İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

STAR POLYMERS WITH POSS VIA AZIDE-ALKYNE CLICK REACTION

M.Sc. Thesis by
Çiğdem BİLİR

Department : Polymer Science & Technology

Programme : Polymer Science & Technology

JANUARY 2010

İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

STAR POLYMERS WITH POSS VIA AZIDE-ALKYNE CLICK REACTION

M.Sc. Thesis by
Çiğdem BİLİR
(515081007)

Date of submission : 25 December 2009
Date of defence examination : 28 January 2010

Supervisor (Chairman) : Prof. Dr. Ümit TUNCA (ITU)
Members of the Examining Committee : Prof. Dr. Metin H. ACAR (ITU)
Members of the Examining Committee : Assis. Prof. Dr. Amitav SANYAL (BU)

JANUARY 2010

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

CLİCK KİMYASI KULLANILARAK POSS İÇEREN YILDIZ POLİMER SENTEZİ

YÜKSEK LİSANS TEZİ

Çiğdem BİLİR
(515081007)

Tezin Enstitüye Verildiği Tarih : 25 Aralık 2009
Tezin Savunulduğu Tarih : 28 Ocak 2010

Tez Danışmanı : Prof. Dr. Ümit TUNCA (İTÜ)
Diğer Jüri Üyeleri : Prof. Dr. Metin H. ACAR (İTÜ)
Diğer Jüri Üyeleri : Yrd. Doç. Dr. Amitav SANYAL (BÜ)

OCAK 2010

ACKNOWLEDGEMENT

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

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

I wish to express my special thanks to my friend and coworker Eda GÜNGÖR for her friendship, helpful and understanding attitudes during my laboratory and thesis study in ITU. It has been a pleasure to work with her.

I would like to also extend my sincere gratitude Hakan DURMAZ for his friendly and helpful attitudes during my laboratory works. In addition, I would like to thank my group member Aydan DAĞ for her support during my laboratory study.

I would like to offer the most gratitude to my family Turhan BİLİR, Aysel BİLİR, Nimet ÇINAR, Nihal ŞUEKİNCİ, Lütfiye BİLİR, Behice BİLİR and Hakan BİLİR and my friends Ceyda Önen YALÇIN, Elif ERDOĞAN, Duygu GÜRSOY, Cansu AKARSU, Volkan KIRMIZI, Başak BULBA and Dila KILIÇLIOĞLU for their patience, understanding and morale support during all stages involved in the preparation of this research.

January 2010

Çiğdem BİLİR
Chemist, M. Sc.

TABLE OF CONTENTS

Page

Page

ABBREVIATIONS

POSS	**:** Polyhedral oligomeric silsesquioxanes
ATRP	**:** Atom Transfer Radical Polymerization
NMP	**:** Nitroxide Mediated Polymerization
RAFT	**:** Reversible Addition-Fragmentation Chain Transfer Polymerization
CRP	**:** Controlled/Living Radical Polymerization
FRP	**:** Free Radical Polymerization
ROP	**:** Ring Opening Polymerization
ROMP	**:** Ring Opening Metathesis Polymerization
PEG	**:** Poly(ethylene glycol)
MMA	**:** Methyl methacrylate
PMMA	**:** Poly(methyl metacrylate)
R_m and R_n	**:** Propagating Radical
P_n and P_m	**:** Terminated Macromolecules
LFRP	**:** Living Free Radical Polymerization
TEMPO	**:** 2, 2', 6, 6'- Tetramethylpiperidinyloxy
PDI	**:** Polydispersity Index
M_t^n	**:** Transition metal
L	**:** Ligand
M_n	**:** Number Average Molecular Weight
M_w	**:** Weight Average Molecular Weight
M_w/M_n	**:** The Molecular Weight Distribution
k_a	**:** Rate constant of activation
k_d	**:** Rate constant of deactivation
k_p	**:** Rate constant of propagation
THF	**:** Tetrahydrofuran
DMAP	**:** 4-dimethylaminopyridine
PMDETA	**:** *N,N,N',N'',N''* - pentamethyldiethylenetriamine
DCC	**:** *N*, *N*'-dicyclohexylcarbodiimide
DMF	**:** *N,N* - dimethylformamide
TEA	**:** Triethylamine
SA	**:** Succinic anhydride
FTIR	**:** Fourier Transform Infrared
GPC	**:** Gel Permeation Chromotography
NMR	**:** Nuclear Magnetic Resonance Spectroscopy
DSC	**:** Differential Scanning Calorimetry

LIST OF TABLE

Page

LIST OF FIGURES

Page

Page

STAR POLYMERS WITH POSS VIA AZIDE-ALKYNE CLICK REACTION

SUMMARY

Cage-like silsesquioxanes are usually called polyhedral oligosilsesquioxanes or Polyhedral Oligomeric Silsesquioxanes, abbreviated as POSS. They can be loosely regarded as the smallest possible silica particles. POSS materials have attained much interest because of their well-defined nanostructure and versatile reactivity. Various types of POSS materials have been used as building blocks for precisely defined nanostructured functional materials, mainly with improved thermal and mechanical properties. POSS molecules have been extensively incorporated into polymer matrices by chemical reaction or physical blending to prepare many POSS-containing hybrids with good properties.

Star polymers have attracted much attention in research over the years due to their unique-three dimensional shape and highly branched structure. The synthesis of well-defined polymers is usually achieved by a living polymerization technique. Controlled/ "Living" Radical Polymerization processes have proven to be versatile for the synthesis of polymers with well-defined structures and complex architectures. Among the CRP processes, Atom Transfer Radical Polymerization (ATRP) and Nitroxide Mediated Polymerization (NMP) are the most efficient methods for the synthesis of special block copolymers and polymers with complex architectures such as stars. Both, ATRP and NMP methods based on the fast equilibrium between active and dormant chains; actually it is the main effect to obtain controlled structure.

One of the advantageous of controlled radical polymerization techniques such as ATRP and NMP is that the molecular weight and the chain end functionality can be controlled. The wide range of functionality can be introduce into the polymer chain and this leads to the synthesis of well-defined copolymers by a sequential two-step or one pot method without any transformation or protection of initiating sites.

Recently, Sharpless and coworkers used Cu (I) as a catalyst in conjunction with a base in Huisgen's 1,3-dipolar cycloadditions ([3 + 2] systems) between azides and alkynes or nitriles and termed them click reactions. Click chemistry strategy was successfully applied to macromolecular chemistry, affording polymeric materials varying from block copolymers to complex macromolecular structures. Click reactions permit C–C (or C–N) bond formation in a quantitative yield without side reactions or requirements for additional purification steps.

In this work, azidopropyl-heptaisobutyl substituted-polyhedral oligomeric silsesquioxane (POSS-N_3) was reacted with 1,1,1-tris[4-(2-propynyloxy)phenyl]-ethane and poly(ethylene glycol) (PEG)-*b*-poly(methyl methacrylate) (PMMA) copolymer with alkyne at its center (PEG-PMMA-alkyne) affording the first time synthesis of 3-arm star POSS and PEG-PMMA-POSS 3-miktoarm star terpolymer, respectively in the presence of CuBr/ *N*, *N*, *N*', *N*'', *N*''-pentamethyldiethylenetriamine (PMDETA) as catalyst and *N*,*N*-dimethylformamide (DMF)/ tetrahydrofuran (THF) as solvent at room temperature. The precursors and

the target star polymers were characterized comprehensively by Hydrogen Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR), Gel Permeation Chromatography (GPC) and Differential Scanning Calorimetry (DSC).

CLİCK KİMYASI KULLANILARAK POSS İÇEREN YILDIZ POLİMER SENTEZİ

ÖZET

POSS olarak kısaltılan kafes benzeri silsesquioksanlar genellikle polihedral oligosilsesquioksanlar veya polihedral oligomerik silsesquioksanlar diye adlandırılır. POSS olabildiğince küçük silika parçacıklar olarak kabul edilebilir. POSS'ın iyi tanımlanmış nano yapıya ve çok yönlü reaktiviteye sahip olması, POSS'a olan ilgiye arttırmıştır. Tanımlı nano yapılı fonksiyonel malzemelerin, ısısal ve mekanik özelliklerini geliştirmek için farklı POSS yapıları kullanılmıştır. İyi özellikleri olan POSS içeren hibrid yapılar elde etmek için POSS molekülleri polimer matrisleri içine kimyasal reaksiyon veya fiziksel karıştırma ile ilave edilirler.

Yıldız polimerler araştırmalarda üç boyutlu ve çok dallanmış yapılarından dolayı yıllardır ilgi çekmektedirler. Yıldız polimerlerin sentezi genellikle yaşayan polimerizasyon yöntemiyle gerçekleştirilmektedir. Kontrollü/ "Yaşayan" Polimerizasyon yöntemlerinin iyi tanımlanmış ve kompleks yapılı polimerlerin sentezinde birçok açıdan faydalar sağladığı bilinmektedir. Kontrollü/ "Yaşayan" Radikal Polimerizasyon yöntemlerinin arasında Atom Transfer Radikal Polimerizasyonu (ATRP) ve Nitroksit Ortamlı Radikal Polimerizasyonu (NMP) özel blok kopolimerler ve yıldız polimerler gibi kompleks yapılı polimerlerin sentezinde en etkili yöntemlerdir. ATRP ve NMP metotlarının her ikisi de aktif ve kararlı zincirler arasındaki hızlı dinamik dengeye dayanır ki kontrolü de sağlayan aslında budur.

ATRP ve NMP gibi kontrollü polimerizasyon tekniklerinin bir avantajı da elde edilen polimerin molekül ağırlığının ve zincir uç grubu fonksiyonalitesinin kontrol edilebilir olmasıdır. Bu teknikler sayesinde polimer uç gruplarına çok çeşitli fonksiyonellikler kazandırılabilir bu da herhangi bir transformasyon reaksiyonu gerektirmeden iyi tanımlı polimerlerin eldesine izin verir.

Son yıllarda, Sharpless ve arkadaşları azidler ve alkin ya da nitriller arasındaki Huisgen 1,3-dipolar siklokatılmalarda ([3 + 2] sistemi) Cu(I)'i baz ile birleştirip kataliz olarak kullandılar ve bu reaksiyonu click reaksiyonu olarak adlandırdılar. Click kimyası blok kopolimerlerden karmaşık makromoleküler yapılara kadar değişen birçok polimerik malzemenin yapılmasına kadar makromolekül kimyasında başarılı bir şekilde uygulandı. Click reaksiyonları, yan reaksiyonlara sebebiyet vermeyecek ve ilave saflaştırma işlemlerine gereksinim duyulmayacak bir şekilde kantitatif verimle C–C (veya C–N) bağ oluşumuna izin vermektedir.

Bu çalışmada, azidpropil-heptaizobutil sübstitüentli polihedral oligomerik silsesquioksan (POSS-N_3), 1,1,1-tris[4-(2-propiniloksi)fenil]-etan ve alkin uç fonksiyonitesine sahip poli(etilen glikol) (PEG)-*b*-poli(metil metakrilat) (PMMA) kopolimeri (PEG-PMMA-alkyne) ile reaksiyona girmesi sonucu 3-kollu yıldız POSS ve 3 farklı kollu yıldız terpolimeri (PEG-PMMA-POSS) sentezlendi. CuBr/ *N*, *N*, *N*', *N*", *N*"-pentametildietilentriamin (PMDETA)'ın katalizör olarak ve N,N-

dimetilformamid (DMF)/ tetrahidrofuran (THF)'ın çözücü olarak kullanıldığı reaksiyon oda sıcaklığında gerçekleştirildi. Elde edilen polimerlerin yapıları ^{1}H NMR, GPC ve DSC yardımıyla aydınlatıldı.

1. INTRODUCTION

Cage-like silsesquioxanes are usually called as polyhedral oligomeric silsesquioxane (POSS). These structures feature well-defined and highly symmetric molecules having size, approximately 1.5 nm in diameter, while including R groups positioned at the silicon-oxygen cage vertex. Therefore, the size of the POSS molecule is comparable to the dimensions of the polymer segments in the solid or molten phase [1]. The POSS molecules having cubic inorganic core with the composition of $R_8Si_8O_{12}$ or $R_1R_7Si_8O_{12}$ are the most studied systems. R groups (organic shell) can be varied from hydrogen to alkyl (methyl, isobutyl, cyclopentyl or cyclohexyl etc), alkylene or arylene. Thus, POSS molecules can be regarded as a truly inorganic core/organic shell architecture, which is compatible with polymers and natural biomaterials. One or more R groups of POSS can be modified by using organic reactions affording the functional groups. These functional groups provide the incorporation of the POSS to the polymer systems. In this approach, a great variety of POSS-polymer architectures is possible. Homo and copolymerization of the POSS macromonomer providing the POSS as pendant and an incorporation of the POSS moiety at the end of the polymer chain affording the block copolymer structure are the most important synthetic routes studied [1-12].

A branched polymer structure is elucidated as a nonlinear polymer with multiple backbone chains growing from junction points [13]. It has been shown that branching results in a more compact structure in comparison to linear counterparts of similar molecular weight, due to its high segment density, which changes the melt, solution and solid-state properties of the polymer [13]. Nonlinear polymers primarily include star, graft, H-type, hyperbranched, dendrimers and dendrimer-like star polymers. Nonlinear polymers had been generally prepared by living anionic and cationic polymerizations until recently [14-16]. In the last decade, with the enormous advances in the living radical polymerization (LRP) routes, e.g. metal catalyzed living radical polymerization often named as atom transfer radical polymerization (ATRP), the nitroxide-mediated free radical polymerization (NMP) and the

reversible addition fragmentation chain transfer (RAFT), the synthesis of polymers having complex architectures and predetermined chemical compositions became possible and received an increased attention due to the variety of applicable monomers and greater tolerance to experimental conditions in comparison with living ionic polymerization routes [17-18].

Additionally, Cu catalyzed Huisgen azide-alkyne 1,3-dipolar cycloaddition as a leading example of the click chemistry has been first adapted to the field of polymer chemistry, because of its quantitative yields, mild reaction condition, and tolerance of a wide range of functional groups [19-22]. Therefore, azide-alkyne click reactions with the combination of LRP and other living polymerization routes, such as ring opening polymerization (ROP) and ring opening metathesis polymerization (ROMP) have been remarkably applied to the preparation of the nonlinear polymers [19-30].

In this study, using this argument given above as a starting point, mono azide functionalized POSS is the first time incorporated as A_3 (3-arm) and ABC (3-miktoarm) star polymers via Cu(I) catalyzed azide-alkyne click reaction strategy. Firstly, 3-arm star POSS was simply achieved via click reaction of mono azide functionalized POSS (POSS-N_3) with tris-alkyne core **(8)** in the presence of Cu(I) salt in DMF at room temperature. Secondly, poly(ethylene glycol) (PEG)-poly(methyl methacrylate) (PMMA)-POSS 3-miktoarm star terpolymer, was prepared by a click reaction of POSS-N_3 with PEG-*b*-PMMA copolymer containing alkyne at its junction point (PEG-PMMA-alkyne) using Cu(I) as catalyst in DMF at room temperature. GPC traces, ^{1}H-NMR and DSC investigations show that both initiator and polymerization were carried out successfully.

2. THEORETICAL PART

2.1. Conventional Free Radical Polymerizations

Conventional free radical polymerization (FRP) has many advantages over other polymerization processes. First, FRP does not require stringent process conditions and can be used for the (co)polymerization of a wide range of vinyl monomers. Nearly 50% of all commercial synthetic polymers are prepared using radical chemistry, providing a spectrum of materials for a range of markets [31]. However, the major limitation of FRP is poor control over some of the key elements of the process that would allow the preparation of well-defined polymers with controlled molecular weight, polydispersity, composition, chain architecture, and site-specific functionality.

As chain reactions, free radical polymerizations proceed via four distinct processes:

1. *Initiation*. In this first step, a reactive site is formed, thereby "initiating" the polymerization.

2. *Propagation*. Once an initiator activates the polymerization, monomer molecules are added one by one to the active chain end in the propagation step. The reactive site is regenerated after each addition of monomer.

3. *Transfer*. Transfer occurs when an active site is transferred to an independent molecule such as monomer, initiator, polymer, or solvent. This process results in both a terminated molecule (see step four) and a new active site that is capable of undergoing propagation.

4. *Termination*. In this final step, eradication of active sites leads to "terminated," or inert, macromolecules. Termination occurs via coupling reactions of two active centers (referred to as combination), or atomic transfer between active chains (termed disproportionation).

The free radical chain process is demonstrated schematically below in Figure 2.1: $R^{\cdot}$ represents a free radical capable of initiating propagation; M denotes a molecule of

monomer; R_m and R_n refer to propagating radical chains with degrees of polymerization of *m* and *n*, respectively; AB is a chain transfer agent; and $P_n + P_m$ represent terminated macromolecules.

Because chain transfer may occur for every radical at any and all degrees of polymerization, the influence of chain transfer on the average degree of polymerization and on polydispersity carries enormous consequences. Furthermore, propagation is a first order reaction while termination is second order. Thus, the proportion of termination to propagation increases substantially with increasing free radical concentrations. Chain transfer and termination are impossible to control in classical free radical processes, a major downfall when control over polymerization is desired. A general free radical polymerization mechanism is given below.

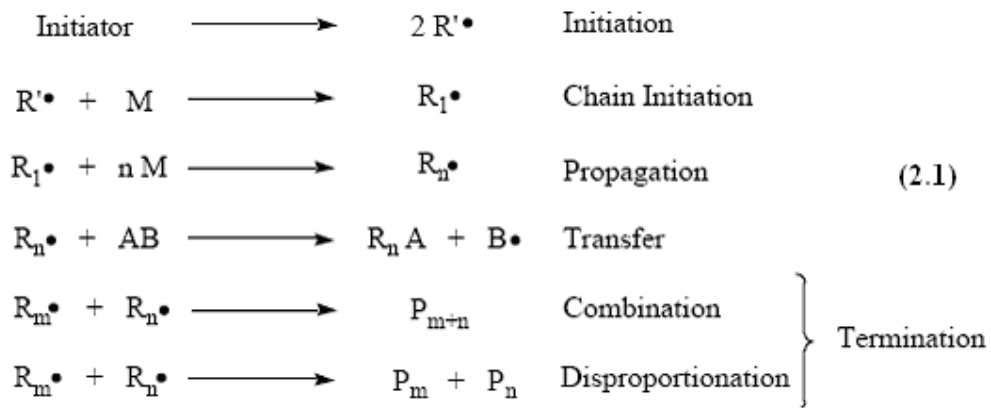


Figure 2.1: General free radical polymerization mechanism.

2.2. Conventional Living Polymerizations

Living polymerizations are characterized by chain growth that matures linearly with time. Inherent in this definition are two characteristics of ionic polymerizations that both liken and distinguish ionic routes from the aforementioned free radical route. In order to grow linearly with time, ionic polymerizations must proceed by a chain mechanism in which subsequent monomer molecules add to a single active site; furthermore, addition must occur without interruption throughout the life of the active site. Thus, the chain transfer mechanisms described above must be absent. Living polymerizations may include slow initiation, reversible formation of species with various activities and lifetimes, reversible formation of inactive (dormant) species, and/or reversible transfer [32]. Living polymerizations must not include

irreversible deactivation and irreversible transfer. Classical living polymerizations occur by the formation of active ionic sites prior to any significant degree of polymerization. A well-suited initiator will completely and instantaneously dissociate into the initiating ions. Dependent on the solvent, polymerization may then proceed via solvent pairs or free ions once a maximum number of chain centers are formed. Solvents of high dielectric constants favor free ions; solvents of low dielectric constants favor ionic pairs. Termination by coupling will not occur in ionic routes due to unfavorable electrostatic interactions between two like charges. Furthermore, chain transfer routes are not available to living polymerizations, provided the system is free of impurities. Polymerization will progress until all of the monomer is consumed or until a terminating agent of some sort is added. On the flip side, ionic polymerizations are experimentally difficult to perform: a system free of moisture as well as oxygen, and void of impurities is needed. Moreover, there is not a general mechanism of polymerization on which to base one's experiment: initiation may occur in some systems before complete dissociation of initiator. Knowledge of the initiating mechanism must be determined *a priori* to ensure a successful reaction. Despite the advantage of molecular control of living systems, the experimental rigor involved in ionic polymerization is often too costly for industrial use and free radical routes are preferred.

2.3. Controlled/ ''Living" Free Radical Polymerizations

Living polymerization was first defined by Szwarc [33] as a chain growth process without chain breaking reactions (transfer and termination). Such a polymerization provides end-group control and enables the synthesis of block copolymers by sequential monomer addition. However, it does not necessarily provide polymers with molecular weight (MW) control and narrow molecular weight distribution (MWD). Additional prerequisites to achieve these goals include that the initiator should be consumed at early stages of polymerization and that the exchange between species of various reactivities should be at least as fast as propagation [34-36]. It has been suggested to use a term controlled polymerization if these additional criteria are met [37]. This term was proposed for systems, which provide control of MW and MWD but in which chain breaking reactions continue to occur as in RP.

However, the term controlled does not specify which features are controlled and which are not controlled. Another option would be to use the term ‘‘living’’ polymerization (with quotation marks) or ‘‘apparently living,’’ which could indicate a process of preparing well-defined polymers under conditions in which chain breaking reactions undoubtedly occur, as in radical polymerization [38,39].

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

Living polymerization is defined as a polymerization that undergoes neither termination nor transfer. A plot of molecular weight vs conversion is therefore linear, as seen in Figure 2.2, and the polymer chains all grow at the same rate, decreasing the polydispersity. The propagating center at 100 % conversion still exists and can be further reacted, which can allow novel block, graft, star, or hyperbranched copolymers to be synthesized. Living polymerizations have been realized in anionic processes where transfer and termination are easy to suppress. Due to the favorable coupling of two radical propagating centers and various radical chain transfer reactions, the design and control of living radical processes is inherently a much more challenging task. The living process of radical polymerization involves the equilibration of growing free radicals and various types of dormant species. By tying up a great deal of the reactive centers as dormant species, the concentration of free radicals decreases substantially and therefore suppresses the transfer and termination steps. These reactions are also denoted as controlled /living polymerizations rather than as true living polymerizations because transfer and termination are decreased but not eliminated. [40]

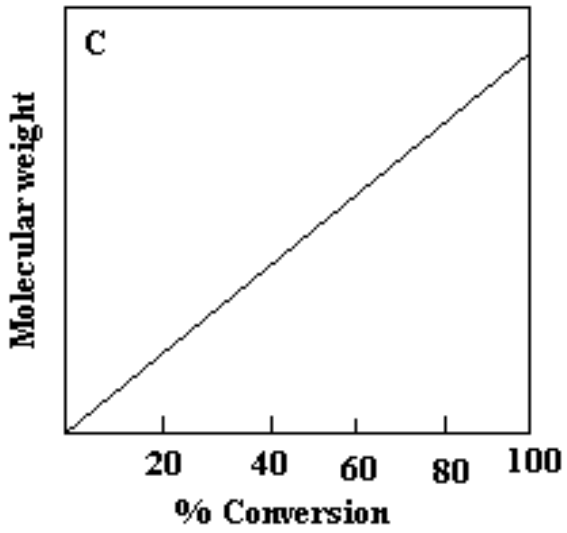


Figure 2.2: Molecular weight vs conversion graph of a typical living polymerization.

Living free radical polymerizations, although only about a decade old, have attained a tremendous following in polymer chemistry. The development of this process has been a long-standing goal because of the desire to combine the undemanding and industrial friendly nature of radical polymerizations with the power to control polydispersities, architectures, and molecular weights that living processes afford. A great deal of effort has been made to develop and understand different living free radical polymerization (LFRP) methods. The methods at the forefront fall into one of three categories: nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition fragmentation chain transfer (RAFT) [40].

2.3.1. Nitroxide-mediated living free radical (NMP)

Nitroxide–mediated living free radical polymerization (NMP) belongs to a much larger family of processes called stable free radical polymerizations. In this type of process, the propagating species (Pn°) reacts with a stable radical (X°) as seen in Figure (2.3). The resulting dormant species (Pn-X) can then reversibly cleave to regenerate the free radicals once again. Once Pn° forms it can then react with a monomer, M, and propagate further. The most commonly used stable radicals have been nitroxides, especially 2,2,6,6-tetramethylpiperidinoxy (TEMPO). The 2,2',6,6'-tetramethylpiperidine-1-oxyl radical (TEMPO) was used as the nitroxide component in these initial studies. The alkoxyamine is formed in situ during the polymerization

process. Shortly thereafter, it was shown that low molecular weight alkoxyamines such as styryl-TEMPO can be used as initiators/regulators for the controlled living radical polymerization of styrene [41]. Although NMP is one of the simplest methods of living free radical polymerization (LFRP), it has many disadvantages. Many monomers will not polymerize because of the stability of the dormant alkoxyamine that forms. Also, since the reaction is kinetically slow, high temperatures and bulk solutions are often required. Also, the alkoxyamine end groups are difficult to transform and require radical chemistry [42].

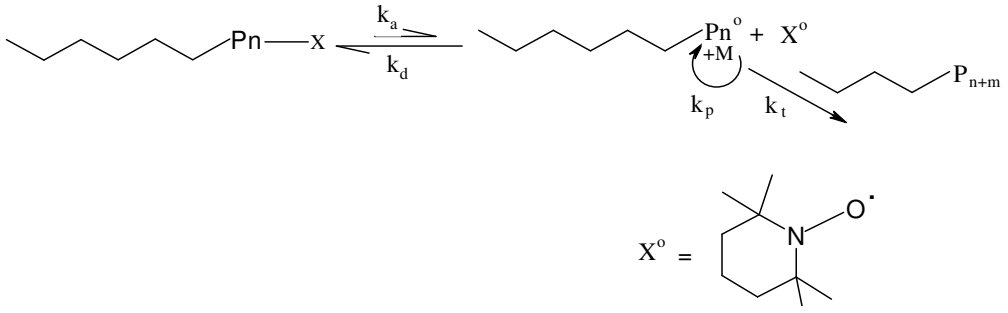


Figure 2.3: Mechanism for nitroxide-mediated living free radical polymerization.

The key to the success is a reversible thermal C═O bond cleavage of a polymeric alkoxyamine to generate the corresponding polymeric radical and a nitroxide. Monomer insertion with subsequent nitroxide trapping leads to chain-extended polymeric alkoxyamine. The whole process is controlled by the so called persistent radical effect (PRE) [43]. The PRE is a general principle that explains the highly specific formation of the cross-coupling product (R_1–R_2) between two radicals R_1 and R_2 when one species is persistent (in NMP the nitroxide) and the other transient (in NMP the polymeric radical), and the two radicals are formed at equal rates (guaranteed in NMP by thermal C═O bond homolysis). The initial buildup in concentration of the persistent nitroxide, caused by the self termination of the transient polymeric radical, steers the reaction subsequently to follow a single pathway, namely the coupling of the nitroxide with the polymeric radical. First, nitroxide mediated polymerizations of styrene were conducted using conventional free radical initiators in the presence of free nitroxide and monomer [44]. In general better results are obtained using preformed alkoxyamines. Defined concentration of the initiator allows a better control of the targeted molecular weight using this approach. Based on the mechanism depicted in Figure 2.3, it is obvious that the

equilibrium constant *K* between the dormant alkoxyamine and the polymeric radical and nitroxide is a key parameter of the polymerization process. The equilibrium constant *K* is defined as *k*a/*k*d (*k*a = rate constant for alkoxyamine C═O bond homolysis; *k*d = rate constant for trapping of the polymeric radical with the given nitroxide). Various parameters such as steric effects, H-bonding and polar effects influence the *K*-value [45]. Since the first TEMPO-mediated polymerizations many nitroxides and their corresponding alkoxyamines have been prepared and tested in NMP. Due to space limitation we cannot give an overview of all alkoxyamines tested so far [46].

The most popular nitroxide used for NMP in the past has been TEMPO. However, TEMPO is limited in the range of monomers which are compatible to polymerize by NMP, mostly due to the stability of the radical. Hawker et. al. recently discovered that by replacing the α-tertiary carbon atom with a secondary carbon atom, the stability of the nitroxide radical decreased which lead to an increased effectiveness in polymerization for many monomers in which TEMPO was uneffective. While TEMPO and TEMPO derivatives are only useful for styrene polymerizations, the new derivatives permit the polymerization of acrylates, acrylamides, 1,3-dienes, and acrylonitrile based monomers with very accurate control of molecular weights and low polydispersities. Another family of nitroxides that have shown to have the same success are phosphonate derivatives designed by Gnanou et.al [47].

The chain end functionalization of polymers synthesized by NMP is a significant problem because dormant chains containing alkoxyamines can regenerate terminal radicals which can depolymerize at high temperatures. A very interesting chain end functionalization process has also been discovered by Hawker et. al. which involves the controlled monoaddition of maleic anhydride or maleimide derivatives to the alkoxyamine chain end. The alkoxyamine can then be easily eliminated and other functional groups can be introduced. This process relies on the resistance of maleic anhydride or maleimide derivatives to homopolymerize and the ability of the precurser to reform the olefin by elimination of the hydroxylamine [48].

2.3.2. Atom transfer radical polymerization

Atom transfer radical polymerization (ATRP) is a living radical polymerization process utilizing transition-metal complexes as catalysts to mediate the propagation of the polymerization. It is a very versatile process and can synthesize a wide spectrum of polymers with controlled structures. Atom transfer radical polymerization (ATRP) is one of the most convenient methods to synthesize well-defined low molecular weight polymers [49]. A general mechanism for ATRP is given below.

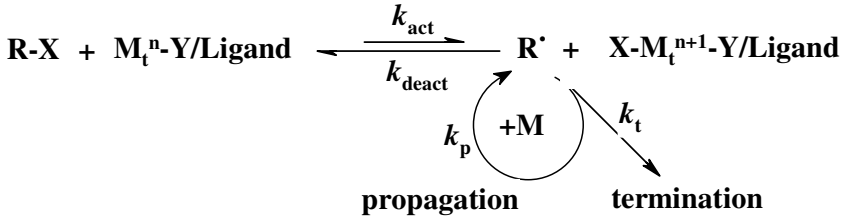


Figure 2.4: General Mechanism for ATRP.

Firstly, initiation should be fast, providing a constant concentration of growing polymer chains. Secondly, because of the persistent radical effect, the majority of the growing polymer chains are dormant species that still presence the ability to grow because a dynamic equilibrium between dormant species. By keeping the concentration of active species of propagating radicals sufficiently low through the polymer, termination is suppressed. ATRP is a radical process that full fills these requirements by using a transition metal in combination with a suitable ligand [50].

Atom transfer radical polymerization (ATRP) involves first a reduction of the initiator by a transition metal complex forming a radical initiating species and a metal halide complex. The reactive center can then initiate the monomer, which can then propagate with additional monomer or abstract the halide from the metal complex forming a dormant alkyl halide species. The alkyl halide species is then activated by the metal complex and propagates once more.

ATRP can be used on a large number of monomers and requires ambient reaction conditions. The reaction is unaffected by the presence of O_2 and other inhibitors. Also, the alkyl halide end groups can be easily transformed by S_N^1, S_N^2, or radical chemistry. The major drawback to ATRP is that a transition metal catalyst which is

used must be removed which after polymerization and possibly recycled. Future work in this field includes the removal and recycling of the catalyst as well as the design of catalysts that react with a larger range of monomers [40].

A transition metal complex, e.g. copper (I) bromide, undergoes an one-electron oxidation with simultaneous homolytic abstraction of the halogen atom from a dormant species (e.g. carbon–halide bond) to generate a radical. The radical propagates monomers with the activity similar to a conventional free radical. The radical is very quickly deactivated to its dormant state—the polymer chain terminally capped with a halide (e.g. P–Br) group. Since the deactivation rate constant is substantially higher than that of the activation reaction $K_{eq} = K_{act} / K_{deact} \sim 10^{-7}$; each polymer chain is protected by spending most of the time in the dormant state, and thereby the permanent termination via radical coupling and disproportionation is substantially reduced. In a well-controlled ATRP, only several percents of the chains become dead via termination.

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 k_p. Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination.

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 polymerization. This process generates oxidized metal complexes, $X\text{-}M_t^{n+1}$, as persistent radicals to reduce the stationary concentration of termination [51]. Polydispersities in ATRP decrease with conversion, with the rate constant of deactivation, k_{deact}, and also with the concentration of deactivator. The molecular conversion and the amount of initiator used, $DP = \Delta[M]/[I]_0$; polydispersities are low, $M_w / M_n < 1{,}3$ [52].

The ATRP system is consisting of the monomer, initiator, and catalyst composed of transition metal species with any suitable ligand.

2.3.2.1. 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. 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 $(K_{eq}=k_{act}/k_{deact})$ determines the polymerization rate.

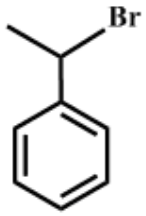
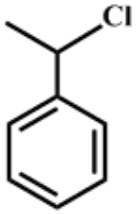
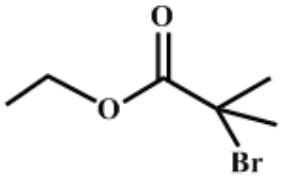
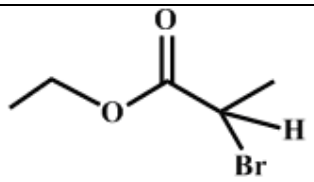
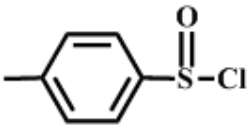
2.3.2.2. Initiators

The main role of the initiator is to determine the number of growing polymer chains. Two parameters are important for a successful ATRP initiating system. First, initiation should be fast in comparison with propagation. Second, the probability of the side reactions should be minimized.

In ATRP, alkylhalides (RX) are typically used as initiator and the rate of 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. When X is either bromine or chlorine, the molecular weight control is the best. Flourine is not used because the C-F bond is too strong to undergo homolytic cleavage.

The most frequently used initiator types in ATRP systems is shown Table 2.1.

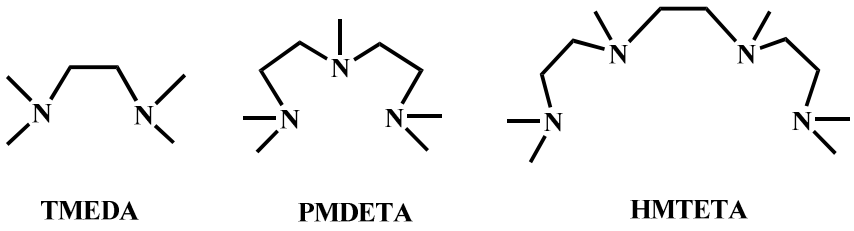
Table 2.1: The most frequently used initiator types in ATRP systems.

• Initiator	• Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 Ethyl-2-bromo isobutyrate	Methyl methacrylate
 Ethyl-2-bromo propionate	Methylacrylate and other acrylates
 p-toluene sulphonyl chloride	Methyl methacrylate

2.3.2.3. Ligands

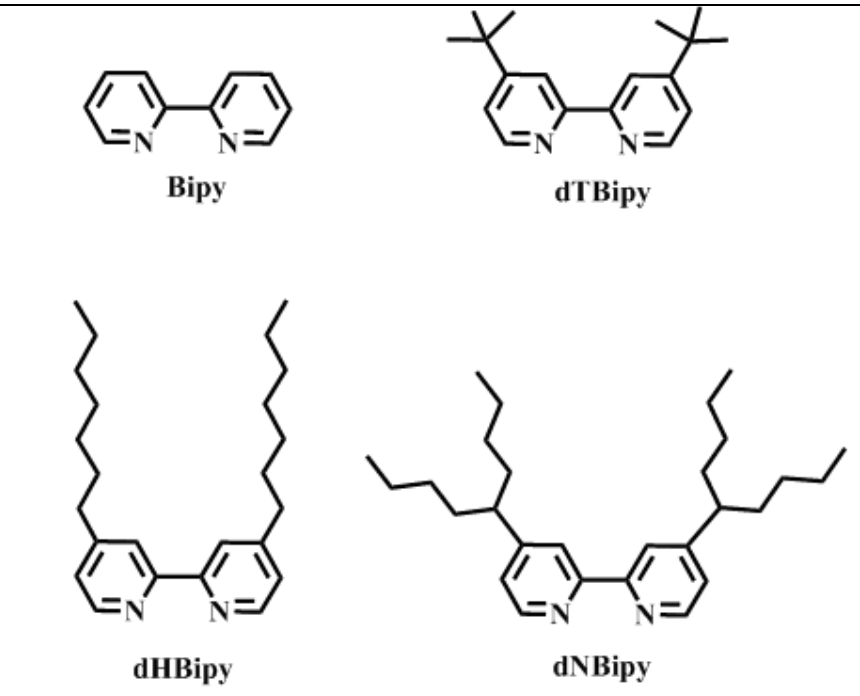
The main role of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential of the metal center for the atom transfer. There are several guidelines for an efficient ATRP catalyst. First, fast and quantitative initiation ensures that all the polymer chains start to grow simultaneously. Second, the equilibrium between the alkylhalide and the transition

metal is strongly shifted toward the dormant species side. This equilibrium position will render most of the growing polymer chains dormant and produce a low radical concentration. As a result, the contribution of radical termination reactions to the overall polymerization is minimized. Third, fast deactivation of the active radicals by halogen transfer ensures that all polymer chains are growing at approximately the same rate, leading to a narrow molecular weight distribution. Fourth relatively fast activation of the dormant polymer chains provides a reasonable polymerization rate. Fifth, there should be no side reactions such as β-H abstraction or reduction/oxidation of the radicals.



(2.5)

Figure 2.5: Nitrogen based ligands.



(2.6)

Figure 2.6: Derivatives of 2,2-bipyridine.

The most widely used ligands for ATRP systems are the derivatives of 2,2-bipyridine and nitrogen based ligands such as *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA), tetramethylethylenediamine (TMEDA), 1,14,7,10,10-hexamethyltriethylenetetraamine (HMTETA), tris[2-(dimethylamino) ethyl]amine (Me_6-TREN) and alkylpyridylmethanimines are also used (Fig. 2.5 and 2.6).

2.3.2.4. Transition metal complexes

Catalyst is the most important component of ATRP. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst. 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. The most important catalysts used in ATRP are; Cu(I)Cl, Cu(I)Br, $NiBr_2(PPh_3)_2$, $FeCl_2(PPh_3)_2$, $RuCl_2(PPh_3)_3$/ $Al(OR)_3$.

2.3.2.5. Solvents

ATRP can be carried out either in bulk, in solution or in a heterogeneous system (e.g., emulsion, suspension). Various solvents such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide and many others have been used for different monomers. A solvent is sometimes necessary especially when the obtained polymer is insoluble in its monomer.

2.3.2.6. Temperature and reaction time

The rate of polymerization also determines the rate of polymerization by effecting both propagation rate constant and the atom transfer equilibrium constant. The k_p/k_t ratio increase as a result of higher temperature thus enables us better control over the polymerization. However this may also increase the side reactions and chain transfer reactions. The increasing temperature also increases the solubility of the catalyst. Against this, it may also poison catalyst by decomposition. Determining the optimum

temperature; monomer, catalyst and the targeted molecular weight should be taken into consideration.

2.3.2.7. Molecular Weight and Molecular Weight Distribution

We can determine the average molecular weight of the polymer by the ratio of consumed monomer and the initiator as in a typical living polymerization ($DP_n=\Delta[M]/[I]_o$, DP=degree of polymerization) while there is a narrow molecular weight distribution ($1.0 < M_w/M_n < 1.5$).

The molecular weight distribution or polydispersity M_w / M_n is the index of the polymer chain distribution. In a well-controlled polymerization, M_w / M_n is usually less than 1.1.

$\mathbf{M_w / M_n = 1 + [[RX]_o k_p / k_d [D]] . [(2/p) - 1]}$	**(2.7)**

Figure 2.7: The polydispersity index in ATRP in the absence of chain termination and transfer.

Where, D: Deactivator, k_p: Propagation rate constant, k_d: Deactivation rate constant, p: Monomer conversion

When a hundred percent of conversion is reached, in other words p=1, it can be concluded that;

i) Polydispersities (molecular weigh distributions) decrease, if the catalyst deactivates the chains faster (smaller k_p / k_d).

ii) For the smaller polymer chains, higher polydispersities are expected to obtain because the smaller chains include little activation-deactivation steps resulting in little control of the polymerization.

iii) Polydispersities decrease as the concentration of the deactivator decreases. (For example, the addition of a small amount of Cu (II) halides in copper-based ATRP decreases the reaction rate thus leads to better controlled polymerizations).

2.3.3. Reversible-addition fragmentation chain transfer (RAFT)

The most recent report of a controlled/"living" free radical polymerization has been reported by Haddleton and co-workers as well as Thang et al. reversible addition-fragmentation chain transfer (RAFT) is achieved by performing a free radical

polymerization in the presence of dithio compounds, which act as efficient reversible addition-fragmentation chain transfer agents. Much like the first two routes, the rapid switching mechanism between dormant and active chain ends affords living polymerization character [53].

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

The greatest advantage to RAFT is the incredible range of polymerizable monomers. As long as the monomer can undergo radical polymerization, the process will most likey be compatible with RAFT. However, there are many major drawback that arise when using this process. The dithio end groups left on the polymer give rise to toxicity, color, and odor and their removal or displacement requires radical chemistry. Also, the RAFT agents are expensive and not commercially available. Another drawback is that the process requires an initiator, which can cause undesired end groups and produce too many new chains which can lead to increased termination rates [40].

2.4. Synthesis of Star-Shaped Polymers

2.4.1 Introduction

Elucidation of structure-property relationships remains an ongoing field of study in polymer science. The introduction of long chain branching is known to affect polymer physical properties and processability as a result of changing the melt, solution, and solid-state properties of polymers [54]. It has been shown that branching results in a more compact structure in comparison to linear polymers of similar molecular weight, due to their high segment density, which alters the crystalline, mechanical, and viscoelastic properties of the polymer. While it is well-known that long chain branching greatly influences polymer physical properties, a fundamental understanding of structure-property relationships remains difficult due to the complexity of branched polymer structures. A branched polymer structure was described as a nonlinear polymer with multiple backbone chains radiating from

junction points [55]. Star-shaped macromolecules constitute the simplest form of branched macromolecules, comprising only one branch point, and as such, have received significant attention in the elucidation of structure property relationships [56]. Although star polymers constitute the simplest branched structure, their synthesis remains challenging, and star polymers are often difficult to synthesize in a well-controlled manner. Due to the complex nature of these macromolecules, controlled polymerization techniques, such as anionic, cationic, living free radical, and group transfer (GTP) polymerization have typically been used to obtain well-defined star-shaped macromolecules. Star polymers are typically synthesized using either a core-first approach, or an arm-first approach. In the core-first synthetic method, a multifunctional initiator is used and the number of arms is proportional to the number of functionalities on the initiator (Fig. 2.8) [57].

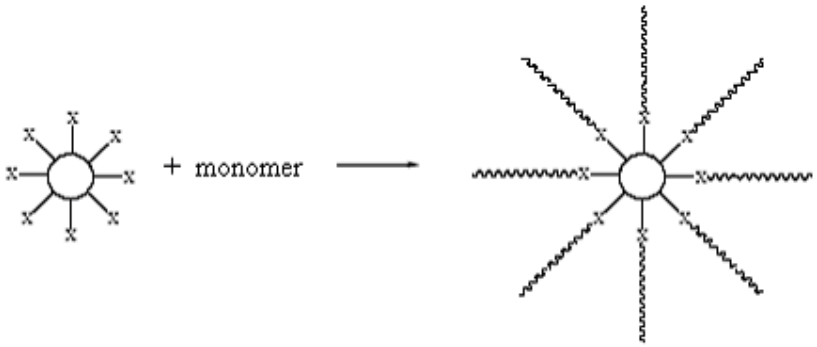


Figure 2.8: Synthesis of star-shaped polymer using the core-first method.

Using the core-first method, well-defined star-shaped macromolecules can be synthesized as long as initiation is rapid relative to propagation. While this approach was used in the first cationic synthesis of star-shaped polymers, containing three or four arms, it tends to yield polymers with broadened molecular weight distributions [58].

In the arm-first synthetic method, linear arm polymers are synthesized and then coupled using a multifunctional linking agent or divinyl compound. In this case, the number of arms depends on the linking efficiency of the arm polymer to the multifunctional core and an alternative method is used to determine the number of arms (Fig. 2.9). This approach is typically used in both living anionic and cationic syntheses of star-shaped polymers [59].

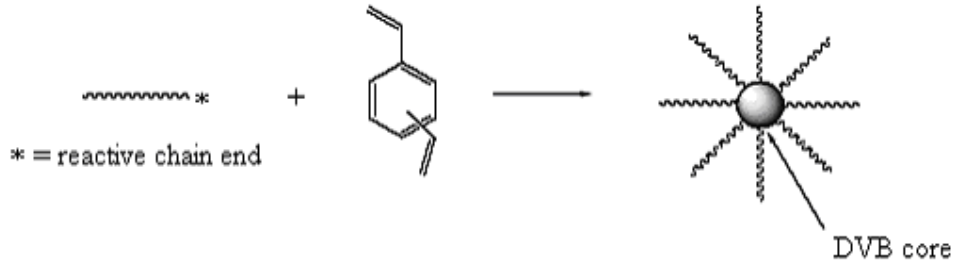


Figure 2.9: Synthesis of star-shaped polymer using the arm-first method.

As discussed previously, living anionic chain ends are very reactive and are used in a variety of chain end functionalization strategy. This characteristic of living chain ends makes living anionic polymerization ideal for the synthesis of complex architectures using chain end coupling reactions. The synthesis of star-shaped polymers using living anionic polymerization has been achieved using a variety of linking agents. Typical linking reagents for coupling of living anionic chain ends are chlorosilanes and their derivatives. However, these types of endcapping reagents are limited in their utility by the necessity for equal reactivity and accessibility of all reactive sites on the linking agent. Use of both silicon tetrachloride and chloromethylated benzenes have been hampered by these limiting factors. Other linking agents are dimethyl phthalate, trisallyloxytriazines, and divinylbenzene. In some cases, the number of arms using the arm first approach is controlled by the number of functionalities on the linking agent, such as trichloromethylsilane or tetrachlorosilane.

In other cases, such as divinylbenzene, the linking agent undergoes homopolymerization to form the core and the number of arms is greater than the functionality of the linker molecule. While the arm-first method is typically used in conjunction with living anionic polymerization to form well-defined star-shaped macromolecules, the core-first methodology has also been used. The core-first method requires the generation of a reactive core molecule prior to polymerization and this oftentimes leads to undesired coupling reactions between core molecules. As the arms grow out from the core, the tendency to couple decreases. The main advantage to the core-first methodology is the ease of chain end functionalization at the star periphery.

More recently, several of the techniques discussed above have been used in conjunction with one another to synthesize novel macromolecular architectures.

For example, Muller et al. reported the use of both cationic and anionic polymerization to synthesize star-shaped block copolymers [60]. The polymerization of isobutylene was initiated using 1,3,5-tricumylchloride and terminated using diphenylethylene and methanol to yield a diphenylethylene methoxy group. This group was then transformed into an initiator for the anionic polymerization of methyl methacrylate using a K/Na alloy.

Star-branched structures in which the arms are comprised of different polymer backbones were achieved using the arm-first approach and a difunctional diphenylethylene derivative. In this approach, the first monomer was polymerized using living anionic techniques and then terminated with the difunctional diphenylethylene derivative. The second monomer was then polymerized from the residual functionality on the diphenylethylene molecule to yield A_2B_2 type macromolecules. When macromolecules with less defined cores are synthesized, a variety of techniques have been employed, including the use of a bromomethylbenzene derivative in the synthesis of *t*-butyl methacrylate star-shaped macromolecules, hyperbranched cores, main chain functional graft sites, and convergent coupling of arm polymers to synthesize dendritically branched polystyrene.

2.4.2. Miktoarm Star Polymers

The term “miktoarm” has been attributed to star polymers with three or more arms, at least two of which are molecularly and chemically different (chemical asymmetry). Miktoarm is a combination of Greek miktos, meaning “mixed”, and arm. This term was proposed by Hadjichristidis in 1992 [61] and was widely accepted by the other research groups all over the world. Although, the terms heteroarm star and A_nB_m-type star were also used for these types of star structures, miktoarm star (μ-star) will be used throughout this work to refer to star polymers with corresponding structure. The most common examples of miktoarm stars are the A_2B, A_3B, A_2B_2, A_nB_n ($n > 2$) and ABC types. Other less common structures, like the ABCD, AB_5, and AB_2C_2 are also available (Fig.2.10).

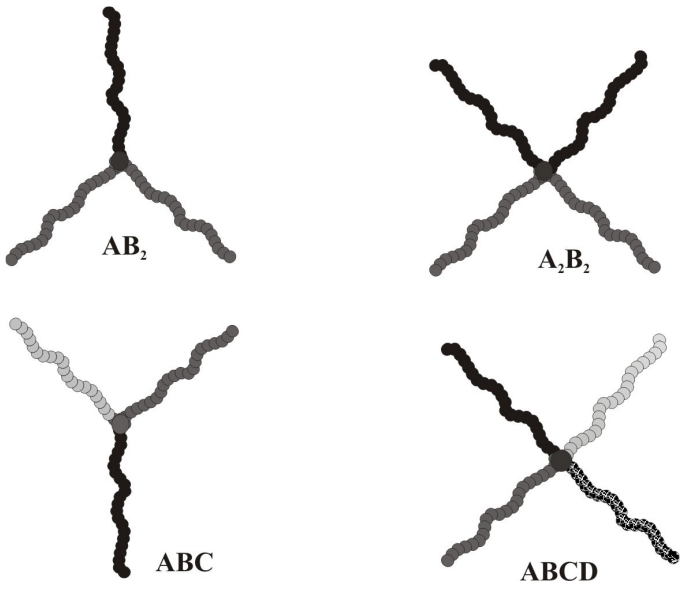


Figure 2.10: Illustration of miktoarm star polymers structures where each letter represents different polymeric arms.

2.4.2.1. ABC terpolymers

In recent years ternary triblock terpolymers have attracted increasing interest owing to their rich variety of bulk morphologies [62].

Emerging technologies in medicine, microelectronics and optics require the availability of novel polymeric materials with ever more sophisticated properties and performances. Living and controlled/ living polymerization methods have allowed for the synthesis of tailor-made macromolecules of varying chemical structure, composition, molecular characteristics and architecture. Among the different architectures, block copolymers definitely play a central role in polymer science.

Following the intense interest in the study of diblock and ABA triblock copolymers, the polymer community starts now to focus on a new type of block copolymers, that of ABC triblock copolymers comprising three blocks, each made of a different monomer repeat unit [63]. In bulk, four different ordered structures can be obtained (alternating lamellae, cylinders, body-centered cubic arrays of spheres and gyroid) depending on the copolymer composition and architecture. Considerably less extended is the work dedicated to the synthesis, solution and bulk properties of triblock terpolymers of the ABC type [64].

Linear ABC triblock terpolymers represent a relatively new class of polymeric materials with an increasing interest for their properties in the bulk and in solution. The three chemically different components of these materials, each placed in a separate block, can confer to the terpolymer three different functions. Another similar, but more novel, and equally interesting class of polymeric materials is that of ABC heteroarm or miktoarm star terpolymers, bearing three arms, each of which is a different homopolymer [65].

The presence of three different monomers placed in different blocks confers to these polymers, three rather than two functions [63]. It is well known that the addition of a third block leads to a much richer variety of phases (over 30 phases have been identified to date in bulk). These materials have the potential to generate a variety of well controlled multiphase microdomain structures with nanosized structural units in bulk and thin films and to provide supramolecular structures in solution with a mesoscopic length scale. Therefore, numerous applications such as multifunctional sensors, multiselective catalysts for sequential or simultaneous chemical reactions, separation membranes, filters, etc., are possible [64].

ABC triblock copolymers comprised mostly of diene-, styrene-, methacrylate-, or pyridine-based monomers have been studied extensively. These well-defined structures have elicited fascination not only for theoreticians modeling phase behavior but also in the physical realm for studying morphological transitions. The phase behavior of these systems is governed by the Flory interaction parameter between two domains, χ, and is strongly influenced by the weight fraction of the various blocks present in the copolymer. The morphological possibilities for these copolymers can range from a basic lamellar structure to highly complex core-shell gyroid morphology and even to a unique knitting pattern. Blending these types of block copolymers with other copolymers enables additional manipulation of the morphological patterns. Until now, however, the monomers comprising the ABC triblock copolymers have been limited to those that can be polymerized either anionically or by group transfer polymerization. Recently, examples of inorganic/organic hybrid ABC triblock copolymers synthesized by combining living anionic ring-opening polymerization with atom transfer radical polymerization (ATRP) have been presented, in addition to ABC triblock copolymers synthesized wholly by ATRP or through reversible addition fragmentation chain transfer

(RAFT). Kelly and Matyjaszewski demonstrated that ABC triblock copolymers of various chain architectures and monomer combinations can be successfully prepared using ATRP methods [66].

The key to the controlled synthesis of block copolymers in ATRP is to maintain high chain end functionality, i.e., limit termination and side reactions, and to balance the reactivity of the end group with that of the monomer, i.e., avoid slow initiation. While the latter consideration is not as problematic as it is in anionic or carbocationic polymerizations and can be overcome through a careful choice of the block order, radical termination cannot be completely avoided due to the nature of the polymerization process. It can be limited, however, through the careful choice of the polymerization conditions and through adjustment of the equilibrium between the active and dormant species, often by adding a "persistent radical" in the form of a higher oxidation state metal. Kelly and Matyjaszewski's report focuses on the preparation of copolymers using these approaches to obtain well-defined multiblock copolymers. Several different catalyst systems, based predominantly on linear amine ligands, as well as different synthetic methodologies (i.e., the halogen exchange technique) were utilized to successfully prepare these copolymers [66].

Recently, the co-terpolymerization reactions, involving two or three monomers for the synthesis of synthetic polymers, have been commonly used. The properties of available polymers can also be changed by these reactions and novel polymers can be obtained by co-terpolymerization reactions. Thus, several useful terpolymers have been synthesized and used for various purposes (Fig. 2.11) [67].

As an important illustration, interesting results have been recently obtained with SBM Nanostrengthw block terpolymers produced on an industrial scale. These triblocks copolymers combine polystyrene (PS), 1–4 polybutadiene (PBu) and polymethylmethacrylate (PMMA) segments. These engineering polymers can, for instance, be used as additives, allowing a much better solubility between incompatible commodity or technical plastics and fine tuning between toughness and stiffness of the host matrix. Detailed characterization of these new block copolymers obtained both by controlled radical polymerization and anionic polymerization represents a real challenge due to their increasing complexity [64].

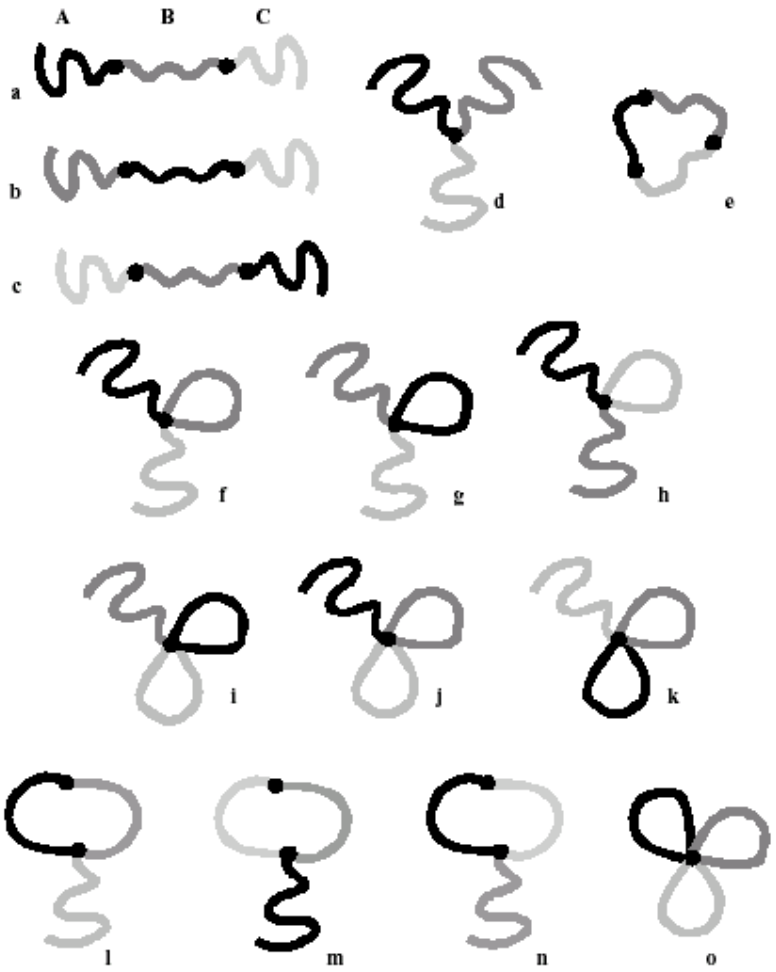


Figure 2.11: Schematic presentation of all possible arrangements for an ABC terpolymer. (a-c) Linear triblock terpolymer, ABC, BAC, CBA, respectively. (d) Miktoarm star terpolymer, (e) Cyclic terpolymer. (f-h) One of the chains is cyclic and the other two linear. (i-k) One chain is linear and the two are cyclic. (l-n) One chain is linear and two chains form one cyclic. (o) All chains are cyclic.

2.5. Click Chemistry

Although demand for new chemical materials and biologically active molecules continues to grow, chemists have hardly begun to explore the vast pool of potentially active compounds. The emerging field of "click chemistry," a newly identified classification for a set of powerful and selective reactions that form heteroatom links, offers a unique approach to this problem [68]. "Click chemistry" is a term used to describe several classes of chemical transformations that share a number of important properties which include very high efficiency, in terms of both conversion and

selectivity under very mild reaction conditions, and a simple workup [69]. It works well in conjunction with structure based design and combinatorial chemistry techniques, and, through the choice of appropriate building blocks, can provide derivatives or mimics of 'traditional' pharmacophores, drugs and natural products. However, the real power of click chemistry lies in its ability to generate novel structures that might not necessarily resemble known pharmacophores [70].

A concerted research effort in laboratories has yielded a set of extremely reliable processes for the synthesis of building blocks and compound libraries:

- Cycloaddition reactions, especially from the 1,3-dipolar family, but also hetero-Diels-Alder (DA) reactions.
- Nucleophilic ring-opening reactions, especially of strained heterocyclic electrophiles, such as epoxides, aziridines, cyclic sulfates, cyclic sulfamidates, aziridinium ions and episulfonium ions.
- Carbonyl chemistry of the non-aldol type (e.g. the formation of oxime ethers, hydrazones and aromatic heterocycles).
- Addition to carbon–carbon multiple bonds; particularly oxidation reactions, such as epoxidation, dihydroxylation, aziridination, and nitrosyl and sulfenyl halide additions, but also certain Michael addition reactions [70].

Huisgen's 1,3-dipolar cycloaddition of alkynes and azides yielding triazoles is, undoubtedly, the premier example of a click reaction [70]. Recently, DA reaction based on the macromolecular chemistry has attracted much attention, particularly for providing new materials. As an alternative route, recently, 1,3-dipolar cycloadditions, such as reactions between azides and alkynes or nitriles, have been applied to macromolecular chemistry, offering molecules ranging from the block copolymers to the complexed macromolecular structures [71].

Sharpless and co-workers have identified a number of reactions that meet the criteria for click chemistry, arguably the most powerful of which discovered to date is the Cu(I)-catalyzed variant of the Huisgen 1,3-dipolar cycloaddition of azides and alkynes to afford 1,2,3-triazoles [68]. Because of Cu(I)-catalyzed variant of the Huisgen 1,3-dipolar cycloaddition of azides and alkynes reactions' quantitative yields, mild reaction condition, and tolerance of a wide range of functional groups, it is very suitable for the synthesis of polymers with various topologies and for polymer

modification [72]. Because of these properties of Huisgen 1,3-dipolar cycloaddition, reaction is very practical. Moreover, the formed 1,2,3-triazole is chemically very stable [73].

In recent years, triazole forming reactions have received much attention and new conditions were developed for the 1,3-dipolar cycloaddition reaction between alkynes and azides [74]. 1,2,3-triazole formation is a highly efficient reaction without any significant side products and is currently referred to as a click reaction [75].

Huisgen 1,3-dipolar cycloadditions are exergonic fusion processes that unite two unsaturated reactants and provide fast access to an enormous variety of five-membered heterocycles. The cycloaddition of azides and alkynes to give triazoles is arguably the most useful member of this family [76].

The copper(I)-catalyzed 1,2,3-triazole formation from azides and terminal acetylenes is a particularly powerful linking reaction, due to its high degree of dependability, complete specificity, and the bio-compatibility of the reactants. With the ~10^6-fold rate acceleration of the copper(I)-catalyzed variant of Huisgen's 1,3-dipolar cycloaddition reaction, the generation of screening libraries has reached a new level of simplicity. Two subunits are reliably joined together by formation of a 1,4-disubstituted 1,2,3-triazole linkage. This ligation process works best in aqueous media without requiring protecting groups for any of the most common functional groups, enabling compound screening straight from the reaction mixtures (i.e. without prior purification) [70].

Azides usually make fleeting appearances in organic synthesis: they serve as one of the most reliable means to introduce a nitrogen substituent through the reaction –R–X→[R–N_3]→R–NH_2. The azide intermediate is shown in brackets because it is generally reduced straightaway to the amine. Despite this azidophobia, this have been learned to work safely with azides because they are the most crucial functional group for click chemistry endeavors. Ironically, what makes azides unique for click chemistry purposes is their extraordinary stability toward H_2O, O_2, and the majority of organic synthesis conditions. The spring-loaded nature of the azide group remains invisible unless a good dipolarophile is favorably presented. However, even then the desired triazole forming cycloaddition may require elevated temperatures and, usually results in a mixture of the 1,4 and 1,5 regioisomers (Fig. 2.12).

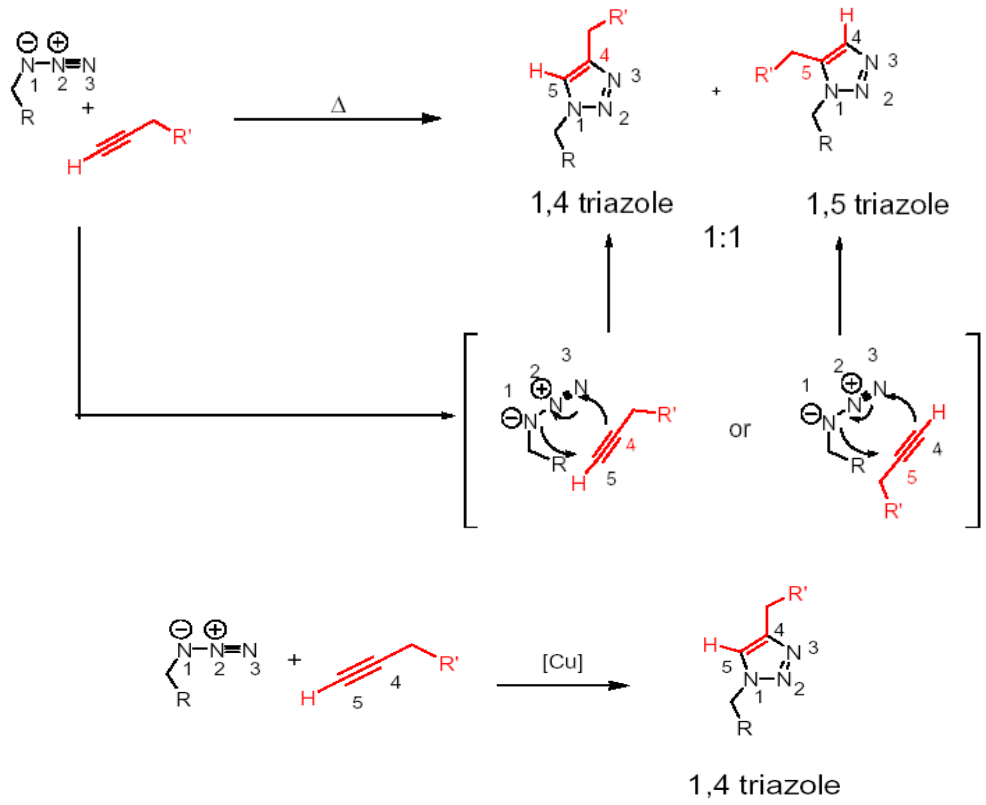


Figure 2.12: Regioselectivity mechanism of triazole forming cycloaddition.

Since efforts to control this 1,4- versus 1,5-regioselectivity problem have so far met with varying success, it was found that copper(I)-catalyzed reaction sequence which regiospecifically unites azides and terminal acetylenes to give only 1,4-disubstituted 1,2,3-triazoles. The process is experimentally simple and appears to have enormous scope [76]. Since the initial discovery of Cu(I)-catalyzed alkyne–azide coupling, numerous successful examples have been recorded in the literature, but as of yet, no systematic study of optimal conditions has been reported. Further, conditions have varied widely, particularly with respect to generation of the active Cu(I) species. Sources of Cu(I) include Cu(I) salts, most commonly copper iodide, in-situ reduction of Cu(II) salts, particularly Cu(II) sulfate, and comproportionation of Cu(0) and Cu(II). Recent reports suggest that nitrogen-based ligands can stabilize the Cu(I) oxidation state under aerobic, aqueous conditions and promote the desired transformation. Steric factors and electronic effects may also play a role in the success of this click chemistry [68].

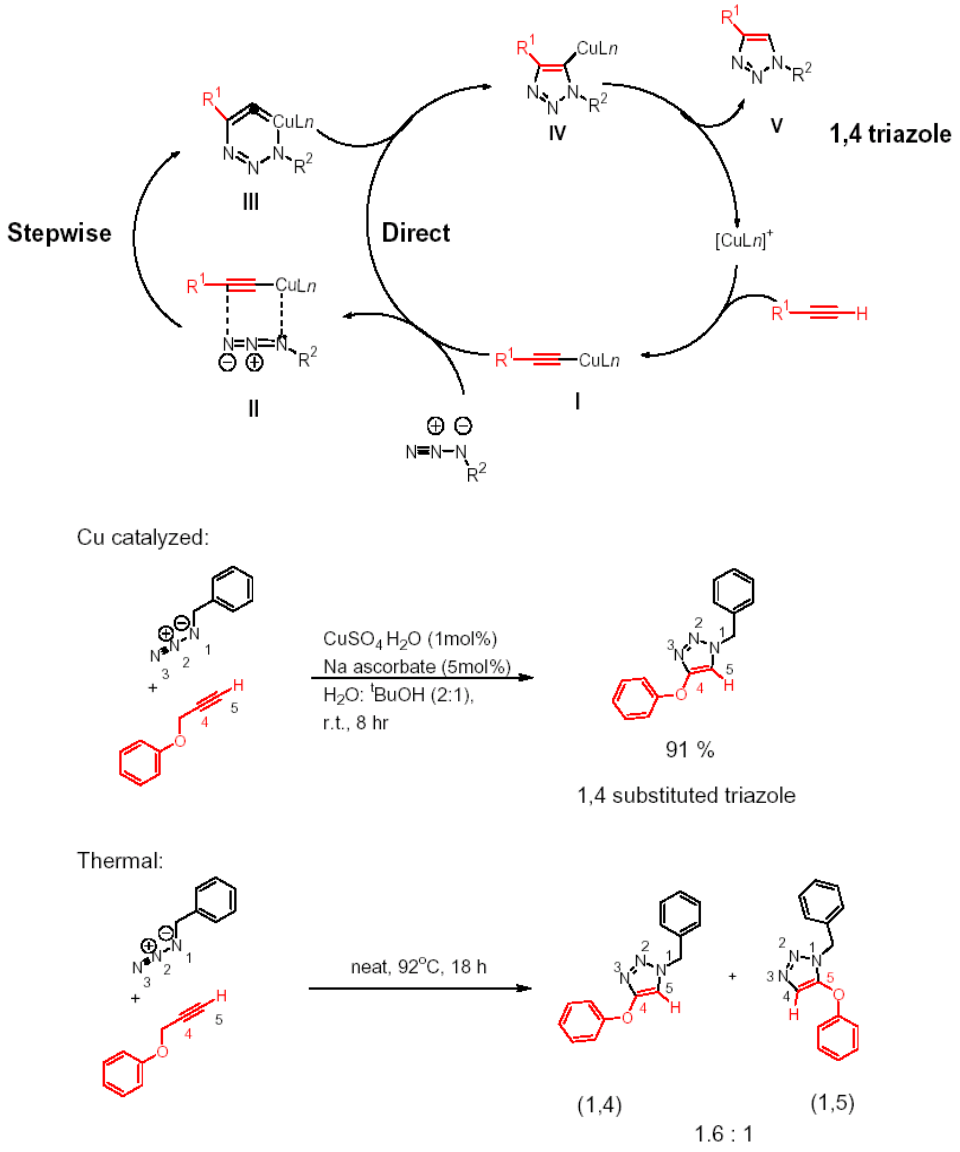


Figure 2.13: Proposed catalytic cycle for the Cu(I)-catalyzed ligation.

The process exhibits broad scope and provides 1,4-disubstituted 1,2,3-triazole products in excellent yields and near perfect regioselectivity (Fig. 2.13) [76].

This ligation process has proven useful for the synthesis of novel polymers and materials in many laboratories, and its unique characteristics make it an ideal reaction for model network crosslinking. Johnson et al. therefore envisioned an azide telechelic macromonomer and a multifunctional small molecule alkyne, the former with a cleavable functionality at its center, as fulfilling the requirements for a degradable model network. Organic azides are most often made from alkyl halides, and several groups have reported the quantitative postpolymerization

transformation(PPT) of polymeric halides to azides for the copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction by treatment with sodium azide in DMF. Atom transfer radical polymerization (ATRP) of various styrenic, acrylic, and methacrylic monomers from halide initiators is well-known to provide polymers of low polydispersity possessing alkyl halide end groups. Therefore, by a sequence of ATRP from a degradable halide-containing initiator, PPT, and CuAAC, one can conveniently prepare model networks of different macromonomer structure (e.g., star polymers, block copolymers) and incorporate a wide variety of functional groups [77].

Some click reactions have already been successfully used in polymer and materials chemistry. The efficient preparation of well-defined polymeric tetrazoles, or dendrimers, amphiphilic block copolymers, cross-linked block copolymer vesicles, and adhesives with triazole units has been reported. Click reactions were also used in the synthesis of functionalized poly(oxynorbornenes) and block copolymers and are a convenient alternative to other coupling reactions applied to polymers prepared by ATRP (such as atom transfer radical coupling or reversible thiol oxidative coupling) for the preparation of high molecular weight polymeric materials [78].

The halogen end group can be converted to other functional groups using standard organic procedures. However, the transformation is preferably carried out under mild conditions, as the substitution must be as free of side reactions as possible and the yield of the transformation reaction must be quantitative. With ATRP, the alkyl group of the alkyl halide initiator remains at one end of the produced polymer chain, a halogen atom is quantitatively transferred to the other end of the chain. By replacement of the halogen end group, several functional groups can be introduced at the polymer chain end [79]. The functionalized polymers can find many applications, for example as macromonomers, telechelics or other specialty polymers [80]. An interesting functional group transformation is the one to azide end groups. Azide groups can produce nitrenes on thermolysis or photolysis, or can be converted to other functionalities such as amines, nitriles, isocyanates, etc [79].

In addition, click strategies have been used as an approach to synthetic cyclodextrins and the decoration of cyclic peptides by glycosylation. Synthetic glycochemicals have attracted increasing interest as carbohydrates are involved in a number of important biological processes involving highly specific events in cell-cell

recognition, cell-protein interactions, and the targeting of hormones, antibodies, and toxins. Sugars are information-rich molecules, and an increasingly large number of known lectins are able to recognize subtle variations of oligosaccharide structure and act as decoders for this carbohydrate-encoded information. Gaining insight into the factors that control these phenomena may open the way for the development of new antiinfective, anti-inflammatory, and anticancer therapeutics and agents [69].

Due to their biological activity of click reactions as anti-HIV and antimicrobial agents, as well as selective β_3 adrenergic receptor agonist, new methods for the regio- and/or stereoselective synthesis of both 1,2,3 triazoles and 1,2,3,4-tetrazoles should be highly valuable [80].

2.6. Polyhedral oligomeric silsesquioxanes (POSS)

Polyhedral oligosilsesquioxane (POSS) is one of many kinds of silsesquioxane molecules. The term silsesquioxane refers to the molecules, whose chemical structure follows the basiccomposition of $R_nSi_nO_{1.5n}$, for example $Me_8Si_8O_{12}$. Here, the R-group, also called the vertex group for polyhedral molecules, may be hydrogen, alkyl, alkylene, aryl arylene, among others. Such silsesquioxanes can form oligomeric organosilsesquioxanes $(CH_3SiO_{1.5})_n$ through chemical reactions and the chemical structures of the derivative silsesquioxanes are quite versatile.The molecular architecture of silsesquioxanes can be classified into two categories: (a) noncaged structure and (b) caged structure, each shown in Figure 2.14 (a) and Figure 2.14 (b). As shown in Figure 2.14 (a), the non-caged silsesquioxane molecules can be further classified into: (i) random structure; (ii) ladder structure, and (iii) partial-cage structure [1].

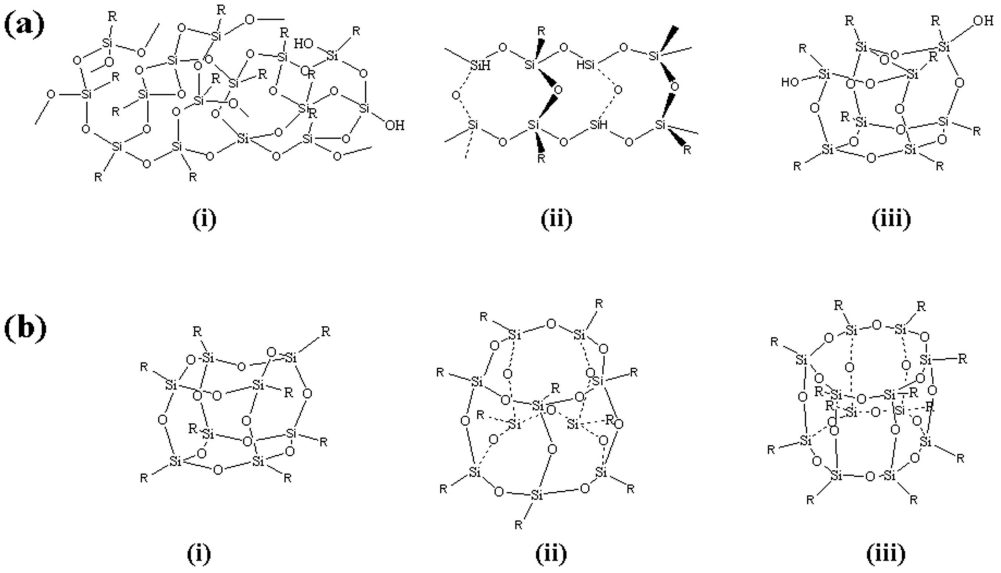


Figure 2.14: Chemical structures of silsesquioxanes. (a) non-caged silsesquioxanes: (i) random, (ii) ladder; (iii) partial caged structures, and (b) caged silsesquioxanes: (i) T_8, (ii) T_{10}, (iii) T_{12} structures.

T_8 POSS series has a cubic core with eight silicon atom at each corner and an oxygen bridge between each silicon atom. Seven silicon atoms bear an organic group that provides solubility, and a reactive group is generally attached to the eighth silicon atom. It is possible to incorporate this ~1.5 nm diameter macromonomer into organic polymers [9].

The mixture of 3-chloropropyltrimethoxysilane, methanol and concentrated HCl led to the formation of octafunctional POSS-$(Cl)_8$ as shown in Figure 2.15 [8].

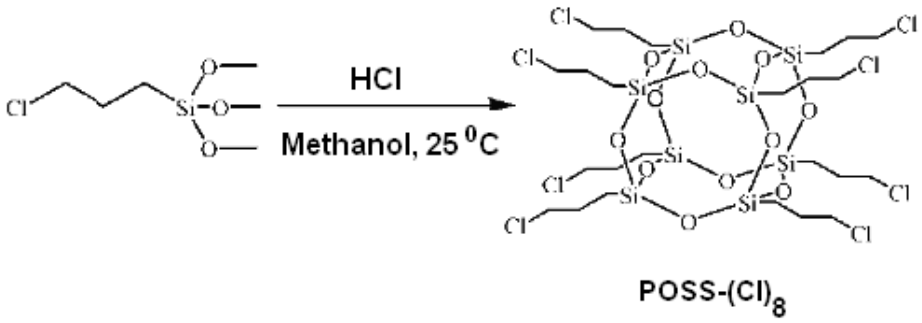


Figure 2.15: Synthesis of Octafunctional POSS-$(Cl)_8$.

Polymeric-inorganic nanocomposites with welldefined architectures have attracted much attention, because of their advantageous performance in mechanical and thermal properties [3]. Polyhedral oligomeric silsesquioxanes (POSS) are inorganic

nanosized particles and are potential candidates to control microstructure. These building blocks are of particular interest due to their molecularly precise structure as well as their solubility in common organic solvents [9]. Thus, the POSS molecules are much more variable in their properties as compared to other inorganic components, such clays or carbon nanotubes. POSS molecules can be extensively incorporated into almost all kinds of the polymer matrices by blending, grafting, cross-linking or copolymerization, to produce POSScontaining organic-inorganic hybrids with many promising properties such as enhanced mechanical and thermal properties, oxidation resistance, and reduced flammability [81].

Random copolymers incorporating POSS have been prepared that are either thermosets or thermoplatics. These represent a category of new hybrid polymers with a tremendous technological potential. Control over the placement of the POSS within an organic polymer is possible using living/controlled polymerization methodologies. Matyjaszweski has incorporated the POSS inorganic particle into both linear and star systems using ATRP [9].

Recently, much attention has focused on using POSS molecules to construct hybrid polymers with novel architectures. Atom transfer radical polymerization (ATRP) has been applied to the preparation of POSS containing polymer hybrids. The homopolymers, triblock copolymers, and star-shaped block copolymers based on POSS monomers have been synthesized using ATRP. POSS molecules were also modified into ATRP initiators to prepare POSS containing hybrid polymers with novel architectures such as star and tadpole-shaped hybrid polymers [3].

3. EXPERIMENTAL WORK

3.1. Materials

Methyl methacrylate (MMA, 99 %, Aldrich) was passed through basic alumina column to remove inhibitor and then distilled over CaH_2 in vacuum prior to use. *N, N, N', N'', N''*-pentamethyldiethylenetriamine (PMDETA, Aldrich) was distilled over NaOH prior to use. Poly (ethylene glycol monomethyl ether) (Me-PEG) (M_n = 2000; Fluka) was dried over anhydrous toluene by azeotropic distillation. Chloropropyl-heptaisobutyl substituted-POSS (97 %, Aldrich), *N*, *N*'-dicyclohexylcarbodiimide (DCC, 99 %, Aldrich), 4-dimethylaminopyridine (DMAP, 99 %, Acros), CuBr (99.9 %, Aldrich), and CuCl (99.9 %, Aldrich) were used as received. Dichloromethane (CH_2Cl_2, J. T. Baker) was used after distillation over P_2O_5. Tetrahydrofuran (THF; 99.8 %, J.T. Baker) was dried and distilled over benzophenone-Na. Other solvents were purified by conventional procedures. All other reagents were purchased from Aldrich and used as received.

3.2. Instrumentation

The ^1H (250 MHz) spectrum was recorded on a Bruker NMR AC 250 Spectrometer in $CDCl_3$. Gel permeation chromatography measurements were obtained from an Agilent instrument (Model 1100) consisting of a pump, a refractive index detector, and four Waters Styragel columns (HR 5E, HR 4E, HR 3, and HR 2). THF was used as eluent at a flow rate of 0.3 mL/min at 30 ^oC and toluene was as an internal standard. Data analyses were performed with PL Caliber Software. The molecular weight of the polymers is calculated on the basis of linear polystyrene (PS) standards (Polymer Laboratories). FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One spectrometer. Differential scanning calorimetry (DSC) was performed on TA Instruments Q1000 with a heating rate of 10 ^oC/ min under nitrogen. Glass transition (T_g) and melting (T_m) temperatures are measured in second heating process.

3.3. Synthesis of initiator

3.3.1. Synthesis of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid [1]

The 2,2-bis(hydroxymethyl)propanoic acid (16 g, 119.36 mmol) along with *p*-TSA (0.9 g, 4.64 mmol), and 2,2-dimethoxypropane (22.4mL, 179.2 mmol) dissolved in 80 mL of dry acetone, and stirred 2h at room temperature. In the vicinity of 2h, while stirring continued the reaction mixture was neutralized with 12 mL of totally NH_4OH (25%), and absolute ethanol (1:5), filtered off by-products and subsequent dilution with dichloromethane (200 mL) , and once extracted with distilled water (80 mL). The organic phase dried with Na_2SO_4, concantrated to yield 14.8 g (71%) as white solid after evaporation of the solvent. ^{1}H NMR ($CDCl_3$, δ) 4.18 (d, *J* = 11.6 Hz, 2H, CC*H*$_2$O), 3.63 (d, *J* = 11.6 Hz, 2H, CC*H*$_2$O), 1.40 (s, 3H, C*CH*$_3$) 1.36 (s, 3H, C*CH*$_3$), 1.18 (s, 3H, C=OC(CH$_2$O)$_2$*CH*$_3$).

3.3.2. Synthesis of propargyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate [2]

Propargyl alcohol (2.53 mL, 43.5 mmol) was dissolved in 30 mL of CH_2Cl_2 and **1** (5 g, 29 mmol), and DMAP (3.54 g, 29 mmol) were added to the reaction mixture in that order. After stirring 5 minutes at room temperature, DCC (8.98 g, 43.5 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 (9:1) to give pale yellow oil (Yield = 4.12 g; 67 %). ^{1}H NMR ($CDCl_3$, δ) 4.72 (d, *J* = 2.4 Hz, 2H, CH≡CC*H*$_2$O), 4.18 (d, *J* = 11.6 Hz, 2H, CC*H*$_2$O), 3.63 (d, *J* = 11.6 Hz, 2H, CC*H*$_2$O), 2.45(t, *J* = 2.4 Hz, 1H, C*H*≡CCH$_2$O), 1.40 (s, 3H, C*CH*$_3$) 1.36 (s, 3H, C*CH*$_3$), 1.18 (s, 3H, C=OC(CH$_2$O)$_2$*CH*$_3$). ^{13}C NMR ($CDCl_3$, δ) 173.47 (C=O), 98.11 (*C*CH$_3$)$_2$,76.58 (CH≡*C*CH$_2$O), 73.03 (*C*H≡CCH$_2$O), 65.84 (*C*H$_2$O), 52.35 (CH≡C*C*H$_2$O), 49.96 (*C*CH$_3$), 25.68 (C*C*H$_3$), 23.66 (C*C*H$_3$), 17.37 (C=OC(CH$_2$O)$_2$*C*H$_3$).

3.3.3. Synthesis of propargyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate [3]

Propargyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (4.0 g, 19 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, Mp = 50 °C (Yield = 3.1 g, 95 %). ^{1}H NMR ($CDCl_3$, δ) 4.72 (d, *J* = 2.4 Hz, 2H, CH≡CC*H*$_2$O), 3.88 (d, *J* = 11.3 Hz, 2H, C*H*$_2$OH), 3.69 (d, *J* = 11.3 Hz, 2H, C*H*$_2$OH), 2.93 (br, 2H, OH), 2.48 (s, 1H, C*H*≡CCH$_2$O), 1.07 (s, 3H, C*CH*$_3$). ^{13}C NMR ($CDCl_3$,δ) 175.08 (C=O), 76.56 (CH≡*C*CH$_2$O), 73.28 (*C*H≡CCH$_2$O), 67.70 (*C*H$_2$OH), 52.52 (*C*CH$_3$), 50.04 (CH≡C*C*H$_2$O), 18.05 (C*C*H$_3$).

3.3.4. Synthesis of propargyl-3-[(2-bromo-2-methylpropanoyl)oxy]-2-(hydroxymethyl)-2-methylpropanoate [4]

Propargyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (3.08 g, 18 mmol) was dissolved in 25 mL of CH_2Cl_2 and triethyl amine (5.5 mL, 39.6 mmol) was added to the mixture and cooled to 0 ^{o}C. 2-Bromoisobutrylbromide (2.22 mL, 18 mmol) in 15 mL of CH_2Cl_2 was added dropwise within 30 minutes. The reaction mixture was stirred 4 h at room temperature. After filtration the mixture was extracted with CH_2Cl_2 and saturated aq. $NaHCO_3$. The aqueous phase was again extracted with CH_2Cl_2 and combined organic phase was dried with Na_2SO_4. The solution was concentrated and the crude product was purified by column chromatography over silica gel eluting with hexane/ethyl acetate (4:1) to give pale yellow oil (Yield = 4.33 g, 75 %). ^{1}H NMR ($CDCl_3$, δ) 4.72 (d, *J* = 2.4 Hz, 2H, CH≡CC*H*$_2$O), 4.43 and 4.30 (dd, *J* = 11.2 Hz, 2H, C*H*$_2$OC=O), 3.75 (d, *J* = 6.3 Hz, 2H, C*H*$_2$OH), 2.47 (t, *J* = 2.4 Hz, 1H, C*H*≡CCH$_2$O), 2.33 (br, 1H, OH), 1.91 (6H, CBr(C*H*$_3$)$_2$), 1.27 (s, 3H, (s, 3H, C*CH*$_3$). ^{13}C NMR ($CDCl_3$,δ) 173.28 (C=O),171.50 (C=O), ,76.53 (CH≡*C*CH$_2$O), 75.29 (*C*H≡CCH$_2$O), 66.93 (*C*H$_2$OC=O), 64.93 (*C*H$_2$OH), 55.42 (*C*Br(CH$_3$)$_2$), 52.54 (*C*CH$_3$), 48.54 (CH≡C*C*H$_2$O), 30.66 (CBr(*C*H$_3$)$_2$), 17.26 (C*C*H$_3$).

3.3.5. Synthesis of COOH-Terminated PEG (PEG-COOH) [5]

PEG_{2000} (10 g, 5 mmol), succinic anhydride (SA) (5 g, 50 mmol), 4-dimethylaminopyridine (DMAP) (0.61 g, 5 mmol), and triethylamine (TEA) (6.97 mL, 50 mmol) were dissolved in (CH_2Cl_2) and reacted for 24 h at room temperature under a nitrogen atmosphere. The molar feed ratio of PEG, SA, DMAP, and TEA was 1:6:1:6, and the solution concentration was 3% (wt/wt). CH_2Cl_2 was removed under vacuum, and the resulting product was dissolved in CCl_4. Unreacted SA was removed by filtering, the filtered solution was precipitated in cold ethyl ether solvent, and the precipitated PEG-COOH was dried under vacuum for more than 12 h. NMR characteristics of PEG-COOH: ^{1}H NMR($CDCl_3$) 4.25 {t, 2H, [OCH_2(CH_2)OCO]}, 3.65{t, 4mH, [O(CH_2CH_2)O]}, 3.38 [s, 3H, (CH_3)], 2.62 {t, 4H, [OCO(CH_2CH_2)OCO]}.

3.3.6. Synthesis of PEG-Macroinitiator [6]

PEG-COOH (2.0 g, 0.95 mmol) was dissolved in 40 mL of dry CH_2Cl_2. **4** (1.2 g, 3.8 mmol) and DMAP (0.23 g, 1.9 mmol) were added to the reaction mixture in that order. After stirring for 5 min at room temperature, DCC (0.589 g, 5.71 mmol) dissolved in 10 mL of CH_2Cl_2 was added. Reaction mixture was stirred overnight at room temperature. After filtration, the solution was concentrated and precipitated in cold diethyl ether and this procedure was repeated two times. Yield: 1.68 g (73%). ($M_{n,theo}$ = 2400; $M_{n,NMR}$ = 2080; $M_{n,GPC}$ = 2180; M_w/M_n = 1.09, relative to PS standards). ^{1}H NMR ($CDCl_3$, d): 4,7 (s, 2H, HCCCH_2O), 4,4–4,2 (m, 6H, CH_2OCO), 3,9 (t,2H,COOC$H_2$$CH_2$-PEG), 3,8–3,5 (m, 4H, C$H_2CH_2$O of PEG), 3,4 (s, 3H, CH_2OCH_3), 2,6 (s, 2H,CO(CH_2) $_2$CO), 2,5 (s, 1H, *H*CCCH_2), 1,9 (s,6H, C(Br)(CH_3)$_2$), 1,3 (s, 3H, COCCH_3) [24].

3.4. Preparation of PEG-*b*-PMMA copolymer with alkyne at the junction point (PEG-PMMA-alkyne) via ATRP of MMA [7]

The synthesis of PEG-*b*-PMMA copolymer with alkyne at its center was accomplished by the ATRP of MMA in toluene using CuCl/PMDETA as a catalyst and the previously obtained PEG as a macroinitiator. The degassed MMA (10.0 mL, 93.5 mmol), PMDETA (0.098 mL, 0.47 mmol), CuCl (4.6 mg, 0.47 mmol), toluene (10 mL), and PEG-macroinitiator (0.31 g, 0.47 mmol) were added into a Schlenk

tube in that order. The reaction mixture was stirred under degassed (three FPT cycles) conditions for 15 minutes at 90 °C. After the specified time, the polymerization mixture was diluted with THF, passed through a column of neutral alumina to remove metal salt. The solution was diluted with THF and precipitated into cold methanol. The obtained copolymer was dried in a vacuum oven for 24 h at 25 °C ($[M]_0/[I]_0 = 200$; $[I]_0:[CuCl]_0:[PMDETA]_0 = 1:1:1$; conversion (%) = 21; $M_{n,theo}$ = 6280, $M_{n,NMR}$ = 7470, $M_{n,GPC}$ = 7130, M_w/M_n = 1.11, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 4.71 (s, 2H, CH≡CCH_2O), 4.22 (m, 6H, PEG-OCH_2CH_2OC=O and CH_2OC=O), 3.89 (t, 2H, PEG-OCH_2CH_2OC=O), 3.67-3.62 (br, 4H, -OCH_2CH_2- of PEG), 3.6-3.5 (br, -OCH_3 of PMMA), 3.36 (s, -OCH_3 end-group of PEG), 2.62 (s, 4H, C=OCH_2CH_2C=O), 2.52 (s, 1H, CH≡CCH_2O), 2.0-0.6 (aliphatic protons).

3.5. Synthesis of 1,1,1-Tris[4-(2-propynyloxy)phenyl]-ethane [8]

1,1,1-Tris(4-hydroxyphenyl)ethane (0.75 g, 2.45 mmol) was dissolved in dimethylformamide (DMF; 10 mL), and propargyl bromide (80% in toluene; 0.97 mL, 9 mmol) and K_2CO_3 (2.4 g, 17.5 mmol) were added to the mixture. The reaction mixture was stirred for 24 h at 110 °C. After the reaction was completed, the mixture was filtered and evaporated in vacuo to remove DMF. CH_2Cl_2 (200 mL) was added, and the reaction mixture was washed three times with distilled water (100 mL x 3). The combined organic phase was dried over Na_2SO_4, filtered, and evaporated. The remaining product was purified by column chromatography over silica gel eluting with ethyl acetate/hexane (1:9) to obtain pure **8** as a yellow-green liquid (0.684 g, 67%). ^{1}H NMR ($CDCl_3$): 7.01–6.96 (m, 6H, ArH), 6.88–6.82 (m, 6H, ArH), 4.66 (d, J = 2.4 Hz, 6H,HCC-CH_2) 2.50 (t, J = 2.4 Hz, 3H, HCC-CH$_2$), 2.09 (s, 3H, CH_3) [82].

3.6. Azidation of chloropropyl-heptaisobutyl substituted-POSS (POSS-N_3) [9]

Chloropropyl-heptaisobutyl substituted-POSS (1.0 g, 1.1 mmol) and 15 mL of DMF were added into a round bottom flask. Sodium azide (0.360 g, 5.55 mmol) was added to the solution. After stirring for 24 h at 80 °C, the reaction mixture was evaporated, diluted with THF and precipitated into methanol. The product was dried in a vacuum oven for 24 h at 25 °C, yielding a white solid (Yield = 0.97 g, 98 %; $M_{n,theo}$ = 900.5; $M_{n,GPC}$ = 677, M_w/M_n = 1.01, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 3.23 (t,

2H, POSS-$CH_2CH_2CH_2N_3$), 1.91-1.66 (br, 9H, POSS-$CH_2CH_2CH_2N_3$ and $SiCH_2CH(CH_3)_2$), 0.94 (d, 42H, -$SiCH_2CH(CH_3)_2$), 0.70-0.57 (br, 16H, POSS-$CH_2CH_2CH_2N_3$ and -$SiCH_2CH(CH_3)_2$).

3.7. Click Reactions

3.7.1. Preparation of 3-arm star POSS via azide-alkyne click reaction of 8 with POSS-N_3 [10]

8 (0.045 g, 0.11 mmol) and POSS-N_3 (0.324 g, 0.360 mmol) were dissolved in nitrogen-purged DMF/THF (1/1 v/v) in a Schlenk tube. CuBr (24.0 mg, 0.165 mmol) and PMDETA (0.0340 mL, 0.165 mmol) were added in that order and the reaction mixture was degassed by three freeze-pump-thaw (FPT) cycles and stirred for 24 h at room temperature. The solution was passed through a column of neutral alumina to remove the copper salt and precipitated into methanol. The product was dried in a vacuum oven at 25 ^oC (Yield = 0.35 g, 95 %; $M_{n,GPC}$ = 3430, M_w/M_n = 1.02, relative to PS standards). ^1H NMR ($CDCl_3$, δ) 7.58 (s, 3H, C*H* of triazole), 7.01-6.85 (m, 12H, ArH), 5.17 (s, 6H, triazole-CH_2O), 4.34 (t, 6H, POSS-$CH_2CH_2CH_2$-triazole), 2.01-1.60 (br, 30H, $(Ph)_3$-C-CH_3, POSS-$CH_2CH_2CH_2$-triazole, and $SiCH_2CH(CH_3)_2$), 0.94 (d, 126H, -$SiCH_2CH(CH_3)_2$), 0.59 (d, 48H, POSS-$CH_2CH_2CH_2$-triazole and $SiCH_2CH(CH_3)_2$).

3.7.2. Preparation of PEG-PMMA-POSS 3-miktoarm star terpolymer via click reaction of POSS-N_3 and PEG-PMMA-alkyne [11]

PEG-PMMA-alkyne copolymer (0.36 g, 0.048 mmol, based on $M_{n,NMR}$) and POSS-N_3 (0.122 g, 0.135 mmol) were dissolved in nitrogen-purged DMF/THF (1/1 v/v) mixture in a Schlenk tube equipped with magnetic stirring bar. CuBr (3.3 mg, 0.023 mmol) and PMDETA (0.048 mL, 0.023 mmol) were added to the tube. The reaction mixture was degassed by three FPT cycles and left in argon and stirred at room temperature for 24 h. After a specified time, the solution was passed through a column of neutral alumina to remove copper salt and precipitated into cold methanol. The polymer was dissolved in THF and precipitated into hexane. The above dissolution-precipitation was repeated for two times. Finally, polymer was dried overnight in vacuum oven at 25 ^oC (Yield = 0.30 g, 70 %; $M_{n,theo}$ = 8370, $M_{n,GPC}$ = 9000; M_w/M_n = 1.19, relative to PS standards). ^1H NMR ($CDCl_3$, δ) 7.66 (bs, 1H, C*H*

of triazole), 5.25 (bs, 2H, triazole-C*H*$_2$OC=O), 4.32-4.22 (br, 8H, POSS-CH$_2$CH$_2$C*H*$_2$-triazole, PEG-OCH$_2$C*H*$_2$OC=O and C*H*$_2$OC=O), 3.87-3.64 (br, 2H, of PEG-OC*H*$_2$CH$_2$OC=O, -OC*H*$_2$C*H*$_2$- and -OC*H*$_3$ repeating units of PEG and PMMA, respectively), 3.36 (s, -OC*H*$_3$ end group of PEG), 2.55 (bs, 4H, C=OC*H*$_2$C*H*$_2$C=O), 2.0-0.6 (aliphatic protons of PMMA and POSS).

4. RESULTS and DISCUSSION

4.1. Synthesis of Initiator

The initiator synthesis was achieved by the following pathways; First of all 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid **(1)** 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.

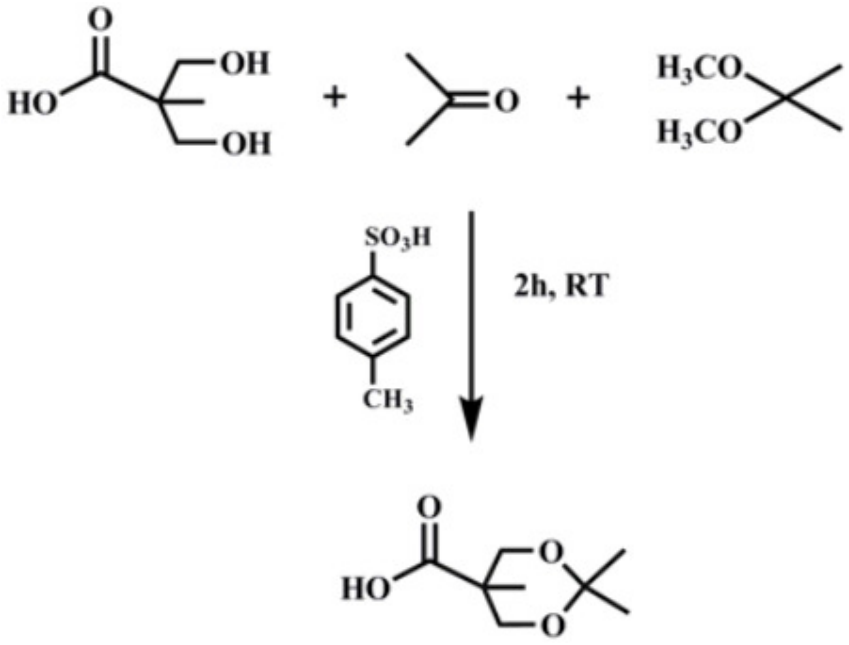


Figure 4.1: Synthesis of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid.

The ^{1}H NMR spectrum of the compound, **(1)**, is shown in Figure 4.2. From the NMR spectrum, the peaks in the range between 3.63 and 4.18 ppm are assigned to methylene protons. The peaks in the range between 1.18 and 1.40 ppm are identified to methyl protons.

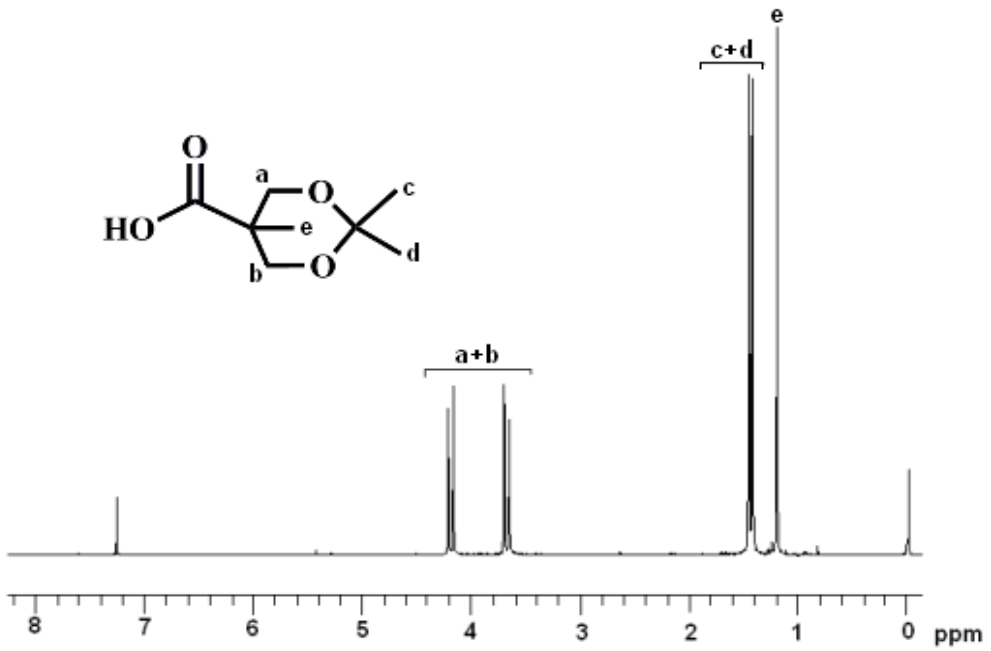


Figure 4.2: The ^{1}H NMR spectrum of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid in $CDCl_3$.

Subsequent esterification reaction between propargyl alcohol and hydroxyl protected acid **(1)** was carried out using DCC as a coupling agent and catalytic amount of DMAP as catalyst and to give propargyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate **(2)**.

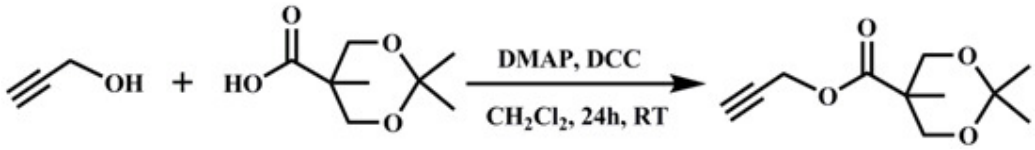


Figure 4.3. Synthesis of propargyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate.

The ^{1}H NMR spectrum of the compound, **(2)**, is shown in Figure 4.4. From the NMR spectrum the new signals appeared at δ 4.72 ppm (CH≡CC*H*$_2$O) and at δ 2.45 ppm (C*H*≡CCH$_2$O) of propargyl alcohol.

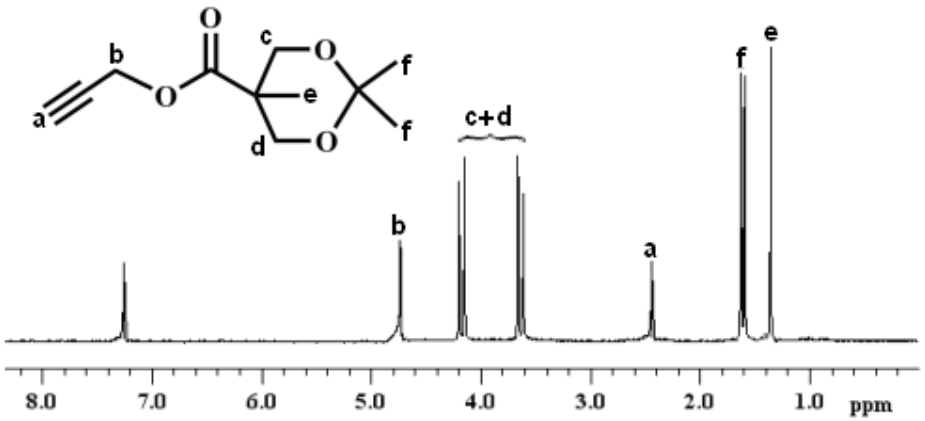


Figure 4.4. The ^{1}H NMR spectrum of propargyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate in $CDCl_3$.

Moreover, deprotection step was easily achieved by acidic hydrolysis using 1 M HCl and THF at room temperature.

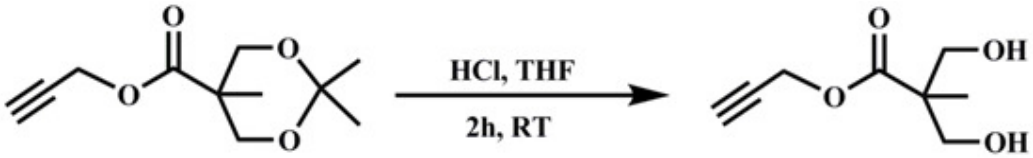


Figure 4.5: Synthesis of propargyl 3-hydroxy-2-(hydroxymethyl)- 2-methyl propanoate.

^{1}H NMR spectrum of the desired compound, **(3),** is illustrated in Figure 4.6. From the NMR spectrum -O*H* protons at δ 2.93 ppm suggests that deprotection step was carried out successfully.

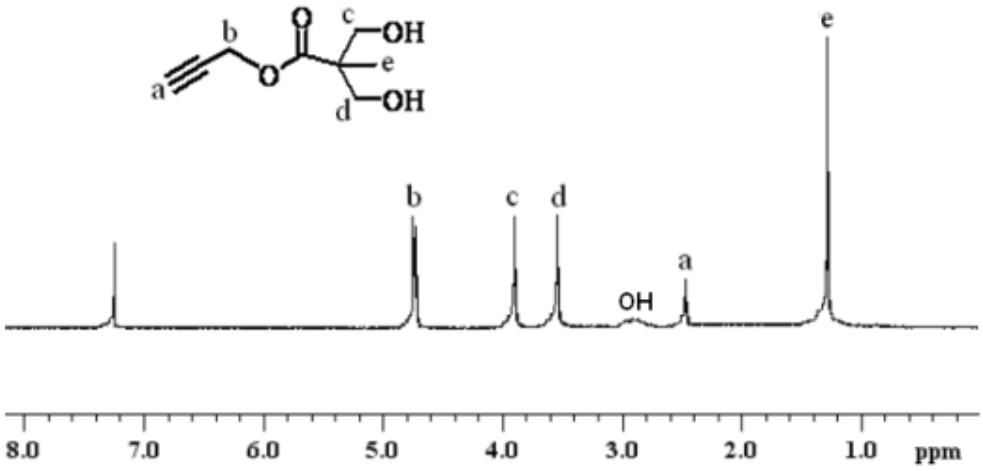


Figure 4.6: The ^{1}H NMR spectrum of propargyl 3-hydroxy-2-(hydroxymethyl)- 2-methylpropanoate in $CDCl_3$.

In order to introduce ATRP functionality into the synthesis, second esterification reaction was achieved. In this connection, it should be pointed out that at this step severe reaction conditions may cause the hydrolysis of the ester groups present in the structure. Therefore, the esterification process was performed at zero temperature and 2-bromoisobutryl bromide was added in a dropwise manner.

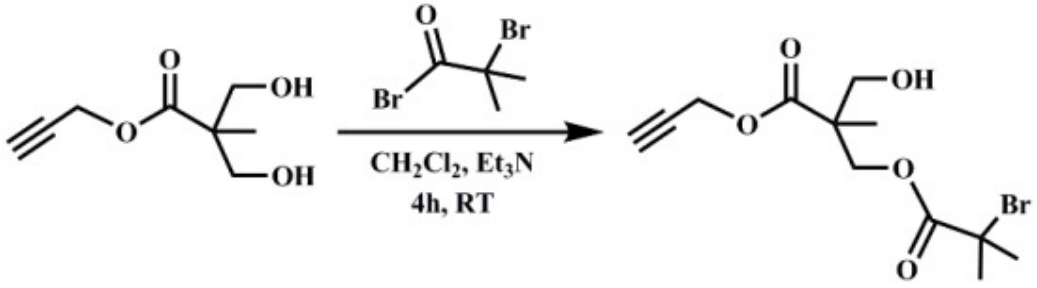


Figure 4.7: Synthesis of propargyl-3-[(2-bromo-2-methylpropanoyl)oxy]-2-(hydroxymethyl)-2-methylpropanoate.

The ^{1}H NMR spectrum of the compound **4** showed the shift of the -CH_2 protons adjacent to ATRP functionality to δ 4.43 and 4.30 ppm and the –CH_3 protons on ATRP functionality at δ 1.91 ppm indicate that esterification reaction was carried out successfully. The ^{1}H NMR spectrum of the resulting compound, **(4),** is shown in Figure 4.8.

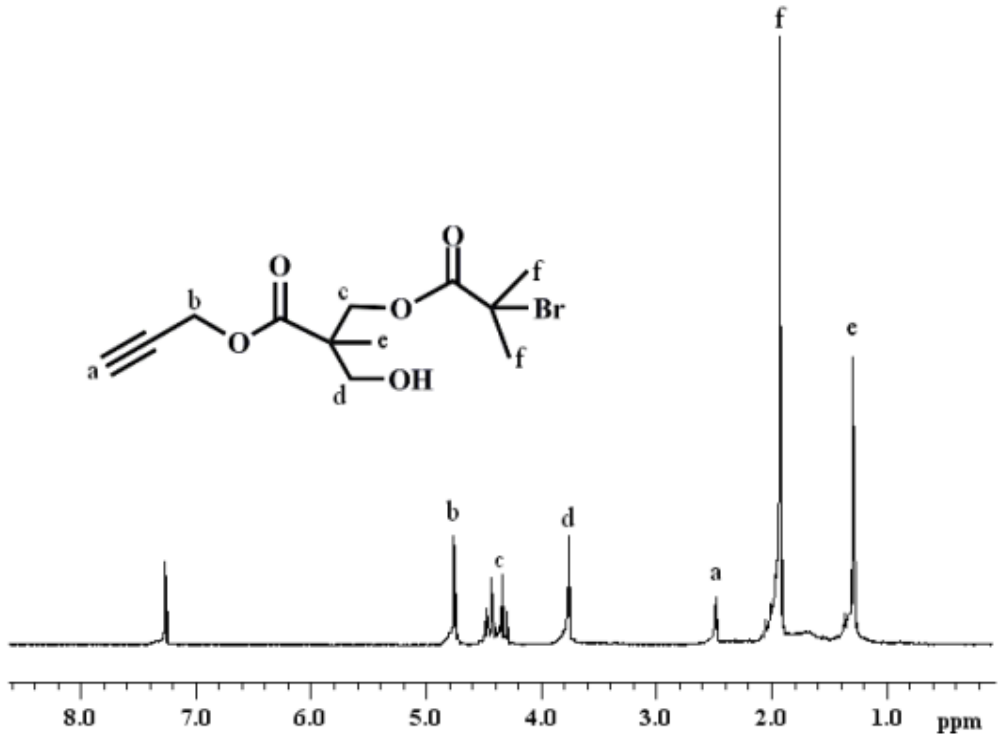


Figure 4.8: The ^{1}H NMR spectrum of propargyl-3-[(2-bromo-2-methylpropanoyl)oxy]-2-(hydroxymethyl)-2-methylpropanoate in $CDCl_3$.

PEG-COOH (5) was obtained from commercially available PEG_{2000} using succinic anhydride.

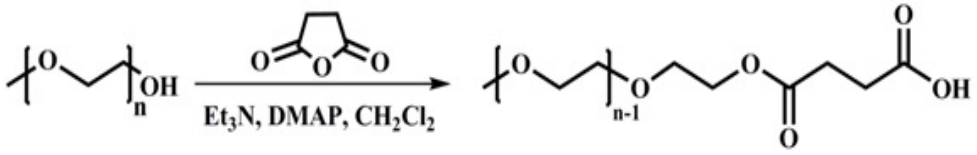


Figure 4.9: Synthesis of PEG mono-carboxylic acid (PEG-COOH).

The ^{1}H NMR spectrum of the compound **(5)** is given in Figure 4.10. From the NMR spectrum, the characteristic peak of the backbone at δ3.62 ppm, CH_2OC=O next to carbonyl at δ 4.23, and C=OCH_2CH_2C=O at δ2.65 ppm suggests that PEG-COOH was obtained succesfully.

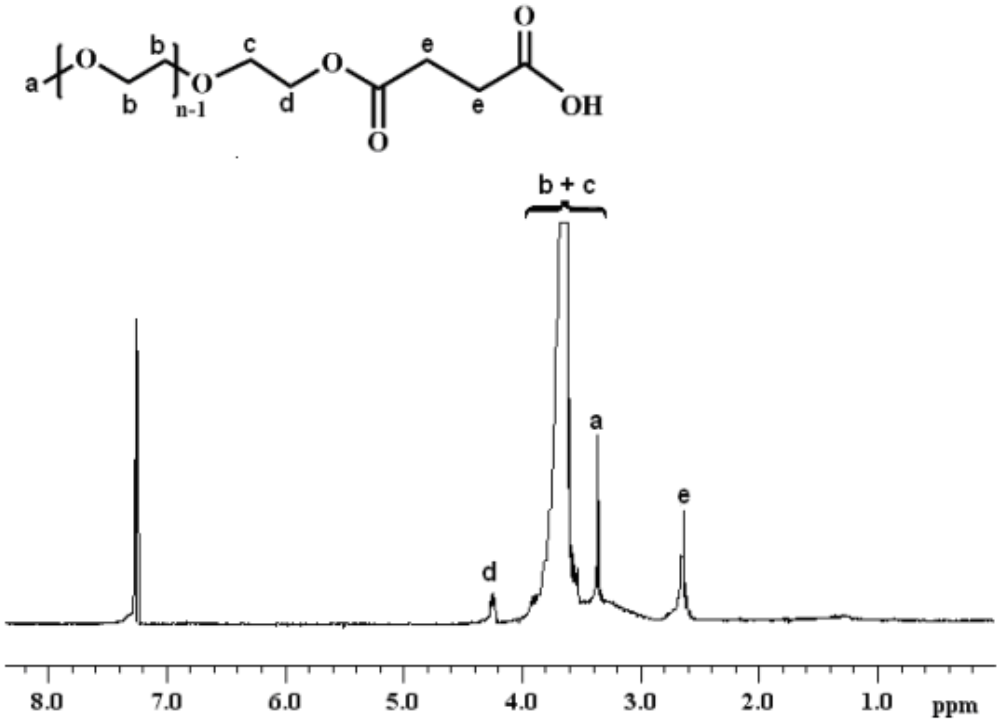


Figure 4.10: The ^{1}H NMR spectrum of PEG mono-carboxylic acid (PEG-COOH) in $CDCl_3$.

Another esterification reaction between compound **4** and compound **5** was carried out using DCC as a coupling agent and catalytic amount of DMAP as catalyst and to give PEG-macroinitiator **(6)** containing both the bromide and alkyne functionalities.

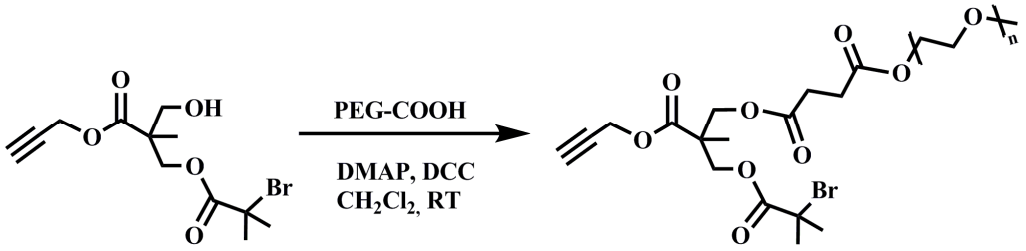


Figure 4.11: Synthesis of PEG-macroinitiator.

The ^{1}H NMR spectrum of the compound, **(6)**, is shown in Figure 4.12. NMR measurement displayed a characteristic peak of PEG in the range between 3.5 and 3.8 ppm. $M_{n,NMR}$ of PEG-macroinitiator was calculated from a ratio of peak areas of CH_2CH_2O repeating unit of PEG at 3.5-3.8 and CH_2 adjacent to alkyne at 4.7 ppm.

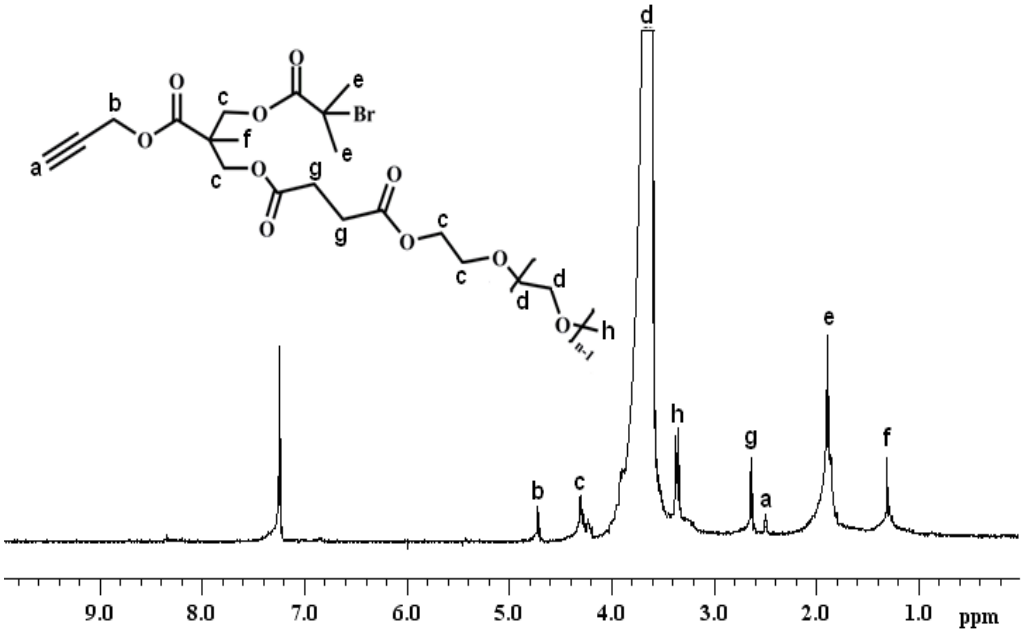


Figure 4.12: The ^{1}H NMR spectrum of PEG-macroinitiator in $CDCl_3$.

4.2. Synthesis of PEG-*b*-PMMA copolymer via ATRP

The obtained PEG-macroinitiator containing both the bromide and alkyne functionalities proper for subsequent ATRP and click reactions were used in ATRP of MMA in toluene using CuCl/ PMDETA as a catalyst for 15 min at 90 ^{o}C affording the synthesis of PEG-*b*-PMMA copolymer with alkyne at its center (PEG-PMMA-alkyne). $M_{n,theo}$ of PEG-PMMA-alkyne copolymer was calculated using the formula $M_{n,theo} = ([M]_0/[I]_0)$ X conv. % X MW of MMA + $M_{n,NMR}$ of PEG-macroinitiator = 200 X 0.21 X 100 + 2080 = 6280. $M_{n,GPC}$ = 7130 and M_w/M_n = 1.11 values were determined from GPC calibrated with PS standards in THF.

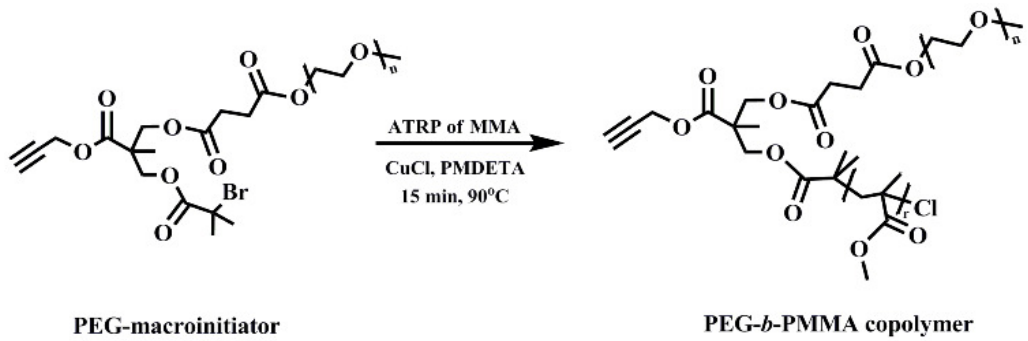


Figure 4.13: Synthesis of PEG-PMMA-alkyne copolymer.

^{1}H NMR analysis clearly revealed an incorporation of MMA segment into the PEG block. $M_{n,NMR}$ = 7470 was calculated using a ratio of an integrated signal at 3.61-3.57 (PMMA and PEG repeating units) to that at 2.62 ppm (C=OCH_2CH_2C=O), while adding the $M_{n,NMR}$ = 2080 of PEG-macroinitiator (Fig. 4.14). Hence, the resulting DP_ns of PEG and PMMA segments are determined to be 40 and 54, respectively.

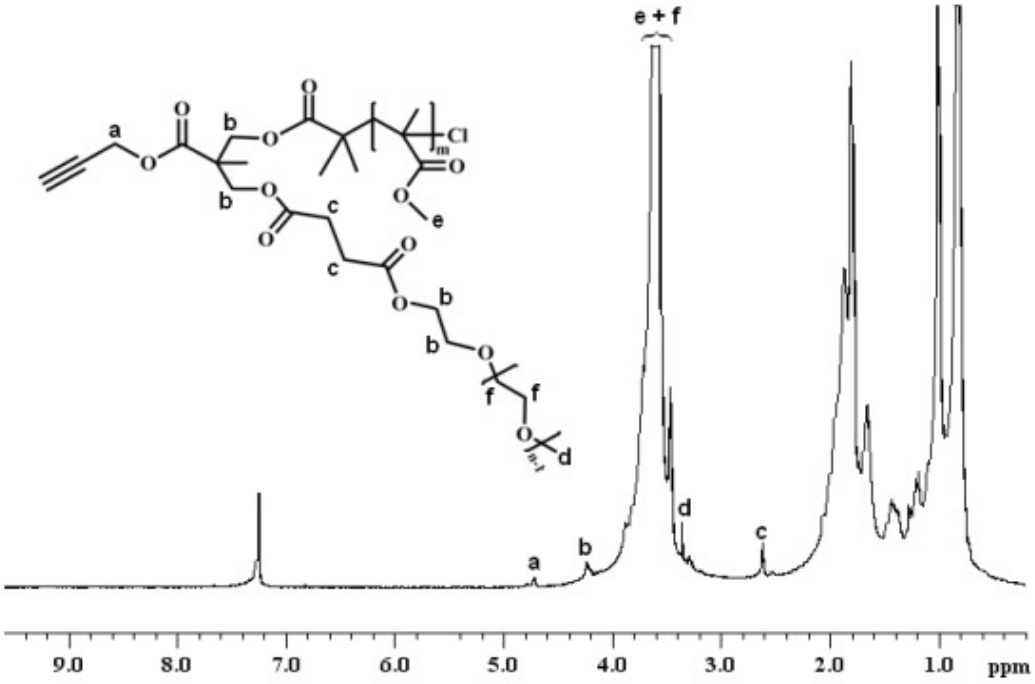


Figure 4.14: The ^{1}H NMR spectrum of PEG-PMMA-alkyne copolymer in $CDCl_3$.

4.3. Synthesis of 1,1,1-Tris[4-(2-propynyloxy)phenyl]- ethane

Trisalkynyl-functional compound **8** was prepared in a 67% yield via an etherification reaction between 1,1,1-tris(4-hydroxyphenyl)ethane and propargyl bromide.

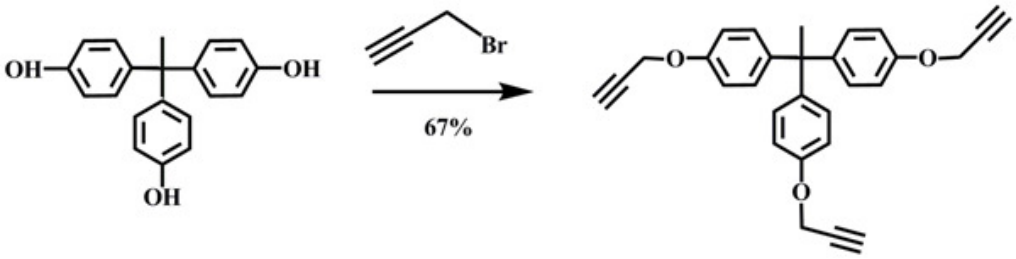


Figure 4.15: Synthesis of 1,1,1-Tris[4-(2-propynyloxy)phenyl]-ethane.

The structure of **8** was confirmed by ^{1}H NMR and elemental analysis. In the ^{1}H NMR spectrum of **8**, it was evident that CH_2 protons of propargyl bromide at 3.86 were shifted to 4.66 ppm as a doublet signal of CH_2O indicating an etherification reaction (Fig. 4.16).

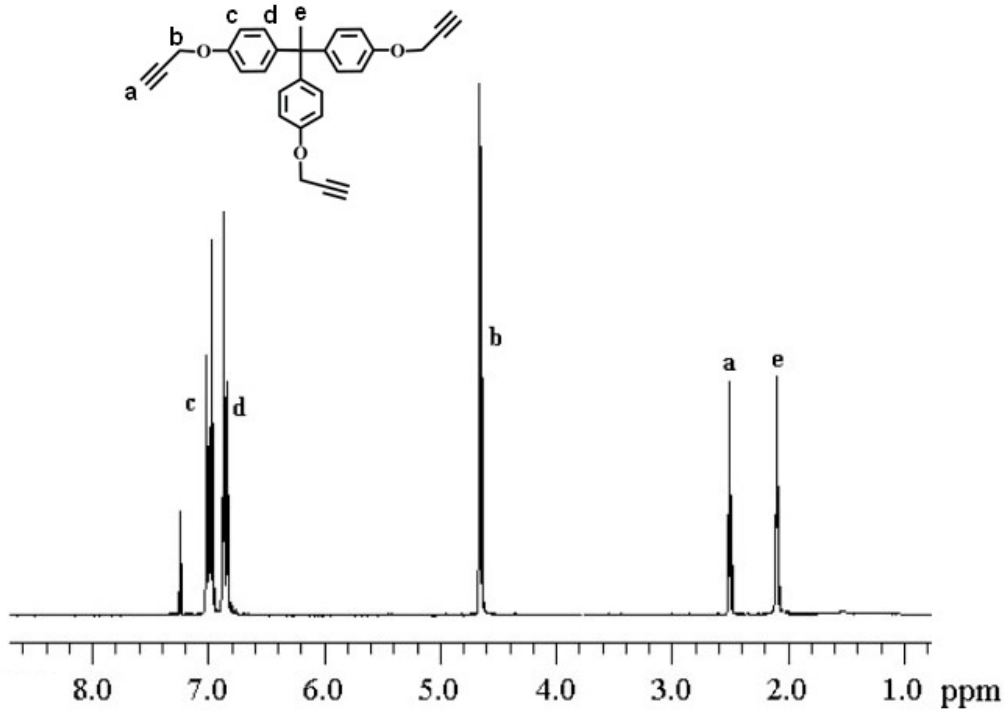


Figure 4.16: The ^{1}H NMR spectrum of 1,1,1-Tris[4-(2-propynyloxy)phenyl]-ethane.

4.4. Azidation of chloropropyl-heptaisobutyl substituted-POSS

POSS-N_3 was prepared by a reaction of chloropropyl-heptaisobutyl substituted-POSS with NaN_3 in DMF for 24 h at 80 ^oC.

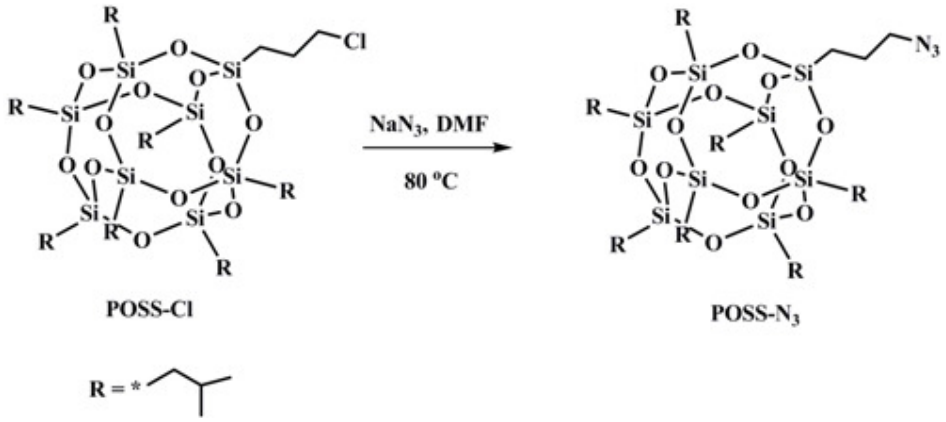


Figure 4.17: Synthesis of POSS-N_3.

Azidation reaction is monitored by the complete disappearance of -CH_2Cl (δ 3.5) and the appearance of -CH_2N$_3$ signal (δ 3.2) via ^{1}H NMR spectroscopy as shown Figure 4.18. This suggested that the azidation reaction is complete. Additionally, FT-IR spectrum of POSS-N$_3$ displayed a characteristic peak of azide group at 2100 cm^{-1}.

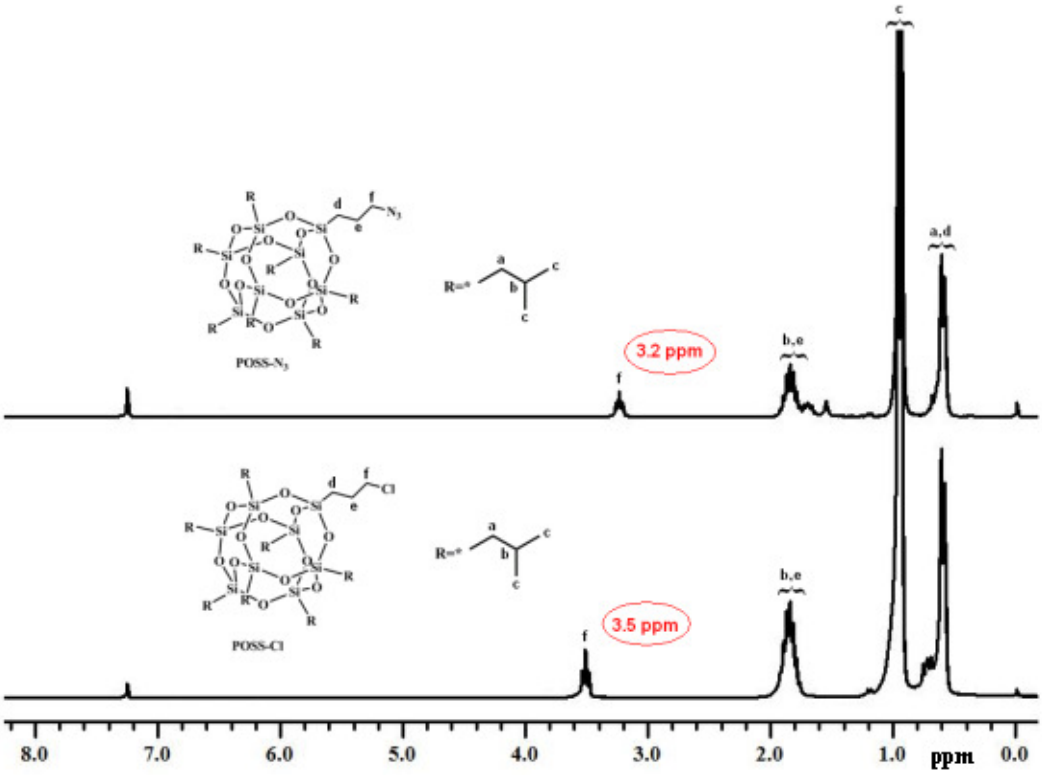


Figure 4.18: The ^{1}H NMR spectrum of POSS-N$_3$.

4.5. Click reactions

4.5.1. Click reaction between POSS-N$_3$ and 1,1,1-Tris[4-(2propynyloxy)phenyl]-ethane

3-arm star POSS was obtained via a reaction of POSS-N$_3$ and **8** under click reaction conditions for 24 h. A total of ~3.3 eq amounts of POSS-N$_3$ compared to that of **8** is used to ensure the complete consumption of alkyne moiety in the mixture of DMF/THF using CuBr/PMDETA as catalyst at room temperature.

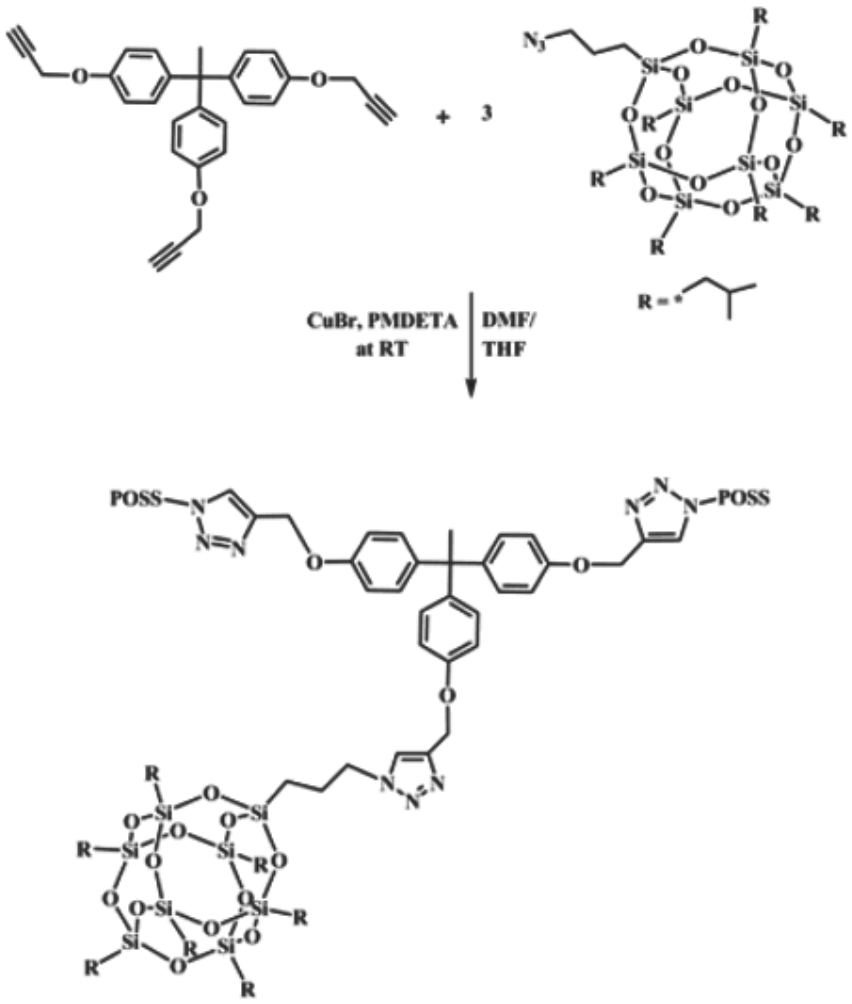


Figure 4.19: Synthesis of 3-arm star POSS.

3-arm star POSS was characterized by ^{1}H NMR and GPC analyses. ^{1}H NMR spectrum of 3-arm star POSS reaction mixture reveals the appearance of a new signal regarding C*H* of 1,2,3-triazole at 7.58, along with the signals appeared at 7.01-6.85, 5.17, and 4.34 ppm assignable to Ar*H* of the core, OCH_2-1,2,3-triazole and CH_2-1,2,3-triazole, respectively (Fig. 4.20). Moreover, a ratio of an integrated signal of the core Ar*H* protons (12H) to that of CH_2-1,2,3-triazole (6H) clearly displayed that the major product was 3-arm star POSS. Moreover, $M_{n,theo}$ of 3-arm star POSS can be calculated using these data ($M_{n,theo}$ = 3 X 900 (MW of POSS-N_3) + 420 (MW of **8**) = 3120), while fitting the $M_{n,GPC}$ of 3-arm star (3430), relative to PS standards.

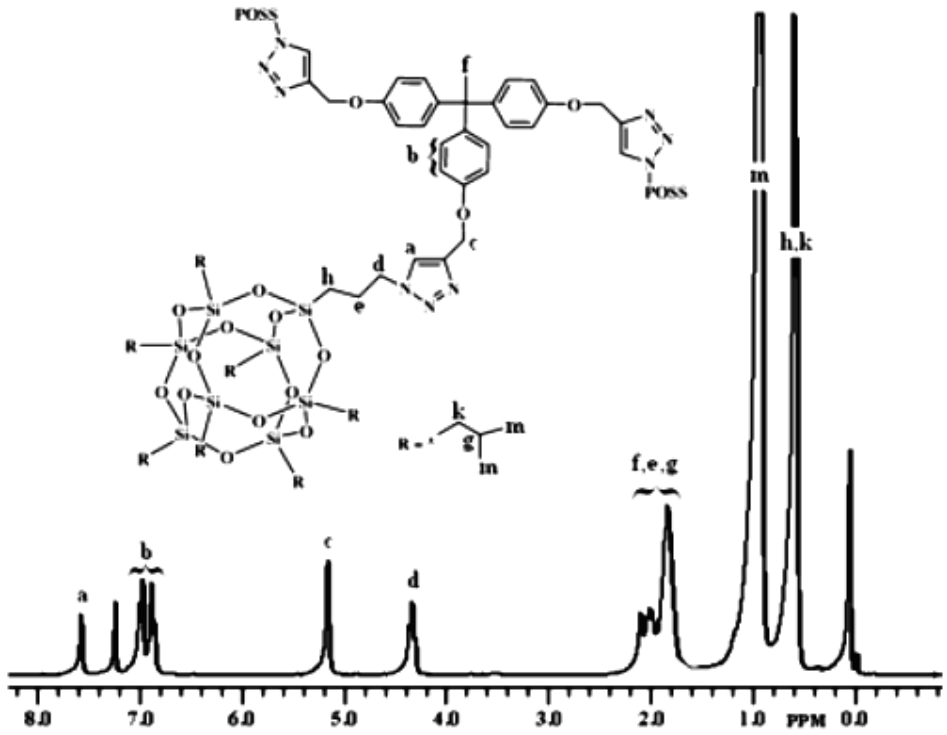


Figure 4.20: The ^{1}H NMR spectrum of 3-arm star POSS in $CDCl_3$.

GPC trace of the click reaction displays a main peak with a tiny tail and a baseline separated small trace (Fig. 4.21). The deconvolution analysis of the GPC trace via Gaussian peak splitting revealed that the area fraction of 3-arm star POSS was 94 %, while those of 2-arm star POSS and POSS precursors were calculated to be 4 and 2 %, respectively. The results inferred from NMR and GPC confirmed the high click reaction efficiency for the production of 3-arm star POSS. It is noted that azide-alkyne click reaction efficiency for 3-arm star POSS is in accordance with those of A_3 star polymers obtained by using various types of click chemistry based on the size of polymeric arm [28, 82, 83].

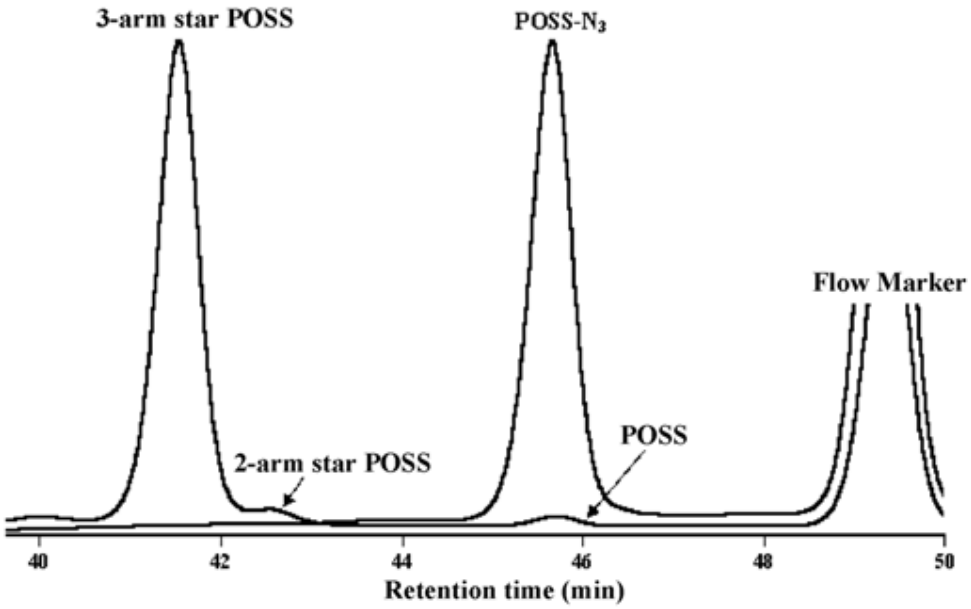


Figure 4.21: GPC curves of POSS and 3-arm star POSS.

DSC thermogram of POSS-N_3 displayed two transitions at 45.6 and 266.7 ^{o}C (Fig. 4.22). These transitions could be due to breaking up of weak aggregates of isobutyl-POSS molecules and melting, respectively [84]. Two melting endotherms for 3-arm star POSS are observed at 201.8 and 217.9 ^{o}C corresponding to crystal structure of POSS (Fig. 4.22).

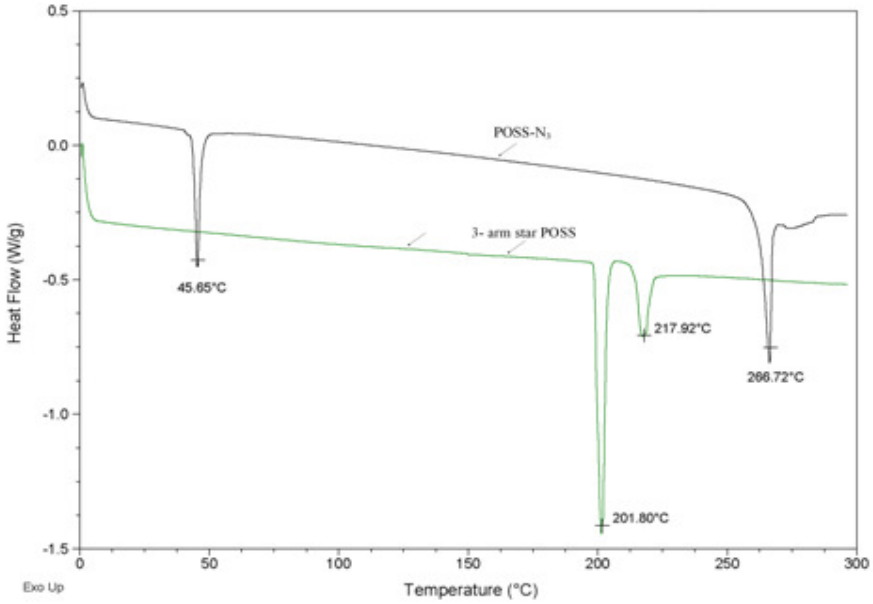


Figure 4.22: DSC thermogram of POSS-N_3 and 3-arm star POSS.

4.5.2. Click reaction between POSS-N_3 and PEG-PMMA-alkyne

POSS-N_3 (~2.5 equiv) and PEG-PMMA-alkyne copolymer (1 equiv) are allowed to click using CuBr/PMDETA in DMF/THF at room temperature for 24 h. Because the unreacted POSS-N_3 molecules could easily be removed by precipitation in hexane, molar excess of POSS-N_3 relative to that of PEG-PMMA-alkyne was deliberately used in order to ensure the reaction completion.

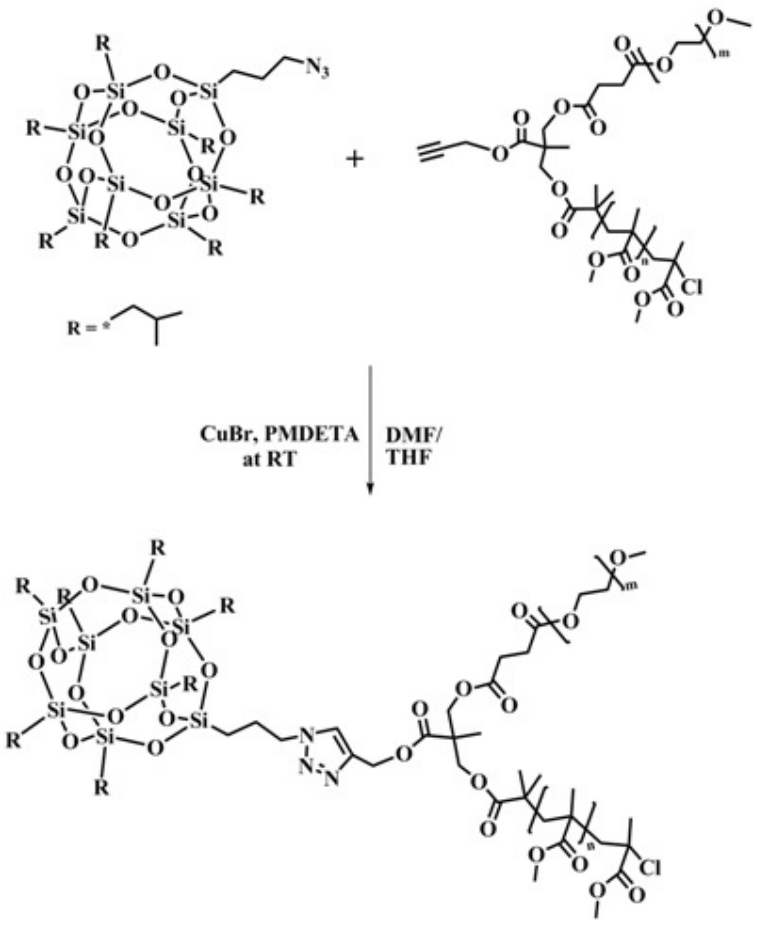


Figure 4.23: Synthesis of PEG-PMMA-POSS 3-miktoarm star polymer.

The obtained PEG-PMMA-POSS 3-miktoarm star polymer was characterized by ^{1}H NMR and GPC analysis. ^{1}H NMR spectrum of 3-miktoarm star terpolymer displays two broad signals at 7.66 and 5.25 ppm assignable to C*H* of 1,2,3-triazole and -C=OOCH_2-1,2,3-triazole, respectively. Additionally, the characteristic signals for PEG, PMMA and POSS segments are observed at 3.9-3.6 (PEG-OCH_2CH$_2$OC=O, -OCH_2CH_2- and -OCH_3 repeating units of PEG and PMMA) and 4.3 ppm (POSS-CH$_2$CH$_2$CH_2-triazole), respectively (Fig. 4.24). $M_{n,theo}$ = 8370 of PEG-PMMA-

POSS 3-miktoarm star polymer are calculated via a sum of $M_{n,NMR}$ of PEG-PMMA-alkyne (7470) and MW of POSS-N_3 (900).

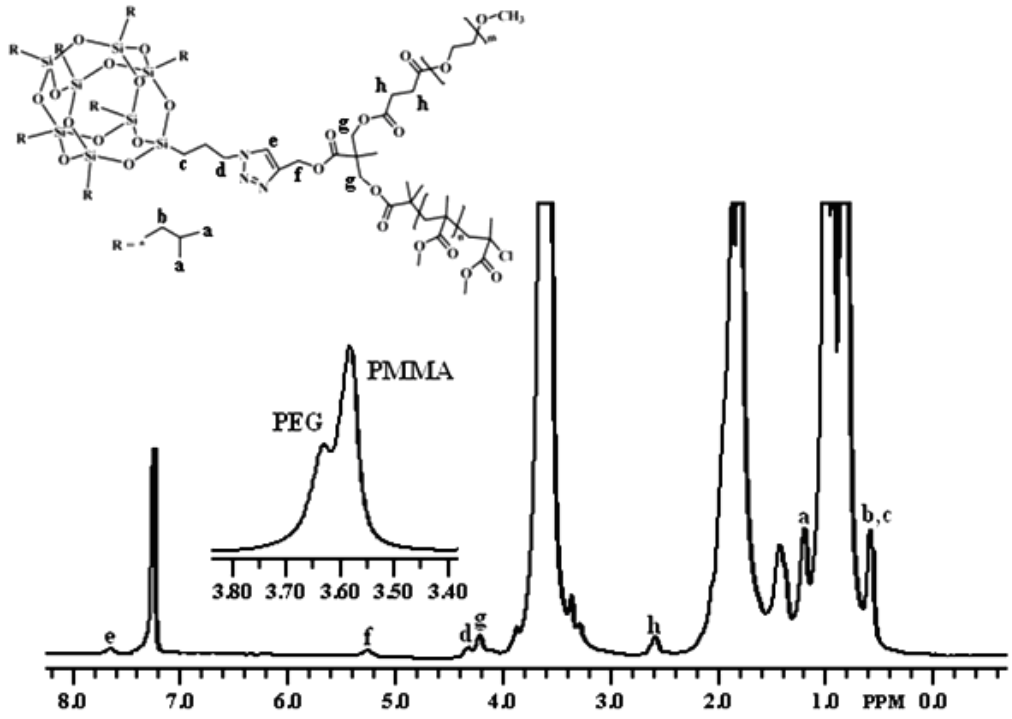


Figure 4.24: The ^{1}H NMR spectrum of PEG-PMMA-POSS 3-miktoarm star polymer in $CDCl_3$.

According to GPC measurement, a clear shift in molecular weight distributions for PEG-PMMA-POSS 3-miktoarm star terpolymer was detected at lower retention time with respect to those of PEG-PMMA-alkyne and POSS-N_3 indicating an efficient click reaction (Fig. 4.25.). Additionally, $M_{n,GPC}$ and M_w/M_n of the target miktoarm star polymer was obtained to be 9000 and 1.19 relative to PS calibrants, respectively.

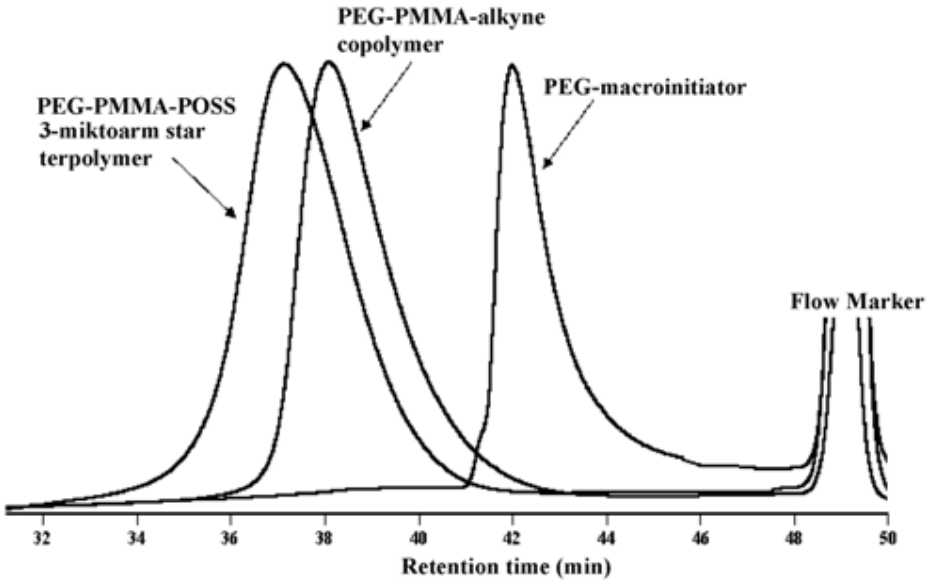


Figure 4.25: GPC traces of PEG-macroinitiator, PEG-PMMA-alkyne copolymer and PEG-PMMA-POSS 3-miktoarm star terpolymer.

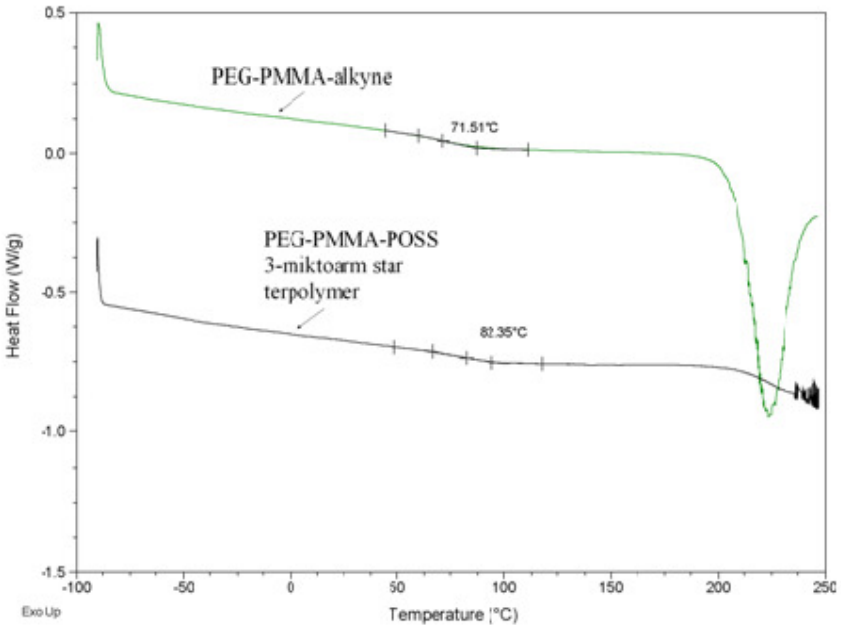


Figure 4.26: DSC thermogram of PEG-PMMA-alkyne copolymer and PEG-PMMA-POSS 3-miktoarm star terpolymer.

For PEG-PMMA-POSS 3-miktoarm star terpolymer, only one T_g is detected at 82.3 ^oC, which is higher than that of PEG-PMMA-alkyne copolymer (T_g = 71.5 ^oC) (Fig. 4.26.). The incorporation of POSS molecule into PEG-PMMA copolymer increased T_g by around 11 ^oC. Moreover, it is noted that both polymers decompose at 200 ^oC.

5. CONCLUSION

In conclusion, POSS-N_3 is clicked simply with tris-alkyne core **8** and PEG-*b*-PMMA copolymer with alkyne at its center (PEG-PMMA-alkyne) affording the synthesis of 3-arm star POSS (A_3) and PEG-PMMA-POSS 3-miktoarm star (ABC) terpolymer, respectively. For this purpose, first, PEG-macroinitiator, with both alkyne and bromide functionalities, was synthesized via a reaction of PEG-COOH with propargyl-3-[(2-bromo-2-methylpropanoyl)oxy]-2-(hydroxymethyl)-2-methyl propanoate. The initiator **6,** thus obtained was used in the subsequent living radical polymerization routes such as ATRP of MMA in order to give PEG-*b*-PMMA copolymer with alkyne at its center (PEG-PMMA-alkyne) with controlled molecular weight and low polydispersity ($M_{n,GPC}$ =7130; $M_{n,NMR}$ = 7470; $M_{n,theo}$ = 6280; M_w/M_n = 1.11). As a second step, POSS-N_3 and 1,1,1-Tris[4-(2-propynyloxy)phenyl]- ethane with trisalkynyl-functionality were synthesized. Third, POSS-N_3 and 1,1,1-tris[4-(2-propynyloxy)phenyl]-ethane **8** are allowed to react affording the synthesis of 3-arm star POSS in the presence of CuBr/PMDETA in DMF/THF at room temperature. In the final step, POSS-N_3 and PEG-PMMA-alkyne copolymer are clicked in order to give POSS-PEG-PMMA 3-miktoarm star terpolymer using CuBr/PMDETA as catalyst in DMF/THF at room temperature.

In this study, highly efficient click reactions are obtained for both cases. The click efficiency for 3-arm star POSS formation is determined to be 94 % from a deconvolution analysis of the GPC trace of the reaction mixture. Additionally, GPC trace of PEG-PMMA-POSS 3-miktoarm star terpolymer also revealed a monomodal distribution confirming a successful click reaction. The click efficiency was calculated to be 93 % from the ratio $M_{n,NMR}$ and $M_{n,theo}$. DSC analysis of 3-arm star POSS revealed two melting peaks of 201.8 and 217.9 ^oC. However, for the case of PEG-PMMA-POSS 3-miktoarm star terpolymer, only one T_g of 82.3 ^oC is detected indicating miscible system.

REFERENCES

[1] **Wu, J.; Mather, P. T.,** 2009. POSS Polymers: Physical Properties and Biomaterials Applications, *J Macromol Sci Part C Polym Rev*, **49**, 25-63.

[2] **Kim, B.-S.; Mather, P. T.,** 2006. Amphiphilic telechelics with polyhedral oligosilsesquioxane (POSS) end-groups: Dilute solution viscometry, *Polymer*, **47**, 6202-6207.

[3] **Zhang, W.; Liu, L.; Zhuang, X.; Li, X.; Bai, J.; Chen, Y.,** 2008. Synthesis and Self-Assembly of Tadpole-Shaped Organic/Inorganic Hybrid Poly(N-isopropylacrylamide) Containing Polyhedral Oligomeric Silsesquioxane via RAFT Polymerization, *J Polym Sci Part A: Polym Chem*, **46**, 7049-7061.

[4] **Pyun, J.; Matyjaszewski, K.,** 2000. The Synthesis of Hybrid Polymers Using Atom Transfer Radical Polymerization: Homopolymers and Block Copolymers from Polyhedral Oligomeric Silsesquioxane Monomers, *Macromolecules*, **33**, 217-220.

[5] **Zhang, L.; Lu, D.; Tao, K.; Bai, R.,** 2009. Synthesis, Characterization and Self-Assembly of Novel Amphiphilic Block Copolymers with a Polyhedral Oligomeric Silsesquioxanes Moiety Attached at the Junction of the Two Blocks, *Macromol. Rapid Commun*, **30**, Early view.

[6] **Huang, C.-F.; Kuo, S.-F.; Lin, F.-J.; Huang, W.-J.; Wang, C.-F.; Chen, W.-Y.; Chang, F.-C.,** 2006. Influence of PMMA-Chain-End Tethered Polyhedral Oligomeric Silsesquioxanes on the Miscibility and Specific Interaction with Phenolic Blends, *Macromolecules*, **39**, 300-308.

[7] **Lee, K. M.; Knight, P. T.; Chung, T.; Mather, P. T.,** 2008. Polycaprolactone-POSS Chemical/Physical Double Networks, *Macromolecules*, **41**, 4730-4738.

[8] **Ge, Z.; Wang, D.; Zhou, Y.; Liu, H.; Liu, S.,** 2009. Synthesis of Organic/Inorganic Hybrid Quatrefoil-Shaped Star-Cyclic Polymer Containing a Polyhedral Oligomeric Silsesquioxane Core, *Macromolecules*, **42**, 2903-2910.

[9] **Cardoen, G.; Coughlin, E. B.,** 2004. Hemi-Telechelic Polystyrene-POSS Copolymers as Model Systems for the Study of Well-Defined Inorganic/Organic Hybrid Materials, *Macromolecules*, **37**, 5123-5126.

[10] **Zhang, X.; Tay, S. W.; Liub, Z.; Honga, L.,** 2009. Restructure proton conducting channels by embedding starburst POSS-g-acrylonitrile

oligomer in sulfonic perfluoro polymer matrix**,** *J Memb Sci*, **329**, 228-235.

[11] **Miao, J.; Cui, L.; Lau, H. P.; Mather, P. T.; Zhu, L.,** 2007. Self-Assembly and Chain-Folding in Hybrid Coil-Coil-Cube Triblock Oligomers of Polyethylene-*b*-Poly(ethylene oxide)-*b*-Polyhedral Oligomeric Silsesquioxane, *Macromolecules*, **40**, 5460-5470.

[12] **Ak, M.; Gacal, B.; Kiskan, B.; Yagci, Y.; Toppare, L.,** 2008. Enhancing electrochromic properties of polypyrrole by silsesquioxane nanocages, *Polymer*, **49**, 2202–2210.

[13] **Roovers, J.,** in Star and Hyperbranched Polymers; **Mishra, M.; Kobayashi, S.** Ed.s, Marcel Dekker, New York 1998, **p. 285**.

[14] **Pitsikalis, M.; Pispas, S.; Mays, J. W.; Hadjichristidis, N.,** 1998. Nonlinear Block Copolymer Architectures, Adv *Polym Sci*, **135**, 1-137.

[15] **Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H.,** 2001. Polymers with Complex Architecture by Living Anionic Polymerization, *Chem Rev*, **101**, 3747-3797.

[16] **Hirao, A.; Hayashi, M.; Loykulnant, S.; Sugiyama, K.; Ryu, S. W.; Haraguchi, N.; Matsuo, A.; Higashihara, T.,** 2005. Precise syntheses of chain-multi-functionalized polymers, star-branched polymers, star-linear block polymers, densely branched polymers, and dendritic branched polymers based on iterative approach using functionalized 1,1-diphenylethylene derivatives**,** *Prog Polym Sci*, **30**, 111-182.

[17] **Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Mays, J.,** 2006. Macromolecular architectures by living and controlled/living polymerizations, *Prog Polym Sci*, **31**, 1068-1132.

[18] **Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Pispas, S.; Avgeropoulos, A.,** 2005. Linear and non-linear triblock terpolymers. Synthesis, self-assembly in selective solvents and in bulk, *Prog Polym Sci*, **30**, 725-782.

[19] **Meldal, M.,** 2008. Polymer ‘‘Clicking’’ by CuAAC Reactions, *Macromol Rapid Commun*, **29**, 1016-1051.

[20] **Lundberg, P.; Hawker, C. J.; Hult, A.; Malkoch, M.,** 2008**.** Click Assisted One-Pot Multi-Step Reactions in Polymer Science: Accelerated Synthetic Protocols, *Macromol Rapid Commun*, **29**, 998-1015.

[21] **Johnson, J. A.; Finn, M. G.; Koberstein, J. T.; Turro, N. J.,** 2008. Construction of Linear Polymers, Dendrimers, Networks, and Other Polymeric Architectures by Copper-Catalyzed Azide-Alkyne Cycloaddition ‘‘Click’’ Chemistry, *Macromol Rapid Commun*, **29**, 1052-1072.

[22] **Lecomte, P.; Riva, R.; Jerome, C.; Jerome, R.,** 2008. Macromolecular Engineering of Biodegradable Polyesters by Ring-Opening Polymerization and ‘Click’ Chemistry, *Macromol Rapid Commun*, 29, 982-997.

[23] **Quemener, D.; Le Halleye, M.; Bisset, C.; Davis, T. P.; Barner-Kowollik, C. Stenzel, M. H.,** 2008. Graft Block Copolymers of Propargyl Methacrylate and Vinyl Acetate via a Combination of RAFT/MADIX and Click Chemistry: Reaction Analysis, *J Polym Sci Part A: Polym Chem*, **46**, 155-173.

[24] **Gungor, E.; Durmaz, H.; Hizal, G.; Tunca, U.,** 2008. H-Shaped (ABCDE Type) Quintopolymer via Click Reaction [3 + 2] Strategy, *J Polym Sci Part A: Polym Chem*, 46, 4459-4468.

[25] **Dag, A.; Durmaz, H.; Demir, E.; Hizal, G.; Tunca, U.,** 2008. Heterograft Copolymers via Double Click Reactions Using One-Pot Technique, *J Polym Sci Part A: Polym Chem*, **46**, 6969-6977.

[26] **Durmaz, H.; Dag, A.; Hizal, A.; Hizal, G.; Tunca, U.,** 2008. One-Pot Synthesis of Star-Block Copolymers Using Double Click Reactions, *Polym Sci Part A: Polym Chem*, **46**, 7091-7100.

[27] **Wang, G.; Liu, C.; Pan, M.; Huang, J.,** 2009. Synthesis and Characterization of Star Graft Copolymers with Asymmetric Mixed ‘‘V-Shaped’’ Side Chains via ‘‘Click’’ Chemistry on a Hyperbranched Polyglycerol Core, J *Polym Sci Part A: Polym Chem*, **47**, 1308-1316.

[28] **Dag, A.; Durmaz, H.; Sirkecioglu, O.; Hizal, G.; Tunca, U.,** 2009. Three-Arm Star Ring Opening Metathesis Polymers via Alkyne-Azide Click Reaction, *J Polym Sci Part A: Polym Chem*, **47**, 2344-2351.

[29] **Shi, G.-Y.; Pan, C.-Y.,** 2009. An Efficient Synthetic Route to Well-Defined Theta-Shaped Copolymers, *J Polym Sci Part A: Polym Chem*, **47**, 2620-2630.

[30] **Zhang, Y.; Li, C.; Liu, S.,** 2009. One-Pot Synthesis of ABC Miktoarm Star Terpolymers by Coupling ATRP, ROP, and Click Chemistry Techniques, *J Polym Sci Part A: Polym Chem*, **47**, 3066-3077.

[31] **Matyjaszewski, K., and Davis, T., (eds.),** 2002. Handbook of Radical Polymerization, John Wiley & Sons, New Jersey.

[32] **Nielsen, L. E.** 1974. Mechanical Properties of Polymers and Composites, **chapter 5** Marcel Dekker: New York**.**

[33] **Szwarc, M.,** 1956. Block copolymers*, Nature,* **178,** 1168.

[34] **Quirk, R. and Lee, B.,** 1992. Terminology and classification of quasiliving polymerizations and ideal living polymerizations on the basis of the logic of elementary polymerization reactions, and comments on using the term controlled, *Polym. Int.,* **27,** 359.

[35] **Matyjaszewski, K. and Lin, C.H.,** 1991. Naming of controlled, living polymerizations, *Makromol. Chem. Macromol. Symp.,* **47,** 221.

[36] **Litvinienko, G. and Müler, A. H. E.,** 1997. General kinetic analysis and comparison of molecular weight distributions for various mechanisms of activity exchange in living polymerizations**,** *Macromolecules,* **30,** 1253.

[37] **Matyjaszewski, K. and Müller**, **A. H. E.,** 1997. AHE naming of controlled, living, and "living" polymerizations, *Polym. Prepr.* **38(1**), 6.

[38] **Wang, J. S.; Matyjaszewski, K.,** 1995. Controlled/"living"radical polymerization. Atom transfer radical polymerization in the presence of transition metal complexes, *J. Am. Chem. Soc.,* **117**, 5614.

[39] **Matyjaszewski, K. and P. Sigwalt**, 1994. Unified approach to living and non-living cationic polymerization of alkenes, *Polym. Int.* **35,** 1.

[40] **Reeves, Ben.** 2001. Recent advances in living free radical polymerization, *University of Florida.*

[41] **Hawker**, 1994. Molecular weight control by a "living" free-radical polymerization process*, C. J. J Am Chem Soc*, **116**, 11185.

[42] **Odian,** 1991. G. Principles of polymerization, p 8, *John Wiley & Sons Inc*.

[43] **Fischer,** 1999. The persistent radical effect in controlled radical polymerizations*, H. J Polym Sci Part A: Polym Chem*, **37**, 1885.

[44] **Solomon, D. H., Rizzardo, E., Cacioli,** 1985. *P. US Patent* 4, **581**, 429.

[45] **Marque,** 2003. Influence of the nitroxide structure on the homolysis rate constant of alkoxyamines: A taft-ıngold analysis, *S. J Org Chem*, **68**, 7582.

[46] **Hawker, C. J.; Bosman**, **A. W., Harth, E.** 2001**.** New polymer synthesis by nitroxide mediated living radical polymerizations*, Chem Rev*, **101**, 3661.

[47] **Benoit, D., Grimaldi, S., Robin, S., Finet, J. P., Tordo, P., Gnanou, Y.,** 2000. Kinetics and mechanism of controlled free-radical polymerization of styrene and *n*-butyl acrylate in the presence of an acyclic -phosphonylated nitroxide, *J. Am. Chem. Soc.*, **122**, 5929.

[48] **Harth, E., Hawker, C. J., Fan, W., Waymouth,** 2001. Chain end functionalization in nitroxide-mediated "living" free radical Polymerizations, *R.M. Macromolecules,* **34**, 3856.

[49] **Grimaud, T.; Matyjaszewski, K.,** 1997. Controlled/'Living' radical polymerization of methyl methacrylate by atom transfer radical polymerization, *Macromolecules*, **30**, 2216.

[50] **Matyjaszewski, K. and Spanswick**, **J.** 2004. Controlled/Living radical polymerization, Handbook of Polymer Synthesis, pp. 895-942, H.Kricheldorf, O. Nuyken, G. Swift, Editors. Dekker, New York,

[51] **Fisher, H.,** 1999. The persistent radical effect in controlled radical polymerizations*, J. Polym. Sci.; Part A: Polym. Chem*, **37**, 1885.

[52] **Matyjaszewski**, **K.,** 2000. Environmental aspects of controlled radical polymerization, *Macromol. Symp.*, **152**, 29-42.

[53] **a) Haddleton, D. M., Topping, C., Hastings, J. J., Suddaby, K. G.,** 1996. Cobalt(II) in catalytic chain transfer polymerization (CCTP), *Macromolecules*, **29**, 481. **b) Chong, Y. K., Le, T. P. T., Moad, G., Rizzardo, E.,** 1999. A more versatile route to block copolymers and other polymers of complex architecture by living radical polymerization: The RAFT process, *S. Macromolecules*, **32**, 2071.

[54] **Long, V. C., Berry, G. C., Hobbs, L. M.,** 1964. Solution and Bulk Properties of Branched Polyvinyl acetates IV—Melt viscosity, *Polymer,* **5**, 517-524.

[55] **Roovers, J. E. L.,** 1985. "Branched polymers." *Encyclopedia of Polymer Science and Engineering*; pp 478 Wiley: New York.

[56] **Hadjichristidis, N., 1999.** Synthesis of miktoarm star (**μ-**star) polymers, *J Polym Sci Part A: Polym Chem***, 37,** 857.

[57] **Zhang, X., Xia, J. and Matyjaszewski, K.,** 2000. End-Functional Poly(*tert*-butyl acrylate) Star Polymers by Controlled Radical Polymerization, *Macromolecules,* **33**, 2340-2345.

[58] **Meneghetti, S. P., P. J. Lutz and D. Rein,** 1999. Star and Hyperbranched Polymers; pp 27 Marcel Dekker: New York.

[59] **Ishizu, K. and K. Sunahara,** 1995. Synthesis of star polymers by organized polymerization of macromonomers, *Polymer,* **36**, 4155.

[60] **Feldthusen, J., B. Ivan and A. H. E. Muller,** 1999. Synthesis of Linear and Star-Shaped Block Copolymers of Isobutylene and Methacrylates by Combination of Living Cationic and Anionic Polymerizations, *Macromolecules,* **31**, 578.

[61] **Iatrou, H., and Hadjichristidis N.,** 1992. Synthesis of a Model 3-Miktoarm Star Terpolymer, *Macromolecules,* **25 (18),** 4649–4651.

[62] **Ludwigs, S., Böker, A., Abetzb, V., Müller, H. E. A., Krauscha, G.,** 2003. Phase behavior of linear polystyrene-block-poly(2-vinylpyridine)-block-poly(tert-butyl methacrylate) triblock terpolymers, *Polymer,* **44**, 6815-6823.

[63] **Triftaridou, A. I., Vamvakaki, M., Patrickios, C. S.,** 2002. Amphiphilic diblock and ABC triblock methacrylate copolymers: synthesis and aqueous solution characterization, *Polymer,* **43**, 2921-2926.

[64] **Hadjichristidis, N., Iatrou, H., Pitsikalis, M., Pispas, S., Avgeropoulos, A.,** 2005. Linear and non-linear triblock terpolymers. Synthesis, self assembly in selective solvents and in bulk, *Progress in Polymer Science,* **30,** 725-782.

[65] **Triftaridou, A. I., Vamvakaki, M., Patrickios, C. S., Stavrouli, N., Tsitsilianis, C.,** 2005. Synthesis of amphiphilic $(ABC)_n$ multiarm star triblock terpolymers, *Macromolecules,* **38**, 1021-1024.

[66] **Davis, K. A., Matyjaszewski, K.,** 2001. ABC triblock copolymers prepared using Atom Transfer Radical Polymerization Techniques, *Macromolecules,* **34**, 2101-2107.

[67] **Boztug, A., Basan, S.,** 2006. The modification and characterization of maleic anhydride-styrene-methyl metacrylate terpolymer by poly(ethyleneadipate), *Journal of Molecular Structure.*

[68] **Bock, V. D., Hiemstra, H., van Maarseveen, J. H.,** 2006. Cu^{I}-Catalyzed Alkyne–Azide "Click" Cycloadditions from a Mechanistic and Synthetic Perspective, *Eur. J. Org. Chem*, 51–68.

[69] **Ladmiral, V., Mantovani, G., Clarkson, G. J., Cauet, S., Irwin, J. L., Haddleton, D. M.,** 2005. Synthesis of Neoglycopolymers by a Combination of "Click Chemistry" and Living Radical Polymerization, *J. Am. Chem. Soc.,* **128**, 4823-4830.

[70] **Kolb, H. C., Sharpless, K. B.,** 2003. The growing impact of click chemistry on drug discovery, *DDT*, **8**, 1128-1137.

[71] **Gacal, B., Durmaz, H., Tasdelen, M.A., Hizal, G., Tunca, U., Yagci, Y., Demirel, A.L.,** 2006. Anthracene-Maleimide-Based Diels-Alder "Click Chemistry" as a Novel Route to Graft Copolymers, *Macromolecoles,* **39**, 5330-5336.

[72] **Liu, Q., Chen, Y.,** 2006. Synthesis of Well-Defined Macromonomers by the Combination of Atom Transfer Radical Polymerization and a Click Reaction, *Journal of Polymer Science: Part A: Polymer Chemistry,* **44,** 6103-6113.

[73] **Lutz, J-F., Börner, H. G., Weichenhan1, K.,** 2005. Combining Atom Transfer Radical Polymerization and Click Chemistry: AVersatile Method for the Preparation of End-Functional Polymers, *Macromol. Rapid Commun.,* **26**, 514–518.

[74] **Kamijo, S., Jinb, T., Yamamotoa, Y.,** 2004. Four-component coupling reactions of silylacetylenes, allyl carbonates, and trimethylsilyl azide catalyzed by a Pd(0)–Cu(I) bimetallic catalyst. Fully substituted triazole synthesis from seemingly internal alkynes, *Tetrahedron Letters*, **45**, 689–691.

[75] **Hotha, S., Anegundi, R.I., Natu, A.A.,** 2005. Expedient synthesis of 1,2,3 triazole-fused tetracyclic compounds by intramolecular Huisgen ('click') reactions on carbohydrate-derived azido-alkynes, *Tetrahedron Letters,* **46**, 4585–4588.

[76] **Rostovtsev, V. V., Green, L. G., Fokin, V. V., Sharpless**, **K. B.,** 2002. A Stepwise Huisgen Cycloaddition Process: Copper(I)-Catalyzed Regioselective "Ligation" of Azides and Terminal Alkynes, *Angew. Chem.,* **41,** 2596-2599.

[77] **Johnson, J. A., Lewis, D. R., Diaz, D. D., Finn, M. G., Koberstein, N. J., Turro, J. T.,** 2006. Synthesis of Degradable Model Networks via ATRP and Click Chemistry, *J. Am. Chem. Soc*., **128**, 6564-6565.

[78] **Tsarevsky, N. V., Sumerlin, B. S., Matyjaszewski, K.,** 2005. Step-Growth "Click" Coupling of Telechelic Polymers Prepared by Atom Transfer Radical Polymerization, *Macromolecules,* **38,** 3558-3561.

[79] **Coessens, V., Nakagawa, Y., Matyjaszewski, K.,** 1998. Synthesis of azido end-functionalized polyacrylates via atom transfer radical polymerization, *Polymer Bulletin,* **40**, 135–142.

[80] **Molteni, G., Buttero, P. D.,** 2005. 1,3-Dipolar cycloadditions of MeOPEG-bounded azides, *Tetrahedron*, **61**, 4983–4987.

[81] **Zhang, W., Fang, B., Walther, A., Muller., H. E.,** 2009. Synthesis via RAFT Polymerization of Tadpole-Shaped Organic/ Inorganic Hybrid Poly(acrylic acid) Containing Polyhedral Oligomeric Silsesquioxane

(POSS) and Their Self-assembly in Water, *Macromolecules,* **42,** 2563-2569.

[82] **Altintas, O., Yankul, B., Hizal, G., Tunca U.,** 2006. A_3-Type Star Polymers via Click Chemistry, *J Polym Sci Part A: Polym Chem*, **44**, 6458–6465.

[83] **Dag, A.; Durmaz, H.; Demir, E.; Hizal, G.; Tunca, U.,** 2008. Preparation of 3-Arm Star Polymers (A3) Via Diels–Alder Click Reaction, *J Polym Sci Part A: Polym Chem*, **46**, 302-313.

[84] **Liu, L.; Tian, M.; Zhang, W.; Zhang, L.; Mark, J. E.;** 2007. Crystallization and morphology study of polyhedral oligomeric silsesquioxane (POSS)/ polysiloxane elastomer composites prepared by melt blending, *Polymer*, **48**, 3201-3212.

CURRICULUM VITA

Candidate's full name: Çiğdem BİLİR

Place and date of birth: İstanbul/Uskudar, 21.05.1985

Permanent Address: Firin Road Altintas Street Eksioglu Apt. No:2/9 34750, K.Bakkalkoy/Atasehir/İSTANBUL

Universities and Colleges attended:

Suadiye Hacı Mustafa Tarman High School 1999-2003

İstanbul Technical University – Faculty of Science and Letters – Chemistry 2003-2008

İstanbul Technical University – Institue of Science And Technology – Polymer Science & Technology Master Programme 2008-2010

Publication:

Gungor, E.; **Bilir, C.;** Durmaz, H.; Hizal, G.; Tunca, U.; 2009. Star Polymers with POSS via Azide-Alkyne Click Reaction, *J Polym Sci Part A: Polym Chem*, 47, 5947-5953.