ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PREPARATION OF GRAFT BLOCK COPOLYMERS VIA COMBINATION OF ROMP, DIELS–ALDER AND NRC CLICK REACTION STRATEGY

M.Sc. THESIS

Dudu EYGAY

Department of Polymer Science and Technology

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Thesis Advisor: Prof. Dr. Gürkan HIZAL

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

HALKA AÇILIMI METATEZ POLİMERİZASYONU, DİELS-ALDER VE NİTROKSİT RADİKAL BİRLEŞME REAKSİYONLARI İLE AŞI BLOK KOPOLİMERLERİ ELDESİ

YÜKSEK LİSANS TEZİ

Dudu EYGAY
(515101007)

Polimer Bilimi ve Teknolojisi Anabilim Dalı

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Tez Danışmanı: Prof. Dr. Gürkan HIZAL

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Dudu EYGAY, a **M.Sc.** student of ITU **GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY** student ID **515101007** successfully defended the **thesis** entitled "**PREPARATION OF GRAFT BLOCK COPOLYMERS VIA COMBINATION OF ROMP, DIELS–ALDER AND NRC CLICK REACTION STRATEGY**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Prof. Dr. Gürkan HIZAL**
İstanbul Technical University

Jury Members : **Prof. Dr. Gürkan HIZAL**
İstanbul Technical University

Prof. Dr. Ümit TUNCA
İstanbul Technical University

Prof.Dr. Nergis ARSU
Yıldız Technical University

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Dudu EYGAY
(Chemical Engineer)

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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
EtOAc : Ethyl acetate
GPC : Gel Permeation Chromatography
MMA : Methyl Methacrylate
NBE : Norbornene
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)
C/LRP : Controlled/Living Radical Polymerization
RAFT : Reversible Addition Fragmentation Chain Transfer
NMP : Nitroxide Mediated Polymerization
ROMP : Ring Opening Metathesis Polymerization
ROP : Ring-opening polymerization
r-DA : retro-Diels-Alder
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
ε-CL : ε-caprolactone
PCL : Poly(ε-caprolactone)
PDI : Polydispersity Index
PEG : Poly(ethylene glycol)
NRC : Nitroxide Radical Coupling
FRP : Free-Radical Polymerization

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PREPARATION OF GRAFT BLOCK COPOLYMERS VIA COMBINATION OF ROMP, DIELS–ALDER AND NRC CLICK REACTION STRATEGY

SUMMARY

Graft polymers have a considerable interest because of having nonlinear architecture with different composition and topology. 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.

In recent years, the use of controlled/living radical polymerization techniques in the synthesis of complex macromolecules (star and dendrimeric polymers) has quickly increased because of the variety of applicable monomers and greater tolerance to experimental conditions in comparison with living ionic polymerization routes. The most widely used methods for C/LRP include atom transfer radical polymerization (ATRP), nitroxide mediated radical polymerization (NMP), and reversible addition-fragmentation chain transfer polymerization (RAFT).

The Ring Opening Metathesis Polymerization (ROMP) has found wide applications in the polymerization of cyclic olefins (norbornene, oxanorbornene, norbornadiene, dicyclopentadiene, etc.). ROMP of cyclic olefins by using metal alkylidene initiators (e.g., molybdenum and ruthenium complex catalysis) has led to a number of well defined architectures including block, graft, star, and cyclic polymers which has controlled moleculer weight and controlled end group.

Nowadays, alternative routes such as Diels-Alder (DA) and the copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC) reactions which can be classified under the term “click chemistry” have emerged as a powerful tool for the preperation of graft polymers. In addition, nitroxide radical coupling reactions (NRC) reaction is considered as a potential click reaction due to its high efficiency and orthogonality in the synthesis of well-defined polymers with different topologies. From this point of view, in this thesis, we describe the synthesis of graft copolymers using subsequently ROMP, DA and NRC reactions.

For this purpose ; oxanorbornenyl PS with ω-anthracene end-functionalized macromonomer was prepared via copper(I) catalyzed azide-alkyne cycloaddition (CuACC) reaction of anthracene-PS-N_3 (heterotelechelic PS) with oxanorbornenyl alkyne. Subsequently, oxanorbornenyl PS with ω-anthracene end-functionalized macromonomer was polymerized via ROMP using the first generation Grubbs’ catalyst in dichloromethane at room temperature and then clicked with maleimide end-functionalized polymer P*t*BA-MI in a Diels-Alder reaction in toluene at 110 ^{o}C to create corresponding graft block copolymer poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA). Next, the third block was introduced onto the graft block copolymer using nitroxyl radical end-functionalized PEG (TEMPO-PEG) and nitroxyl radical end-functionalized PCL (TEMPO-PCL) by nitroxide radical coupling (NRC) technique to

give poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA-*b*-PEG) and poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA-*b*-PCL.

HALKA AÇILIMI METATEZ POLİMERİZASYONU VE DİELS-ALDER VE NİTROKSİT RADİKAL BİRLEŞME REAKSİYONLARI İLE AŞI BLOK 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.

Kontrollü kompozisyon ve yapılarda iyi tanımlanmış makromoleküllerin sentezi polimer biliminde yeni bir alan açan iyonik polimerizasyon yöntemlerinin gelişimine kadar sorun olmuştu. Ancak, iyonik polimerizasyon araştırmalarının gelişimi zorlu işlem koşulları; yüksek saflık ve çeşitli fonksiyonel monomerlerle uyumsuzluk söz konusu olduğundan bazı ciddi engeller ile karşılaşmaktadır. Serbest radikal polimerizasyonu safsızlıklara daha toleranslıdır ve çok çeşitli vinil monomerlerinin polimerleştirilmesi yeteneğine sahiptir fakat en büyük dezavantajı iyonik polimerizasyondaki gibi polimer yapı ve fonksiyonalite kontrolünün aynı derecede mümkün olmamasıdır. Bu nedenle, kaydadeğer çabalar serbest radikal polimerizasyonunu kontrollü bir şekilde gerçekleştirmek için harcanmıştır. Neyse ki, serbest radikal polimerizasyonunundaki devrim herhangi bir zorlu deneysel koşul gereksinimleri olmayan, iyi tanımlanmış makromoleküllerin inşasına erişim kolaylığı sağlayan kontrollü/"yaşayan" radikal polimerizasyon (C/LRP) yöntemlerinin gelişimlerine yol açmıştır. Günümüzde, en etkili ve en sık kullanılan üç C/LRP yöntemi: kararlı serbest radikal polimerleşmesi (SFRP) veya en sık kullanılan ifadesi ile nitroksit ortamlı radikal polimerleşmesi (NMP), atom transfer radikal polimerleşmesi (ATRP), ve tersinir eklenme-ayrılma zincir transfer (RAFT) polimerleşmesidir. Sonuç olarak, bu yöntemlerin polimer sentezinde geniş bir yelpazede yaygın olarak kabulu ve yararlanılması iyi tanımlanmış makromoleküllerin kontrollü kompozisyon, yapı ve fonksiyonalitede yapılmasındaki sınırsız potansiyellerine dayanır.

Kontrollü /yaşayan polimerizasyon tekniklerinden biri olan ATRP kendinden önceki önceki kontrollü radikal polimerizasyon yöntemlerinden (iyonik ,kararlı serbest radikal polimerizasyonu gibi), karmaşık polimer yapıları üretimine izin vermesi ile ayrılır. Bu polimerizasyon yöntemi, sıcaklık gibi reaksiyon parametrelerinin kontrolü ile kolayca durdurulup yeniden başlatılabilir. ATRP'den önce ortaya çıkan kontrollü polimerleşme yöntemlerinde her çeşit monomer kullanılamamasına karşın, ATRP mekanizmasında geniş bir monomer yelpazesine kullanılabilir. Kontrollü ve düzenli büyüyen polimer zinciri ve düşük molekül ağırlığı dağılımı (*polidispersite*), ATRP mekanizması sırasında kullanılan metal bazlı katalizör sayesinde elde edilir.

Her ne kadar halka açılımı metatez polimerizasyonu **(**ROMP**)** polimer kimyası alanında yeni olmasına rağmen, makromoleküler malzemelerin sentezi için, güçlü ve geniş uygulanabime alanı olan, bir yöntem olarak ortaya çıkmıştır.

En genel ROMP polimerleri norbornen tipi monomerlerden türetilir. Norbornen yapısı fonksiyonel grupların polimerlerdeki çeşitliliğini belirtmek için kullanılır. Yüksek camsı geçiş sıcaklığı ve iyi ısıl kararlılığı gibi önemli özellikleri polinorbornen iskeleti ile ilişkilidir. Tek dezavantajı hava ile temasında çabuk okside olmasıdır, bu da hidrojenerasyonla engellenebilir.

ROMP, metal alkilidin başlatıcılar (molibdenyum ve rutenyum kompleks katalizi gibi) kullanılarak elde edilen halkalı olefinlerin (norbornen, oksanorbornen, norbornadien, ve disiklopentadien vs.) yaşayan polimerizasyonu için çok yönlü ve etkili bir sentez yöntemidir. Metal alkilidin kullanarak siklik olefinlerin ROMP polimerizasyonu ile blok, aşı, yıldız ve siklik polimerler gibi uç grup kontrolü, moleküler ağırlık kontrolü gibi özelliklere sahip birçok iyi tanımlı yapılar elde edilebilir.

Ayrıca serbest radikal polimerizasyonu gibi diğer ticari polimerizasyon teknikleri karşılaştırıldığında ROMP polimerizasyonu sistemi çok daha üstündür. Radikal polimerizasyonunun en büyük problemlerinden biri zincir transferi ve sonlandırma basamağında molekül ağırlığı kontrolüdür. Kontrollü/yaşayan serbest radikal polimerizasyonu nitroksit ortamlı radikal polimerizasyonu ve atom transfer radikal polimerizasyonu ile sağlanır. Fakat bu yaşayan polimerizasyonların genellikle tamamlanması için uzun reaksiyon süresi gerekir. Molekül ağırlığı kontrolü yaşayan iyonik polimerizasyonlar da başarılı olunabilir.

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. Günümüzde, "click kimyası" terimi altında sınıflandırılan Diels-Alder (DA) ve bakır katalizli azid-alkin siklokatılma (CuAAC) tepkimeleri blok kopolimerlerden karmaşık makromoleküler yapılara kadar değişen birçok polimerik malzemenin sentezinde başarılı bir şekilde uygulandı ve blok, aşı ve yıldız polimerlerin eldelerinde güçlü bir alternatif yöntem olarak ortaya çıktı.

Buna ek olarak , yine "click kimyası" terimi altında sınıflandırılan nitroksit radikal birleşme reaksiyonları (NRC), moleküllerin birbirlerine seçici ve hızlı bir şekilde bağlanmasını sağlamak amacıyla molekül uçlarında TEMPO ve türevlerinin kullanıldığı bir tepkimedir. TEMPO uç fonksiyonlu polimer malzemeler ışık, şok ve ısı değişikliklerine daha az duyarlı olduklarından, azid uç grubu taşıyan polimerlere göre daha kararlıdırlar. Farklı topolojilere uygulanabilirliği ve yüksek verimlilikleri nedeniyle iyi tanımlanmış polimerlerin sentezi için potansiyel bir click reaksiyonu olarak kabul edilir.

Üstün özellikler gösteren ileri polimer malzemelerin sentezi konusunda yoğun çaba harcanmaktadır. Daha gelişmiş fiziksel ve mekanik özellikleri bir arada bulundurmalarından dolayı blok kopolimerler ve aşı polimerler en çok rağbet edilen ileri malzemelerdir.

Aşı kopolimerler blok kopolimerlerin tüm özelliklerine sahiptirler ve sentezlenmeleri daha kolaydır. Aşı polimerler genel olarak 3 farklı yöntemle elde edilirler zincirden aşılama "grafting from", makromonomer aşılama "grafting through" ya da zincire aşılama "grafting onto".

Zincirden aşılama tekniğinde polimer zinciri fonksiyonlanmış aktif bölgeden büyür. Bu bölge başlatıcı görevini üstlenir. Bu aktif bölgelerdeki polimerizasyonunda polimerik aşı formu aşı kopolimere dönüşür. Bu yolla yüksek yoğunluklu fırça tipi graft kopolimer elde edilebilir.

Makromonomere aşılama yönteminde önceden fonksiyonlandırılmış makromonomerler aşı kopolimeri elde etmek için polimerize edilir. Makromonomerler genel olarak polimerizasyona uygun son grup taşıyan polimerik ya da oligomerik zincirlerdir.

Zincire aşılama metodunda iskelet ve kollar polimerizasyon yöntemleri ile ayrı ayrı hazırlanır. Yaşayan kısımlar ile reaksiyona girecek olan fonksiyonel gruplar polimer zinciri boyunca dağılmıştır. Uygun deneysel koşullar altında iskelet ve yaşayan dallanmalar bağlanma reaksiyonu ile aşı kopolimerlerin oluşumu sağlanır.

Bu noktadan hareketle bu tezde ROMP, DA click ve NRC click reaksiyonlarının birlikte kullanılmasıyla iyi tanımlanmış aşı blok kopolimerlerinin zincire aşılama metoduyla sentezi tanımlanmıştır.

Bu amaçla, birinci basamakta önce ω-antrasen uç-fonksiyonlandırılmış okzanorbornenil PS makromonomeri, ω-anthracene-PS-N_3 ve oksanorbornil alkinin Cu(I) katalizinde azid-alkin siklik katılması reaksiyonu ile oda sıcaklığında ile hazırlandı. Sırasıyla ω-antrasen uç-fonksiyonlandırılmış okzanorbornenil PS makromonomeri oda sıcaklığında diklorometan içerisinde birinci jenerasyon Grubbs katalizörü kullanılarak halka açılma metatez polimerizasyonu ile sentezlendi. Sonra 110 ^{o}C' de toluende Diels-Alder reaksiyonu ile maleimid uç-fonksiyonlu polimer P*t*BA-MI ile poly(oxanorbornen)-*g*-(PS-*b*-P*t*BA) aşı blok kopolimeri sentezlendi. Son olarak bu aşı blok kopolimeri nitrokisit radikal birleşmesi yöntemiyle TEMPO uç fonksiyonlu polimerler PEG ve PCL ile poly(oxanorbornen)-*g*-(PS-*b*-P*t*BA-*b*-PEG) ve poly(oxanorbornen)-*g*-(PS-*b*-P*t*BA-*b*-PCL) aşı blok kopolimerleri sentezlendi.

Aşı blok kopolimerizasyonun Diels-Alder click reaksiyonu etkinliği UV-Vis spektroskopisi ile gözlemlendi. Sentezlenen aşı blok kopolimerinin yapıları Hidrojen Nükleer Magnetik Rezonans Spektroskopisi (^{1}H-NMR) ve Jel Geçirgenlik Kromatografisi (GPC) ile karakterize edildi. Hidrojen Nükleer Magnetik Rezonans Spektroskopisi (^{1}H-NMR)'den elde edilen verilerden yola çıkılarak aşı blok kopolimerlerinin d*n*/d*c* değerleri hesaplandı ve bu değerler üçlü dedektör GPC (TD-GPC) cihazına tanıtılarak molekül ağırlıkları, intrinsik viskozite ([η]) and hidrodinamik yarıçapı (Rh) değerleri elde edildi.

1. INTRODUCTION

Graft copolymers with a large number of side chains chemically attached onto a linear backbone are endowed with unusual properties thanks to their confined and compact structures, including wormlike conformation, compact molecular dimensions and notable chain end effects [1].

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 [2, 3].

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) [4-22].

The concept of click chemistry, introduced by Sharpless and co-workers has attracted widespread attention in polymer science due to its high specificity, quantitative yields, and fidelity in the presence of a wide variety of solvents and functionalities [23]. The great potential of click reactions combination with their compatible partner of C/LRP processes for the construction of novel macromolecular architectures such as graft and star polymers has been pursued by synthetic polymer chemists in recent years, and is now the subject of intensive research in polymer science.

Nitroxide radical coupling reaction is considered as a potential click reaction due to its high efficiency and orthogonality in the synthesis of well-defined polymers with different topologies. The NRC click reaction proceeds between a halide- and a 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO)-terminated polymers in the presence of CuBr and ligand under mild reaction temperature based on the ATRP mechanism [24].

In this thesis we synthesised of well-defined graft copolymers generated from a combination of ROMP, Diels-Alder click reaction and NRC reaction. The ROMP technique is specially chosen for the construction of a well-defined main backbone. Oxanorbornenyl PS with ω-anthracene end-functionalized macromonomer were 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 polymer P*t*BA-MI in a Diels-Alder reaction in toluene at 110 ^{o}C to create corresponding graft block copolymer poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA). Corresponding graft block copolymer with bromide pendant groups that are for further grafting via the NRC reaction applied. TEMPO end-functionalized PEG and TEMPO end-functionalized PCL were grafted as side chains onto the ROMP generated graft copolymer poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA) to obtain poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA-*b*-PEG) and poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA-*b*-PCL) (figure 1.1) .

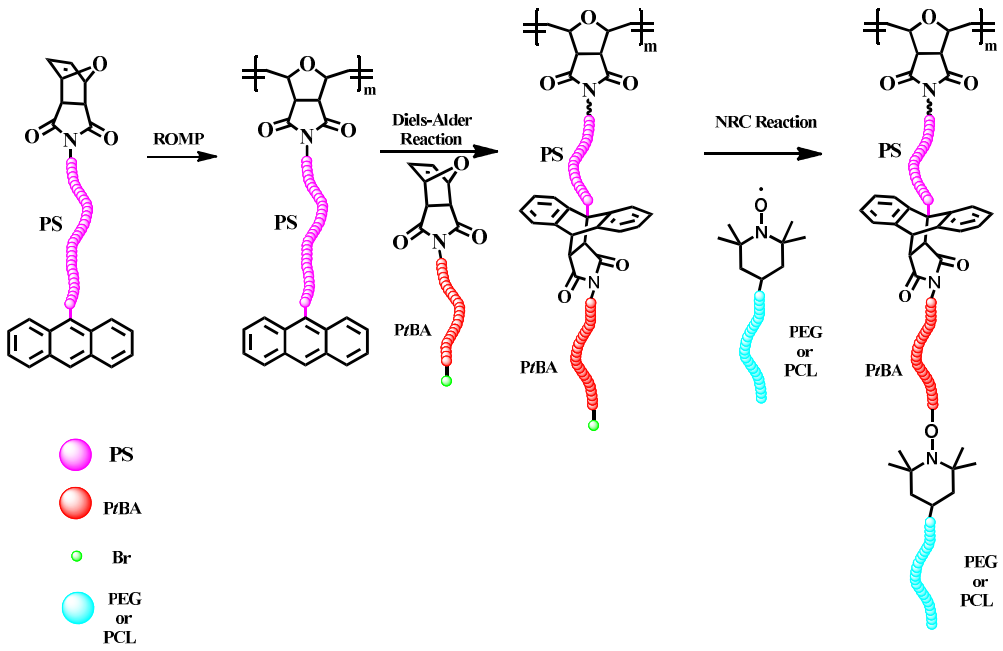


Figure 1.1 : Synthesis of graft block copolymers via ROMP, Diels–Alder click reaction and NRC click reaction.

2. THEORETICAL PART

2.1 Living Polymerization

The considerable attention to the field of living polymerization techniques is due to the increasing demand for well-defined functional polymers with fully controllable molecular characteristics. Living polymerization, the concept of which was first introduced by Szwarc in 1956, is one of the most promising ways for the synthesis of well-defined polymers [25, 26]. A living polymerization is defined as a chain polymerization that proceeds in the absence of chain transfer and chain termination as indicated by Szwarc. His pioneering work on the anionic polymerization of St initiated with sodium naphthalenide opened the field of living polymers with controlling the molecular weight and molecular weight distributions as well as the structure of the end-groups.

After the discovery of living anionic polymerization, critical research on cationic polymerization was performed in the "living" era**.** An equimolar mixture of HI/I_2 was the first system used for the initiation of such polymerizations of vinyl ethers [27]**.** In this system, the initially formed adduct of HI to a vinyl ether is activated by iodine. The fast initiation realized ideal living cationic polymerization of alkyl vinyl ethers. Thus, homopolymers and block copolymers with narrow molecular weight distributions were first synthesized in cationic polymerization.

Since then, much progress has been made in these living ionic polymerization techniques and polymerization of various monomers have been examined, for which numerous types of initiators have been developed. While these techniques are undoubtedly successful, they do suffer from rigorous synthetic requirements including the use of very pure reagents and the total exclusion of water and oxygen and incompatibility with a variety of functional monomers. Definitely, with so many parameters to control, such requirements represent a grand challenge to synthetic polymer chemists and somewhat delay their practical use. Aware of the intrinsic limitations of ionic polymerizations, many efforts have been made to find new routes which could address the development of a free radical polymerization. This process

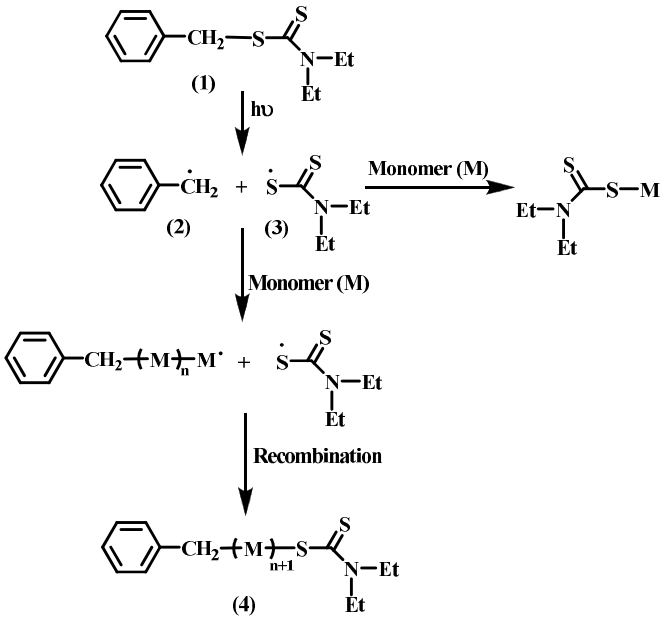
is tolerant to impurities, very versatile with respect to compatibility with broad range of functional monomers, and relatively easy to implement in an industrial plant.

2.2 Controlled/Living Radical Polymerization (C/LRP)

Conventional free-radical polymerization (FRP) techniques are very convenient commercial process for the synthesis of high molecular weight polymers since it can be employed for the polymerization of numerous vinyl monomers under mild reaction conditions, requiring an oxygen free medium, but tolerant to water, and can be conducted over a large temperature range (-80 to 250^{o}C). Furthermore, a wide range of monomers can easily be copolymerized through a radical route, and this leads to an infinite number of copolymers with properties dependent on the proportion of the incorporated comonomers. Moreover, the polymerization does not require rigorous process conditions. The major drawbacks of conventional radical polymerizations are related to the lack of control over the polymer structure. Due to the slow initiation, fast propagation and subsequent irreversible transfer or irreversible termination, polymers with high molecular weights and high polydispersities are generally produced.

In order to overcome the disadvantages of FRP without sacrificing the above-mentioned advantages, it was recognized that a living character had to be realized in conjunction with the free radical mechanism. The concept of “iniferters” (*ini*tiator-trans*fer* agent-termina*tor*) was introduced by Otsu in 1982 which was arguably the first attempt to develop a true living free-radical polymerization (LRP) technique [28]. In this case, disulfides **1** including diaryl and dithiuram disulfides, were proposed as photo initiators where cleavage can occur at the C-S bond to give a carbon-based propagating radical **2** and the mediating thio radical **3**. While the propagating radical **2** can undergo monomer addition followed by recombination with a primary sulfur radical **3** to give a dormant species **4** it may also undergo chain transfer to the initiator itself. As opposed to FRP, which results in chain termination, even at low conversion, this technique provides rudimentary characteristics of typical living systems, such as a linear increase in molecular weight with conversion (2.1). In addition, the monofunctional, or α,ω-bifunctional chains, can be considered as telechelic polymers, giving the possibility to prepare block copolymers. Nevertheless, other features of a true living system such as accurately controlled

molecular weights and low polydispersities could not be obtained since a thio radical **3** can also initiate polymerization.

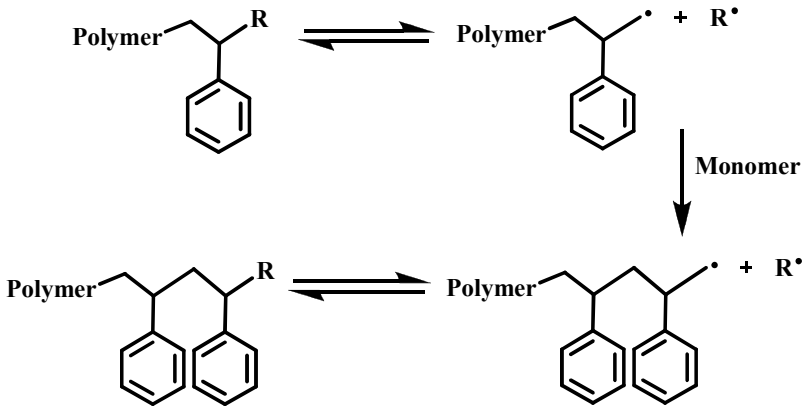


(2.1)

Otsu's pionering works have opened a way to develop the three main controlled/living radical polymerization (C/LRP) methods. Georges and co-workers first introduced true nitroxide mediated radical polymerization (NMP) in 1993 [29], Matyjaszewski and Sawamoto developed metal catalzed (Cu, Ru) living radical polymerization also called atom transfer radical polymerization (ATRP) in 1995 [30, 31], and Moad, Rizzardo and Thang reported reversible addition-fragmentation chain transfer polymerization (RAFT) in 1998 [32].

2.2.1 Nitroxide mediated radical polymerization (NMP)

The pioneering iniferter work provided the basis for the development of LRP and it is interesting to note a similarity between the iniferter mechanism and the general outline of a successful living free radical mechanism (2.2).



(2.2)

R• :Mediating Radicals

In this general mechanism, the reversible termination of the growing polymeric chain is the key step for reducing the overall concentration of the propagating radical chain end. In the absence of other reactions leading to initiation of new polymer chains (i.e., no reaction of the mediating radical with the vinylic monomer), the concentration of reactive chain ends is extremely low, minimizing irreversible termination reactions, such as combination or disproportionation. All chains would be initiated only from the desired initiating species and growth should occur in a living fashion, allowing a high degree of control over the entire polymerization process with well-defined polymers being obtained. The identity of the mediating radical, R·, is critical to the success of living free radical procedures and a variety of different persistent, or stabilized radicals have been employed.

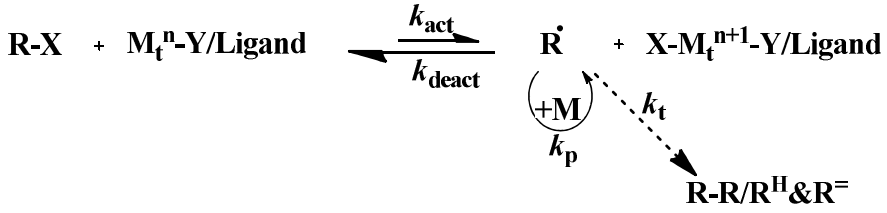
The most commonly used stable radicals have been nitroxides, especially 2,2,6,6-tetramethylpiperidinoxy (TEMPO). The 2,2',6,6'- tetramethylpiperidine-1-oxyl radical (TEMPO) was used as the nitroxide component in these initial studies. The alkoxyamine is formed in situ during the polymerization process. 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 [33]. 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 [34].

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 [35].

2.2.2 Atom transfer radical polymerization (ATRP)

The Transition-metal mediated controlled/‘‘living” radical polymerization, reported independently by Matyjaszewski [36], Sawamoto [31] and Percec [37] in 1995, is one of the most powerful techniques to obtain polymers with high control over compositions, architectures, and functionalities. The polymerization, which is mechanistically similar to atom transfer radical addition (ATRA), therefore, is often termed as atom transfer radical polymerization (ATRP).

A general mechanism for ATRP is shown in Scheme 2.3. ATRP is based on the reversible homolytic cleavage of carbon-halogen bond by a redox reaction. Homolytic cleavage of the alkyl (pseudo)halogen bond (RX) by a transition metal complex (activator, M_t^n –Y / ligand, where Y may be another ligand or a counterion) in the lower oxidation state generates an alkyl radical ($R^{\bullet}$) and a transition metal complex (deactivator, $X–M_t^{n+1}$ / ligand) in the higher oxidation state. The formed radicals can initiate the polymerization by adding across the double bond of a vinyl monomer, propagate, terminate by either coupling or disproportionation, or be reversibly deactivated by the transition metal complex in the higher oxidation state to reform the dormant species and the activator.



(2.3)

This process occurs with a rate constant of activation, k_{act}, and deactivation k_{deact}, respectively. Polymer chains grow by the addition of the free radicals to monomers

in a manner similar to a conventional radical polymerization, with the rate constant of propagation, k_p. Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. Other side reactions may additionally limit the achievable molecular weights.

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

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

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

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

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

Equation 2.2, which shows how the polydispersity index in ATRP (in the absence of chain termination and transfer) relates to the concentrations of initiator (RX) and deactivator (M_t^{n+1}), the rate constants of propagation (k_p), deactivation (k_{deact}), and monomer conversion (p). Lower polydispersities are obtained at higher conversion, higher k_{deact} relative to k_p, higher concentration of deactivator, and higher monomer to initiator ratio, $[M]_0/[I]_0$ [38, 39, 40].

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

2.2.2.1 Basic components of ATRP

Monomers

Most vinyl monomers used in free radical polymerizations have been successfully polymerized via ATRP, e.g. St derivates, (meth)acrylates, (meth)acrylamides, dienes, and acrylonitrile which contain substituents that are capable of stabilizing the propagating radicals [41]. ATRP is tolerant to many functional polar groups in monomers, however, a few monomers can not be polymerized with currently available ATRP catalysts. Some groups react rapidly with the catalyst system (such as acids; (meth)acrylic acid) creating metal carboxylates which are ineffective catalysts for ATRP. Some other monomers may be difficult to polymerize since they exhibit side reactions. An example of such a monomer is 4-vinyl pyridine (4-VP), which can undergo quaternization by the (alkyl halide) initiator [42]. Monomers often have a major effect on the ATRP, several variables can account for the influence of the used monomer. For each monomer the rates of activation and deactivation (k_{act} and k_{deact}) are unique, and these in combination with the rate of propagation k_p determine the polymerization rate. The most common monomers in the order of their decreasing ATRP reactivity are methacrylates, acrylonitrile, styrenes, acrylates, (meth)acrylamides [43].

Initiators

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

To obtain well-defined polymers with narrow molecular weight distributions, the (pseudo)halide group, X, must rapidly and selectively migrate between the growing chain and the transition metal complex. Thus far, bromine and chlorine are the halogens that afford the best molecular weight control. Iodine works well for acrylate polymerizations; however, in styrene polymerizations the heterolytic elimination of

hydrogen iodide is too fast at high temperatures. Fluorine is not used because the carbon–fluorine bond is too strong to undergo homolytic cleavage. As for other X groups, some pseudohalogens, specifically thiocyanates, have been used successfully in polymerization of acrylates and styrenes [44-46].

Initiator efficiency is of prime importance for succesful ATRP. Generally, alkyl halides RX with resonance stabilizing substituents are efficient initiators for ATRP. Often, the structure of the initiator is analogous to the structure of the halogenated polymer chain end to obtain similar reactivity of the carbon-halogen bond. For example, styrene polymerizations often incorporate 1-phenylethyl chlorides or bromides as the initiators [30]. However, this guideline does not always hold as demonstrated in the polymerization. The use of sulfonyl chlorides as universal initiator in ATRP of styrene and methacrylates was reported [47].

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

Catalysts

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

Various transition metals, such Re [48], Ru [31, 49], Rh [50], Fe[51-56], Ni [57,58], Pd [59] and Cu [60, 61] has been successfully used as catalysts for ATRP. Among them, Cu seems to be the most efficient metal as determined by the successful application of its complexes as catalysts in the ATRP of a broad range of monomers in diverse media [62].

Ligands

Ligand plays a critical role in the activation/deactivation equilibrium in ATRP. The type of a ligand including electronic, steric and solubility characters, greatly affects the reactivity of the catalyst complex and control over the polymerization [30,63]. The main role of a 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, and should also allow expansion of the coordination sphere, and should allow selective atom transfer without promoting other reactions.

Ligands for ATRP systems include multidentate alkyl amines, pyridines, pyridineimines, phosphines, ethers or half-metallocene species. Copper complexes with various multidentate N-containing ligands are most often used as ATRP catalysts such as PMDETA, and tris[2-(dimethylamino) ethyl]amine (Me6-TREN) [64]. The ATRP catalytic activity of Cu(I) complexes increases in the order bipyridine (bpy)< 1, 1, 4, 7, 10, 10- hexamethyltriethylene tetramine (HMTETA)< PMDETA< tris(2-pyridylmethyl)amine (TPMA)< Me6-TREN< dimethyl cross-bridge cyclam (DMCBCy). The most active complex known to date is derived from the cross-bridged cyclam ligand DMCBCy [38].

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

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) [34] and solvent-assisted side reactions, such as elimination of HX from polystyryl halides, which is more pronounced in a polar solvent [65], should be minimized.

2.2.3 Reversible addition–fragmentation chain transfer process (RAFT)

Reversible addition-fragmentation chain transfer (RAFT) polymerization is one of the most efficient methods in C/LRP [32, 66]. An important advantage of this method over ATRP and NMP is its tolerance to a wide range of functionalities, monomer and solvent [66-68]. This offers the possibility of performing the polymerization under a wide range of reaction conditions and polymerizing or copolymerizing a wide range of monomers in a controlled manner. In contrast to the previously described NMP and ATRP, this system relies on chain transfer for the exchange between active and dormant chains. The chain end of a dormant chain carries a thiocarbonylthio moiety, which is chain-transfer-active. Upon chain transfer, the thiocarbonylthio moiety is transferred to the previously active chain, which now becomes dormant, and the previously dormant chain carries the radical activity and is able to propagate [32].

The RAFT system consists of a small amount of RAFT agent and monomer and a free-radical initiator. Radicals stemming from the initiator are used at the very beginning of the polymerization to trigger the degenerative chain transfer reactions that dominate the polymerization. Free radicals affect both the molecular weight distribution of the polymer as the dead polymer chains of uncontrolled molecular weight are formed and the rate of polymerization. Therefore, the concentration of free radicals introduced in the system needs to be carefully balanced [69]

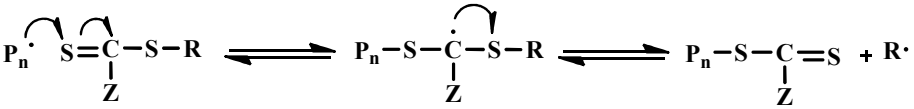
The mechanism of RAFT polymerization with the thiocarbonylthio-based RAFT agents involves a series of addition–fragmentation steps as depicted below (reaction 2.10 a-e) [32, 69]. Initiation and radical–radical termination occur as in conventional radical polymerization. Initiation starts with decomposition of an initiator leads to formation of propagating chains. In the early stages of the polymerization, addition of a propagating radical (P_n•) to the to the thiocarbonylthio compound [S=C(Z)SR] followed by fragmentation of the intermediate radical gives rise to a polymeric RAFT agent and a new radical (R•). The radical R• reinitiates polymerization by

reaction with monomer to form a new propagating radical (P_m•). In the presence of monomer, the equilibrium between the active propagating species (P_n• and P_m•) with the dormant polymeric RAFT compound provides an equal probability for all the chains to grow. This feature of the RAFT process offers the production of narrow polydispersity polymers. When the polymerization is complete, most of the chains retain the thiocarbonylthio end-group (scheme 2.4 e) which has been identified by ^{1}H NMR and UV–vis spectroscopy [70]. Additional evidence for the proposed mechanism was provided by the identification of the intermediate thioketal radical ((A) and/or (B), scheme 2.4 b,d) by ESR spectroscopy [71].

Initiation and propagation

(2.4a)

Addition to RAFT agent



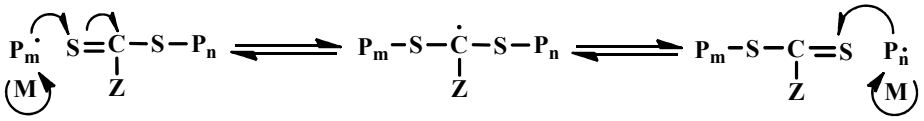
(2.4b)

(A)

Reinitiation

(2.4c)

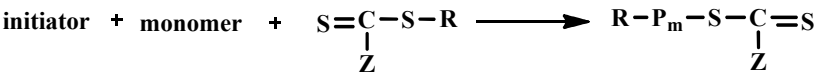
Chain equilibration by reversible addition fragmentation



(2.4d)

(B)

Overall



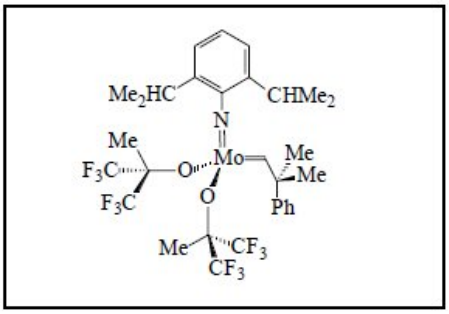
(2.4e)

2.3 Ring-opening metathesis polymerization (ROMP)

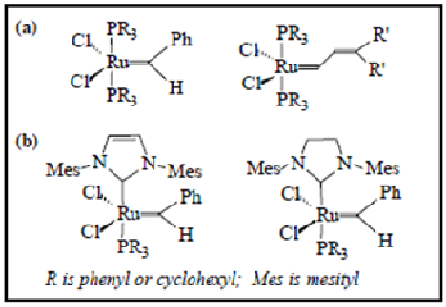
Although a relatively new player on the field of polymer chemistry, ring-opening metathesis polymerization (ROMP) has emerged as a powerful and broadly applicable method for synthesizing macromolecular materials. The origins of ROMP can be traced to the mid-1950s when various metals and reagents were combined to

uncover new transformations and reactivities involving olefins. However, the rapid rise in popularity and utility of this polymerization technique is the result of extensive work on the identification and isolation of key intermediates involved in the general olefin metathesis reaction. This led to the development of well-defined ROMP catalysts and ultimately enabled the synthesis of a wide range of polymers with complex architectures and useful functions [4].

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 **(2.5)**, and the 1st and 2nd generation of ruthenium-alkylidene catalysts, by R. H. Grubbs **(2.6)** [72].



(2.5)

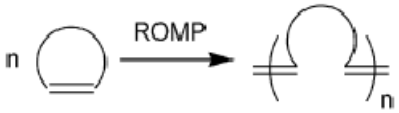


(2.6)

2.3.1 . ROMP essentials: mechanism and thermodynamics

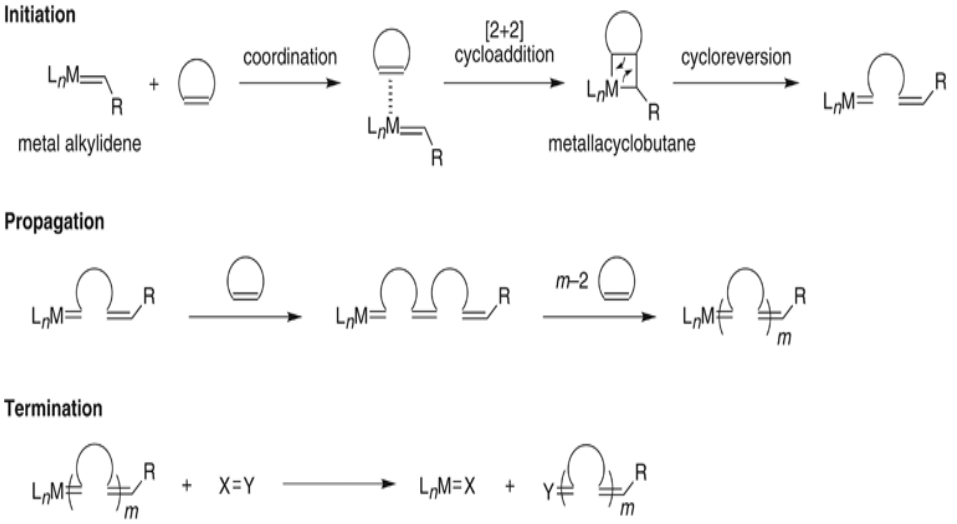
The word metathesis comes from the Greek *meta* (change) and *tithemi* (place). In olefin chemistry, it refers to the pair-wise exchange of substituents on a carbon-carbon double bond [73]. Ring-opening metathesis polymerization (ROMP) is a chain growth polymerization process where a mixture of cyclic olefins is converted to a polymeric material **(2.7)**. 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).



(2.7)

Chauvin proposed a general mechanism for ROMP in 1971 [16]. Initiation begins with coordination of a transition metal alkylidene complex to a cyclic olefin (2.8)



(2.8)

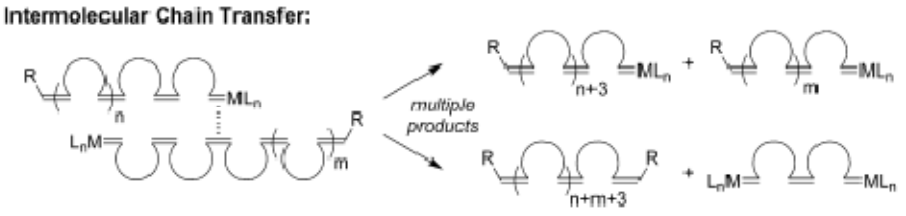
After formation of the metal-carbene complex, subsequent [2+2] cycloaddition forms a highly strained metallacyclobutane intermediate. The ring in the intermediate opens to give a new metal alkylidene. The chain growth process proceeds during the propagation stage until all monomer is consumed. Then living 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 [4].

In addition to the general ROMP mechanism illustrated in equation (2.8) (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 (2.9) and (2.10)**.** 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.



(2.9)

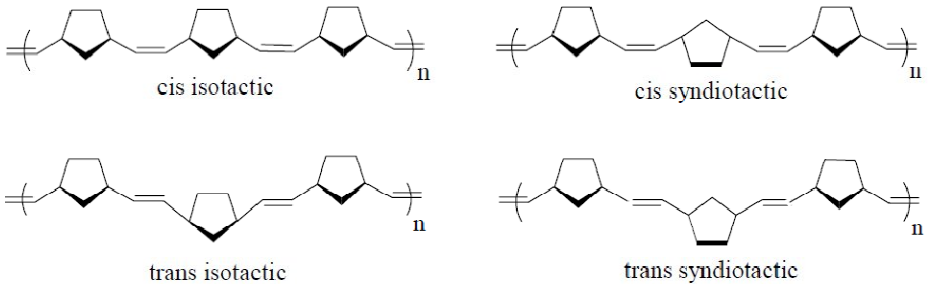
(2.10)

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 [4].

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



(2.11)

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 [73].

2.3.2 Well-Defined catalysts for ROMP

The studies of two groups deserve particular attention – as recognized by the award of the 2005 Nobel Prize for chemistry to R.H. Grubbs and R.R. Schrock. The award was shared with Y. Chauvin , who was honored for his fundamental studies on metathesis. The investigations of Grubbs and Schrock led to the development of well-defined transition metal alkylidenes that rapidly outrivaled any other initiator or initiation system, particularly those consisting of an often serendipitous mixture of transition metal salts, alcohols and tin alkyls [74].

2.3.2.1 Schrock-type initiators

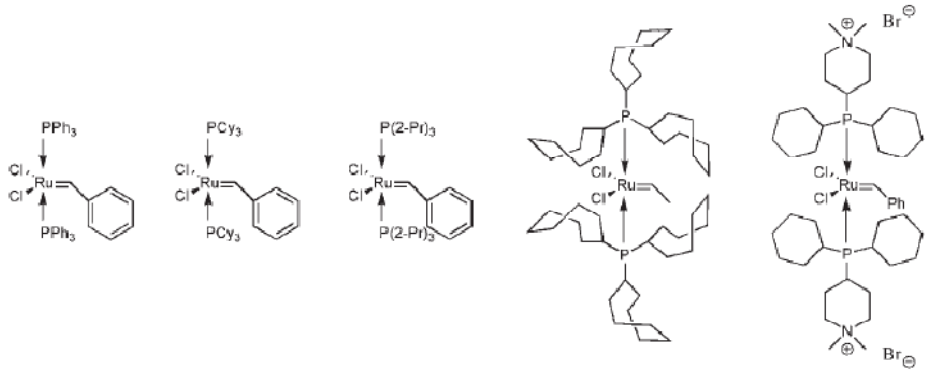
The synthesis of well-defined, high-oxidation state molybdenum alkylidenes was first reported by Schrock and coworkers in 1990 . These, and the analogous tungsten systems, are now commonly named 'Schrock-catalysts'. The systems possess the general formula $M(NAr')(OR')_2(CHR).L$, where M= Mo,W; Ar′= 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) [74].

The Schrock type catalysts are very active and somewhat tolerant with functional groups during ring open metathesis polymerization [75]. 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 [76].

2.3.2.2 Grubbs-type initiators

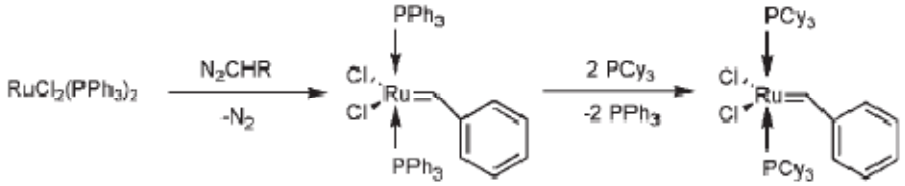
In 1992, Grubbs described the synthesis of the first well-defined ruthenium alkylidene. Thus, the reaction of $RuCl_2(PPh_3)_3$ and $RuCl_2(PPh_3)_4$, respectively, with 2,2-diphenylcyclopropene in benzene or methylene chloride yielded the desired ruthenium carbene complex $RuCl_2(PPh_3)_2(CH=CH=CPh_2)$. 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 (2.12) [74].



(2.12)

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 (2.13) [74].



(2.13)

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 [74].

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

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

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

The first homogeneous well-defined Ru complex for ROMP was $(PPh_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$ [77].

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) [15].

2.3.3 Norbornene: the traditional ROMP monomer

Most common ROMP polymers are derived from norbornene-type monomers. The norbornene structure has recently been used extensively to introduce a variety of functional groups into polymers [78].

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

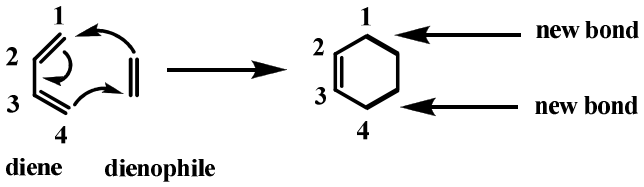
atom transfer radical polymerization (ATRP) [79]. But, those living polymerizations usually require long reaction time for completion. Molecular weight control can also be achieved with living ionic polymerizations but the stringent conditions limit their utility to non-functionalized monomers.

2.4 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 [23]. 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.

2.4.1 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 (2.14). This reaction is named for Otto Diels and Kurt Alder, who received the 1950 Nobel prize for discovering this useful transformation [80-82].

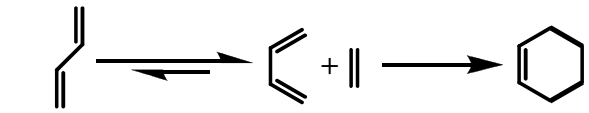


(2.14)

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 [83].

2.4.1.1 Stereochemistry of Diels-Alder reaction

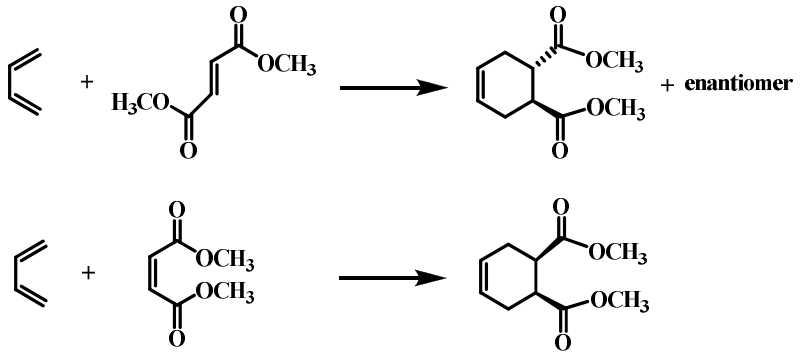
There are stereochemical and electronic requirements for the DA reaction to occur smoothly. First, the diene must be in an s-*cis* conformation instead of an s-*trans* conformation to allow maximum overlap of the orbitals participating in the reaction (2.15).



(2.15)

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.

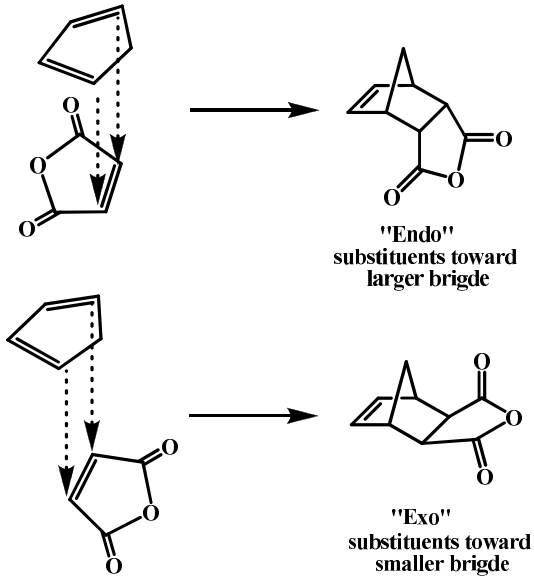
Since the reaction proceeds in a concerted fashion (*i.e.,* bonds are being formed and broken at the same time), substituents that are *cis* on the dienophile will also be *cis* in the product, and substituents that are *trans* on the dienophile will be *trans* in the product (2.16) [83-87].



(2.16)

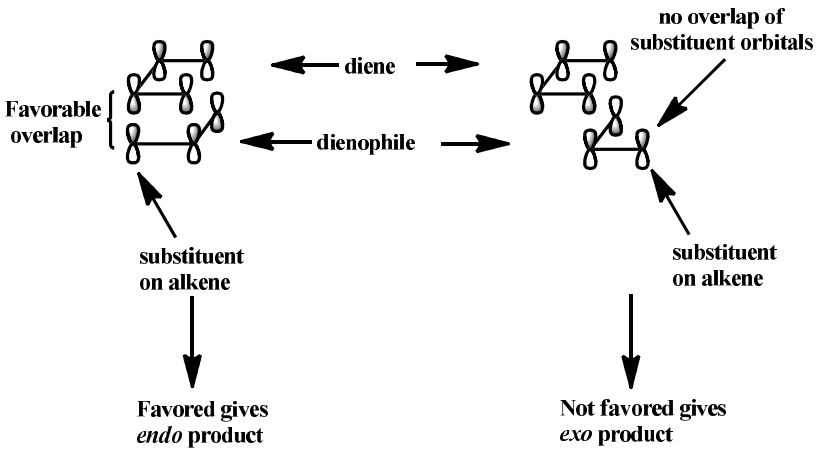
A unique type of stereoselectivity is observed in DA reactions when the diene is cyclic. In the reaction of maleic anhydride with cyclopentadiene, for example, the *endo* isomer is formed (the substituents from the dienophile point to the larger bridge) rather than the *exo* isomer (the substituents from the dienophile point away from the larger bridge) (2.17).

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 [85, 86].



(2.17)

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 (2.18).

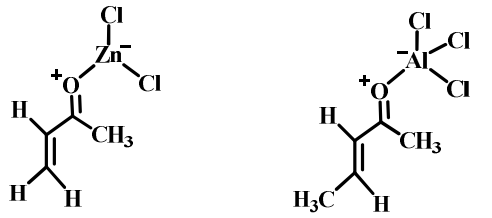


(2.18)

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.

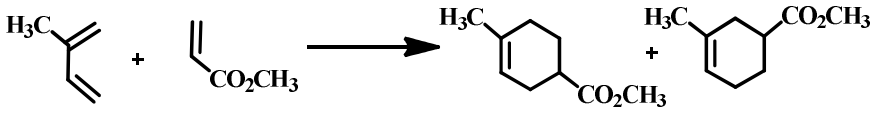
2.4.1.2 Catalysis of Diels-Alder reactions by Lewis acids

The DA reactions are catalyzed by many Lewis acids, including $SnCl_4$, $ZnCl_2$, $AlCl_3$ and derivatives of $AlCl_3$ [83]. 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 (2.19) [88].



(2.19)

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 [89]. 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 (2.20).



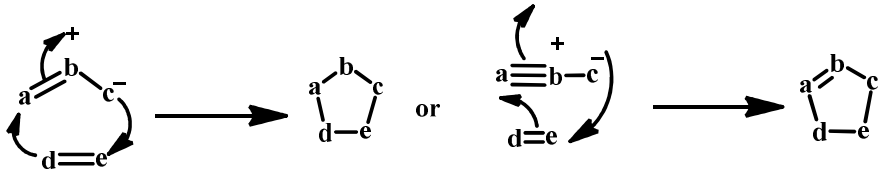
(2.20)

	"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 [90-93]. The accelerating effect of water is attributed to "enforced hydrophobic interactions" [91]. That is, the strong hydrogenbonding network in water tends to exclude nonpolar solutes and forces them together, resulting in higher effective concentrations.

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

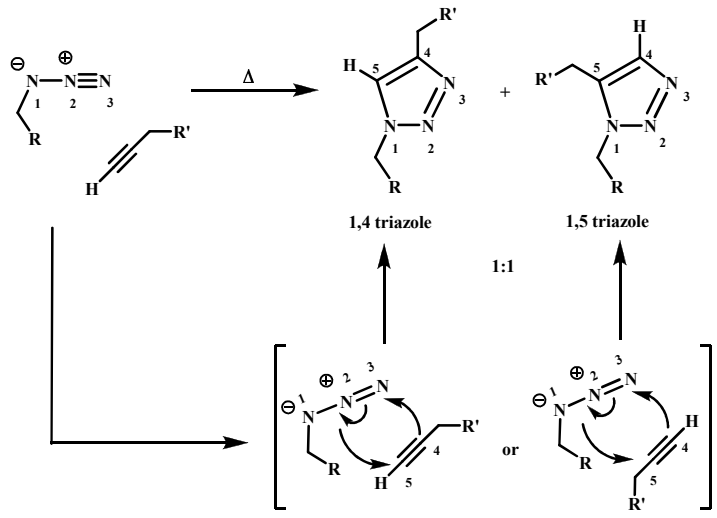
There is a large class of reactions known as 1,3-dipolar cycloaddition reactions (1,3-DPCA) that are analogous to the Diels-Alder reaction in that they are concerted [4π+2π] cycloadditions [94, 95]. 1,3-DPCA reactions can be represented as shown in the following diagram. The entity a-b-c is called the *1,3-dipole* and d-e is the *dipolarophile* (2.21).



(2.21)

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

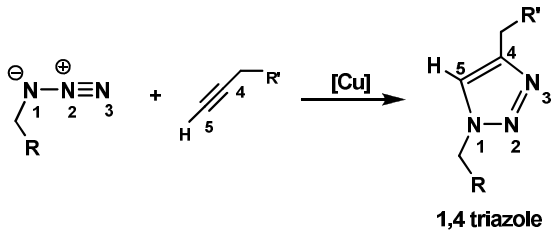
least one charge-separated resonance structure with opposite charges in a 1,3-relationship. It is this structural feature that leads to the name 1,3-dipole for this class of reactants. The dipolarophiles are typically substituted alkenes or alkynes but all that is essential is a π bond, and other multiply 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) [96]. 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 (2.22) [97].



(2.22)

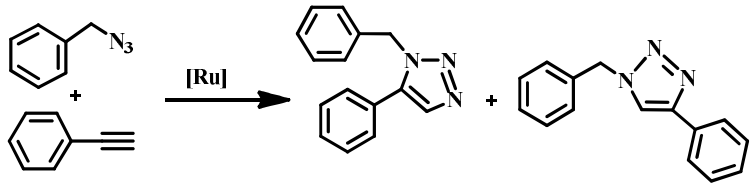
Thus, only following the recent discovery of the advantages of Cu(I)-catalyzed alkyne–azide coupling, reported independently by the Sharpless and Meldal groups,

did the main benefits of this cycloaddition become clear [98, 99]. Cu(I) catalysis dramatically improves regioselectivity to afford the 1,4-regioisomer exclusively (2.23) and increases the reaction rate up to 10^7 times eliminating the need for elevated temperatures [100]. 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 [93, 99]. 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.



(2.23)

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) [101]. 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 (2.24).

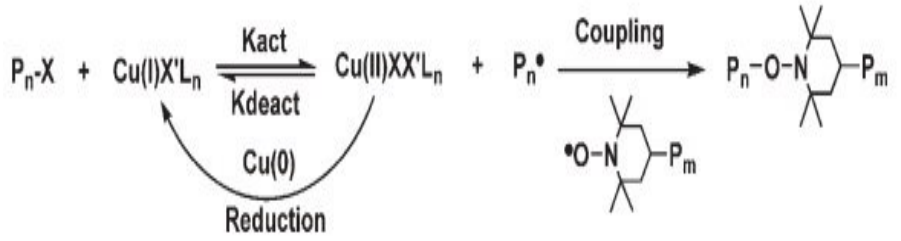


(2.24)

$Ru(OAc)_2(PPh_3)_2$	-	100%
$CpRuCl(PPh_3)_2$	85%	15%
$CpRuCl(PPh_3)_2$	100%	-
CpRuCl(NBD)	100%	-

2.5 Nitroxide Radical Coupling Click

A new reversible coupling strategy termed nitroxide radical coupling (NRC) [102-109] has the attributes of a "click" reaction. In which the bromine end-functional group of one polymer served as oxidant is reduced to bromine anion and carbon radical is formed. The Cu^{1+} is oxidized to Cu^{2+} in the presence of CuBr/ ligand. Then polymeric radical is immediately captured by another TEMPO end-functional polymer, and alkoxyamine is formed between the two polymers [109]. (2.25). In NRC reaction, CuBr participated in the reaction was served as reactant and its action was quite different from the ATRP. If some Cu(0) was added, the Cu(0) would react with the formed Cu^{2+} and the Cu^{+} was regenerated, which promoted the reaction completely. Thus, under the NRC conditions (such as the Cu(0)/CuBr/PMDETA system), the graft, [104] the star-shaped, [102] and the linear copolymer [105] were prepared successfully with high efficiency.



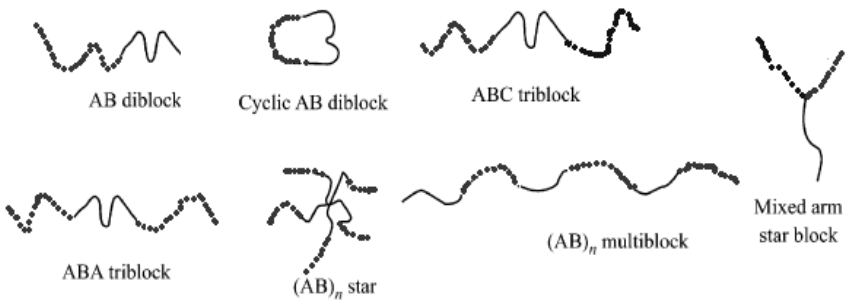
(2.25)

This reaction involves formation of a carbon centered radical by an atom transfer reaction with Cu(I)Br and trapping of this radical with a persistent nitroxide radical at close to diffusion-controlled rates. The unique aspect of this reaction is its reversibility, in which the product alkoxyamine can readily be converted to the starting incipient radical and parent nitroxide at elevated temperatures (>100 ^{0}C when TEMPO-type nitroxides are used) [110-112]. This methodology has been used to synthesize degradable and reversibly coupled linear multiblock copolymers, block and graft copolymers in the presence of a 10-fold molar excess of copper species per halide end group [108]. The rate determining step in the coupling reaction is the speed (k_{act}) at which the halide end groups on the polymer chains convert (or are activated) to the carbon-centered radical via atom transfer reactions with Cu(I) species.

2.6 Topology

2.6.1 Block copolymers

Block copolymers, or more general segmented copolymers, are a fascinating class of polymeric materials made by covalent bonding of two or more chemically different polymeric chains that, in most cases, are thermodynamically incompatible giving rise to a rich variety of microstructures in bulk and in solution. In this way, versatile properties can be combined, leading to the possibility of using block copolymers as compatibilizers, impact modifiers, surface modifiers, coating materials, antistatic agents, adhesives, for drug delivery and information storage [113, 114]. Their properties, including their mechanical, thermal, and solubility behavior, can be controlled through their composition. Another well-known application field is their use as thermoplastic elastomers in which soft and rigid segments are covalently combined. Block copolymers can be synthesized by various ways such as sequential addition of monomers to a living polymerization system, transformation approach, the use of dual or heterofunctional initiator and coupling reactions.



(2.26)

2.6.2 Graft copolymers

Graft polymers refer to the special type of branched polymers in which branched chains are structurally distinct from the main chain. The main chain is commonly called as the backbone and the branches as the side chains which are distributed along the backbones either randomly or uniformly.

When graft polymers characterized by a high density of grafted chains they were named ‘‘macromolecular brushes’’. In terms of chemical composition, macromolecular brushes can be categorized into homopolymer brushes and

copolymer brushes. The latter typically consist of two or more types of polymer side chains. When only two types of polymer grafts are involved, they can be arranged in a random, alternating, block, and "centipede" manner.

Graft copolymers have been the subject of continuously increasing interest due to their unique specific properties (morphology, phase behaviour, etc.). In general, graft copolymers can be prepared following three main strategies: (a) the "grafting onto", (b) the "grafting from", and (c) the "grafting through" strategies which differentiate from each other based on the formation principle. The different pathways are schematically depicted in Figure 2.1 and will be discussed in the context of the ensuing sections.

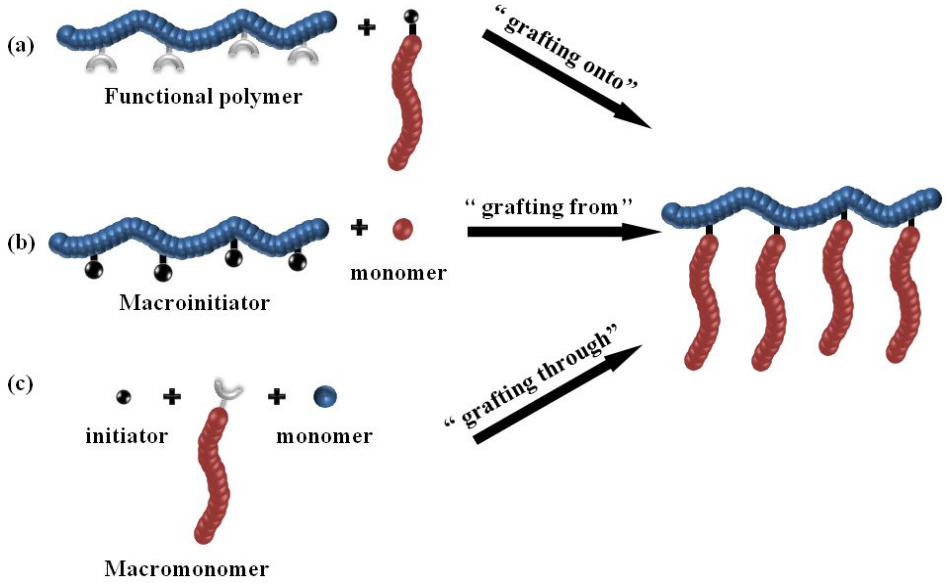


Figure 2.1 : Strategies for the synthesis of graft copolymer: (a) ''grafting onto'', (b) ''grafting from'', and (c) ''grafting through''.

2.6.2.1 General synthetic routes

The ''grafting onto'' strategy

The ''*grafting onto*'' method (a) relying on grafting of preformed side chains onto a backbone is carried out via a coupling reaction between the pendant functional groups distributed randomly on the backbone and the complementary end-functional groups of side chains.

The primary advantage of this method is that both backbone and side chains are prepared separately via different living polymerization techniques allowing the more

accurate characterization of the resulting polymer with respect to their backbone and side chains. On the other hand, the number of grafted polymer chains is limited due to the steric hindrance and low reactivity of functional groups of the polymer chains resulting in insufficient grafting efficiency.

Usually, ‘‘g*rafting onto*’’ reactions involve the preparation of well-defined side chains by living anionic polymerization and their subsequent reaction with a backbone of monomer units that are susceptible to nucleophilic attack. Examples of such functional groups include esters, anhydrides, benzylic halides, nitriles, chlorosilanes, and epoxides. So far, polymers bearing highly reactive benzylic halides, particularly poly(chloromethylstyrene)s, have been largely used as backbones subsequent reaction with the living polymers [115-118]. Beside the above mentioned anionic polymerization techniques, so far, extensive attempts for the preparation of graft copolymers using ‘‘click’’ chemistry and combined with some of the other C/LRP techniques that have been used to construct a graft architecture applying a ‘‘*grafting onto*” concept. Click reactions are expected to efficiently attach side chains to a backbone in ‘‘*grafting onto*’’ method. Obviously, this technique offering unique opportunities to improve the grafting efficiency have been explored. However, the problems for controlling the grafting density remain a challenge especially when clicking long or ‘‘thick’’ chains to the backbone.

The ‘‘g*rafting from*’’ strategy

In the “*grafting from*” (b) method, a polymer backbone (macroinitiator) with a predetermined number of initiation sites is generated, followed by grafting the side chains from the macroinitiator. The number of grafted chains can be controlled by the number of initiation sites generated along the backbone assuming that each one participates in the formation of one branch.

The “*grafting from*” approach has been extensively used in the synthesis of well-defined macromolecular grafts and brushes. For instance, PI-*g*-PS and PBd-*g*-PS well-defined copolymers were synthesized several years ago employing anionic polymerization [119, 120].

C/LRP techniques are suitable for polymer brush synthesis via grafting from method since low concentration of instantaneous propagating species limit the coupling and termination reactions and the gradual growth of side chains can effectively decrease

the steric effect which is inevitable for either ‘‘*grafting-onto*’’ or ‘‘*grafting-through*’’ strategies.

The ‘‘g*rafting through*’’ strategy

The ‘‘g*rafting through*’’ approach (c) is based on the synthesis of a terminally functional polymer chain followed by a polymerization of this macromonomer.

The attractive feature of this method is that the length of side chains and the grafting density can be controlled by adjusting the degree of polymerization of side chains and backbone, respectively. Also, because the macromonomers are prepared separately, the side chains can be characterized prior to polymerization. This method allows preparation of macromolecular brushes with well-defined grafting density and side-chain length. However, the ‘‘g*rafting through*’’ method suffers from the degree of polymerization of the backbone being dependent on the macromonomer length and type. Additionally, due to the necessarily low concentration of polymerizable end groups and high steric hindrance of the propagating chain end, polymerizations can be slow and not proceed to high conversion [121].

2.6.3 Synthesis of 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 [104].

ROMP has been considered to be an efficient way to synthesize polymacromonomer with complete conversion as well as with a uniform molecular weight distribution since the ring strain and a larger space of ring functional group provide a favorable environment for polymerization. Grubbs et al. firstly prepared a variety of polymers including PS, PMMA, and P*t*BA, via ATRP [122].

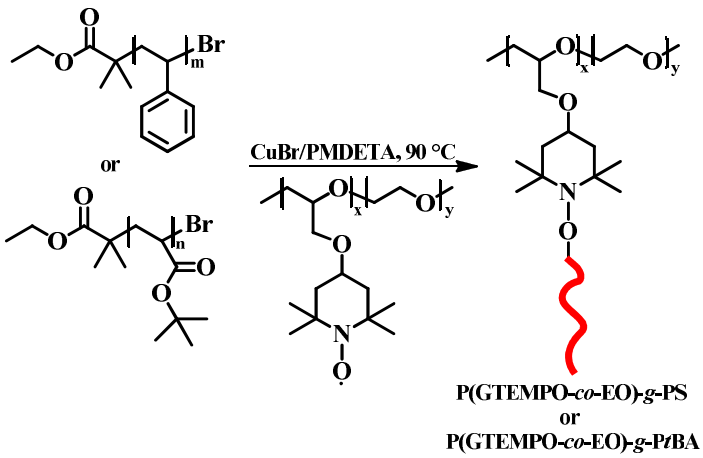
The past few years have witnessed the rapid growth of synthesis of graft copolymers using click type reactions.

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 [123].

Nitroxide radical coupling reaction is considered as a potential click reaction due to its high efficiency and orthogonality in the synthesis of well-defined polymers with different topologies. The NRC click reaction proceeds between a halide- and a TEMPO-terminated polymers in the presence of CuBr and ligand under mild reaction temperature based on the ATRP mechanism[24]

Well-defined poly(GTEMPO-co-EO)-*g*-PS/P*t*BA heterograft copolymers were prepared in one-pot by NRC 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.(2.19) This approach can afford a useful strategy for synthesis of heterograft copolymers with various compositions and well-defined structures [104].



(2.19)

The combination of ATRP with ROMP and NRC 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 [124].

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

Styrene (St, 99%, Aldrich), *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. Furan (99%, Aldrich), maleic anhydride (99%, Aldrich), ethanolamine (99.5%, Aldrich), succinic anhydride (97%, Aldrich), 9-anthracene methanol (97%, Aldrich), α-bromoisobutryl bromide (98%, Aldrich), triethylamine (Et_3N, 99.5%, Aldrich), *N,N'*-dicyclohexylcarbodiimide (DCC, 99 %, Aldrich), 4-dimethylaminopyridine (DMAP, 99 %, Acros), 9-Anthracene methanol (97%, Aldrich), 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. ε-Caprolactone (ε-CL, 99%, Aldrich). 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 ^{o}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 Synthetic Procedures

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 (**4**) were prepared according to published procedures. 4-Hydroxy-TEMPO initiator was used as received.

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, NC*H*$_2$C*H*$_2$OH), 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$_2$C*H*$_2$OC=O), 3.79 (t, *J* =5.2 Hz, 2H, NC*H*$_2$CH$_2$OC=O), 2.85 (s, 2H, C*H*-C*H*, bridge protons), 1.87 (s, 6H, C(C*H*$_3$)$_2$-Br).

3.3.4 Synthesis of 9-anthyrylmethyl 2-bromo-2-methyl propanoate (4)

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 ^{o}C. 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 ^{o}C 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 **4** 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, CH_2-anthracene), 1.86 (s, 6H, C(CH_3)$_2$-Br).

3.3.5 Synthesis of PEG-COOH

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

^{1}H NMR ($CDCl_3$, δ) 4.2 (d, 4H, C=OOCH_2), 3.65-3.5 (m, -OCH_2CH_2O-, PEG backbone), 3.35 (s, 3H, OCH_3), 2.6 (bs, 4H, C=OCH_2CH_2C=O).

3.3.6 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 (20.0 mL, 174 mmol), PMDETA (0.182 mL, 0.872 mmol), CuBr (0.1252 g, 0.872 mmol) and **4** (0.311g, 0.872 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. (%) = 22, $M_{n,theo}$ = 5000, $M_{n,NMR}$ = 5300, $M_{n,GPC}$ = 5550, M_w/M_n = 1.09, 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 (3.25g, 0.61 mmol, $M_{n,NMR}$ = 5300) dissolved in DMF (15 mL) and NaN_3 (1.195g, 18.4 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 = 3 g, 92 %; $M_{n,GPC}$ = 5500, 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).

3.3.7 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. (%) = 20.5 $M_{n,theo}$ = 2950, $M_{n,NMR}$ = 3000, $M_{n,GPC}$ = 3100, M_w/M_n= 1.24, (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).

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

PEG-COOH (1.00 g, 1.53 mmol, based on $M_{n,theo}$ = 650) was dissolved in 20 mL of dry CH_2Cl_2. 4-Hydroxy-TEMPO (0.79 g, 4.61 mmol) and DMAP (0.186 g, 1.n53

mmol) were added to the reaction mixture in that order. After stirring for 5 minutes at room temperature, DCC (0.95 g, 4.61 mmol) in 10 mL of CH_2Cl_2 was added to solution. The reaction was continued via stirring for 24 h at room temperature. Reaction solution was concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel eluting first with CH_2Cl_2/ethyl acetate (1/1), then CH_2Cl_2/CH_3OH (10/1) in order to give red oil (Yield = 1.05 g, 85 %; $M_{n,theo}$ = 800; $M_{n,GPC}$ = 650; M_w/M_n = 1.06, relative to PS standards).

3.3.9 Synthesis of TEMPO end-functionalized PCL (PCL-TEMPO)

The PCL-TEMPO was prepared by ROP of ε-CL (5.0 mL, 0.047 mol) in bulk using tin(II)-2-ethylhexanoate (0.01 mL, 0.03 mmol) as catalyst and 4-hydroxy-TEMPO (0.270 g, 1.57 mmol) as initiator at 110 °C for 4 h. The degassed monomer, catalyst, and the initiator were added to a previously flamed Schlenk tube equipped with a magnetic stirring bar in the given order. The tube was degassed with three FPT cycles, left in argon, and placed in a thermostated oil bath. After the polymerization, the mixture was diluted with THF, and precipitated into an excess amount of cold methanol. The PCL-TEMPO was isolated by filtration and dried at 40 °C in a vacuum oven for 24 h ($[M]_0/[I]_0$ = 30; conv. = 78 %; $M_{n,theo}$= 3300, $M_{n,GPC}$= 6650 ($M_{n,PCL}$= 0.259x$M_{n,GPC}^{1.073}$, after correction formula), M_w/M_n = 1.16, relative to PS standards).

3.3.10 Synthesis of Oxanorbornenyl Alkyne, (5)

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 **5** 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, $C=OCH_2CH_2C\equiv CH$), 1.9 (s, 1H, $C=OCH_2CH_2C\equiv CH$).

3.3.11 Synthesis of α-anthracene-ω-oxanorbornene end-functionalized PS macromonomer (Anth-PS-oxanorbornene) (6)

Linear anthracene-PS-N_3 (see supporting information; 3 g, 0.55 mmol, $M_{n,NMR}$ = 5500) dissolved in *N*,*N*-dimethyl formamide (DMF; 15 mL), **5** (0.47 g, 1.64 mmol), PMDETA (0.11 mL, 0.55 mmol) and CuBr (0.08 g, 0.55 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 = 2.8 g; $M_{n,GPC}$ = 5600, 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), 7.6 (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, $NCH_2CH_2OC=O$), 3.7 (m, 2H, $NCH_2CH_2OC=O$), 2.8 (br, 4H, triazole-$CH_2CH_2C=O$ and $CH_2NC=OC$*H*-C*H*, bridge protons), 2.6 (m, 2H, $CH_2CH_2C=O$), 2.0-0.8 (m, C*H* and CH_2 of PS and CH_3).

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

$(PCy_3)_2(Cl)_2$-RuCHPh (0.0183 g, 0.022 mmol) was placed in a Schlenk tube and dissolved in 3 mL of anhydrous CH_2Cl_2 in a glove box. Anthracene-PS-oxanorbornene macromonomer **(6)** (2.50 g, 0.446 mmol, $Mn_{,GPC}$ = 5600) was dissolved in 12 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 2 h. The polymer solution was precipitated in methanol-ether (1/3) 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 = 20; yield (%) = 34; Mn,theo = 112000; $Mn_{,GPC}$ = 42000; Mw/Mn = 1.164, 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).

3.3.13 Synthesis of Polyoxanorbornene-(PS-*g*-P*t*BA) via Diels–Alder Click Reaction

A solution of MI-P*t*BA (0.0105 g, 0.035 mmol, $M_{n,NMR}$= 3000) in 10 mL of toluene was added to a 10 mL solution of poly(oxanorbornene)-PS-Anthracene (0.4 g, 0.0023 mmol $M_{w,TD\text{-}GPC}$= 168000) 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. ^{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).

3.3.14 Synthesis of poly(oxanorbornene)-*g*-(PS-*b*-PtBA-*b*-PEG) via ATNRC

Polyoxanorbornene-*g*-(PS-*g*-P*t*BA) (0,1 g, 0.581 μmol, $M_{n,theo}$ = 172000) was dissolved in DMF (3 mL) in 10 mL of Schlenk tube. PEG-TEMPO (0.023 g, 0.029 mmol, based on $M_{n,theo}$=800, 50 eq.) was then added to this solution and the mixture was stirred at room temperature for 10 minutes. After that, Cu(0) (0.0046 g, 0.072 mmol, 125 eq.), CuBr (0.002 g, 0.0145 mmol, 25eq.) and PMDETA (0.003 mL, 0.0145mmol, 25 eq.) were added immediately. Reaction mixture was degassed by three FPT cycles, left in vacuum and stirred for 24 h at room temperature. After reaction, the mixture was diluted with THF, filtered through a column filled with neutral alumina to remove the copper complex and precipitated in cold diethyl ether. The polymer was dried at 40 °C in a vacuum oven for 24 h. (Yield= 0.091 g, yield (%) = 34,$M_{n,theo}$ = 178000 $M_{n,GPC}$ = 37500; M_w/M_n = 1.068, relative to PS standards). ^{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), 4.0-3.5 (-OCH_2CH_2O-, PEG backbone)

4.1 (C=OOCH_2CH$_2$N), 3.6-3.0 (C=OOCH_2CH_2N, and C*H*-C*H*), 3.35 (-OCH_3 end group of PEG) 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, CH_3CH$_2$OC=O, C=OC(CH_3)$_2$, NC(CH_3)$_2$ and (CH_2)$_2$CHOC=O).

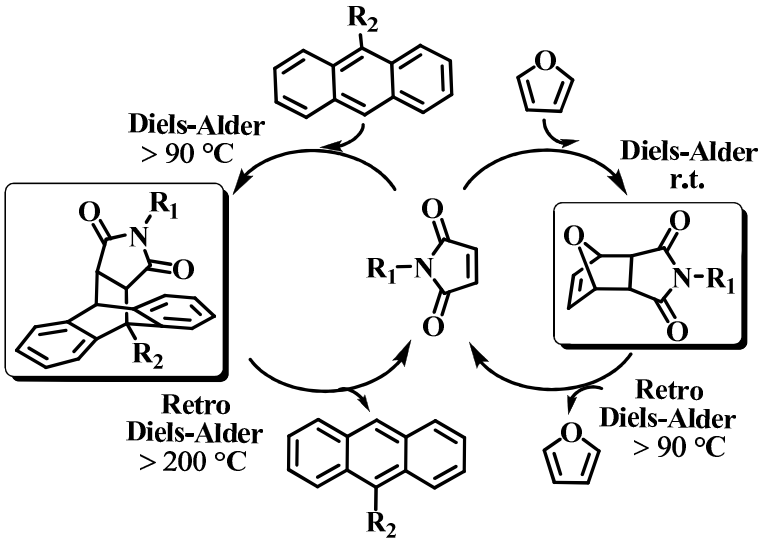
3.3.15 Synthesis of poly(oxanorbornene)-*g*-(PS-b-PtBA-b-PCL) via ATNRC

Polyoxanorbornene-(PS-*g*-P*t*BA) (0,2g, 1.162 μmol , based on $M_{n,theo}$ = 172000) was dissolved in DMF (5 mL) in 10 mL of Schlenk tube. PCL-TEMPO (0.115 g, 0.0348 mmol, based on $M_{n,theo}$ = 3300, 30eq.) was then added to this solution and the mixture was stirred at room temperature for 10 minutes. After that, Cu(0) (0.0095 g, 0.145 mmol, 125 eq.), CuBr (0.00416 g, 0.0290 mmol, 25 eq.) and PMDETA (0.00606 mL, 0.0290 mol, 25 eq.) were added immediately. Reaction mixture was degassed by three FPT cycles, left in vacuum and stirred for 24 h at room temperature. After reaction, the mixture was diluted with THF, filtered through a column filled with neutral alumina to remove the copper complex and precipitated in 2:1 methanol-diethyl ether. The polymer was dried at 40 °C in a vacuum oven for 24 h. (yield (%) = 34,$M_{n,theo}$ =221000 ; $M_{n,GPC}$ = 83000; M_w/M_n = 1.22, relative to PS standards). ^{1}H NMR (250 MHz, CDCl$_3$, δ) 7.4-6.2 (Ar*H* of PS), 5.4 (br, 2H, CH_2-Diels-Alder adduct), 5.2-4.8 (br, 2H C*H*(Ph)-triazole and C*H*O-C=O), 4.7 (br, 1H, C*H*, bridge-head proton), 4.0 (br, CH_2OC=O of PCL and CH_2OC=OC(CH$_3$)$_2$-TEMPO), 3.8-3.0 (br, NCH_2CH$_2$OC=O, NCH$_2$CH_2OC=O, C*H*-C*H*, bridge protons, CH_2OH, end group of PCL, and CH_2OC=OC(CH$_3$)$_2$-PS), 2.8 (br, 2H, triazole-CH_2CH$_2$C=O), 2.5 (br, 2H, triazole-CH$_2$CH_2C=O), 2.3 (br, 2H, C=OCH_2 of PCL), 2.0-0.8 (CH_2 of PCL, CCH_3 and CH$_2$OC=O-C(CH_3)$_2$-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).

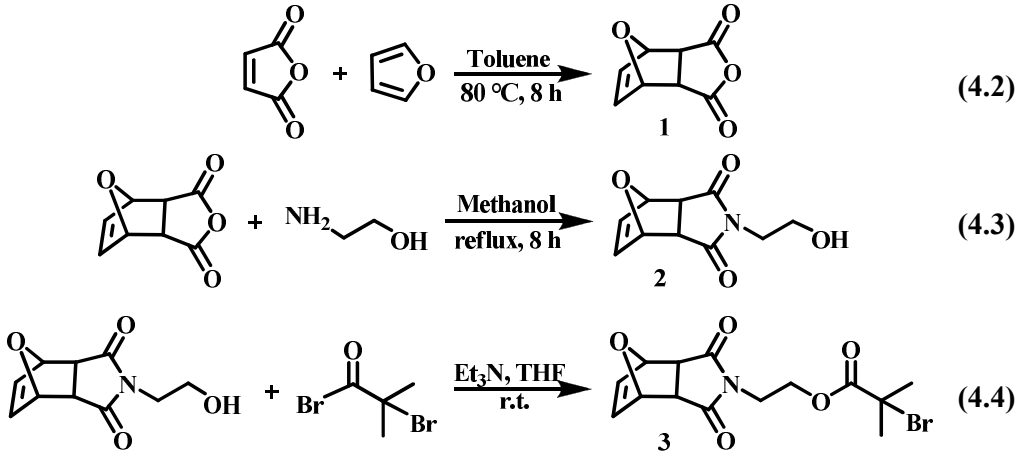


(4.1)

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 Copolymer 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).



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.

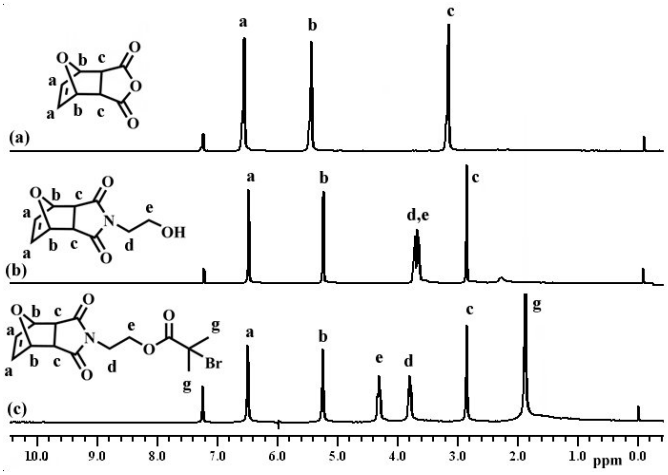
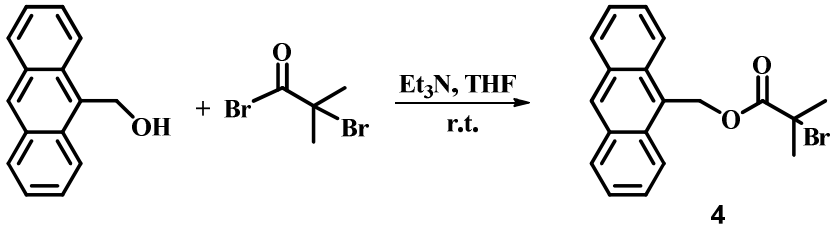


Figure 4.1 : ^{1}H NMR spectra of **a)** 4,10-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione **(1)**; **b**) 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (**2**); **c**) 2-bromo-2-methyl propionic acid 2-(3,5-Dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl) ethyl ester **(3)** in $CDCl_3$.

In addition, 9-anthyrylmethyl 2-bromo-2-methyl propanoate (**4)** (4.5), was synthesized by a similar way as described for **3**.



(4.5)

4

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 **4** was successfully obtained.

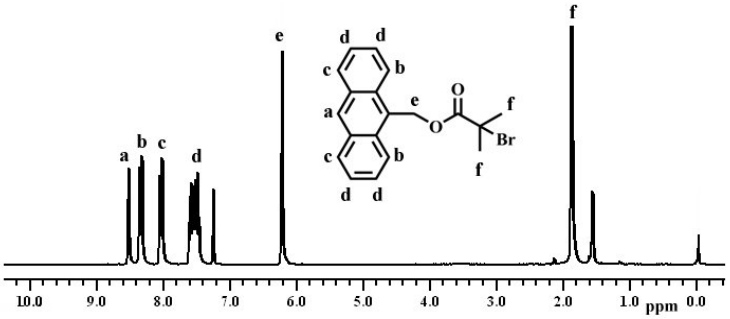
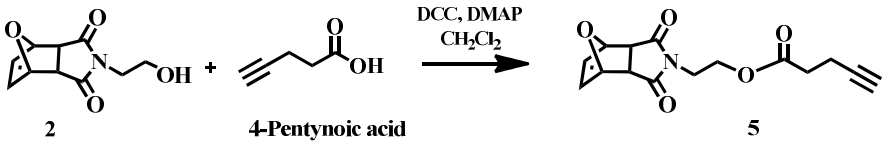


Figure 4.2 : ^{1}H NMR spectrum of 9-anthyrylmethyl 2-bromo-2-methyl propanoate **(4)** in $CDCl_3$.

Oxanorbornenyl Alkyne (**5)** was obtained via an esterification between 4-Pentynoic acid and compound **(2)** in CH_2Cl_2. And it was purified by column chromatography over silica gel eluting with ethyl acetate/hexane (1:1) to give **5** as a white solid (4.6).



2 4-Pentynoic acid 5 **(4.6)**

It was observed from ^{1}H NMR spectrum of **(5)** Alkyne proton was detected at 1.95 pmm and the methylene protons next to the ester unit at 4.2 ppm. Moreover, the the characteristic protons of the adduct were also detected at 6.5 ppm (bridge vinyl protons), 5.2 ppm (bridge-head protons) and 2.85 ppm (bridge protons) respectively. These results confirmed that the synthesis of **5** was achived .

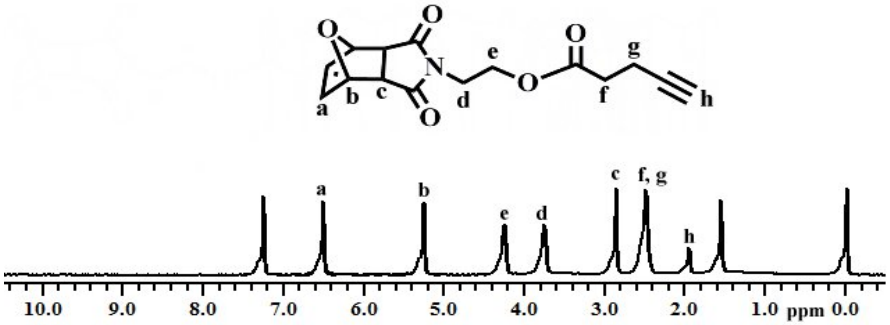
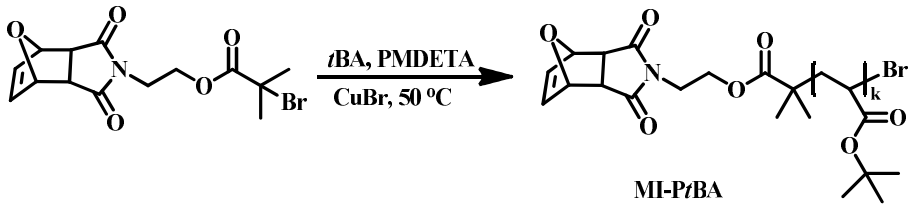
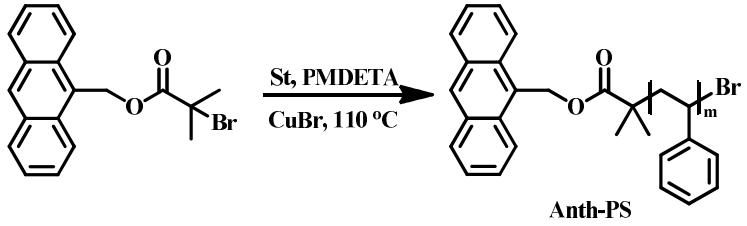


Figure 4.3 : ^{1}H NMR spectrum of Oxanorbornenyl Alkyne(**5)** in $CDCl_3$.

MI-P*t*BA (4.7) Anth-PS (4.8) and were obtained by ATRP of St and *t*BA using **3** and **4** as initiators. Since furan protection was easily deprotected at elevated temperatures, the polymerization temperature for *t*BA was 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-P*t*BA was in fairly good agreement with the theoretical one ($M_{n,theo}$) indicating that the initiations were not quantitative under these polymerization conditions.



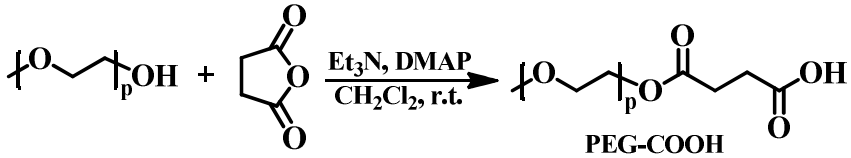
(4.7)



(4.8)

The $M_{n,NMR}$ of MI-P*t*BA was determined from a ratio of integrated peaks at 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.

Mono carboxylic acid functional PEG (PEG-COOH) was synthesized with a reaction of PEG-OH in the presence of succinic anhydride. When DMAP, Et_3N and CH_2Cl_2 were used as the catalysts and the solvent respectively, the reaction proceeded efficiently, and PEG-COOH were obtained in high yield.



(4.9)

Figure 4.4 depicts the ^{1}H NMR spectrum of PEG with a COOH end group. The methylene proton of PEG is assigned as 4.25 ppm because of the introduction of succinic anhydride. The methylene proton formed by the ring opening of succinic anhydride is assigned as 2.65 ppm.

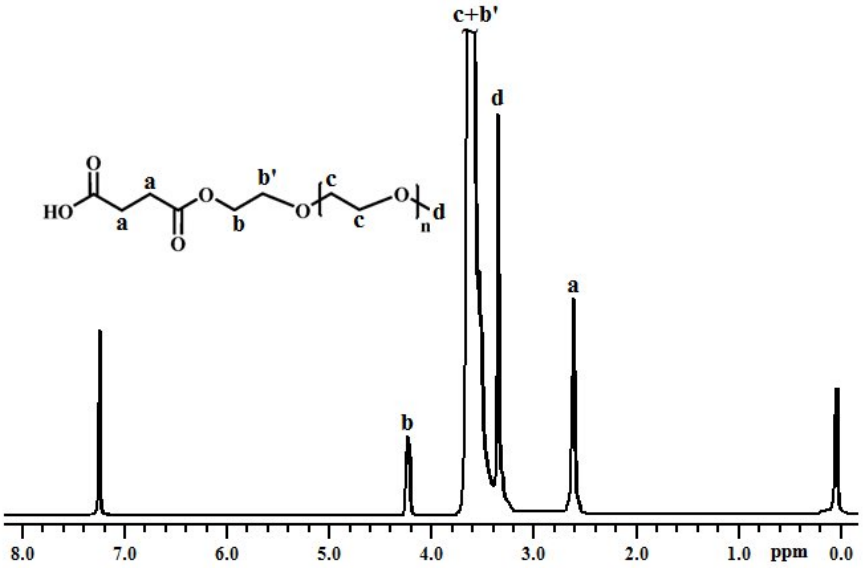


Figure 4.4 : ^{1}H NMR spectrum of PEG-COOH in $CDCl_3$.

Next, PEG-COOH used as a monomer to obtained nitroxyl radical end-functionalized PEG (TEMPO-PEG) by using 4-hyroxy-TEMPO as an initiator.

(4.10)

TEMPO-PCL was prepared by Ring Opening Polymerization(ROP) of ε-CL (in bulk using tin(II)-2-ethylhexanoate as a catalyst and 4-hyroxy-TEMPO as an initiator at 110 °C

(4.11)

Table 4.1 : The conditions and the results of linear polymers used in the synthesis of block copolymers via DA and NRC 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]	**4**	25	22	5550	1.09	5000[f]	5300
MI-P*t*BA[b]	**3**	270	21	3100	1.24	2950[f]	3000
TEMPO-PEG[c]	**5**	-	85	650	1.06	800[f]	750
TEMPO-PCL[d]	**5**	-	78	3280[g]	1.16	3300[f]	3000

[a] $[M]_0:[I]_0:[CuBr]:[PMDETA] = 200:1:1:1$; polymerization was carried out at 110 ^oC.

[b] $[M]_0:[I]_0:[CuBr]:[PMDETA] = 100:1:1:1$; polymerization was carried out at 50 ^oC. *t*BA / EC = 10 (w/w).

[c] Obtained by the reaction of compound **5** and PEG-COOH.

[d] $[M]_0:[I]_0 = 20:1$;polymerization was carried out at 110 ^oC

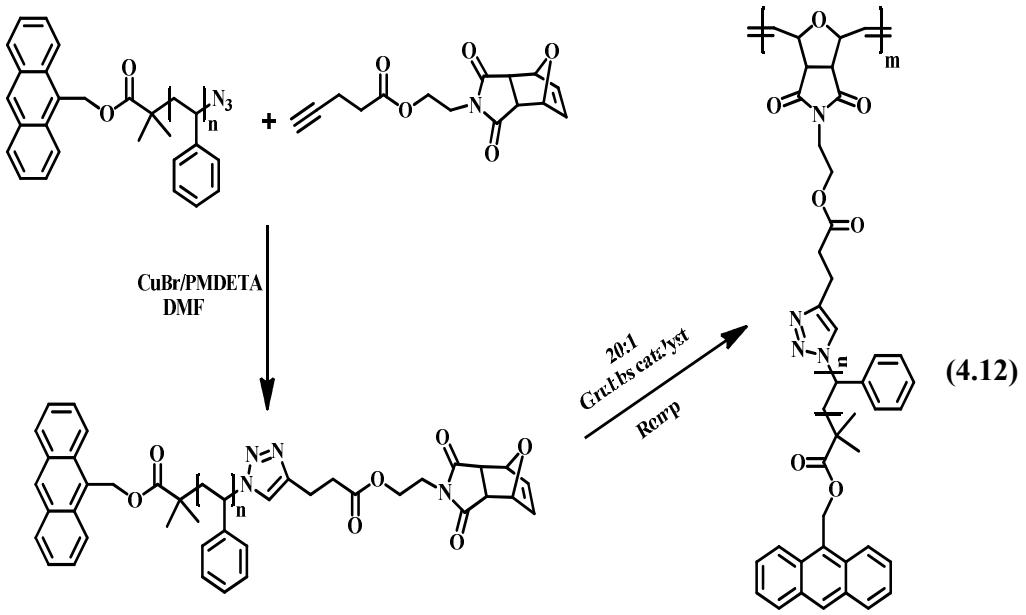
[e] Determined by gravimetrically.

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

[g] $M_{n,PCL} = 0{,}259 \text{ X } M_{n,GPC}^{1.073}$ ($M_{n,PCL}$=6650)

4.2 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 **(5)** catalyzed by CuBr/PMDETA in DMF at room temperature overnight (4.12). The quantitative azide-alkyne click reaction was here exploited to functionalize the chain-end of the anthracene-PS with an oxanorbornene group.



(4.12)

^{1}H NMR spectroscopy confirmed that polymers were appropriately prepared with controlled molecular weight, low polydispersity index (PDI), and desired end group functionalities.

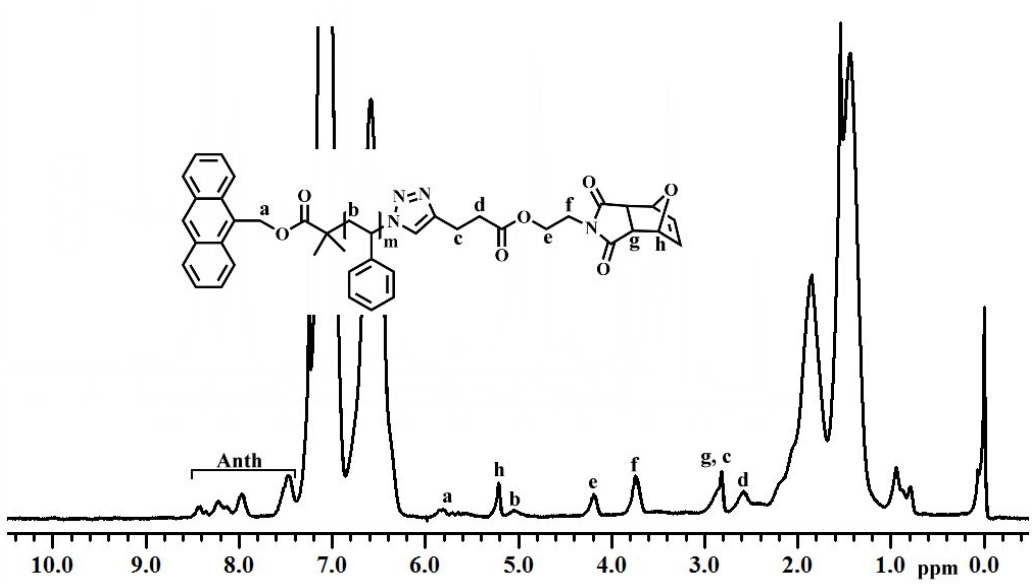


Figure 4.5 : ^{1}H NMR spectrum of Anthracene-PS-oxanorbornene macromonomer

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.

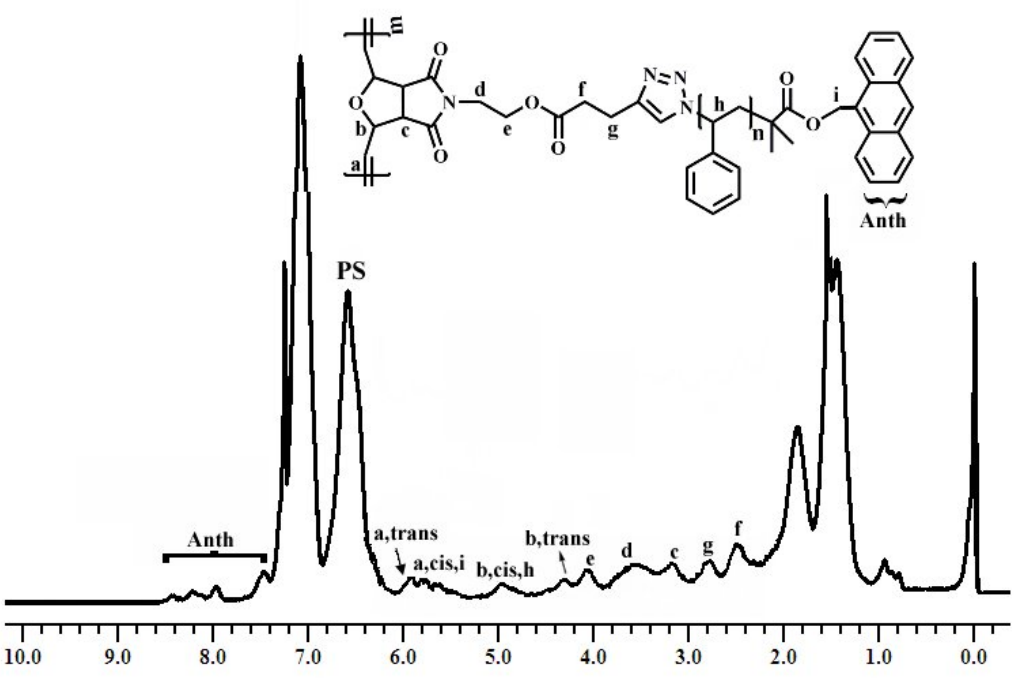
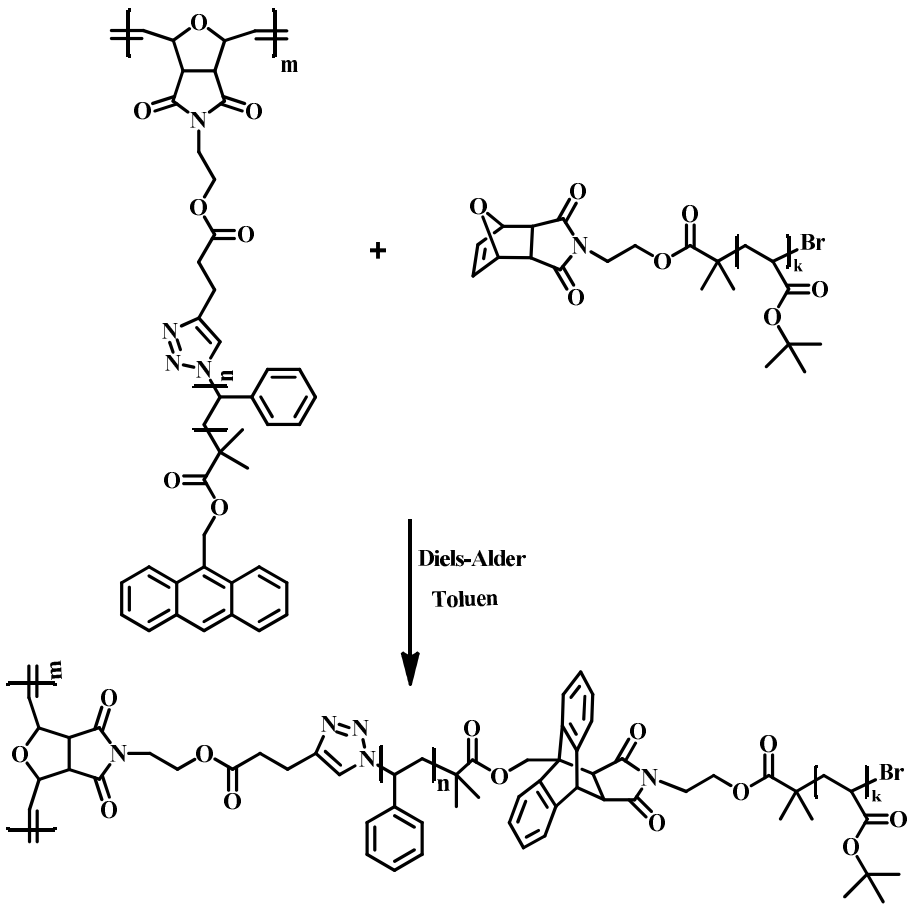


Figure 4.6 : ^{1}H NMR spectrum of poly(oxanorbornene)-*g*-PS-anthracene

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,$M_{n,TDGPC}$=122200 (M_w/M_n = 1.37) is obtained for poly(oxanorbornene)-*g*-PS-anthracene, which is close to a $M_{n,theo}$ = 112000 (Table 4.2).

The poly(oxanorbornene)-*g*-PS-anthracene copolymer (DP_n = 20 calculated from $M_{n,theo}$) was then clicked with 1.5 equiv of P*t*BA-MI, per anthracene unit in toluene at 110 ^{o}C for 48 h to yield graft block copolymers (4.13). In addition, after Diels-Alder click reaction, graft block copolymers were purified by simply dissolution and precipitation procedure.



(4.13)

^{1}H NMR spectra of graft block copolymer display characteristic signals of P*t*BA, along with those of oxanorbornene segment as seen in Figure 4.7

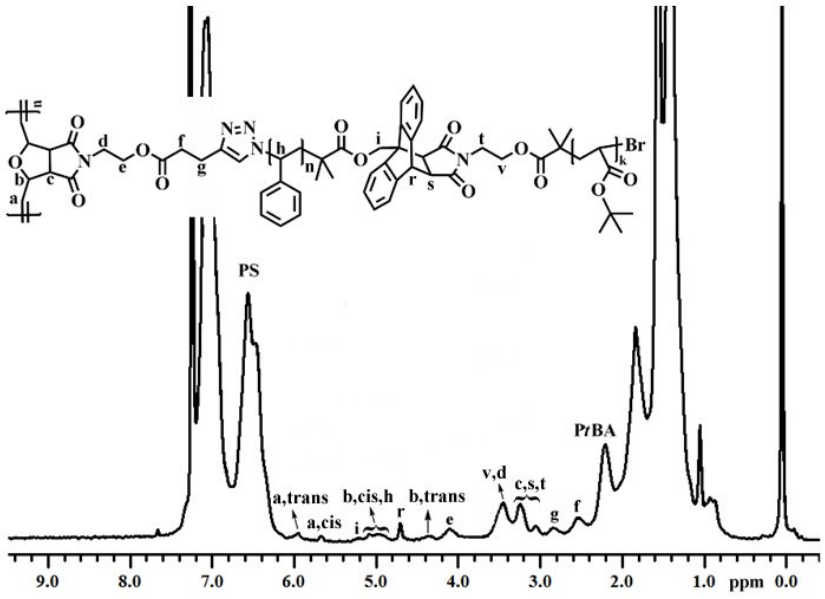


Figure 4.7 : ^{1}H NMR spectrum of poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA) in $CDCl_3$.

Monomodal GPC traces with narrow polydispersity display a clear shift to a lower retention time as compared to those of starting precursor, thus proving the synthesis of graft block copolymer as seen in Figures 4.8.

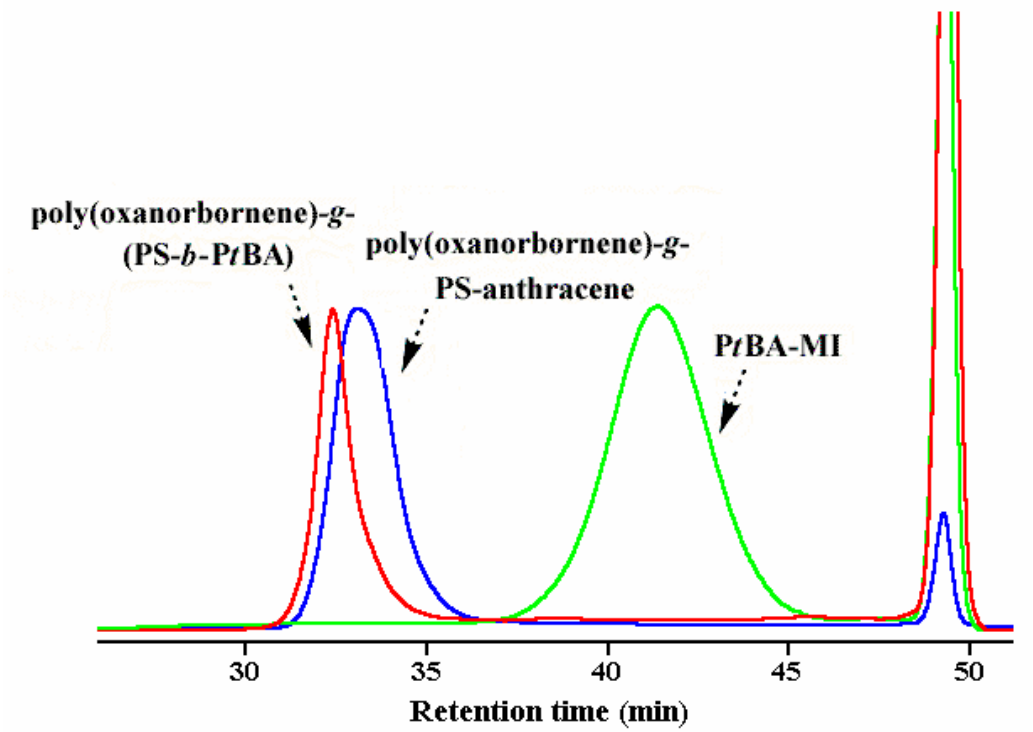


Figure 4.8 : Evolution of GPC traces: P*t*BA-MI, poly(oxanorbornene)-*g*-PS-anthracene and poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA)

Diels-Alder click reaction efficiency was also monitored by UV spectroscopy after the decrease in absorbance of anthracene at 366 nm and 4.6×10^{-6} M in the reaction medium as seen in Figure 4.9 Diels–Alder efficiency was calculated by following anthracene Conv. % = (1 – A*t*/A0), where A0 and A*t* are initial and final absorbance values of anthracene and found to be 87%

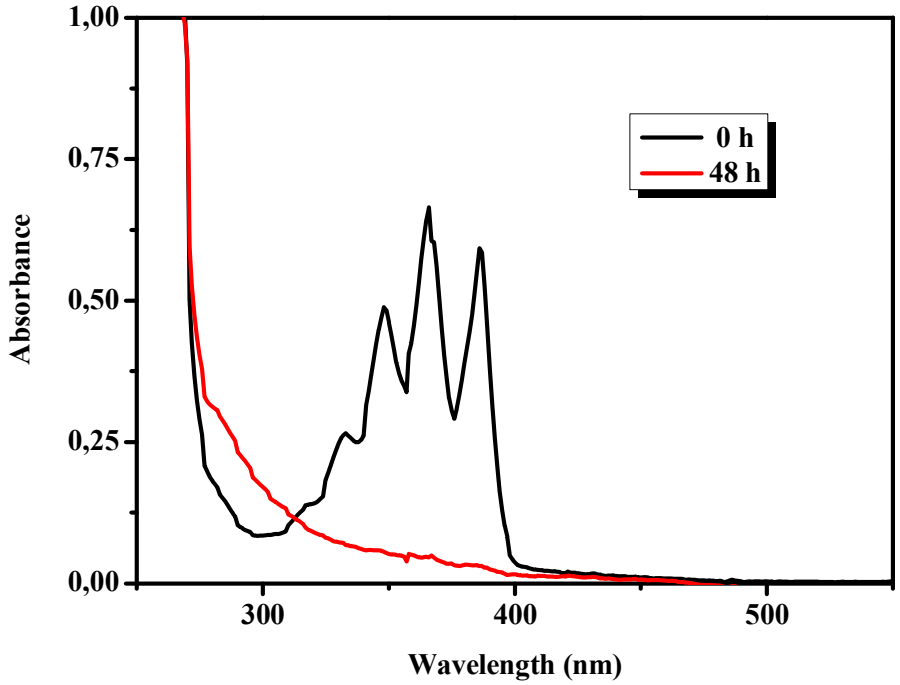


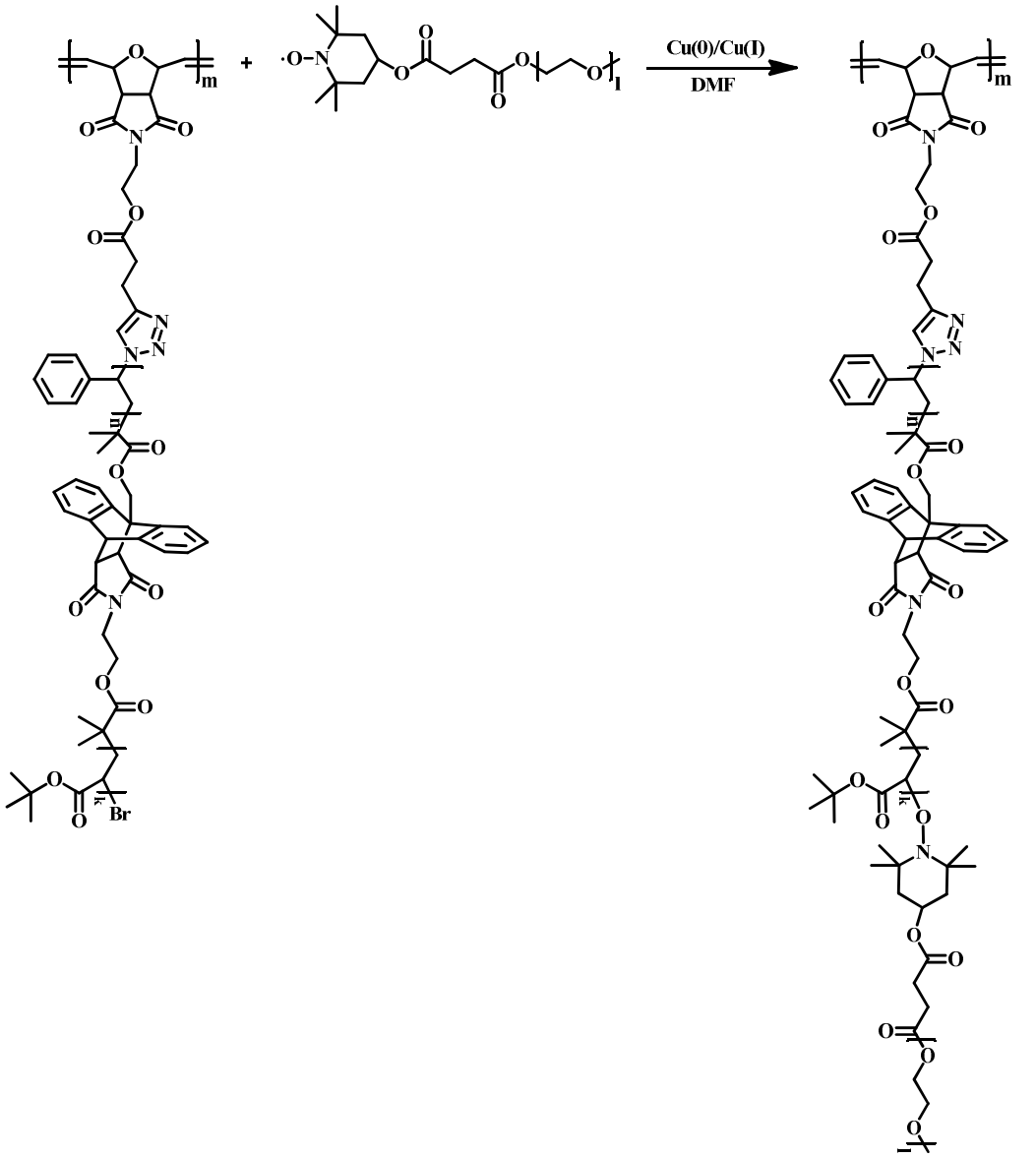
Figure 4.9 : UV spectra to monitor the efficiency of Diels-Alder reaction of poly(oxanorbornene)-*g*-PS-anthracene with PtBA-MI after 0 h and 48 h in CH_2Cl_2

Next, the NRC click reaction strategy was applied to the preparation of the final graft block copolymers poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA-*b*-PEG) and poly(oxanorbornene)-g-(PS-*b*-PtBA-*b*-PCL).

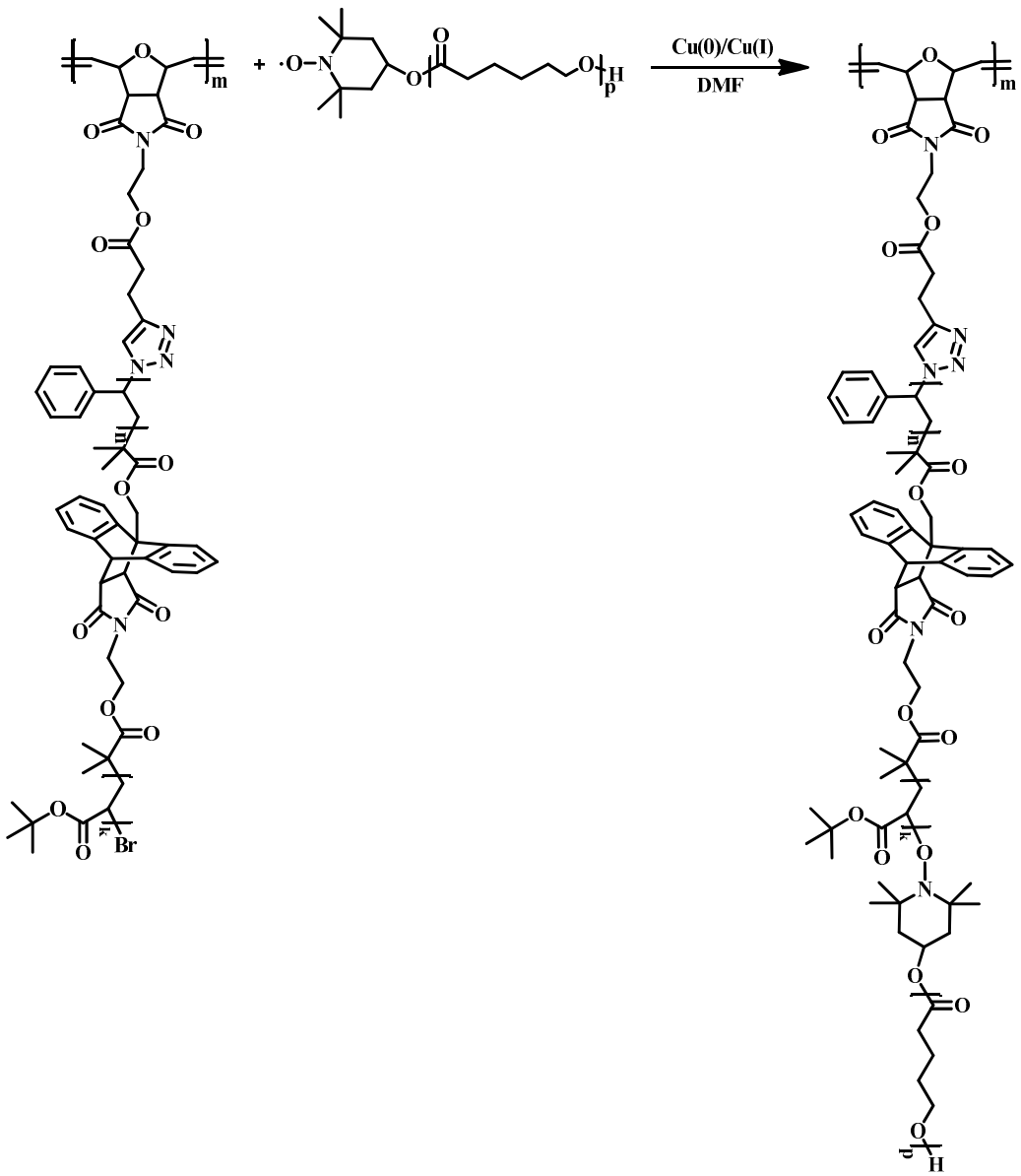
Graft block copolymers, poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA-*b*-PEG) and poly(oxanorbornene)-g-(PS-*b*-PtBA-*b*-PCL) were simply obtained via a grafting-onto technique, in which poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA) main chain was clicked with a TEMPO-PEG or a TEMPO-PCL graft in a NRC reaction to yield related graft block copolymers in the presence of Cu(0) and Cu(I)/PMDETA in DMF at room temperature for 24 h (4.14 and 4.15).

In the NRC grafting-onto reaction, a 25% molar excess of a TEMPO-PEG or a TEMPO-PCL graft with respect to that of the main backbone was deliberately used for the reaction completion. Additionally, it should be noted that unreacted grafts were easily removed from the reaction medium via dissolution–precipitation cycle. It

is noted that an excess amount of Cu(0) compared with Cu(I) was added to the system to promote the efficiency of whole NRC reactions proceeded in this work [125].



(4.14)



(4.15)

GPC analysis of poly(oxanorbornene)-*g*-(PS-*b*-*t*BA-*b*-*PEG*) graft block copolymer showed a monomodal peak, however, which shifted to higher retention time with respect to that of poly(oxanorbornene)-*g*-(PS-*b*-*t*BA) graft block copolymer (Figure 4.10).

This may be due to that adsorption of the PEG segment on the stationary phase caused a shift to lower molecular weight region. Moreover, from Table 4.2, it is deduced that hydrodynamic radius (R_h) of graft block copolymer is slightly higher

than that of, poly(oxanorbornene)-*g*-(PS-*b*-*t*BA) graft block copolymer indicating that GPC trace shift is not the result of a decrease in the hydrodynamic volume.

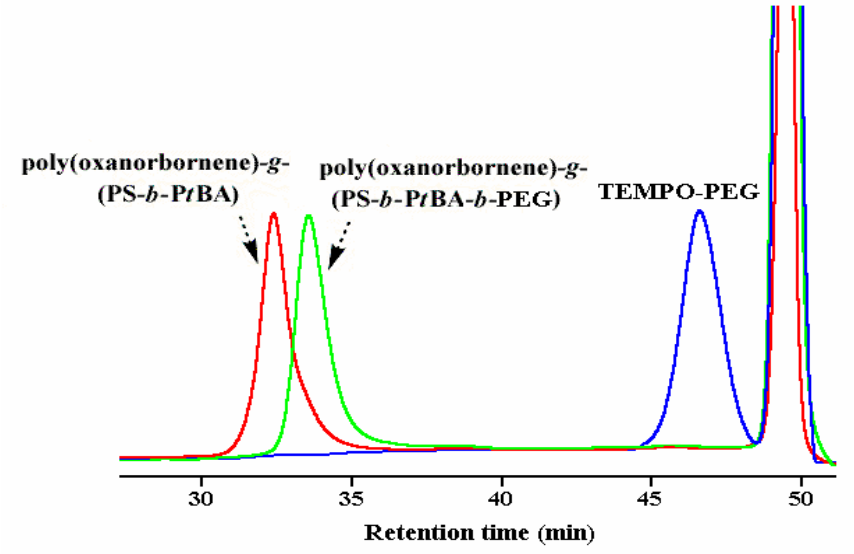


Figure 4.10 : Evolution of GPC traces: TEMPO-PEG, poly(oxanorbornene)-g-(PS-b-tBA) and poly(oxanorbornene)-g-(PS-b-tBA-b-PEG)

^{1}H NMR spectra displayed that an incorporation of the PEG graft onto the poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA) main backbone by appearance of the characteristic signals of the PEG (δ 4.0–3.5) (Figure 4.11)

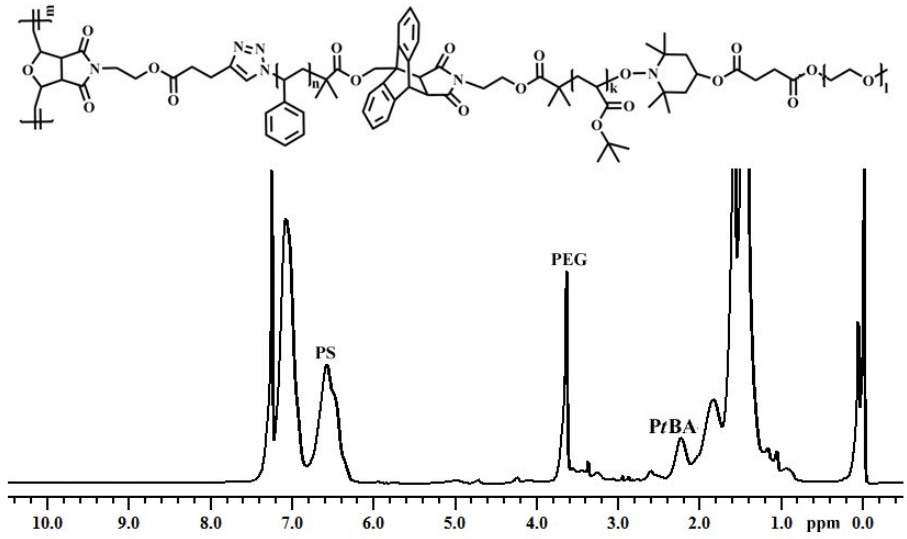


Figure 4.11 : ^{1}H NMR spectrum of poly(oxanorbornene)-g-(PS-*b*-PtBA-*b*-PEG) in $CDCl_3$

The d*n*/d*c* = 0.12 mL/g for poly(oxanorbornene)-g-(PS-*b*-PtBA-*b*-PEG) was determined by ^{1}H NMR spectrum and introduced into the OmniSec software to yield molecular weights, intrinsic viscosity ([η]) and hydrodynamic radius (R_h).

The $M_{n,theo}$ = 178000 was calculated by following equation;

$M_{n,theo}$ =$M_{n,theo}$ poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA) + (DA efficiency X DP_n of poly(oxanorbornene)-g-PS-anthracene X $M_{n,theo}$ of TEMPO-PEG) and were close to $M_{n,TDGPC}$ =184000 (Table 4.2).

GPC analysis of poly(oxanorbornene)-*g*-(PS-*b*-*t*BA-*b*-PCL) graft block copolymer showed a monomodal peak, which shifted to lower retention time with respect to that of poly(oxanorbornene)-*g*-(PS-*b*-*t*BA) graft block copolymer (Figure 4.12).

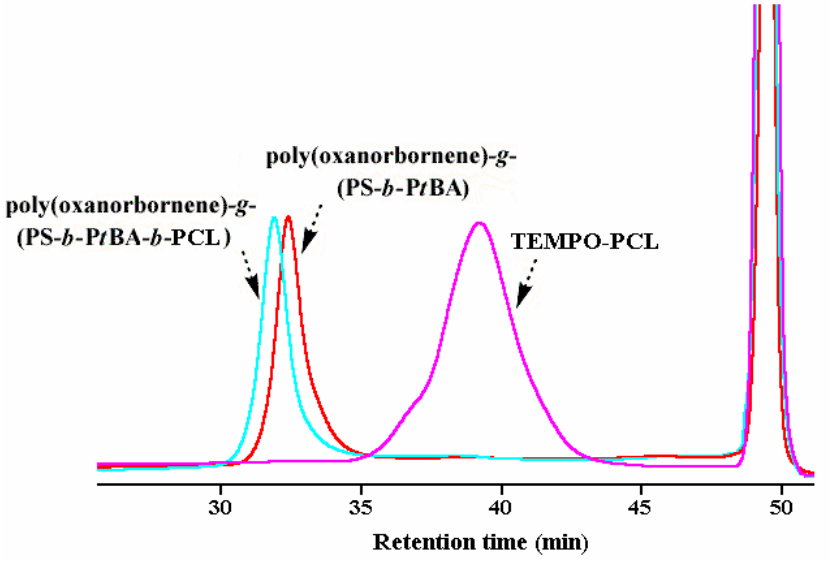


Figure 4.12 : Evolution of GPC traces: TEMPO-PCL, poly(oxanorbornene)-g-(PS-b-tBA) and poly(oxanorbornene)-g-(PS-b-tBA-b-PCL)

^{1}H NMR spectrum confirmed the incorporation of PCL into the block copolymer by appearance of the characteristic signals of the PCL segment at 4.0, 2.3 and 1.8–1.2 ppm, (Figure 4.13)

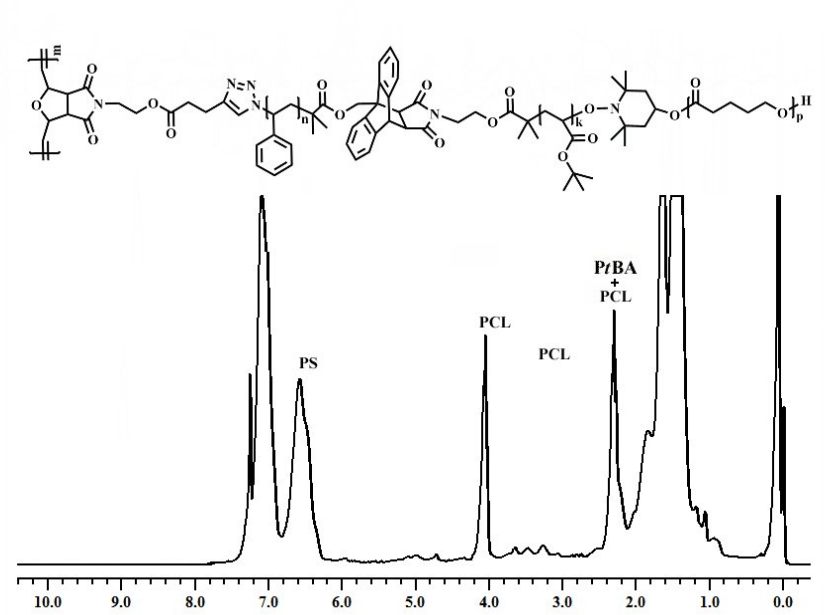


Figure 4.13 : ^{1}H NMR spectrum of poly(oxanorbornene)-g-(PS-*b*-PtBA-*b*-PCL) in $CDCl_3$

The d*n*/d*c* =0.12 mL/g for poly(oxanorbornene)-g-(PS-*b*-PtBA-*b*-PCL) was determined by ^{1}H NMR spectrum and introduced into the OmniSec software to yield molecular weights, intrinsic viscosity ([η])and hydrodynamic radius (R_h). The $M_{n,theo}$ =221000 was calculated by following equation;

$M_{n,theo}$ =$M_{n,theo}$ poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA) + (DA efficiency X DP_n of poly(oxanorbornene)-g-PS-anthracene X $M_{n,theo}$ of PCL-TEMPO) and were close to $M_{n,TDGPC}$ =225000 (Table 4.2).

The d*n*/d*c* values of graft block copolymers were determined by ^{1}H NMR spectrum and these 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 4.2).

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

Table 4.2 : The characterization of graft block copolymers and their precursor

Entry	Polymer	$M_{n,GPC}$[a] (g/mol)	$M_{n,theo}$ (g/mol)	TD-GPC[b] M_n (g/mol)	TD-GPC[b] M_w (g/mol)	TD-GPC[b] d*n*/d*c*[g] (mL/g)	TD-GPC[b] [η] (dL/g)	TD-GPC[b] R_h (nm)
1	**poly(oxanorbornene)-g-PS-anthracene**	42000	112000[c]	122200	168000	0.185	0.1357	6.99
2	**poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA)**	65900	164000[d]	172000	192000	0.130	0.1787	8.034
3	**poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA-*b*-PEG)**	37500	178000[e]	184000	198500	0.127	0.1808	8.186
4	**poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA-*b*-PCL)**	83000	221000[f]	222500	256000	0.120	0.2724	10.13

[a]Determined by conventional GPC, calibrated on the basis of linear PS standards in THF at 30°C.
[b]Calculated from triple-detection GPC in THF at 35°C.
[c] $M_{n,theo}$ of poly(oxanorbornene)-g-PS-anthracene = (macromonomer/catalyst) X $Mn_{,GPC}$ of macromonomer.
[d]$M_{n,theo}$ of graft block copolymers = $M_{n,theo}$ of poly(oxanorbornene)-g-PS-anthracene + (DA efficiency X DP_n of poly(oxanorbornene)-g-PS-anthracene X $Mn_{,NMR}$ of PtBA)
[e]$M_{n,theo}$ of graft block copolymers = $M_{n,theo}$ poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA) + (DA efficiency X DP_n of poly(oxanorbornene)-g-PS-anthracene X $M_{n,theo}$ of PEG-TEMPO)
[f]$M_{n,theo}$ of graft block copolymers = $M_{n,theo}$ poly(oxanorbornene)-*g*-(PS-*b*-P*t*BA) + (DA efficiency X DP_n of poly(oxanorbornene)-g-PS-anthracene X $M_{n,theo}$ of PCL-TEMPO)
[g]Determined by ^{1}H NMR spectrum and these 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.

5. CONCLUSIONS

In this thesis, we aimed to describe the synthesis route is a versatile and simple strategy for preparation of graft block copolymer with well-defined architecture. This graft block copolymers were successfully prepared via first time combining ROMP and Diels-Alder and NRC click reaction strategys

In the first step, ROMP carried out at room temperature within relatively short times enables the synthesis of block copolymer structure with pendant anthryl groups.

In the second step, the linear precursors were introduced onto the block copolymer backbone via Diels-Alder reactions. UV spectroscopy indicated that DA efficiencies of the reactions were quantitative which is highly efficient (over 87 %).

The final step , NRC click reaction strategy applied the graft block copolymer. In the NRC grafting-onto reaction, a 25% molar excess of a TEMPO-PEG or a TEMPO-PCL graft with respect to that of the main backbone was deliberately used for the reaction completion. GPC traces of poly(oxanorbornene)-*g*-(PS-*b*-*t*BA-*b*-PEG) graft block copolymer showed a monomodal peak, however, which shifted to higher retention time with respect to that of poly(oxanorbornene)-*g*-(PS-*b*-*t*BA) graft block copolymer. This may be due to that adsorption of the PEG segment on the stationary phase caused a shift to lower molecular weight region. Moreover, The absolute molecular weights, [g] and Rh of polymers were measured by introducing their experimentally determined dn/dc values into the TD-GPC software and it is deduced that hydrodynamic radius (R_h) of graft block copolymer is slightly higher than that of, poly(oxanorbornene)-*g*-(PS-*b*-*t*BA) graft block copolymer indicating that GPC trace shift is not the result of a decrease in the hydrodynamic volume. On the other hand GPC traces of poly(oxanorbornene)-*g*-(PS-*b*-*t*BA-*b*-PCL) graft block copolymer showed a monomodal peak which is incorporation with TD-GPC results.

As a conclusion , we proved that ROMP and Diels-Alder and NRC click reaction strategys was versatile and simple strategy for the preparation of well-defined graft block copolymer.

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CURRICULUM VITAE

Name Surname:	**Dudu EYGAY**
Place and Date of Birth:	**KUMRU 15.01.1985**
Address:	**Osmangazi cad. Tuna mah. 698.sok.No:18 Esenler/İstanbul**
E-Mail:	**dudueygay@hotmail.com**
B.Sc.:	**Gazi Univercity/ Chemical Engineering**