ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

BROMINATION of POLYOXANORBORNENE BACKBONE and SUBSEQUENT POST-FUNCTIONALIZATION via ATOM TRANSFER NITROXIDE RADICAL COUPLING REACTION

M.Sc. THESIS

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Department of Chemistry

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

POLİOKSANORBORNEN ANA ZİRCİRİNİN BROMLANMASI ve ATOM TRANSFER NİTROKSİT RADİKAL BİRLEŞMESİ REAKSİYONU İLE FONKSİYONLANDIRILMASI

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OCAK 2015

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Date of Submission : **15 December 2014**
Date of Defense : **21 January 2015**

To my dearest family and my friends,

FOREWORD

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

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December 2014

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ABBREVIATIONS

^{1}H NMR	**:** Hydrogen Nuclear Magnetic Resonance Spectroscopy
ROMP	**:** Ring Opening Metathesis Polymerization
ATNRC	**:** Atom Transfer Nitroxide Radical Coupling
$CDCl_3$	**:** Deuterated chloroform
CH_2Cl_2	**:** Dichloromethane
C/LRP	**:** Controlled/Living Radical Polymerization
CuAAC	**:** Copper catalyzed azide-alkyne cycloaddition
DA	**:** Diels-Alder
DMF	**:** *N*,*N*-dimehthylformamide
EtOAc	**:** Ethyl acetate
GPC	**:** Gel Permeation Chromatography
PDI	**:** Polydispersity Index
PEG	**:** Poly(ethylene glycol)
PMDETA	**:** *N, N, N',N'', N''*-Pentamethyldiethylenetriamine
RAFT	**:** Reversible Addition Fragmentation Chain Transfer
NMP	**:** Nitroxide Mediated Polymerization
ATRP	**:** Atom Transfer Radical Polymerization
ROP	**:** Ring-opening polymerization
Et_3N	**:** Triethylamine
TEMPO	**:** 2,2,6,6-Tetramethylpiperidine-*N*-oxyl
THF	**:** Tetrahydrofuran
PONB	**:** poly(oxanorbornene)
PBONB	**:** poly(butyloxanorbornene)
TBABS	**:** Tetrabutylammonium bisulfate

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BROMINATION of POLYOXANORBORNENE BACKBONE and SUBSEQUENT POST-FUNCTIONALIZATION via ATOM TRANSFER NITROXIDE RADICAL COUPLING REACTION

SUMMARY

Living/Controlled radical polymerization (L/CRP) is among the most rapidly developing areas of chemistry and polymer science. It has always been desirable to prepare, by a free radical mechanism, well-defined block and graft copolymers, gradient and periodic copolymers, stars, combs, networks, end-functional polymers and many other materials under mild conditions from a larger range of monomers than available for ionic living polymerizations. This emergent ability to prepare long desired materials is the main reason for the explosion of academic and industrial research on L/CRP.

The Ring Opening Metathesis Polymerization (ROMP) of cyclic olefins by using metal alkylidene initiators has led to a number of well defined architectures including block, graft, star, and cyclic polymers which has controlled moleculer weight and controlled end group.

Graft polymers have a considerable interest because of having nonlinear architecture with different composition and topology. Because of their branched structure they generally have also lower melt viscosities, which is advantageous for processing. Also, graft polymers have a better physical and chemical properties than their linear polymers.

In 2001, Sharpless et al. described a new concept for conducting organic reactions, which was based upon the premise that organic synthesis should take advantage of the long history of development and progress during the 20th century and focus attention on highly selective, simple orthogonal reactions that do not yield side products and that give heteroatom-linked molecular systems with high efficiency under a variety of mild conditions. Several efficient reactions, which are capable of producing a wide catalogue of functional synthetic molecules and organic materials have been grouped accordingly under the term click reactions. Characteristics of modular click reactions include:

High yields with by-products (if any) that are removable by nonchromatographic processes, regiospecificity and stereospecificity, insensitivity to oxygen or water, mild, solventless (or aqueous) reaction conditions, orthogonality with other common organic synthesis reactions and amenability to a wide variety of readily available starting compounds.

The most popular click reactions are the copper catalyzed azide–alkyne cycloaddition (CuAAC), Diels–Alder cycloaddition, thiol-ene, thiol-yne, and nitroxide radical coupling (NRC) reactions.

Atom transfer nitroxide radical coupling (ATNRC) is a reaction in which TEMPO derivatives are used to end-cap polymer chains. ATNRC reaction is considered as a potential click reaction due to its high efficiency and orthogonality in the synthesis of well-defined polymers with different topologies. When compared with azide group, TEMPO group is less sensitive to light, shock, and thermal changes, which makes the polymer materials stable.

In this thesis, butyloxanorbornene monomer was first polymerized via ring opening metathesis polymerization (ROMP) using the first generation Grubbs' catalyst in chloroform at room temperature and then, bromine were reacted with PBONB in chloroform at room temperature for 4h **.** Afterward bromide functionalized PBONB clicked with acrylate functionalized TEMPO via Atom Transfer Nitroxide Radical Coupling (ATNRC) reaction in the presence of PMDETA, CuBr and Cu (0) catalyst system and DMF as solvent , to create corresponding graft polymer, poly(BONB-acrylate). Subsequently, thiophenol functionalized polybutyloxanorbornene was successfully prepared by using nucleophilic (Michael) thiol-ene "click" reaction.

Next, mono carboxylic acid functional PEG (PEG-COOH) was synthesized with a reaction of PEG-OH in the presence of succinic anhydride. Afterward, PEG-COOH and 4-hydroxy-TEMPO were reacted to obtain nitroxyl radical functionalized PEG (TEMPO-PEG)**.** Then, bromide functionalized PBONB clicked with PEG functionalized TEMPO via ATNRC reaction in the presence of PMDETA, CuBr and Cu (0) catalyst system and DMF as solvent , to create corresponding graft polymer, poly(BONB-PEG).

Afterward, epoxy functionalized poly(BONB) was carried out by ATNRC reaction between 4-glycidyl-2,2,6,6-tetramethylpiperidin-1-oxyl and poly(BONB-bromide). The Bromide functionality of PBONB was converted to epoxy in the presence of PMDETA, CuBr and Cu (0) catalyst system and DMF as solvent in order to give poly(BONB-epoxy).

Finally, the ATNRC reaction of PBONB-bromide was carried out using without TEMPO groups in the presence of Cu(0), Cu(Br) and PMDETA catalyst system and DMF as solvent at room temperature for 24 h. We observed the original signals belong to PBONB which means in this condition bromine functionalized polymer completely turned into original form. The obtained polymers were characterized by ^{1}H-NMR and gel permeation chromatograpy (GPC).

POLİOKSANORBORNEN ANA ZİNCİRİNİN BROMLANMASI VE ATNRC REAKSİYONLARI İLE FONKSİYONLANDIRILMASI

ÖZET

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.

Metal alkilidin kullanarak siklik olefinlerin Halka Açılma Metatez Polimerizasyonu (ROMP) ile blok, aşı, yıldız ve siklik polimerler gibi uç grup kontrolü, moleküler ağırlık kontrolü gibi özelliklere sahip birçok iyi tanımlı yapılar elde edilebilir. Halka açılma metatez polimerizasyonu siklik olefinlerden doğrusal makromoleküler yapıdaki bileşiklerin kısa sürede elde edilme imkanı veren polimerizasyon türüdür. Bu polimerizasyonda olefin metatez için gerekli iki olefinden biri monomer diğeri ise katalizördür. Monomer olarak bir siklik olefin ve katalizör olarak metal alkilidin kullanılır.

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

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

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 kopolimerler lineer polimerlere kıyasla daha iyi fiziksel ve kimyasal özelliklere sahiptirler.

2001 yılında Sharpless ve çalışma arkadaşları organik reaksiyonları yürütmek için yeni bir kavram ortaya atmışlardır. Bu yeni kavramın temelinde, organik sentezlerin, 20. yüzyıl boyunca olan bütün gelişmelerden yararlanması ve yüksek seçicilikte, basit ortogonal reaksiyonlara odaklanması yer almaktadır. Bu reaksiyonlar ılımlı reaksiyon koşullarında, yan ürünler olmaksızın, yüksek verimle heteroatoma bağlı moleküler sistemler oluşturabilmelidir. Geniş yelpazede, fonksiyonel sentetik molekülleri ve organik maddeleri üretebilen birkaç etkili reaksiyon "Click" reaksiyonlar kavramı altında gruplandırılmıştır. Modüler click reaksiyonları şu özelliklere sahip olmalıdır:

Yüksek verimli olması; eğer yan ürünler var ise, bu ürünlerin kromatografik olmayan yöntemlerle uzaklaştırılabilir olması, regioseçici ve stereoseçici olması, oksijen ve suya karşı hassas olmaması, ılımlı, çözücüsüz (veya sulu) reaksiyon koşullarında gerçekleşebiliyor olması, diğer bilinen organik sentez reaksiyonları ile uyumlu olabilmesi ve çok çeşitli ve kolay elde edilebilen çıkış bileşiklerine karşı yatkın olabilmesi.

En yaygın kullanılan click reaksiyonları, bakır katalizli azid-alkin siklokatılma (CuAAC) reaksiyonu, Diels-Alder siklokatılma reaksiyonu, tiyol-en ve tiyol-in reaksiyonları ve nitroksit radikal birleşme reaksiyonlarıdır.

Atom Transfer Nitroksit Radikal Birleşmesi (ATNRC); moleküllerin birbirlerine seçici ve hızlı bir şekilde bağlanmasını sağlamak amacıyla molekül uçlarında TEMPO ve türevlerinin kullanıldığı bir tepkimedir. ATNRC tepkimesi; farklı topolojilere uygulanabilirliği ve yüksek verimlilikleri nedeniyle iyi tanımlanmış polimerlerin sentezi için potansiyel bir "click" reaksiyonu olarak nitelendirilir. TEMPO uç grubu taşıyan polimer malzemeleri ışık, şok ve ısı değişikliklerine daha az duyarlı olduklarından, azid uç grubu taşıyan polimerlere göre daha kararlıdırlar.

Bu çalışmada, ilk olarak butiloksanorbornen monomeri Grubbs katalizörü eşliğinde halka açılma metatez polimerizasyonu yöntemi ile polimerleştirildi ve brom ile reaksiyonu gerçekleştirildi. Sonrasında, brom fonksiyonlu PBONB ve akrilat fonksiyonlu TEMPO arasında click reaksiyonu, ilgili aşı polimerini elde etmek amacıyla ATNRC yöntemi ile PMDETA, CuBr ve Cu (0) katalizör sistemi varlığında gerçekleştirildi.

PEG-OH ve süksinik anhidritin reaksiyonu ile karboksilik asit fonksiyonlu PEG (PEG-COOH) sentezlendi. Sonrasında, PEG-COOH ve 4-hidroksi-TEMPO arasında, nitroksi radikal fonksiyonlu PEG (TEMPO-PEG) elde etmek amacıyla reaksiyon gerçekleştirildi.Brom fonksiyonlu PBONB ve PEG fonksiyonlu TEMPO arasında click reaksiyonu, ilgili aşı polimeri sentezlemek amacıyla ATNRC yöntemi ile gerçekleştirildi.

Epoksi fonksiyonlu PBONB, 4-glycidyl-2,2,6,6-tetramethylpiperidin-1-oxyl ile PBONB-bromide arasında ATNRC reaksiyonu ile sentezlendi. PBONB brom fonksiyonu, ilgili aşı polimerini elde etmek amacıyla ATNRC yöntemi ile PMDETA, CuBr ve Cu (0) katalizör sistemi varlığında epoksi halkasına dönüştürüldü.

Son olarak, brom fonksiyonlu PBONB herhangi bir TEMPO grubu kullanılmadan , PMDETA, CuBr ve Cu (0) katalizör sistemi varlığında reaksiyon ortamına konuldu. Orijinal polimerdeki vinilik sinyalin tekrar ortaya çıktığı ve polimerin tamamen orijinal yapısına döndüğü gözlemlendi. Elde edilen polimerler ^{1}H-NMR ve GPC ile karakterize edilmiştir.

1. INTRODUCTION

Living polymerization techniques, e.g., ionic polymerizations, living/ controlled radical polymerizations (L/CRPs), ring opening polymerization (ROP), and ring opening metathesis polymerization (ROMP) may provide polymers with well-defined properties, such as precise control of composition, molecular weight, polydispersity, and endfunctionality [1-18].

A combination of "click" reactions and their compatible partner living polymerization methods allows increasingly the synthesis of the complex macromolecular structures, such as star, cyclic, hyperbranched polymers, dendrimers, and graft copolymers, with well-defined molecular weight, composition, topology and functional groups [19-31]. It is well known that complex architectures display different properties both in bulk and solution, i.e. morphology and assembly in solution and in bulk, and the solution and the melt viscosity, while compared to their linear counterparts.

Among living polymerization methods, ring opening metathesis polymerization (ROMP) is a versatile and an efficient synthetic strategy for the polymerization of cyclic olefins (such as norbornene norbornadiene, and dicyclopentadiene etc.) by using metal alkylidene initiators (e.g. molybdenum and ruthenium complex catalysis) [32-50]. Although there have been many published studies on the synthesis of graft copolymers by using a combination of ROMP and other living polymerization techniques, relatively few publications have emerged in the literature based on combining ROMP and "click" reactions [51-68].

Graft copolymers can be obtained with three general methods: (i) grafting-onto, in which side chains are preformed, and then attached to the backbone; (ii) grafting-from, in which the monomer is grafted from the backbone; and (iii) grafting-through, in which the macromonomers are copolymerized [69,70].

The click reaction defined by Sharpless and co-workers in 2001 should display high stereo- and regioselectivity, high yield under mild reaction conditions, simple

recovery of the main product, a capability of working in a wide range of solvents, and tolerance of a wide range of functional groups [72]. The most popular click reactions are the copper catalyzed azide–alkyne cycloaddition (CuAAC), Diels-Alder cycloaddition, thiol-ene, thiol-yne, and nitroxide radical coupling (NRC) reactions [71].

Huang and coworkers proved that atom transfer nitroxide radical coupling (ATNRC) reaction between a halide- and a 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-terminated polymers in the presence of CuBr and ligand at elevated temperature based on the ATRP mechanism was very efficient in the preparation of well-defined linear ABC-type triblock terpolymers together with the CuAAC "click" reaction [73]. Huang and coworkers [74–78] extended this strategy to the synthesis of graft and star polymers. It should be noted that the ATNRC reaction is considered as a potential "click" reaction due to its high efficiency and orthogonality in the synthesis of well-defined polymers with different topologies.

The goals of this thesis can be collected under two main topics: i) bromination of polyoxanorbornene (PBONB) backbone ii) subsequent post-functionalization via ATNRC "click" reaction. For this purpose, PBONB was synthesized by ROMP. Thereafter, this polymer was quantitatively reacted with bromine to obtain bromide functionalized PBONB. Finally, ATNRC reactions were carried out between bromide functionalized PBONB and functionalized TEMPO (TEMPO-acrylate, TEMPO-PEG and TEMPO-epoxy) to achieve various different functionalities on PBONB backbone. The functionalized polymers were characterized by ^{1}H-NMR and Gel Permeation Chromatography (GPC) measurements.

2. THEORETICAL PART

2.1 Controlled/ ‘‘Living” Polymerizations

Living polymerization, the concept of which was first introduced by Szwarc in 1956, is one of the most promising ways for the synthesis of well-defined polymers. A living polymerization is defined as a chain polymerization without chain transfer and chain termination [79,80]. These chain breaking processes were avoided with the development of special high vacuum techniques to minimize traces (<1 ppm) of moisture and air in the anionic polymerization of non-polar vinyl monomers [81]. Until recently, ionic polymerizations (anionic or cationic) were the only living techniques that efficiently controlled the structure and architecture of vinyl polymers. These polymerization techniques ensure low polydispersity materials, controlled molecular weight and defined chain ends but they are not useful for the polymerization and copolymerization of a wide range of functionalized vinylic monomers [82]. Furthermore, these techniques require stringent reaction conditions and pure reagents. To overcome all these limitations polymer chemists developed new concepts. These new concepts are often called controlled radical polymerization, living radical polymerization, control/“living” radical polymerization [83,84]. Living or controlled/”living” polymerization techniques allow the synthesis of well-defined polymers with controlled molecular weight, polydispersities, and terminal functionalities. The polymerization proceeds until all of the monomer has been consumed, and further additions of monomer result in continued polymerization.

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 [85-87].

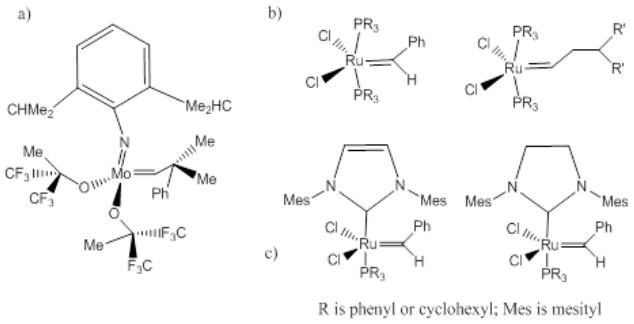
2.2 Controlled/ ‘‘Living” Radical Polymerizations

Living free radical polymerizations have attained a tremendous following in polymer chemistry. A great deal of effort has been made to develop and understand different living free radical polymerization (LFRP) methods.Georges and co-workers first introduced true nitroxide mediated polymerization (NMP) in 1993, Matyjaszewski and Sawamoto developed metal catalzed (Cu, Ru) living radical polymerization also called atom transfer radical polymerization (ATRP) in 1995, and Moad, Rizzardo and Thang reported reversible addition-fragmentation chain transfer polymerization (RAFT) in 1998 [88-90].

2.3 Ring-Opening Metathesis Polymerization (ROMP)

Although a relatively new player on the field of polymer chemistry, ring-opening metathesis polymerization (ROMP) has emerged as a powerful and broadly applicable method for synthesizing macromolecular materials. The origins of ROMP can be traced to the mid-1950s when various metals and reagents were combined to uncover new transformations and reactivities involving olefins. However, the rapid rise in popularity and utility of this polymerization technique is the result of extensive work on the identification and isolation of key intermediates involved in the general olefin metathesis reaction. This led to the development of well-defined ROMP catalysts and ultimately enabled the synthesis of a wide range of polymers with complex architectures and useful functions [91].

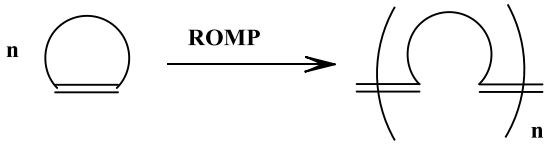
It was only in 1971 that a metal-carbene intermediate was proposed by Y. Chauvin, to explain – satisfactorily for the first time – the mechanism. This extraordinary mechanistic proposal, rationalising Chauvin’s astonishing new observations, was immediately embraced by the metathesis community and prompted studies on metal-carbene initiators culminating in the creation of the molybdenum- alkylidene catalysts by R. R. Schrock **(2.1a)**, and the 1st and 2nd generation of ruthenium-alkylidene catalysts, by R. H. Grubbs **(2.1b, 2.1c)** [92].



(2.1)

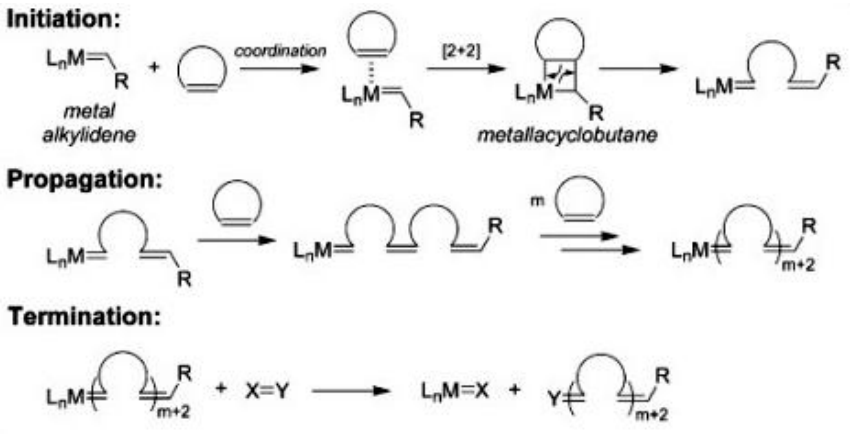
2.3.1 ROMP essentials: mechanism and thermodynamics

The word metathesis comes from the Greek *meta* (change) and *tithemi* (place). In olefin chemistry, it refers to the pair-wise exchange of substituents on a carbon-carbon double bond [93]. Ring-opening metathesis polymerization (ROMP) is a chain growth polymerization process where a mixture of cyclic olefins is converted to a polymeric material **(2.2)**. The mechanism of the polymerization is based on olefin metathesis, a unique metal-mediated carbon‑carbon double bond exchange process. As a result, any unsaturation associated with the monomer is conserved as it is converted to polymer. This is an important feature that distinguishes ROMP from typical olefin addition polymerizations (e.g. ethylene → polyethylene).



(2.2)

Chauvin proposed a general mechanism for ROMP in 1971 [91]. Initiation begins with coordination of a transition metal alkylidene complex to a cyclic olefin **(2.3)**.



(2.3)

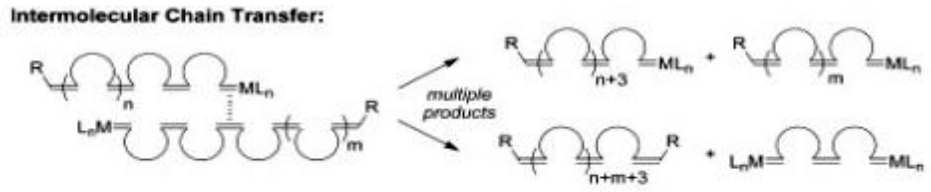
After formation of the metal-carbene complex, subsequent [2+2] cycloaddition forms a highly strained metallacyclobutane intermediate. The ring in the intermediate opens to give a new metal alkylidene. The chain growth process proceeds during the propagation stage until all monomer is consumed. Then living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

There are three important features regarding metal-mediated ROMP reactions. First, it is important to note that the propagating metal centers on the growing polymer chains may exist in either the metallacyclobutane or metal alkylidene form. This difference depends on the transition metal and its associated ligands, as well as the reaction conditions. Second, like most olefin metathesis reactions, ROMP reactions are generally reversible. Third, although most ROMP reactions are reversible, they are equilibrium-controlled and the position of the equilibrium (monomer vs. polymer) can be predicted by considering the thermodynamics of the polymerization. As with other ring-opening polymerizations, the reaction is driven from monomer to polymer by the release of strain associated with the cyclic olefin (so-called 'ring strain') balanced by entropic penalties. The most common monomers used in ROMP are cyclic olefins which possess a considerable degree of strain (45 kcal/mol) such as cyclobutene, cyclopentene, cis-cyclooctene, and norbornene.

Generally, the most favorable conditions for a successful ROMP reaction is to use the highest monomer concentration at the lowest temperature possible, due to enthalpic contribution from the relief of ring strain [91].

In addition to the general ROMP mechanism illustrated in equation **2.5** (and its related depolymerization mechanism), the equilibria noted above can be established via other metathetical pathways, including intermolecular chain-transfer and intramolecular chain-transfer (so-called 'backbiting') reactions. Examples of these types of secondary metathesis reactions are shown in equations **2.4** and **2.5**. In an intermolecular chain-transfer reaction, one polymer chain containing an active metal alkylidene on its terminus can react with any olefin along the backbone of a different polymer chain in the same reaction vessel. Although the total number of polymer chains remains the same, the molecular weights of the individual polymers will increase or decrease accordingly. In a backbiting reaction, the active terminus of a polymer chain reacts with itself to release a cyclic species and a polymer chain of

reduced molecular weight. Collectively, these chaintransfer reactions effectively broaden molecular weight distribution (or polydispersity) of the system.



(2.4)

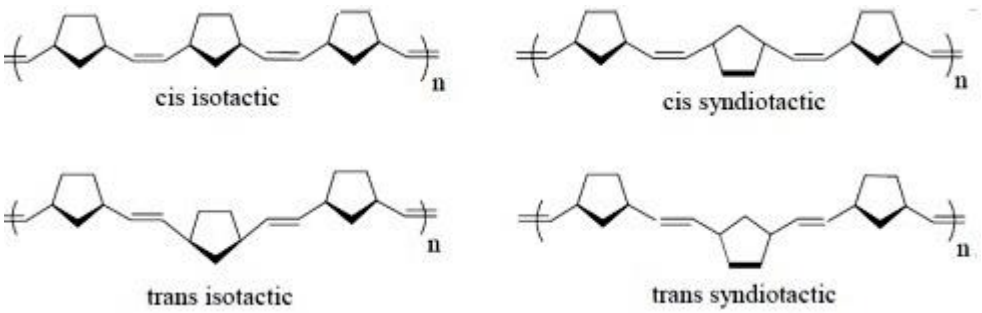
(2.5)

Another implication of equilibrium controlled polymerizations such as ROMP is the propensity to form cyclic oligomers. According to the Jacobson‐ Stockmayer theory of ring‐chain equilibria, the formation of cyclic oligomers will always accompany the formation of high molecular weight polymer. The total amount of cyclic species present will depend on factors such as solvent, cis/trans ratio of the polymer backbone, rigidity of the monomer, reaction time, and concentration. Formation of cyclic species is favored at higher temperatures and lower concentrations with a critical value dependent on the factors noted above. While these side reactions challenge the realization of living polymerizations based on ROMP, they can be advantageous. For example, cyclic oligomers can be synthesized in high yields by simply conducting the ROMP reaction under relatively dilute conditions.

A "living polymerization" was defined by Swarzc as a reaction proceeding without chain transfer or termination. Besides Swarzc's original concept of the living polymerization, a ROMP reaction requires three more features for its living and controlled reaction. First, the initiation should be fast and complete. Second, there should be a linear relationship between polymer formation and monomer consumption. Third, polymers should be narrowly polydispersed with PDIs<1.5 [91].

ROMP polymers can display a very rich microstructure. Depending on the monomer, three main characteristics can be observed: cis/trans isomerism, tacticity, and head-to-tail bias. Cis/trans isomerism is present in all ROMP polymers and relatively easy to quantify using spectroscopic techniques. Analysis of tacticity has only been

successful with polymers made from prochiral monomers **(2.6)**. Head-to-tail bias can be observed with non-symmetrical monomers.



(2.6)

2.3.2 Well-Defined catalysts for ROMP

The studies of two groups deserve particular attention – as recognized by the award of the 2005 Nobel Prize for chemistry to R.H. Grubbs and R.R. Schrock. The award was shared with Y. Chauvin , who was honored for his fundamental studies on metathesis. The investigations of Grubbs and Schrock led to the development of well-defined transition metal alkylidenes that rapidly outrivaled any other initiator or initiation system, particularly those consisting of an often serendipitous mixture of transition metal salts, alcohols and tin alkyls [94].

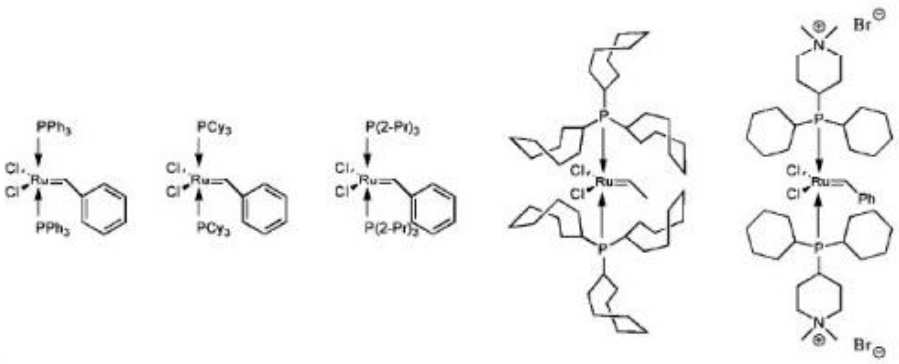
2.3.2.1 Schrock-type initiators

The synthesis of well-defined, high-oxidation state molybdenum alkylidenes was first reported by Schrock and coworkers in 1990 . These, and the analogous tungsten systems, are now commonly named 'Schrock-catalysts'. The systems possess the general formula $M(NAr')(OR')_2(CHR).L$, where M= Mo,W; Ar′= phenyl or a substituted phenyl group; R= ethyl, phenyl, trimethylsilyl, CMe_2Ph or t-butyl; R′= CMe_3, CMe_2CF_3, $CMe(CF_3)_2$, $C(CF_3)_2$, aryl, and so on, while L = quinuclidine, trialkylphosphane and tetrahydrofuran (THF) [95].

The Schrock type catalysts are very active and somewhat tolerant with functional groups during ring open metathesis polymerization [96]. In 1993, first chiral molybdenum carbene catalyst was introduced. Then, Schrock and Hoveyda developed more active chiral molybdenum carbene catalyst system, they are so-called the Schrock-Hoveyda catalysts [97].

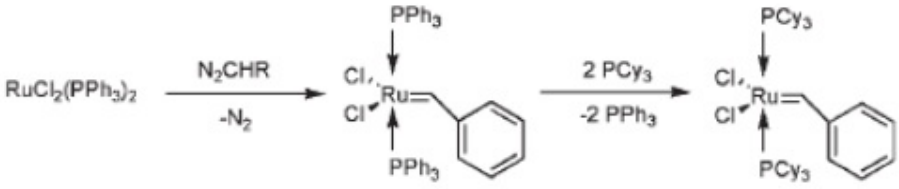
2.3.2.2 Grubbs-type initiators

In 1992, Grubbs described the synthesis of the first well-defined ruthenium alkylidene. Thus, the reaction of $RuCl_2(PPh_3)_3$ and $RuCl_2(PPh_3)_4$, respectively, with 2,2-diphenylcyclopropene in benzene or methylene chloride yielded the desired ruthenium carbene complex $RuCl_2(PPh_3)_2(CH{=}CH{=}CPh_2)$. As is the case of Schrock-type catalysts, the alkylidene proton in $RuCl_2(PPh_3)_2(CH{=}CH{=}CPh_2)$ experiences an agostic interaction with the metal, resulting in downfield NMR shifts for H_α and C_α to δ=17.94 and 288.9 ppm, respectively (both in C_6D_6). Despite a ratio of k_i/k_p <1 (k_p= rate constant of polymerization, k_i= rate constant of initiation), the compound was found to be a quite efficient initiator for the polymerization of norbornene (NBE) and substituted NBEs. The comparably low activity of the bis(triphenylphosphane)-derivative for other cyclic olefins than NBE such as bicyclo [3.2.0]hept-6-ene or trans-cyclo-octene was successfully enhanced by phosphane exchange with more basic analogues, for example tricyclohexylphosphane and tri-(2-propyl)phosphane **(2.7)** [94].



(2.7)

An alternative route to ruthenium alkylidenes that avoided the preparation of 2,2-diphenylcyclopropene was elaborated by Schwab and Grubbs.The synthetic protocol entailed the reaction of $RuCl_2(PPh_3)_3$ with an diazoalkane **(2.8)** [95].



(2.8)

Via this route, the resulting compounds of the general formula $RuCl_2(PR_3)_2(CHPh)$, (R=Ph, Cy_3)– which today are well known as the first-generation Grubbs catalyst– are accessible in high yields [94].

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

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

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

The first homogeneous well-defined Ru complex for ROMP was $(PPh_3)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$ [98]. Although this catalyst has a broad range of functional group tolerance and mediates living ROMP reaction with norbornene and cyclobutene monomers, the catalytic activities for other olefines are reduced. To increase the catalytic activities, the bulky and electron-rich phosphine ligands were substituted. The catalysts containing phosphine are tolerant to a broader range of functional groups, such as water and alcohols. However, ROMP reactions of norbornene with the catalyst containing phosphine are not controlled. Because of the different reaction rates between initiation and propagation, the catalyst is not able to provide the desired polymers. Besides, chain transfer reactions occur to yield broadly polydispersed polymers (PDI > 2) [99].

2.3.3 Norbornene: the traditional ROMP monomer

Most common ROMP polymers are derived from norbornene-type monomers. The norbornene structure has recently been used extensively to introduce a variety of functional groups into polymers [100].

Interesting properties are associated with the polynorbornene backbone itself: high glass transition temperature and good thermal stability for example. One

disadvantage could be its tendency to easily oxidize in air, but the unsaturation can be removed by hydrogenation.

Also, as compared to other commercial polymerization techniques such as free radical polymerizations, the current ROMP-norbornene system is very attractive. One major problem of radical polymerization is molecular weight control because of chain transfer and termination processes. Controlled/"living" free radical polymerization can be obtained by nitroxyl radical-mediated polymerization and atom transfer radical polymerization (ATRP) [101]. But, those living polymerizations usually require long reaction time for completion. Molecular weight control can also be achieved with living ionic polymerizations but the stringent conditions limit their utility to non-functionalized monomers.

2.4 Click Chemistry

”Click chemistry” is a chemical term introduced by Sharpless in 2001 and describes chemistry tailored to generate substances quickly and reliably by joining small units together [102]. “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.

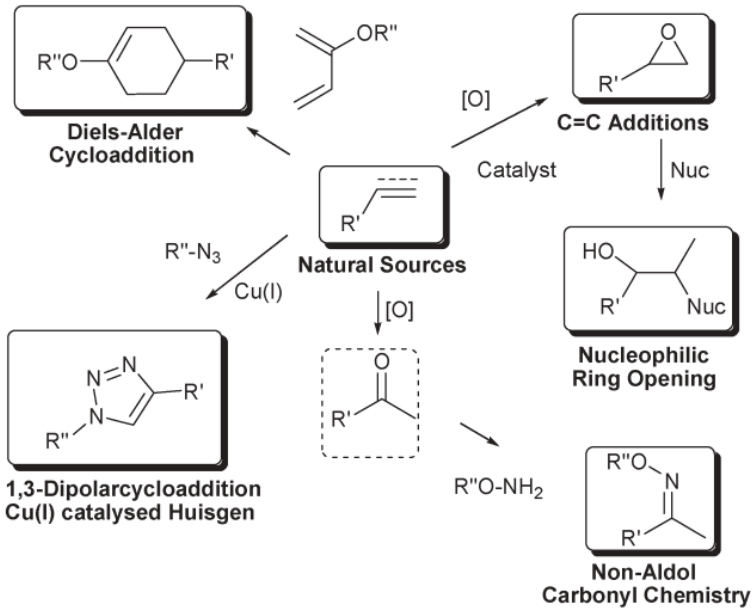
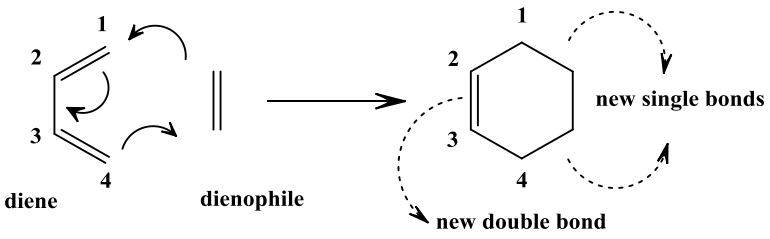


Figure 2.1 : A selection of reactions which match the Click Chemistry criteria

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 **(2.9)**. This reaction is named for Otto Diels and Kurt Alder, who received the 1950 Nobel prize for discovering this useful transformation [103-105].



(2.9)

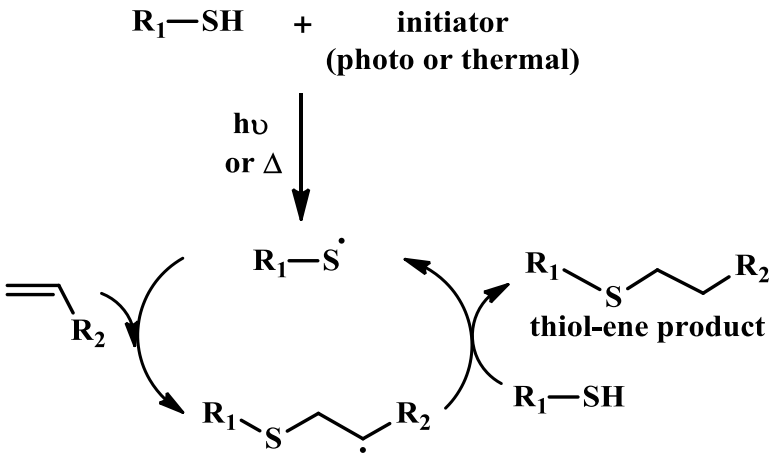
Typically, the DA reaction works best when either the diene is substituted with electron donating groups (like -OR, -NR_2, etc) or when the dienophile is substituted with electron-withdrawing groups (like -NO_2, -CN, -COR, etc). Many different

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 [106].

2.4.2 Thiol-ene reaction

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

The thiol-ene chemistry, which involves the hydrothiolation of a C=C bond, can be induced photochemically or thermally at ambient temperature to mainly give an anti-Markownik-type product. Generally, the thiol-ene reaction follows a radical-mediated process, with initiation, propagation and termination steps. Initiation involves the treatment of a thiol with an initiator, under irradiation or heat, subsequently generating a thiyl radical, $RS^{\cdot}$, via hydrogen abstraction, plus other byproducts **(2.10)**. Propagation then occurs in two step which involves first the direct addition of the thiyl radical to the C=C bond producing an intermediate thioether carbon radical followed by chain transfer to a second molecule of thiol to give the thiol-ene addition product with the concomitant generation of a new thiyl radical. Termination is believed to ocur through the radical-radical recombination of the thioether carbon and/or thiyl radicals.



(2.10)

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

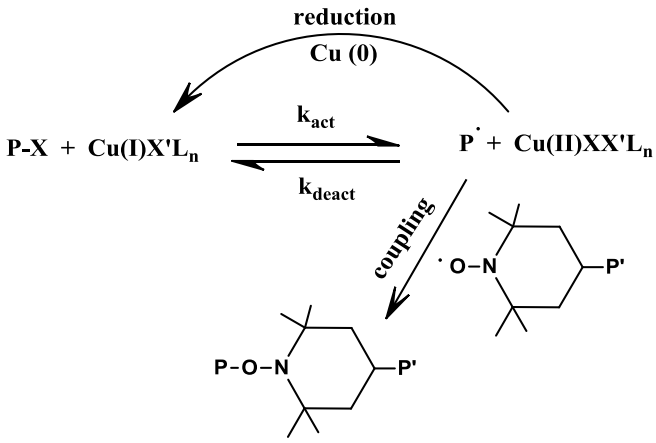
The thiol-ene ''click'' reactions, through either a radical or nucleophilic mechanism, provide efficient hydrothiolation routes across virtually any double bond [107-111].

Over the years, the thiol-ene ''click'' reaction has been extensively exploited in polymer chemistry since it can be conducted under various conditions without any metal catalyst. The UV-induced crosslinking of unsaturated polymers (photocuring) by reaction with multifunctional thiols is currently employed in surface coating owing to a number of advantages over other curing methods. Biomaterials for application in medicine, especially dentistry, have been prepared by using this process. Only recently, however, has the "click" aspect of the thiol-ene ''click'' reaction been fully appreciated in the field of polymer science. The use of thio-Michael addition as a "click" reaction was recently reported by Lowe et al. for the synthesis of star polymers [112]. The great potential of thiol–ene chemistry was exploited by Hawker and co-workers in the synthesis of poly(thioether) dendrimers [113]. Consequently, numerous examples are available in the literature for polymer end group and backbone modification [114-116], many of which are covered in various excellent reviews [108,117,118].

2.4.3 Atom transfer nitroxide radical coupling reaction (ATNRC)

A new reversible coupling strategy termed atom transfernitroxide radical coupling (ATNRC) [119-124] has the attributes of a "click" reaction. In which the bromine end-functional group of one polymer served as oxidant is reduced to bromine anion and carbon radical is formed. The Cu^{1+} is oxidized to Cu^{2+} in the presence of CuBr/ ligand. Then polymeric radical is immediately captured by another 2,2,6,6-tetramethyl-piperidinyl-1-oxy (TEMPO) end-functional polymer, and alkoxyamine is formed between the two polymers [125] **(2.11)**. In ATNRC reaction, CuBr participated in the reaction was served as reactant and its action was quite different

from the ATRP. If some Cu(0) was added, the Cu(0) would react with the formed Cu^{2+} and the Cu^{+} was regenerated, which promoted the reaction completely. Thus, under the ATNRC conditions (such as the Cu(0)/CuBr/PMDETA system), the graft, [120] the star-shaped, [122] and the linear copolymer [119] were prepared successfully with high efficiency.



(2.11)

This reaction involves formation of a carboncentered radical by an atom transfer reaction with Cu(I)Br and trapping of this radical with a persistent nitroxide radical at close to diffusion-controlled rates. The unique aspect of this reaction is its reversibility, in which the product alkoxyamine can readily be converted to the starting incipient radical and parent nitroxide at elevated temperatures (>100 ^{0}C when TEMPO-type nitroxides are used) [126-128]. This methodology has been used to synthesize degradable and reversibly coupled linear multiblock copolymers, block and graft copolymers in the presence of a 10-fold molar excess of copper species per halide end group [129]. The rate determining step in the coupling reaction is the speed (kact) at which the halide end groups on the polymer chains convert (or are activated) to the carbon-centered radical via atom transfer reactions with Cu(I) species.

2.5 Polymer Topology

The need to synthesize polymers with new and/or improved properties properties has driven the effort to design polymers with novel macromolecular architectures. The properties of polymers depend strongly on their topologies, and finding facile and feasible synthetic methods for polymers with different topological structures remains a goal for polymer chemists. 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**.

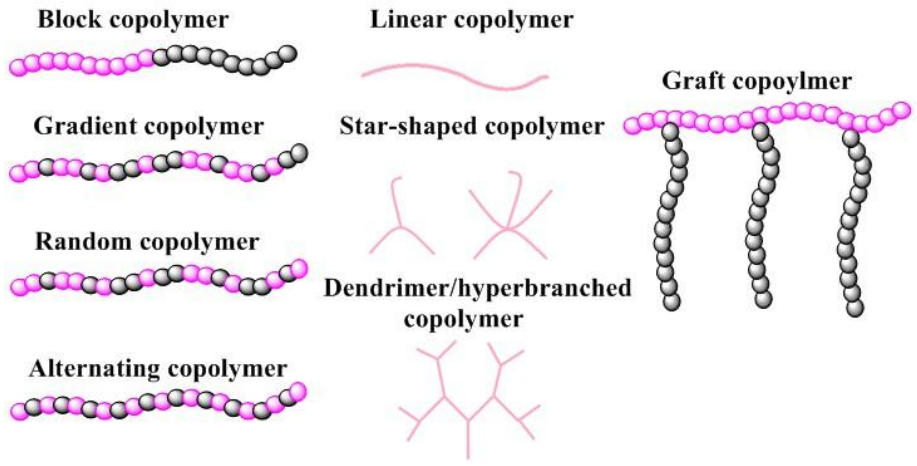


Figure 2.2 : Schematic represantation of selected (co)polymer architectures.

C/LRP techniques are well suited for preparation of polymers with precisely controlled architectures, including graft and star polymers as well as branched, dendritic, network, and cyclic type structures. In addition to versatile polymerization chemistry, the synthesis of such complex macromolecules often requires the use of efficient and specific postpolymerization modification techniques to incorporate functionality potentially incompatible with the polymerization conditions and to build novel structures by coupling preformed polymers. In this respect, "click" reactions are especially well conformed for such advanced macromolecular design. Indeed, "click" strategies have served as a complementary tools for most of the major synthetic polymerization techniques, such as ring opening polymerization (ROP), ring opening metathesis polymerization (ROMP), polycondensation, conventional free-radical polymerization, and C/LRPs.

2.5.1 Graft copolymers

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

When graft polymers characterized by a high density of grafted chains they were named ‘‘macromolecular brushes’’. In terms of chemical composition, macromolecular brushes can be categorized into homopolymer brushes and copolymer brushes. The latter typically consist of two or more types of polymer side chains. When only two types of polymer grafts are involved, they can be arranged in a random, alternating, block, and “centipede” manner.

Graft copolymers have been the subject of continuously increasing interest due to their unique specific properties (morphology, phase behaviour, etc.). In general, graft copolymers can be prepared following three main strategies: (a) the “*grafting onto*”, (b) the “*grafting from*”, and (c) *the* “*grafting through*” strategies which differentiate from each other based on the formation principle. The different pathways are schematically depicted in **Figure 2.3** and will be discussed in the context of the ensuing sections.

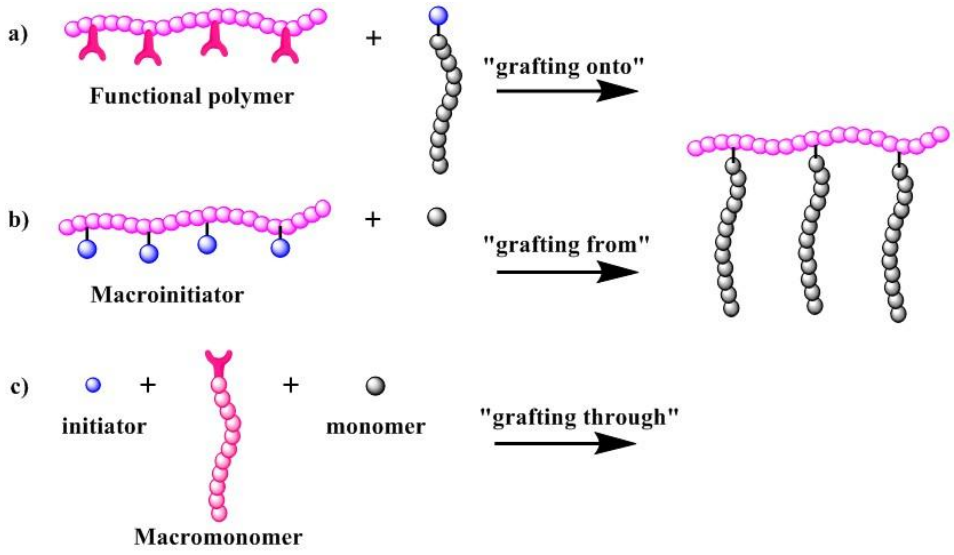


Figure 2.3 : Strategies for the synthesis of graft copolymer: (a) ‘‘grafting onto’’, (b) ‘‘grafting from’’, and (c) ‘‘grafting through’’.

The ‘‘*grafting onto*’’ strategy involves the attachment of preformed polymer chains via chemical reaction with reactive side chains of a polymer backbone. Secondly, the ‘‘*grafting from*’’ strategy, consists in a polymerization of the grafts from a polymer backbone bearing initiating sites. The last approach is the ‘‘grafting through’’ strategy which relies on polymerization of appropriate macromonomers.

Each of these strategies controls different structural parameters, including chemical composition, grafting density, degree of polymerization (DP) of side chains, and DP of the backbone. Even though each strategy demonstrates distinct advantages with respect to the molecular design, there are also limitations from a synthetic perspective. There are several strategies that have been employed to synthesize graft polymers thus, increasing interest in their various possible applications. Graft copolymers can be synthesized using any of the various polymerization techniques available including: anionic polymerization, ROMP, conventional radical polymerization, C/LRPs, and various coupling reactions (‘‘click chemistry’’).

2.5.1.1 “Grafting onto” method

One of the methods widely used for the synthesis of graft copolymers is the ‘‘grafting onto’’ method, i.e. reaction of preformed polymeric chains bearing functional groups with other polymeric chains bearing active chain ends as seen in Figure 2.3 (a). In most cases, the incorporation of functional groups is performed by chemical modification of the backbone. Characterization of the backbone and the preformed side chains can be performed separately from the graft copolymer, thus allowing for the detailed characterization of the final structure.

2.5.1.2 “Grafting from” method

In the ‘‘grafting from’’ method, the backbone is chemically modified in order to introduce active sites capable of initiating the polymerization of a second monomer as seen in Figure 2.3 (b). The number of grafted chains can be controlled by the number of active sites generated along the backbone assuming that each one participates in the formation of one branch [130].

2.5.1.3 “Grafting through” method

In the grafting through method, preformed macromonomers are copolymerized with another monomer in order to produce the graft copolymer as seen in Figure 2.3 (c). Macromonomers are oligomeric or polymeric chains that have a polymerizable end group. In this case, the macromonomer comprises the branch of the copolymer and the backbone is formed in situ. The number of branches per backbone can be generally controlled by the ratio of the molar concentrations of the macromonomer and the comonomer [131].

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

Furan (99%, Aldrich), maleimide (99%, Aldrich), succinic anhydride (97%, Aldrich), bromine (99.5%, Aldrich), triethylamine (Et_3N, 99.5%, Aldrich), *N,N'*-dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Aldrich), propargyl bromide (80 wt. % in toluene, Aldrich), 4-Hydroxy-TEMPO (97%, Aldrich), TEMPO (98%, Aldrich), 1-bromobutane (99%, Aldrich), sodium azide (99 %, Acros) and CuBr (99.9%, Aldrich) were used as received. *N*, *N*, *N*', *N*", *N*"-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) was distilled over NaOH prior to use. Poly(ethylene glycol) monomethylether (PEG-OH, M_n = 550, Acros) were dried by azeotropic distillation with anhydrous toluene. Tetrahydrofuran (THF, 99.8%, J.T. Baker) was dried and distilled from benzophenone-Na. *N*,*N*-dimethylformamide (DMF, 99.8%, Aldrich) was dried and distilled under vacuum over CaH_2. Dichloromethane (CH_2Cl_2, 99%, J. T. Baker) was dried and distilled over and P_2O_5. Diethyl ether (99.7%, Aldrich) and methanol (99.8%, Aldrich) were used without further purification. Ethyl acetate (EtOAc) and hexane were in technical grade and distilled prior to use. All other reagents were purchased from Aldrich and used as received without further purification.

3.2 Instrumentation

^1H NMR measurements were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using a Bruker AC250 (250 MHz) instrument. ^{13}C NMR (62.89 MHz) spectra were recorded on a Bruker NMR AC 250 Spectrometer in $CDCl_3$.

The conventional Gel Permeation Chromatography (GPC) measurements were conducted in THF at 30 °C using an Agilent instrument (Model 1100) consisting of a pump (0.3 mL/min) and four Waters Styragel columns (guard, HR 5E, HR 4E, HR 3, HR 2), (4.6 mm internal diameter, 300 mm length, packed with 5 μm particles) in series with two detection systems: a refractive index and UV detectors). Toluene was

used as an internal standard. The determination of apparent molecular weights for the polymers was based on linear PS standards (Polymer Laboratories), whereas linear PMMA standards (Polymer Laboratories) were only used for the molecular weight determination of the PMMA homopolymer using PL Caliber Software from Polymer Laboratories.

The second GPC system (TD-GPC) is equipped with an Agilent model isocratic pump, four Waters Styragel columns (guard, HR 5E, HR 4, HR 3, and HR 2), and a Viscotek TDA 302 triple detector (RI, dual laser light scattering (LS) (λ = 670 nm, 90° and 7°) and a differential pressure viscometer). TD-GPC was conducted to measure the absolute molecular weights in THF with a flow rate of 0.5 mL/min at 35 °C. All three detectors were calibrated with a PS standard having narrow molecular weight distribution (M_n = 115,000 g/mol, M_w/M_n = 1.02, [η] = 0.519 dL/g at 35 °C in THF, dn/dc = 0.185 mL/g) provided by Viscotek company. Typical sample concentrations for GPC-analysis were in the range of 1–10 mg/mL depending on molecular weight of analyzed polymers. Data analyses were performed with OmniSec 4.5 software from Viscotek Company.

The differential scanning calorimetry (DSC) measurements were performed on a DSC Q1000 (TA Instruments) and a Diamond DSC (Perkin Elmer) instrument with a heating rate of 10 ^{0}C/min under nitrogen. All data were collected from a second heating cycle, and the glass transition (T_g) and the melting temperatures (T_m) were calculated as a midpoint and a peak apex of thermograms, respectively.Mass spectroscopy was performed on Thermo LCQ-Deca ion trap mass instrument.

3.3 Synthetic Procedures

Exo-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione **(1)**, butyloxanorbornene (BONB) **(2)**, polybutyloxanorbornene P(BONB) **(3)**, brom fuctionalized P(BONB) **(4)**, 4-acryloxy-2,2,6,6-tetramethylpiperidine-1-oxyl **(5)**, P(BONB-acrylate) **(6)**, P(BONB-thiophenol) **(7)**, carboxylic acid end-functionalized PEG **(**PEG-COOH) **(8)**, TEMPO end-functionalized PEG (TEMPO-PEG) **(9)**, P(BONB-PEG) **(10)**, 4-glycidyl-2,2,6,6-tetramethylpiperidin-1-oxyl **(11)** P(BONB-epoxy) **(12)** P(BONB-TEMPO) (**13**) and P(BONB) without TEMPO (**14**) were prepared according to literature procedures.

3.3.1 Synthesis of exo-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (1)

Maleimide (7.0 g, 0.052 mol, 1 equiv.) was suspended in 40 mL of toluene and the mixture warmed to 80 °C. Furan (7.48 mL, 0.103 mol, 2 equiv.) 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 100 mL of hexane afforded **1** as white needless. Yield: 7.31 g (86 %). ^{1}H NMR ($CDCl_3$, δ) 8.10 (br, 1H, -N*H)*, 6.51 (s, 2H, C*H*=C*H*, bridge protons), 5.30 (s, 2H, C*H*O, bridge-head protons), 2.88 (s, 2H, C*H*-C*H*, bridge protons).

3.3.2 Synthesis of butyloxanorbornene (BONB) (2)

1 (3.0 g, 18.17 mmol, 1 equiv.) was dissolved in 30 mL of DMF. K_2CO_3 (5.02 g, 36.33 mmol, 2 equiv.) and 1-bromobutane (3.9ml, 36.33 mmol) were added to the reaction mixture in that order. The reaction mixture was stirred for overnight at 60 ^{o}C. After cooling the mixture to ambient temperature, solvent was removed under reduced pressure, and residue was dissolved in 50 mL of CH_2Cl_2 and washed with 3 × 30 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 chromatography eluting with EtOAc /hexane (1:1) to give **2** as a white solid. (Yield: 3.38 g, 84 %).^{1}H NMR ($CDCl_3$): δ 6.51 (s, 2H, C*H*=C*H*, bridge protons), 5.27 (s, 2H, C*H*O, bridge-head protons), 3.47 (t, 2H, NCH_2), 2.83 (s,2H, C*H*-C*H*, bridge protons), 1.56 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.28 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.91 (t, 3H, $NCH_2CH_2CH_2CH_3$). 13C NMR ($CDCl_3$): δ 176.1, 136.4, 80.7, 47.2, 38.8, 31.1, 27.4, 26.1, 22.3, 13.8

3.3.3 Synthesis of poly(butyloxanorbornene) (PBONB) via ROMP of 2 (3)

The first generation Grubbs' catalyst $(PCy_3)_2(Cl)_2$-RuCHPh (0.3 g, 0.36 mmol, 1 equiv.) was placed in a Schlenk tube and dissolved in 2 mL of $CHCl_3$ in a glove box. **2** (2.0 g, 9.05 mmol, 25 equiv.) was dissolved in 3 mL of $CHCl_3$ in another Schlenk tube and added to the catalyst solution via syringe. The flask was capped with a septum and removed from glove box. The polymerization was allowed to stir at room temperature for 30 min. then butyl vinyl ether (0.5 mL) was added to quench the polymerization and stirred additional for 30 min. Finally, the polymer solution was precipitated in methanol and the obtained polymer was dried for 24 h in a vacuum oven at 40 °C (**2**/catalyst = 25; conv. (%) = 100 %; $M_{n,theo}$ = 5560; $M_{n,GPC}$ = 6980;

$M_{n,NMR}$ = 6500; M_w/M_n = 1.28 (RI detector relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.5-7.2 (m, 5H, Ar*H*), 6.08 (bs, C*H*=C*H*, trans), 5.80 (bs, C*H*=C*H*, cis), 5.03 (bs, =CH-C*H*O, cis), 4.47 (bs, =CH-C*H*O, trans), 3.47 (bs, NCH_2), 3.32 (bs, C*H*-C*H* bridge-protons), 1.55 (bs, $NCH_2CH_2CH_2CH_3$), 1.31 (bs, $NCH_2CH_2CH_2CH_3$), 0.93 (bs, $NCH_2CH_2CH_2CH_3$).

3.3.4 Bromination of PBONB backbone (4)

3 (0.75 g, 0.13 mmol, $M_{n,theo}$=5560, 1 equiv.) was dissolved in 80 mL of $CHCl_3$. The reaction mixture was then cooled to 0 ^{o}C. Bromine (0.33 mL, 6.5 mmol, 50 equiv.) in 20 mL of $CHCl_3$ was added dropwise within 30 min. to this solution under nitrogen. The reaction mixture was stirred for 15 min. at 0 ^{o}C then for 4h at room tempeature. The solvent was evaporated under reduced pressure. The remaining residue was diluted with THF, and precipitated in hexane/diethyl ether. This procedure (THF/ hexane-diethyl ether) was repeated two times. The polymer was filtered and dried for 24 h in a vacuum oven at 40 ^{o}C. (Yield: 1.23 g, 95 %). $M_{n,theo}$ = 9560; $M_{n,GPC}$ = 6885; $M_{n,NMR}$ = 9560; M_w/M_n = 1.29 (RI detector relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.5-7.2 (m, 5H, Ar*H*), 4.73 (br, C*H*O and C*H*Br), 3.77 (bs, NCH_2), 3.54 (bs, C*H*-C*H* bridge-protons), 1.58 (bs, NCH_2CH_2), 1.33 (bs, $NCH_2CH_2CH_2$), 0.94 (bs, $NCH_2CH_2CH_2CH_3$).

3.3.5 Synthesis of 4-acryloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (5)

To a 100-mL round bottom flask equipped with a magnetic stir bar, 4-hyroxy-TEMPO (3.0 g, 0.017 mol) and Et_3N (4.85 mL, 0.034 mol) were dissolved in 20 mL dry THF. The flask was cooled in an ice-bath, and acryloyl chloride (2.83 mL, 0.034 mol) was then added dropwise. After 15 h stirring, the mixture was filtered to remove the salt and the filtrate was concentrated. The residual was purified by column chromatography (silica gel) using a MeOH/DCM mixture (5/95, v/v) eluent. The product fraction was collected, concentrated and recrystallised in hexane. Yield: 1.35 g (35 %). ^{1}H NMR ($CDCl_3$): δ 6.47 (br, 1H, C*H*=CH_2), 6.18 (br, 1H, CH=CH_2), 5.94 (br, 1H, CH=CH_2).

3.3.6 Synthesis of PBONB-acrylate via ATNRC reaction (6)

4 (0.4 g, 0.042 mmol, $M_{n,theo}$=9560 , 1 equiv.) was dissolved in DMF (10 mL), **5** (0.95 g, 4.18 mmol, 100 equiv.), PMDETA (0.44 mL, 2.09 mmol, 50 equiv.), CuBr (0.3 g, 2.09 mmol, 50 equiv.) and Cu (0) (0.67 g, 10.45 mmol, 250 equiv.) were added in a 25 mL of Schlenk tube. The reaction mixture was degassed by three FPT cycles, left in vacuum and stirred at room temperature overnight. The solution was diluted with THF and filtered through a column filled with neutral alumina to remove copper complex and finally precipitated in hexane/diethyl ether. The dissolution–precipitation (THF/hexane-diethyl ether) procedure was repeated two times. After decantation, the obtained polymer was dried overnight in a vacuum oven at 40 °C. (Yield = 0.1 g, 36 %) $M_{n,theo}$ = 6804; $M_{n,GPC}$ = 3788; $M_{n,NMR}$ = 7943; M_w/M_n = 1.39 (RI detector relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.5-7.2 (m, 5H, Ar*H*), 6.38 (br, 1H, C*H*=CH_2), 6.08 (bs, C*H*=C*H*), 5.93 (br, 1H, CH=CH_2), 5.81 (br, 1H, CH=CH_2), 5.05 (C*H* of TEMPO), 4.48 (br, NOC*H* and C*H*O), 3.49 (bs, NCH_2), 3.33 (bs, C*H*-C*H* bridge-protons), 1.49 (bs, $NCH_2CH_2CH_2CH_3$), 1.31 (bs, $NCH_2CH_2CH_2CH_3$), 0.93 (bs, $NCH_2CH_2CH_2CH_3$).

3.3.7 Synthesis of PBONB-thiophenol via thiol-ene (Michael) click reaction (7)

6 (0.1 g, 0.015 mmol, $M_{n,theo}$=6804, 1 equiv.) was dissolved in 5 mL of THF. To the reaction mixture were added thiophenol (0.15 mL, 1.5 mmol, 100 equiv.) and Et_3N (0.021 mL, 0.15 mmol, 10 equiv.) in that order under nitrogen. The reaction mixture was stirred for 2 h at room temperature. The mixture was diluted with THF (5 mL), and precipitated in diethyl ether. The dissolution–precipitation (THF-Diethyl ether) procedure was repeated two times. After decantation, the obtained polymer was dried overnight in a vacuum oven at 40 °C. (Yield = 0.1 g, 100 %) $M_{n,theo}$ = 7410; $M_{n,GPC}$ = 4743; $M_{n,NMR}$ = 8646; M_w/M_n = 1.33 (RI detector relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.5-7.2 (m, 5H, Ar*H*), 6.08 (bs, C*H*=C*H*), 5.02 (C*H* of TEMPO), 4.47 (br, NOC*H* and C*H*O), 3.48 (bs, NCH_2), 3.33 (bs, C*H*-C*H* bridge-protons), 2.99 (br, 2H, C=OCH_2CH_2S-Ar), 2.90 (br, 2H, C=OCH_2), 1.55 (bs, $NCH_2CH_2CH_2CH_3$), 1.30 (bs, $NCH_2CH_2CH_2CH_3$), 0.93 (bs, $NCH_2CH_2CH_2CH_3$).

3.3.8 Synthesis of carboxylic acid end-functionalized PEG (PEG-COOH) (8)

PEG-OH (5 g, 9.09 mmol, M_n = 550, 1 equiv.) was dissolved in 150 mL of CH_2Cl_2. Succinic anhydride (1.82 g, 18.18 mmol, 2 equiv.), triethylamine (Et_3N) (6.32 mL, 45.45 mmol, 5 equiv.) and DMAP (2.22 g, 18.18 mmol, 2 equiv.) were added to the reaction mixture. After stirring overnight at room temperature, solution was poured into ice-cold water (150 mL) and extracted with CH_2Cl_2. The organic layer was washed with 1 M HCl (150 mL) and then with distilled water. Finally, organic phase was dried with anhydrous Na_2SO_4 and the solvent was removed in vacuum to give mono carboxylic acid end-functionalized PEG (PEG-COOH) as colorless oil. Yield = 5.6 g (95%); $M_{n,theo}$ = 650 g/mol; $M_{n,NMR}$ = 615 g/mol; $M_{n,GPC}$ = 450 g/mol; M_w/M_n = 1.1, relative to PS standards. ^{1}H NMR ($CDCl_3$, δ) 4.25 (d, 4H, C=OOCH_2), 3.55-3.64 (m, 4H, -OCH_2CH_2O-, PEG backbone), 3.37 (s, 3H, OCH_3), 2.64 (s, 4H, C=OCH_2CH_2C=O).

3.3.9 Synthesis of TEMPO end-functionalized PEG (TEMPO-PEG) (9)

PEG_{550}-COOH (5 g, 7.7 mmol, 1 equiv.), 4-Hydroxy-TEMPO (3.97 g, 0.023 mol, 3 equiv.) and DMAP (0.94 g ,7.7 mmol, 1 equiv.) were dissolved in 25 ml of dry CH_2Cl_2. After stirring 5 min at room temperature, DCC (4.75 g, 0.023 mol, 3 equiv.) dissolved in 100 mL of CH_2Cl_2 was added to the reaction mixture. The reaction mixture was stirred overnight at room temperature. After filtration off the salt, the solution was concentrated and the viscous brown color product was purified by column chromatography over silica gel eluting with CH_2Cl_2/EtOAc mixture (1:1, v/v) and then with CH_2Cl_2/methanol (1:1, v/v) to obtain PEG-Tempo as viscous brown oil.(Yield:4.58 g 82%) $M_{n,theo}$ = 820 g/mol; $M_{n,GPC}$ = 650 g/mol; M_w/M_n = 1.06, relative to linear PS. ^{1}H NMR ($CDCl_3$, δ) 4.33 (d, 4H, C=OOCH_2), 3.61-3.71 (m, 4H, -OCH_2CH_2O-, PEG backbone), 3.44 (s, 3H, OCH_3), 2.75 (s, 4H, C=OCH_2CH_2C=O).

3.3.10 Synthesis of PBONB-PEG via ATNRC reaction (10)

4 (0.2 g, 0.02 mmol, $M_{n,theo}$=9560 , 1 equiv.) was dissolved in DMF (10 mL), **9** (1.51 g, 2.09 mmol, 100 equiv.), PMDETA (0.21 mL, 1.05 mmol, 50 equiv.), CuBr (0.14 g, 1 mmol, 50 equiv.) and Cu (0) (0.32 g, 5 mmol, 250 equiv.) were added in a 25 mL of Schlenk tube. The reaction mixture was degassed by three FPT cycles, left in vacuum and stirred at room temperature overnight. The solution was diluted with

THF and filtered through a column filled with neutral alumina to remove copper complex and finally precipitated in diethyl ether. The dissolution–precipitation (THF-diethyl ether) procedure was repeated two times. After decantation, the obtained polymer was dried overnight in a vacuum oven at 40 °C. (Yield = 0.05 g, 29 %) $M_{n,theo}$ = 8088; $M_{n,GPC}$ = 6843; $M_{n,NMR}$ = 9432; M_w/M_n = 1.25 (RI detector relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.5-7.2 (m, 5H, Ar*H*), 6.08 (bs, C*H*=C*H*), 5.05 (C*H* of TEMPO), 4.47 (br, NOC*H* and C*H*O), 3.65 (m, 4H, -OCH_2CH_2O-, PEG backbone), 3.48 (bs, NCH_2), 3.33 (bs, C*H*-C*H* bridge-protons), 2.62 (br, 4H, C=OCH_2CH_2C=O), 1.55 (bs, $NCH_2CH_2CH_2CH_3$), 1.31 (bs, $NCH_2CH_2CH_2CH_3$), 0.93 (bs, $NCH_2CH_2CH_2CH_3$).

3.3.11 Synthesis of 4-glycidyl-2,2,6,6-tetramethylpiperidin-1-oxyl (11)

First, 10 mL of NaOH (50 wt% aqueous solution) followed by (5 mL, 0.064 mol, 130 equiv.) epichlorohydrin and (0.168 g 0.49 mmol, 1 equiv.) TBABS were added to a 50 mL round bottom flask. With vigorous stirring, (2.0 g, 12 mmol, 24 equiv.) HTEMPO was then added, and left to stir for 16 h at room temperature. Upon stopping any stirring, phase separation between the water and organic red phase occurred. The separate organic phase was dissolved in diethyl ether, washed with brine, dried over MgSO4 and concentrated by using rotary evaporation. The concentrate was purified by column chromatography (silica gel) using methanol/DCM mixture (5/95, v/v) as the eluent. The product fraction at an Rf of 0.45 was collected, concentrated and dried under vacuum. Dark red crystal product (2.5 g) was obtained with yield as 91.2%. ^{1}H NMR ($CDCl_3$, δ) 3.76 (m, 1H; C*H* of epoxide group), 3.35 (m, 2H; -OC*H*2-epoxide), 2.74 (m, 2H; CH_2 of epoxide group), 2.56 (m, 2H; CH_2 of epoxide group).

3.3.12 Synthesis of PBONB-epoxy via ATNRC reaction (12)

4 (0.4 g, 0.042 mmol, $M_{n,theo}$=9560 , 1 equiv.) was dissolved in DMF (10 mL), **11** (0.96 g, 4.2 mmol, 100 equiv.), PMDETA (0.44 mL, 2.1 mmol, 50 equiv.), CuBr (0.30 g, 2.1 mmol, 50 equiv.) and Cu (0) (0.66 g, 10.52 mmol, 250 equiv.) were added in a 25 mL of Schlenk tube. The reaction mixture was degassed by three FPT cycles, left in vacuum and stirred at room temperature overnight. The solution was diluted with THF and filtered through a column filled with neutral alumina to remove copper complex and finally precipitated in methanol. The dissolution–precipitation

(THF-MeOH) procedure was repeated two times. After decantation, the obtained polymer was dried overnight in a vacuum oven at 40 °C. (Yield = 0.07 g, 27 %) $M_{n,theo}$ = 6130; $M_{n,GPC}$ = 6171; $M_{n,NMR}$ = 7162; M_w/M_n = 1.24 (RI detector relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.5-7.2 (m, 5H, Ar*H*), 6.08 (bs, C*H*=C*H*), 5.02 (m, 1H ; C*H* of TEMPO group), 4.47 (br, NOC*H* and C*H*O), 3.48 (bs, NCH_2), 3.33 (bs, C*H*-C*H* bridge-protons and C*H* of epoxide group), 3.10 (m, 2H; -OC*H*2-epoxide), 2.78 (m, 2H; CH_2 of epoxide group), 2.58 (m, 2H; CH_2 of epoxide group), 1.55 (bs, $NCH_2CH_2CH_2CH_3$), 1.30 (bs, $NCH_2CH_2CH_2CH_3$), 0.93 (bs, $NCH_2CH_2CH_2CH_3$).

3.3.13 Synthesis of PBONB-TEMPO (13)

4 (0.7 g, 0.074 mmol, $M_{n,theo}$=9560 , 1 equiv.) was dissolved in DMF (10 mL), TEMPO (2.3 g, 14.7 mmol, 200 equiv.), PMDETA (1.54 mL, 7.4 mmol, 100 equiv.), CuBr (1.06 g, 7.4 mmol, 100 equiv.) and Cu (0) (2.35 g, 37 mmol, 250 equiv.) were added in a 25 mL of Schlenk tube. The reaction mixture was degassed by three FPT cycles, left in vacuum and stirred at room temperature overnight. The solution was diluted with THF and filtered through a column filled with neutral alumina to remove copper complex and finally precipitated in hexane/diethyl ether. The dissolution–precipitation (THF/hexane-diethyl ether) procedure was repeated two times. After decantation, the obtained polymer was dried overnight in a vacuum oven at 40 °C. (Yield = 0.29 g, 65 %) $M_{n,theo}$ = 5990; $M_{n,GPC}$ = 6171; $M_{n,NMR}$ = 6980; M_w/M_n = 1.26 (RI detector relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.5-7.2 (m, 5H, Ar*H*), 6.08 (bs, C*H*=C*H*), 4.47 (br, NOC*H* and C*H*O), 3.48 (bs, NCH_2), 3.32 (bs, C*H*-C*H* bridge-protons), 1.55 (bs, $NCH_2CH_2CH_2CH_3$), 1.31 (bs, $NCH_2CH_2CH_2CH_3$), 0.93 (bs, $NCH_2CH_2CH_2CH_3$).

3.3.14 Synthesis of PBONB without TEMPO (14)

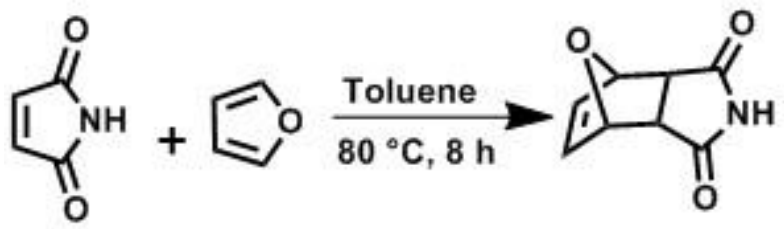
4 (0.2 g, 0.021 mmol, $M_{n,theo}$=9560 , 1 equiv.) was dissolved in DMF (10 mL), PMDETA (0.22 mL, 1.1 mmol, 50 equiv.), CuBr (0.15 g, 1.1 mmol, 50 equiv.) and Cu (0) (0.33 g, 5.26 mmol, 250 equiv.) were added in a 25 mL of Schlenk tube. The reaction mixture was degassed by three FPT cycles, left in vacuum and stirred at room temperature overnight. The solution was diluted with THF and filtered through a column filled with neutral alumina to remove copper complex and finally precipitated in hexane. The dissolution–precipitation (THF/hexane) procedure was

repeated two times. After decantation, the obtained polymer was dried overnight in a vacuum oven at 40 °C. (Yield = 0.07 g, 27 %) $M_{n,theo}$ = 5560; $M_{n,GPC}$ = 4257; $M_{n,NMR}$ = 6500; M_w/M_n = 1.3 (RI detector relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.5-7.2 (m, 5H, Ar*H*), 6.08 (bs, C*H*=C*H*), 4.48 (br, NOC*H* and C*H*O), 3.48 (bs, NCH_2), 3.33 (bs, C*H*-C*H* bridge-protons), 1.54 (bs, $NCH_2CH_2CH_2CH_3$), 1.29 (bs, $NCH_2CH_2CH_2CH_3$), 0.93 (bs, $NCH_2CH_2CH_2CH_3$).

4. RESULTS AND DISCUSSION

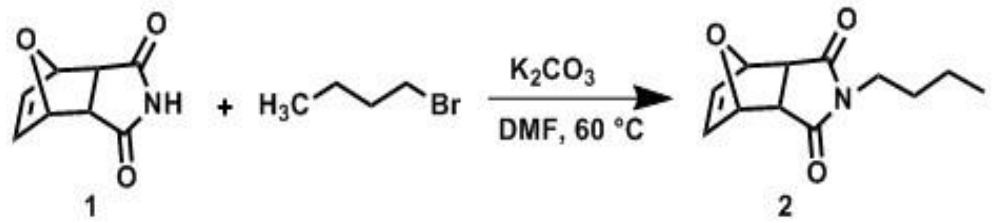
4.1 Preparation of PBONB

First of all, maleimide and furan were reacted in toluene at reflux temperature for 8 h to give exo-10-oxa-4-azatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione **(1) (4.1)**. The maleimide adduct **1** was obtained as small white needless.



(4.1)

Butyl-functionalized oxanorbornene (BONB) monomer **2** was synthesized via reaction of **1** and 1-bromobutane catalyzed by K_2CO_3 in DMF at 60 ^oC overnight **(4.2)**.



(4.2)

The compound **2** was simply purified by flash chromatography eluting with EtOAc/hexane (1/1) and its structure was identified by ^1H NMR spectroscopy. ^1H NMR spectroscopy confirmed clearly the structure of **2** by appearance of characteristic signals of butyl protons (δ 3.47, 1.54,1.31 and 0.91 ppm) and adduct

protons at 6.51 ppm (bridge vinyl protons), 5.26 ppm (bridge-head protons) and 2.83 ppm (bridge protons)as seen in **Figure 4.1.**

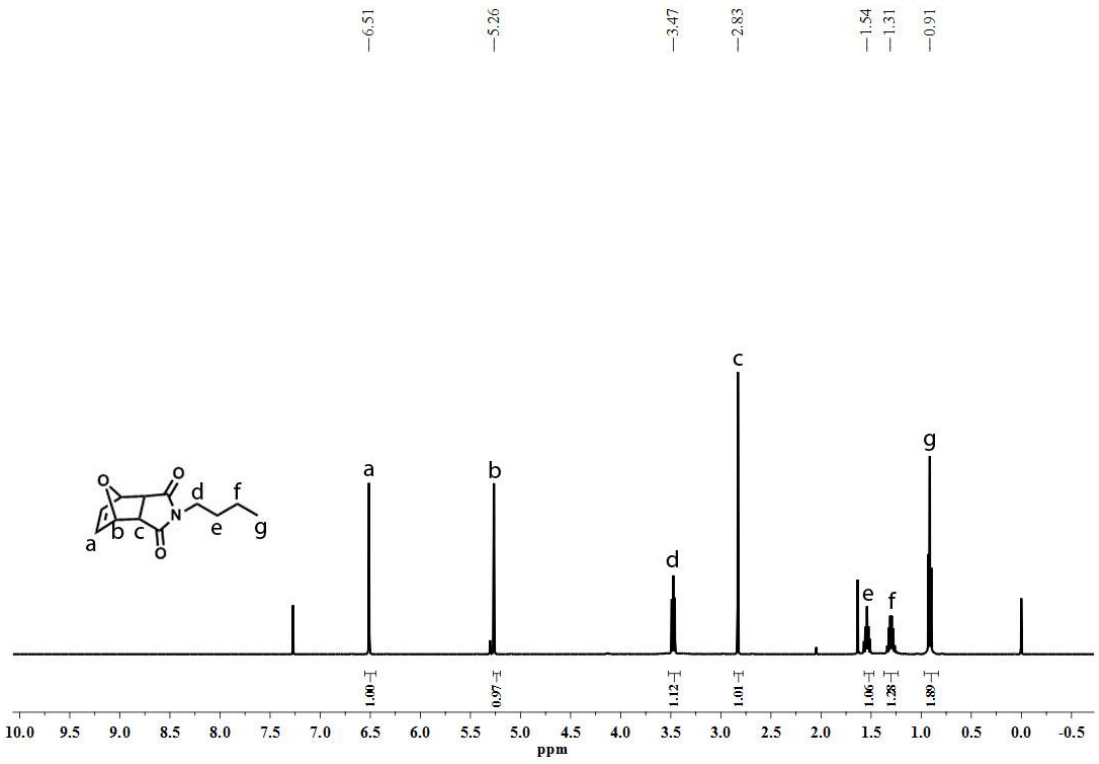
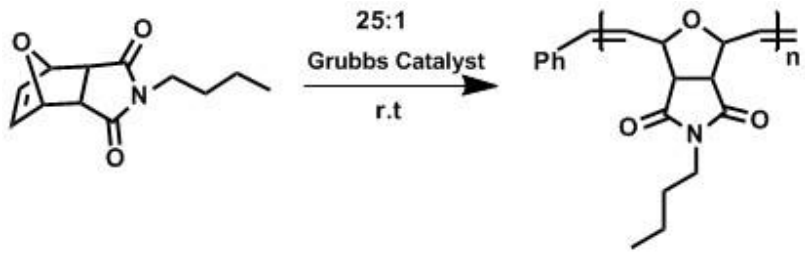


Figure 4.1 : ^{1}H NMR spectrum of BONB (**2**) in $CDCl_3$.

Next, poly(butyloxanorbornene) (PBONB) was obtained via ROMP of **2** using the first generation Grubbs' catalyst $(PCy_3)_2(Cl)_2$-RuCHPh in $CHCl_3$ at room temperature for 30 min, followed by a reaction with butyl vinyl ether as a terminating agent for additional 30 min **(4.3)**.



(4.3)

GPC, ^{1}H NMR and ^{13}C NMR spectroscopy confirmed that PBONB was appropriately prepared with controlled molecular weight, low polydispersity index (PDI) and desired butyl pendant groups. The number-average theoretical molecular weight ($M_{n,theo}$ = 5560), did not fit the number-average molecular weight by

conventional GPC ($M_{n,GPC}$ = 6980, with M_w/M_n = 1.28) relative to linear PS standards. In the NMR spectrum, the shift of the vinyl protons (6.5 ppm) to the 6.08 (C*H*=C*H*, trans) and 5.8 (C*H*=C*H*, cis) were observed upon the ROMP of **2**, which revealed that PBONB had occurred as seen in **Figure 4.2**.

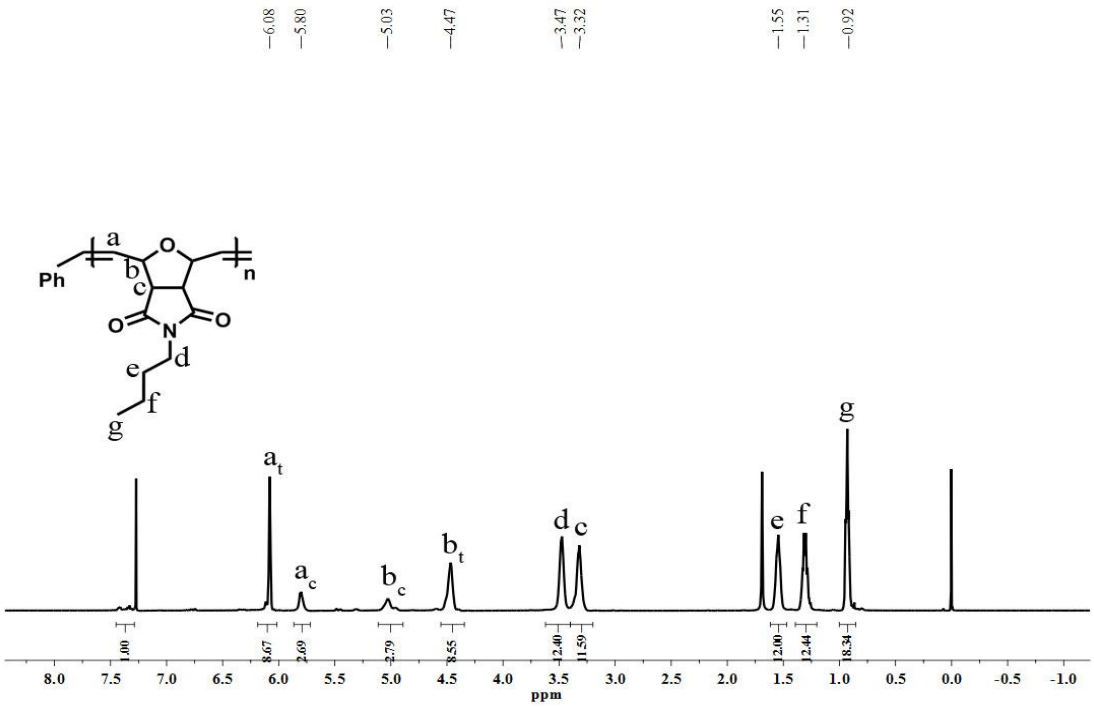


Figure 4.2 : ^{1}H NMR spectrum of PBONB (**3**) in $CDCl_3$.

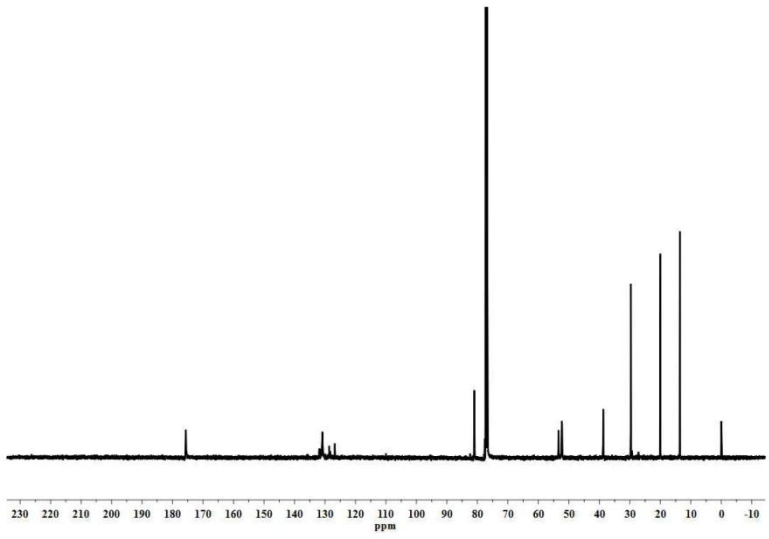
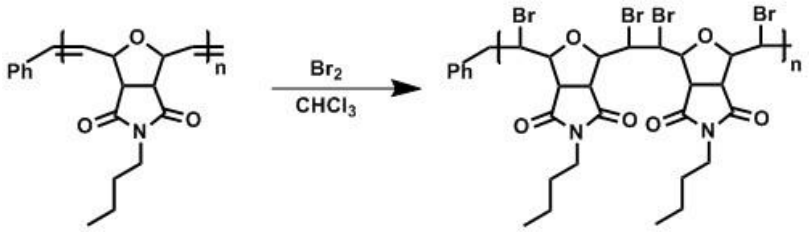


Figure 4.3 : ^{13}C NMR spectrum spectrum of PBONB (**3**) in $CDCl_3$.

To synthesize bromide functionalized polybutyloxanorbornene, **3** and Bromine were reacted in $CHCl_3$ at room temperature for 4h **(4.4).** Finally, compound **4** was obtained.



(4.4)

GPC , ^{1}H NMR and ^{13}C NMR spectroscopy confirmed that PBONB-Br was appropriately prepared with controlled molecular weight, low polydispersity index (PDI) and desired bromide pendant groups. ^{1}H NMR spectrum revealed the structure of PBONB-Br displaying characteristic methine groups attached to the bromine at 4.73 ppm (C*H*Br). It should be noted that vinyl protons of the PBONB at 6.08 (C*H*=C*H*, trans) and 5.80 ppm (C*H*=C*H*, cis) were completely removed on the bromination of **3 (Figure 4.4)**.

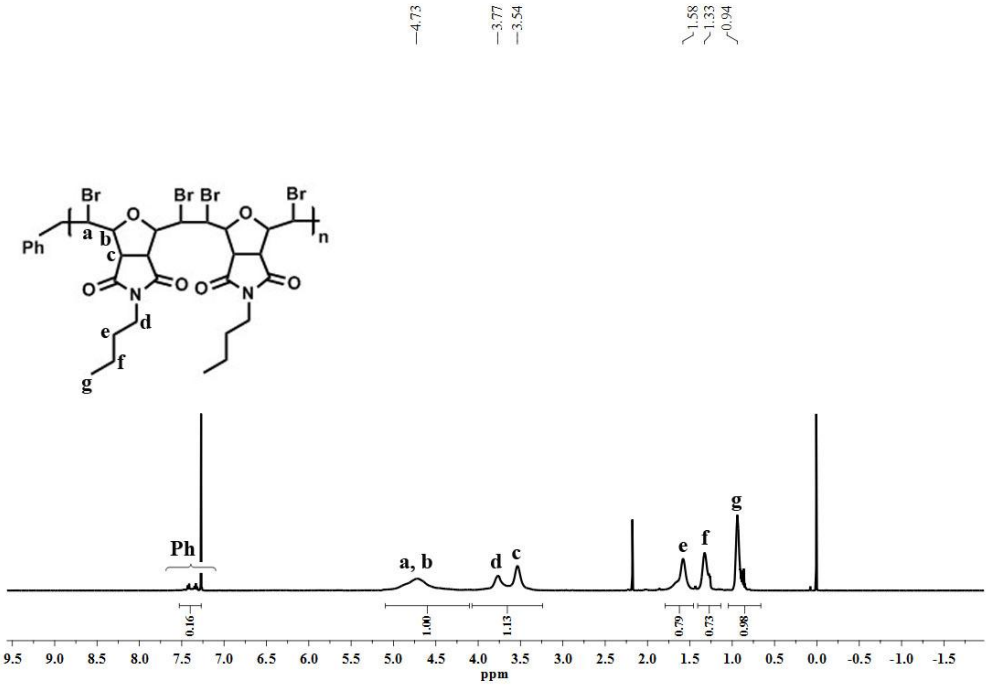


Figure 4.4 : ^{1}H NMR spectrum of PBONB-Br **(4)** in $CDCl_3$.

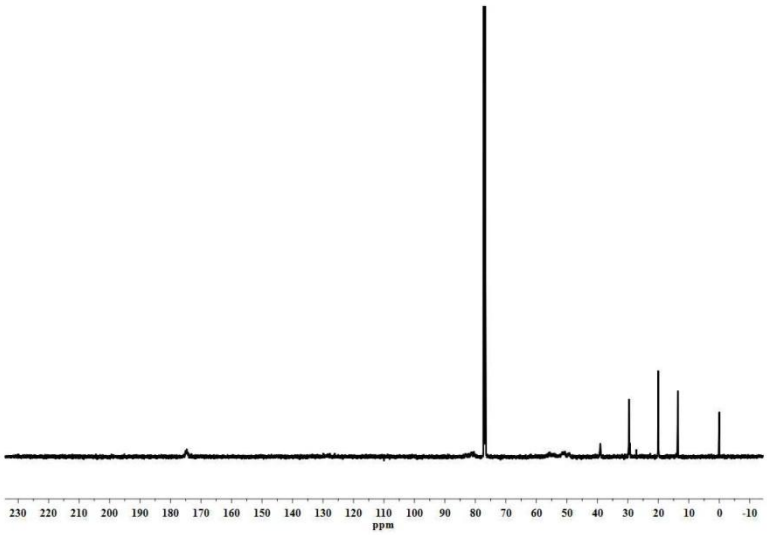
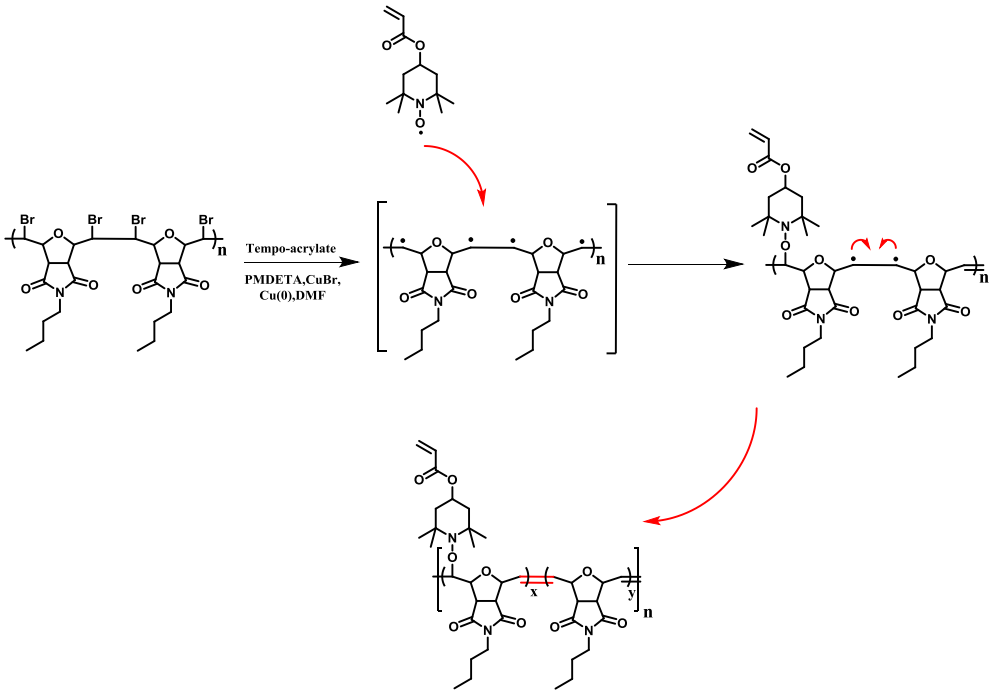


Figure 4.5 : ^{13}C NMR spectrum spectrum of PBONB-Br (**4**) in $CDCl_3$.

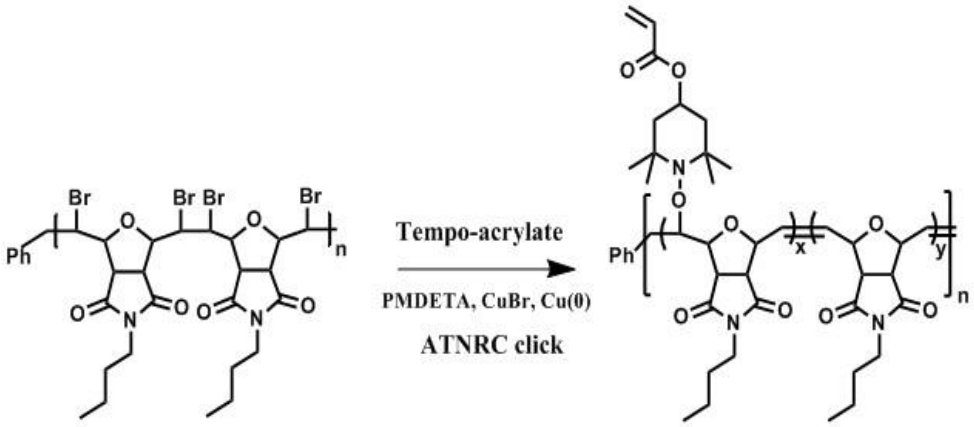
$M_{n,theo}$ was calculated to have 9560 g/mol from the following equation: $M_{n,theo}$ = $M_{n,theo}$ of **3** + (25 x MW of bromine). The number-average molecular weight obtained by GPC ($M_{n,GPC}$ = 6885 g/mol, with M_w/M_n = 1.29), relative to linear PS standarts.

4.2 Synthesis of PBONB-Acrylate via ATNRC Reaction and Subsequent Post-functionalization via Michael thiol-ene Click Reaction

Next, PBONB-bromide was clicked with 4-acryloxy-2,2,6,6-tetramethylpiperidine-1-oxyl **(5)** via ATNRC "click" reaction to yield PBONB Acrylate. The Bromide functionality of **4** was converted to acrylate via a reaction with **5** in the presence of PMDETA, CuBr and Cu (0) catalyst system and DMF as solvent in order to give **6 (4.6)**. $M_{n,theo}$ of **6** was calculated to be 6804 g/mol from an equation, $M_{n,theo}$ = 5560 g/mol ($M_{n,theo}$ of **3**) + 25 x (MW of **5**). Surprisingly, ^1H NMR spectrum of 6 showed vinylic signal at 6.09 ppm indicated formation of double bond as in original polymer. We attributed this behavior to combination of preformed radicals under this conditions.



(4.5)



(4.6)

Figure 4.6 shows the ^{1}H NMR spectrum of **6.** The appearance of CH_3 and CH_2 protons of TEMPO between 2.1-0.7 ppm and olefin protons of acrylate pendants (C=OC*H*=CH_2) of **5** in the range of 6.39 to 5.81 ppm are detected confirming the occurrence of ATNRC "click" reaction.

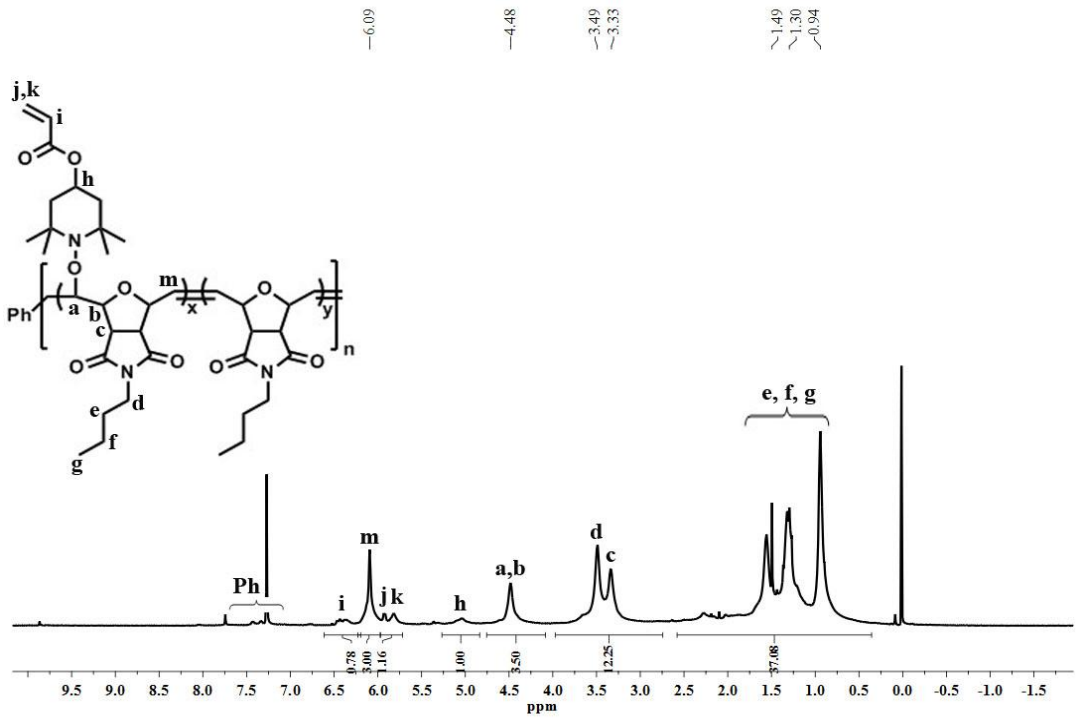
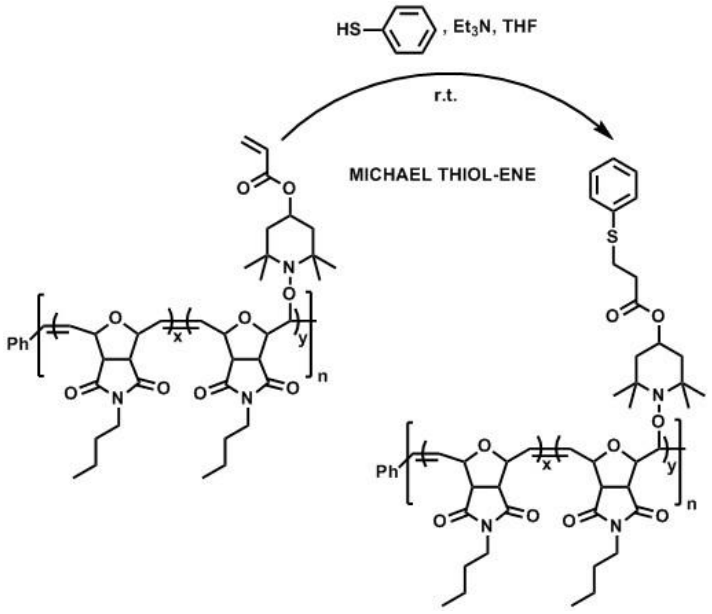


Figure 4.6 : ^{1}H NMR spectrum of PBONB-acrylate **(6)** in $CDCl_3$.

The percentage of acrylate was found to be 22% from ^{1}H NMR by the integral ratios of methine proton (C*H*OC=O) at 5.05 ppm to total area of methine protons (NOC*H* and C*H*O) at 4.48 ppm.

After ATNRC "click" reaction, the obtained polymer **6** was reacted with thiophenol, THF as solvent at room temperature in the presence of Et_3N **(4.7)**.



(4.7)

We can observe the nucleophilic (Michael) thiol-ene "click" reaction by the complete disappearance of characteristic C*H*=CH_2 protons for **6**, as compared to that of **7**. Moreover, the appearance of characteristic multiplet signals of benzyl protons at 7.3 ppm and signals of methylene protons (C=OCH$_2$C*H*$_2$S-Ar and C=OC*H*$_2$CH$_2$S-Ar) at 2.90 and 2.99 ppm respectively, can be seen in **Figure 4.7.**

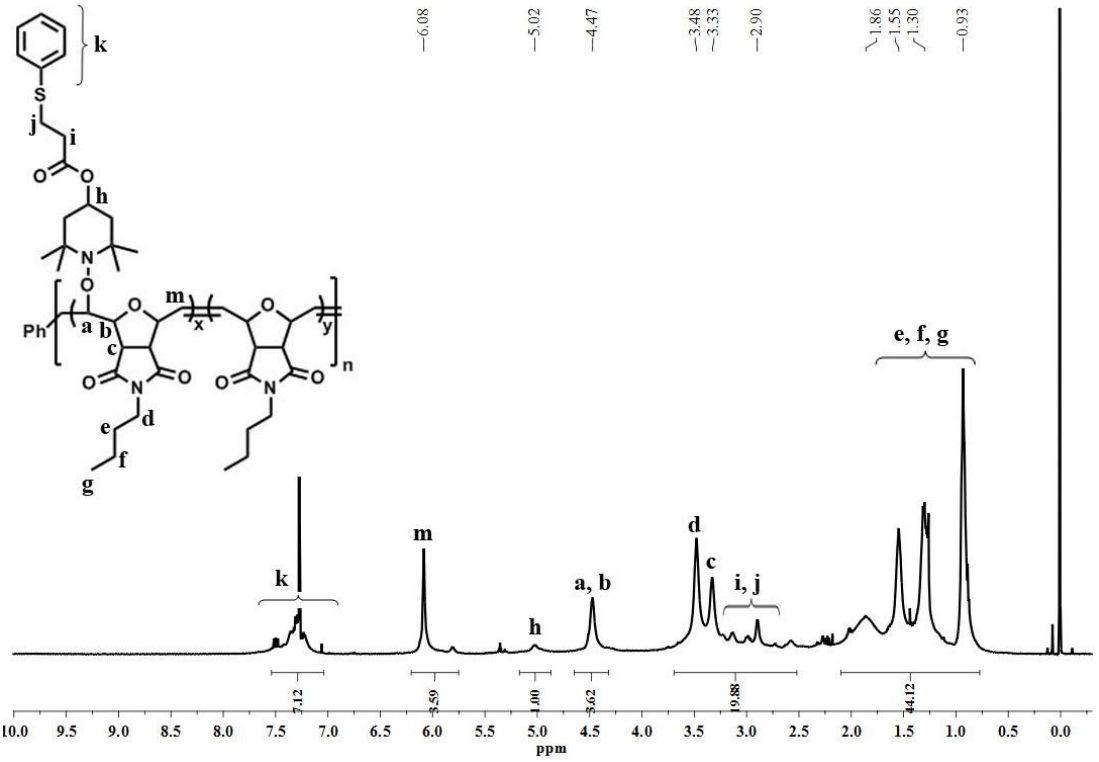


Figure 4.7 : ^{1}H NMR spectrum of PBONB-thiophenol **(7)** in $CDCl_3$.

The $M_{n,theo}$ of **7** was calculated from the following equation $M_{n,theo} = M_{n,theo}$ of **6** + (25 x MW of thiophenol) = 7410 g/mol. The number-average molecular weight obtained by GPC ($M_{n,GPC}$ = 4743 g/mol) relative to linear PS standarts (with M_w/M_n = 1.33) which did not fit the $M_{n,theo}$ =7410.

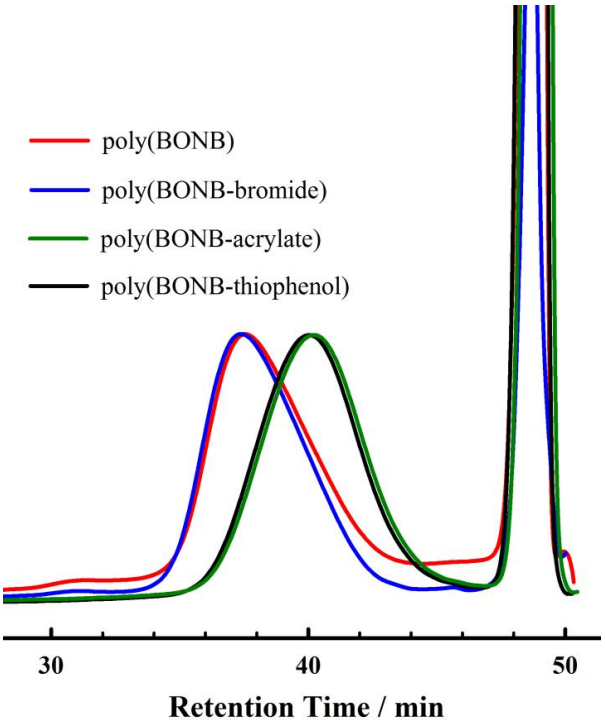
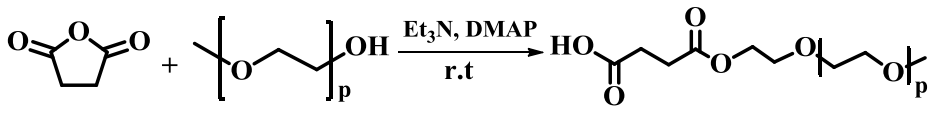


Figure 4.8 : GPC traces of poly(butyloxanorbornene) (PBONB), PBONB-bromide, PBONB-acrylate and PBONB-thiophenol using RI detector in THF at 30 ^{o}C.

GPC analysis showed a shift to low molecular weight region after ATNRC and subsequent Michael reaction could be attributed to decrease in hydrodynamic volume of final structure.

4.3 Synthesis of PBONB-PEG via ATNRC Reaction

Mono carboxylic acid functional PEG (PEG-COOH) was synthesized with a reaction of PEG-OH in the presence of succinic anhydride. When DMAP, Et_3N and CH_2Cl_2 were used as the catalysts and the solvent respectively **(4.8)**.



(4.8)

Figure 4.9 depicts the ^{1}H NMR spectrum of PEG with a COOH end group. The methylene proton of PEG is assigned as 4.25 ppm because of the introduction of succinic anhydride. The methylene proton formed by the ring opening of succinic anhydride is assigned as 2.64 ppm and OCH_2CH_2 repeating unit of PEG observed at 3.64 ppm.

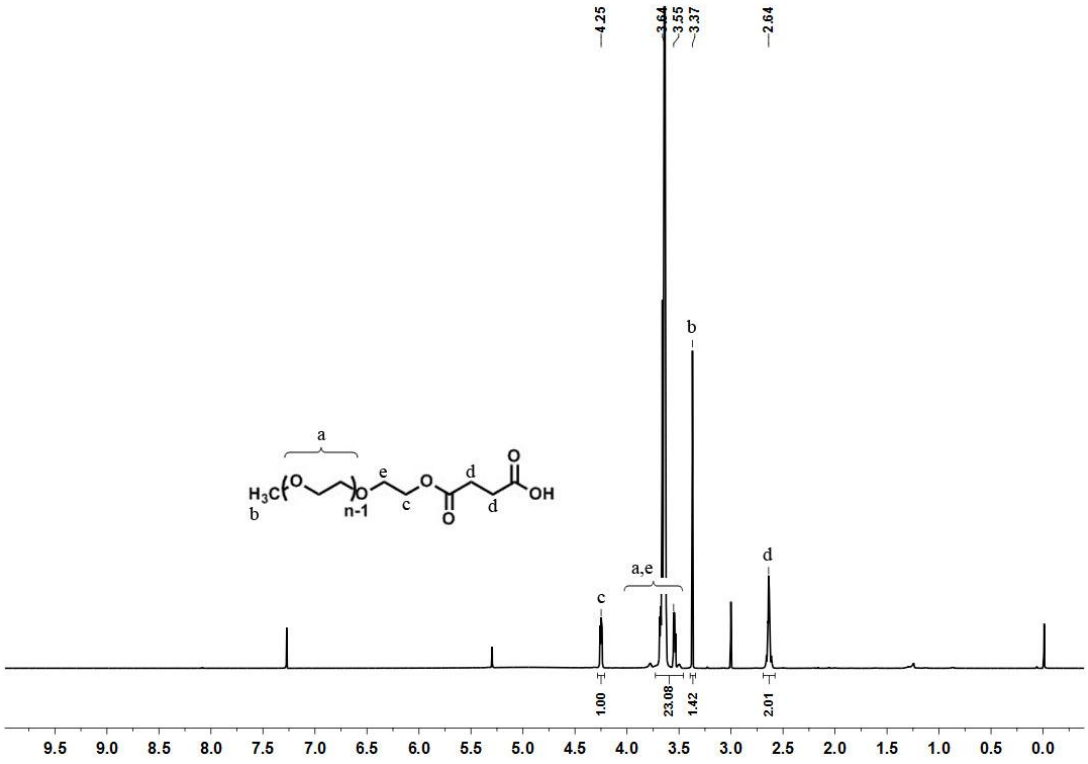
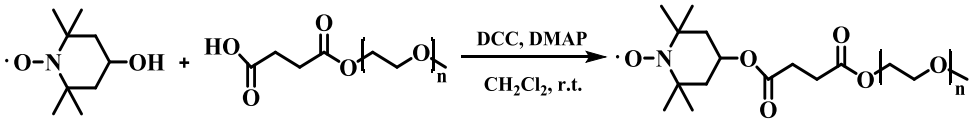


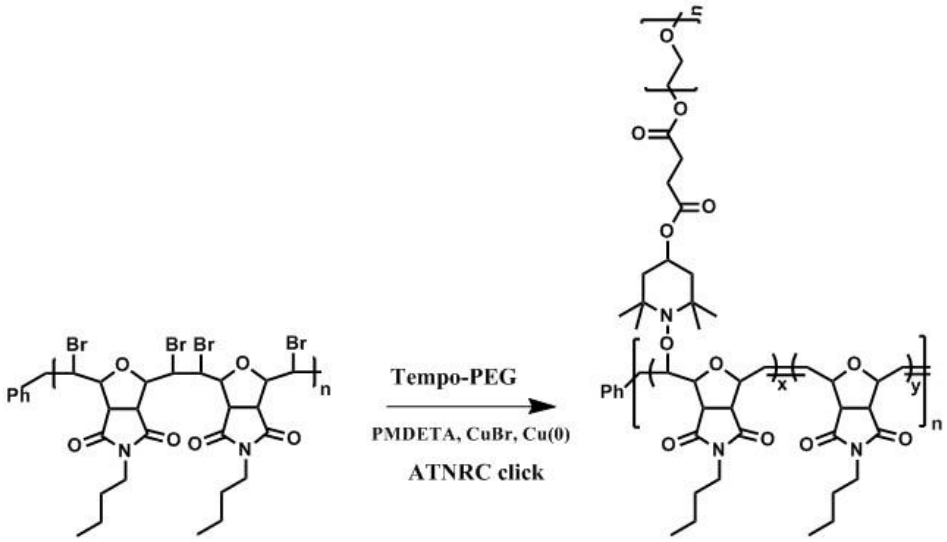
Figure 4.9 : ^{1}H NMR spectrum of PEG-COOH **(8)** in $CDCl_3$.

Next, PEG-COOH used as a polymer to obtained nitroxyl radical functionalized PEG (TEMPO-PEG) **(9)** via using 4-hydroxy-TEMPO as an initiator **(4.9)**. The number-average molecular weight obtained by GPC ($M_{n,GPC}$ = 650 g/mol, relative to linear PS standarts) ($M_{n,theo}$ = 820 g/mol) .



(4.9)

Afterward, PBONB-PEG **(10)** was simply obtained via grafting-onto technique, in which PBONB-bromide main chain was clicked with a TEMPO-PEG by ATNRC "click" reaction **(4.10)**. The ATNRC reaction was carried out using Cu(0), Cu(Br)/PMDETA as catalyst in DMF at room temperature for 24 h. The crude product was purified by two dissolution-precipitation cycles in THF-diethyl ether, respectively, due to that the unreacted PEG could be easily removed from the product.



(4.10)

The structure of PEG functionalized PBONB was identified by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of the **10** is shown in **Figure 4.10**. Repeating unit of PEG ($OCH_2CH_{2)}$ and methine proton of TEMPO observed at 3.65 and 5.02 ppm respectively .

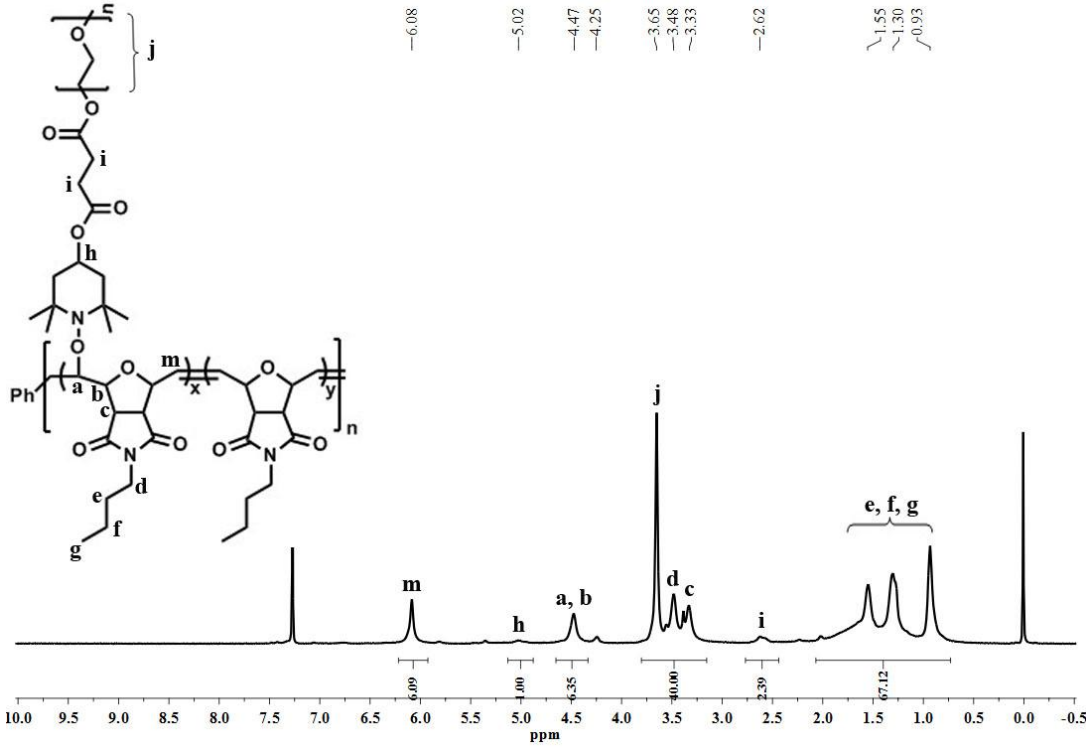


Figure 4.10 : ^{1}H NMR spectrum of PBONB-PEG **(10)** in $CDCl_3$.

The percentage of PEG was found to be 14% from ^{1}H NMR by the integral ratios of methine proton (C*H*OC=O) at 5.02 ppm to total area of methine protons (NOC*H* and C*H*O) at 4.47 ppm.

$M_{n,theo}$ of **10** was calculated to be 8088 g/mol from an equation, $M_{n,theo}$ = 5560 g/mol ($M_{n,theo}$ of **3**) + 25 x (MW of **9**). Furthermore, the number-average molecular weight obtained by GPC ($M_{n,GPC}$ = 6843 g/mol, with M_w/M_n = 1.25, relative to linear PS standarts).

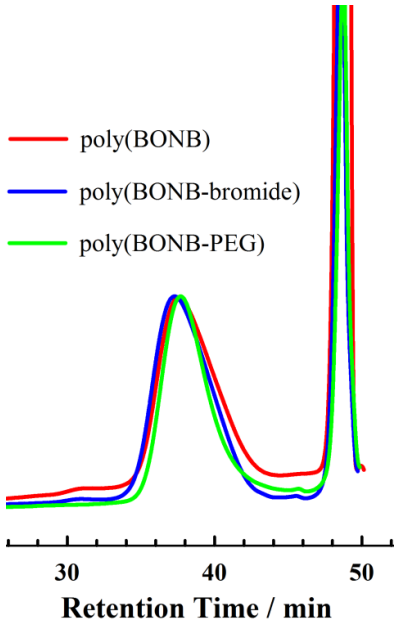
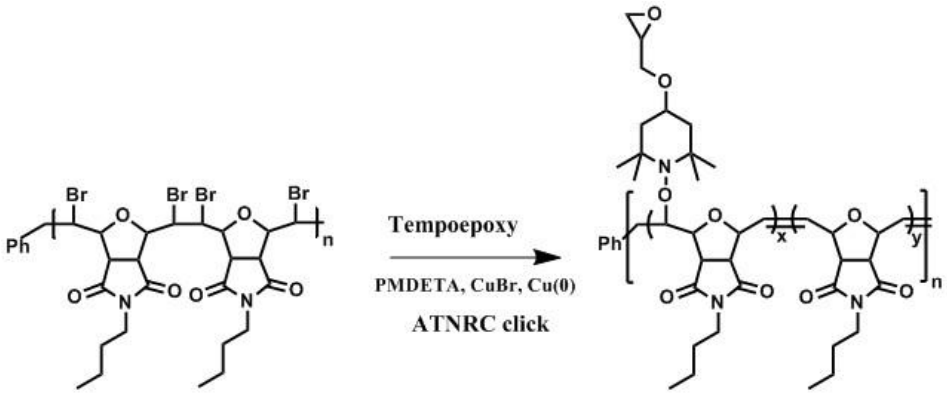


Figure 4.11 : GPC traces of poly(butyloxanorbornene) (PBONB), PBONB-Bromide and PBONB-PEG using RI detector in THF at 30 ^{o}C.

A clear shift was not shown for GPC traces of these polymers , which means the obtained products and its unmodified polymer precursor have same hydrodynamic volume.

4.4 Synthesis of PBONB-Epoxy via ATNRC Reaction

Epoxy functionalized poly(BONB) was carried out by ATNRC "click" reaction between 4-glycidyl-2,2,6,6-tetramethylpiperidin-1-oxyl **(11)** and poly(BONB-bromide). The Bromide functionality of **4** was converted to epoxy via a reaction with **11** in the presence of PMDETA, CuBr and Cu (0) catalyst system and DMF as solvent in order to give **12 (4.11)**



(4.11)

The structure of epoxy functionalized PBONB was identified by ^{1}H NMR and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of the **12** is shown in **Figure 4.12**. The appearance of epoxy protons (C*H* of epoxy ring, – OCH_2-epoxy and CH_2 of epoxy ring), at 3.10, 2.78 and 2.58 ppm respectively, are detected confirming the occurrence of ATNRC "click" reaction.

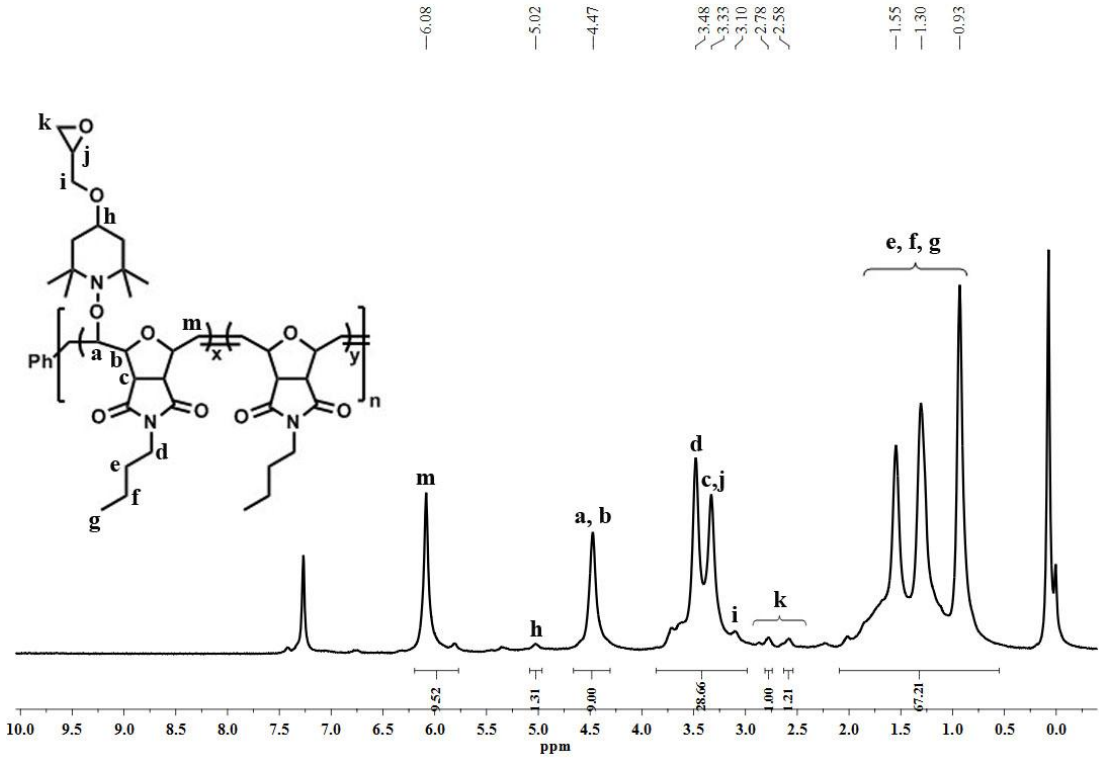


Figure 4.12 : ^{1}H NMR spectrum of PBONB-Epoxy **(12)** in $CDCl_3$.

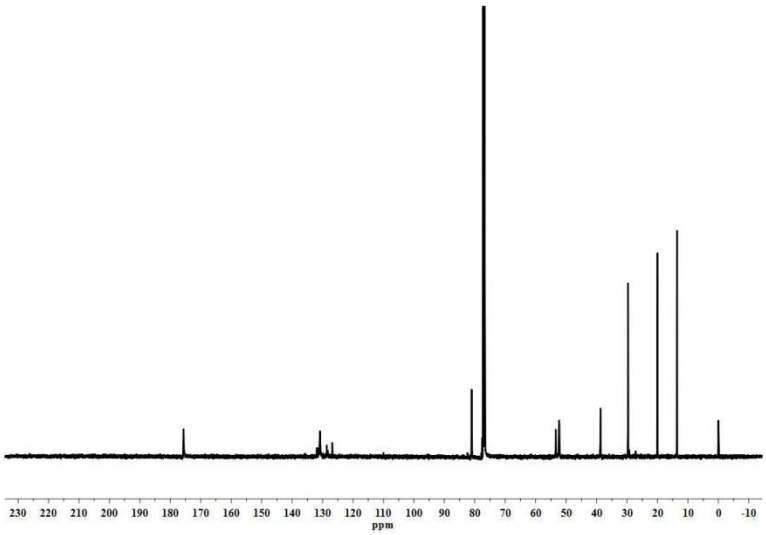


Figure 4.13 : ^{13}C NMR spectrum spectrum of PBONB-Epoxy (**12**) in $CDCl_3$.

The percentage of epoxy was found to be 10% from ^{1}H NMR by the integral ratios of methine proton (C*H*OCH_2) at 5.02 ppm to total area of methine protons (NOC*H* and C*H*O) at 4.47 ppm.

Again $M_{n,theo}$ of **12** was calculated from an equation, $M_{n,theo} = M_{n,theo}$ of **3** + (25 x MW of **11**) = 6130 g/mol. Furthermore, the number-average molecular weight obtained by GPC ($M_{n,GPC}$ = 6171 g/mol, with M_w/M_n = 1.23 relative to linear PS standarts). It was found good agreement between $M_{n,theo}$ and $M_{n,GPC.}$

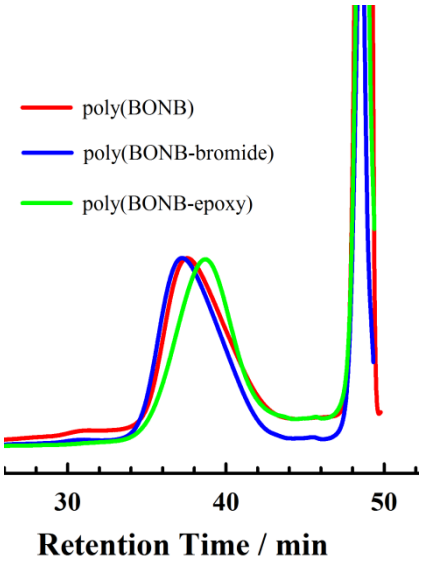
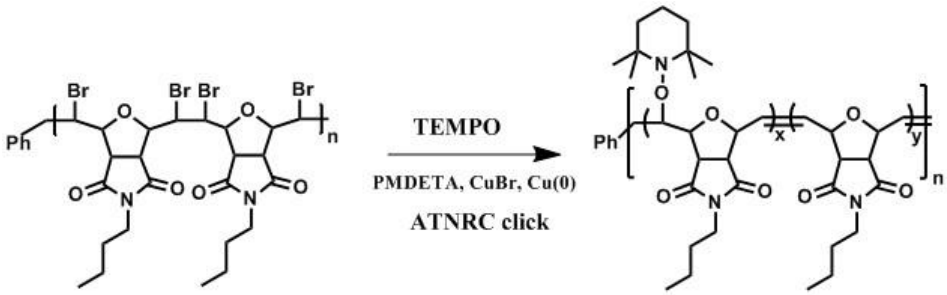


Figure 4.14 : GPC traces of poly(butyloxanorbornene) (PBONB), PBONB-Bromide and PBONB-epoxy using RI detector in THF at 30 ^{o}C.

GPC analysis showed a shift to low molecular weight region compared to PBONB and PBONB-bromide. This may be attributed to decrease in hydrodynamic volume of final structure.

4.5 Synthesis of PBONB-TEMPO via ATNRC Reaction

TEMPO functionalized poly(BONB) was carried out by ATNRC "click" reaction between TEMPO and poly(BONB-bromide). The Bromide functionality of **4** was converted to TEMPO in the presence of PMDETA, CuBr and Cu (0) catalyst system and DMF as solvent in order to give **13 (4.12)**.



(4.12)

The structure of TEMPO functionalized PBONB was identified by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of the **13** is shown in **Figure 4.15**. The appearance of methine protons (NOC*H* and C*H*O) at 4.47 ppm and disappearance of methine protons attached to the bromine at 4.73 ppm (C*H*Br) are detected confirming the occurrence of ATNRC "click" reaction.

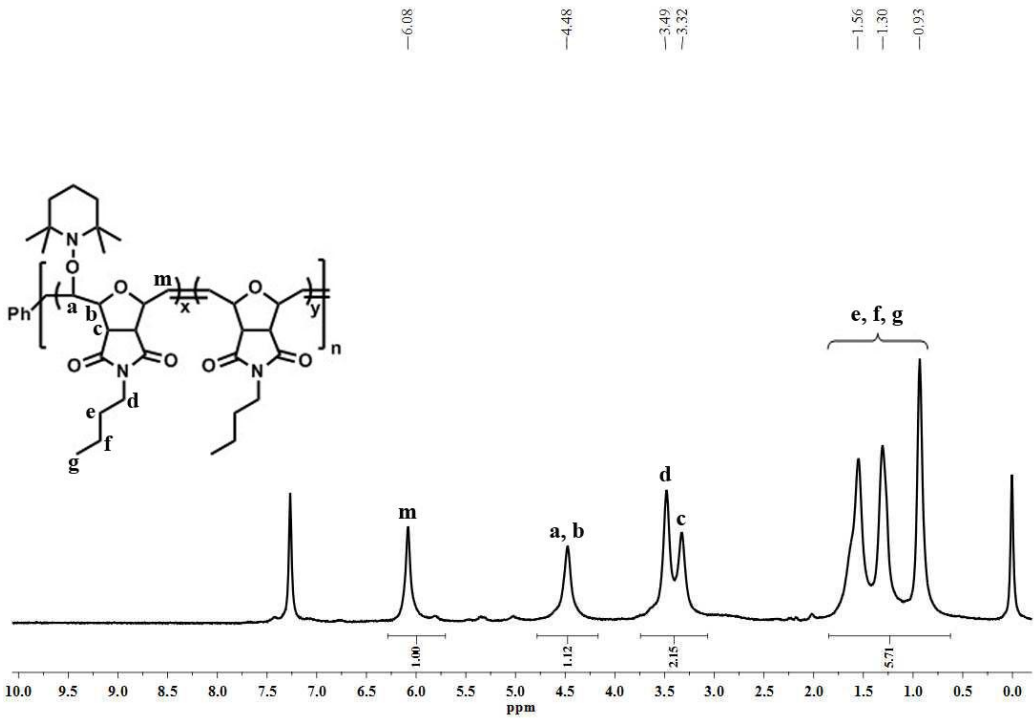


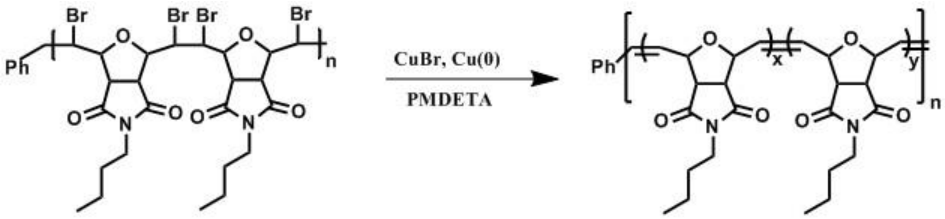
Figure 4.15 : ^{1}H NMR spectrum of PBONB-Epoxy **(12)** in $CDCl_3$.

The percentage of TEMPO was found to be 12% from ^{1}H NMR by the integral ratios of vinyl protons (C*H*=C*H*) at 6.08 ppm to total area of methine protons (NOC*H* and C*H*O) at 4.47 ppm.

Again $M_{n,theo}$ of **13** was calculated from an equation, $M_{n,theo} = M_{n,theo}$ of **3** + (25 x MW of **TEMPO**) = 6028 g/mol. Furthermore, the number-average molecular weight obtained by GPC ($M_{n,GPC}$ = 4671 g/mol, with M_w/M_n = 1.36 relative to linear PS standarts). It was found good agreement between $M_{n,theo}$ and $M_{n,GPC.}$

4.6 Synthesis of PBONB without TEMPO via ATNRC Reaction

Finally, the ATNRC reaction of PBONB-bromide was carried out using without TEMPO groups in the presence of Cu(0), Cu(Br) and PMDETA catalyst system and DMF as solvent at room temperature for 24 h. We observed the original signals belong to PBONB which means in this condition bromine functionalized polymer completely turned into original form.



(4.13)

From ^{1}H NMR spectrum of **14**, the disappearance of methine protons attached to the bromine at 4.73 ppm (C*H*Br) and appearance of vinyl protons (C*H*=C*H*) at 6.08 ppm were detected **(Figure 4.16).**

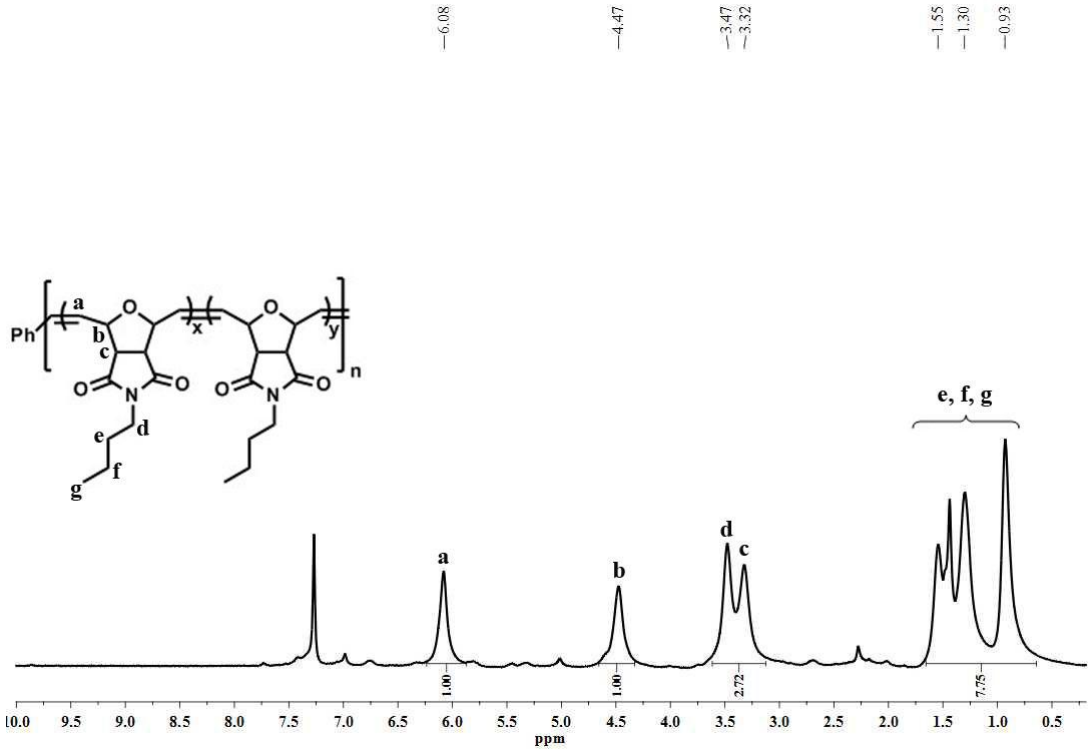


Figure 4.16 : ^{1}H NMR spectrum of PBONB without TEMPO **(14)** in $CDCl_3$.

The number-average molecular weight obtained by GPC ($M_{n,GPC}$ = 4257 g/mol, with M_w/M_n = 1.3 relative to linear PS standarts).

CONCLUSIONS

In this study, a well defined PBONB was obtained through ROMP of BONB monomer. Then, PBONB was quantitatively reacted with bromine to obtain bromide functionalized PBONB. The bromide functionalized PBONB backbone was reacted with several functionalized TEMPO compounds (TEMPO-acrylate, TEMPO-PEG and TEMPO-epoxy) using ATNRC "click" reactions. Surprisingly, ^{1}H NMR spectrum of modified polymers showed vinylic signal at 6.09 ppm indicated formation of double bond as in original polymer. We attributed this behavior to combination of preformed radicals under this conditions. The percentage of acrylate, PEG and epoxy were found to be 22%, 14% and 10% respectively, from ^{1}H NMR by the integral ratios of related areas. PBONB-Acrylate was further reacted with thiophenol via thiol-ene (Michael) click reaction to demonstrate second post-functionalization. Finally, we tested our reaction condition without using any TEMPO groups and we observed that bromine functionalized polymer completely turned into original PBONB.The obtained polymers were characterized by ^{1}H-NMR and GPC. The GPC traces of all polymers showed mostly shift to low molecular weight region unlike expecting to higher molecular weight region after functionalizations might be attributed to decrease in hydrodynamic volume of final structures.

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