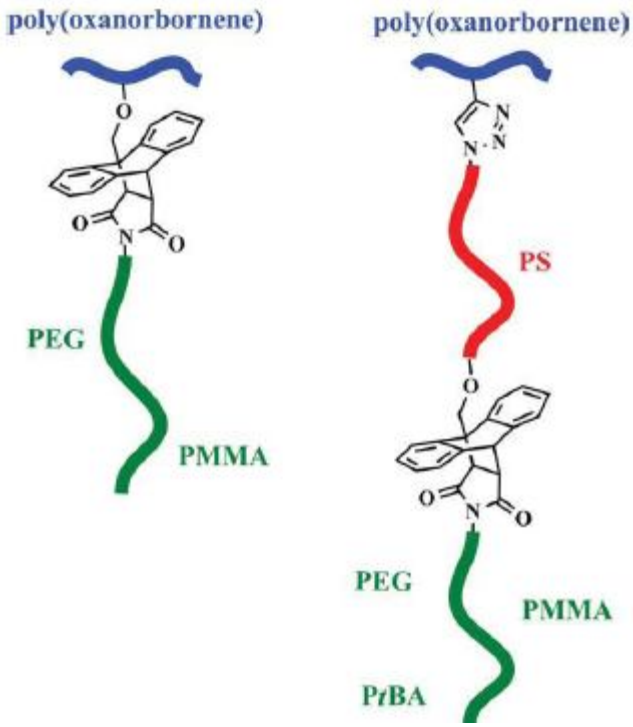


Figure 1.1: General scheme for the preparation of graft copolymers and graft block copolymers via ROMP and Diels–Alder click reaction.

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 [59]. 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) [60]. 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 [61-63]. It has been suggested to use a term controlled polymerization if these additional criteria are met [64]. 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 [65, 66].

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 [67].

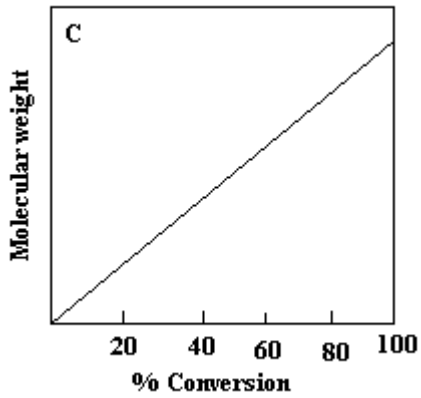
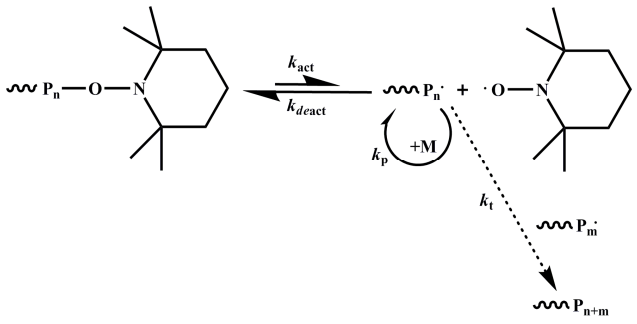


Figure 2.1: Molecular weight vs. conversion graph of a typical living polymerization

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) [67].

2.1.1.1 Nitroxide mediated radical polymerization (NMP)

Nitroxide–mediated living free radical polymerization (NMP) belongs to a much larger family of processes called stable free radical polymerizations. In this type of process, the propagating species (Pn°) reacts with a stable radical (X°) as seen in equation **2.1**. The resulting dormant species (Pn-X) can then reversibly cleave to regenerate the free radicals once again. Once Pn° 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-tetramethylpiperidinoxy (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 [68]. Although NMP is one of the simplest methods of living free radical polymerization (LFRP), it has many disadvantages. Many monomers will not polymerize because of the stability of the dormant alkoxyamine that forms. Also, since the reaction is kinetically slow, high temperatures and bulk solutions are often required. Also, the alkoxyamine end groups are difficult to transform and require radical chemistry [69].



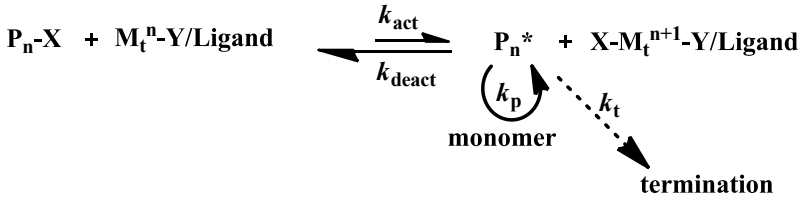
(2.1)

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 [70].

2.1.1.2 Atom transfer radical polymerization (ATRP)

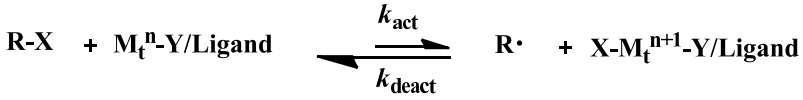
Atom transfer radical polymerization (ATRP) is a living radical polymerization process utilizing transition-metal complexes as catalysts to mediate the propagation of the polymerization. It is a very versatile process and can synthesize a wide spectrum of polymers with controlled structures. Atom transfer radical polymerization (ATRP) is one of the most convenient methods to synthesize well-defined low molecular weight polymers [71].



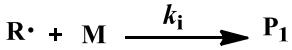
(2.2)

Equation **2.2** represents the general mechanism of ATRP. The radicals, i.e., the propagating species P_n*, are generated through a reversible redox process catalyzed by a transition metal complex (activator, M_t^n –Y / ligand, where Y may be another ligand or a counterion) which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo)halogen atom, X, from a dormant species, P_n–X. Radicals react reversibly with the oxidized metal complexes, X–M_t^{n+1} / ligand, the deactivator, to reform the dormant species and the activator. These processes are rapid, and the dynamic equilibrium that is established favors the dormant species. By this way, all chains can begin growth at the same time, and the concentration of the free radicals is quite low, resulting in reduced amount of irreversible radical-radical termination. Also chain growth 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. Elementary reactions consisting of initiation, propagation, and termination are illustrated below in equations **2.3-2.7** [72].

Initiation

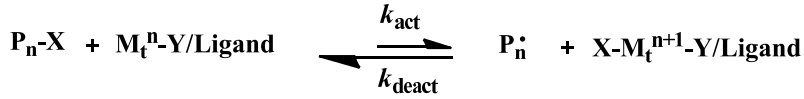


(2.3)

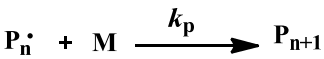


(2.4)

Propagation



(2.5)



(2.6)

Termination

(2.7)

Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. 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 [73]. 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 rates of polymerization and polydispersity in ATRP, assuming steady-state kinetics, are given in equations **2.8** and **2.9**, respectively [74-76].

$$R_p = k_p.K_{eq}\frac{[\text{R-X}][\text{Mt}^n]}{[\text{Mt}^{n+1}]}[\text{M}] \quad \text{or} \quad \ln\left(\frac{[\text{M}_0]}{[\text{M}]}\right) = \frac{k_p.k_{act}[\text{R-X}][\text{Mt}^n]}{k_{deact}[\text{Mt}^{n+1}]}t = k_{app}t \tag{2.8}$$

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_p[\text{R-X}]}{k_{deact}[\text{Mt}^{n+1}]}\right)\left(\frac{2}{\text{p}} - 1\right) = 1 + \frac{2}{k_{act}[\text{Mt}^n]\,t} \tag{2.9}$$

From equation **2.8**, the rate of polymerization, R_p, is directly proportional to the equilibrium constant, K_{eq}, and the propagation rate constant. The proper selection of the reaction components of an ATRP process led to establishment of an appropriate equilibrium between activation and deactivation processes. The equilibrium constant ($K_{eq} = k_{act}/k_{deact}$) plays an important role in the fate of ATRP because it determines

the concentration of radicals and, therefore, the rates of polymerization and termination. K_{eq} must be low to maintain a low stationary concentration of radicals; thus, the termination reaction is suppressed. For the ATRP system, the rate of polymerization, R_p, is first order with respect to the monomer [M] and the activator [Mt^n] concentrations and increases with the concentrations of activator, monomer, and initiator [R-X] and decreases with the increasing deactivator [Mt^{n+1}] concentration. Equation **2.9** shows that lower polydispersities are obtained at higher conversion, higher k_{deact} relative to k_p, higher concentration of deactivator, and higher monomer to initiator ratio, $[M]_0/[I]_0$.

As a multicomponent system, ATRP includes the monomer, an initiator with a transferable (pseudo)halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Both activating and deactivating components of the catalytic system must be simultaneously present. Sometimes an additive is used. Basic components of ATRP, namely, monomers, initiators, catalysts, ligands, and solvents are discussed as follows:

Monomers

A variety of monomers have been successfully polymerized using ATRP: styrenes, (meth)acrylates, (meth)acrylamides, dienes, and acrylonitrile, which contain substituents that can stabilize the propagating radicals [72]. Each monomer has its own equilibrium constant, K_{eq}, which determined the polymerization rate in ATRP according to equation **2.8**. In fact, all vinyl monomers are susceptible to ATRP except for a few exceptions. Notable exceptions are unprotected acids (e.g. (meth)acrylic acid). Some other monomers may be difficult to polymerize since they exhibit side reactions, which may be affected by the choice of reaction conditions, nature of the catalyst, etc. An example of such a monomer is 4-vinyl pyridine (4-VP), which can undergo quaternization by the (alkyl halide) initiator [77]. The most common monomers in the order of their decreasing ATRP reactivity are methacrylates, acrylonitrile, styrenes, acrylates, (meth)acrylamides [78].

Initiators

Organic halides having a labile carbon-halogen bond are the most successfully employed initiators in ATRP. In general, these organic halides possess electron withdrawing groups and/or atoms such as carbonyl, aryl, cyano, or halogens at α-

carbon to stabilize the generated free radicals. The common way to initiate is via the reaction of an activated (alkyl) halide with the transition-metal complex in its lower oxidation state. To obtain well-defined polymers with narrow molecular weight distributions, the halide atom, X, should rapidly and selectively migrate between the growing chain and the transition metal complex. Thus far, when X is either bromine or chlorine, the molecular weight control is best. Iodine works well for acrylate polymerizations in copper-mediated ATRP and has been found to lead to controlled polymerization of St in ruthenium and ruthenium-based ATRP [79-81]. The carbon–fluorine bond strength is too strong for the fast activation–deactivation cycle with atom transfer. To obtain similar reactivity of the carbon-halogen bond in the initiator and the dormant polymer end, the structure of the alkyl group, R, of the initiator should be similar to the structure of the dormant polymer end. Typical examples would be the use of ethyl 2-bromoisobutyrate and a Cu(I) complex for the initiation of a methacrylate polymerization, or 1-phenylethyl chloride for the initiation of a styrene polymerization [82,65]. In addition, Percec and co-workers reported the use of sulfonyl chlorides as universal initiators in ATRP [83]. Also the use of di-, tri-, or multifunctional initiators is possible, which will result in polymers growing in two, three, or more directions. Besides, some pseudohalogens, specifically thiocyanates and thiocarbamates, have been used in the polymerization of acrylates [84].

The alternative way to initiate ATRP is via a conventional free-radical initiator, which is used in conjunction with a transition-metal complex in its higher oxidation state. Typically one would use AIBN in conjunction with a Cu(II) complex. Upon formation of the primary radicals and/or their adducts with a monomer unit, the Cu(II) complex very efficiently transfers a halogen to this newly formed chain. In doing so the copper complex is reduced, and the active chain is deactivated. This alternative way of initiation was termed “reverse ATRP” [85].

Catalysts

Catalyst is another important component of ATRP. It plays a key role in 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. First, the catalyst should react with initiator fast and quantitatively to ensure that all the polymer chains start to add monomer at the

same time. Second, the catalyst must have moderate redox potential to ensure an appropriate equilibrium between dormant and active species. In general, a low redox potential of the catalyst leads to formation of the high Cu(II) concentration (equilibrium is shifted toward transient radicals). Consequently, a fast and uncontrolled polymerization is observed. In contrast, high redox potential strongly suppresses Cu(II) formation (equilibrium is shifted toward dormant species) via a halogen atom abstraction process leading to very slow polymerization. Third, the catalyst should be less sterically hindered, because large steric congestion around the metal center of catalyst results in a reduction of the catalyst activity. Fourth, a good catalyst should not afford side reactions such as Hoffman elimination, β-H abstraction, and oxidation/reduction of radicals [86].

A variety of transition metal complexes with various ligands have been studied as ATRP catalysts. The majority of work on ATRP has been conducted using copper as the transition metal. Apart from copper-based complexes, iron, nickel, rhenium, ruthenium, rhodium, and palladium have been used to some extent [81, 87-89]. Recent work from Sawamoto and co-workers shows that the Ru-based complexes can compete with the Cu-based systems on many fronts. A specific Fe-based catalyst has also been reported to polymerize vinyl acetate via an ATRP mechanism [92].

Ligands

The major roles of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex strongly with the transition metal, should also allow expansion of the coordination sphere, and should allow selective atom transfer without promoting other reactions.

The most common ligands for ATRP systems are substituted bipyridines, alkyl pyridylmethanimines and multidentate aliphatic tertiary amines such as N,N,N′,N″,N″ pentamethyldiethylenetriamine (PMDETA), and tris[2-(dimethylamino) ethyl]amine (Me_6-TREN) [65, 93]. In addition to those commercial products, it has been demonstrated that hexamethyltriethylene tetramine (HMTETA) provides better solubility of the copper complexes in organic media and entirely homogeneous reaction conditions [94]. Since copper complexes of this new ligand

are almost insoluble in water, ATRP technique can be employed in preparing poly(acrylate esters) in aqueous suspensions [95].

Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Common solvents, including nonpolar (toluene, xylene, benzene), polar aprotic (diphenyl ether, dimetoxy benzene, anisole, *N,N*-dimethylformamide, ethylene carbonate, acetonitrile), and polar protic (alcohols, water), are employed not only for solubilizing the monomers, the produced polymers, and the catalyst, but also to achieve the controlled polymerization condition. A solvent is sometimes necessary, especially when the polymer is insoluble in its monomer (e.g., polyacrylonitrile). ATRP has also been successfully carried out under heterogeneous conditions in (mini)emulsion, suspension, or dispersion. Several factors affect the solvent choice. Chain transfer to solvent should be minimal. In addition, potential interactions between solvent and the catalytic system should be considered. Catalyst poisoning by the solvent (e.g., carboxylic acids or phosphine in copper-based ATRP) and solvent-assisted side reactions, such as elimination of HX from polystyryl halides, which is more pronounced in a polar solvent, should be minimized [96, 97].

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 [98].

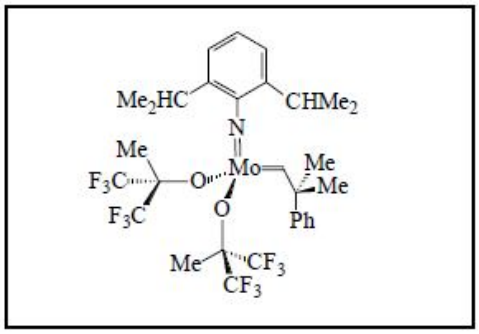
Reversible addition-fragmentation chain transfer (RAFT) incorporates compounds, usually dithio derivatives, within the living polymerization that react with the propagating center to form a dormant intermediate. The dithio compound can release the alkyl group attached to the opposite sulfur atom which 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 likey 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 [67].

2.1.2 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 [16].

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 **(2.10)**, and the 1st and 2nd generation of ruthenium-alkylidene catalysts, by R. H. Grubbs **(2.11)** [99].



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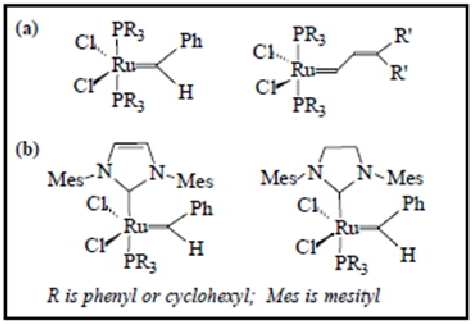
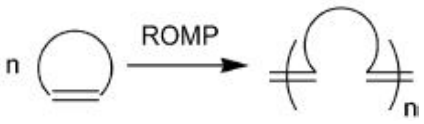


(2.11)

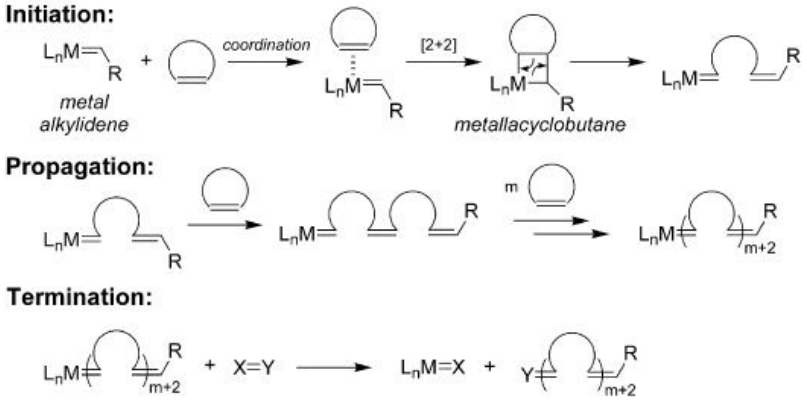
2.1.2.1 ROMP essentials: mechanism and thermodynamics

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 [100]. Ring-opening metathesis polymerization (ROMP) is a chain growth polymerization process where a mixture of cyclic olefins is converted to a polymeric material **(2.12)**. 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).



(2.12)

Chauvin proposed a general mechanism for ROMP in 1971 [16]. Initiation begins with coordination of a transition metal alkylidene complex to a cyclic olefin **(2.13)**



(2.13)

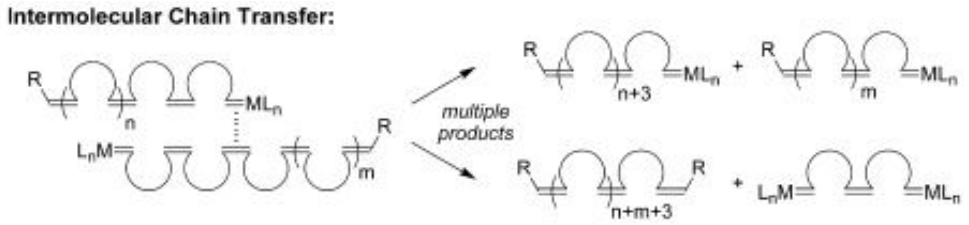
After formation of the metal-carbene complex, subsequent [2+2] cycloaddition forms a highly strained metallacyclobutane intermediate. The ring in the intermediate opens to give a new metal alkylidene. The chain growth process proceeds during the propagation stage until all monomer is consumed. Then living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

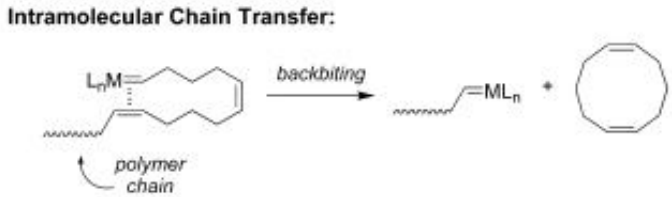
Generally, the most favorable conditions for a successful ROMP reaction is to use the highest monomer concentration at the lowest temperature possible, due to enthalpic contribution from the relief of ring strain [16].

In addition to the general ROMP mechanism illustrated in equation **2.13** (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 **2.14** and **2.15**. 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.



(2.14)

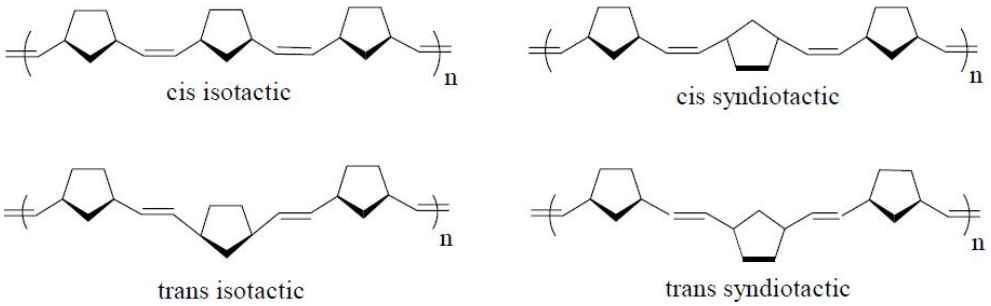


(2.15)

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 Swarzc as a reaction proceeding without chain transfer or termination. Besides Swarzc'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 [16].

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 **(2.16)**. Head-to-tail bias can be observed with non-symmetrical monomers.



(2.16)

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 [100].

2.1.2.2 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 [101].

Schrock-type initiators

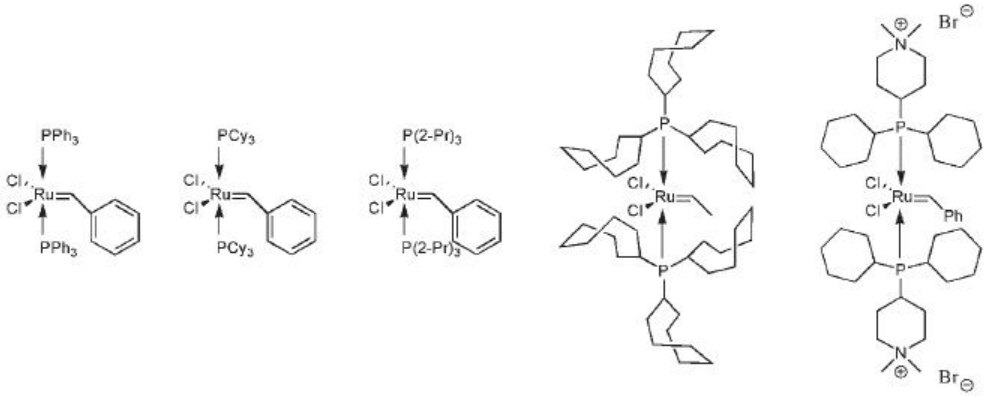
The synthesis of well-defined, high-oxidation state molybdenum alkylidenes was first reported by Schrock and coworkers in 1990 . These, and the analogous tungsten systems, are now commonly named ‘Schrock-catalysts’. The systems possess the general formula $M(NAr')(OR')_2(CHR).L$, where M= Mo,W; Ar′= 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) [101].

The Schrock type catalysts are very active and somewhat tolerant with functional groups during ring open metathesis polymerization [102]. 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 [103].

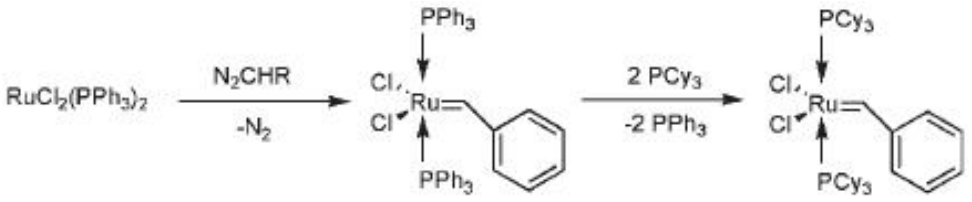
Grubbs-type initiators

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 δ=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 **(2.17)** [101].



(2.17)

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 $RuCl_2(PPh_3)_3$ with an diazoalkane **(2.18)** [101].



(2.18)

Via this route, the resulting compounds of the general formula $RuCl_2(PR_3)_2(CHPh)$, (R=Ph, Cy_3)– which today are well known as the first-generation Grubbs catalyst– are accessible in high yields [101].

The Ru-based catalysts have exceptional functional group tolerances compared to other transition metal-based catalysts, especially toward polar functionalities (Table 2.1).

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

Reactivity	Ti/Ta	W	Mo	Ru
↑	acids	acids	acids	**olefins**
	alcohols	alcohols	alcohols	acids
	aldehydes	aldehydes	aldehydes	alcohols
	ketones	ketones	**olefins**	aldehydes
	esters/amides	**olefins**	ketones	ketones
	olefins	esters/amides	esters/amides	esters/amides

The first homogeneous well-defined Ru complex for ROMP was $(PPh_3)_2Cl_2Ru=CH-CH=CPh_2$ [104]. 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 olefines are reduced. To increase the catalytic activities, the bulky and electron-rich phosphine ligands were substituted. 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) [27].

2.1.2.3 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 [105].

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) [106]. 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.

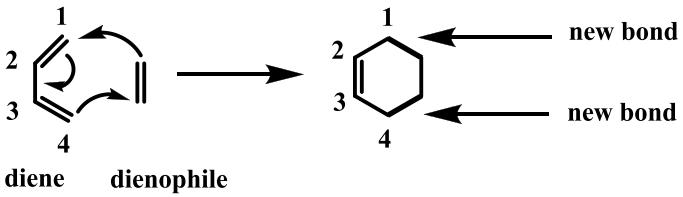
2.2 Click Chemistry

“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 [107]. Click chemistry can be summarized only one sentence: “Molecules that are easy to make”. Sharpless also introduced some criteria in order to fullfill the requirements as reactions that: are modular, wide in scope, high yielding, create only inoffensive by-products, are stereospecific, simple to perform and that require benign or easily removed solvent. Nowadays there are several processes have been identified under this term in order to meet these criterias such as nucleophilic ring opening reactions; non-aldol carbonyl chemistry; thiol additions to carbon–carbon multiple bonds (thiol-ene and thiol-yne); and cycloaddition reactions. Among these selected reactions, copper(I)-catalyzed azide-alkyne (CuAAC) and Diels-Alder (DA)

cycloaddition reactions 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 [4π+2π] 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 **(2.19)**. This reaction is named for Otto Diels and Kurt Alder, who received the 1950 Nobel prize for discovering this useful transformation [108-110].

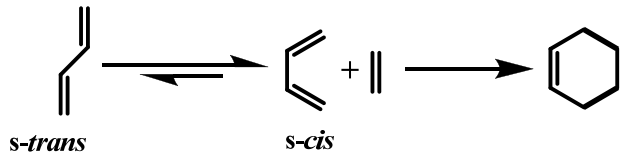


(2.19)

Typically, the DA reaction works best when either the diene is substituted with electron donating groups (like -OR, $-NR_2$, etc) or when the dienophile is substituted with electron-withdrawing groups (like $-NO_2$, -CN, -COR, etc). 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 [111].

2.2.1.1 Stereochemistry of Diels-Alder reaction

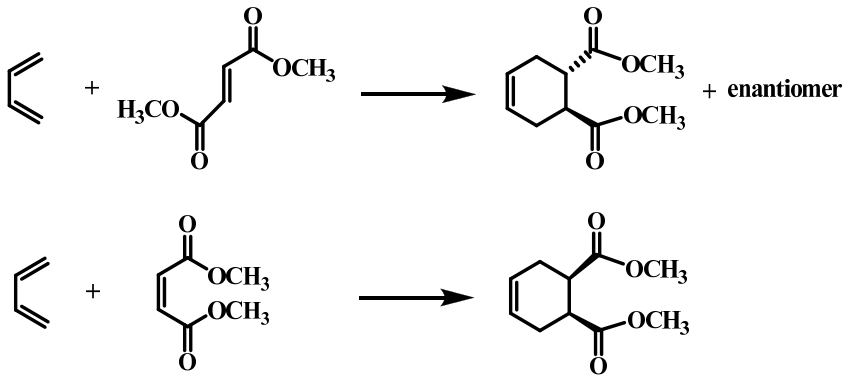
There are stereochemical and electronic requirements for the DA reaction to occur smoothly. First, the diene must be in an s-*cis* conformation instead of an s-*trans* conformation to allow maximum overlap of the orbitals participating in the reaction **(2.20)**.



(2.20)

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.

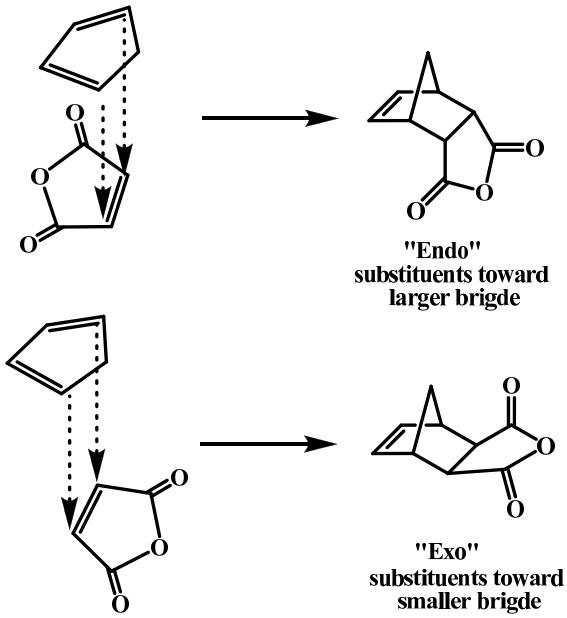
Since the reaction proceeds in a concerted fashion (*i.e.,* bonds are being formed and broken at the same time), substituents that are *cis* on the dienophile will also be *cis* in the product, and substituents that are *trans* on the dienophile will be *trans* in the product **(2.21)** [111-115]:



(2.21)

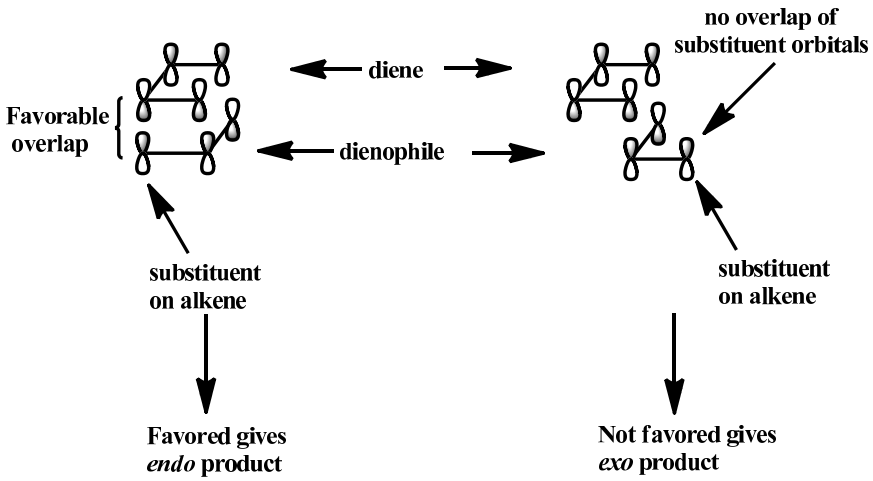
A unique type of stereoselectivity is observed in DA reactions when the diene is cyclic. In the reaction of maleic anhydride with cyclopentadiene, for example, the *endo* isomer is formed (the substituents from the dienophile point to the larger bridge) rather than the *exo* isomer (the substituents from the dienophile point away from the larger bridge) **(2.22)**.

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 [113,114].



(2.22)

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 **(2.23)**:



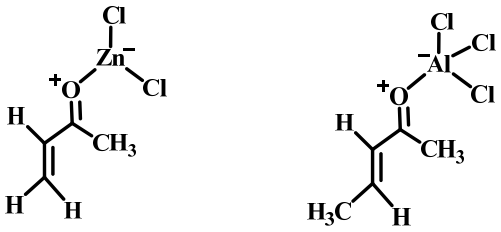
(2.23)

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.

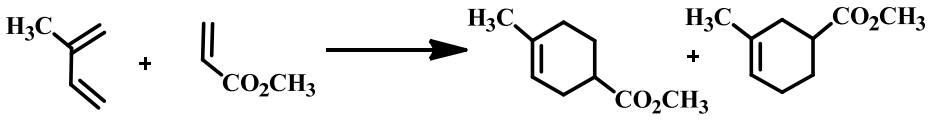
2.2.1.2 Catalysis of Diels-Alder reactions by Lewis acids

The DA reactions are catalyzed by many Lewis acids, including $SnCl_4$, $ZnCl_2$, $AlCl_3$, and derivatives of $AlCl_3$ [111]. 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 **(2.24)** [116].



(2.24)

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 [117]. 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 **(2.25)**.



(2.25)

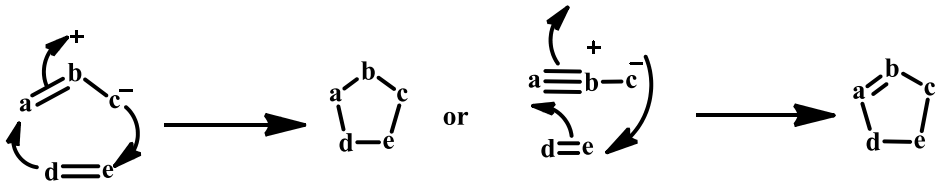
	"para"	"meta"
Uncatalyzed reaction, 120 ^{0}C, 6h	**70%**	**30%**
$AlCl_3$-catalyzed 20 ^{0}C, 3h	**95%**	**5%**

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 [118-121]. The accelerating effect of water is attributed to "enforced hydrophobic interactions" [119]. 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)

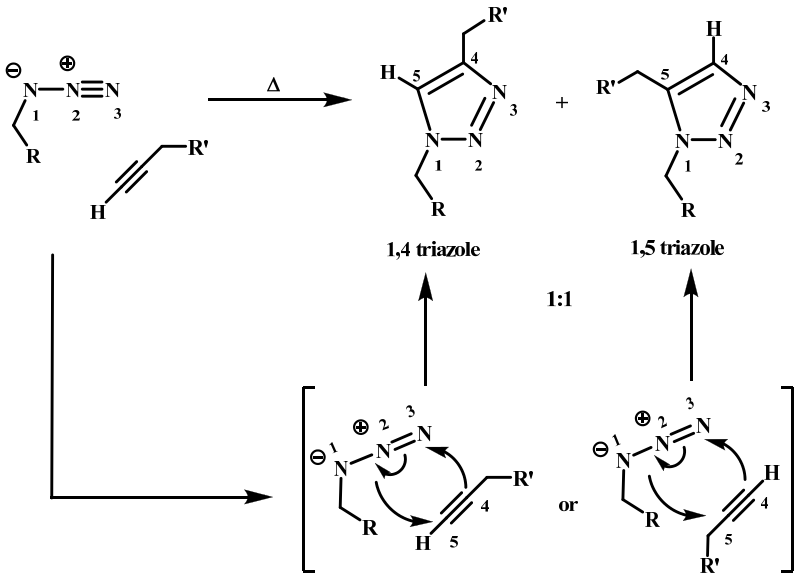
There is a large class of reactions known as 1,3-dipolar cycloaddition reactions (1,3-DPCA) that are analogous to the Diels-Alder reaction in that they are concerted [4π+2π] cycloadditions [122,123]. 1,3-DPCA reactions can be represented as shown in the following diagram. The entity a-b-c is called the *1,3-dipole* and d-e is the *dipolarophile* **(2.26)**.



(2.26)

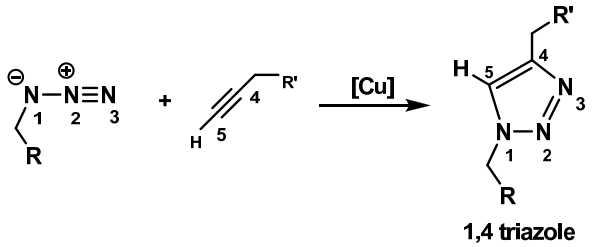
The 1,3-dipoles have a π-electron system consisting of two filled and one empty orbital and are analogous with the allyl or propargyl anion. Each 1,3-dipole has at least one charge-separated resonance structure with opposite charges in a 1,3-relationship. It is this structural feature that leads to the 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) [124]. 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 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 **(2.27)** [125].



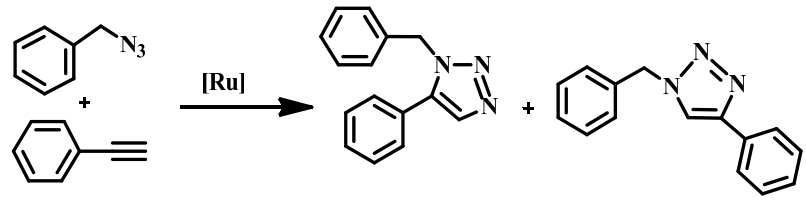
(2.27)

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 [126, 127]. Cu(I) catalysis dramatically improves regioselectivity to afford the 1,4-regioisomer exclusively **(2.28)** and increases the reaction rate up to 10^7 times eliminating the need for elevated temperatures [128]. 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 [126,127]. 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.



(2.28)

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) [129]. 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 **(2.29)**.



(2.29)

	1-5 triazole	1-4 triazole
$Ru(OAc)_2(PPh_3)_2$	-	100%
$CpRuCl(PPh_3)_2$	85%	15%
$CpRuCl(PPh_3)_2$	100%	-
CpRuCl(NBD)	100%	-

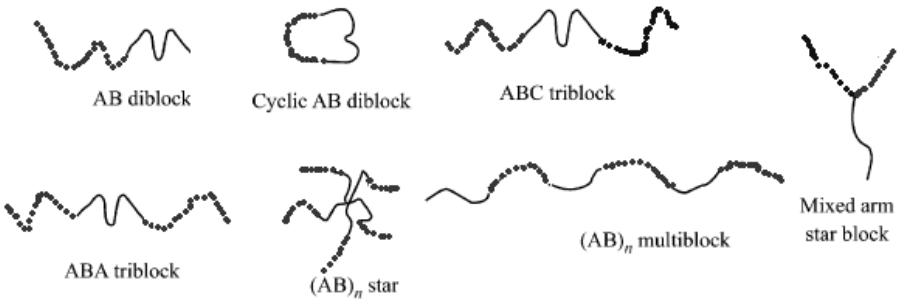
2.3 Polymer Topology

The control over molecular weight and functionality obtained in living or C/LRP have allowed for the synthesis of polymers with various architectures. With the exception of linear polymers, architectural differences lie in branched structures with regard to the number of branches and their relative placement in the macromolecule. However, these variations, inconjunction with changes in composition, may provide dramatic differences in the properties of the materials. At first glance, polymer topology includes linear, block, graft, star, cyclic, hyperbranched etc. [130]. Among them, the synthesis of block and the synthesis of graft polymers will be summarized due to their importance both in academically and industrially.

2.3.1 Block copolymers

A diblock copolymer is a linear-chain molecule consisting of two sub-chains joined covalently to each other. One of the sub-chains is made of monomers of type A and the other of type B. Block copolymers comprise a particularly interesting class of materials constituted by two or more blocks of different polymer chains where each block presents sequences of 50–1000 repetitive units, linked by covalent bonds. When the blocks are miscible, these materials are homogeneous and exhibit disordered domains with properties intermediate with respect to the constituent blocks. In contrast, local a wide range of microstructured materials such as nanoporous materials, membranes, nanoparticles and drug carriers, in a controlled way [60].

Block copolymers are useful in many applications where a number of different polymers are connected together to yield a material with hybrid properties. For example, thermoplastic elastomers are block copolymers containing a rubbery matrix (polybutadiene or polyisoprene) containing glassy hard domains (often polystyrene). The block copolymer, a kind of polymer alloy, behaves as a rubber at ambient conditions, but can be moulded at high temperatures due to the presence of the glassy domains that act as physical crosslinks. Linear block copolymers comprise two or more polymer chains in sequence, whereas a star block copolymer comprises more than two linear block copolymers attached at a common branch point. Polymers containing at least three homopolymers attached at a common branching point have been termed mixed arm block copolymers. In the following, block copolymers prepared by controlled polymerization methods only are considered, primarily di- and tri-block copolymers. Multiblock copolymers such as polyurethanes and poly (urethane- ureas) prepared by condensation polymerisation are not discussed. While these materials do exhibit microphase separation, it is only short range in spatial extent due to the high polydispersity of the polymers. A standard notation for block copolymers is becoming accepted, whereby X-b-Y denotes a diblock copolymer of polymer X and polymer Y. However, sometimes the b is replaced by the full term block, or alternatively is omitted, and the diblock is denoted X-Y. A number of texts covering general aspects of block copolymer science and engineering appeared in the 1970s and 1980s and these are listed elsewhere . More recently, specialised reviews have appeared on block copolymer melts and block copolymer solutions [64].



(2.30)

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 [131, 132]. 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 [133].

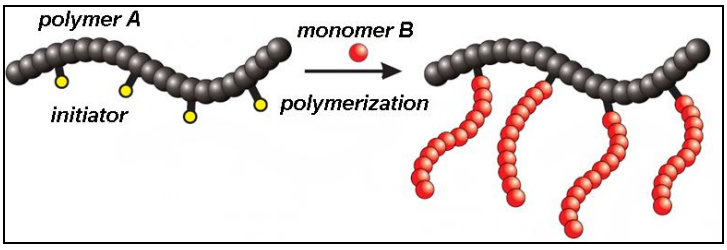


Figure 2.2: Illustration of the synthesis of graft copolymers by "grafting-from" method.

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 [134].

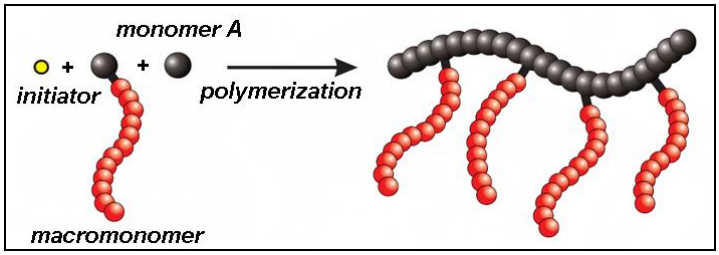


Figure 2.3: Illustration of the synthesis of graft copolymers by “grafting-through” method.

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.

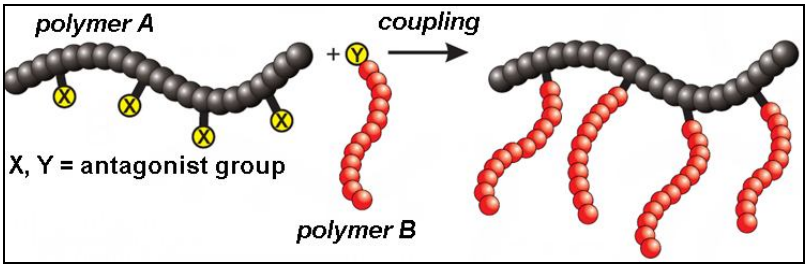


Figure 2.4: Illustration of the synthesis of graft copolymers by “grafting-onto” method.

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 [135].

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 [136].

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/P*t*BA 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 [135].

1,3-dipolar azide-alkyne [3 + 2] and thermoreversible Diels–Alder (DA) [4 + 2] click reactions have been successfully combined for the synthesis of polymers bearing side-chain TX photoactive groups. One of the consequences of the method is that such modification causes a dramatic change in the photochemistry of the precursor TX-A. Generally, the in-situ double click chemistry strategy described here is simple and quantitative and may permit a wide range of derivatives of polymers with various functional groups to be prepared in high yields [136].

A new synthetic approach for the preparation of well-defined graft copolymers on the basis of the DA "click chemistry" between copolymers bearing anthryl pendant groups and maleimide as end-functionalized polymers have been demonstrated . The grafting processes were carried out at the reflux temperature of toluene with a quantitative yield and without need for an additional purification step [55].

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 [137].

3. EXPERIMENTAL WORK

3.1 Materials

Styrene (St, 99%, Aldrich), methyl methacrylate (MMA, 99%, Aldrich) and *tert*-butyl acrylate (*t*BA, 99 %, Aldrich) were passed twice through basic alumina column to remove inhibitor and then distilled over CaH_2 in vacuum prior to use. Poly(ethylene glycol monomethyl ether) (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. Tetrabutylammonium fluoride (TBAF, 1 M in THF, 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. 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. 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 and ^{13}C NMR spectra were recorded on Bruker AC250 spectrometer (250 MHz for proton and 68.2 MHz for carbon). The conventional gel permeation chromatography (GPC) measurements were carried out with an Agilent instrument (Model 1100) consisting of a pump, refractive index (RI), 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) (λ = 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, [η] = 0.519 dL/g at 35°C in THF, d*n*/d*c* = 0.185 mL/g) provided by Viscotek company. UV spectra were recorded on a Shimadzu UV-1601 spectrophotometer in CH_2Cl_2.

3.3 Synthesis Methods

4,10-dioxatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-3,5-dione (**1**), 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-3,5-dione (**2)**, 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**), 9-anthyrylmethyl 2-bromo-2-methyl propanoate (**5**) and succinic acid mono-anthracen-9-ylmethyl-ester (**6**) were prepared according to published procedures [138-140].

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 needless. Yield: 80.2 g (80%). ^{1}H NMR ($CDCl_3$, δ) 6.57 (s, 2H, C*H*=C*H*, bridge protons), 5.45 (s, 2H, -C*H*O, bridge-head protons), 3.17 (s, 2H, C*H*-C*H*, 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 CH_2Cl_2 and washed with 3 × 100 mL of water. The organic layer was separated, dried over Na_2SO_4 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%). ^{1}H NMR ($CDCl_3$, δ) 6.51 (s, 2H, C*H*=C*H*, bridge protons), 5.26 (s, 2H, -C*H*O, bridge-head protons), 3.74-3.68 (m, 4H, NCH_2CH_2OH), 2.88 (s, 2H, C*H*-C*H*, 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 Et_3N (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%). ^{1}H NMR ($CDCl_3$, δ) 6.49 (s, 2H, C*H*=C*H*, bridge protons), 5.24 (s, 2H, -C*H*O, bridge-head protons), 4.31 (t, *J* = 5.2 Hz, 2H, NCH$_2$CH_2OC=O), 3.79 (t, *J* =5.2 Hz, 2H, NCH_2CH$_2$OC=O), 2.85 (s, 2H, C*H*-C*H*, bridge protons), 1.87 (s, 6H, C(CH_3)$_2$-Br).

3.3.4 Synthesis of 4-(2-{[(3-acetyl-7-oxabicyclo[2.2.1]hept-yl)carbonyl]amino} ethoxy)-4-oxobutanoic acid (4)

2 (5 g, 23.9 mmol) was dissolved in 150 mL of 1,4-dioxane. To the reaction mixture were added Et_3N (16.58 mL, 119.6 mmol), DMAP (4.38 g, 35.8 mmol), and succinic anhydride (9.56 g, 95.6 mmol) in that order. The reaction mixture was stirred for overnight at 50 ^{o}C, then poured into ice-cold water and extracted with CH_2Cl_2. The organic phase was washed with 1 M HCl, dried over Na_2SO_4 and concentrated. The crude product was crystallized from ethanol to give **4** as white crystal. Yield: 5.9 g (80%). ^{1}H NMR ($CDCl_3$, δ) 6.50 (s, 2H, C*H*=C*H,* bridge protons), 5.25 (s, 2H, -C*H*O, bridge-head protons), 4.25 (t, *J* = 5.2 Hz, 2H, NCH$_2$CH_2OC=O), 3.74 (t, *J*

=5.2 Hz, 2H, NC*H*$_2$CH$_2$OC=O), 2.87 (s, 2H, C*H*-C*H*, bridge protons), 2.66-2.53 (m, 4H, C=OC*H*$_2$C*H*$_2$C=OOH).

3.3.5 Synthesis of 9-anthyrylmethyl 2-bromo-2-methyl propanoate (5)

9-Anthracene methanol (1.50 g, 7.18 mmol) and DMAP (0.175 g, 1.44 mmol) were dissolved in 50 mL of CH_2Cl_2, and Et_3N (1.2 mL, 8.6 mmol) was added. The reaction mixture was then cooled to 0 ^oC. 2-bromo isobutyryl bromide (1.82 g, 7.89 mmol) was added dropwise within 30 minutes to this solution. The reaction mixture was stirred for 15 min. at 0 ^oC then for overnight at room tempeature. The ammonium salt was filtered off and the solvent was evaporated under reduced pressure. The remaining residue was extracted with CH_2Cl_2, and saturated aqueous $NaHCO_3$. The aqueous phase again extracted with CH_2Cl_2, and combined organic phases dried over Na_2SO_4. The solution was concantrated, and the crude product was purified by column chromatography over silica gel eluting with hexane/EtOAc (10:1) to give **5** as yellow solid. Yield: 1.78 g (70%). ^{1}H NMR ($CDCl_3$, δ) 8.51 (s, 1H, Ar*H* of anthracene), 8.33 (d, *J* = 8.7 Hz, 2H, Ar*H* of anthracene), 8.03 (d, *J* = 8.2 Hz, 2H, Ar*H* of anthracene), 7.60-7.45 (m, 4H, Ar*H* of anthracene), 6.21 (s, 2H, C*H*$_2$-anthracene), 1.86 (s, 6H, C(C*H*$_3$)$_2$-Br).

3.3.6 Synthesis of succinic acid mono-anthracen-9-ylmethyl-ester (6)

9-Anthracene methanol (4.16 g, 20 mmol) was dissolved in 150 mL of CH_2Cl_2. To the reaction mixture were added Et_3N (14 ml, 100 mmol), 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 seperating funnel. The organic phase was extracted with 1M HCl (150 mL). The aqueous phase extracted with CH_2Cl_2 and combined organic phases dried over Na_2SO_4 and concentrated to give **6** as a green solid. Yield: 5.85 g (95%). ^{1}H NMR ($CDCl_3$, δ) 8.50 (s, 1H, Ar*H* of anthracene), 8.32 (d, *J* = 8.8 Hz, 2H, Ar*H* of anthracene), 8.02 (d, *J* = 8.2 Hz, 2H, Ar*H* of anthracene), 7.60-7.45 (m, 4H, Ar*H* of anthracene), 6.18 (s, 2H, C*H*$_2$-anthracene), 2.69-2.62 (m, 4H, C=OC*H*$_2$C*H*$_2$C=OOH).

3.3.7 General procedure for the synthesis of α-anthracene-ω-azide end-functionalized PS (Anth-PS-N_3)

In a 50 mL of Schlenk tube, St (30.0 mL, 260 mmol), PMDETA (0.273 mL, 1.309 mmol), CuBr (0.1878 g, 1.309 mmol) and **5** (0.468 g, 1.309 mmol) were added and the reaction mixture was degassed by three freeze-pump-thaw (FPT) cycles and left in vacuum. The tube was then placed in a thermostated oil bath at 110 ^{o}C for 25 min. The dark-green polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated into methanol. The polymer was dried for 24 h in a vacuum oven at 40 ^{o}C. ($[M]_0/[I]_0$ = 200, $[I]_0$:$[CuBr]_0$:$[PMDETA]_0$ = 1:1:1, conv. (%) = 17, $M_{n,theo}$ = 3700, $M_{n,NMR}$ = 3850, $M_{n,GPC}$ = 3900, M_w/M_n = 1.15, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.4 (Ar*H* of anthracene), 8.3 (Ar*H* of anthracene), 7.9 (Ar*H* of anthracene), 7.5 (Ar*H* of anthracene), 6.5-7.5 (Ar*H* of PS), 5.8 (CH_2-anthracene), 4.4 (C*H*(Ph)-Br), 2.2-0.8 (m, C*H* and CH_2 of PS and CH_3).

Next, anth-PS-Br (4.3 g, 1.11 mmol, $M_{n,NMR}$ = 3850) dissolved in DMF (15 mL) and NaN_3 (0.363 g, 5.5 mmol) was added to the flask. After stirring overnight at room temperature, CH_2Cl_2 and water were added to the mixture. The organic layer was extracted three times with water and dried over Na_2SO_4. The excess CH_2Cl_2 was evaporated under reduced pressure and the obtained product was precipitated into an excess amount of methanol. The recovered polymer anth-PS-N_3 was dried for 24 h in a vacuum oven at 40 °C (Yield = 4.1 g, 95 %; $M_{n,GPC}$ = 4000, M_w/M_n = 1.10 , relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.4 (Ar*H* of anthracene), 8.3 (Ar*H* of anthracene), 7.9 (Ar*H* of anthracene), 7.4 (Ar*H* of anthracene), 6.5-7.5 (Ar*H* of PS), 5.8 (CH_2-anthracene), 3.9 (m, C*H*(Ph)-N_3), 2.2-0.8 (m, C*H* and CH_2 of PS and CH_3).

3.3.8 Synthesis of maleimide end-functionalized PEG (MI-PEG)

Me-PEG (M_n = 550) (2.0 g, 3.63 mmol) was dissolved in 50 mL of CH_2Cl_2. To the reaction mixture were added DMAP (0.044 g, 0.363 mmol) and **4** (2.24 g, 7.27 mmol) in that order. After stirring 5 min at room temperature, a solution of DCC (1.49 g, 7.27 mmol) in 10 mL of CH_2Cl_2 was added. Reaction mixture was stirred for 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 CH_2Cl_2/EtOAc mixture (1:1, v/v) and

then with CH_2Cl_2/methanol (90:10, v/v) to obtain MI-PEG as viscous brown oil. $M_{n,GPC}$ = 550; M_w/M_n = 1.10 (RI detector, relative to PS standards); $M_{n,theo}$ = 840; $M_{n,NMR}$ =750). ^{1}H NMR ($CDCl_3$, δ) 6.5 (s, 2H, vinyl protons), 5.2 (s, 2H, C*H*C*H*=C*H*C*H*, bridge-head protons), 4.2 (m, 4H, NCH_2CH_2OC=O and C=OOCH_2CH_2), 3.9–3.5 (m, OCH_2CH_2, repeating unit of PEG and NCH_2CH_2OC=O), 3.4 (s, 3H, OCH_3, end group of PEG), 2.8 (s, 2H, CH_2NC=OC*H*-C*H*, bridge protons), 2.6 (m, 4H, OC=OCH_2CH_2C=OO).

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, 46.7 mmol), PMDETA (0.196 mL, 0.940 mmol), CuCl (0.093 g, 0.94 mmol), toluene (5 mL), and **3** (0.336 g, 0.940 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. 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. ($[M]_0/[I]_0$ = 50, [I]:[CuCl]:[PMDETA] = 1:1:1, conv. (%) = 30, $M_{n,theo}$ = 1850, $M_{n,NMR}$ = 2950, $M_{n,GPC}$ = 2850, M_w/M_n= 1.24, (RI detector, relative to PMMA standards). ^{1}H-NMR ($CDCl_3$, δ): 6.5 (s, 2H, vinyl protons), 5.3 (s, 2H, C*H*CH=CHC*H*, bridge-head protons), 4.1 (m, 2H, NCH$_2$CH_2OC=O), 4.0–3.2 (m, OCH$_3$ of PMMA and NCH_2CH$_2$OC =O), 2.9 (s, 2H, CH$_2$NC= OC*H*-C*H*, bridge protons), 2.5– 0.5 (m, CH$_2$ and CH$_3$ protons of PMMA).

3.3.10 General procedure for the synthesis of α-furan protected maleimide end-functionalized P*t*BA (MI-P*t*BA)

In a 25 mL of Schlenk tube, *t*BA (10.0 mL, 68.3 mmol), PMDETA (0.142 mL, 0.680 mmol), CuBr (0.098 g, 0.68 mmol), ethylene carbonate (0.88 g) and the initiator **3** (0.024 g, 0.68 mmol) were added, and the reaction mixture was degassed by three FPT cycles, and left in argon. The tube was then placed in a thermostated oil bath at 50 °C for predetermined times. The polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst. The excess of THF was evaporated under reduced pressure and the mixture was precipitated into cold methanol/water (80/20; v/v). After decantation, the polymer was dissolved in

CH_2Cl_2, extracted with water and the water phase was again extracted with CH_2Cl_2, and combined organic phase was dried over Na_2SO_4. Finally, the organic phase was evaporated to give MI-P*t*BA. The polymer was dried for 24 h in a vacuum oven at 40 °C. $[M]_0/[I]_0$ = 100; $[I]_0$:[CuBr]:[PMDETA] =1:1:1; conv. (%) = 11. $M_{n,theo}$ = 1850, $M_{n,NMR}$ = 2300, $M_{n,GPC}$ = 2050, M_w/M_n= 1.18, (RI detector, relative to PS standards). ^{1}H-NMR ($CDCl_3$, δ) 6.5 (s, 2H, vinyl protons), 5.2 (s, 2H, C*H*CH=CHC*H*, bridge-head protons), 4.3–4.0 (bs, NCH_2CH_2OC=O and C*H*Br end group of P*t*BA), 3.7 (m, 2H, NCH_2CH_2OC=O), 2.9 (s, 2H, CH_2NC=OC*H*-C*H*, bridge protons), 2.2 (bs, C*H* of P*t*BA), 2.0–1.0 (m, CH_2 and CH_3 of P*t*BA).

3.3.11 Synthesis of Oxanorbornenyl Anthracene, (7)

Compounds **2** (1.63 g, 7.80 mmol, 1.2 equiv), **6** (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 CH_2Cl_2. After stirring 5 min at room temperature, DCC (1.6 g, 7.8 mmol, 1.2 equiv) 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, the solvent was removed and the remaining product was extracted with CH_2Cl_2/water. The aqueous phase was again extracted with CH_2Cl_2 and the combined organic phases were dried with Na_2SO_4, and concentrated to dryness. The crude product was purified by column chromatography over silica gel eluting with CH_2Cl_2 to give **5** as a yellow solid (Yield = 2.6 g; 80%). ^{1}H NMR ($CDCl_3$, δ): 8.5 (s, 1H, Ar*H* of anthracene), 8.3 (d, 2H, Ar*H* of anthracene), 8.0 (d, 2H, Ar*H* of anthracene), 7.5 (m, 4H, Ar*H* of anthracene), 6.4 (s, 2H, vinyl protons), 6.1 (s, 2H, CH_2-anthracene), 5.2 (s, 2H, C*H*CH=CHC*H*, bridge-head protons), 4.2 (t, 2H, NCH_2CH_2OC=O), 3.7 (t, 2H, NCH_2CH_2OC=O), 2.8 (s, 2H, C*H*-C*H*, bridge protons), 2.6 (s, 4H, C=OCH_2CH_2C=O).

3.3.12 Synthesis of Oxanorbornenyl Alkyne, (8)

4-Pentynoic acid (1.12 g, 11.5 mmol, 1.2 equiv), DMAP (0.58 g, 4.78 mmol, 0.5 equiv) and **2** (2.00 g, 9.56 mmol, 1 equiv) were dissolved in 40 mL of dry CH_2Cl_2. After stirring 5 min at room temperature, DCC (2.40 g, 11.5 mmol, 1.5 equiv) dissolved in 15 mL of CH_2Cl_2 was added to the solution. After stirring overnight at room temperature, the reaction mixture was filtered, and then solvent was evaporated, the remaining product was extracted with CH_2Cl_2/water. The aqueous phase was again extracted with CH_2Cl_2 and the combined organic phases were dried

with Na_2SO_4, and concentrated to dryness. The crude product was purified by column chromatography over silica gel eluting with ethyl acetate/hexane (1:1) to give **6** as a white solid (Yield: 2.6 g; 94 %). ^{1}H NMR ($CDCl_3$, δ) 6.5 (s, 2H, vinyl protons), 5.2 (s, 2H, C*H*CH=CHC*H*, bridge-head protons), 4.2 (t, 2H, NCH_2CH_2OC=O), 3.7 (t, 2H, NCH_2CH_2OC=O), 2.8 (s, 2H, C*H*-C*H*, bridge protons), 2.5 (bs, 4H, C=OCH_2CH_2C≡CH), 1.9 (s, 1H, C=OCH_2CH_2C≡C*H*).

3.3.13 Synthesis of Poly(oxanorbornenyl anthracene) via ROMP of 7

The first generation Grubbs' catalyst $(PCy_3)_2(Cl)_2$-RuCHPh (0.082 g, 0.10 mmol) was placed in a Schlenk tube and dissolved in 2 mL of anhydrous CH_2Cl_2 in a glove box.Compound **7** (1.0 g, 2.0 mmol) was dissolved in 8 mL of anhydrous CH_2Cl_2 in another Schlenk tube and 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 20 min, then butyl vinyl ether (0.2 mL) was added to quench the polymerization and stirred additional for 20 min. Finally, the polymer solution was precipitated in methanol and the obtained polymer was dried for 24 h in a vacuum oven at 40 °C (**7**/catalyst = 20; conv. (%) = 100%; $M_{n,theo}$ = 10000; $M_{n,GPC}$ = 6100; M_w/M_n = 1.07, RI detector, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.4 (bs, 1H, Ar*H* of anthracene), 8.2 (bs, 2H, Ar*H* of anthracene), 7.9 (bs, 2H, Ar*H* of anthracene), 7.5 (bs, 2H, Ar*H* of anthracene), 7.4 (bs, 2H, Ar*H* of anthracene), 6.0 (s, 2H, CH_2-anthracene), 5.9 (s, 2H, C*H*=C*H*, trans), 5.6 (bs, 2H, C*H*=C*H*, cis), 4.9 (bs, 2H, =CH-C*H*-O, cis), 4.3 (s, 2H, =CH-C*H*-O, trans), 4.1 (bs, 2H, C=OOCH_2CH_2N), 3.5 (bs, 2H, C=OOCH_2CH_2N), 3.1 (bs, 2H, C*H*-C*H*), 2.5 (s, 4H, C=OCH_2CH_2C=O).

3.3.14 Synthesis of Poly(oxanorbornene)-*g*-PEG via Diels-Alder click reaction

A solution of PEG-MI (0.19 g, 0.25 mmol, $M_{n,NMR}$ = 750) in 10 mL of toluene was added to a 10 mL dioxane solution of poly(oxanorbornenyl anthracene) (0.1 g, 0.001) mmol, $M_{n,theo}$ = 10000) in a Schlenk tube. The reaction mixture was bubbled with nitrogen for 30 min and refluxed for 48 h at 110 °C in the dark. After that specified time, toluene was evaporated under vacuum, and residual solid was dissolved in THF, subsequently precipitated in methanol. The dissolution-precipitation procedure was repeated two times. The obtained product was dried in a vacuum oven at 40 °C for 24 h ($M_{n,GPC}$ = 3400, M_w/M_n = 1.26, relative to linear PS). ^{1}H NMR ($CDCl_3$, δ) 7.5-7.0 (m, 8H, Ar*H*), 6.0 (s, 2H, C*H*=C*H*, trans), 5.7 (bs, 2H, C*H*=C*H*, cis), 5.4 (bs,

2H, CH_2-adduct), 5.0 (bs, 2H, =CH-C*H*-O, cis), 4.7 (s, 1H, CH, bridge head proton), 4.4 (s, 2H, =CH-C*H*-O, trans), 4.2 (bs, 4H, C=OOCH_2CH$_2$N), 3.6 (OCH_2CH_2 of PEG, C=OOCH$_2$CH_2N and C=OOCH_2), 3.5-3.0 (m, 7H, OCH_3 of PEG and C*H*-C*H*), 2.5 (m, 8H, C=OCH_2CH_2C=O and H_2O).

3.3.15 Synthesis of poly(oxanorbornene)-*g*-PMMA via Diels-Alder click reaction

A solution of PMMA-MI (0.74 g, 0.25 mmol, $M_{n,NMR}$ = 2950) in 10 mL of toluene was added to a 10 mL dioxane solution of poly(oxanorbornenyl anthracene) (0.1 g, 0.001mmol, $M_{n,theo}$= 10000) in a Schlenk tube. The mixture was bubbled with nitrogen for 30 min and refluxed for 48 h at 110 °C in the dark. After the specified time, toluene was evaporated under vacuum. Residual solid was dissolved in THF, and subsequently precipitated into methanol. This dissolution-precipitation procedure was repeated two times. The obtained product was dried in a vacuum oven at 40 °C for 24 h ($M_{n,GPC}$ = 18700, M_w/M_n = 1.08, relative to linear PS). ^{1}H NMR ($CDCl_3$, δ) 7.5-7.0 (m, 8H, Ar*H*), 6.0 (s, 2H, C*H*=C*H*, trans), 5.7 (bs, 2H, C*H*=C*H*, cis), 5.4 (bs, 2H, CH_2-adduct), 5.0 (bs, 2H, =CH-C*H*-O, cis), 4.7 (s, 1H, CH, bridge head proton), 4.4 (s, 2H, =CH-C*H*-O, trans), 4.2 (bs, 6H, C=OOCH_2CH$_2$N and C=OOCH_2), 4.0-3.0 (OCH_3 of PMMA, C*H*-C*H*, and C=OOCH_2CH_2N), 2.5 (C=OCH_2CH_2C=O), 2.0-1.0 (CH_2 and CH_3 of PMMA).

3.3.16 Synthesis of α-anthracene-ω-oxanorbornene end-functionalized PS macromonomer (Anth-PS-oxanorbornene) (9)

Linear anthracene-PS-N_3 (see supporting information; 4 g, 1 mmol, $M_{n,NMR}$ = 3850) dissolved in *N*,*N*-dimethyl formamide (DMF; 15 mL), **8** (0.9 g, 3.0 mmol), PMDETA (0.21 mL, 1.0 mmol) and CuBr (0.143 g, 1.00 mmol) were added in a 25 mL of Schlenk tube. The reaction mixture was degassed by three freeze-pump-thaw (FPT) cycles, left in vacuum and stirred at room temperature overnight. After the specified time, the solution was diluted with THF, filtered through a column filled with neutral alumina to remove copper complex and finally precipitated in methanol in order to give anth-PS-oxanorbornene (Yield = 3.94 g; $M_{n,GPC}$ = 4100, M_w/M_n = 1.12, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.4 (Ar*H* of anthracene), 8.3 (Ar*H* of anthracene), 7.9 (Ar*H* of anthracene), 7.6 (C*H* of triazole), 7.5 (Ar*H* of anthracene), 7.5-6.5 (Ar*H* of PS), 5.8 (CH_2-anthracene), 5.2 (s, 2H, C*H*CH=CHC*H*, bridge-head protons), 5.1 (br, 1H, C*H*(Ph)-triazole), 4.2 (m, 2H, NCH$_2$CH_2OC=O),

3.7 (m, 2H, NCH_2CH$_2$OC=O), 2.8 (br, 4H, triazole-CH_2CH$_2$C=O and CH$_2$NC=OC*H*-C*H*, bridge protons), 2.6 (m, 2H, CH$_2$CH_2C=O), 2.0-0.8 (m, C*H* and CH_2 of PS and CH_3).

3.3.17 Synthesis of poly(oxanorbornene)-*g*-PS-anthracene via ROMP

$(PCy_3)_2(Cl)_2$-RuCHPh (0.041 g, 0.05 mmol) was placed in a Schlenk tube and dissolved in 2 mL of anhydrous CH_2Cl_2 in a glove box. Anthracene-PS-oxanorbornene macromonomer (2.0 g, 0.5 mmol, $M_{n,GPC}$ = 4100) was dissolved in 8 mL of anhydrous CH_2Cl_2 in another Schlenk tube and 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 24 h, and then butyl vinyl ether (0.2 mL) was added to quench the polymerization and stirred for 20 min. The polymer solution was precipitated in methanol-ether (1/2) and recovered polymer was dissolved in THF, precipitated in methanol and finally dried for 24 h in a vacuum oven at 40 °C (macromonomer/catalyst = 10; conv. (%) = 90; $M_{n,theo}$ = 36900; $M_{n,GPC}$ = 19900; M_w/M_n = 1.10, RI detector, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.4-7.5 (Ar*H* of anthracene and C*H* of triazole), 7.5-6.5 (Ar*H* of PS), 6.0-5.6 (CH_2-anthracene, C*H*=C*H*, trans, and C*H*=C*H*, cis), 5.0 (=CH-C*H*-O, cis and C*H*Ph-triazole), 4.4 (=CH-C*H*-O, trans), 4.1 (C=OOCH_2CH$_2$N), 3.6 (C=OOCH$_2$CH_2N), 3.2 (C*H*-C*H*), 2.8 (triazole-CH_2CH$_2$C=O), 2.5 (CH$_2$CH_2C=O), 2.0-0.8 (C*H* and CH_2 of PS and CH_3).

3.3.18 Synthesis of poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA) via Diels-Alder click reaction

A solution of P*t*BA-MI (0.086 g, 0.0375 mmol, $M_{n,NMR}$ = 2300) in 10 mL of toluene was added to a 10 mL of toluene solution of poly(oxanorbornene)-*g*-PS-anthracene (0.10 g, 0.0025 mmol, $M_{w,TDGPC}$ = 40300) in a Schlenk tube. The mixture was bubbled with nitrogen for 30 min and refluxed at 110 °C in the dark for 48 h. After that time toluene was evaporated under vacuum and residual solid was dissolved in THF, and subsequently precipitated in methanol. The dissolution-precipitation procedure was repeated two times. The obtained product was dried in a vacuum oven at 40 °C for 24 h. ($M_{n,GPC}$ = 28350, M_w/M_n = 1.12, relative to linear PS). ^{1}H NMR ($CDCl_3$, δ) 7.7 (C*H* of triazole), 7.5-6.5 (Ar*H* of PS), 6.0 (C*H*=C*H*, trans), 5.7 (C*H*=C*H*, cis), 5.2 (CH_2-adduct), 5.1-4.8 (=CH-C*H*-O, cis and C*H*Ph-triazole), 4.7

(C*H* of adduct), 4.4 (=CH-C*H*-O, trans), 4.1 (C=OOCH_2CH$_2$N), 3.6-3.0 (C=OOCH_2CH_2N, and C*H*-C*H*), 2.8 (triazole-CH_2CH$_2$C=O), 2.5 CH$_2$CH_2C=O), 2.2 (CH of P*t*BA), 2.0-0.8 (C*H*, CH_2 and CH_3 of PS and P*t*BA).

3.3.19 Synthesis of poly(oxanorbornene)-*g*-(PS-*b*-PMMA) via Diels-Alder click reaction

A solution of PMMA-MI (0.110 g, 0.0375 mmol) in 10 mL of toluene was added to a 10 mL solution of poly(oxanorbornene)-*g*-PS-anthracene (0.1 g, 0.0025 mmol) in toluene in a Schlenk tube. The mixture was bubbled with nitrogen for 30 min and refluxed for 48 h at 110 °C in the dark, and then toluene was evaporated under vacuum and residual solid was dissolved in THF, and subsequently precipitated into methanol. This procedure was repeated two times. The obtained product was dried in a vacuum oven at 40 °C for 24 h. ($M_{n,GPC}$ = 24700, M_w/M_n = 1.11, relative to linear PS). ^{1}H NMR (CDCl$_3$, δ) 7.7 (CH of triazole), 7.5-6.5 (Ar*H* of PS), 6.0 (C*H*=C*H*, trans), 5.7 (C*H*=C*H*, cis), 5.2-4.8 (CH_2-adduct, =CH-C*H*-O, cis and C*H*Ph-triazole), 4.7 (C*H* of adduct), 4.4 (=CH-C*H*-O, trans), 4.1 (C=OOCH_2CH$_2$N), 4.0-3.0 (C*H*-C*H*, OCH_3 of PMMA, and C=OOCH_2CH_2N), 2.8 (triazole-CH_2CH$_2$C=O), 2.5 ((CH$_2$CH_2C=O), 2.0-0.8 (C*H*, CH_2 and CH_3 of PS and PMMA).

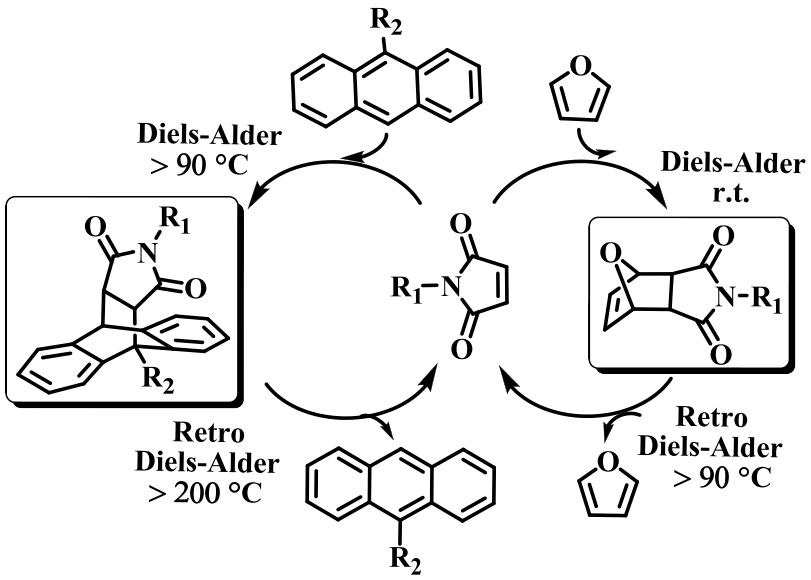
3.3.20 Synthesis of poly(oxanorbornene)-*g*-(PS-*b*-PEG) via Diels-Alder click reaction

A solution of PEG-MI (0.028 g, 0.0375 mmol) in 10 mL of toluene was added to a 10 mL solution of poly(oxanorbornene)-*g*-PS-anthracene (0.1 g, 0.0025 mmol) in toluene in a Schlenk tube. The mixture was bubbled with nitrogen for 30 min and refluxed for 48 h at 110 °C in the dark. After that time, solution was evaporated under vacuum, and residual solid was dissolved in THF, and subsequently precipitated into methanol. This dissolution-precipitation procedure was repeated two times and finally the obtained product was dried in a vacuum oven at 40 °C for 24 h ($M_{n,GPC}$ = 20250, M_w/M_n =1.10, relative to linear PS). ^{1}H NMR (CDCl$_3$, δ) 7.6 (C*H* of triazole), 7.5-6.5 (Ar*H* of PS), 6.0 (C*H*=C*H*, trans), 5.7 (C*H*=C*H*, cis), 5.4-4.8 (CH_2-adduct, =CH-C*H*-O, cis and C*H*Ph-triazole), 4.7 (C*H* of adduct), 4.4 (=CH-C*H*-O, trans), 4.3-4.0 (ester CH_2), 4.0-3.0 (OCH_2CH_2 of PEG, ester CH_2, N-CH_2, C*H*-C*H* and OCH_3 of PEG), 2.8 (triazole-CH_2CH$_2$C=O), 2.5 (CH_2C=O), 2.0-0.8 (C*H* and CH_2 of PS).

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)**.



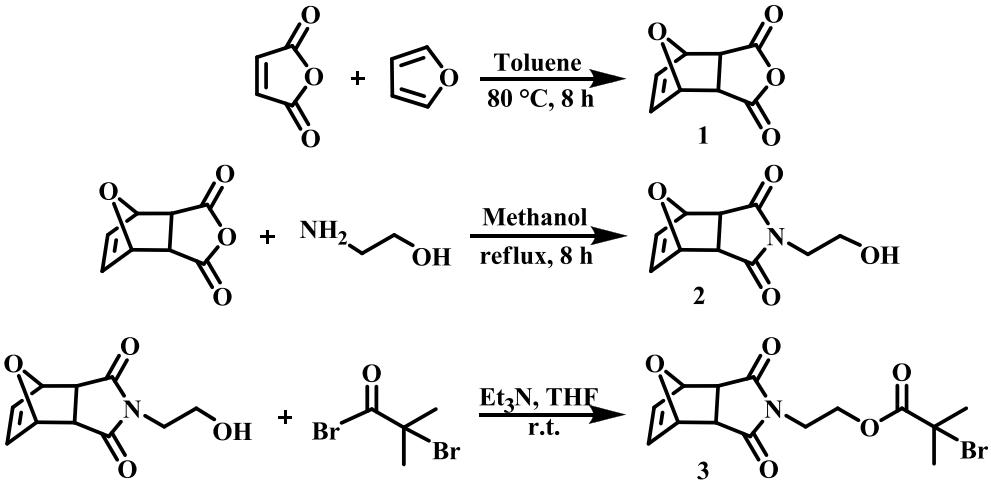
(4.1)

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 ^{o}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 Block Copolymers via Diels-Alder Click Reaction

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[5.2.1.02,6]dec-8-en-4-yl) ethyl ester **(3)** was first synthesized within three steps. Furan and maleic anhydride were reacted in toluen at 80 ^{o}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)**.



(4.2)

(4.3)

(4.4)

From overlay ^{1}H 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 achived.

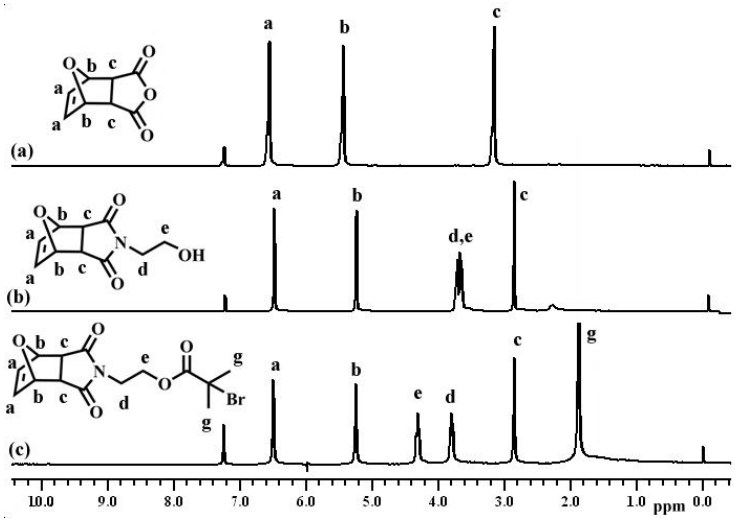
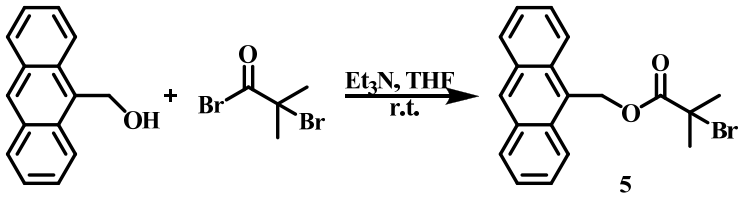


Figure 4.1: ^{1}H NMR spectra of: **a**) 3-acetyl-N-(2-hydroxyethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid **(1)**; **b**) 3-acetyl-N-(2-hydroxyethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxamide (**2)**; **c**) 2-bromo-2- methyl-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-en-4-yl) ethyl ester **(3)** (c) in $CDCl_3$.

In addition, 9-anthyrylmethyl 2-bromo-2-methyl propanoate (**5) (4.5)**, was synthesized by a similar way as described for **3**.



5 **(4.5)**

Along with anthracene protons between 8.51 and 7.45 ppm, from ^{1}H NMR spectrum as seen in Figure 4.2, methylene protons adjacent to the anthracene and methyl protons next to Br were detected at 6.21 ppm and 1.86 ppm, respectively. These results confirmed that **5** was successfully obtained.

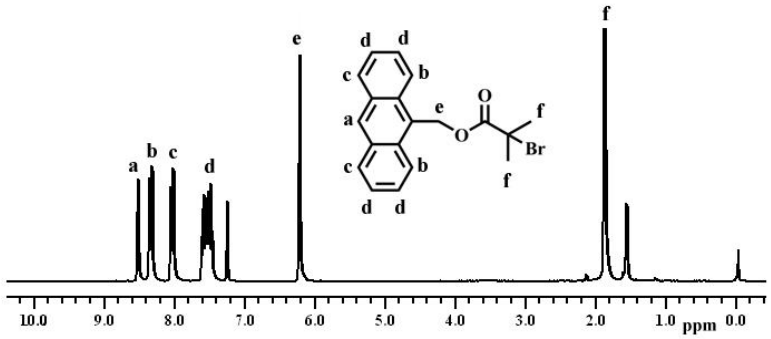


Figure 4.2: ^{1}H NMR spectrum of 9-anthyrylmethyl 2-bromo-2-methyl propanoate (**5**) in $CDCl_3$.

The hydoxyl functionality of **2** was converted to carboxylic acid via a reaction with succinic anhydride in the presence of Et_3N/DMAP catalyst system and 1,4-dioxane as solvent in order to give **4 (4.6)**.

(4.6)

From ^{1}H NMR spectrum as seen in Figure 4.3 of **4**, methylene protons next to the ester ($NCH_2CH_2OC{=}O$) and methylene protons adjacent to nitrogen ($NCH_2CH_2OC{=}O$) appeared at 4.25 ppm and 3.74 ppm respectively. Moreover, the multiplet peaks around 2.66-2.53 ppm confirmed successful conversion of hydroxyl group to carboxylic acid.

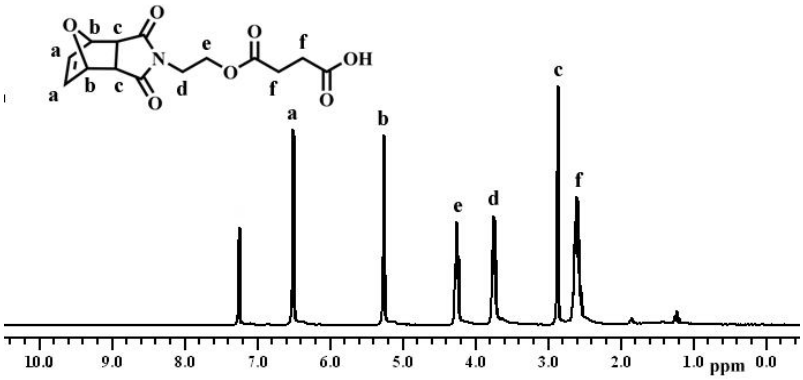
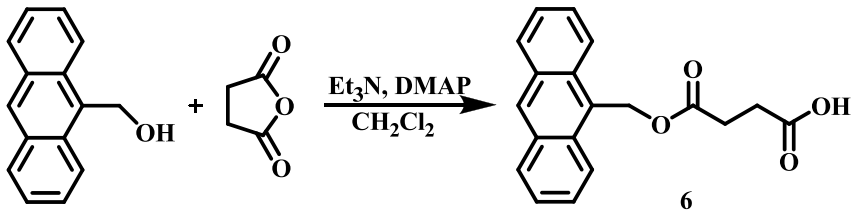


Figure 4.3: ^{1}H NMR spectrum of 4-(2-{[(3-acetyl-7-oxabicyclo[2.2.1]hept-yl)carbonyl]amino}ethoxy)-4-oxobutanoic acid **(4)** in $CDCl_3$.

A similar procedure was applied to the synthesis of **6**. In this case, 9-anthracene methanol was used as starting material **(4.7)**.



(4.7)

Again, the structure was confirmed by ^{1}H NMR spectrum as seen in Figure 4.4. 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 aasigned to C=OCH_2CH_2OC=O clearly indicated that **6** was achieved.

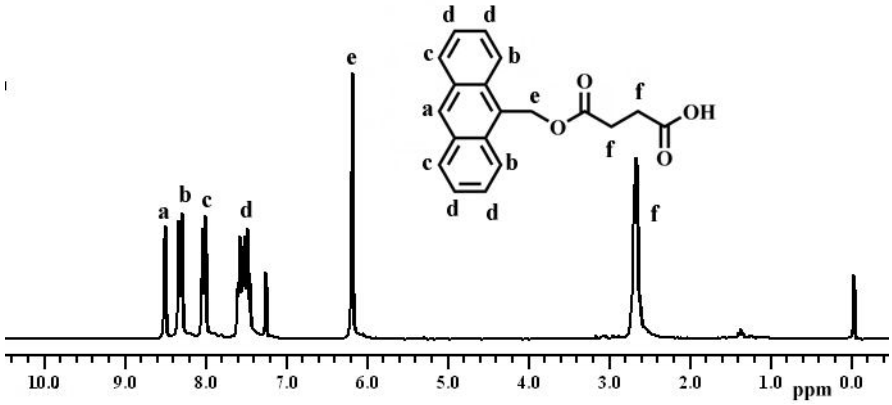
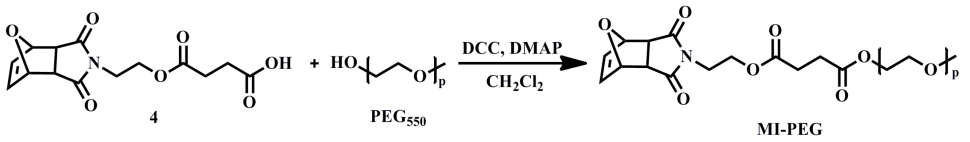


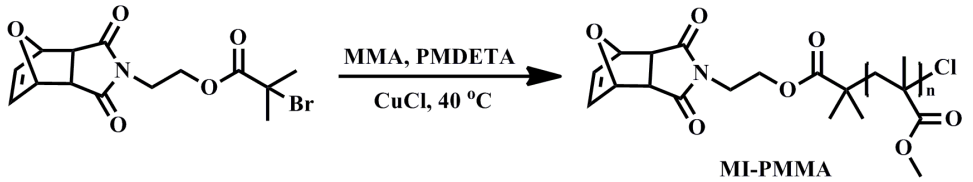
Figure 4.4: ^{1}H NMR spectrum of succinic acid mono-anthracen-9-ylmethyl-ester **(6)** in $CDCl_3$.

Before ATRP of the precursor polymers, condensation reaction of PEG precursors was carried out. MI-PEG was obtained as brown oil after esterification reaction between **4** and Me-PEG (550) **(4.8)**. From ^{1}H NMR spectrum of the polymer, the bridge and bridge-head protons were detected at 6.5, 5.2 and 2.8 ppm respectively. The $M_{n,NMR}$= 750 of MI-PEG was determined from a ratio of integrated peaks at 3.62 ppm (OCH_2CH_2 protons of PEG) to 6.5 ppm (vinyl end protons).

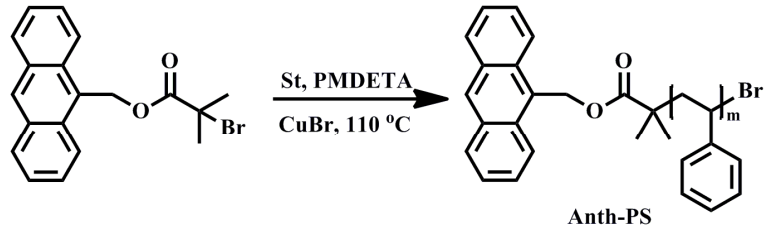


(4.8)

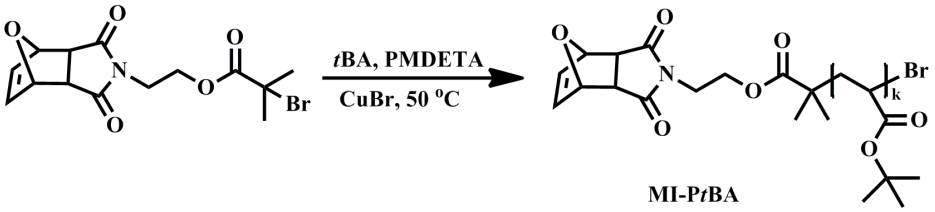
Next, MI-PMMA **(4.9)**, Anth-PS **(4.10)** and MI-P*t*BA **(4.11)** were obtained by ATRP of MMA, St and *t*BA using **3** and **5** as initiators. Since furan protection was easily deprotected at elevated temperatures, the polymerization temperature for *t*BA and MMA were purposely kept low in order to prevent possible copolymerization of maleimide and monomers during polymerization. Number-average molecular weight calculated by GPC ($M_{n,GPC}$) of MI-PMMA and MI-P*t*BA were in fairly good agreement with the theoretical one ($M_{n,theo}$) indicating that the initiations were not quantitative under these polymerization conditions.



(4.9)



(4.10)



(4.11)

The $M_{n,NMR}$ of MI-PMMA and MI-P*t*BA were determined from a ratio of integrated peaks at 3.58 ppm (OCH_3 protons of MMA) and 2.2 ppm (C*H* protons of P*t*BA) to 6.5 ppm (vinyl end protons). Molecular weight of **3** was added to this value. $M_{n,NMR}$ values were consistent with those of the $M_{n,GPC}$ (Table 4.1). Besides, $M_{n,NMR}$ of Anth-PS was calculated by comparing of the integrals of the aromatic protons of PS at 6.0-7.5 ppm and that of two protons of anthracene end group at 7.9 ppm. From Table 4.1. It was found good agreement between $M_{n,theo}$ $M_{n,NMR}$ and $M_{n,GPC}$ values.

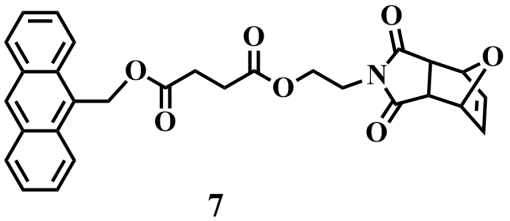
Table 4.1: The conditions and the results of linear polymers used in the synthesis of block copolymers via DA click reaction.

Polymer	Ini.	Time (min)	Conv.[e] (%)	$M_{n,GPC}$ (g/mol)	M_w/M_n	$M_{n,theo}$ (g/mol)	$M_{n,NMR}$ (g/mol)
Anth-PS[a]	**5**	25	17	3900	1,15	3700[f]	3850
MI-PMMA[b]	**3**	270	30	2850	1,24	1850[f]	2950
MI-P*t*BA[c]	**3**	150	11	2050	1,18	1850[f]	2300
MI-PEG[d]	**-**	-	-	550	1,10	840[g]	750

[a] $[M]_0:[I]_0:[CuBr]:[PMDETA] = 200:1:1:1$; polymerization was carried out at 110 °C.
[b] $[M]_0:[I]_0:[CuCl]:[PMDETA] = 50:1:1:1$; polymerization was carried out at 40 °C. MMA / toluene = 1 (v/v).
[c] $[M]_0:[I]_0:[CuBr]:[PMDETA] = 100:1:1:1$; polymerization was carried out at 50 °C. *t*BA / EC = 10 (w/w).
[d] Obtained by an esterification reaction between compound **4** and Me-PEG (550).
[e] Determined by gravimetrically.
[f] $M_{n,theo} = ([M]_o/[I]_o)$ X conversion % X MW of monomer + MW of initiator.
[g] $M_{n,theo} = M_n$ of Me-PEG (550) + MW of **4**.

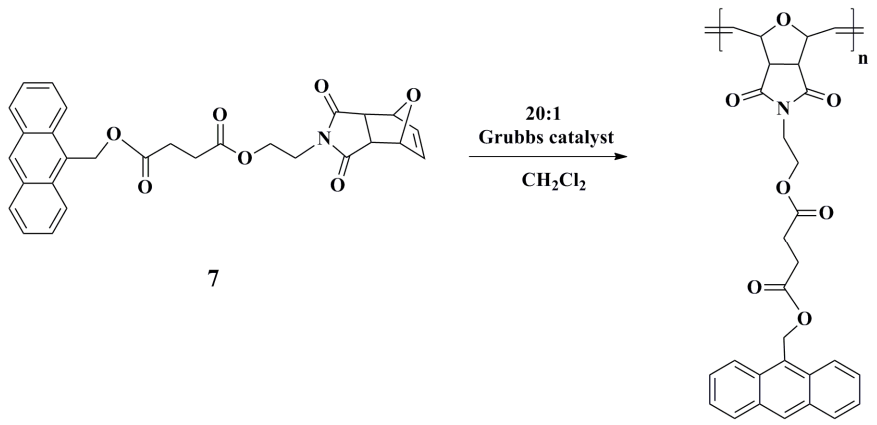
4.2 Preparation of Graft Copolymers via Combination of ROMP and Diels-Alder Click Reaction

Anthracene-functionalized oxanorbornene (oxanorbornenyl anthracene) monomer **7** was synthesized via esterification reaction of **2** and **6** catalyzed by DCC and DMAP in CH_2Cl_2 at room temperature overnight **(4.12)**.



7 **(4.12)**

^{1}H NMR spectroscopy confirmed clearly the structure of **7** by appearance of characteristic signals of anthracene (δ 8.5-7.5) and vinyl protons (δ 6.4). Next, poly(oxanorbornenyl anthracene) was obtained via ROMP of **7** using the first generation Grubbs' catalyst $(PCy_3)_2(Cl)_2$-RuCHPh in CH_2Cl_2 at room temperature for 20 min, followed by a reaction with butyl vinyl ether as a terminating agent for additional 20 min **(4.13)**.



7

poly(oxanorbornenyl anthracene)

(4.13)

GPC and ^{1}H NMR spectroscopy confirmed that poly(oxanorbornenyl anthracene) was appropriately prepared with controlled molecular weight, low polydispersity index (PDI) and desired anthracene pendant groups. The number-average theoretical molecular weight ($M_{n,theo}$ = 10000), which did not fit with the number-average molecular weight by conventional GPC ($M_{n,GPC}$ = 6100) relative to linear PS standards was comparable to that obtained from three detection GPC ($M_{n,TDGPC}$ = 11200). In the NMR spectrum, the shift of the vinyl protons (6.4 ppm) to the 5.9 (C*H*=C*H*, trans) and 5.6 ppm (C*H*=C*H*, cis) was observed upon the ROMP of **7**, which revealed that poly(oxanorbornenyl anthracene) had occurred as seen in Figure 4.5.

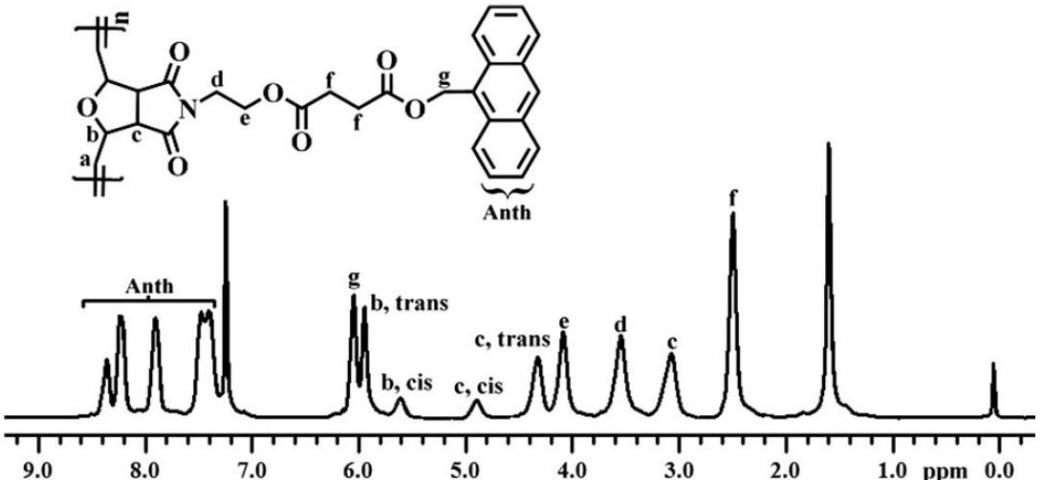


Figure 4.5: ^{1}H NMR spectrum of of poly(oxanorbornenyl anthracene) in $CDCl_3$.

Absolute molecular weight ($M_{w,TDGPC}$ = 13100) of poly(oxanorbornenyl anthracene) was measured by using TD-GPC in THF at 35 ^oC, after an introducing of

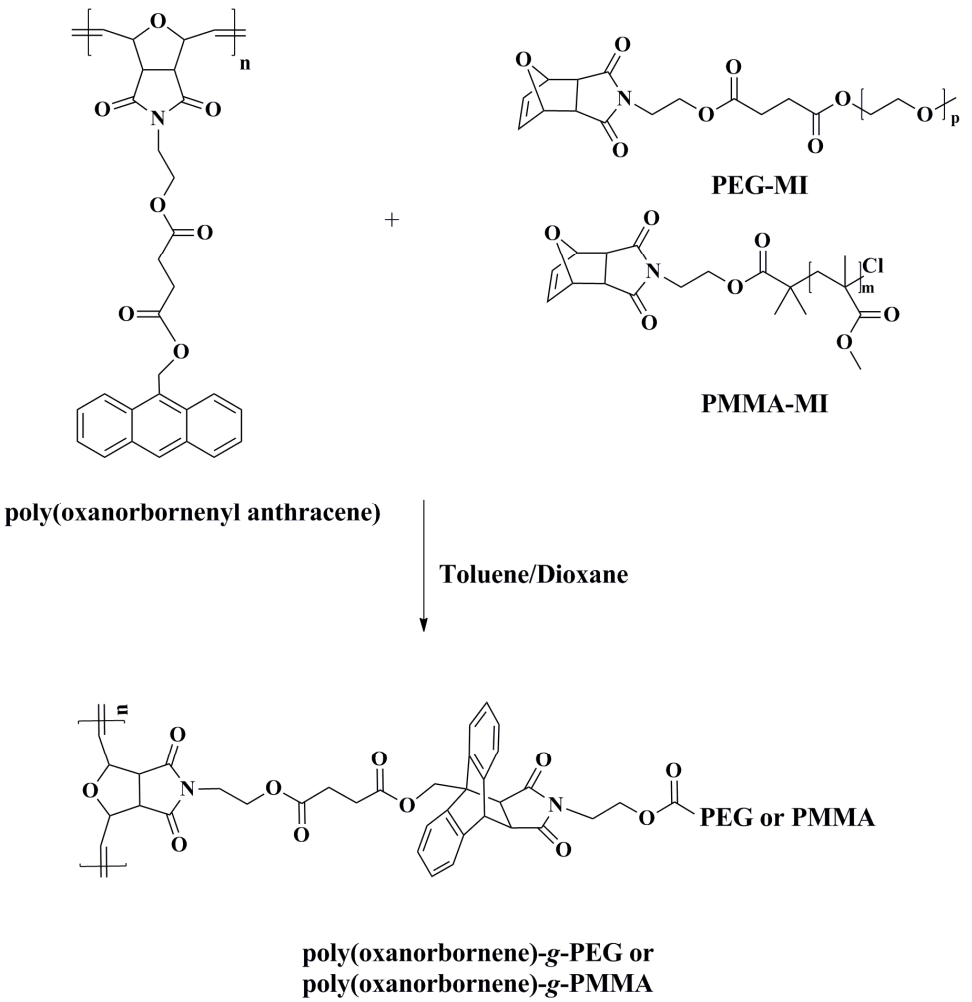
experimentally dn/dc = 0.166 mL/g into the software. This experimental dn/dc was determined from a slope of RI Area-concentration (g/mL) linear plot containing at least four different polymer concentrations and based on an assumption that truly size-exclusion mechanism was operative in the columns of TD-GPC (Table 4.2).

Table 4.2: The characterization of graft copolymers and their precursor

Entry	Polymers	DA eff. (%)	$M_{n,theo}$[a] (g/mol)	TD-GPC				
				M_n (g/mol)	M_w (g/mol)	d*n*/d*c* (mL/g)	[η] (dL/g)	R_h (nm)
1	**Poly(oxanorbornenyl-anthracene)**	-	10000	11200	13100	0.166[b]	0.05	2.16
2	**Poly(oxanorbornene)-*g*-PEG**	97	24500	29000	34000	0.120[c]	-	-
3	**Poly(oxanorbornene)-*g*-PMMA**	98	68000	56000	74000	0.101[b]	0.10	4.68

[a] $M_{n,theo}$ of poly(oxanorbornene) = (monomer/catalyst) X conv. % X MW of oxanorbornene;
$M_{n,theo}$ of graft copolymer = $M_{n,theo}$ of poly(oxanorbornenyl-anthracene) + DA efficiency X
DP_n of poly(oxanorbornenyl-anthracene) X $M_{n,NMR}$ of PEG or PMMA;
[b]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;
[c] Calculated from Diels-Alder efficiency depending on assumption that d*n*/d*c* value correlates linearly with composition of block copolymer.

Next, poly(oxanorbornenyl anthracene) was clicked with PEG-MI and PMMA-MI via Diels-Alder reaction to yield poly(oxanorbornene)-*g*-PEG and poly(oxanorbornene)-*g*-PMMA, respectively **(4.14)**.



(4.14)

A 1.25 equiv of PEG-MI and PMMA-MI per anthracene unit was employed in Diels-Alder click reaction, because of the DP_n of the poly(oxanorbornenyl anthracene) was calculated to be 20 based on the $M_{n,theo}$= 10000. Meanwhile, it should be noted that unreacted PEG and PMMA precursors were easily removed from the reaction mixture by dissolution-precipitation.

^{1}H NMR analysis of poly(oxanorbornene)-*g*-PEG indicated that the PEG 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. Interestingly, a GPC trace of poly(oxanorbornene)-*g*-PEG showed a shift to the higher retention time region as compared to that of poly(oxanorbornenyl

anthracene). This may be due to adsorption of the graft copolymer to the stationary phase rather than selective permeation as seen in Figure 4.6.

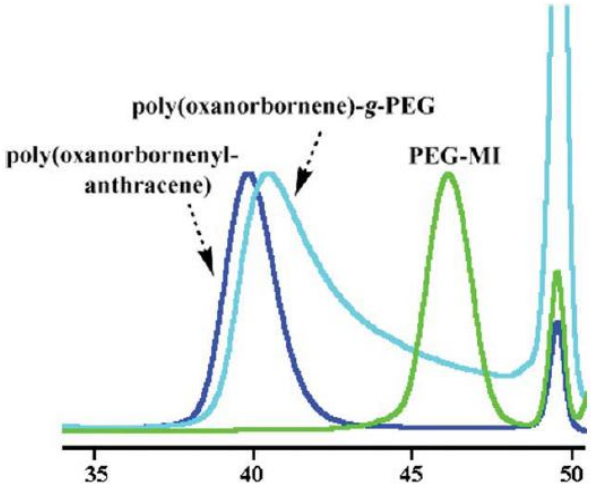


Figure 4.6: Evolution of GPC traces: PEG-MI, poly(oxanorbornenyl-anthracene), and poly(oxanorbornene)-*g*-PEG obtained from RI detection of conventional GPC at 30°C in THF

Moreover, because of an experimental d*n*/d*c* of this graft copolymer could not be obtained correctly, TD-GPC measurement was performed by introducing a d*n*/d*c* = 0.120 mL/g derived from Diels-Alder click efficiency into the instrument and subsequent the $M_{w,TDGPC}$ value was calculated as 34000 (Table 4.2). ^{1}H NMR spectrum of the second graft copolymer poly(oxanorbornene)-*g*-PMMA confirmed the grafting of PMMA segment into the poly(oxanorbornenyl anthracene) displaying the signals corresponding to the both segments as seen in Figure 4.7.

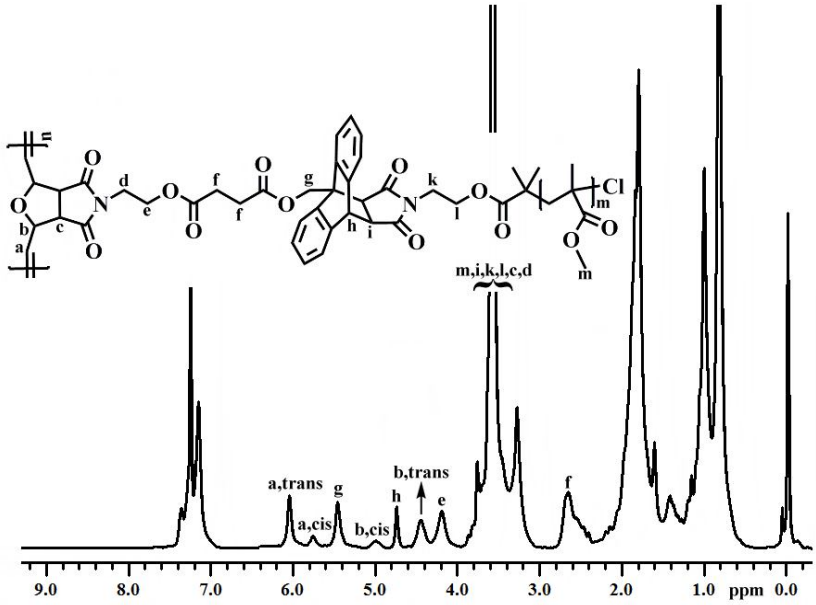


Figure 4.7: ^{1}H NMR spectrum of poly(oxanorbornene)-*g*-PMMA in $CDCl_3$.

In the GPC trace of poly(oxanorbornene)-*g*-PMMA, a clear shift to higher molecular weights was observed as compared to that of poly(oxanorbornenyl anthracene), thus proving a successful grafting as seen in Figure 4.8. The d*n*/d*c* value, 0.101 mL/g, for poly(oxanorbornene)-*g*-PMMA obtained by experimentally was introduced to the instrument so as to give $M_{w,TDGPC}$ = 74000. The experimental determination depends on a slope of RI area-polymer concentrations linear plot assuming that truly size exclusion mechanism was operative through the columns of TD-GPC (Table 4.2).

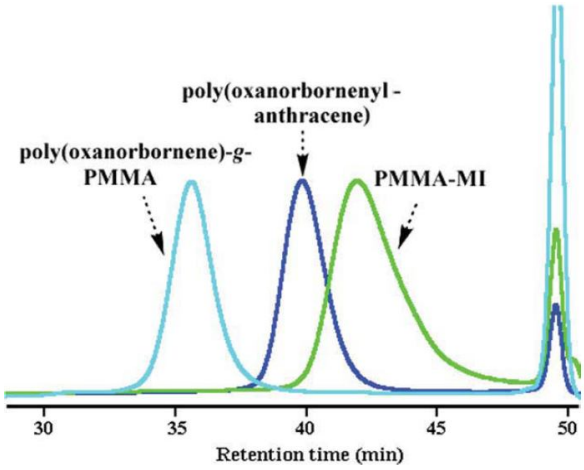


Figure 4.8: Evolution of GPC traces: MI-PMMA, poly(oxanorbornenyl anthracene), and poly(oxanorbornene)-*g*-PMMA obtained from RI detection of conventional GPC at 30 ^{o}C in THF.

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 4.9 and 4.10. 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 and at 4.44×10^{-6} and 6.86×10^{-6} M , respectively. Diels-Alder click reaction efficiencies were calculated by monitoring the disappearance of the signals corresponding to the anthracene group and found to be 97 and 98 %, respectively.

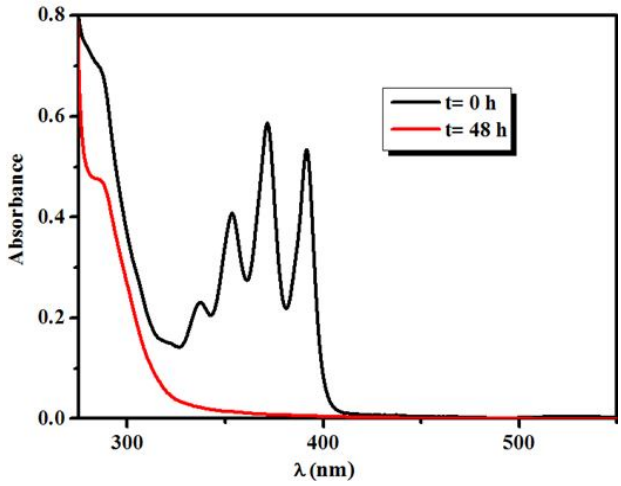


Figure 4.9: UV spectra to monitor the efficiency of Diels-Alder reaction of poly(oxanorbornenyl-anthracene) with PMMA-MI after 0 h and 48 h in CH_2Cl_2.

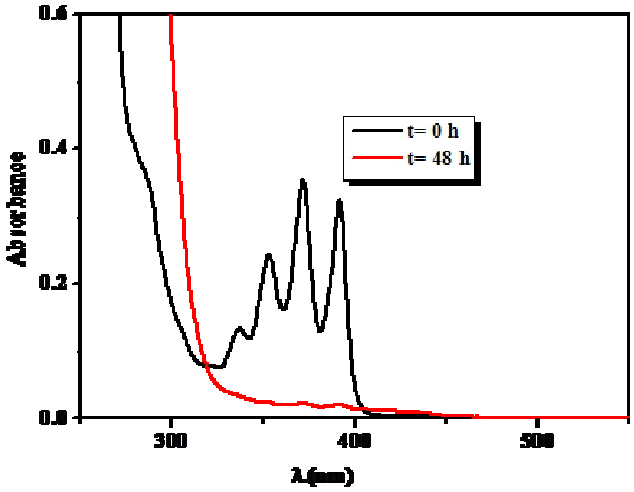
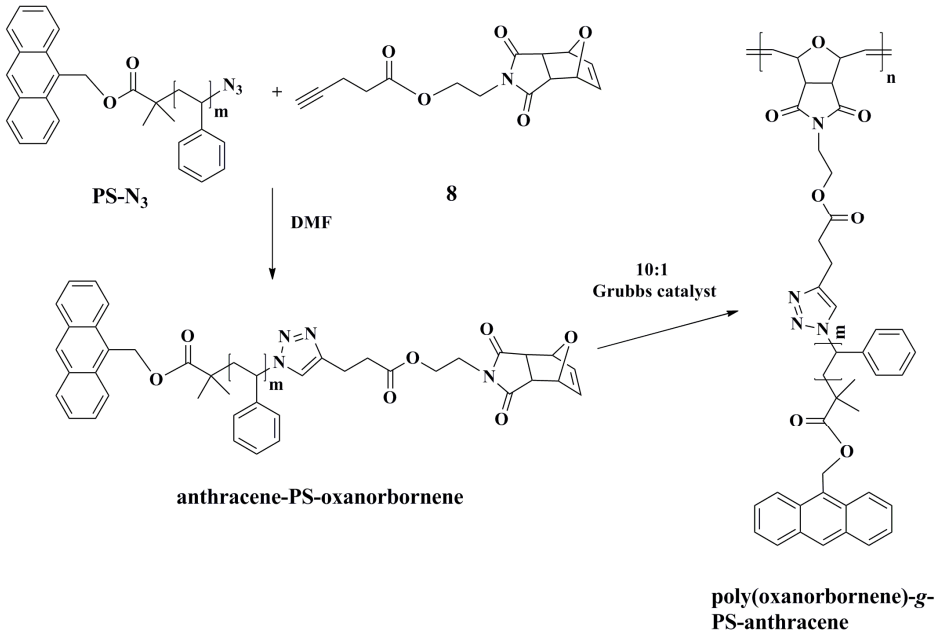


Figure 4.10: UV spectra to monitor the efficiency of Diels-Alder reaction of poly(oxanorbornenyl-anthracene) with PEG-MI after 0 h and 48 h in CH_2Cl_2.

4.3 Preparation of Graft Block Copolymers via Combination of ROMP and Diels-Alder Click Reaction

Anthracene-PS-oxanorbornene macromonomer was prepared via azide-alkyne click reaction of anthracene-PS-N_3 with oxanorbornenyl alkyne catalyzed by CuBr/PMDETA in DMF at room temperature overnight **(4.15)**. The quantitative azide-alkyne click reaction was here exploited to functionalize the chain-end of the anthracene-PS with an oxanorbornene group. Subsequent ROMP of anthracene-PS-oxanorbornene macromonomer affords the synthesis of poly(oxanorbornene)-*g*-PS-anthracene by using the first generation Grubbs' catalyst in CH_2Cl_2 at room temperature for 24 h.

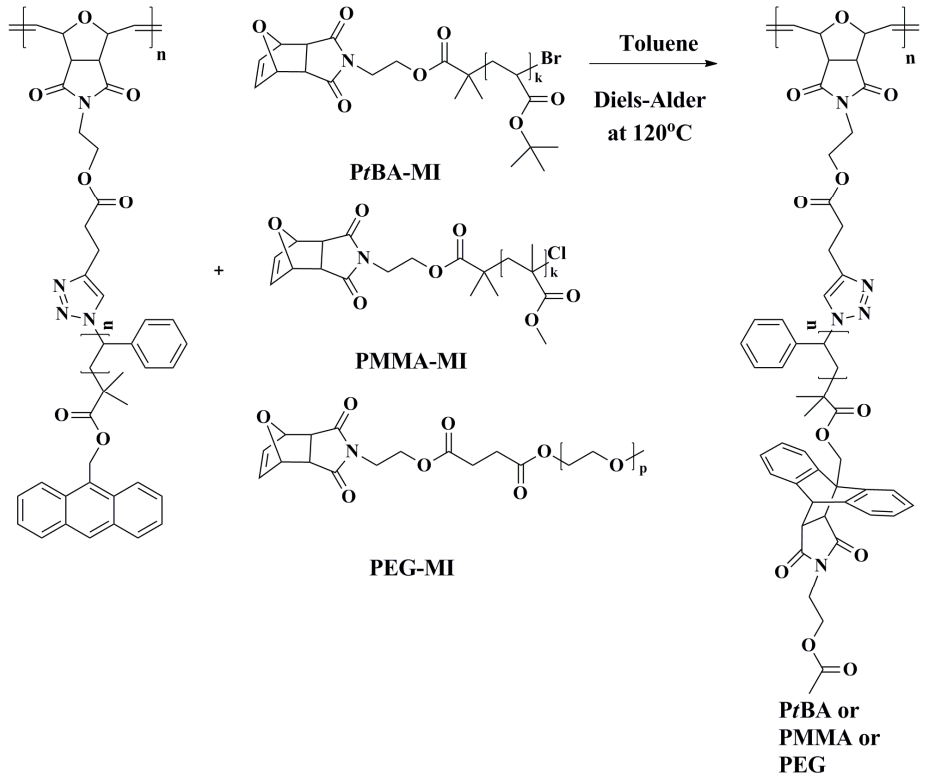


(4.15)

Although ^{1}H NMR spectrum of poly(oxanorbornene)-*g*-PS-anthracene 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 anthracene-PS-oxanorbornene. Moreover, when the d*n*/d*c* = 0.185 mL/g was introduced into the software of TD-GPC, a $M_{w,TDGPC}$ = 40300 (M_w/M_n = 1.17) is obtained for poly(oxanorbornene)-*g*-PS-anthracene, which is close to a $M_{n,theo}$ = 36900(Table 4.3).

The poly(oxanorbornene)-*g*-PS-anthracene copolymer (DP_n = 9 calculated from $M_{n,theo}$) was then clicked with 1.5 equiv of P*t*BA-MI, PMMA-MI and PEG-MI per anthracene unit in toluene at 110 ^oC for 48 h to yield final graft block copolymers

(4.16). In addition, after Diels-Alder click reaction, final graft block copolymers were purified by simply dissolution and precipitation procedure.



(4.16)

^{1}H NMR spectra of all graft block copolymers display characteristic signals of P*t*BA, PMMA and PEG along with those of oxanorbornene segment as seen in Figure 4.11.

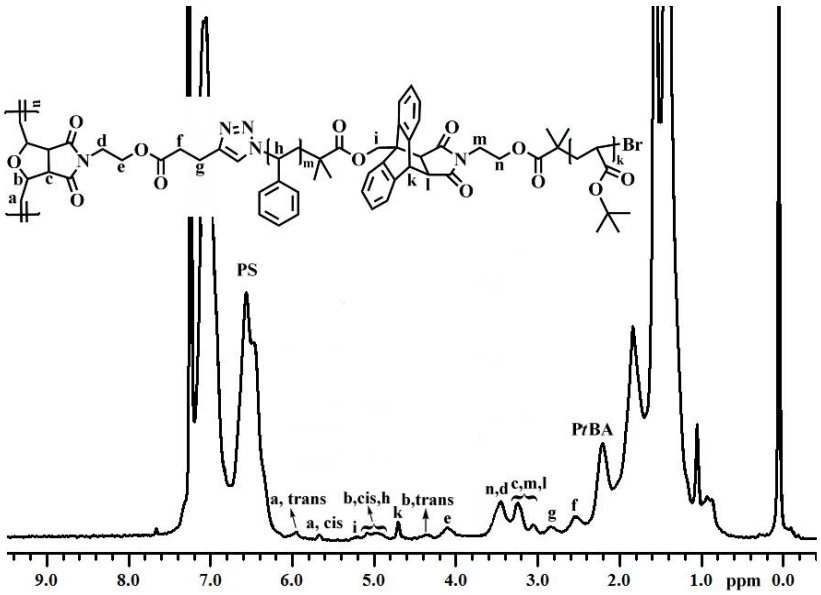


Figure 4.11: ^{1}H NMR spectrum of poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA) in $CDCl_3$.

Monomodal GPC traces with narrow polydispersity display a clear shift to a lower retention time as compared to those of starting precursors, thus proving the synthesis of final graft block copolymers as seen in Figures 4.12-4.14.

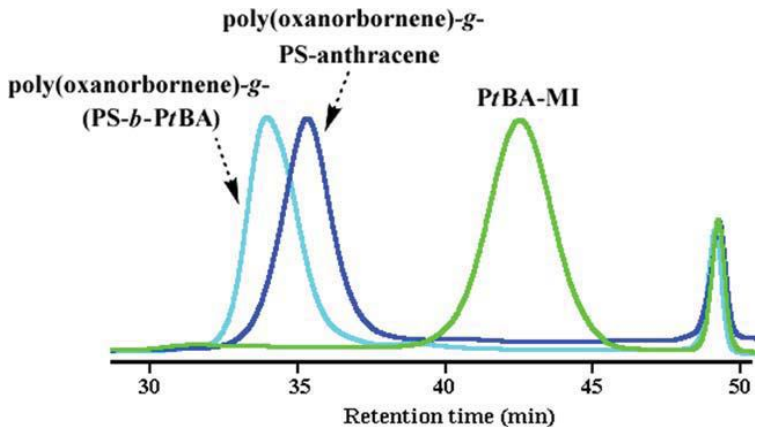


Figure 4.12: Evolution of GPC traces: P*t*BA-MI, poly(oxanorbornene)-*g*-PS-anthracene, and poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA).

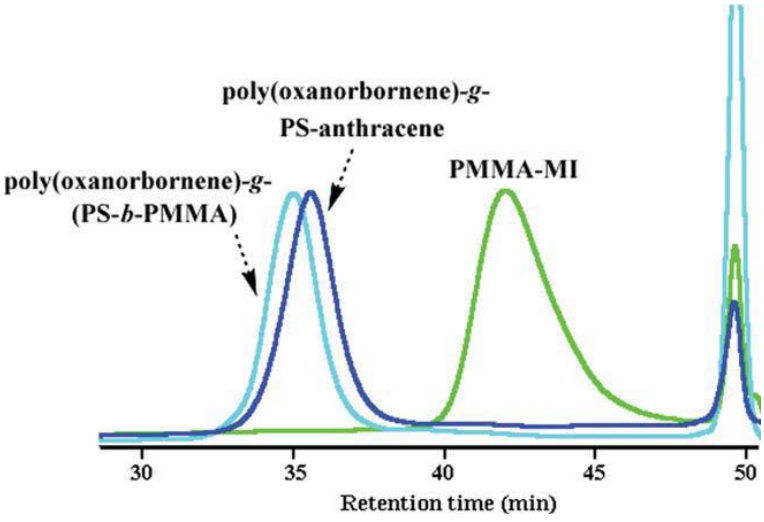


Figure 4.13: Evolution of GPC traces: PMMA-MI, poly(oxanorbornene)-*g*-PS-anthracene, and poly(oxanorbornene)-*g*-(PS-*b*-PMMA).

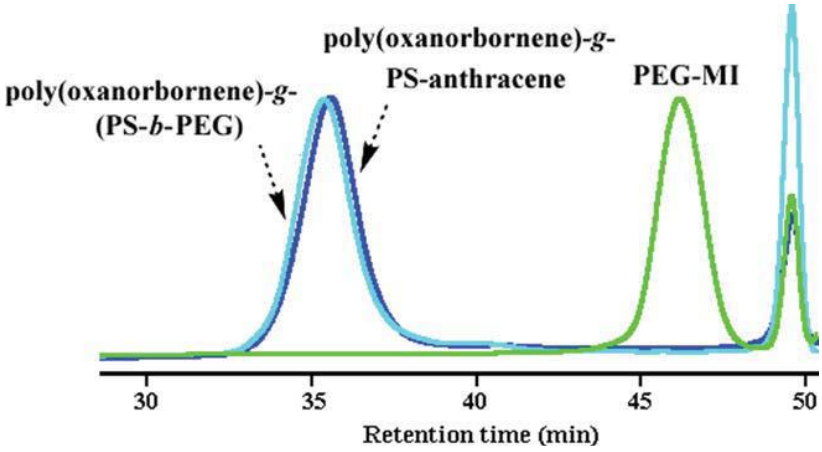


Figure 4.14: Evolution of GPC traces: PEG-MI, poly(oxanorbornene)-*g*-PS-anthracene, and poly(oxanorbornene)-*g*-(PS-*b*-PEG).

The d*n*/d*c* values of graft 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 d*n*/d*c* values are subsequently introduced to the OmniSec software of the TD-GPC to yield $M_{w,TDGPC}$, [η] and R_h of the analyzed graft block copolymers (Table 4.3). It should be noted that the obtained molecular weights ($M_{n,TDGPC}$) are close to $M_{n,theo}$ values, thus displaying target well-defined graft block copolymers.

Table 4.3: The characterization of graft block copolymers and their precursor

Entry	Polymer	DA eff. (%)	$M_{n,theo}$[a] (g/mol)	TD-GPC				
				M_n (g/mol)	M_w (g/mol)	d*n*/d*c* (mL/g)	[η] (dL/g)	R_h (nm)
1	**poly(oxanorbornene)-g-PS-anthracene**	-	36900	34500	40500	0.185	0.12	4,18
2	**poly(oxanorbornene)-*g*-(PS-*b*-PEG)**	95	43500	42500	47000	0.171[b]	-	-
3	**poly(oxanorbornene)-*g*-(PS-*b*-PMMA)**	90	61000	63400	71000	0.121[c]	0.11	5,17
4	**poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA)**	92	56000	60300	66000	0.135[c]	0.15	5,30

[a] $M_{n,theo}$ of poly(oxanorbornene)-*g*-PS-anthracene = (macromonomer/catalyst) X conv. % X $M_{n,GPC}$ of macromonomer;
$M_{n,theo}$ of graft block copolymer= $M_{n,theo}$ of poly(oxanorbornene)-*g*-PS-anthracene + DA efficiency X DP_n of poly(oxanorbornene)-*g*-PS-anthracene X $M_{n,NMR}$ of PEG, PMMA or P*t*BA;
[b]Calculated from ^{1}H NMR depending on assumption that dn/dc value correlates linearly with composition of block copolymer;
[c]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.

Next, the formation of graft block copolymer was followed over time by UV spectroscopy upon the disappearance of the signal of anthryl groups at 371 nm and $5.6x10^{-5}$ M. Monitoring of Diels-Alder click reaction using UV-Vis spectroscopy revealed high reaction efficiencies (90-95%) as seen in Figures 4.15.

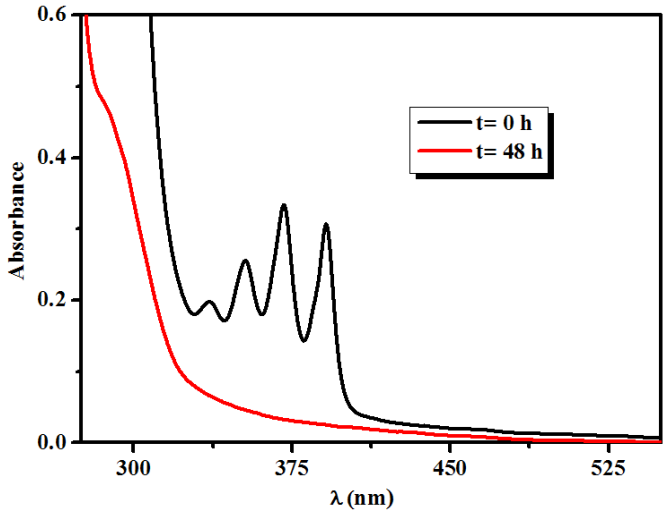


Figure 4.15: UV spectra to monitor the efficiency of Diels-Alder reaction of poly(oxanorbornene)-*g*-PS-anthracene with PMMA-MI after 0 h and 48 h in CH_2Cl_2.

5. CONCLUSION

As a conclusion, we here described that graft copolymers and graft block copolymers were successfully prepared via first time combining ROMP and Diels-Alder reaction 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 graft and graft block copolymers showed a clear shift when compared to their linear precursors, proving that graft reactions were carried out. However, poly(oxanorbornene)-*g*-PEG sample displayed a different behavior, probably due to its adsorption on the column stationary phase. The graft and graft block copolymers were prepared with $M_{n,TDGPC}$ of 30-63 kg/mol and polydispersities 1.1-1.3. It should be noted that $M_{n,theo}$ values are of between $M_{w,TDGPC}$ and $M_{n,TDGPC}$.

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▪ Durmaz, H., Dag A., **Cerit, N.,** Sirkecioglu, O., Hizal, G., Tunca U., 2010, Graft copolymers via ROMP and Diels–Alder click reaction strategy, *Polym. Chem*., **48**, 5982-5991. *International Congress - 8th Hellenic Polymer Society Symposium, Hersonissos*, October 24-29, 2010 Crete, Greece.