ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

POLYCARBONATES CONTAINING GRAFT COPOLYMERS VIA DIELS-ALDER CLICK REACTIONS

M.Sc. THESIS

Mehtap AYDIN

Department of Chemistry

Chemistry Programme

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

DIELS-ALDER CLICK REAKSİYONLARI İLE POLİKARBONAT İÇERİKLİ AŞI KOPOLİMERLERİ ELDESİ

YÜKSEK LİSANS TEZİ

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FOREWORD

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December 2011 Mehtap AYDIN
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ABBREVIATIONS

^{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
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
TEA **:** Triethylamine
TEMPO **:** 2,2,6,6-Tetramethylpiperidine-*N*-oxyl
THF **:** Tetrahydrofuran
UV **:** Ultra Violet
PCL **:** Poly(ε-caprolactone)
NRC **:** Nitroxide Radical Coupling
FRP **:** Free-Radical Polymerization
TD-GPC **:** Triple Detector- Gel Permeation Chromatography

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SUMMARY

Increasing attention has been paid to biocompatible, biodegradable, or bioresorbable polymers because of their potential uses in biomedical and environmental applications, such as medical implants and drug-delivery systems. As a kind of surface erosion biodegradable materials, aliphatic polycarbonates are usually derived from ring-opening polymerization (ROP) and have gained increasing interest for their potential use in biomedical and pharmaceutical applications due to their favorable biocompatibility, biodegradability, and nontoxicity.

The ionic polymerizations (anionic or cationic) were the only living systems available until last decade. These systems provide polymers with controlled molecular weight, well-defined chain ends, and low polydispersity. In recent years, the use of controlled/living radical polymerization (C/LRP) methods for the synthesis of complex macromolecules has fast increased because of the variety of applicable monomers and more tolerant experimental conditions than the living ionic polymerization routes require.

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 block and graft copolymers.

Click chemistry has some advantages of fast, effective, reliable, selective, etc., and is widely used in new drug research and biochemistry. One of the most popular reactions within the click chemistry philosophy is theHuisgen 1,3-dipolar cycloaddition reaction of azide and alkyne using a Cu(I) catalyst at room temperature, which has attracted more and more attention because of simple reaction conditions, high yields (no byproducts), easy purification, etc. Since the first report by Emrick et al. on the chemical modification of a biodegradable aliphatic polyester by Huisgen’s cycloaddition, a steadily increasing number of works have been devoted to the macromolecular engineering of biodegradable polyesters by ROP and click chemistry. In contrast, examples of modification on polycarbonates by click chemistry are relatively rare.

Copolymerization has developed as one of the most used strategies to adjust the properties of polymeric materials. The combination of two polymers into a single entity is generally advantageous because the copolymers may integrate the merits of the original homopolymers. Graft copolymers, also called molecular brushes, have attracted considerable interest for their distinguished conformation and properties.

More attractively, by design, polycarbonate copolymers with a wide variety and accurate controllability in the physical and mechanical properties are readily provided via facile ring-opening copolymerization. Ring-opening polymerization (ROP) of carbonates seems of the most effective method to fabricate polycarbonates

with good reproducibility and high quality (high molecular weight and low polydispersity). From this point of view, in this thesis, the design and synthesis of graft copolymers of PC-Anth with a well-defined molecular architecture and molecular weight was described. The study presented in this thesis is aimed at describing the anthracene-maleimide-based DA "click reaction" as a novel route to prepare well-defined graft copolymers.

Here, anthracene-functionalized carbonate monomer polymerized for the purpose to prepare high molecular weight PC-Anth via ring opening polymerization (ROP) using the thiourea/DBU catalyst and benzyl alcohol initiator in dichloromethane at room temperature for 5 h and then clicked with maleimide end-functionalized linear polymers, PMMA-MI, PEG-MI, PMMA-MI/PEG-MI and PS-MI in a Diels-Alder reaction in toluene at 110 ℃ for 36 h to create corresponding graft copolymers, PC-*g*-PMMA, PC-*g*-PEG, PC-*g*-PMMA/PEG and PC-*g*-PS, respectively. Diels-Alder click reaction efficiency for graft copolymerization was monitored by UV-Vis spectroscopy. The d*n*/d*c* values of graft copolymers were experimentally obtained using a triple detection GPC (TD-GPC).

DIELS-ALDER CLICK REAKSİYONLARI İLE POLİKARBONAT İÇERİKLİ AŞI KOPOLİMERLERİ ELDESİ

ÖZET

Son zamanlarda biyolojik olarak uyumluluk, kolay parçalanabilme veya yüksek emilim gibi birtakım özellikli polimerlere olan ilgi artmıştır. Bu polimerler medikal implantlar ve ilaç-taşıma sistemleri gibi biyomedikal ve çevresel uygulama alanlarında kullanılmaktadır.

Yüzey erozyonunun bir çeşidi olan biyo çözünür malzemelerden olan alifatik polikarbonatlar genellikle halka açılma polimerizasyonu (ROP) yoluyla elde edilir. Ayrıca sahip oldukları biyolojik uyumluluk, kolay parçalanabilme ve toksik olmama özelliklerinden dolayı biyomedikal ve ilaç uygulamalarında tercih edilir.

Kontrollü kompozisyon ve yapılarda iyi tanımlanmış makromoleküllerin sentezi polimer biliminde yeni bir alan açan iyonik polimerizasyon yöntemlerinin gelişimine kadar kimyagerler için 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.

Hem kimyasal yapısı hem de moleküler mimarisi iyi tanımlanmış, fonksiyonel grupları isteğe göre kontrol edilebilen polimerleri sentezleyebilmek polimer bilimiyle uğraşan araştırmacıların en büyük hayalidir. Yaşayan polimerizasyon mekanizmalarını kullanarak bu hayalin bir kısmını gerçekleştirmek ve polimer zincirini kontrollü byütmek mümkündür.

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 sahiptirler.

Son yıllara kadar, elde bulunan sistemler yaşayan iyonik polimerizasyonlardı (anyonik ve katyonik) . Bu sistemler sayesinde moleküler ağırlığı kontrol edilebilen, zincir sonu olan ve düşük polidipersiteye sahip polimerler elde edilebilir. Son yıllarda ise kompleks makromoleküllerin sentezinde kullanılan kontrollü/yaşayan

polimerizasyon metotlarının kullanımı arttı. İyonik polimerizasyona göre monomerlerin fazla çeşitli olması ve deney koşullarının daha rahat olması bunun başlıca sebebidir.

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. Polimerizasyon (ATRP) yakın dönemde birçok akademik araştırmaya konu olmuştur. Yüksek maliyetli ve hazırlık esnasında kolaylıkla oksitlenebilen düşük oksidasyon basamağındaki metal tuzları katalizliğinde gerçekleşmesi ATRP'nin en büyük dezavantajlarındandır.

Halka açılma polimerizasyonu (ROP) siklik monomerin lineer polimer oluşturmak üzere açıldığı tek polimerizasyon yöntemidir. Halka-açılma polimerleşmeleri genelde anyonik ve katyonik polimerleşmede kullanılan başlatıcılarla başlatılır. Başlatıcıya ek olarak, monomerin reaksiyona girebilirliliğini arttırmak için bu tip sistemlerde katalizör kullanımı da yaygındır. Halkalı bileşiklerin bazıları metatez, ya daradikalik halka-açılma gibi mekanizmalarla da polimerize edilebilir. Halka açılma polimerizasyonunu tetiklemek için hangi başlatıcıların kullanılacağı bilinmesine rağmen, kullanılan başlatıcının nasıl bir tepkime yolu çizdiği tam olarak anlaşılamamıştır.

Bilimsel literatürde, halka-açılma polimerizasyonunun ilerleyişinin iki farklı mekanizmayla gerçekleştiği düşünülür. Birinci mekanizmada halkanın açılmadığı, monomer ve katalizörün etkileşimi sonucu başlatıcının oluştuğu düşünülür. Oluşan bu başlatıcının bir ara ürün olduğuna inanılır. Genellikle oksonyum iyonu olarak oluşan bu ara ürün başlatıcı görevi yaparak polimerizasyonun başlamasını sağlar.

İkinci mekanizmada ise, başlatıcı ve katalizörün doğrudan halkayı açtığı ve oluşan iyonik merkezin başka bir monomerle tepkimeye girerek polimerizasyon reaksiyonunu gerçekleştirdiği düşünülür.

Lactide, carbonate gibi siklik esterlerin halka açılma polimerizasyonu kontrollü poliester sentezinde genel ve etkin bir metottur. Polimerizasyon yöntemlerine ek olarak, düşük polidispersite indisleri ve uç gruplarda yüksek uyumluluk gibi birçok gelişmiş uygulama, ağır metaller gibi istenmeyen kirliliklerin katalizörlerden uzaklaştırılmasını gerektirir. Bu amaçla siklik esterlerin metalsiz halka açılma reaksiyonlarına organokatalitik yaklaşımlarda bulunulmuştur.

Günümüzde, "click kimyası" terimi altında sınıflandırılan Diels-Alder (DA) ve bakır katalizli azid-alkin siklokatılma (CuAAC) tepkimeleri blok ve aşı 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.

Click kimyası hızlı, etkin, güvenilir ve seçici olmak gibi özelliklere sahip olmasının yanı sıra yeni ilaç araştırma ve biyokimya çalışmalarında geniş olarak kullanılır. Click kimyasında en popüler reaksiyonlardan biri Huisgen 1,3-dipolar siklik

katılması reaksiyonudur. Oda sıcaklığında olan azid ve alkin nin reaksiyonunda Cu(I) kataliz olarak kullanılır. Bu reaksiyonun çok tercih edilmesinin sebebi reaksiyon şartlarının basit olması, yan ürün olmaması, verimin yüksek olması ve saflaştırmanın kolay olmasıdır. Bu reaksiyon mekanizması ile ilgili Emrick in yaptığı ilk çalışmalardan bu yana, biyolojik olarak click kimyası ve halka açılma polimerizasyonu metotlarının kullanıldığı bir çok çalışma yapılmıştır. Fakat, click kimyası kullanılarak polikarbonatların modifikasyonun içeren çalışmaların sayısı azdır.

Kopolimerizasyon, polimerik malzemelerin özelliklerini değiştirme ve ayarlama da kullanılan önemli bir yöntemdir. İki polimerin tek olacak şekilde bir araya gelmesi, kopolimerlerin orijinal polimerin meritlerine kadar girebilmesi nedeniyle avantajlıdır. Aşı kopolimerler, moleküler fırça olarak da bilinirler, sahip oldukları özellikler ve şekilleri sayesinde oldukça popülerdirler. İki veya daha fazla monomer birlikte polimerleştiğinde kompleks bir polimer oluşur.

Kopolimerlerin fiziksel özellikleri homopolimerlerden farklıdır ve bu farkın ölçüsü kopolimerin bileşimine bağımlıdır. Genelde rastgele ve alternatif kopolimerler kendilerini oluşturan homopolimerlerin özellikleri arasında özelliklere sahiplerken, blok ve aşı kopolimerler homopolimerlerinin herikisinin özelliklerini de gösterirler. Çünkü onların segmentleri polimer zincir boyunca düzensiz olarak yerleşmiş olup kopolimerler düzenli bir şekle sahip değildir. Bu nedenle de; pekçok kopolimer amorftur. Bununla beraber, eğer taktisite ya da segmentlerin yerleri nedeniyle yeterince düzenlilik sağlanırsa kristalize kopolimerler hazırlanabilir.

Basit halka açılma kopolimerizasyonu ile kontrollü olarak fiziksel ve mekanik özellikleri belirlenebilen polikarbonat kopolimerler elde edilir. Karbonatların halka açılma polimerizasyonu ile yüksek kaliteli (yüksek moleküler ağırlık ve düşük polidispersite) polikarbonatların elde edilmesi oldukça oldukça etkili bir metottur. Bu çalışmada, belirlenebilir moleküler ağırlığa ve yapıya sahip olan PC-Anth aşı kopolimerlerinin dizaynı ve sentezi konu edilmiştir ve antresan-maleimid-bazlı DA "click reaksiyonu" aşı kopolimer hazırlanmasında kullanılmıştır.

Deney 3 aşamada gerçekleştirildi. İlk olarak, Antresen uç fonksiyonlu karbonat monomeri sentezlendi. ^{1}H NMR ve ^{13}C NMR spectrumları bakılarak sentezin gerçekleşip gerçekleşmediği kontrol edildi.

Antresen uç fonksiyonlu monomer, thiourea/DBU kataliz sistemi ve benzil alkol başlatıcısı kullanılarak halka açılma polimerizasyon (ROP) reaksiyonuyla yüksek molekül ağırlıklı polikarbonat elde edildi.

Daha sonra, hazırlanan maleimid uç fonksiyonlu polimerleri, PMMA-MI, PEG-MI, PMMA-MI/PEG-MI ve PS-MI, Diels-Alder reaksiyonu ile antresen uç fonksiyonlu polikarbonata takıldı ve PC-*g*-PMMA, PC-*g*-PEG, PC-*g*-PMMA/PEG, PC-*g*-PS aşı kopolimerleri elde edildi. Aşı kopolimerleri için Diels-Alder reaksiyon etkinliği UV-vis spektroskopisi yardımıyla belirlendi. Aşı kopolimerlerinin d*n*/d*c* değerlerine deneysel olarak ulaşıldı ve sonuçlar GPC ve TD-GPC ile görüntülendi.

1. INTRODUCTION

Most of the attention has long been devoted to polymers made from cyclic diesters or lactones such as lactide or ε-caprolactone. Yet, rising awareness toward polycarbonates has recently emerged because of the renewed attention for green and sustainable development in polymer science.

Recent advances in controlled/living radical polymerization (CRP) allow the synthesis of welldefined block and graft copolymers [1-3]. The three processes that have been developed for CRP are nitroxide-mediated polymerization [4, 5]. The reversible addition–fragmentation chain-transfer (RAFT) process [6] and atom transfer radical polymerization (ATRP) [7, 8].ATRP has been actively used for the polymerization of many functional monomers, along with end-functional polymers or macromonomers, to produce a variety of polymer architectures [1, 9-13]. An increasing interest in segmented copolymers has led to the application of this technique for the synthesis of graft copolymers with a macroinitiator (grafting-from technique) [14–16] and a macromonomer (grafting through technique), [17–20] which were first prepared by other methods.

Ring-Opening polymerization occurs under milder reaction conditions, and it sometimes proceeds in a “living” manner that is, without side reactions to give polyesters of controlled molecular weight.

Recent advances in metal-free organocatalytic living ring-opening polymerization (ROP) of cyclic carbonate monomers, in particular, have provided an extremely effi cient, biofriendly, and cost-effective means to prepare carbonate-based polymers of predictable molecular weights and narrow polydispersities appropriate for biomedical applications [21-23].

It is quite favorable since cyclic carbonates have a variety of advantages in the light of actual applications, such as ease of molecular design and synthesis, diversity of polymerization mode, mild polymerization condition, high polymerization efficiency, and so on, in comparison with the hitherto recognized expandable

monomers [24, 25]. So, it can be expected that cyclic carbonates may be utilized in many polymer material fields.

This strategy is particularly attractive for ring-opening polymerization (ROP) as the inventiory of carbonate monomers available are limited. To improve hydrophilicity, degradation rate, and mechanical properties of polycarbonates, various functional groups such as carboxyl [26-28], amino [29-31], hydroxyl [33-34], etc. were introduced through copolymerization with functional carbonate monomers.

In this study, more attractively, by design, polycarbonate copolymers with a wide variety and accurate controllability in the physical and mechanical properties are readily provided via facile ring-opening copolymerization.

Firstly, the anth-carbonate was synthesized for the purpose to prepare high molecular weight PC-Anth via ROP. Next stage is that many of linear polymers were synthesized by DA click reaction between furan protected maleimide end-functionalized polymers: poly(methyl methacrylate) (MI-PMMA), poly(ethylene glycol), (MI-PEG) and poly(styrene) (MI-PS) at reflux temperature of toluene for 36 h. Diels-Alder click reactions of anthracene with maleimide end-groups are extended to the preparation of intended graft copolymers, PC-*g*-PMMA, PC-*g*-PEG, PC-*g*-PMMA/PEG and PC-*g*-PS (Figure 1.1).

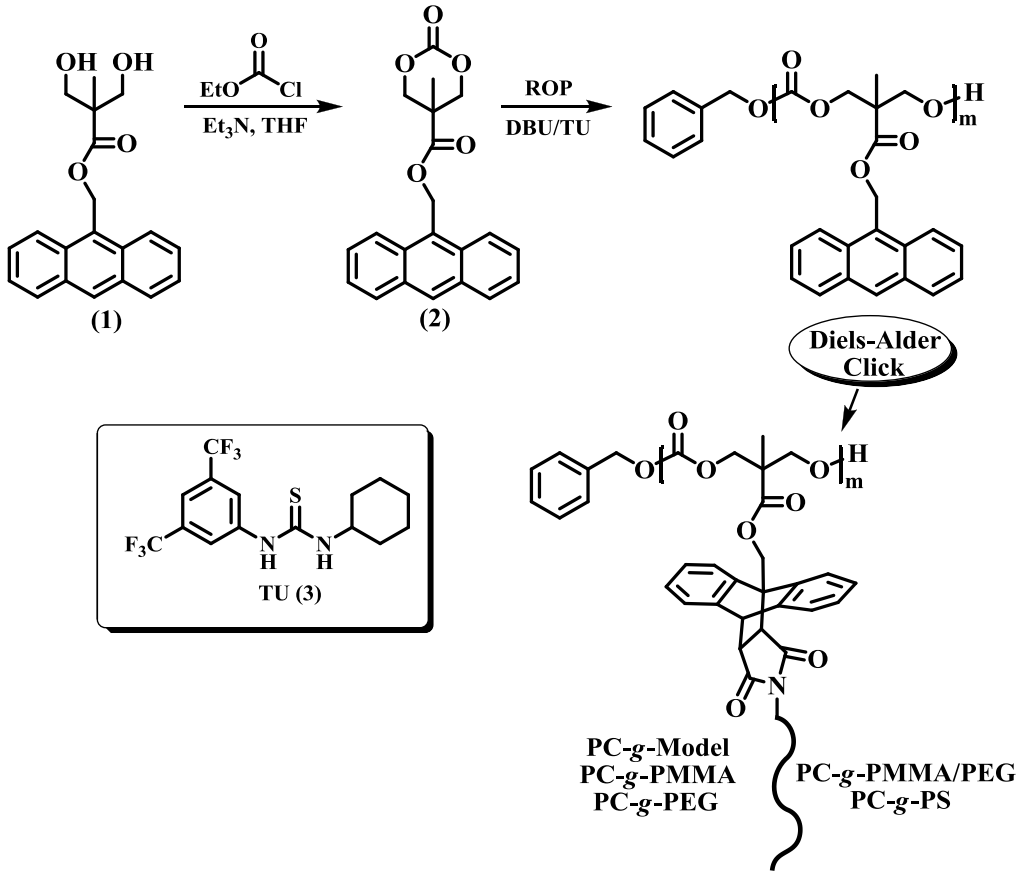


Figure 1.1 : Synthesis of graft copolymers, PC-*g*-PMMA, PC-*g*-PEG, PC-*g*-PMMA/PEG and PC-*g*-PS, via DA click reaction.

2. THEORETICAL PART

In recent years, the main scientific and applied interest in polymeric materials is focused on the novel synthetic methods that allow control over the composition, functionality, molecular structure, molecular weight and glass transition temperature.

2.1 Living Polymerization

The name "living polymerization" was coined for the method by Szwarc in 1956 [35] because the chain ends remain active untilled killed. (The term has nothing to do with living in the biological sense.) Before Szwarc's classical work, Flory [36] had described the properties associated with living polymerization of ethylene oxide initiated with alkoxides. Flory noted that since all of the chain ends grow at the same rate, the molecular weight is determined by the amount of initiator used versus monomer.

Another property of polymers produced by living polymerization is the very narrow molecular weight distribution [36]. The polydispersity (PDI) has a Poisson distribution, PDI = M_w/M_n; M_w and M_n can be determined by gel permeation chromatography (GPC).

A living polymerization can be distinguished from free radical polymerization or from a condensation polymerization by plotting the molecular weight of the polymer versus conversion. In a living polymerization, the molecular weight is directly proportional to conversion (Figure, 2.1 (A)). In a free radical or other nonliving polymerization, high molecular weight polymer is formed in the initial stages (Figure, 2.1(B)), and in a condensation polymerization, high molecular weight polymer is formed only as the conversion approaches 100% (Figure 2.1, (C)) [37].

Living polymerization provides end-group control and enables the synthesis of block copolymers by sequential monomer addition. However, it does not necessarily provide polymers with molecular weight (MW) control and narrow molecular weight distribution (MWD). To obtain well defined polymers the initiator should be

consumed at early stages of polymerization and that the exchange between species of various reactivities should be at least as fast as propagation [38-40].

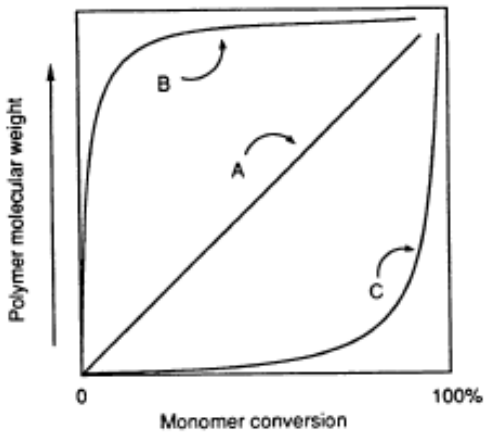


Figure 2.1 : Molecular weight conversion curves for various kinds of polymerization methods: (A) living polymerization; (B) free radical polymerization; and (C) condensation polymerization.

Much of the academic and industrial research on living polymerization has focused on anionic, cationic, coordination, and ring-opening polymerizations. The development of controlled/living radical polymerization (CRP) methods has been a long-standing goal in polymer chemistry, as a radical process is more tolerant of functional groups and impurities and is the leading industrial method to produce polymers [41]. Despite its tremendous industrial utility, CRP has not been realized until recently, largely due to the inevitable, near diffusion-controlled bimolecular radical coupling and disproportionation reactions.

2.2 Controlled/Living Radical Polymerization (C/LRP)

The ability to accurately control macromolecular architecture is becoming an increasingly important aspect of polymer chemistry. Typically well-defined macromolecular architectures are prepared by stepwise, [42] transition-metal-catalyzed, [43] or anionic processes. [44] However, a long-term goal of synthetic polymer chemists has been the development of a radical polymerization process which possesses many of the desired characteristics of these more challenging methods and leads to well-defined materials. Specifically, these characteristics are molecular weight control, end group control, ability to form block copolymers, and a "living" nature. Recently, Georges et al. [45] have reported that low polydispersity

(PDI) polymers can be prepared by free-radical chemistry using a system that can be considered to be a living polymerization.

Matyjaszewski and Sawamoto developed metal catalzed (Cu, Ru) living radical polymerization also called atom transfer radical polymerization (ATRP) in 1995 [46-48].

The past few years have witnessed the rapid growth in the development and understanding of new CRP methods [49, 50] All of these methods are based on establishing a rapid dynamic equilibration between a minute amount of growing free radicals and a large majority of the dormant species. The dormant chains may be alkyl halides, as in atom transfer radical polymerization (ATRP) or degenerative transfer (DT), thioesters, as in reversible addition fragmentation chain transfer processes (RAFT), alkoxyamines, as in nitroxide mediated polymerization (NMP) or stable free radical polymerization (SFRP), and potentially even organometallic species. Free radicals may be generated by the spontaneous thermal process (NMP, SFRP) via a catalyzed reaction (ATRP) or reversibly via the degenerative exchange process with dormant species (DT, RAFT).

2.2.1 Atom transfer radical polymerization(ATRP)

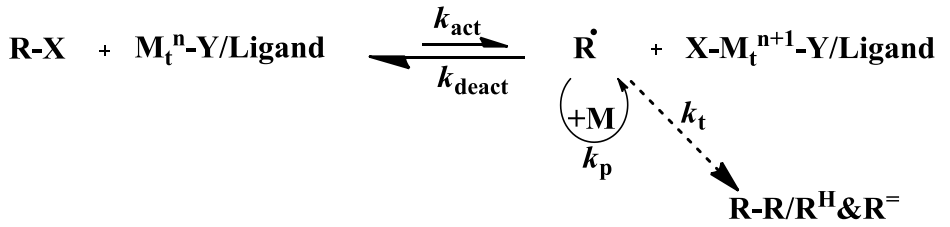
The ATRP process involves an equilibrium reaction between a low concentration of active radicals and a much greater concentration of dormant species. The radicals or the active species, are generated through a reversible redox process catalyzed by a transition metal complex (Mt*n*-Y/Ligand where Y may be another ligand or the counterion) which undergoes a one electron oxidation with concomitant abstraction of a (pseudo) halogen atom, X, from a dormant species, R-X. This process occurs with a rate constant of activation, k_{act} and deactivation k_{deact}. Polymer chains grow by the addition of the intermediate radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation kp. 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. Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. This process generates oxidized metal complexes, M_t^{n+1}, as

persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination [51]. A successful ATRP will have not only a small contribution of terminated chains, but also a uniform growth of all the chains, which is accomplished through fast initiation and rapid reversible deactivation.

The name ATRP originates from the atom transfer step, which is the key elementary reaction responsible for the uniform growth of the polymeric chains. ATRP also has roots in the transition metal catalyzed telomerization reactions [52]. These reactions, however, do not proceed with efficient exchange, which results in a nonlinear evolution of the molecular weights with conversions and polymers with high polydispersities. ATRP also has connections to the transition metal initiated redox processes as well as inhibition with transition metal compounds [53-55]. These two techniques allow for either an activation or deactivation process, however, without efficient reversibility.

ATRP was developed by designing an appropriate catalyst (transition metal compound and ligands), using an initiator with the suitable structure, and adjusting the polymerization conditions such that the molecular weights increased linearly with conversion and the polydispersities were typical of a living process [56-60]. This allowed for an unprecedented control over the chain topology (stars, combs, branched), the composition (block, gradient, alternating, statistical), and the end functionality for a large range of radically polymerizable monomers [58, 61-65].

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.



(2.1)

Equation 2.2 shows that lower polydispersities are obtained at higher conversion, higher k_{deact} relative to k_p, higher concentration of deactivator, and higher monomer to initiator ratio, $[M]_0/[I]_0$.

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 (2.3).

$$R_p = k_p.K_{eq}\frac{[R\text{-}X][M_t^n]}{[M_t^{n+1}]}.[M] \quad (2.2)$$

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_p[R\text{-}X]}{k_{deact}[M_t^{n+1}]}\right)\left(\frac{2}{p} - 1\right) = 1 + \frac{2}{k_{act}[M_t^n]t} \quad (2.3)$$

As a multicomponent system, ATRP is composed of the monomer, an initiator with a transferable (pseudo) halogen, and a catalyst (composed of a transition metal species with any suitable ligand). Sometimes an additive is used. For a successful ATRP, other factors, such as solvent and temperature, must also be taken into consideration.

2.2.1.1 Monomers

A variety of monomers have been successfully polymerized using ATRP. Typical monomers include styrenes, (meth)acrylates, (meth)acrylamides, and acrylonitrile, which contain substituents that can stabilize the propagating radicals [63, 64]. Ring-opening polymerization has been also successful [66, 67]. Even under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. In the absence of any side reactions other than radical termination by coupling or disproportionation, the magnitude of the equilibrium constant (K_{eq}) determines the polymerization rate. ATRP will not occur or occur very slowly if the equilibrium constant is too small. In contrast, too large an equilibrium constant will lead to a large amount of termination because of a high radical concentration. This will be accompanied by a large amount of deactivating higher oxidation state metal complex; which will shift the equilibrium toward dormant species and may result in the apparently slower polymerization [68]. Each monomer possesses its own intrinsic radical propagation rate. Thus, for a specific monomer, the concentration of propagating radicals and the rate of radical deactivation need to be adjusted to maintain polymerization control.

2.2.1.2 Initiators

The main role of the initiator is to determine the number of growing polymer chains. If initiation is fast and transfer and termination negligible, then the number of growing chains is constant and equal to the initial initiator concentration. The theoretical molecular weight or degree of polymerization (DPn) increases reciprocally with the initial concentration of initiator in a living polymerization (2.4).

$$DPn = [M]_0 / [initiator]_0 \times conversion \quad \textbf{(2.4)}$$

In ATRP, alkyl halides (RX) are typically used as the initiator and the rate of the polymerization is first order with respect to the concentration of RX. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, must rapidly and selectively migrate between the growing chain and the transition-metal complex. Thus far, when X is either bromine or chlorine, the molecular weight control is the best. Iodine works well for acrylate polymerizations in copper-mediated ATRP [69] and has been found to lead to controlled polymerization of styrene in ruthenium- and rhenium-based ATRP [70, 71]. Fluorine is not used because the C-F bond is too strong to undergo homolytic cleavage. Some pseudohalogens, specifically thiocyanates and thiocarbamates, have been used successfully in the polymerization of acrylates and styrenes [69, 72, 73]. Initiation should be fast and quantitative with a good initiator. In general, any alkyl halide with activating substituents on the R-carbon, such as aryl, carbonyl, or allyl groups, can potentially be used as ATRP initiators. Polyhalogenated compounds (e.g. CCl_4 and $CHCI_3$) and compounds with a weak R-X bond, such as N-X, S-X, and O-X, can also be used as ATRP initiators. When the initiating moiety is attached to macromolecular species, macroinitiators are formed and can be used to synthesize block/graft copolymers [62]. Similarly, the efficiency of block/graft copolymerization may be low if the apparent rate constant of cross-propagation is smaller than that of the subsequent homopolymerization. It should be noted, however, that R-X bonds can be cleaved not only homolytically but also heterolytically, which depends mostly on the initiator structure and the choice of the transition metal catalyst.

2.2.1.3 Catalysts

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. First, the metal center must have at least two readily accessible oxidation states separated by one electron. Second, the metal center should have reasonable affinity toward a halogen. Third, the coordination sphere around the metal should be expandable upon oxidation to selectively accommodate a (pseudo) halogen. Fourth, the ligand should complex the metal relatively strongly. Eventually, the position and dynamics of the ATRP equilibrium should be appropriate for the particular system.

2.2.1.4 Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g.emulsion, suspension). A solvent is sometimes necessary, especially when the obtained polymer is insoluble in its monomer (e.g. polyacrylonitrile). Several factors affect the solvent choice. Chain transfer to solvent should be minimal. In addition, interactions between solvent and the catalytic system should be considered. Catalyst poisoning by the solvent (e.g. carboxylic acids or phosphine in copperbased ATRP) [74] and solvent-assisted side reactions, such as elimination of HX from polystyryl halides, which is more pronounced in a polar solvent [75], should be minimized.

2.2.1.5 Temperature and reaction time

The rate of polymerization in ATRP increases with increasing temperature due to the increase of both the radical propagation rate constant and the atom transfer equilibrium constant. As a result of the higher activation energy for the radical propagation than for the radical termination, higher k_p/k_t ratios and better control ("livingness") may be observed at higher temperatures. However, chain transfer and other side reactions become more pronounced at elevated temperatures [75, 76]. In general, the solubility of the catalyst increases at higher temperatures; however, catalyst decomposition may also occur with the temperature increase [77, 78]. The

optimal temperature depends mostly on the monomer, the catalyst, and the targeted molecular weight.

2.3 Ring-Opening Polymerization (ROP)

Metal alkoxide or metal carboxylate initiators and catalysts generating controlled ring-opening polymerizations are frequently utilized in synthesis of polymers with

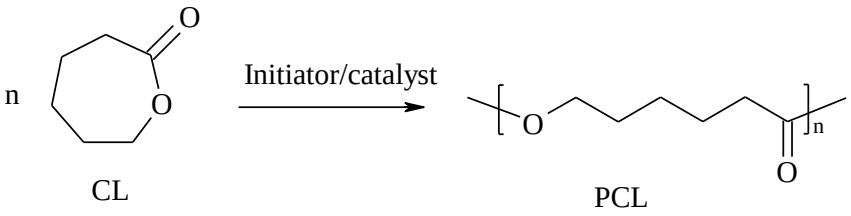
predictable molecular weight, narrow molecular weight distribution, and desirable end groups [79]. A diverse variety of functionalized initiators have been developed during the past decade utilized in the production of new biodegradable materials. Extensive work has also been carried out to understand the polymerization mechanism and kinetics of the ROP [80-82].

Polymerization catalysis, in addition to the general issues of turnover frequency, turnover number, and selectivity (chemo-, regio-, and stereoselectivity), poses additional challenges such as the need to control the molecular weight and the molecular weight distribution of the macromolecules, the nature and number of polymer end groups (end-group fidelity), the topology of the macromolecule (linear, branched, cyclic, concatenated, the presence and/or degree of crosslinking), and the functionality and sequence of monomers along the polymer chain.

The thermodynamics of ROP is driven by the release of the ring strain of the monomer. The selectivity of the catalyst is critical to facilitate ring-opening relative to transesterification and other side reactions (chain shuffling and termination). Traditional thermal and hydrolytic ROPs are poorly controlled and often induce a great amount of side reactions. Hence, efficient catalysts that accelerate ring-opening of cyclic monomers are needed for controlled ROP. Conventionally, mechanisms for ROP are divided into cationic and anionic polymerization according to the ionic charge of active propagating species [83].

2.3.1 Controlled ring-opening polymerization of cyclic esters

Aliphatic poly(ester)s can be either synthesized by polycondensation of hydroxyl-carboxylic acids or by the ring-opening polymerization (ROP) of cyclic esters. The polycondensation technique yields low molecular weight polyesters (Mn<30.000) with poor control of specific end groups [74]. In contrast, high molecular weight aliphatic polyesters can be prepared in short periods of time by ROP. There has been much research directed towards the controlled ROP of commercially available cyclic esters including glycolide, lactide, ε-caprolactone (2.5) and carbonate resulting in aliphatic poly(ester)s with high molecular weights [84].



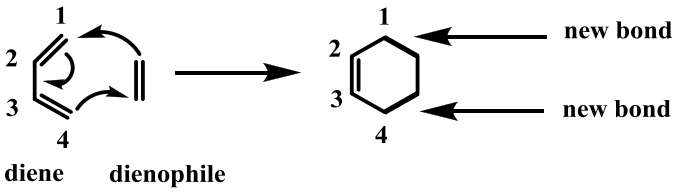
(2.5)

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 [85]. 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 (2.6). This reaction is named for Otto Diels and Kurt Alder, who received the 1950 Nobel prize for discovering this useful transformation [86-88].

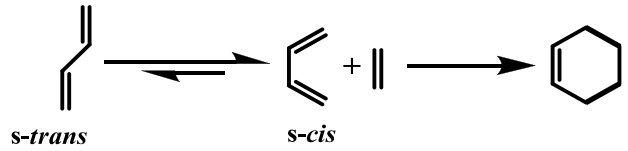


(2.6)

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 [89].

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 (2.7).

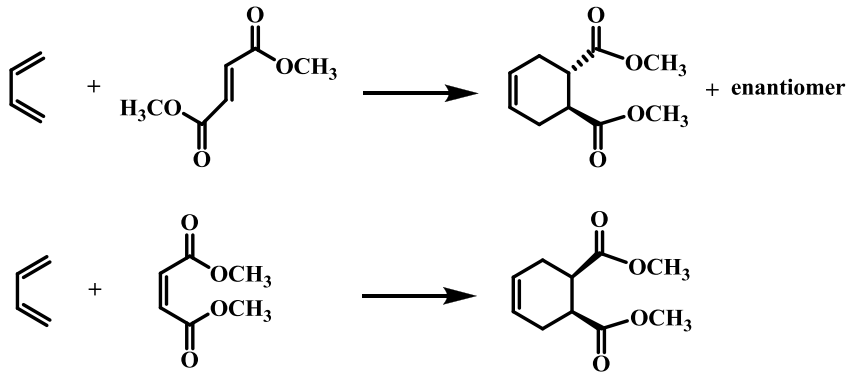


(2.7)

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.

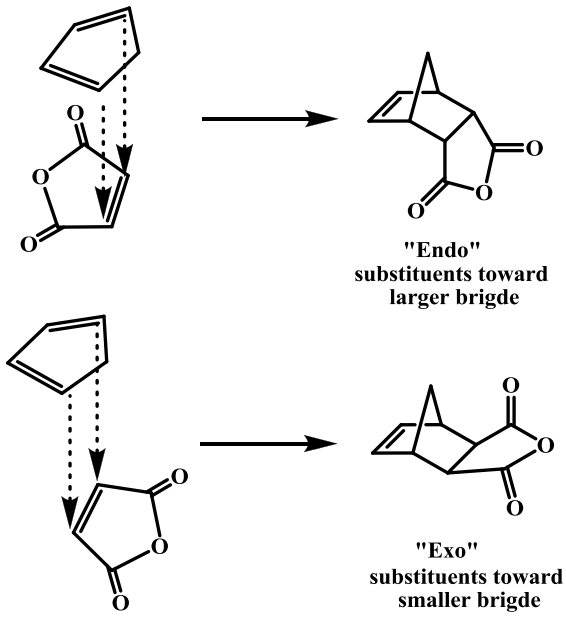
Since the reaction proceeds in a concerted fashion (*i.e.*, bonds are being formed and broken at the same time), substituents that are *cis* on the dienophile will also be *cis* in the product, and substituents that are *trans* on the dienophile will be *trans* in the product (2.8) [89-93].

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) (2.9).



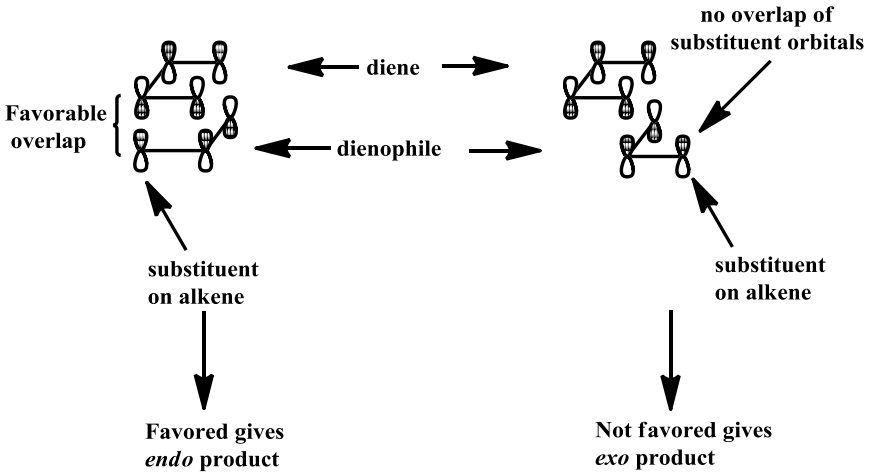
(2.8)

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 [91, 92].



(2.9)

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 (2.10). 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.

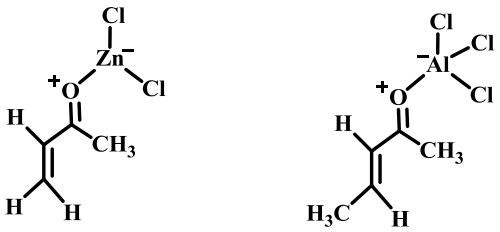


(2.10)

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

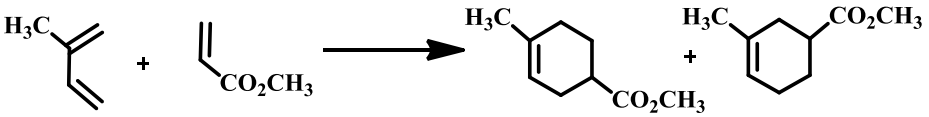
The DA reactions are catalyzed by many Lewis acids, including $SnCl_4$, $ZnCl_2$, $AlCl_3$ and derivatives of $AlCl_3$ [83]. A variety of other Lewis acids is effective catalysts. The types of dienophiles that are subject to catalysis are typically those with carbonyl substituents. Lewis acids form complexes at the carbonyl oxygen and this increases the electron-withdrawing capacity of the carbonyl group (2.11) [94].



(2.11)

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 [95]. 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 (2.12).



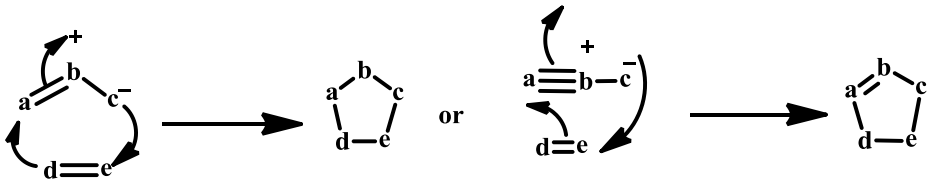
(2.12)

	"para"	"meta"
Uncatalyzed reaction, 120 ^{o}C, 6h	**70%**	**30%**
$AlCl_3$-catalyzed 20 ^{o}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 [96-99]. The accelerating effect of water is attributed to "enforced hydrophobic interactions" [97]. 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)

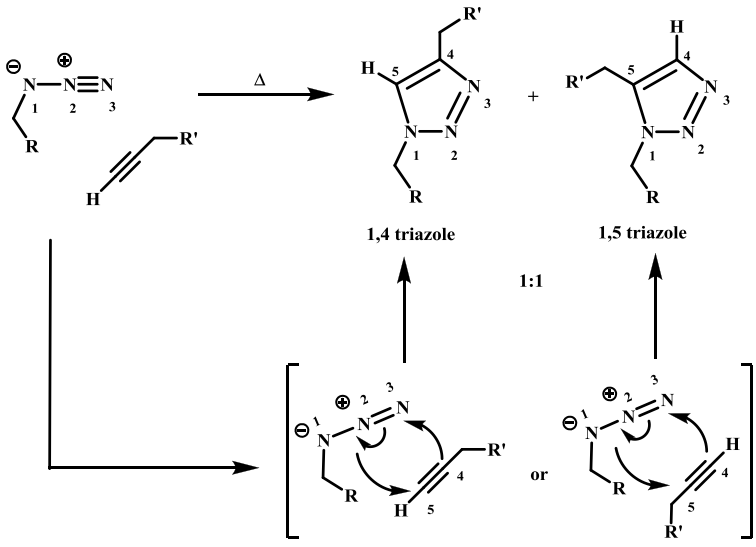
There is a large class of reactions known as 1,3-dipolar cycloaddition reactions (1,3-DPCA) that are analogous to the Diels-Alder reaction in that they are concerted [4π+2π] cycloadditions [100, 101]. 1,3-DPCA reactions can be represented as shown in the following diagram. The entity a-b-c is called the *1,3-dipole* and d-e is the *dipolarophile* (2.13).



(2.13)

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. This structural feature 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

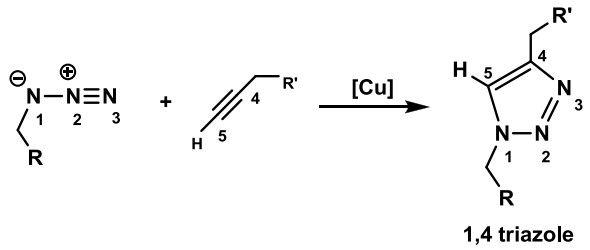
carbonyl, imine, azo, and nitroso can also act as dipolarophiles. The reactivity of dipolarophiles depends both on the substituents present on the π bond and on the nature of the 1,3-dipole involved in the reaction. Owing to the wide range of structures that can serve either as a 1,3-dipole or as a dipolarophile, 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) [102]. 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 (2.14) [103].



(2.14)

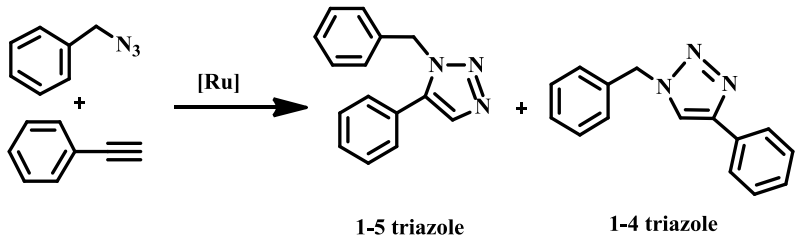
Thus, only following the recent discovery of the advantages of Cu(I)-catalyzed alkyne–azide coupling, reported independently by the Sharpless and Meldal groups, did the main benefits of this cycloaddition become clear [104, 105]. Cu(I) catalysis dramatically improves regioselectivity to afford the 1,4-regioisomer exclusively (2.15) and increases the reaction rate up to 10^7 times eliminating the need for elevated temperatures [106]. 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 [99, 105]. 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.



(2.15)

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) [107]. 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 (2.16).



(2.16)

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

2.5 Topology

The need to synthesize polymers with new and/or improved properties properties has driven the effort to design polymers with novel macromolecular architectures. Polymer topology can be generally defined as the fabrication of complex macromolecular structures with defined composition, functionality, and architecture

(e.g. telechelic polymers, block copolymers, macromolecular brushes, stars, and networks) as depicted in Figure 2.2.

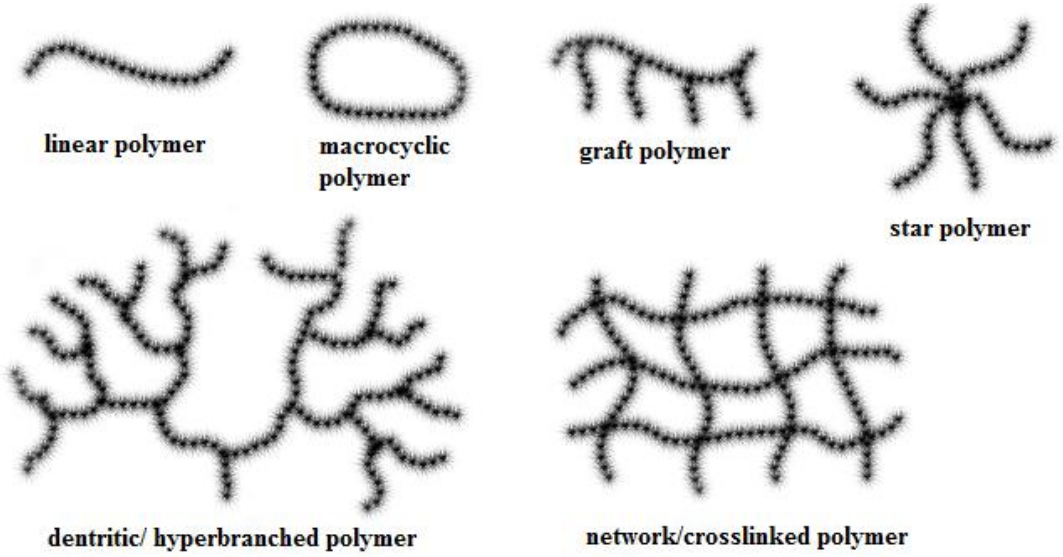


Figure 2.2 : Illustration of polymers with various topologies

2.5.1 Block copolymers

Block copolymers display remarkable phase behavior and are industrially important as thermoplastic elastomers, [108] impact modifiers, [109] compatibilization agents, [110] and surfactants [111]. The novel properties that arise in block copolymers when compared to random copolymers result from microphase separation of the components. A generally recognized prerequisite for well-defined phase behavior is to have low PDIs for each of the blocks (generally PDI < 1.3), and especially precise synthetic techniques are required for control of molecular weight and PDI.

In particular, anionic polymerization has been successfully applied for block copolymer synthesis [112] Several other routes have been realized as well, including controlled radical polymerization [113-116], living cationic polymerization [117-119],group transfer [120-122], metathesis polymerization [123, 124], ring-opening polymerization [125-127] or combinations of these techniques. Recently, block copolymers and, in particular, block co- (polyesters) have shown great promise in both nanoscale patterning of microelectronics and biomedical applications, due to the variety of two- and three-dimensional morphologies that can be constructed and the (bio)degradability of polyester segments. Organocatalytic strategies that avoid introducing any metallic catalysts appear highly advantageous.

2.5.2 Graft copolymers

The synthesis of graft copolymers can be accomplished through one of three routes: “grafting from” reactions (utilizing polymerization of grafts from a macroinitiator with pendant functionality), “grafting through” processes (operating by homo- or copolymerization of a macromonomer) and “grafting onto” (occurring when the growing chain is attached to a polymer backbone). The first two methods have been used in conjunction with ATRP in the design of graft copolymers and underscore the versatility of this controlled radical polymerization technique to synthesize a variety of (co)polymers.

2.5.2.1 “Grafting from ” method

In the “*grafting from*” 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 [128, 129].

2.5.2.2 “Grafting trough ” method

The "grafting through" method (or macromonomer method) (Figure 2.3) is one of the simplest ways to synthesize graft copolymers with well defined side chains. In a "grafting through" copolymerization the reactivity ratio of monomers and macromonomers may be affected by micro-inhomogeneity of the reaction mixture in addition to the reaction mechanism. This has often been observed in macromonomer copolymerization, or "grafting through" copolymerization for preparation of graft copolymers that would be expected to undergo phase separation. [130].

Typically a low molecular weight monomer is radically copolymerized with a (meth)acrylate functionalized macromonomer. This method permits incorporation of macromonomers that have prepared by other controlled polymerization processes into a backbone prepared by a CRP.

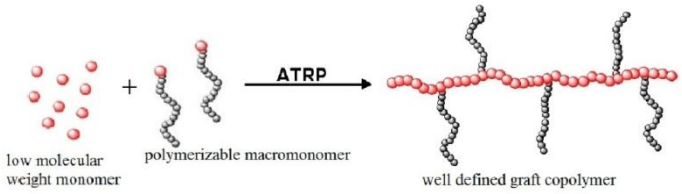


Figure 2.3 : Synthesis of well-defined graft copolymer via grafting through method

Macromonomers are short polymer chains possessing a polymerizable group at one terminus. A great variety of methods involving living polymerization techniques, chain transfer reactions, and end chain modifications have been developed to synthesize such species. In this case the macromonomer comprises the branch of the copolymer, and the backbone is formed in situ. The number of branches per backbone can be generally controlled by the ratio of the molar concentrations of the macromonomer and the comonomer. Several other factors have to be considered. Among them the most important one is the copolymerization behavior of the macromonomer and the comonomer forming the backbone.

2.5.2.3 “Grafting onto ” method

Due to steric congestion between reactive polymeric sidechains and backbones, the grafting density of polymeric brushes (number-average ratio of brush sidechains to backbone monomer units) prepared by the “grafting onto” method is usually low[54]. An excess of reactive sidechains can be employed to increase the grafting density, although it is not easy to purify the final brush polymers by repeated fractionation to remove the unreacted linear chains. In order to increase the grafting density during the “grafting onto” synthesis, two factors should be considered. One is to use a reactive polymeric sidechain with a “thinner” structure, which can decrease the steric hindrance during grafting reactions. The other is to perform an organic reaction with high efficiency, which assures a fastcoupling reaction between reactive sidechains and backbones.

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

Anthracen-9-ylmethyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate **7** [131], 1-(3,5-bis(trifloromethyl)phenyl)-3-cyclohexylthiourea (TU) **9** [132] and 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** [133] were prepared according to published procedures.

3.3.1 Synthesis of 4,10-dioxatricyclo[5.2.1.02,6]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%). Mp: 114-115 ^{o}C (DSC). ^{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). ^{13}C NMR ($CDCl_3$, δ) 170.18, 137.29, 82.46, 48.88. Mass spectrometry (+EI) *m*/*z* (%): 167 [MH+] (50), 144 (35), 130 (20).

3.3.2 Synthesis of 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.02,6]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%). Mp = 138-139 °C (DSC). ^{1}H NMR ($CDCl_3$, δ) 6.51 (s, 2H, C*H*=C*H*, bridge protons), 5.26 (s, 2H, -C*H*O, bridge-head protons), 3.74-3.68 (m, 4H, NCH_2CH_2OH), 2.88 (s, 2H, C*H*-C*H*, bridge protons). ^{13}C NMR ($CDCl_3$, δ) 177.03, 136.60, 81.09, 60.53, 47.74, 42.03. Mass spectrometry (+EI) *m*/*z* (%): 210 [MH+] (50), 145 (22), 142 (100), 124 (17).

3.3.3 Synthesis of 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)

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%). Mp = 81-82 °C (DSC). ^{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_2CH_2OC=O), 3.79 (t, *J* =5.2 Hz, 2H, NCH_2CH_2OC=O), 2.85 (s, 2H, C*H*-C*H*, bridge protons), 1.87 (s, 6H, C(CH_3)$_2$-Br). ^{13}C NMR ($CDCl_3$, δ) 176.12, 171.55, 136.83, 81.09, 62.36, 55.96, 47.74, 37.69, 30.83. Mass spectrometry (+EI) *m*/*z* (%): 360 [MH+] (100).

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

2 (5 g, 23.9 mmol) was dissolved in 150 mL of 1,4-dioxane. To the reaction mixture were added Et_3N (16.58 mL, 119.6 mmol), DMAP (4.38 g, 35.8 mmol), and succinic anhydride (9.56 g, 95.6 mmol) in that order. The reaction mixture was stirred for

overnight at 50 ^{o}C, then poured into ice-cold water and extracted with CH_2Cl_2. The organic phase was washed with 1 M HCl, dried over Na_2SO_4 and concentrated. The crude product was crystallized from ethanol to give **4** as white crystal. Yield: 5.9 g (80%). M.p. = 122-123 ^{o}C (DSC). ^{1}H NMR ($CDCl_3$, δ) 6.50 (s, 2H, C*H*=C*H*, bridge protons), 5.25 (s, 2H, -C*H*O, bridge-head protons), 4.25 (t, *J* = 5.2 Hz, 2H, NCH_2CH_2OC=O), 3.74 (t, *J* =5.2 Hz, 2H, NCH_2CH_2OC=O), 2.87 (s, 2H, C*H*-C*H*, bridge protons), 2.66-2.53 (m, 4H, C=OCH_2CH_2C=OOH). ^{13}C NMR ($CDCl_3$, δ) 177.26, 176.35, 172.01, 136.83, 81.09, 61.22, 47.74, 37.92, 29.24. Mass spectrometry (+EI) *m*/*z* (%): 310 [MH+] (100), 242 (100), 142 (18), 124 (13).

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

In a 25 mL of Schlenk tube, MMA (5.00 mL, 46.7 mmol), PMDETA (0.196 mL, 0.940 mmol), CuCl (0.093 g, 0.94 mmol), toluene (5 mL), and **3** (0.336 g, 0.940 mmol) were added, and the reaction mixture was degassed by FPT cycles, and left in argon. The tube was then placed in a thermostated oil bath at 40 °C for predetermined times. The polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated into hexane. The polymer was dried for 24 h in a vacuum oven at 40 °C. ^{1}H NMR ($CDCl_3$, δ) 6.5 (s, 2H, C*H*=C*H*, bridge protons), 5.3 (s, 2H, -C*H*O, bridge-head protons), 4.1 (m, 2H, NCH_2CH_2OC=O), 4.0-3.2 (br, OCH_3 of PMMA and NCH_2CH_2OC=O), 2.9 (s, 2H, C*H*-C*H*, bridge protons), 2.5-0.5 (br, aliphatic protons of PMMA). $M_{n,theo}$=2100, $M_{n,NMR}$ = 3200, $M_{n,GPC}$ =3100, M_w/M_n =1.31 (relative to PMMA standards).

3.3.6 Synthesis of furan protected maleimide end-functionalized PEG (PEG-MI)

Me-PEG (M_n = 550) (2.0 g, 3.63 mmol) was dissolved in 50 mL of CH_2Cl_2. To the reaction mixture were added DMAP (0.044 g, 0.363 mmol) and **4** (2.24 g, 7.27 mmol) in that order. After stirring 5 min at room temperature, a solution of DCC (1.49 g, 7.27 mmol) in 10 mL of CH_2Cl_2 was added. Reaction mixture was stirred for overnight at room temperature. After filtration off the salt, the solution was concentrated and the viscous brown color product was purified by column chromatography over silica gel eluting with CH_2Cl_2/EtOAc mixture (1:1, v/v) and then with CH_2Cl_2/methanol (90:10, v/v) to obtain MI-PEG as viscous brown oil. Yield: 2.7 g (88%). ^{1}H NMR ($CDCl_3$, δ) 6.50 (s, 2H, C*H*=C*H* as bridge protons),

5.25 (s, 2H, -C*H*O, bridge-head protons), 4.23 (m, 4H, CH_2OC=O), 3.75-3.51 (m, OCH_2CH_2 repeating unit of PEG, C=ONCH_2, and CH_2-PEG repeating unit), 3.36 (s, 3H, PEG-OCH_3), 2.87 (s, 2H, C*H*-C*H*, bridge protons) 2.61-2.56 (m, 4H, C=OCH_2CH_2C=O). $M_{n,theo}$= 840, $M_{n,NMR}$= 860, $M_{n,GPC}$= 550, M_w/M_n= 1.09 (relative to PS standards).

3.3.7 Synthesis of azide-terminated polystyrene (PS-N_3)

PS was achieved by ATRP of St. St (15.0 mL, 130 mmol), PMDETA (0.136 mL, 0.65 mmol), CuBr (0.094 g, 0.65 mmol) and ethyl 2-bromo isobutyrate (EIBr) (0.096 g, 0.65 mmol) were added in a 50 mL of Schlenk tube and the reaction mixture was degassed by three freeze-pump-thaw (FPT) cycles and left in vacuum. The tube was subsequently placed in a thermostated oil bath at 110 °C for 45 min. The darkgreen polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated in methanol. The polymer was dried for 24 h in a vacuum oven at 40 °C. $[M]_0/[I]_0$ = 200, $[I]_0$:$[CuBr]_0$:$[PMDETA]_0$ = 1:1:1; (conv. = 19%; $M_{n,theo}$ = 4200; $M_{n,NMR}$ = 4350; $M_{n,GPC}$ = 4550; M_w/M_n = 1.10, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ), 4.4 (br, 1H, C*H*(Ph)-Br end group of PS), 3.7-3.4 (br, 2H, CH_3CH_2O), 2.2-0.8 (m, aliphatic protons of PS and CH_3).

Next, previously obtained PS (1.50 g, 0.33 mmol, $M_{n,GPC}$ = 4550 g/mol) dissolved in DMF (15 mL) and NaN_3 (0.43 g, 6.6 mmol) was added to the flask. After stirring overnight at room temperature, the mixture was precipitated into an excess amount of methanol. The recovered polymer PS-N_3 was dried in a vacuum oven at 40 °C for 24 h (Yield = 1.7 g, 98 %; $M_{n,GPC}$ = 5000 g/mol; M_w/M_n = 1.08 , relative to PS standards). ^{1}H NMR ($CDCl_3$, δ), 3.9 (br, 1H, C*H*(Ph)-N_3 end group of PS), 3.7-3.4 (br, 2H, CH_3CH_2O), 2.2-0.8 (m, aliphatic protons of PS and CH_3).

3.3.8 Synthesis of furan protected maleimide end-functionalized PS (PS-MI)

PS-N_3 (1.00 g, 0.200 mmol, $M_{n,GPC}$= 5000), **7** (0.173 g, 0.600 mmol), PMDETA (0.042 mL, 0.200 mmol), CuBr (0.028 g, 0.200 mmol), and DMF (10 mL) were added in a 50 mL of Schlenk tube, and the reaction mixture was degassed by three FPT cycles, left in vacuum and then stirred overnight at room temperature. After the specified time, polymer solution was passed through neutral alumina column to remove copper salt, precipitated in methanol for two times, and dried in a vacuum

oven at 40 °C. (Yield = 1 g; $M_{n,theo}$ = 5300, $M_{n,GPC}$= 5200, M_w/M_n= 1.07 (relative to PS standards).

3.3.9 Synthesis of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid (5)

The 2,2-bis(hydroxymethyl)propanoic acid (8 g, 59.6 mmol) along with *p*-TSA (0.45 g, 2.32 mmol), and 2,2-dimethoxypropane (11.2 mL, 89.4 mmol) dissolved in 40 mL of dry acetone, and stirred 2h at room temperature. In the vicinity of 2h, while stirring continued the reaction mixture was neutralized with 6 mL of totally NH_4OH (25%), and absolute ethanol (1:5), filtered off by-products and subsequent dilution with dichloromethane (100 mL), and once extracted with distilled water (40 mL). The organic phase dried with Na_2SO_4, concantrated to yield 7.4 g (71%) as white solid after evaporation of the solvent. ^{1}H NMR ($CDCl_3$, δ) 4.18 (d, 2H, CC*H*$_2$O), 3.63 (d, 2H, CC*H*$_2$O), 1.38 (s, 3H, C*CH*$_3$) 1.36 (s, 3H, C*CH*$_3$), 1.18 (s, 3H, C=OC(CH_2O)$_2$*CH*$_3$).

3.3.10 Synthesis of anthracen-9ylmethyl 2,2,5-trimethyl-[1,3]dioxane-5-carboxylate (6)

9-Anthracene methanol (2 g, 9.6 mmol) was dissolved in 50 mL of CH_2Cl_2 and **6** (2 g, 11.5 mmol), and DMAP (1.17 g, 9.6 mmol) were added to the reaction mixture in that order. After stirring 5 minutes at room temperature, DCC (2.37 g, 11.5 mmol) dissolved in 20 mL of CH_2Cl_2 was added. Reaction mixture was stirred overnight at room temperature and urea byproduct was filtered. Then reaction mixture was extracted with water/ CH_2Cl_2 (1:4) two times and combined organic phase was dried with Na_2SO_4. Solvent was evaporated and the remaining product was purified by column chromatography over silica gel eluting with hexane/ethyl acetate (4:1) to give pale yellow oil (Yield = 2.97 g; 85 %). ^{1}H NMR ($CDCl_3$, δ) 8.50 (s, 1H, Ar*H* of anthracene), 8.32 (d, 2H, Ar*H* of anthracene), 8.02 (d, 2H, Ar*H* of anthracene), 7.60-7.45 (m, 4H, Ar*H* of anthracene), 6.2 (s, 2H, *CH*$_2$-anthracene), 4.14 (d, 2H, CC*H*$_2$O), 3.58 (d, 2H, CC*H*$_2$O), 1.38 (s, 3H, C*CH*$_3$), 1.35 (s, 3H, C*CH*$_3$), 1.08 (s, 3H, C=OC(CH_2O)$_2$*CH*$_3$).

3.3.11 Synthesis of anthracen-9ylmethyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (7)

9-anthrylmethyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (2.95 g, 8.1 mmol) was dissolved in a mixture of 20 mL of THF and 10 mL of 1 M HCl. The reaction mixture was stirred for 2 h at room temperature. The precipitated product was filtered off and reaction mixture was concentrated and extracted with 160 mL of CH_2Cl_2 and 40 mL of water. The combined organic phase was dried with Na_2SO_4 and concentrated. Hexane was added to the reaction mixture and it was kept in deep freeze overnight to give white solid (Yield = 2.4 g, 91 %). ^{1}H NMR ($CDCl_3$, δ) 8.52 (s, 1H, Ar*H* of anthracene), 8.30 (d, 2H, Ar*H* of anthracene), 8.03 (d, 2H, Ar*H* of anthracene), 7.60-7.45 (m, 4H, Ar*H* of anthracene), 6.2 (s, 2H, *CH*$_2$-anthracene), 3.85 (d, 2H, C*H*$_2$OH), 3.66 (d, 2H, C*H*$_2$OH), 2.17(br, 2H, OH), 1.01 (s, 3H, C*CH*$_3$).

3.3.12 Synthesis of anthracen-9-ylmethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (8)

In a 250 mL of three-neck round bottom flask were added **8** (5.0 g, 0.015 mol) in 100 mL of THF. The solution was cooled to 0 °C, and a solution of ethyl chloroformate (4.40 mL, 0.045 mol) in 25 mL of THF was added dropwise to the reaction mixture. Then a solution of triethylamine (6.25 mL, 0.045 mmol) in 25 mL of THF was added dropwise (20 min). The white suspension was stirred for 2 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 yellow residue that was further purified by crystallization from dry THF to give white powder. Yield: 4 g (80%). Mp = 164-165 °C (DSC). ^{1}H NMR ($CDCl_3$, δ) 8.5 (s, 1H, Ar*H* of anthracene), 8.2 (d, 2H, Ar*H* of anthracene), 8.0 (d, 2H, Ar*H* of anthracene), 7.60-7.50 (m, 4H, Ar*H* of anthracene), 6.2 (s, 2H, C*H*$_2$-anthracene), 4.6 (d, 2H, CC*H*$_2$OC=O), 4.1 (d, 2H, CC*H*$_2$OC=O), 1.2 (s, 3H, C=OC(CH_2O)$_2$*CH*$_3$).

^{13}C NMR ($CDCl_3$, δ) 171.2 (Anth-CH_2O*C*=O), 147.4 (O*C*=OO), 131.3 (Ar*C* of anthracene), 131 (Ar*C* of anthracene), 129.7 (Ar*C* of anthracene), 129.2 (Ar*C* of anthracene), 127 (Ar*C* of anthracene), 125.2 (Ar*C* of anthracene), 124.8 (Ar*C* of anthracene), 123.4 (Ar*C* of anthracene), 72.9 (*C*H_2OC=OO), 60.7 (Anth-*C*H_2), 40.4 (*C*CH_2OC=O), 17.6 (C*C*H_3).

3.3.13 1-(3,5-bis(trifloromethyl)phenyl)-3-cyclohexylthiourea (TU) (9)

Cyclohexylamine (1.85 g, 18.5 mmol) was added dropwise at room temperature to a stirring solution of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (5.0 g, 19 mmol) in THF (20 mL). After the solution was stirred for 4 h, the solvent was evaporated. The white residue was recrystallized from hexane to give **10** as a white powder. Yield: 5.90 g (86%). ^{1}H NMR: δ = 7.52 (s, 1H, 5-ArH), 7.33 (s, 2H, 2,6-ArH), 6.50 (s, 1H, ArNH), 5.17 (s, 1H, CyNH), 4.40 (br 1H, NCyH), 2.03-0.86 (10H, CyH).

3.3.14 Preparation of pendant anthracene-functionalized polycarbonate (PC-Anth)

PC-Anth was prepared by ROP of Ant-Carbonate (1 g, 2.85 mmol) using both DBU (0.021 mL, 0.143 mmol) and **10** (0.053 g, 0.143 mmol) as catalyst and benzyl alcohol (0.015 mL, 0.143 mmol) as an initiator at room temperature for 5 h. The degassed monomer in CH_2Cl_2 (14 mL), catalyst, and initiator were added to a 25 mL 2-neck round bottom flask that had been flame-dried under vacuum and purged with argon. The tube was degassed with three freeze-pump-thaw (FPT) and left in vacumm. After the polymerization, the mixture was concentrated and precipitated into an excess amount of methanol at ambient temperature. Recovered polymer, redissolved in THF and precipitated in methanol/diethyl ether (1/1) then THF/methanol. It was isolated by filtration and dried at 40 ^{o}C in a vacuum oven for 24 h. ^{1}H NMR ($CDCl_3$, δ) 8.3 (br, Ar*H* of anthracene), 8.1 (br, Ar*H* of anthracene), 7.8 (bs, Ar*H* of anthracene), 7.4-7.2 (br, Ar*H* of anthracene and Ar*H* of Ph), 6.0 (bs, C*H*$_2$-anthracene), 5.0 (s, 2H, OC*H*$_2$-Ph) 4.1 (bs, C*H*$_2$OC=O of PC), 3.5 (br, 2H, C*H*$_2$OH, end-group of PC), 2.5 (br, 1H, CH_2O*H*), 1.0 (bs, C=OC(CH_2O)$_2$*CH*$_3$). $M_{n,theo}$ = 5600; $M_{n,GPC}$ = 3400, $M_{n,NMR}$ = 5950, M_w/M_n = 1.18 (relative to PS standards).

3.3.15 Diels-Alder click reaction of PC-Anth with 3

PC-Anth (0.100 g, 0.016 mmol, $M_{n,TD\text{-}GPC}$ = 6000) was dissolved in 20 mL of toluene. **3** (0.149 g, 0.416 mmol) in 10 mL of toluene was added to the solution. The mixture was bubbled with nitrogen for 30 minutes and refluxed for 24 h at 110 ^{o}C in the dark. After the specified time, solution was evaporated to dryness and the residual solid was dissolved in THF, and subsequently precipitated in methanol. This dissolution–precipitation procedure was repeated two times. The obtained product

was dried in a vacuum oven at 40 ^{o}C for 24 h. ^{1}H NMR ($CDCl_3$, δ), 7.6-7.0 (br, Ar*H*), 5.5 (bs, CH_2-Diels-Alder adduct), 5.0 (s, 2H, Ph-CH_2-O), 4.7 (s, C*H*, bridge head proton), 4.2 (bs, CH_2OC=O of PC), 3.8–3.4 (br, C=OOCH_2CH$_2$N and CH_2OH of PC), 3.4-3.2 (br, C=OOCH$_2$CH_2N and C*H*-C*H* bridge protons), 1.8 (s, CBr(CH_3)$_2$), 1.2 (bs, CH$_2$C(CH_3)CH$_2$).

3.3.16 Diels-Alder click reaction of PC-Anth with PMMA-MI

PC-Anth (0.050 g, 0.008 mmol, $M_{n,TD\text{-}GPC}$ = 6000, 1equiv) was dissolved in 20 mL of toluene. PMMA-MI (0.667 g, 0.208 mmol, $M_{n,NMR}$ = 3200, 25 equiv) in 10 mL of toluene was added to the solution. The mixture was bubbled with nitrogen for 30 minutes and refluxed for 36 h at 110 ^{o}C in the dark. After the specified time, solution was evaporated to dryness and the residual solid was dissolved in THF, and subsequently precipitated in methanol then methanol/diethyl ether (1/1, v/v) mixture. The obtained product was dried in a vacuum oven at 40 ^{o}C for 24 h. ^{1}H NMR ($CDCl_3$, δ) 7.6-7.0 (br, Ar*H*), 5.5 (br, CH_2-Diels-Alder adduct), 4.7 (bs, C*H*, bridge head proton), 4.2 (bs, CH_2OC=O of PC), 3.8–3.0 (m, OCH_3 of PMMA, C=OOCH_2CH$_2$N, C=OOCH$_2$CH_2N, and C*H*-C*H* bridge protons), 2.2-0.6 (CH_2 and CH_3 of PMMA).

3.3.17 Diels-Alder click reaction of the PC-Anth with PEG-MI

PC-Anth (0.100 g, 0.016 mmol, $M_{n,TD\text{-}GPC}$ = 6000, 1equiv) was dissolved in 20 mL of toluene. PEG-MI (0.350 g, 0.416 mmol, $M_{n,theo}$ = 840, 25 equiv) in 10 mL of toluene was added to the solution. The mixture was bubbled with nitrogen for 30 minutes and refluxed for 36 h at 110 ^{o}C in the dark. After the specified time, solution was evaporated to dryness and the residual solid was dissolved in THF, and subsequently precipitated in methanol. This dissolution–precipitation procedure was repeated two times. The obtained product was dried in a vacuum oven at 40 ^{o}C for 24 h. ^{1}H NMR ($CDCl_3$, δ) 7.6-7.0 (br, Ar*H*), 5.5 (br, CH_2-Diels-Alder adduct), 4.7 (bs, C*H*, bridge head proton), 4.2 (bs, 4H, CH_2OC=O of PC and C=OOCH_2CH$_2$), 3.8–3.0 (m, OCH_2CH_2, PEG repeating unit, C=OOCH_2CH$_2$N, C=OOCH$_2$CH_2N, OCH_3 end-group of PEG and C*H*-C*H* bridge protons), 2.6 (br, C=OCH_2CH_2C=O) , 1.2 (bs, CH$_2$C(CH_3)CH$_2$).

3.3.18 Diels-Alder click reaction of the PC-Anth with PMMA-MI and PEG-MI

PC-Anth (0.100 g, 0.016 mmol, $M_{n,TD\text{-}GPC}$ = 6000, 1equiv) was dissolved in 10 mL of toluene. PMMA-MI (0.800 g, 0.249 mmol, $M_{n,NMR}$ = 3200, 15 equiv) and PEG-MI (0.210 g, 0.249 mmol mmol, $M_{n,\ theo}$ =840, 15 equiv) in 20 mL of toluene was added to the solution. The mixture was bubbled with nitrogen for 30 minutes and refluxed for 36 h at 110 ^{o}C in the dark. After the specified time, solution was evaporated to dryness and the residual solid was dissolved in THF, and subsequently precipitated in methanol then methanol/diethyl ether (1/1, v/v) mixture. The obtained product was dried in a vacuum oven at 40 ^{o}C for 24 h. ^{1}H NMR ($CDCl_3$, δ) 7.6-7.0 (br, Ar*H*), 5.5 (br, CH_2-Diels-Alder adduct), 4.7 (bs, C*H*, bridge head proton), 4.2 (bs, CH_2OC=O of PC and C=OOCH_2CH$_2$), 3.8–3.0 (m, OCH_2CH_2, PEG repeating unit, OCH_3 of PMMA, C=OOCH_2CH$_2$N, C=OOCH$_2$CH_2N, OCH_3 end-group of PEG and C*H*-C*H* bridge protons), 2.5 (br, 4H, C=OCH_2CH_2C=O), 2.2-0.6 (CH_2 and CH_3 of PMMA).

3.3.19 Diels-Alder click reaction of PC-Anth with PS-MI

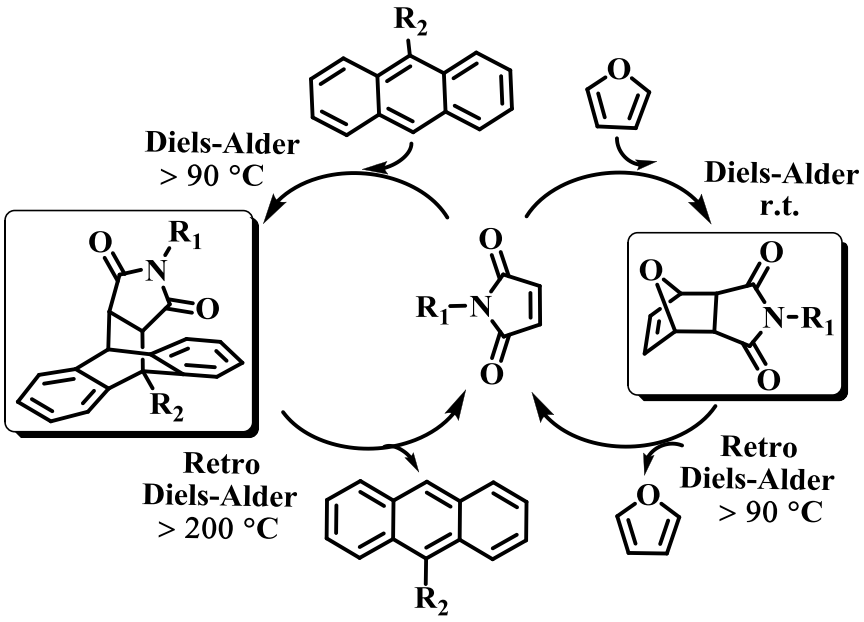
PC-Anth (0.050 g, 0.008 mmol, $M_{n,TD\text{-}GPC}$ = 6000, 1 equiv) was dissolved in 10 mL of toluene. PS-MI (1.083 g, 0.208 mmol, $M_{n,GPC}$ = 5200, 25 equiv) in 20 mL of toluene was added to the solution. The mixture was bubbled with nitrogen for 30 minutes and refluxed for 36 h at 110 ^{o}C in the dark. After the specified time, solution was evaporated to dryness and the residual solid was dissolved in THF, and subsequently precipitated in methanol/diethyl ether (1/3, v/v) mixture then in methanol. The obtained product was dried in a vacuum oven at 40 ^{o}C for 24 h. ^{1}H NMR ($CDCl_3$, δ) 7.8 (br, C*H* of triazole), 7.5–6.2 (Ar*H* of PS), 5.4 (br, CH_2-Diels-Alder adduct), 5.0 (br, C*H*(Ph)-triazole, end group of PS), 4.7 (br, C*H*, bridge head proton), 4.2 (br, CH_2OC=O of PC), 3.9-3.0 (m, NCH$_2$CH_2OC=O, CH$_3$CH_2O, NCH_2CH$_2$OC=O, C*H*-C*H* and bridge protons), 2.7 (br, triazole-CH_2CH$_2$C=O), 2.4 (br, triazole-CH$_2$CH_2C=O), 2.2-0.6 (CH_2 and CH_3 of PS).

4. RESULTS AND DISCUSSION

The synthesis of polymers with well-defined compositions, architectures, and functionalities has long been of great interest in polymer chemistry. Typically, living ionic polymerization techniques have been employed where the polymerizations proceed in the absence of irreversible chain transfer and chain termination [1,2]. The development of C/LRP methods has been a long-standing goal in polymer chemistry, since a radical process is more tolerant of functional groups and impurities and is the leading industrial method to produce polymers. Recent advances in C/LRP techniques have facilitated access to polymers with complex architectures, and precisely positioned functional groups [3,4].

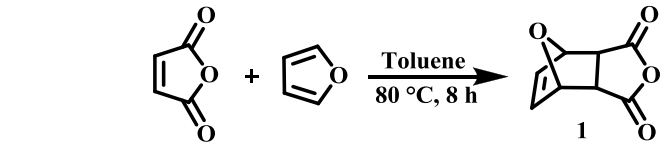
Polymer-polymer conjugation is often the only viable means to prepare complex chain topologies with the assist of efficient synthetic organic chemistry. Click reactions, as coined by Sharpless [5], are highly efficient and specific reactions, have emerged as a powerful tool for polymer chemists in order to build such architectures. In fact, CuAAC click reaction has drawn a particular interest for this purpose and extensively been used either in synthetic organic chemistry or in polymer chemistry. In addition, our group's recent studies have proved that the DA reactions are also the convenient way to prepare polymers with well-defined topologies (*vide infra*). Undoubtedly, DA reactions have many attractive features for polymer chemists, but the unique one is its thermo responsive behavior. This feature has been utilized in polymer science as a method for producing reversible cross-linked gels [6-12], polymers featuring self-healing abilities [13-19], dendrimers [20-22], and even as a polymerization technique itself [23-28]. However, the utilization of DA reaction by the combination of C/LRP methods for polymer-polymer conjugation remained as a *virgin* area until our works. The reason behind this fact lies in the radical sensitivity of the double bonds of both dienes and dienophiles. Therefore, radicals produced in C/LRP inevitably add to these bonds. In order to prevent such an addition, protection-deprotection methods have been developed and utilized particularly for bioconjugation of the well-defined polymers [29,30,31].

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 in reaction (4.1).

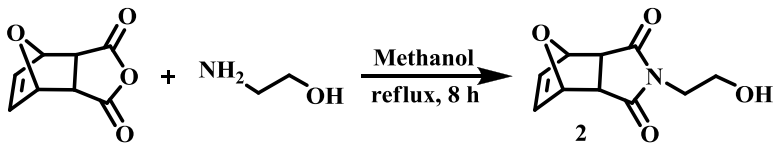


(4.1)

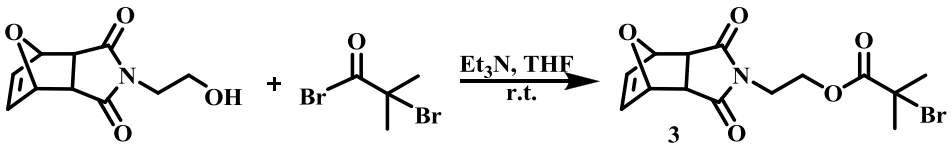
The initiator with proper functionality for Diels-Alder reaction was first prepared. The synthesis of 2-bromo-2-methyl-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-en-4-yl) ethyl ester**, 3** consists mainly of three steps. In the first step, furan and maleic anhydride were reacted in toluene at 80 ºC, and thus obtained adduct **1,** (4.2), was utilized for the synthesis of **2** by adding the solution 2-amino ethanol in methanol into dispersion of **1** in methanol, (4.3). Finally, **3**, was obtained via an esterification reaction between **2** and 2-bromoisobutryl bromide in THF at room temperature (4.4).



(4.2)



(4.3)



(4.4)

From overlay ^{1}H NMR spectra (Figure 4.1) of 3, 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.

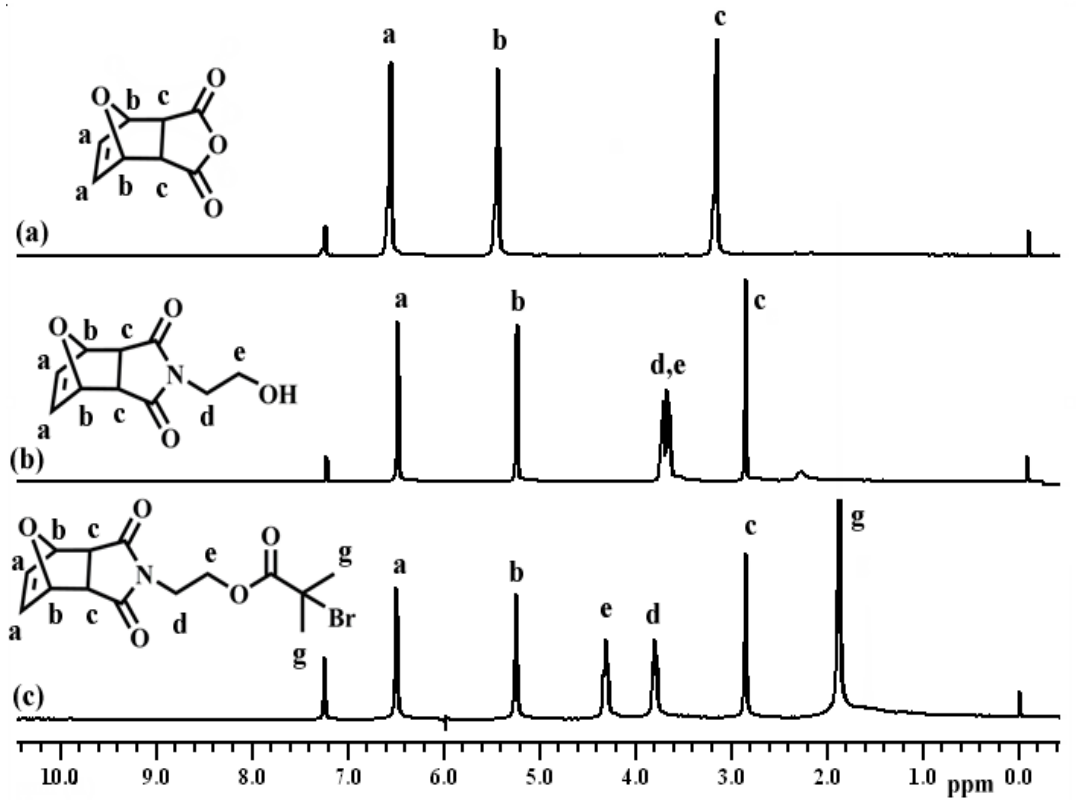
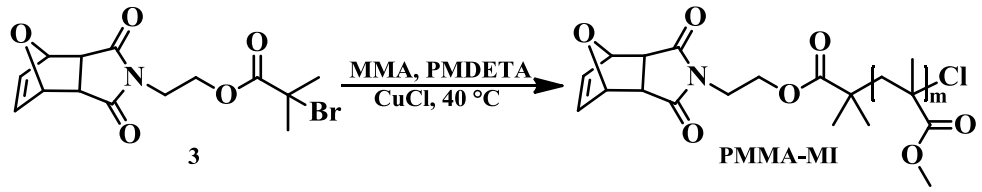


Figure 4.1 : ^{1}H NMR spectra of a) 4,10-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (1); b) 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (2); c) 2-bromo-2-methyl propionic acid 2-(3,5-Dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl) ethyl ester (3) in $CDCl_3$.

Then compound **3** was used as an initiator in ATRP of MMA in the presence of CuCl/PMDETA as a catalyst system at 40 ºC to obtain MI-PMMA as one of the graft chains (4.5). The maleimide functional group of the **3** was protected with furan in order to prevent radical copolymerization of maleimide with MMA during polymerization. The polymerization temperature was deliberately kept low avoiding furan deprotection at elevated temperatures.



(4.5)

The join of the MI to the PMMA was easily monitored by ^{1}H NMR (Figure 4.2). The $M_{n,NMR}$ of PMMA-MI ($M_{n,NMR}$=3200 g/mol) was calculated from a ratio of integrated peaks at 3.58 ppm (OCH_3 protons of MMA) to 6.5 ppm (vinyl end protons) and molecular weight of **3** (357 g/mol) was added to this value.

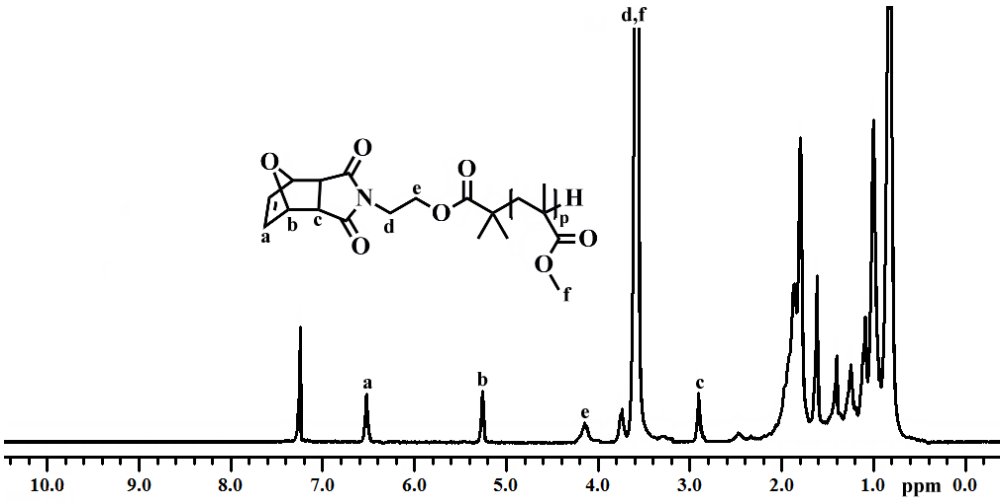
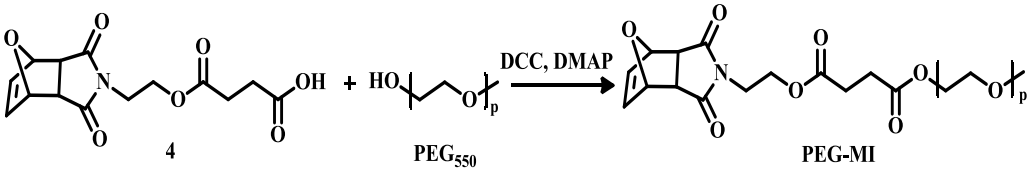


Figure 4.2 : ^{1}H NMR spectra of PMMA-MI in $CDCl_3$.

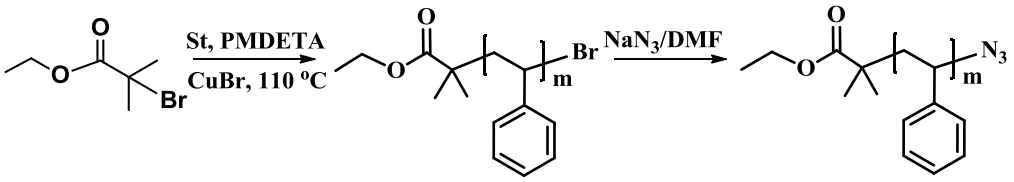
The number-average molecular weight calculated by GPC ($M_{n,GPC}$=3100 g/mol, relative to linear PMMA standards) is in fairly good agreement with $M_{n,NMR}$ indicating that the initiations were not quantitative under these polymerization conditions. Moreover, M_w/M_n = 1.31 calculated from GPC displays narrow molecular weight distribution.

Next, PEG-MI was obtained after esterification reaction between **4** and Me-PEG (550) (4.6). From ^{1}HNMR spectrum of the polymer, the bridge and bridge-head protons were detected at 6.5, 5.25 and 2.87 ppm respectively. The $M_{n,NMR}$ ($M_{n,NMR}$ = 750 g/mol) of PEG-MI was determined from a ratio of integrated peaks at 3.62 ppm (OCH_2CH_2 protons of PEG) to 6.5 ppm (vinyl end protons).



(4.6)

Then, azide end-functionalized PS (PS-N_3) was prepared in two steps by succesive reaction (4.7). PS was obtained via ATRP and then bromide-end of PS converted to azide in the presence of NaN_3/DMF at room temperature.



(4.7)

The structure of PS-N_3 was further supported by the observation of the azide stretching band at 2094 cm^{-1} from FT-IR spectrum.

Azide functional PS was converted then the PS-MI via click reaction between PS-N_3 and **5** using PMDETA/CuBr catalyzing system in DMF. $M_{n,NMR}$ of PS-MI was shown at 6.0-7.5 ppm (Figure 4.3).

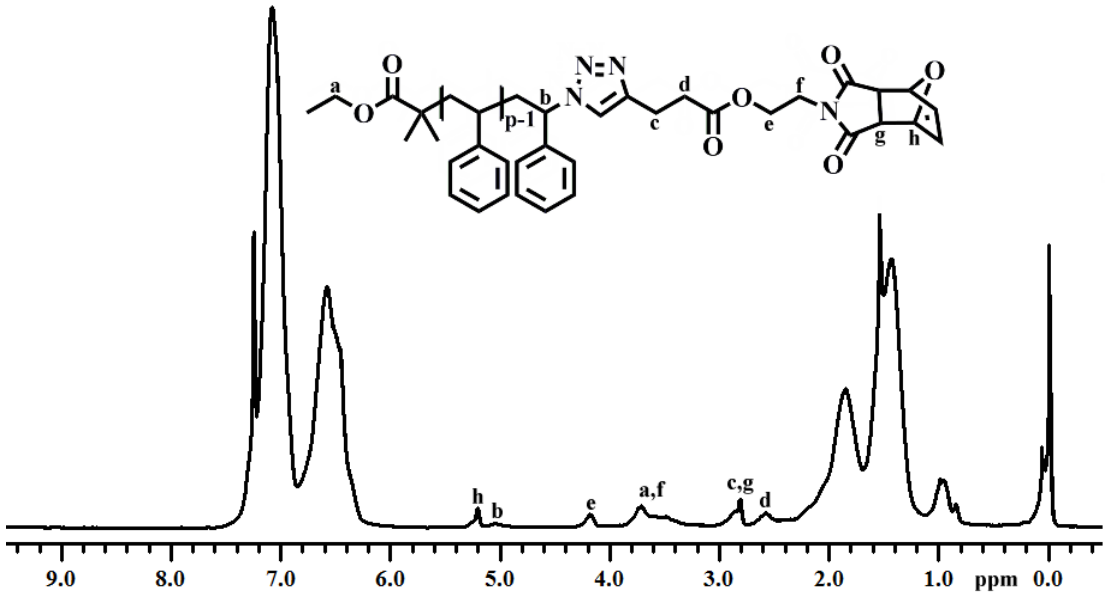


Figure 4.3 : ^{1}H NMR spectrum of PS-MI in $CDCl_3$.

$M_{n,NMR}$ values were consistent with those of the $M_{n,GPC}$ (Table 4.1). From Table 4.1, It was found good agreement between $M_{n,theo}$ $M_{n,NMR}$ and $M_{n,GPC}$ values.

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

Polymer	$M_{n,GPC}$ (g/mol)	M_w/M_n	$M_{n,theo}$[d] (g/mol)	$M_{n,NMR}$ (g/mol)
MI-PS[a]	5200	1.07	5300[d]	-
MI-PMMA[b]	3100	1.31	2100[d]	3200
MI-PEG[c]	550	1.09	840[e]	860

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

[b] $[M]_0:[I]_0:[CuCl]:[PMDETA] = 50:1:1:1$; polymerization was carried out at 40 ^oC. MMA / toluene = 1 (v/v).

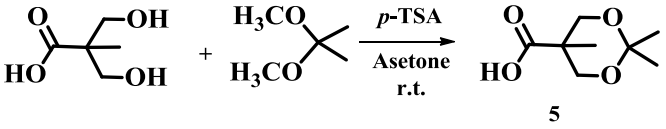
[c] Obtained by an esterification reaction between compound **4** and Me-PEG (550).

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

[e] $M_{n,theo}$ = M_n of Me-PEG (550) + MW of **4**

4.1 Synthesis of Initiators

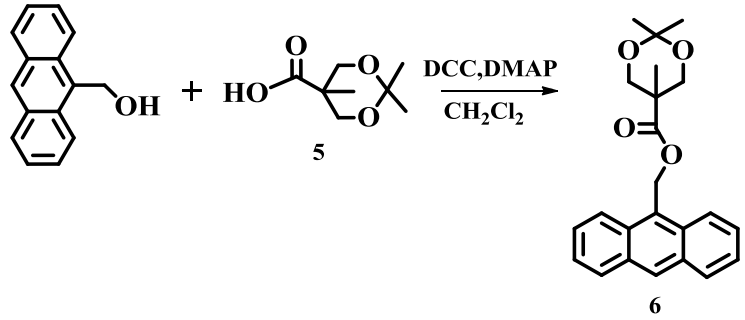
First of all 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid **(5)** was synthesized by this way; 2, 2-bis (hydroxymethyl)-propanoic acid was reacted with excess amount of dry acetone using *p*-toluene sulfonic acid as catalyst. Additionally, 2,2-dimethoxy-propane was deliberately used to provide acetone during the reaction. Process is given below schematically (4.8).



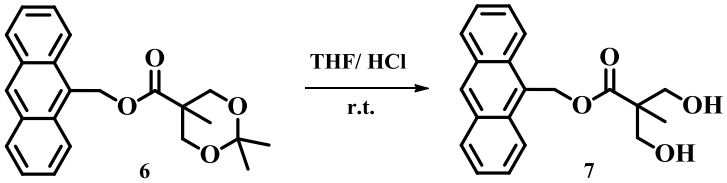
5 **(4.8)**

After that, esterification reaction of anthracen-9-ylmethanol and 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid was prepared to synthesize **6** (anthracen-9-ylmethyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate) by catalyzing DCC and DMAP in CH_2Cl_2 at room temperature overnight (4.9).

Next, (anthracen-9-ylmethyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate) **6** was hydrolized in THF by adding HCl solution stirring for 2 hours at room temperature. Thus, anthracen-9-ylmethyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate **7** was obtained (4.10).



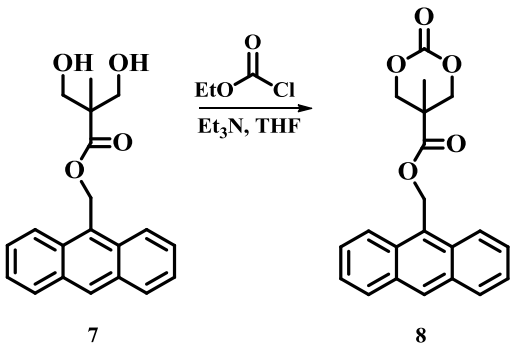
(4.9)



(4.10)

^{1}H NMR spectroscopy confirmed clearly the structure of **7** by appearance of characteristic signals of anthracene (δ 8.5 – 7.5) . It is obviously seen that the peak of methylene protons neighbouring to hydroxyl group is between 3.63 and 3.85 ppm.

In the following step, Anth-carbonate monomer (anthracen-9-ylmethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate) was synthesized (4.11). The cyclization was performed in the presence of ethyl chloroformate in dilute anhydrous THF solution via dropwise addition of triethylamine.



(4.11)

^{1}H NMR spectroscopy confirmed clearly the structure of **8** by appearance of characteristic signals of anthracene (δ 8.5-7.5). The double doublets at δ 4.10/4.66 were attiributable to the methylene protons next to the carbonate. Importantly, no peak at δ 3.63-3.85 assignable to the methylene protons adjacent to the hydroxyl group was detected. The ^{1}H NMR and elemental analysis of Anth-carbonate showed similar outcome (Figure 4.4).

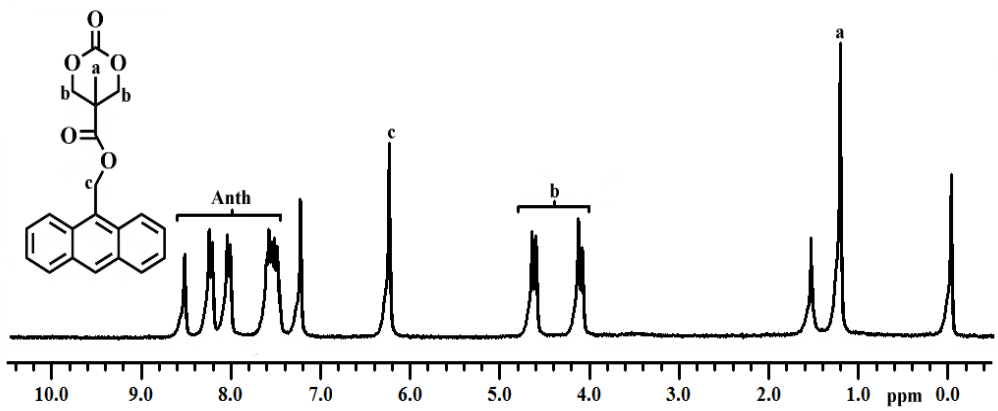


Figure 4.4 : ^{1}H NMR spectrum of Anth-Carbonate in $CDCl_3$.

In addition, ^{13}C NMR spectroscopy indicated a peak at 147.4 ppm that proved the cyclic carbonate formation (Figure 4.5).

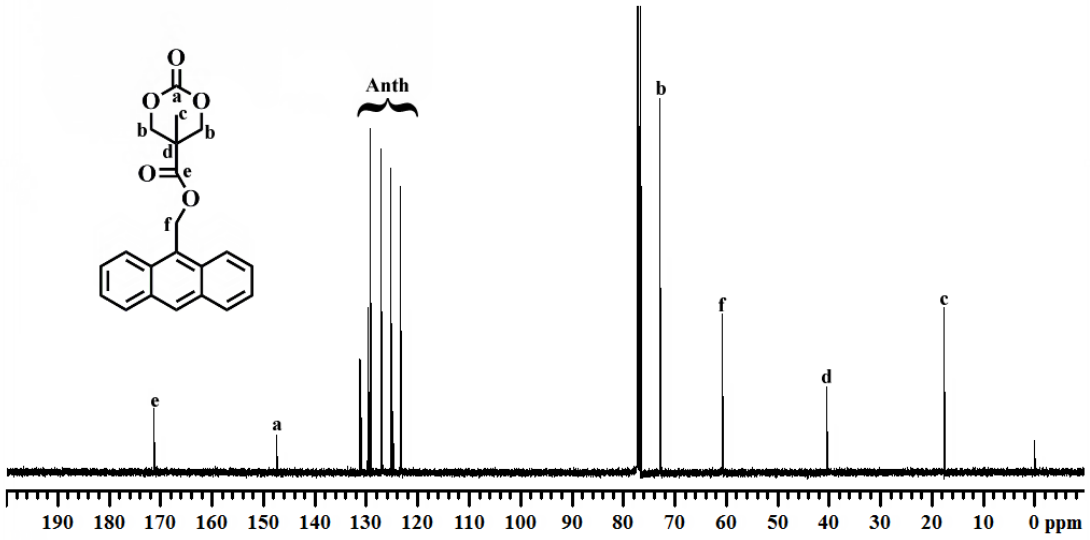
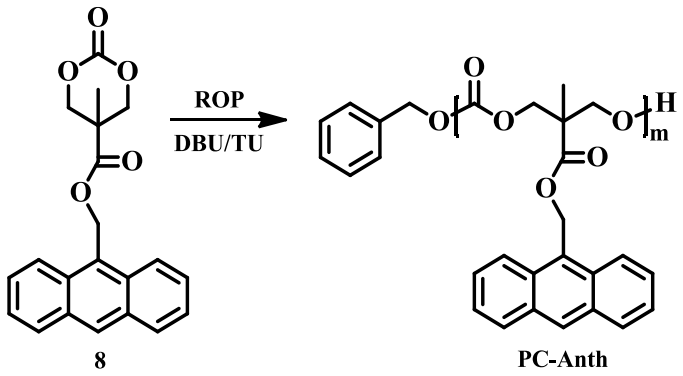


Figure 4.5 : ^{13}C NMR spectroscopy of Anth-Carbonate in $CDCl_3$.

4.2 Preparation of the Graft Copolymers via Combination of ROP and DA Click Reaction

Well-defined anthracene-functional poly(carbonate), PC-Anth, was synthesized via organocatalytic ring-opening polymerization of **8** (anthracen-9-ylmethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate) in CH_2Cl_2 using the dual 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea and DBU catalyst system at room temperature overnight (4.12)**.** It is shown from the GPC and ^{1}H NMR (Figure 4.6) results that the PC-Anth was properly prepared with controlled molecular weight, low polydispersity index (PDI) and desired anthracene pendant groups.



(4.12)

The number average theoretical molecular weight ($M_{n,theo}$ =5600), which did not match with the number-average molecular weight by conventional GPC ($M_{n,GPC}$ = 3400) relative to linear PS standards was comparable to that obtained from three detection GPC.

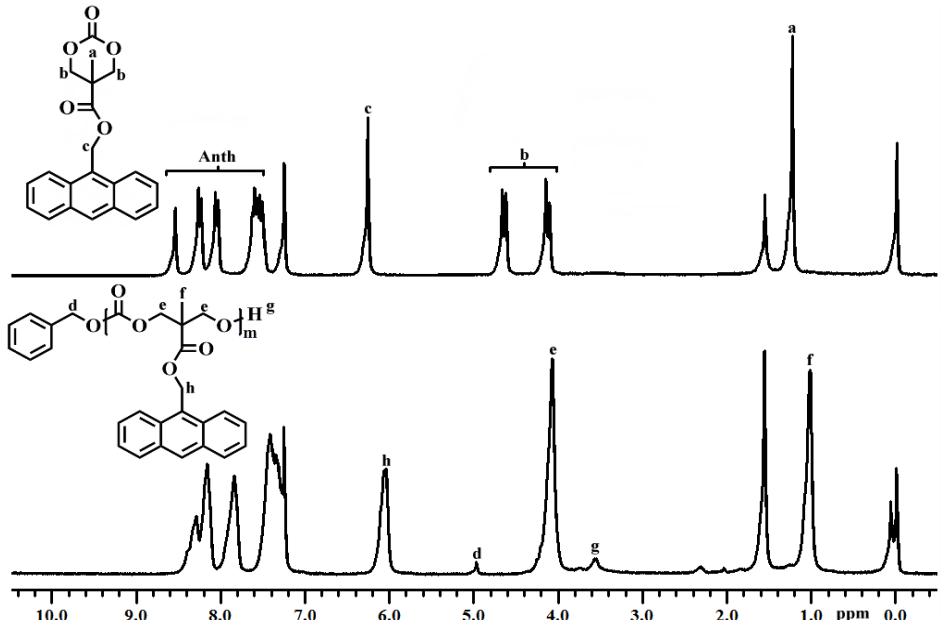


Figure 4.6 : Comparison of the ^{1}H NMR spectra of Anth-Carbonate and PC-Anth in $CDCl_3$.

Absolute molecular weight ($M_{w,TDGPC}$ = 6200) of PC-Anth was measured by using TD-GPC in THF at 35℃, after an introducing the experimentally derived d*n*/d*c* (0.190 mL/g) value into the software.

A model reaction was carried out to evaluate the efficiency of DA reaction before the synthesis of graft copolymers. For this purpose, both maleimide fuctional initiator (3) and PC-Anth were reacted at reflux temperature of toluene in the dark for 36 h. PC-g-model was obtained in a quantitative yield after purification. DA adduct formation

was also monitored by UV spectroscopy by following the disappearance of characteristic five-finger absorbance of Anth-PC at 300-400 nm (Figure 4.7).

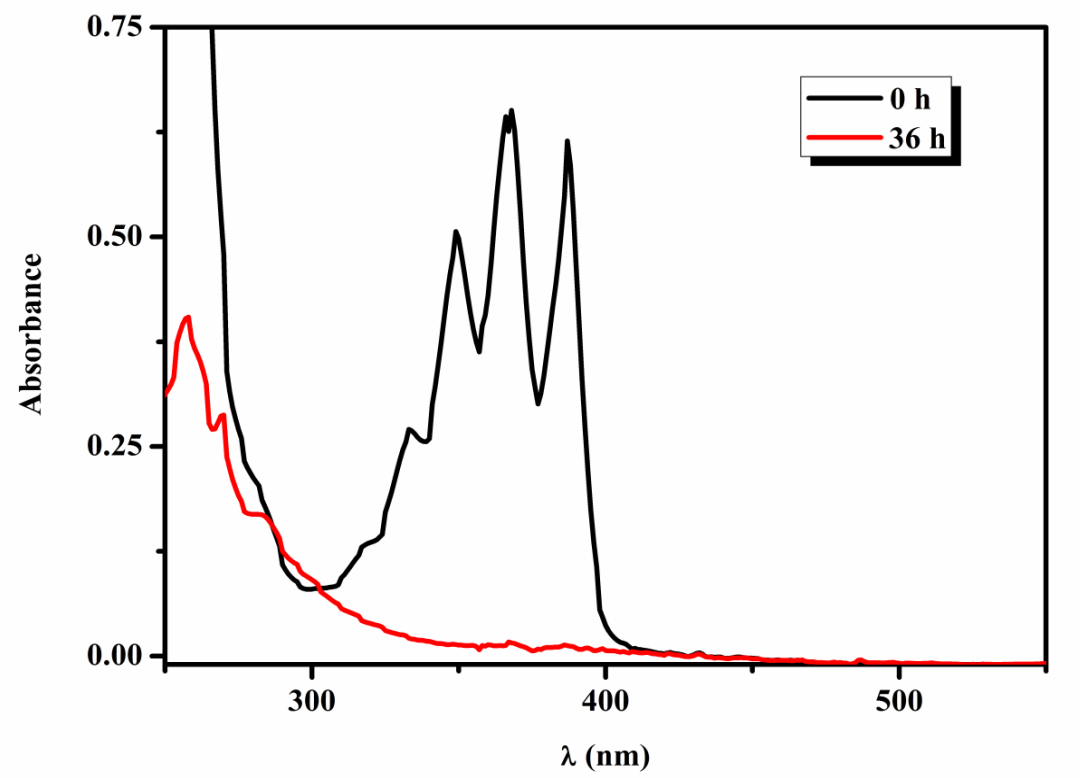


Figure 4.7 : UV spectra of PC-Anth during the synthesis of PC-*g*-model in CH_2Cl_2.

The structure of PC-*g*-model was identified by GPC and ^{1}H NMR. The complete disappearance of aromatic protons of anthracene between 8.5-7.5 ppm. Moreover, new peaks corresponding to C*H*$_2$ protons adjacent to new adduct and a bridgehead proton (C*H*) of the compound were primarily detected at 5.5 ppm and 4.7 ppm, respectively (Figure 4.8). Thus, confirmed structure of PC-*g*-Model proves DA click reaction having a potential in the preparation of graft copolymers.

Additionaly, GPC traces indicates that the PC-*g*-model shifts through the high molecular weight region (Figure 4. 9).

After that, DA click reaction was carried out between PC-Anth and PMMA-MI, PEG-MI, PS-MI or PMMA-MI/PEG-MI mixture in toluene for 36 hours.

In the case of PC-*g*-PMMA polymer (4.13), the DA efficiency was found to be quantitative (98%) from the UV measurement with a ratio of final absorbance at 36 h and initial absorbance.

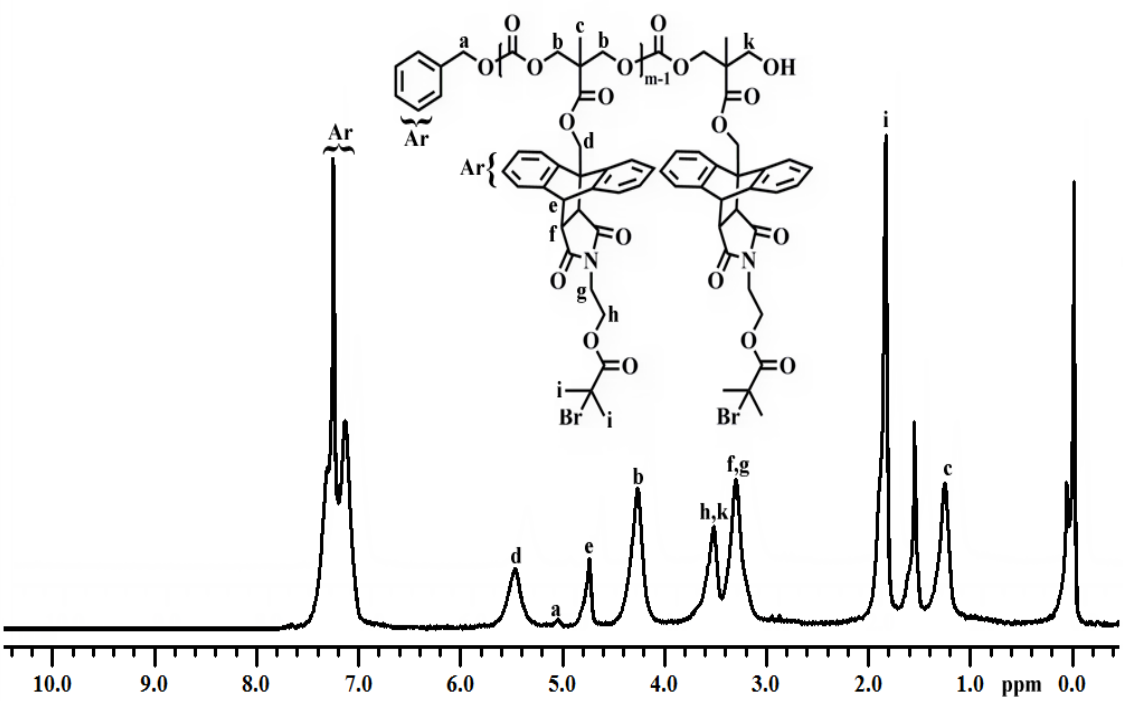


Figure 4.8 : ^{1}H NMR spectrum of model reaction between 3 and PC-Anth in $CDCl_3$

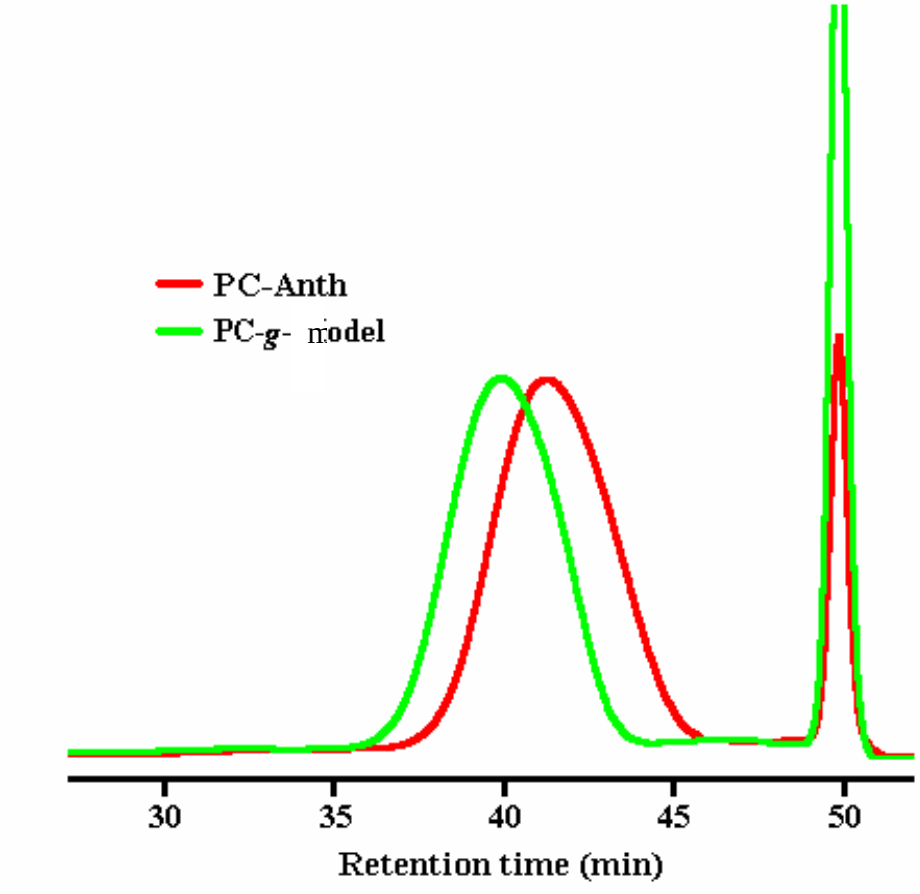
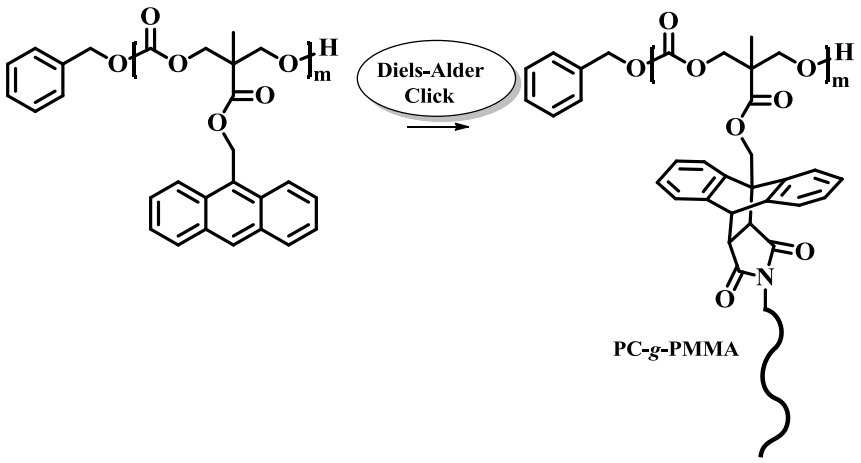


Figure 4.9 : Evolution of GPC traces of PC-*g*-model and its precursor in THF at 30 °C



(4.13)

After purification, a clear shift to higher molecular weight region was observed from GPC measurement without tail or shoulder proved the formation of graft copolymer (Figure 4.10).

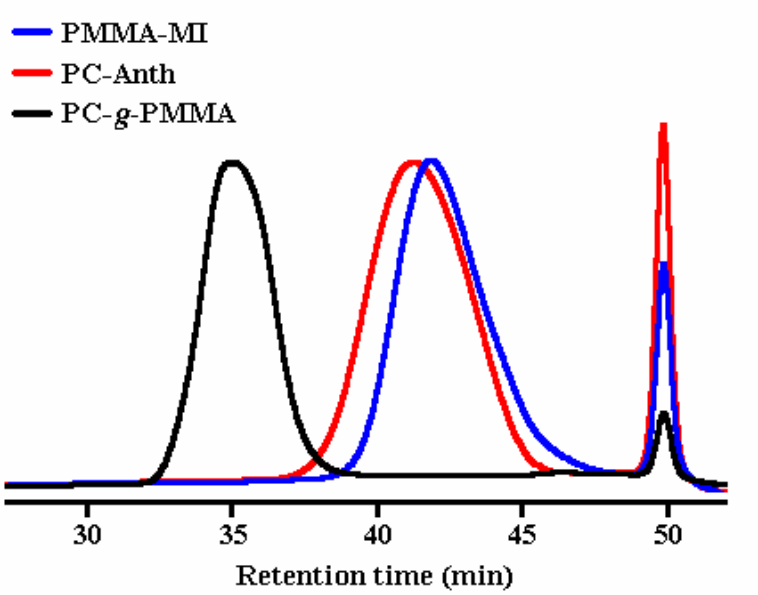


Figure 4.10 : GPC traces of PMMA-MI, PC-Anth and PC-*g*-PMMA in THF at 30 °C

From ^{1}H NMR spectra of the PC-*g*-PMMA polymer, it was observed that the peaks between 8.3-7.4 ppm corresponding to aromatic protons of anthracene were disappeared due to the cycloaddition and only multiplet peaks for the phenyl rings remained in the range of 7.4-7.0 ppm (Figure 4.11). Additionally, methylene protons next to cycloadduct were detected at 5.5 ppm and the bridge-head proton at 4.77 ppm confirmed the graft copolymer formation.

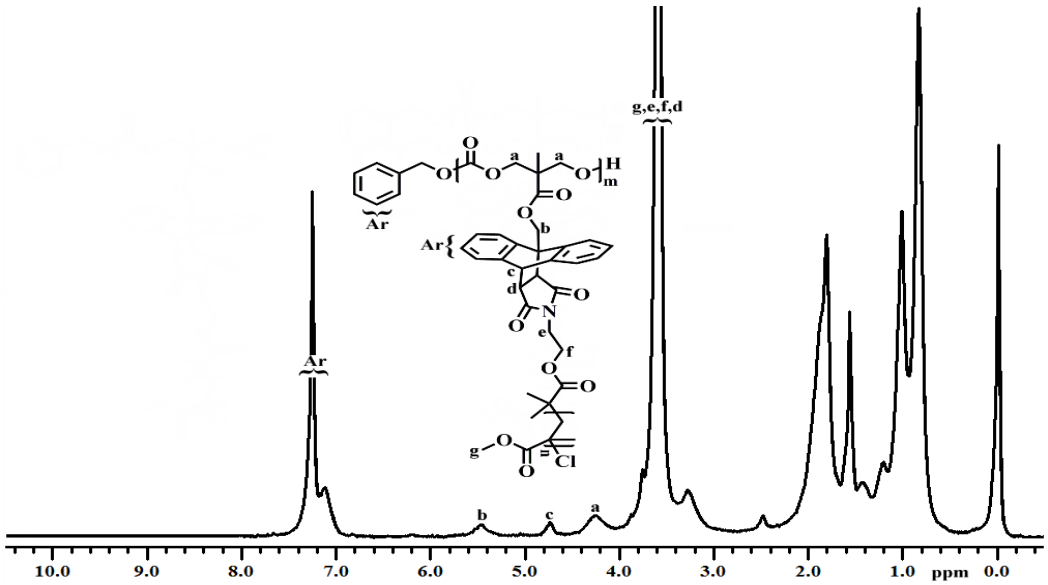
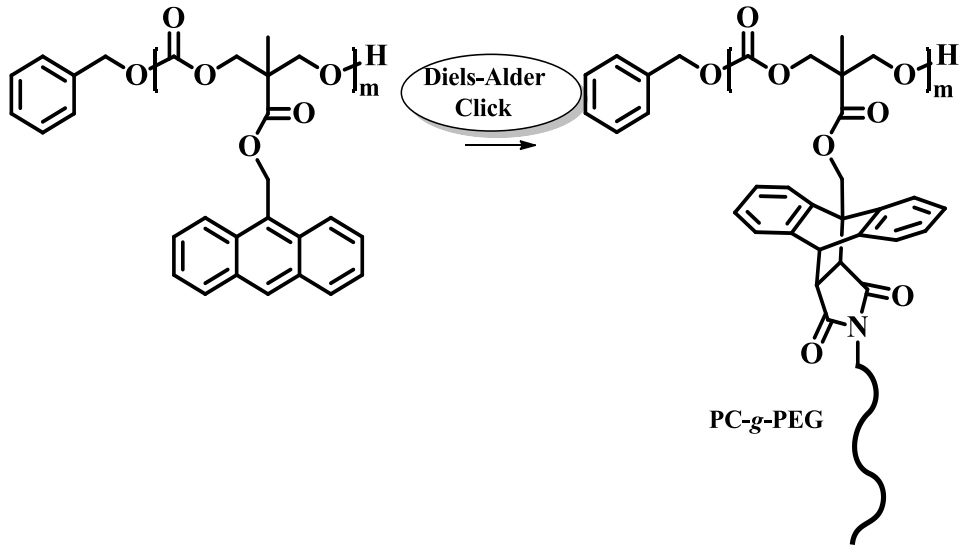


Figure 4.11 : ^{1}H NMR spectrum of PC-*g*-PMMA in $CDCl_3$

As a second example of graft copolymers, PC-*g*-PEG was synthesized via DA click reaction (4.14). The efficiency of DA reaction was found to be 98% after 36 h. Since PEG is soluble in methanol, PC-*g*-PEG polymer was easily purified by precipitation in methanol after DA click reaction. Unimodal curve without low molecular weight tail indicated that quantitative purification of resulting graft copolymer was achieved. Moreover, due to the adsorption of the PEG segment caused a small shift of graft copolymer to higher molecular weight region in GPC measurement (Figure 4.12).

In addition to the complete disappearance of anthracene protons, the join of the maleimide to the anthracene ring was easily monitored by ^{1}H NMR.



(4.14)

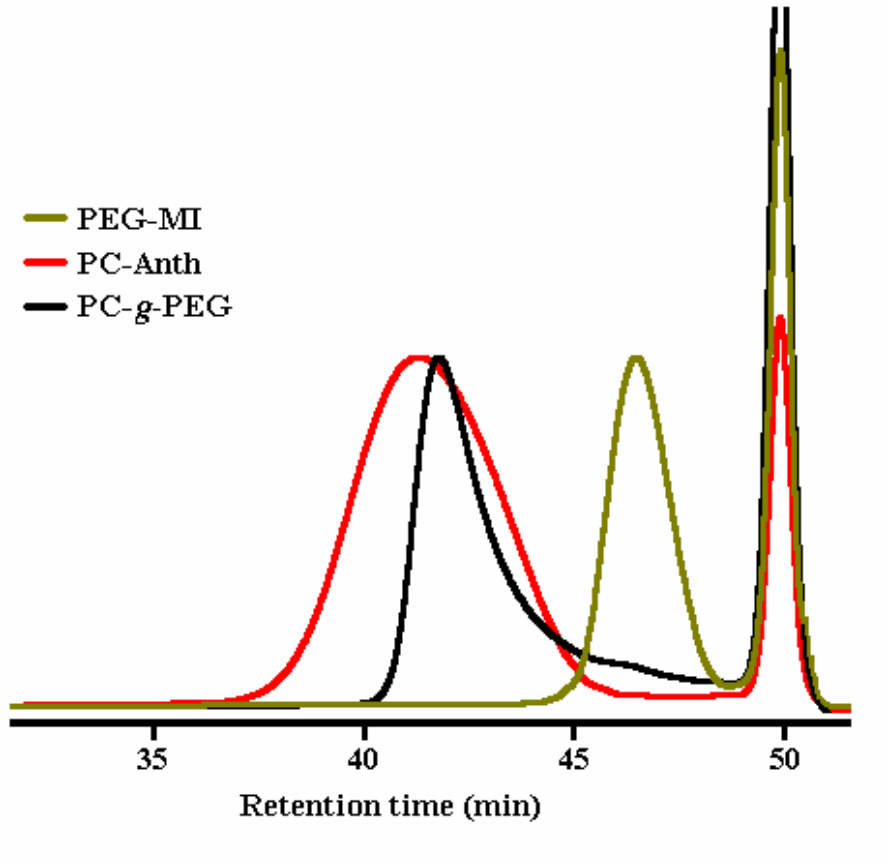


Figure 4.12 : GPC traces of PEG-MI, PC-Anth and PC-*g*-PEG in THF at 30 ^{o}C

As shown in ^{1}H NMR spectra (Figure 4.13), the peaks corresponding to bridge protons (6.5 and 2.9 ppm) and bridge-head protons (5.2 ppm) of PEG-MI completely disappeared. Moreover, new peak for bridge head proton of the cycloadduct was detected at 4.7 ppm.

Additionally, good correlation between $M_{n,theo}$ and $M_{n,GPC}$ values was found for PC-*g*-PEG (Table 4.2). These results signified successful synthesis of structurally well-defined graft copolymer.

Subsequently, PC-*g*-PEG/PMMA polymer was prepared via DA click reaction of PC-Anth and PEG/PMMA mixture (4.15).

As shown in the GPC traces, PC-*g*-PMMA/PEG polymer shifts through the high molecular weight region and PEG-MI has a smaller molecular weight than the PMMA-MI (Figure 4.14).

According to the characteristic integration peaks of the ^{1}H NMR spectrum, PC-*g*-PEG/PMMA polymer consists of 8.5 units of PMMA polymer and 7.5 units of PEG polymer (Figure 4.15).

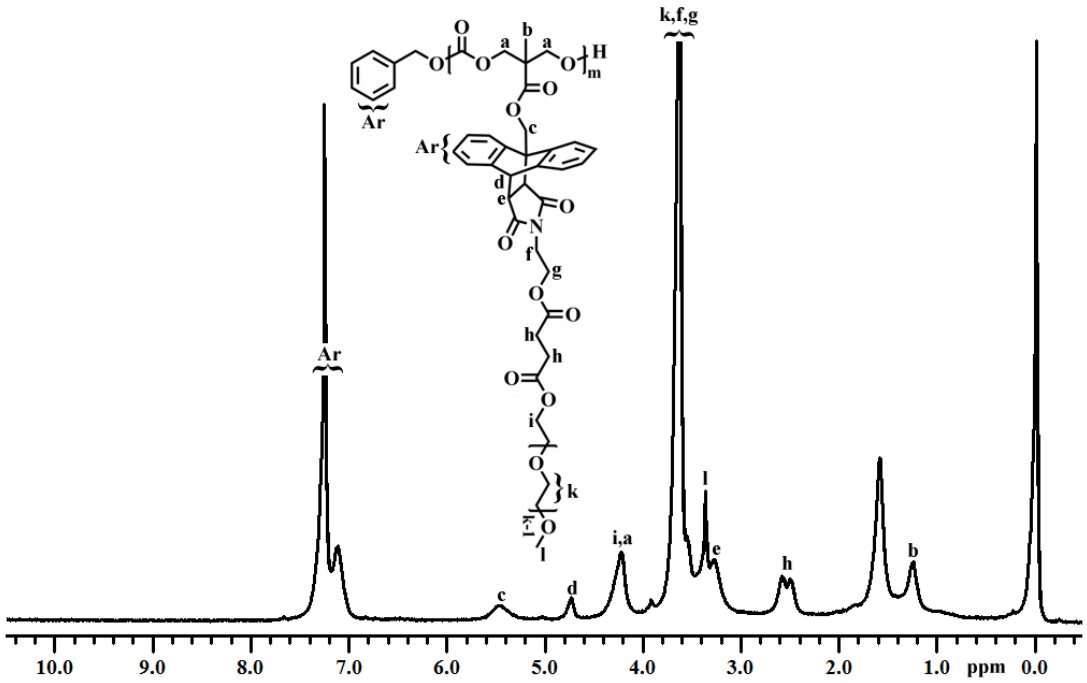
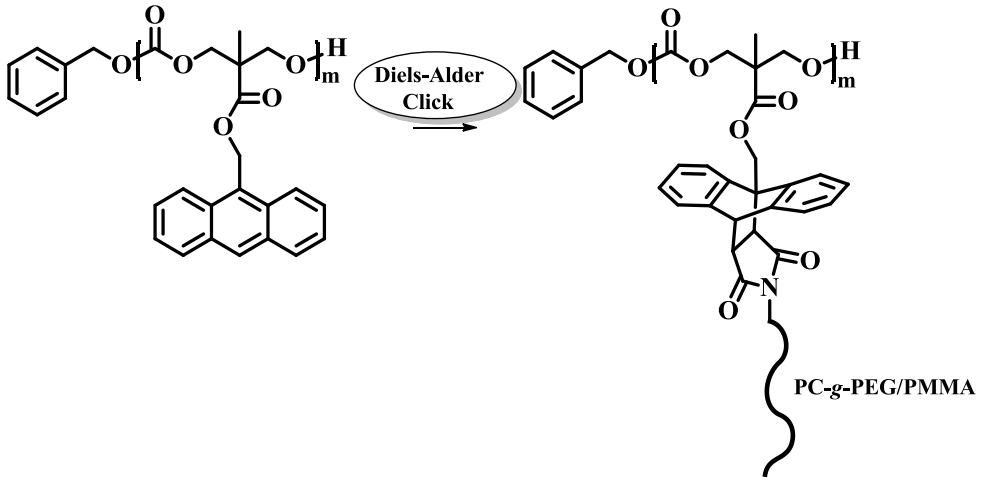


Figure 4.13 : ^{1}H NMR spectra of PC-*g*-PEG in $CDCl_3$.



(4.15)

Finally, PC-*g*-PS polymer was prepared using similar reaction strategy (4.16). In the case of PC-*g*-PS polymer, the DA efficiency was found to be quantitative (95%) from the UV measurement.

After purification, a clear shift to higher molecular weight region was observed from GPC measurement without tail or shoulder proved the formation of graft copolymer (Figure 4.16).

Moreover, the aromatic protons of styrene present on each repeating unit was detected at 6.5-7.5 ppm (Figure 4.17).

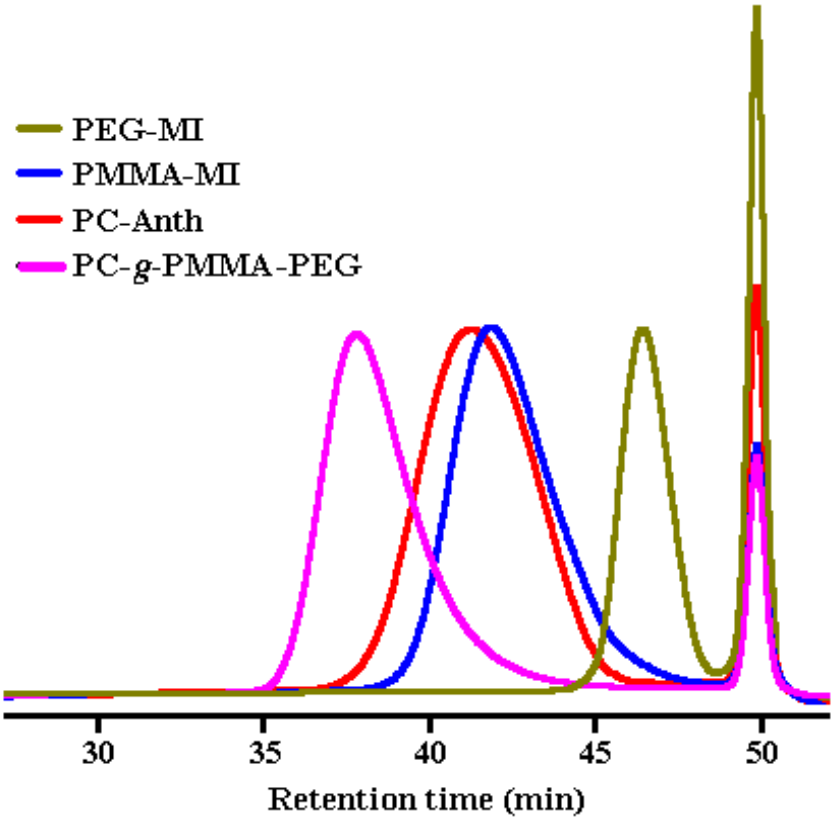


Figure 4.14 : GPC traces of PEG-MI, PMMA-MI, PC-Anth and PC-*g*-PMMA/PEG in THF at 30 ℃

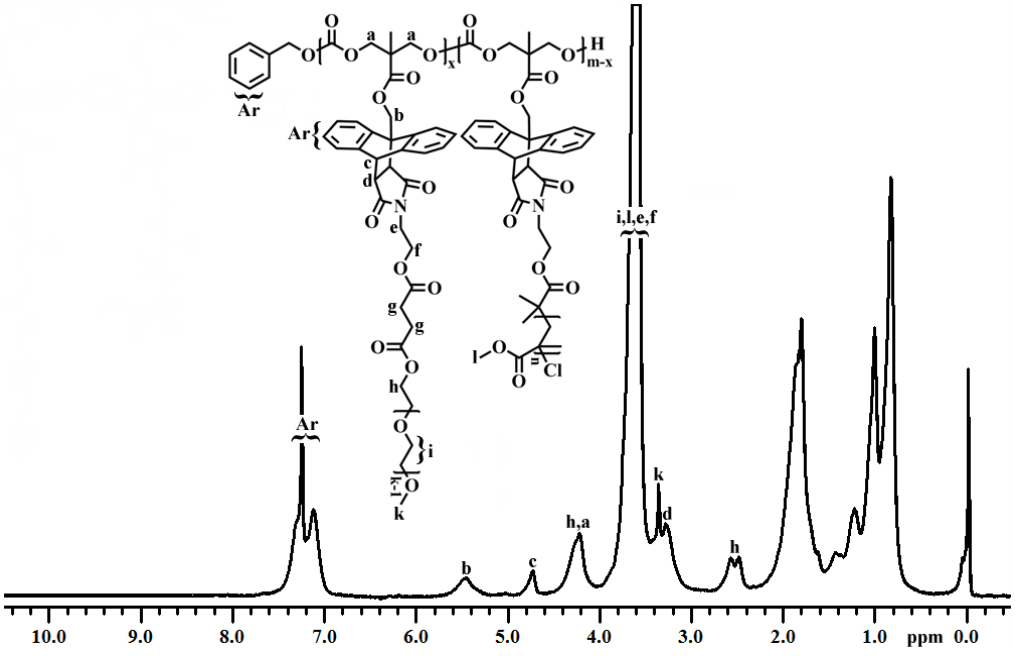
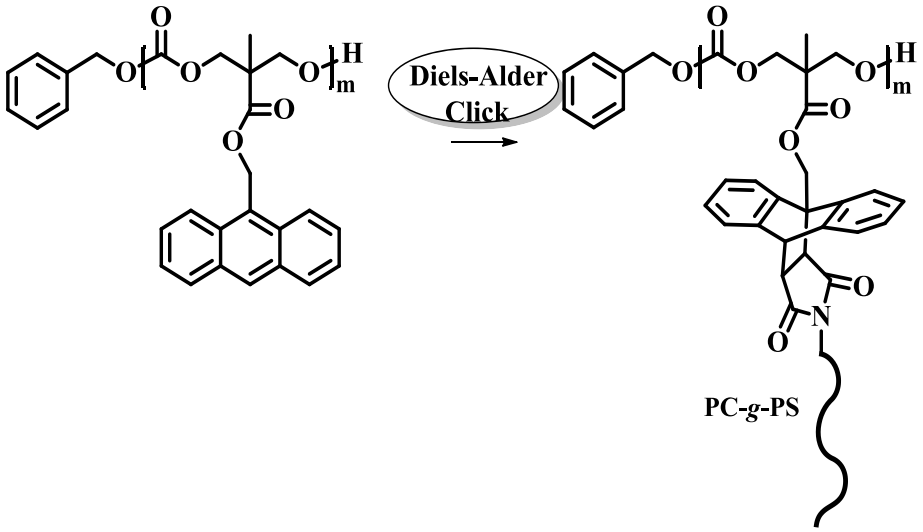


Figure 4.15 : ^{1}H NMR spectrum of PC-*g*-PMMA/PEG polymer in $CDCl_3$

The glass transition temperature (T_g) of graft copolymers were measured by DSC at a heating rate of 10 ^{o}C/min under nitrogen atmosphere. As demonstrated in Figure 4.18, T_g for PEG segment of graft copolymer was the shortest compared to those of

PS and PMMA. Two Tg values were an evident at -26 ^{o}C and 90 ^{o}C corresponding to the PEG/PMMA segments for PC-*g*-PMMA/PEG.



(4.16)

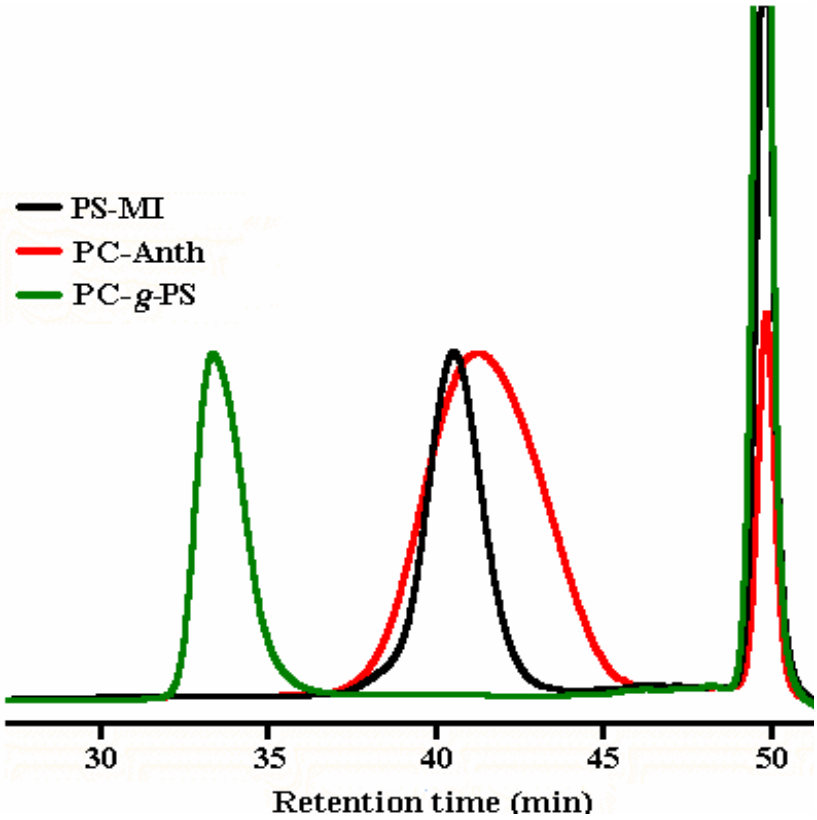


Figure 4.16 : GPC traces of PS-MI, PC-Anth and PC-*g*-PS in THF at 30 ^{0}C

Additionally, d*n*/dc values for all graft copolymers were calculated experimentally from a slope of RI area-concentration (g/mL) linear plot containing at least four different polymer concentrations. The calculation was based on an assumption that truly size-exclusion mechanism was operative in the columns of GPC.

The experimental d*n*/d*c* values were subsequently introduced to the TD-GPC to give their corresponding $M_{n,TD\text{-}GPC}$, [η] and R_h of the analyzed graft copolymers. The molecular weight details of all graft copolymers after DA reactions were tabulated in Table 4.2.

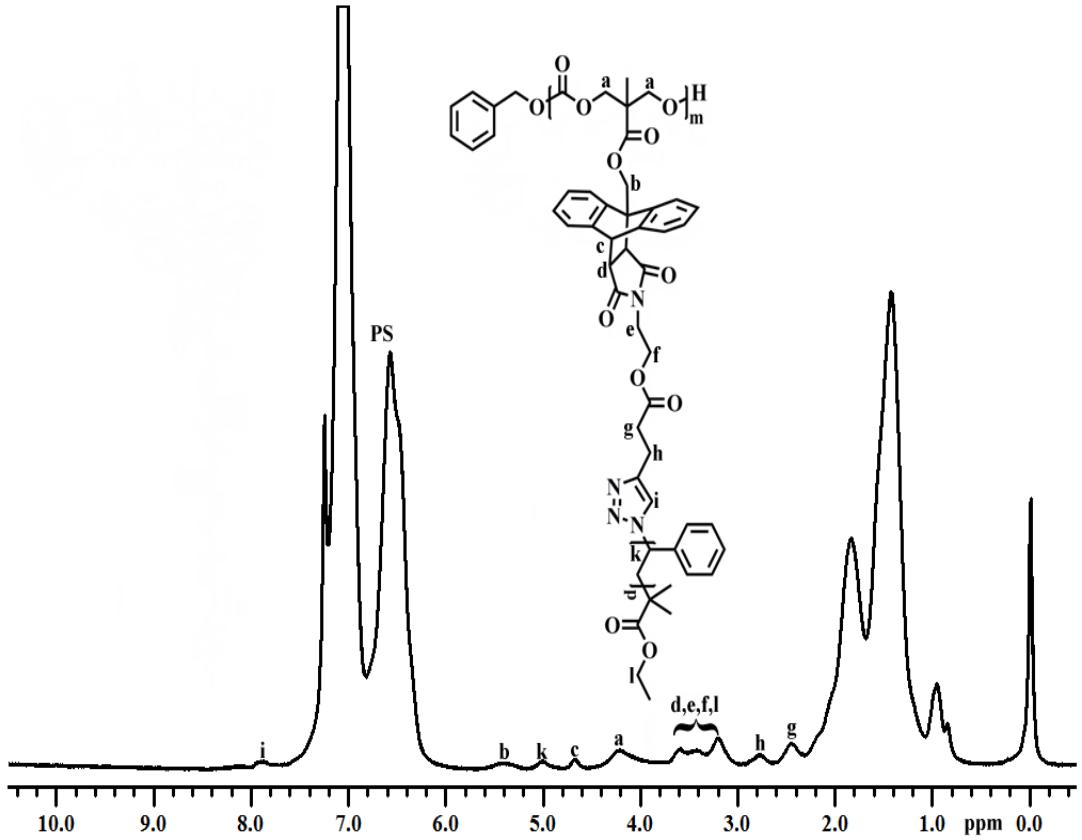


Figure 4.17 : ^{1}H NMR spectrum of PC-*g*-PS in $CDCl_3$.

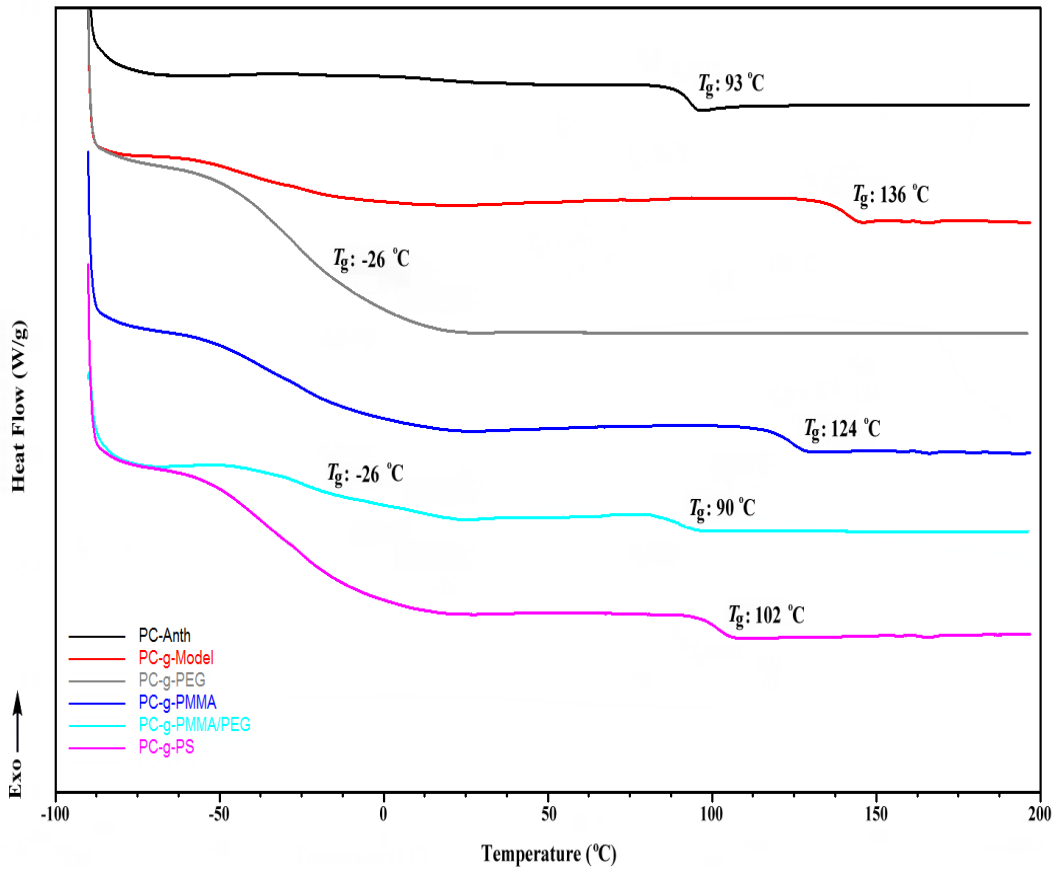


Figure 4.18 : DSC thermograms of PC-Anth, PC-*g*-model, PC-*g*-PEG, PC-*g*-PMMA, PC-*g*-PMMA/PEG, PC-*g*-PS polymers at a heating rate of 10 °C/ min under nitrogen. The glass transition (T_g) was calculated as a midpoint and a peak apex of thermograms.

Table 4.2 : Chracterization of graft copolymers after DA Click Reaction

Polymers	GPC[a]		TD-SEC[b]					DA *eff*[d] *(%)*	$M_{n,theo}$ (g/mol)
	M_n (g/mol)	M_w/M_n	M_n (g/mol)	M_w (g/mol)	[η] (dL/g)	*Rh* (nm)	d*n*/dc[c] (mL/g)		
PC-*g*-Model	5700	1.18	11500	13500	0.045	2.10	0.124	>99	11750[e]
PC-*g*-PMMA	24100	1.17	59000	72300	0.085	4.51	0.084	98	54500[f]
PC-*g*-PEG	2400	1.27	-	-	-	-	-	98	19050[g]
PC-*g*-PMMA/PEG	8700	1.23	39900	46500	0.088	3.94	0.091	97	35300[h]
PC-*g*-PS	43500	1.11	89100	95500	0.146	5.99	0.185	95	85050[i]

[a] Determined by conventional GPC calibrated relative to linear PS standards in THF at 30 °C.

[b] Calculated from TD-GPC in THF at 35 °C.

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

[d] Determined by UV measurements with a ratio of final absorbance (A_t) at36 h and initial absorbance (A_0); DA *eff*= **(**1-A_t/A_0)x100

[e] $M_{n,theo}$ = 6000 ($M_{n,TD\text{-}GPC}$) + (MW of **4** X 16) X DA *eff*

[f] $M_{n,theo}$ = 6000 ($M_{n,TD\text{-}GPC}$) + ($M_{n,GPC}$ X 16) X DA *eff*

[g] $M_{n,theo}$ = 6000 ($M_{n,TD\text{-}GPC}$) + ($M_{n,theo}$ X 16) X DA *eff*

[h] $M_{n,theo}$ = 6000 ($M_{n,TD\text{-}GPC}$) + ($M_{n,GPC}$ of PMMA X 47% + $M_{n,theo}$ of PEG X 53%) X 16 X DA *eff*

[i] $M_{n,theo}$ = 6000 ($M_{n,TD\text{-}GPC}$) + ($M_{n,GPC}$ X 16) X DA *eff*

5. CONCLUSIONS

In this M.Sc thesis, the synthesis of various graft copolymers were obtained via ROP and highly efficient DA click reactions .

In the first stage, series of well-defined linear polymers were first time synthesized and click reactions were applied with furan protected maleimide.

The second step was comprised of the DA click reaction between furan protected maleimide and anthracene end-functionalized carbonate polymer in reflux temperature of toluene.

UV spectroscopy indicated that DA efficiencies of the reactions were quantitative. Moreover, both GPC and ^{1}H NMR analysis confirmed a successful graft copolymer formation.

It was obviously seen from the DSC analysis that the graft copolymers had high glass transition temperature values except copolymers with PEG.

It was obvious that DA click reaction was a versatile and efficient method for the preparation of well-defined polymeric structures.

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