İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF MULTI MIKTOARM STAR BLOCK COPOLYMER THROUGH DOUBLE CLICK REACTIONS

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Programme : Polymer Science & Technology

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ÇOK VE FARKLI KOLLU YILDIZ BLOK KOPOLİMERLERİN ÇİFT CLICK REAKSİYONLARI İLE SENTEZİ

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ABBREVIATIONS

ATRP	**:** Atom Transfer Radical Polymerization
NMP	**:** Nitroxide Mediated Polymerization
RAFT	**:** Reversible Addition-Fragmentation Chain Transfer Polymerization
DVB	**:** Divinyl Benzene
CRP	**:** Controlled/Living Radical Polymerization
St	**:** Styrene
MMA	**:** Methyl methacrylate
***t*BA**	**:** *tert*-butylacrylate
PS	**:** Polystyrene
PMMA	**:** Poly(methyl metacrylate)
P*t*BA	**:** Poly(*tert*-butyl acrylate)
R_m and R_n	**:** Propagating Radical
P_n and P_m	**:** Terminated Macromolecules
LFRP	**:** Living Free Radical Polymerization
CTA	**:** Chain Transfer Agent
TEMPO	**:** 2, 2', 6, 6'- Tetramethylpiperidinyloxy
PDI	**:** Polydispersity Index
PRE	**:** Persistent Radical Effect
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
FTIR	**:** Fourier Transform Infrared
GPC	**:** Gel Permeation Chromotography
NMR	**:** Nuclear Magnetic Resonance Spectroscopy
UV-Vis.	**:** Ultra Violet-Visible Spectroscopy

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SYNTHESIS OF MULTI MIKTOARM STAR BLOCK COPOLYMER THROUGH DOUBLE CLICK REACTIONS

SUMMARY

Star polymers have attracted much attention in research over the years due to their unique-three dimensional shape and highly branched structure. There are two general strategies used to produce star polymers: the arm-first and core-first techniques. In the arm-first strategy, a polymer with a proper end-group functionality is reacted with an appropriate multifunctional core to give a star polymer. In the second strategy (core-first), the polymer chain is simultaneously grown from a multifunctional initiator. Previously, living ionic polymerization was the only system for the preparation of star polymers with controlled structures. However, in recent years, the use of controlled/living radical polymerization techniques in the synthesis of complex macromolecules (star and dendrimeric polymers) has quickly increased because of the variety of applicable monomers and greater tolerance to experimental conditions in comparison with living ionic polymerization routes.

The 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 polymers with complex architectures. 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.

Nitroxide mediated radical polymerization based on the use of stable nitroxide free radicals and Mtn(Metat)/ligand catalyst- mediated living radical polymerization, which is often called atom transfer radical polymerization (ATRP), are versatile methods among living radical polymerizations. Recently, Sharpless and coworkers used Cu(I) as a catalyst in conjunction with a base in Huisgen’s 1,3-dipolar cycloadditions ([3 + 2] systems) between azides and alkynes or nitriles and termed them click reactions. Later, click chemistry strategy was successfully applied to macromolecular chemistry, affording polymeric materials varying from block copolymers to complex macromolecular structures. Click reactions permit C–C (or C–N) bond formation in a quantitative yield without side reactions or requirements for additional purification steps.

In this study, first of all, by using two types of different initiator at the same flask well defined anthracene and trimethyl silyl end functionalized polystyrene arms were

synthesized. After producing star from these arms, the arms of the resulted multi arm star polymer bear 47% three methyl silyl and the rest of the 53% anthracene end fucntinality. Secondly, multi arm star polymer was hydrolized and by this, alkyne functionality was gained to the arms of the multi arm star polymer. Then, Click reaction was applied between well defined azide end functionalized poly(*tert*-butyl acrylate) (P*t*BA-N_3) and hydrolized multi arm star polymer. Latter step is follwed by a 'Diels-Alder' click reaction between obtained $(PtBA)_m$-$(PS)_n$-polyDVB multi miktoarm star block copolymer and a well defined maleimide functionalized poly(methyl metacrylate) (Maleimide-PMMA-Br). As a consequence $(PMMA)_k$-$(PtBA)_m$-$(PS)_n$-polyDVB multi miktoarm star block copolymer is obtained via double click raections. The resulted products were characterized by Gel Permeation Chromatography (GPC), Nuclear Magnetic Resonance (NMR) and Ultra Violet-Visible (UV-Vis.).

ÇOK VE FARKLI KOLLU YILDIZ BLOK KOPOLİMERLERİN ÇİFT CLICK REAKSİYONLARI İLE SENTEZİ

ÖZET

Yıldız polimerler araştırmalarda üç boyutlu ve çok dallanmış yapılarından dolayı yıllardır ilgi çekmektedirler. Yıldız polimerlerin elde edilmesinde kullanılan iki genel yöntem vardır: kol öncelikli ve çekirdek öncelikli yöntemleri. Kol öncelikli yönteminde, uygun uç grup fonksiyonalitesine sahip polimer ona uygun çok fonksiyonlu bir çekirdekle yıldız polimer elde etmek için reaksiyona sokulur. İkinci yöntemde (çekirdek öncelikli) ise, polimer zinciri çok fonksiyonlu bir başlatıcıdan eşzamanlı bir şekilde büyümektedir. Önceleri yaşayan iyonik polimerizasyon, yıldız polimer hazırlanmasında kullanılan tek sistemdi. Fakat son yıllarda kompleks makromoleküllerin sentezinde kontrollü/yaşayan polimerizasyon tekniklerinin kullanılması, yaşayan iyonik polimerizasyon yöntemiyle mukayese edildiğinde deneysel koşullara çok daha toleranslı olması ve çok çeşitli monomerlere uygulanabilir olması nedeniyle hızlı bir şekilde arttı.

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) 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.

Kararlı nitroksit serbest radikallerin kullanımına dayanan Nitroksit Ortamlı Radikal Polimerizasyonu ve genellikle Atom Transfer Radical Polimerizasyonu (ATRP) olarak bilinen Mtn(Metat)/ligand kataliz ortamlı radikal polimerizasyonu yaşayan radikal polimerizasyon yöntemleri arasında çok yönlü metotlardır. Son yıllarda, Sharpless ve arkadaşları azidler ve alkin/nitriller arasındaki Huisgen 1,3-dipolar siklokatılmalarda ([3 + 2] sistemi) Cu(I)'i baz ile birleştirip kataliz olarak kullandılar ve bu reaksiyonu click reaksiyonu olarak adlandırdılar. Daha sonra click kimyası blok kopolimerlerden karmaşık makromoleküler yapılara kadar değişen birçok polimerik malzemenin 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, ilk olarak, aynı balonda iki farklı başlatıcı kullanılarak antrasen ve üç metil silil uç fonsiyonelitesine sahip polistiren kollar sentezlendi. Bu kollardan

yıldız polimer elde edildikten sonra, sonuç ürün olan çok kollu yıldız polimerin kollarının 53%'ü üç metil silil ve kalan 47%'si antrasen uç fonksiyonelitesini taşır. Sonra, iyi tanımlanmış azid uç fonksiyonlu poli(*tersiyer*-butil akrilat) (P*t*BA-N_3) ile hidrolize edilmiş çok kollu yıldız polimer arasında 'Click Reaksiyonu' uygulandı. Sonraki basamak elde edilen çok ve farklı kollu yıldız blok kopolimer $(PtBA)_m$-$(PS)_n$-polyDVB ile iyi tanımlanmış antrasen uç fonksiyonelitesi taşıyan poli(metil metakrilat)'ın (Maleimid-PMMA-Br) 'Diels-Alder' click reaksiyonu ile takip edildi. Sonuç olarak $(PMMA)_k$-$(PtBA)_m$-$(PS)_n$-polyDVB çok ve farklı kollu yıldız blok kopolimeri çift click reaksiyonları ile sentezlendi. Sonuçlanan ürünler ise Jel Geçirgenlik Kromatografisi (GPC), Nükleer Magnetik Rezonans Spektroskopisi (NMR) ve Ultra Viole Görünür Bölge Spektroskopisi (UV-Vis.) cihazları ile karakterize edildi.

1. INTRODUCTION

A star structure is defined as a nonlinear polymer that consists of multiple backbone chains existing from junction points [1]. Star polymers show different crystalline, mechanical, and viscoelastic properties in comparison with their corresponding linear analogues.

Interest in star polymers arises from their compact structure and globular shape, which predetermines their low viscosity when compared to linear analogues and makes them suitable materials for several applications. Synthesis of star polymers, which began in the 1950s with living anionic polymerization, has recently received increased attention due to the development of controlled/living radical polymerization (CRP) [2,3]. Typically, star polymers are synthesized via CRP by one of two strategies: core-first and arm-first. The arm-first strategy can be further subcategorized according to the procedure employed for star formation. One method is chain extension of a linear arm precursor with a multivinyl crosslinking agent, and the other is coupling linear polymer chains with a multifunctional linking agent or "grafting-onto" a multifunctional core. Although both methods were successfully used for star synthesis in anionic polymerization, to date only the former procedure, using a multivinyl cross-linking agent, has been applied in CRP for synthesis of star polymers containing multiple arms and/or functionalities [4,5].

Much of the academic and industrial research on living polymerization has focused on anionic, cationic, coordination, and ring-opening polymerizations. The development of controlled/living radical polymerization (CRP) methods has been a long-standing goal in polymer chemistry, as a radical process is more tolerant of functional groups and impurities and is the leading industrial method to produce polymers [6].

Atom transfer radical polymerization (ATRP) is a particularly attractive CRP process for synthesis of chain-end functionalized polymers [7,8]. The polymers produced by ATRP preserve terminal halogen atom(s) that can be successfully converted into

various desired functional chain-end groups through appropriate transformations, especially nucleophilic substitutions. The modified chain-end group, such as a hydroxyl group or an amino group, cannot react with itself but can react with an appropriate functional group on the multifunctional coupling agent, such as a carboxylic acid group by esterification, to form a star polymer. However, a commonly encountered drawback, when using such a method, is a low yield of star products due to the slow and inefficient reactions between the modified polymer chain ends and multifunctional linking agents. In other words, highly efficient site-specific organic reactions are required in order for star synthesis to be highly successful [5].

In the past few years, “click reactions”, as termed by Sharpless et al., have gained a great deal of attention due to their high specificity, quantitative yields, and near-perfect fidelity in the presence of most functional groups. The most popular click chemistry reaction is the copper-catalyzed Huisgen dipolar cycloaddition reaction between an azide and an alkyne leading to 1,2,3-triazole [9-12].

The Diels-Alder reaction is an organic chemical reaction (specifically, a cycloaddition) between a conjugated diene and a substituted alkene, commonly termed the dienophile, to form a substituted cyclohexene system [13, 14].

The reaction can proceed even if some of the atoms in the newly-formed ring are not carbon. Some of the Diels-Alder reactions are reversible; the decomposition reaction of the cyclic system is then called the Retro-Diels-Alder. For example, Retro-Diels-Alder compounds are commonly observed when a Diels Alder product is analyzed via mass spectrometry [14].

Otto Paul Hermann Diels and Kurt Alder first documented the novel reaction in 1928 for which they were awarded the Nobel Prize in Chemistry in 1950 for their work on the eponymous reaction [16]. The Diels-Alder reaction is generally considered the "Mona Lisa" of reactions in organic chemistry since it requires very little energy to create the very useful cyclohexene ring [15-18].

In this thesis, we prepared miktoarm star polymer by the combination of ATRP, Click and Diels-Alder click reactions based on the arm-first method. For this purpose polystyrene is synthesized from the initiators **1** and **2** at the same flask by one pot. Star polymer, with an alkyne and anthracene functionality at the periphery, was

obtained by the reaction of **6** and DVB as a cross-linker. This is followed by the hydrolisation of the star to give the polymer, **7**. Then "Click" reaction strategy is followed between **7** and well defined azide-end-functionalized poly(*tert*-butyl acrylate), **9**. The resulted polymer, **10**, is reacted with well defined, maleimide-end-functionalized poly(methyl methacrylate), **11**, (PMMA-Maleimide) via Diels-Alder Click reaction and our final multi miktoarm star block copolymer, **12**, is produced. The efficiency of the Click reaction has been investigated by gel permeation chromatography measurements (refractive-index detector). On the other hand, the efficiency of the Diels-Alder Click reaction has been investigated by gel permeation chromatography measurements (refractive-index detector) and UV measurements.

2. THEORETICAL

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 [19]. 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 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 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.

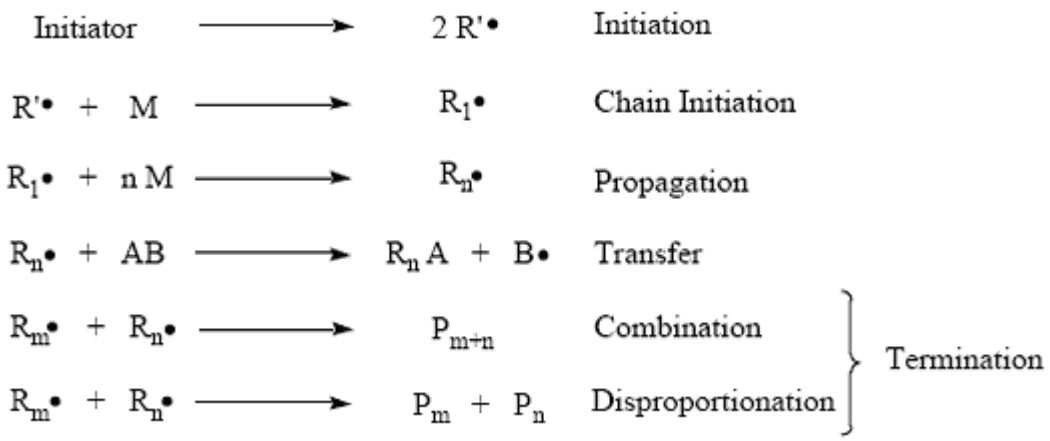

Figure 2.1 : General free radical polymerization mechanism.

2.2. 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 [20]. 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 [21] 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 [22-24]. It has been suggested to use a term controlled polymerization if these additional criteria are met [25]. 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 [26,27].

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 a living radical processes is inherently a much more challenging task. The living process of radical polymerization involves the equilibration of growing free radicals and various types of dormant species. By tying up a great deal of the reactive centers as dormant species, the concentration of free radicals decreases substantially and therefore suppresses the transfer and termination steps. These reactions are also denoted as controlled /living polymerizations rather than as true living polymerizations because transfer and termination are decreased but not eliminated. Three processes, NMP, ATRP, and RAFT, will now be introduced [28].

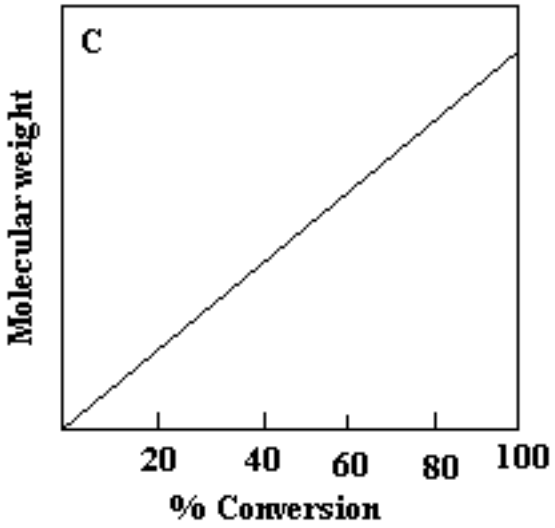

Figure 2.2 : Molecular weight vs. conversion graph of a typical living polymerization.

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) [28].

2.3.1. Nitroxide-mediated living free radical polymerization

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 [29]. 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 [30].

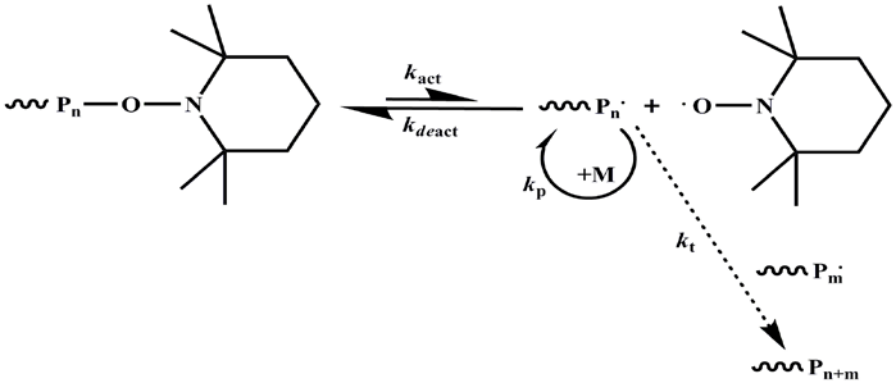

Figure 2.3 : Mechanism for nitroxide-mediated living free radical polymerization.

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) [31]. 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 [32]. 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 [33]. 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 [34].

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 ineffective. 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 [35].

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 precursor to reform the olefin by elimination of the hydroxylamine [36].

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 [37]. A general mechanism for ATRP is given below.

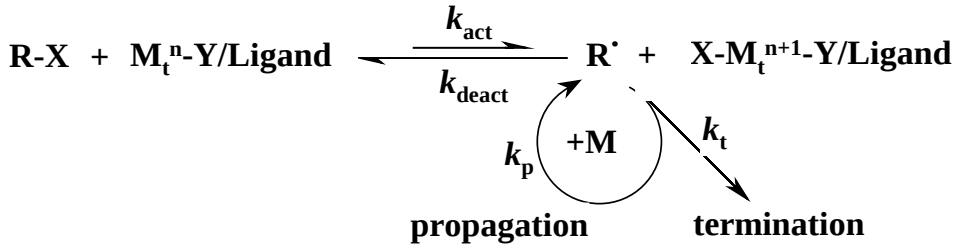

Figure 2.4 : General mechanism for ATRP.

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 [38].

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 uneffected 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 [38]. 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 [39]. 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, $M_w / M_n < 1{,}3$ [40]. The ATRP system is consisting of the monomer, initiator, and catalyst composed of transition metal species with any suitable ligand.

ATRP has been successfully used in living polymerizations of a wide range of monomers, such as styrenic monomers, acrylates, methacrylates, (meth)acryl amides, acrylonitrile and vinyl chloride in bulk, solution using organics or water as solvents, and emulsion, supercritical carbon dioxide, producing polymers with well-controlled molecular weights and structures. For example, polystyrene with polydispersity as narrow as those of PS standards synthesized by living anionic polymerization was obtained by copper-catalyzed ATRP [41]. The amount of the initiator in the ATRP determines the final molecular weight of the polymer at full monomer conversion. Multifunctional initiators may provide chain growth in several directions. The main

role of the initiator is to determine the number of growing polymer chains. If initiation is fast and transfer and termination negligible, then the number of growing chains is constant and equal to the initial initiator concentration. The theoretical molecular weight or degree of polymerization (DP) increases reciprocally with the initial concentration of initiator in a living polymerization (Scheme 2.1).

$$DP = [M]_0 / [I]_0 \times \text{Conversion} \quad \textbf{(2.1)}$$

In ATRP, alkyl halides (RX) are typically used as the initiator and the rate of the polymerization is first order with respect to the concentration of RX. To obtain well-defined polymers with narrow molecular weight distributions, the halide group X, must rapidly and selectively migrate between the growing chain and the transition-metal complex.

Initiation should be fast and quantitative with a good initiator. In general halogenated alkanes, benzylic halides, α-halo esters, α-halo ketones, α-halo nitriles and sulfonyl halides are used as ATRP initiators [42].

The most frequently used initiator types used in the atom transfer radical polymerization systems are, 1-Bromo-1-phenyl ethane (Styrene), 1-Chloro-1-phenyl ethane (Styrene), Ethyl-2-bromo propionate (Methyl methacrylate) and Ethyl-2-bromo isobutyrate (Methyl methacrylate). Two parameters are important for a successful ATRP initiating system; first, initiation should be fast in comparison with propagation. Second, the probability of side reactions should be minimized [42]. Transition metal catalysts are the key to ATRP since they determine the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. The main effect of the ligand is to solubilise the transition-metal salt in organic media and to regulate the proper reactivity and dynamic halogen exchange between the metal center and the dormant species or persistent radical. Ligands, typically amines or phosphines, are used to increase the solubility of the complex transition metal salts in the solution and to tune the reactivity of the metal towards halogen abstraction. Linear amines with ethylene linkage like tetramethylethylenediamine (TMEDA), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA), and 1,1,4,7,10,10 hexamethyltriethylenetetramine (HMTETA) were synthesized and examined for ATRP as ligands [43]. Reasons for examining of these type of ligands are, they are not expensive, due to the absence of the extensive π-

bonding in the simple amines, the subsequent copper complexes are less colored and since the coordination complexes between copper and simple amines tend to have lower redox potentials than the copper-by complex, the employment of simple amines as the ligand in ATRP may lead to faster polymerization rates.

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 strong.

The most important catalysts used in ATRP are; Cu(I)Cl, Cu(I)Br, $NiBr_2(PPh_3)_2$, $FeCl_2(PPh_3)_2$, $RuCl_2(PPh_3)_3$/ $Al(OR)_3$.

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 [44].

2.3.3. Reversible-addition fragmentation chain transfer

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 [45].

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 [28].

2.4. 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 [46]. “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 [47]. 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 [48].

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 [48].

Huisgen's 1,3-dipolar cycloaddition of alkynes and azides yielding triazoles is, undoubtedly, the premier example of a click reaction [48]. 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 [49].

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 [46]. 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 [50]. 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 [51].

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 [52]. 1,2,3-triazole formation is a highly efficient reaction without any significant side products and is currently referred to as a click reaction [53].

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 [54].

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) [48].

One of the most popular reactions within the click chemistry philosophy is the azide alkyne Huisgen cycloaddition using a Cu catalyst at room temperature discovered concurrently and independently by the groups of K. Barry Sharpless and Morten Meldal. This was an improvement over the same reaction first popularized by Rolf Huisgen in the 1970s, albeit at elevated temperatures in the absence of water and without a Cu catalyst (it is explained fully in 1,3-Dipolar Cycloaddition Chemistry, published by Wiley and updated in 2002). Copper and Ruthenium are the commonly used catalysts in the reaction. The use of Copper as a catalyst results in the formation of 1,4- regioisomer whereas Ruthenium results in formation of the 1,5- regioisomer.

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.

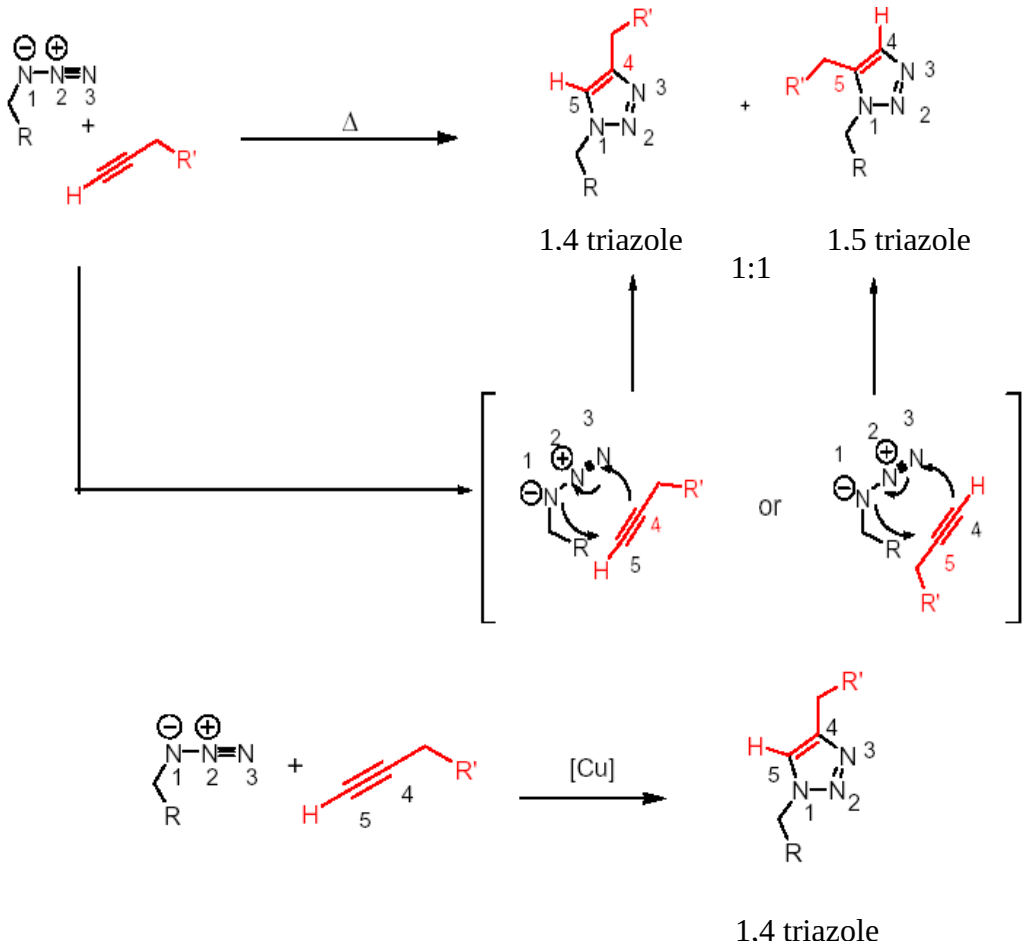

Figure 2.5 : Regioselectivity mechanism of triazole forming cycloaddition.

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 [54]. 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 [46].

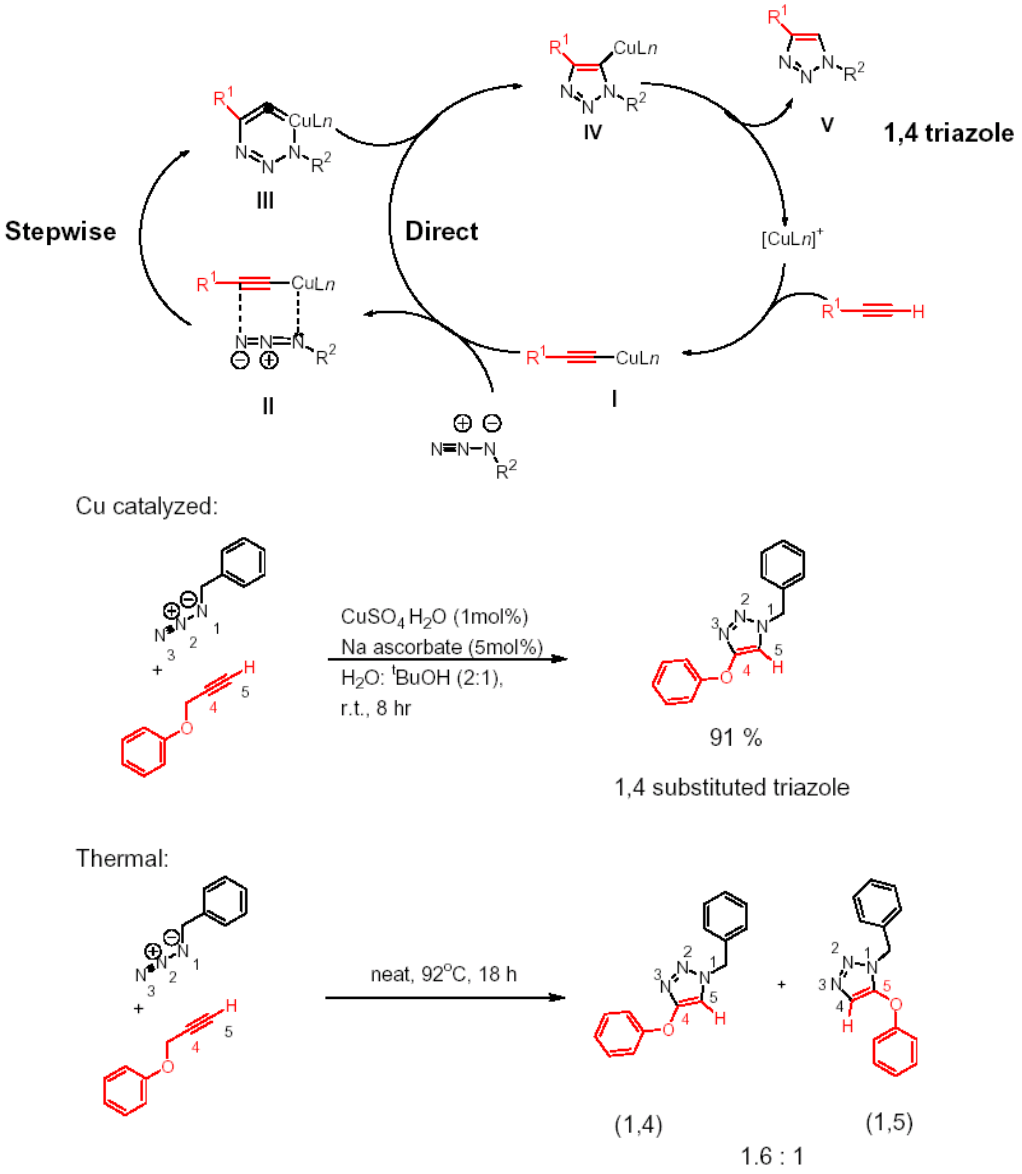

Figure 2.6 : Proposed catalytic cycle for the Cu(I)-catalyzed ligation. The process exhibits broad scope and provides 1,4-disubstituted 1,2,3-triazole products in excellent yields and near perfect regioselectivity [54].

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 [55].

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 [56].

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 [57]. The functionalized polymers can find many applications, for example as macromonomers, telechelics or other specialty polymers [58]. 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 [59].

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 [47].

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 [58].

2.5. Diels-Alder Reactions

The Diels-Alder reaction has both enabled and shaped the art and science of total synthesis over the last few decades to an extent which, arguably, has yet to be eclipsed by any other transformation in the current synthetic repertoire. With myriad applications of this magnificent pericyclic reaction, often as a crucial element in elegant and programmed cascade sequences facilitating complex molecule construction, the Diels-Alder cycloaddition has afforded numerous and unparalleled solutions to a diverse range of synthetic puzzles provided by nature in the form of natural products [60].

The Diels-Alder reaction is a concerted [$4\pi+2\pi$] cycloaddition reaction of a conjugated diene and a dienophile. This reaction belongs to the larger class of pericyclic reactions, and provides several pathways towards the simultaneous construction of substituted cyclohexenes with a high degree of regioselectivity, diastereoselectivity and enantioselectivity. Since its discovery in 1928, the Diels-Alder reaction has been amongst the most important carbon-carbon bond forming reactions available [61].

The original version of the Diels-Alder reaction, Figure 2.7, joins together a wide variety of conjugated dienes and alkenes with electron withdrawing groups (the dienophiles), to produce a cyclohexene ring in which practically all six carbon atoms can be substituted as desired.

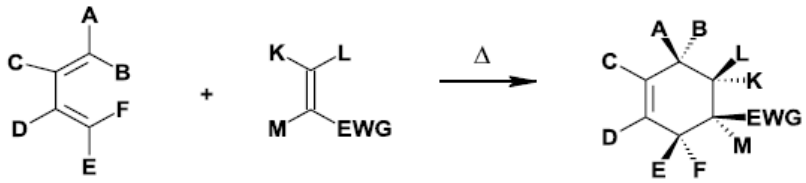

Figure 2.7 : The original version of the Diels-Alder reaction.

The reaction may be executed under relatively simple reaction conditions by heating together the two components, diene and dienophile, in non-polar solvents, followed by evaporation which leads usually to high yields of the product(s). The reaction is disciplined by the Woodward-Hoffmann rules [62] as a [$_{\pi}4_{s}+_{\pi}2_{s}$] cycloaddition occurring in a concerted but probably not symmetrically synchronous fashion, thus leading to highly predictable product structures in which two new carbon-carbon sigma bonds are formed in a stereospecific manner with the creation of up to four new stereogenic centres. The classical empirical rules have now found strong theoretical basis in the Woodward- Hoffmann rules, with regards to regiochemistry ("*ortho*" and "*para*" orientations) and stereochemistry (*endo* transition state kinetically favoured over the *exo* transition state in most of the reactions). The practising synthetic organic chemist will certainly be well aware of the kinds of dienes and dienophiles that may be combined successfully, and by way of simple frontier orbital theory be perfectly capable of predicting the major (or unique) product to be expected from the reaction. The reverse process of retrosynthetic analysis is also well established for transforming cyclohexene/cyclohexane containing structures into appropriate diene dienophile combinations.

The Diels-Alder reaction has now become an important research area for theoretical chemists, with regard to the finer details of the transition state and the energetics of the process, and with special concern for entropy and activation energies [60].

2.5.1. Mechanism of Diels–Alder reactions with anthracene

The mechanism of the thermal [4+2] cycloaddition reaction of anthracene with a dienophile has been the source of much conjecture. The stereochemistry of the reaction involves exclusive cis addition of the dienophile to anthracene where the cis or trans stereochemistry of the dienophile is retained in the product. The retention of stereochemistry has led many groups to postulate a concerted mechanism, where the new σ bonds are formed simultaneously either by direct addition, or via an intermediate charge–transfer complex or an electron donor–acceptor molecular

complex. Another possibility is a two-step reaction mechanism where the reaction proceeds via a zwitterionic or diradical intermediate. For a two-step mechanism to occur with retention of stereochemistry, the second step of the reaction would have to be much faster than the rotation about the C–C σ bond of the intermediate formed in the first step.

Many studies have noted the production of a transient colour that disappears as the thermal Diels–Alder reaction proceeds. This has been attributed to the formation of a charge–transfer complex during the course of the reaction and seems, therefore, to provide evidence for a concerted mechanism. Studies carried out with 1,4-dithiins 1 and anthracene 2 and its derivatives 3–5 (Figure 2.8) have shown that the formation of the Diels–Alder adducts 6 can in fact occur either via a charge–transfer complex or by direct addition, depending on the properties of the anthracene derivative used.

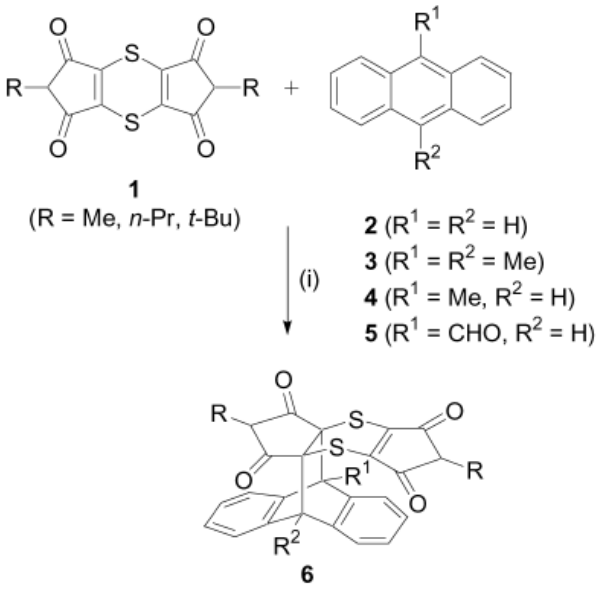

Figure 2.8 : Reagents and conditions: (i) C_6H_6, Δ.

The effect of solvent on the rate of reaction has been studied by many groups. The electron-donating ability of the solvent has been shown to be an important factor that affects the rate of reaction. Electron-donating solvents increase solvation of the dienophile that can in turn decrease the reaction rate. Solvents that are electron accepting can, in some cases, increase the rate of reaction by stabilization of the transition state, which can be regarded as being electron rich. Aromatic solvents produce large increases in reactivity with dienophiles that are capable of very strong charge–transfer interactions, while salt effects have been observed for reactions performed in water. However, in general, the influence of the solvent on the rate of

reaction, independent of the system investigated, has been shown to be relatively small, rarely above a factor of ten. This can be seen as evidence for a concerted mechanism as solvent effects would be expected to be large if a stepwise mechanism was in operation due to solvent stabilisation/ destabilisation of zwitterionic or diradical intermediates. However, the use of highly-fluorinated solvents has been shown to have a dramatic effect on the rate of the Diels–Alder reaction of 9-hydroxymethylanthracene and N-ethylmaleimide. Additionally, changes in the solvent can also have an effect on the endo/exo selectivity of the Diels–Alder reaction by a complex combination of solvent solvophobicity, dipolarity and hydrogen bond-donating effects The rate of the Diels–Alder reaction of anthracene appears to be governed much more by temperature and substituent effects. As the Diels–Alder reaction of anthracene is an equilibrium process, changes in temperature have a decisive effect on the position of the equilibrium. Lower reaction temperatures coupled with an excess of dienophile can increase the forward reaction rate, whereas higher temperatures can actually favour the retro Diels–Alder reaction [63].

2.6. Star Polymers

Polymer properties are influenced by their structure and topology. Therefore, the synthesis of complex macromolecular architectures to control polymer properties is an ongoing field of study in polymer science. Branching in polymers is a useful structural variable that can be used advantageously to modify polymer physical properties and the processing characteristics as a result of changing the melt, solution, and solid-state properties of polymers [64]. 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 affects the crystalline, mechanical, and viscoelastic properties of the polymer. A branched polymer structure was described as a nonlinear polymer comprised of molecules with more than one backbone chain radiating from branch points (junction points; atoms or small group from which more than two long chains emanate) [65]. *Star polymers* constitute the simplest form of branched macromolecules where all the chains as arm segments of one molecule are linked to a centre, which is called the core (Fig. 2.9).

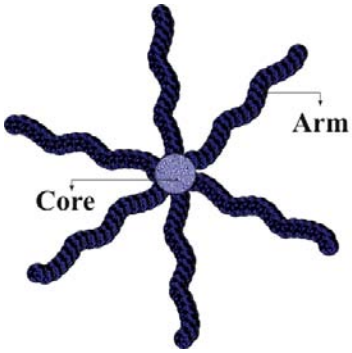

Figure 2.9 : Illustration of a symmetric (regular) star polymer.

The core of the star polymer can be composed of a multifunctional low molar mass compound [66-69], a dendrimer [70], a hyperbranched polymer [71, 72], an arborescent structure [73] and a crosslinked microgel [74, 75]. When the core is big enough, the stars obtained are called core-shell structures. They exhibit interesting properties, especially when the chemical differentiation between internal and external parts occurs. There are two general types of star polymers:

a) Symmetric or regular, star polymers, which have n branches of the same length and composition (A), each connected a single site (core), represented as A_n.

b) Asymmetric star polymers, which are a special class of stars that is characterized by an asymmetry factor compared to the classical symmetric stars, represented as A_nB_m. The following categories of asymmetric stars are defined in the literature [76-78].

-Stars with molecular weight asymmetry: The arms are chemically identical but differ in molecular weight.

-Stars with chemical asymmetry: The arms differ in chemical nature. The term *miktoarm stars* (coming the Greek word miktos means mixed) or heteroarm star polymers has been adopted for the stars with chemical asymmetry. Stars having similar chemical nature but different end groups also belong to this category (functional group asymmetry).

-Stars with topological asymmetry: The arms of the star are block copolymers that may have the same molecular weight and composition but differ with respect to the polymeric block that is covalently attached to the core of the star. The schematic representation of these structures is depicted in Figure 2.10.

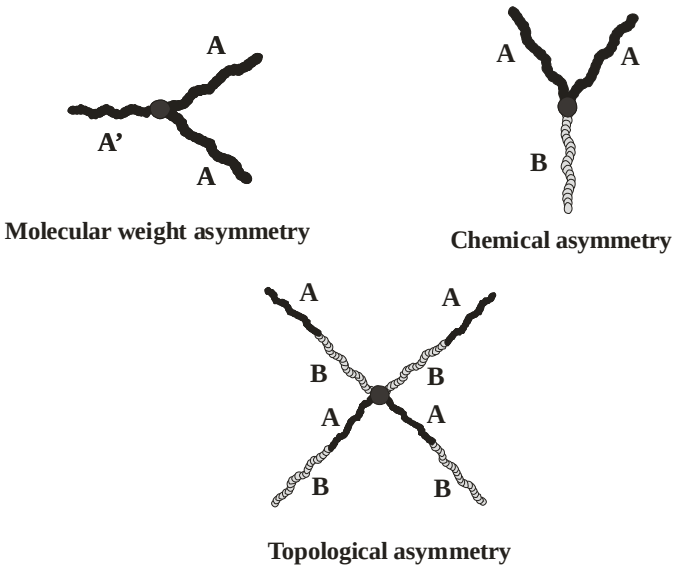

Figure 2.10 : The schematic representation of asymmetric star structures.

2.7. Preparation of Star Polymers

Star polymers consist of a central core, from which a given number of chains radiate attracted the attention of scientists so as to they constitute the simplest form of branching. The earliest attempt to prepare a model star polymer was that by Schaefgen and Flory [79]. They were able to synthesize four- and eight-armed polyamide stars by condensation polymerization of with either a tetrafunctional acid (cyclohexanone tetrapropionic acid) or an octafunctional acid (dicyclohexanone octapropionic acid) as multifunctional reactants.

Living polymerizations provide the most versatile synthetic routes for the preparation of a wide variety of well-defined polymer structure. The methodology of living polymerization is ideally suited for the preparation of star polymers since it is possible to vary and control important structural parameters such as molecular weight, molecular weight distribution, copolymer composition and microstructure, tacticity, chain end functionality and the number of branches per molecule. Because termination and chain transfer reactions are absent and the chain-ends may be stable for sufficient time periods, these polymerizations have the following useful synthetic attributes for star polymer synthesis:

I. One polymer is formed for each initiator molecule, so that the number average molecular weight of polymers or block segments can be predicted from the reaction

stoichiometry. Multifunctional initiators with functionality *n* can form stars with *n* arms.

II. If the rate of initiation is rapid or competitive with the rate of propagation, polymers (precursor arms) with narrow molecular weight distributions are formed [80].

III. When all of the monomer has been consumed, the product is a polymer with reactive chain ends that can be participate in a variety of post polymerization reactions:

a. block copolymerization by addition of a second monomer, and/or

b. end-linking with multifunctional linking agents to form the corresponding star polymers with uniform arm lengths.

Although a variety of mechanistic types of living chain reaction polymerization have been developed [81] such as cationic, group transfer, or living ring opening metathesis polymerization for the synthesis of star-shaped polymers, until recently anionic polymerization was one of the best methods to obtain well-defined star-shaped macromolecules of predetermined branch molar mass. However, in recent years there has been rapid growth in the area of growing controlled/“living” radical polymerizations (CRP), which have some advantages over anionic polymerization, in that they do not require rigorous experimental conditions and are applicable to a wide range of monomers. The detailed historical background regarding the basic concepts of CRP will be given in the following sections of this book. First, the general methods for the synthesis of star-shaped polymers will be described based on living anionic polymerization. There are three general synthetic methods for the preparation of star-shaped polymers. These methods have been based on two approaches: arm-first and core-first.

I. End linking with multifunctional linking agent (arm-first),

II. Use of multifunctional initiators (core-first),

III. Use of difunctional monomers (arm-first).

2.7.1. Synthesis of star block copolymers

Star-block copolymers are star polymers in which each arm is a diblock (or a triblock) copolymer (Fig. 2.11). They can be prepared by all the methods described earlier. The best way involves the linking reaction of a living diblock copolymer, prepared by sequential anionic polymerization of the two monomers, with a suitable linking agent. Using this method and chlorosilane linking agents, Fetters and collaborators synthesized star-block copolymers (polystyrene-*b*-polyisoprene)$_n$, where n=4, 8, 12, 18 [82, 83].

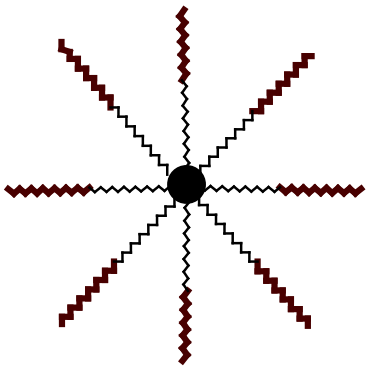

Figure 2.11 : Schematic representation of star-block structure.

2.8. 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 [84] 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. 2.12).

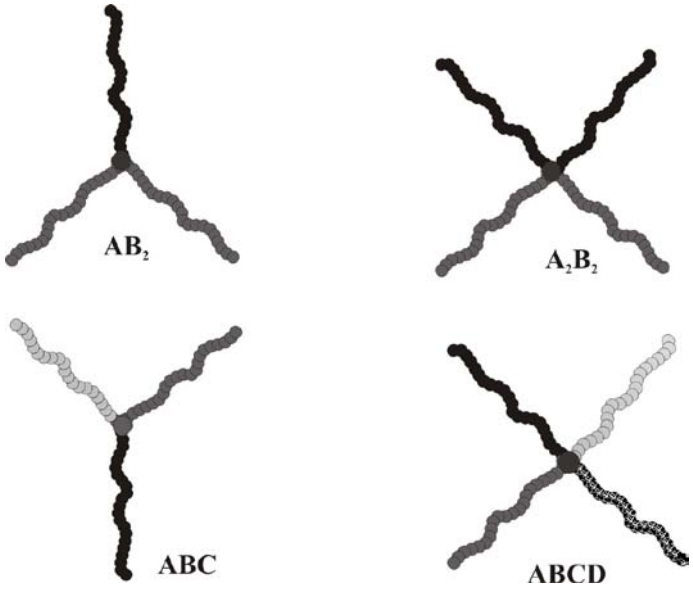

Figure 2.12 : Illustration of miktoarm star polymers structures where each letter represents different polymeric arms.

2.9. Synthesis of Miktoarm Star Polymers by Combination of Controlled Polymerization Methods

It was a major challenge to synthesize well-defined complex macromolecular architectures such as block and graft copolymers and star polymers via radical polymerizations until the discovery of controlled/"living" radical polymerization (CRP) techniques. Although these architectures have been prepared mainly by truly living systems (anionic, cationic), the radical polymerization method is more convenient because it does not require strict purification of monomers and solvents, and allows the presence of functional groups. The combination of various controlled polymerization techniques to produce novel polymer architectures is quite important because of the synthetic limitations of the pure living systems. CRP combines the advantages offered by truly living systems with the experimental easiness characterizing free radical processes.

The synthesis of miktoarm star polymers by controlled polymerization methods can be accomplished by those explained for the synthesis miktoarm star polymers by anionic polymerization. Although miktoarm star polymers have been synthesized mainly by the anionic polymerization [76-78, 81], the recent development in the CRP [85-89] has brought about a drastic change in the synthetic methodology for miktoarm star polymers for the last 5 years [89, 90]. They are essentially two approaches to synthesize star polymers by CRP methods: core-first and arm-first

method [85-89]. The core first method exploits simultaneous growth from the multifunctional initiators to give star polymers with constant arm number and constant arm length as in living ionic polymerization.

The arm-first approach involves the linking reaction of linear living polymers obtained by CRP with a divinyl compound. This gives a crosslinked gel core and a random distribution of the number of arms per polymer molecule [91-102]. The mechanism of divinyl compound method is shown in Figure 2.13. Firstly, a few units of divinyl reagents add to the reactive macroinitiators (arms) to form short block copolymers with hanging vinyl groups. Then, the reactive macroinitiator chain ends react with the hanging vinyl groups to form a microgel core or add to a sterically accessible star core. Finally, core–core coupling reaction can occur to form a higher-order star polymer. The star polymer thus obtained still carries a number of active sites within its microgel core, which is theoretically equal to the number of incorporated arms of the star polymer. These 'core' active sites can initiate the living polymerization of another monomer to grow new arms from the core, yielding a miktoarm star polymer with A_nB_n type. Using this method, miktoarm star polymers have been synthesized also by CRP methods [85-89]. In the following, the readers can find a historical background for the preparation of miktoarm star polymers based on controlled polymerization methods and combination of those.

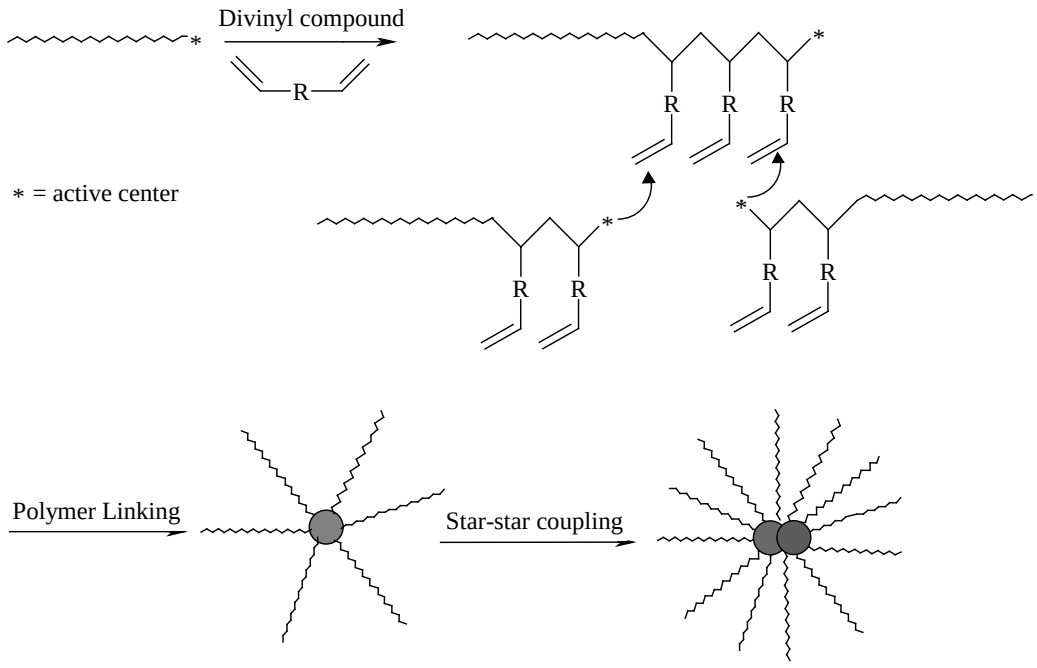

Figure 2.13 : The mechanism of divinyl compound and star coupling.

2.9.1. Synthesis of miktoarm star polymers by atom transfer radical polymerization

Gnanou and coworkers [103] synthesized AB_2 type miktoarm star polymers by combination of atom transfer radical polymerization (ATRP) and chemical modification of the termini of ATRP derived polymers (Fig. 2.14). The first step involved the preparation of ω-bromo PS chains by ATRP using ethyl 2-bromoisobutyrate as initiator. Next, the bromo end groups of the resulting PS chains were derivatized into twice as many bromoisobutyrates in order to obtain ω,ω′-bis(bromo)-PS chains. The last step consisted of growing two poly(*tert*-butyl acrylate) (P*t*BA) blocks by ATRP, This methodology enabled to synthesize PS(P*t*BA)$_2$ stars with chemically different PS and P*t*BA arms. They further performed the selective cleavage of *tert*-butyl groups from PS(P*t*BA)$_2$ stars under acidic conditions. This resulted amphiphilic PS(PAA)$_2$ miktoarm stars carrying one hydrophobic PS branch and two ionizable poly(acrylic acid) (PAA) arms.

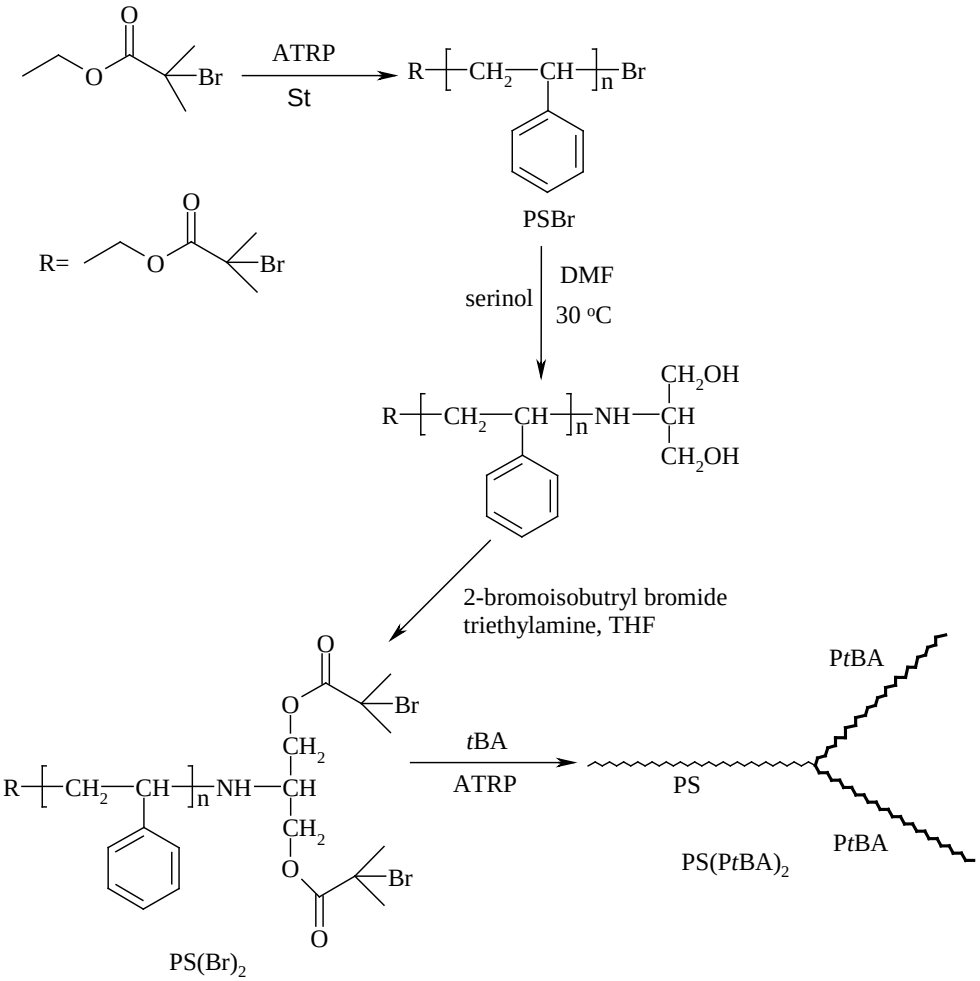

Figure 2.14 : Chemical modification of ATRP derived polymers.

In 2003, Matyjaszewski reported the synthesis of miktoarm star polymer by arm-first approach using ATRP [104]. The coupling of living P*t*BA arms with DVB and subsequent growth of poly(n-butyl acrylate), PBA arms from the core gave multiarm $(P\textit{t}BA)_n$-$(PBA)_n$ miktoarm star polymer (Fig. 2.15).

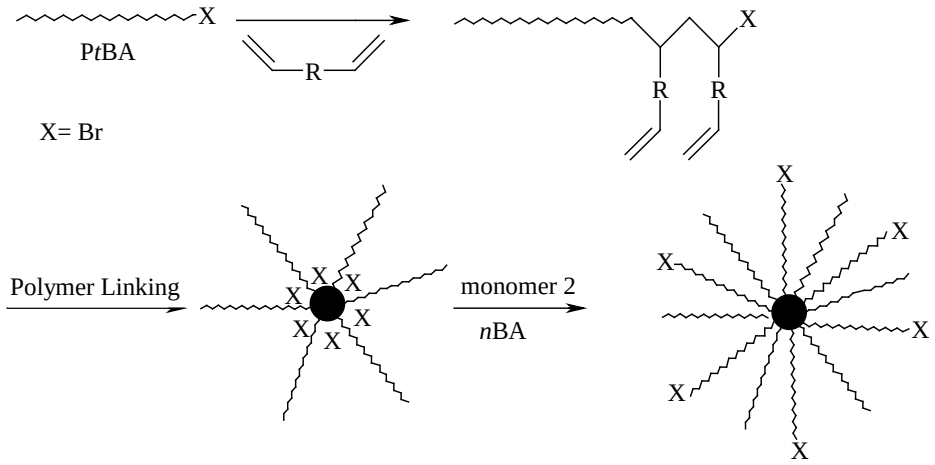

Figure 2.15 : Synthesis of multiarm $(P\textit{t}BA)_n$-$(PBA)_n$ miktoarm star polymer.

Using the same methodology, Chen and coworkers [105] prepared $(PCL)_n$-$(PS)_n$ miktoarm star polymer by ATRP. For this purpose, they first synthesized PCL star polymer with a cross-linked microgel core by ATRP of DVB using mono-2-bromoisobutyryl PCL ester as a macroinitiator. Then $(PCL)_n$-$(PS)_n$ miktoarm star polymer was produced subsequently by grafting PS from the core of PCL star polymer in which the initiating groups were inherited from PCL star formation using ATRP as shown in Figure 2.16. The same group also reported the synthesis of $(PEO)_n$-$(PS)_n$ miktoarm star polymer where PEO is poly(ethylene oxide) using the similar approach [106].

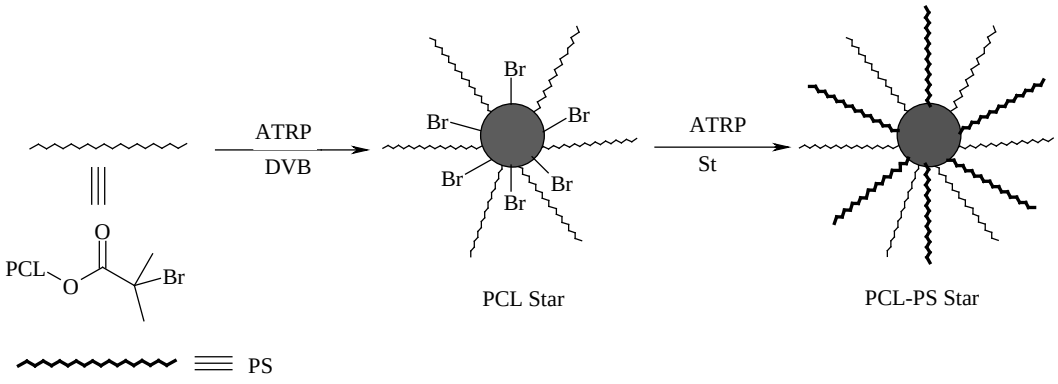

Figure 2.16 : Synthesis of $(PCL)_n$-$(PS)_n$ miktoarm star.

With a slightly different strategy, Wu et al. [107] have been prepared $(PS)_n$-$(PEA)_m$ miktoarm star polymer where PEA represents poly(ethyl acrylate) arms. In their

work, star polystyrene PS, was first synthesized by the arm- first method via ATRP using a preformed PS macroinitiator in the presence of DVB. Then, the residual vinyl groups in the gel core were converted to 1-bromoethylbenzene groups by hydrobromination. Lastly, miktoarm star polymer, $(PS)_n$-$(PEA)_m$, where the arm number of PEA was greater than that of PS, was prepared by ATRP of ethyl acrylate

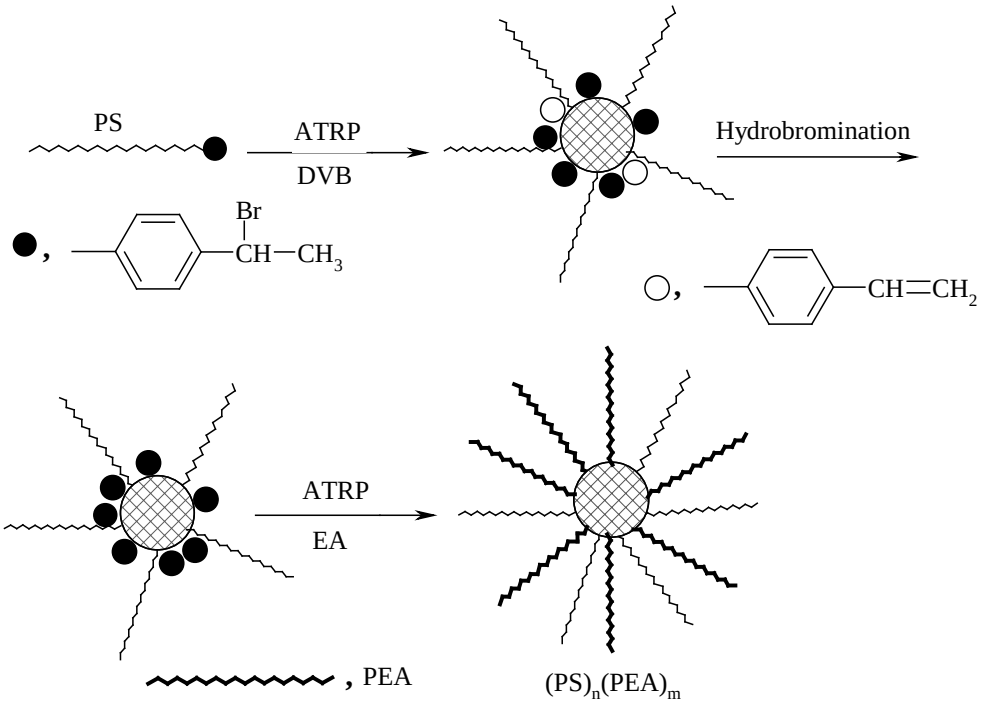

Figure 2.17 : Hydrobromination of residual vinyl groups in star.

from 1-bromoethylbenzene initiating sites, obtained by both the addition of linear PS macrointiators to vinyl groups of DVB and by hydrobromination of residual vinyl groups (Fig. 2.17).

2.9.2. Synthesis of miktoarm star polymers by combination of ATRP and ring opening polymerization

Hedrick and coworkers [108] reported the production of miktoarm star copolymers with alternating PCL and PMMA arms from miktofunctional initators using consecutive ATRP and living ring opening polymerization (ROP) via core-first approach. The key to this technique is the initiator molecule, since it determines the structure of the resulting copolymer. They employed a building block containing initiating sites for both ROP and ATRP (Fig. 2.17). Coupling of this building block to a multifunctional core leads to a multiarm initator with initiating sites arranged in

an alternating fashion for the synthesis of corresponding miktoarm star copolymer as illustrated in Figure 2.18.

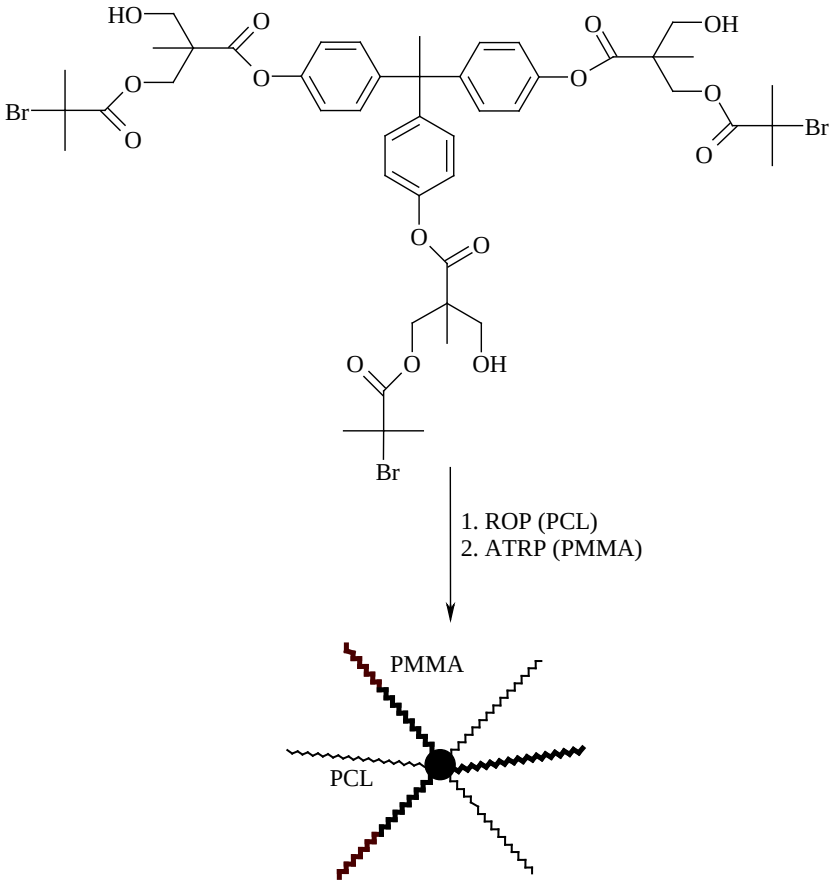

Figure 2.18 : Combination of ROP and ATRP in the synthesis of miktoarm star polymers.

The same methodology can also be applied for the preparation of other types of miktoarm star structures such as AB_2 μ-stars by differentiation of the building block. Erdogan et al. [109] have reported the facile synthesis of AB_2 type miktoarm star copolymers with poly(ε-caprolactam) (PCL) and P*t*BA or PMMA arms by combination of ROP and ATRP processes. They employed a novel miktofunctional intiator (Fig. 2.18) possessing one initiating site for ROP and two initiating sites for ATRP. The successive ROP and ATRP processes yield the desired AB_2 miktoarm star polymer (Fig. 2.19). The details of this work will be represented in the results and discussions part of this book. The described core-first approach provides another level of control to the preparation of miktoarm star polymers by employing different miktofunctional initiators.

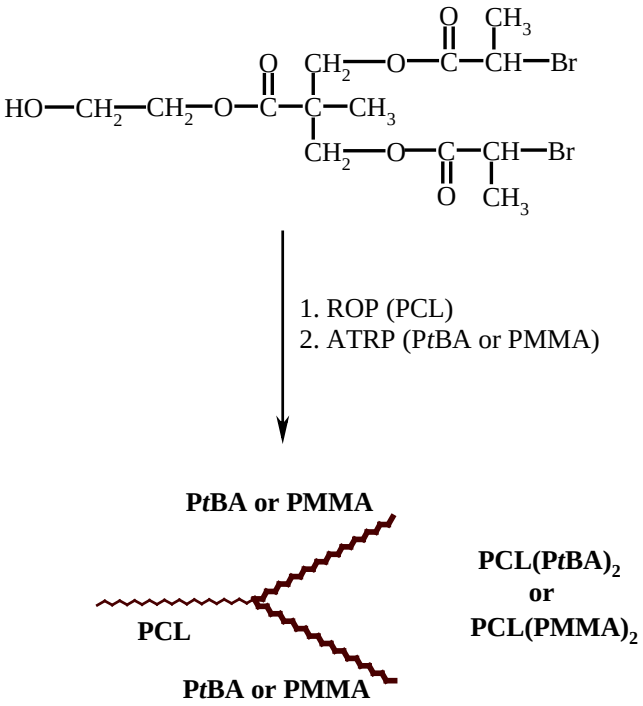

Figure 2.19 : AB_2 miktoarm star polymer by miktofunctional initiator.

2.9.3. Synthesis of miktoarm star polymers by combination of ATRP and nitroxide-mediated radical polymerization

Tunca et al. [110] synthesized miktoarm stars of the AB_2C_2 type, where "A" is PS, "B" is P*t*BA and "C" is PMMA by using the trifunctional initiator. They used a combination of nitroxide mediated radical polymerization (NMP) and atom transfer radical polymerization (ATRP) techniques and a three-step reaction sequence. In the first step, polystyrene macroinitiator with dual ω-bromo functionality was obtained by NMP of styrene in bulk at 125 ºC. This precursor was subsequently used as the macroinitiator for the ATRP of *tert*-butylacrylate (*t*BA) in the presence of copper bromide (CuBr) and pentamethyldiethylenetriamine (PMDETA) at 80 ºC, to produce the miktoarm star of the (PS)(P*t*BA)$_2$. This two armed precursor was the macroinitiator for the subsequent polymerization of methly methacrylate (MMA), giving the miktoarm star polymer (PS)(P*t*BA)$_2$(PMMA)$_2$. All the steps of the synthesis of the miktoarm star polymer scheme is shown in Figure 2.20.

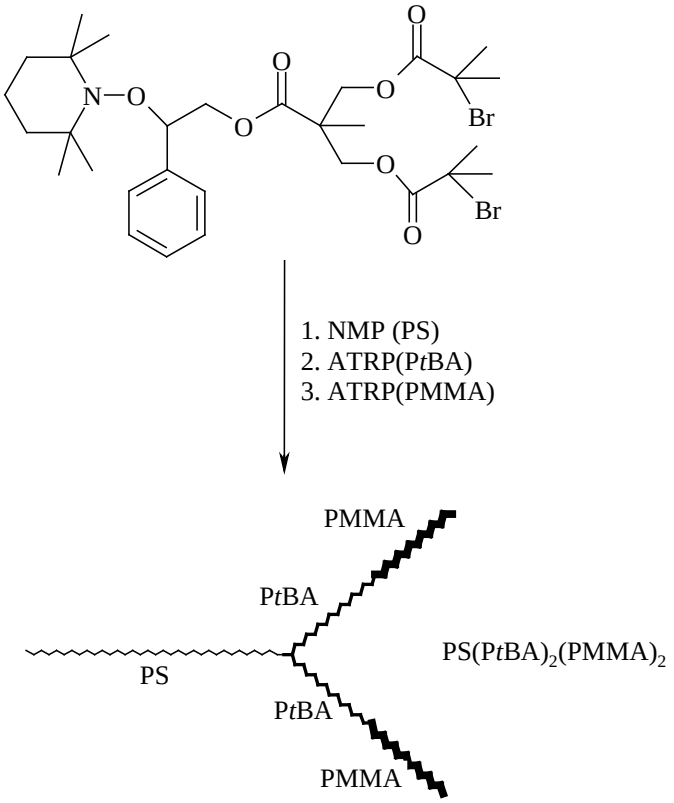

Figure 2.20 : Star produced by combination of ATRP and NMP.

More recently, the same group reported the preparation of A_3B_3 type $(PS)_3$-$(PMMA)_3$ miktoarm star polymers via combination of nitroxide mediated polymerization and atom transfer radical polymerization routes [111]. They synthesized a novel initiator having initiating sites for both nitroxide mediated polymerization and atom transfer radical polymerization and first used in the preparation of A_3 type polystyrene (PS) macroinitiator by nitroxide mediated polymerization. Next, using this macroinitiator, the synthesis of A_3B_3 type $(PS)_3$–$(PMMA)_3$ miktoarm star polymers was carried out by atom transfer radical polymerization of methyl methacrylate as shown in Figure 2.21. As can be seen in the given studies, the core-first approach does not need any chemical transformation of functional end-groups in order to obtain proper functionality for a succeeding polymerization step.

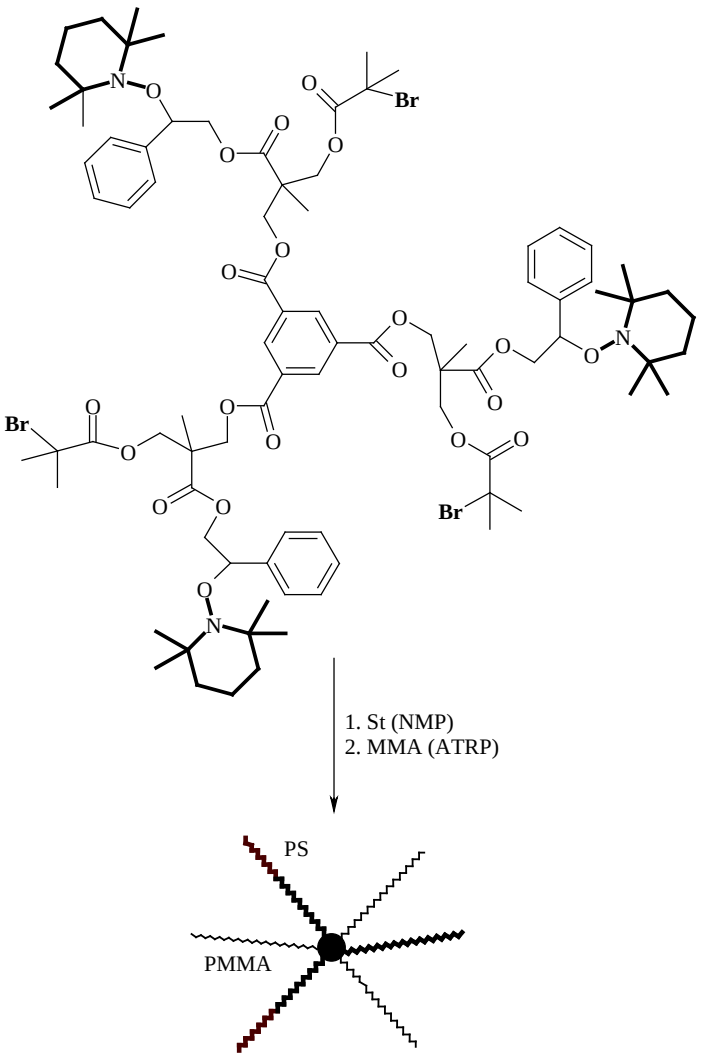

Figure 2.21 : A novel miktoarm star copolymer with an azobenzene unit at the core.

Using the same approach, Erdoğan et al. [112] prepared a novel miktoarm star copolymer with an azobenzene unit at the core as shown in Figure 2.22. For this purpose, first, miktofunctional initiator, with tertiary bromide (for atom transfer radical polymerization) and 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) (for nitroxide mediated polymerization) functionalities and an azobenzene moiety at the core was synthesized. The initiator thus obtained was used in atom transfer radical polymerization of methyl methacrylate and nitroxide mediated polymerization of styrene, respectively, to give A_2B_2 type miktoarm star copolymer, $(PMMA)_2$-$(PS)_2$ with an azobenzene unit at the core.

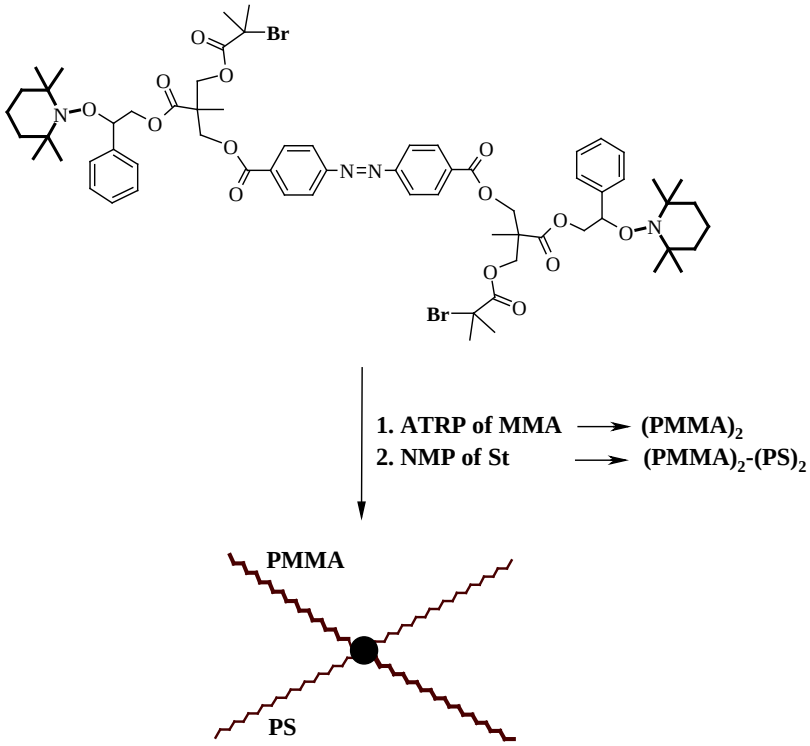

Figure 2.22 : A_2B_2 type miktoarm star copolymer.

3. EXPERIMENTAL WORK

3.1. Materials

Styrene (St, 99%, Acros), methyl methacrylate (MMA, 99%, Aldrich) and *tert*-butylacrylate (*t*BA, 99%, Aldrich) were passed twice through basic alumina column to remove inhibitor and then distilled over CaH_2 in vacuo prior to use. Divinylbenzene (DVB, 80%, Aldrich) was purified twice by passing through a column filled with basic alumina to remove the inhibitor. N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, Aldrich) was distilled over NaOH prior to use. CuBr (99.9%, Aldrich), CuCl (99.9%, Aldrich) were used as received. Dichloromethane (CH_2Cl_2) was purchased from Aldrich and 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 without further purification.

3.2. Instrumentation

The conventional size exclusion chromatography (SEC) measurements were carried out with an Agilent instrument (Model 1100) consisting of a pump, refractive index, and UV detectors. Four Waters Styragel columns (HR 5E, HR 4E, HR 3, HR 2), (4.6 mm internal diameter, 300 mm length, packed with 5 μm particles) were used in series. The effective molecular weight ranges were 2000- 4.000.000, 50-100.000, 500-30.000, and 500–20.000, respectively. THF was used as eluent at a flow rate of 0.3 mL/min at 30 °C. Toluene was used as an internal standard. The apparent molecular weights and polydispersities were determined with a calibration based on linear PS or PMMA standards using PL Caliber Software from Polymer Laboratories. The second SEC system with an Agilent model isocratic pump, four Waters Styragel columns (guard, HR 5E, HR 4, HR 3, and HR 2), and a Viscotek

TDA 302 triple detector (RI, dual laser light scattering (LS) (λ = 670 nm, 90° and 7°) and a differential pressure viscometer), (TD-SEC) was conducted to measure the absolute molecular weights in THF with a flow rate of 0.5 mL/min at 35 °C. All three detectors were calibrated with a PS standard having narrow molecular weight distribution (M_n = 115,000 g/mol, M_w/M_n = 1.02, [η] = 0.519 dL/g at 35 °C in THF, dn/dc = 0.185 mL/g) provided by Viscotek company. Data was collected using Omni-Sec version 4.5 software from Viscotek Company. DVB conversion was determined using the Agilent 6890N gas chromatograph, equipped with an FID detector using a wide-bore capillary column (HP5, 30m x 0.32mm x 0.25 μm, J and W Scientific). Injector and detector were kept constant at 280 and 285 °C, respectively. UV spectra were recorded on a Shimadzu UV-1601 spectrophotometer in CH_2Cl_2.

3.3. Synthesis of Initiators

9-Anthyryl methyl 2-bromo-2-methyl propanoate **1** [113], and 3-(trimethylsilyl)prop-2-ynyl 2-bromo-2-methylpropanoate **2** [114], and 2-bromo-2-methyl-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-en-4-yl)-ethyl ester **5** [115] were prepared according to published procedures. Ethyl 2-bromo-2-methylpropanoate (EIBr) was a commercial chemical and was directly used.

3.3.1. Synthesis of 9-anthyryl methyl 2-bromo-2-methyl propanoate (1)

In a 250 mL of round bottom flask, equipped with a magnetic stirrer, 9-Anthracene methanol (4 g, 19.2 mmol), DMAP (1.17 g, 9.6 mmol), and Et_3N (7.25 mL, 50.7 mmol) were dissolved in 30 mL of dry THF, then flask was connected with dropping funnel where there is a solution of 2-bromo-2-methylpropanoyl bromide (2,84 mL, 23 mmol) in 70 mL THF. The solution was dropped into a flask, as one drop per second under nitrogen gas and was stirred in ice bath at 0 ^oC while all the solution in dropping funnel was consumed. Dropping was finished over a period of 45 minute, the solution was stirred at room temperature for overnight in the dark. Then THF was evaporated on rotary and the crude product was dissolved in dichloromethane and washed successfully with dilute Na_2CO_3 (sodium carbonate) aqueous solution for three times and dried over anhydrous sodium sulfate (Na_2SO_4). CH_2Cl_2 was removed and the yellow oil was crystallized from hexane two times. Light yellow crystals

were obtained with 65% of yield. ^{1}H NMR ($CDCl_3$), δ 7.43–8.52 (m, 9 ArH of anthracene), 6.21 (s, 2*H* of CH_2-O), 1.87 (s, (CH_3)$_2$-C-Br).

3.3.2. Synthesis of 3-(trimethylsilyl)prop-2-ynyl 2-bromo-2-methylpropanoate (2)

In a 250 mL of necked round bottom flask, equipped with a magnetic stirrer, 3-(trimethylsilyl)prop-2-yn-1-ol (2.28 mL, 15.6 mmol), DMAP (0.95 g, 7.8 mmol), and Et_3N (3.34 mL, 23.4 mmol) were dissolved in 30 mL CH_2Cl_2, then flask was connected with dropping funnel where there is a solution of 2-bromo-2-methylpropanoyl bromide (2,3 mL, 18.7 mmol) in 70 mL CH_2Cl_2. The solution was dropped into a flask as one drop per second and was stirred in ice bath while all the solution in dropping funnel was consumed. For the first ten minute, yellow color was changed into an orange one and for the second half hour the color was changed from orange to brick color. After droping was finished, the solution was stirred at ambient temperature for 24 hour. Then mixture was extracted with distilled water, the combined organic phase was dried with Na_2SO_4 and solvent was evaporated. Obtaining material was passed through the silica gel column with ethyl acetate-hexane (1/4; v/v) as a mobile phase.

3.3.3. Synthesis of 4,10-dioxatricyclo[5.2.1.0 ^{2,6}]dec-8-ene-3,5-dione (3)

Maleic anhydride (30.0 g, 306 mmol) was suspended in 150 mL of toluene and the mixture warmed to 80 °C. Furan (33.4 mL, 459 mmol) was added via syringe and the turbid solution stirred for 6 hour. The mixture was then cooled to ambient temperature and the stirring stopped. After 1 hour, the resulting white crystals were collected by filtration and washed with 2 × 30 mL of petroleum ether. Obtained was 44.4 g (267 mmol, 87% yield) of as small white needless.

3.3.4. Synthesis of 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.0 ^{2,6}]dec-8-ene-3,5- dione (4)

The anhydride **3** (10.00 g, 60.0 mmol) was suspended in MeOH (150 mL) and the mixture cooled to 0 °C. A solution of ethanolamine (3.6 mL, 60 mmol) in 30 mL of MeOH was added dropwise (10 min), and the resulting solution was stirred for 5 min at 0 °C, then 30 min. at ambient temperature, and finally refluxed for 6 hour. After cooling the mixture to ambient temperature, the solvent was removed under reduced

pressure, and the white residue was dissolved in 150 mL of CH_2Cl_2 and washed with 3 × 100 mL of water. The organic layer was dried over $MgSO_4$ and filtered. Removal of the solvent under reduced pressure furnished an off-white residue that was purified by flash chromatography to give (4.9 g , 25 mmol, 40% yield) as a white solid.

3.3.5. Synthesis of 2-bromo-2-methyl propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo [5.2.1.0 ^{2,6}] dec-8-en-4-yl) ethyl ester (5)

A solution of the alcohol **4** (2.00 g, 9.55 mmol) and Et_3N (1.44 mL, 10.54 mmol) in 100 mL of THF (the solution remained slightly turbid) was cooled to 0 °C, and a solution of 2-bromo isobutyryl bromide (1.26 mL, 10 mmol) in 25 mL of THF was added dropwise (30 min). The white suspension was stirred for 3 hour at 0 °C and subsequently at ambient temperature overnight. The ammonium salt was filtered off and the solvent removed under reduced pressure to give a pale-yellow residue that was purified by flash chromatography . Obtained was 1.86 g (55% yield) of as a white solid. ^{1}H NMR ($CDCl_3$, O) 6.49 (t, 2H, CH_{vinyl}), 5.23 (t, 2H, CHO), 4.30 (t, 2H, OCH_2), 3.78 (t, 2H, NCH_2), 2.84 (s, 2H, CH9, 1.86 (s, 6H, CH_3).

3.4. One Pot Synthesis of α-Silyl Protected Alkyne- and α-Anthracene-end-capped PS Using Double Initiator (6)

In this synthesis, both initiators **1** and **2** were added into the same Schlenk tube to polymerize styrene in ATRP conditions. Styrene (20.0 mL, 175 mmol), PMDETA (0.182 mL, 0.872 mmol), CuBr (0.125 g, 0.871 mmol) and, **1** (0.313 g, 877 mmol) and **2** (0.242 g, 877 mmol) were added in a 50 mL of Schlenk tube and the reaction mixture was degassed by three freeze-pump-thaw (FPT) cycles and left in vacuum. The tube was then placed in a thermostated oil bath at 110 ^{o}C for 40 min. The dark green polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated in methanol. The polymer was dried for 24 hour in a vacuum oven at 40 ^{o}C. $([M]_0/[I]_0$ = 200, $[I]_0$:$[CuBr]_0$:$[PMDETA]_0$=1:1:1 and $[I]_0$= 0.5 mol **1** + 0.5 mol **2**, conversion = 23%, $M_{n,theo}$ = 5100, $M_{n,NMR}$ = 6030 (47% α-anthracene-end-capped and 53% α-silyl protected alkyne-end-capped PS), $M_{n,GPC}$ = 5400, M_w/M_n = 1.10, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.4 (bs, 1H, Ar*H* of anthracene), 8.3 (bs, 2H, Ar*H* of anthracene), 7.9 (bs, 2H, Ar*H* of anthracene), 7.5 (bs, 4H, Ar*H* of anthracene), 7.5 -

6.5 (Ar*H* of PS), 5.8 (CH_2-anthracene), 4.4 (C*H*(Ph)-Br), 0.6–2.2 (aliphatic protons of PS). 7.5-6.5 (Ar*H*), 4.4 (C*H*Br), 4.1 (≡CC H_2O), 2.0-0.9 (CH_2 and C*H*), 0.17 ((CH_3)$_3$Si-).

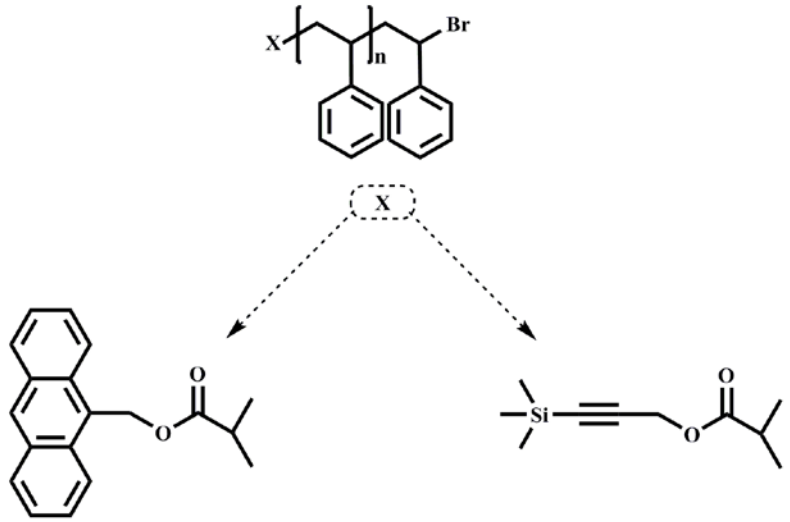

Figure 3.1 : One Pot ATRP of Styrene via both initiators **1** and **2** at the same Schlenk tube.

3.5. Synthesis of Alkyne- and Anthracene-end-capped (PS)$_n$-polyDVB Multi Arm Star Polymer (Core) (7)

Macroinitiator, **6**, (2.1 g, 0.38 mmol), anisole (13.0 mL), PMDETA (80 µL, 0.380 mmol), DVB (0.815 mL, 5.72 mmol), and CuBr (0.055 g, 0.38 mmol) were charged to a Schlenk tube equipped with a magnetic stirrer bar under argon atmosphere. The first sample was quickly taken from the reaction mixture for GC measurement, before it was degassed by using three FPT cycles. The reaction flask was back-filled with argon and immersed in a 110 ^{o}C oil bath. At timed intervals, samples were taken from the reaction mixture with argon purged-syringe under positive argon atmosphere. The samples were diluted with THF and purified by passing through short neutral alumina column to remove the copper salt and then filtered through poly(tetrafluoro ethylene) (PTFE) filter (0.2 µm pore size) prior to GC and GPC analyses. When DVB conversion reached up to 94%, the reaction was stopped after 12 hour via exposure to air. The reaction mixture was diluted with THF, then filtered through a column filled with neutral alumina to remove the copper complex and the star polymer was precipitated in methanol. The crude product was dissolved in THF and then reprecipitated in methanol/diethyl ether mixture. Finally, the polymer was dried under vacuum at 40 ^{o}C for 24 hour.

Subsequently, tetrabutyl ammonium fluoride (TBAF) 20 µL was added to a 20 mL solution of multiarm anthracene and trimethyl silyl-end functionalized $(PS)_n$-polyDVB (1.2 g, 4.80 µmol) multi arm star polymer in THF in a 25 mL of Schlenk tube. Star polymer hydrolyzed overnight. The crude product was dissolved in THF and precipitated into methanol. Finally, the obtained white product, **7**, was dried in a vacuum oven at 40 ^{o}C for 24 hour.

3.6. ATRP of P*t*BA From Ethyl 2-bromo-2-methylpropanoate (P*t*BA-Br) (8)

P*t*BA-Br was prepared by ATRP of *t*BA via initiator EIBr. *t*BA (12.0 mL, 82.3 mmol), PMDETA (0.173 mL, 0.830 mmol), CuBr (0.120 g, 0.83 mmol), ethylene carbonate (1.06 g) and the initiator EIBr (0.121 mL, 0.83 mmol) were added in a 25 mL of Schlenk tube and the reaction mixture was degassed by three FPT cycles, and left in argon. The tube was then placed in a thermostated oil bath at 80 ^{o}C for 30 min. The polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst. The excess of THF was evaporated under reduced pressure and the mixture was precipitated into cold methanol/water (80/20; v/v). After decantation, the polymer was dissolved in CH_2Cl_2, extracted with water and the water phase was again extracted with CH_2Cl_2 and combined organic phase was dried over Na_2SO_4. Finally, the organic phase was evaporated to give P*t*BA-Br. The polymer was dried for 24 hour in a vacuum oven at 40 ^{o}C. ($[M]_0/[I]_0$ = 100, $[I]_0$:$[CuBr]_0$:$[PMDETA]_0$=1:1:1, conversion = 25%, $M_{n,theo}$ = 3400, $M_{n,NMR}$ = 5100, $M_{n,GPC}$ = 3500, M_w/M_n = 1.16, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ), 4.3–4.0 (m, CH_3CH_2OC=O and C*H*Br end group of P*t*BA), 2.2 (bs, C*H* of P*t*BA), 2.0–1.0 (m, CH_2 and CH_3 of P*t*BA).

3.7. Synthesis ω-Azide Functional P*t*BA (P*t*BA-N_3) (9)

Previously obtained P*t*Ba-Br, **8**, (2.65 g, 0.76 mmol) was dissolved in DMF (10 mL), and NaN_3 (1.0 g, 15.4 mmol) was added to the reaction mixture. After stirring the reaction mixture for overnight at 50 ^{o}C, the product was precipitated into cold methanol/water (80/20; v/v). After decantation, the polymer was dissolved in CH_2Cl_2, extracted with water and the water phase was again extracted with CH_2Cl_2 and combined organic phase was dried over Na_2SO_4. Finally, the organic phase was evaporated to give P*t*BA-N_3. The polymer was dried for 24 hour in a vacuum oven at

40 ^{o}C. (Yield = 2.63 g, 99%). $M_{n,theo}$ = 3350, $M_{n,NMR}$ = 5100, $M_{n,GPC}$ = 3800, M_w/M_n = 1.10, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ), 4.05 (d, CH_3CH_2OC=O), 2.2 (bs, C*H* of P*t*BA), 2.0–1.0 (m, CH_2 and CH_3 of P*t*BA).

3.8. Synthesis of (P*t*BA)$_m$-(PS)$_n$-polyDVB Multi Miktoarm Star Block Copolymer via Click Reaction (10)

A solution of P*t*BA-N_3, **9**, (0.122 g, 0.024 mmol) in 8 mL of DMF was added to a solution of multiarm anthracene- and alkyne-end-functionalized $(PS)_n$-polyDVB, **7**, (0.3 g, 1.20 µmol) star polymer in a Schlenk tube. Then, the reaction mixture was degassed by three FPT cycles and left in argon then stirred at room temperature for overnight. Polymer solution was passed through neutral alumina column to remove copper salt and precipitated into methanol. The crude product was dissolved in THF and then reprecipitated in methanol/diethyl ether mixture (1/1 v/v). Finally, the polymer was dried in a vacuum oven at 40 ^{o}C for 24 hour.

3.9. Synthesis of Furan Protected Maleimide Terminated PMMA (PMMA-MI) (11)

PMMA-MI was prepared by ATRP of MMA via initiator **5**. MMA (5.0 mL, 46.9 mmol), PMDETA (0.196 mL, 0.94 mmol), CuCl (0.93 g, 0.94 mmol), toluene (5 mL), and **5** (0.336 g, 0.94 mmol) were added in a 50 mL of Schlenk tube and the reaction mixture was degassed by three FPT cycles, and left in argon. The tube was then placed in a thermostated oil bath at 40 ^{o}C for 4 hour. The polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst and precipitated in hexane. The polymer was dried for 24 hour in a vacuum oven at 40 ^{o}C. ($[M]_0/[I]_0$ = 50, $[I]_0$:$[CuBr]_0$:$[PMDETA]_0$=1:1:1, conversion = 56%, $M_{n,theo}$ = 2800, $M_{n,NMR}$ = 3000, $M_{n,GPC}$ = 3900, M_w/M_n = 1.17, relative to PS standards). ^{1}H–NMR ($CDCl_3$, δ) 6.5 (s, 2H, vinyl protons), 5.3 (s, 2H, C*H*CH=CHC*H*, bridge-head protons), 4.1 (m, 2H, NCH_2CH_2OC=O), 4.0–3.2 (m, OCH_3 of PMMA and NCH_2CH_2OC=O), 2.9 (s, 2H, CH_2NC=OC*H*-C*H*, bridge protons), 2.5–0.5 (m, CH_2 and CH_3 protons of PMMA).

3.10. Synthesis of $(PMMA)_k$-$(Pt BA)_m$-$(PS)_n$-polyDVB Multi Miktoarm Star Block Copolymer via Diels-Alder Click Reaction (12)

A solution of PMMA-MI (0.025g, 8.33 mmol) in 10 mL of toluene was added to a multi miktoarm anthracene-end capped $(PtBA)_m$-$(PS)_n$-polyDVB, **10**, (0.15 g, 0.422 µmol) star polymer in a Schlenk tube. The reaction mixture was bubbled with nitrogen for 30 min. and then stirred and refluxed temperature for 48 hour in the dark. At the end of the reaction, toluene was evaporated under vacuum and the reaction mixture the residual solid dissolved in THF, and subsequently precipitated into methanol for two times and dried in a vacuum oven at 40 ^{o}C for 24 hour.

4. RESULTS AND DISCUSSION

4.1. Synthesis of Initiators

First of all, the synthesis of 9-Anthyryl methyl 2-bromo-2-methyl propanoate, **1**, was carried out by the reaction of 9-Anthracene methanol with 2-bromo-2-methylpropanoyl bromide in the presence of the DMAP, Et_3N and as a solvent THF for 24 hour.

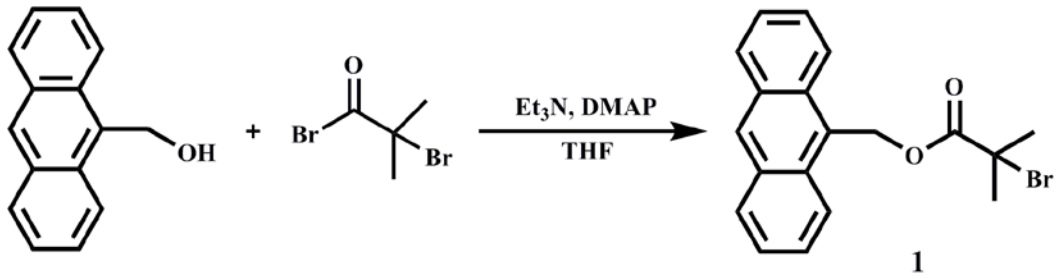

Figure 4.1 : Synthesis of 9-Anthyryl methyl 2-bromo-2-methyl propanoate, **1**.

In this reaction, the excess of 2-bromo-2-methylpropanoyl bromide was used to achieve complete bromination of 9-Anthracene methanol and 4-dimethyl aminopyridine (DMAP) was used as a catalyst of this esterification reaction. The existence of HBr as a byproduct in this reaction, was captured by Et_3N as to form a salt in the solution. By this, it is easy to remove inorganic byproduct from system by the extraction of organic molecule.

Moreover, after purification procedures of the obtained initiator, **1**, a sample was taken from it for ^{1}H NMR. It can be seen that 9 *H* of anthracene unit on ^{1}H NMR spectrum as multiplet peaks are between 7.43–8.52 ppm. Also we can see 6 *H* of $(CH_3)_2$-C-Br unit as singlet peak at 1.87 ppm. Peak between 7.2-7.3 ppm comes from $CHCl_3$ that is presented in $CDCl_3$ which is the solvent of the ^{1}H NMR. And peak which is observed at 0.2 ppm belongs to tetramethylsilane (TMS). There is no another peak observed on spectrum so this shows the reaction was successfully done and the obtained product is pure.

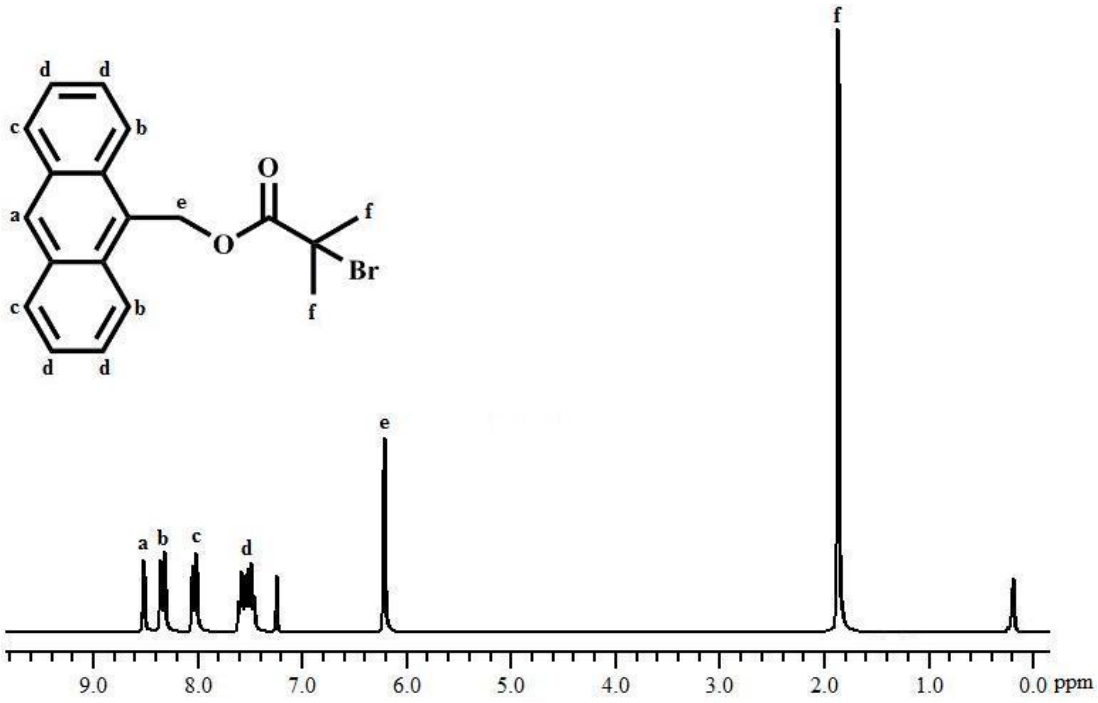

Figure 4.2 : ^{1}H NMR spectrum of 9-Anthyryl methyl 2-bromo-2-methyl propanoate, **1**, in $CDCl_3$.

Secondly, the synthesis of 3-(trimethylsilyl)prop-2-ynyl 2-bromo-2-methyl propanoate, **2**, was done. For this purpose, 3-(trimethylsilyl)prop-2-yn-1-ol was reacted with 2-bromo-2-methylpropanoyl bromide in the presence of the DMAP, Et_3N and CH_2Cl_2 as a solvent for overnight.

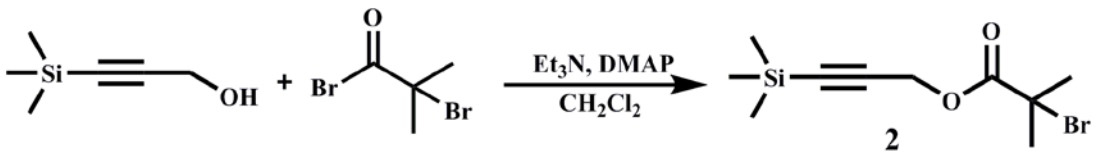

Figure 4.3 : Synthesis of 3-(trimethylsilyl)prop-2-ynyl 2-bromo-2-methylpropanoate, **2**.

Like in the synthesis of **1**, DMAP and Et_3N were used because of the same reasons. Then initiator **2** was purified by silica gel column with ethyl acetate-hexane (1/4; v/v) as a mobile phase.

On the other hand, ^{1}H NMR spectrum also shows that reaction is done because we can see sharp singlet peak of 9 *H* of $-Si(CH_3)_3$ at 0.165 ppm.

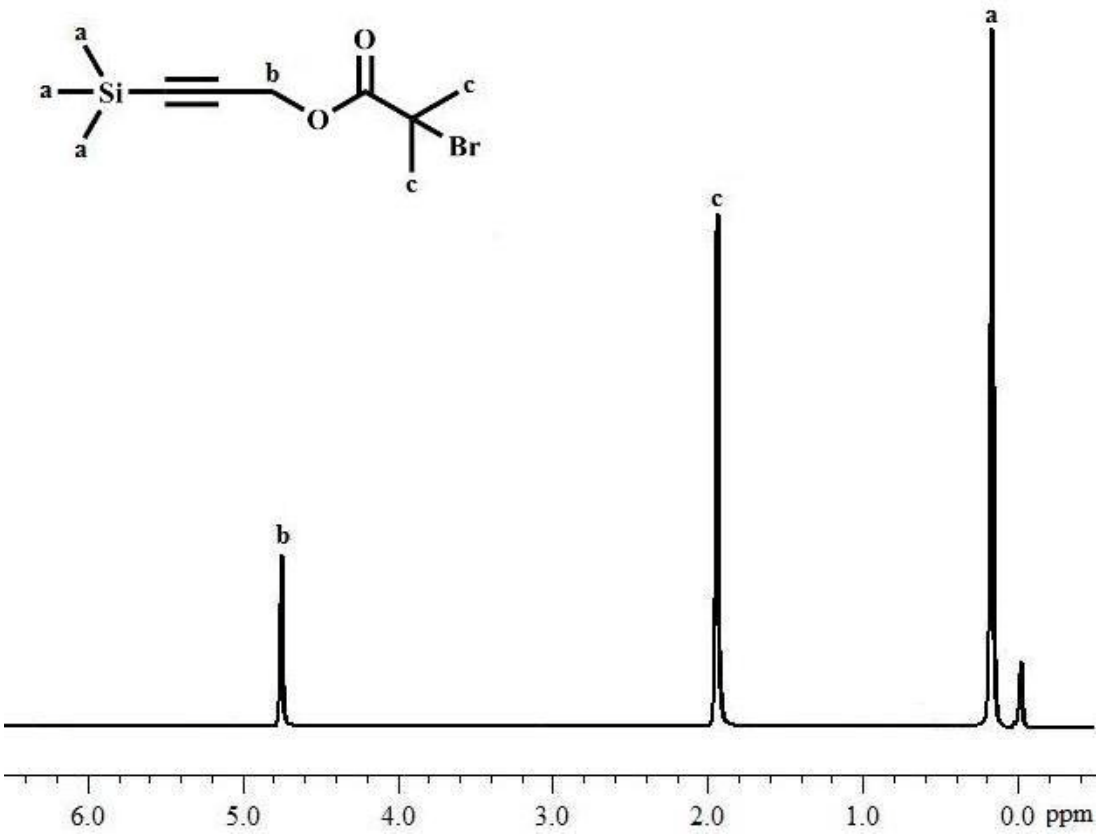

Figure 4.4 : ^{1}H NMR Spectrum of 3-(trimethylsilyl)prop-2-ynyl 2-bromo-2-methylpropanoate, **2**, in $CDCl_3$.

As it is seen from ^{1}H NMR spectrum of **2**, there is no other peak comes from other compounds. So reaction was fully done.

Finally, maleic anhydride and furan were reacted in toluene at reflux temperature for 6 hour to give 4,10-Dioxatricyclo[5.2.1.0 ^{2,6}]dec-8-ene-3,5-dione, **3**. The anhydride **3** was obtained as small white needless. The reaction of the anhydride **3** was then carried out to give the 4-(2-Hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5- dione, **4.** In this reaction, the anhydride **3** was suspended in MeOH and a solution of ethanolamine in MeOH was added at 0 ^{o}C, then the mixture refluxed for 6 hour. Finally, compound **4** was obtained as a white solid. Subsequent this reaction, compound **4** and Et_3N was mixed in THF. Additionally, a solution of 2-bromo isobutyryl bromide was added in THF at 0 °C. After this process, the reaction was carried out at ambient temperature overnight. Finally**,** 2-bromo-2-methyl propionic acid 2-(3,5-Dioxo-10-oxa-4 azatricyclo[5.2.1.0 ^{2,6}] dec-8-en-4-yl) ethyl ester **5** was obtained as a white solid.

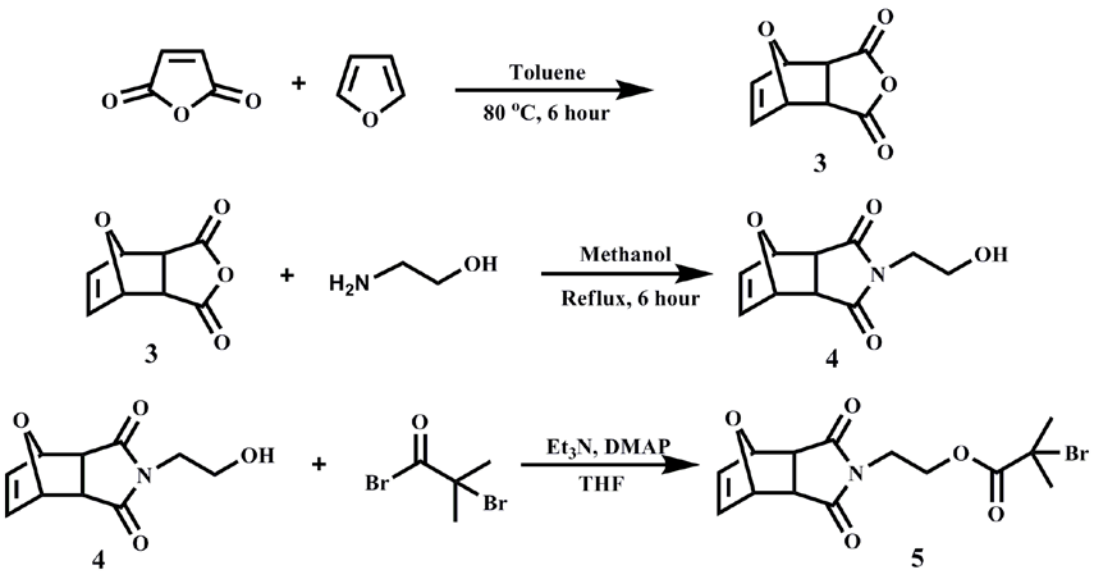

Figure 4.5 : All the steps of the synthesis of the 2-(3,5-Dioxo-10-oxa-4- azatricyclo [5.2.1.0 ^{2,6}] dec-8-en-4-yl) ethyl ester, **5**.

The ^{1}H NMR spectrum of the compound **5** is shown in Figure 4.6.

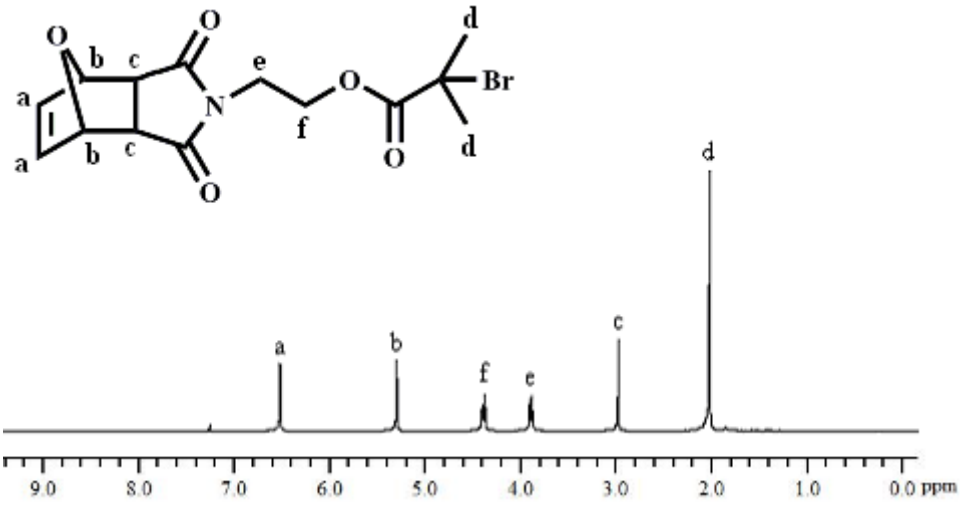

Figure 4.6 : ^{1}H NMR spectrum of the compound the 2-(3,5-Dioxo-10-oxa-4-azatricyclo [5.2.1.0 ^{2,6}] dec-8-en-4-yl) ethyl ester, **5,** in $CDCl_3$.

4.2. One Pot Synthesis of α-Silyl Protected Alkyne- and α-Anthracene-end-capped PS Macroinitiator

For this purpose both of initiators **1**, and **2** were used to polymerize styrene. ATRP method is followed and therefore CuBr, PMDETA is also used as the catalyst of the ATRP at 110 ^{o}C. And the resulted polymer chains carried both α-silyl protected alkyne- and α-anthracene-end-capped functionality as shown in Figure 4.7.

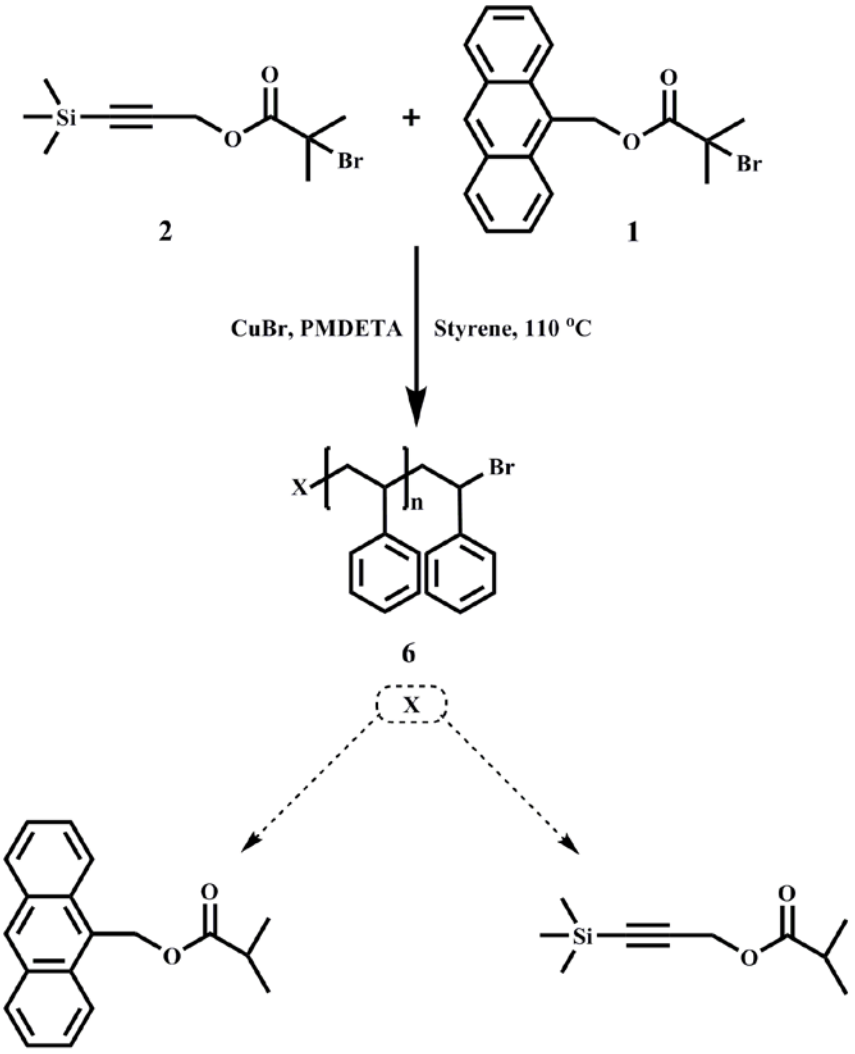

Figure 4.7 : Synthesis of One Pot α-silyl protected alkyne- and α-anthracene-end-capped PS Macroinitiator, **6**.

The ^{1}H NMR spectrum of the macroinitiator **6** showed that the resulting polymer bears both of the α-silyl protected alkyne- and α-anthracene-end-capped. We can see both of the multiplet 9 *H* peaks of anthracene between 7.43–8.52 ppm and singlet peak of 9 *H* of –Si(C*H*$_3$)$_3$ at 0.165 ppm as shown in Figure 4.8. And also peak that is observed between 3.6-3.7 ppm belongs to aliphatic protons near to ester bond. Peaks between 6.1-7.3 ppm belongs to protons of aromatic ring, phenyl groups. Peaks between 0.9-2.2 ppm belongs to aliphatic protons presented on polymer chain. On ^{1}H NMR spectrum, we can both observe anthracene and trimethyl silyl units and aliphatic parts. At the same time we can observe *H* peak between 4.2-4.3 ppm that is near to bromine. So the reaction was also successfully completed according to spectrum.

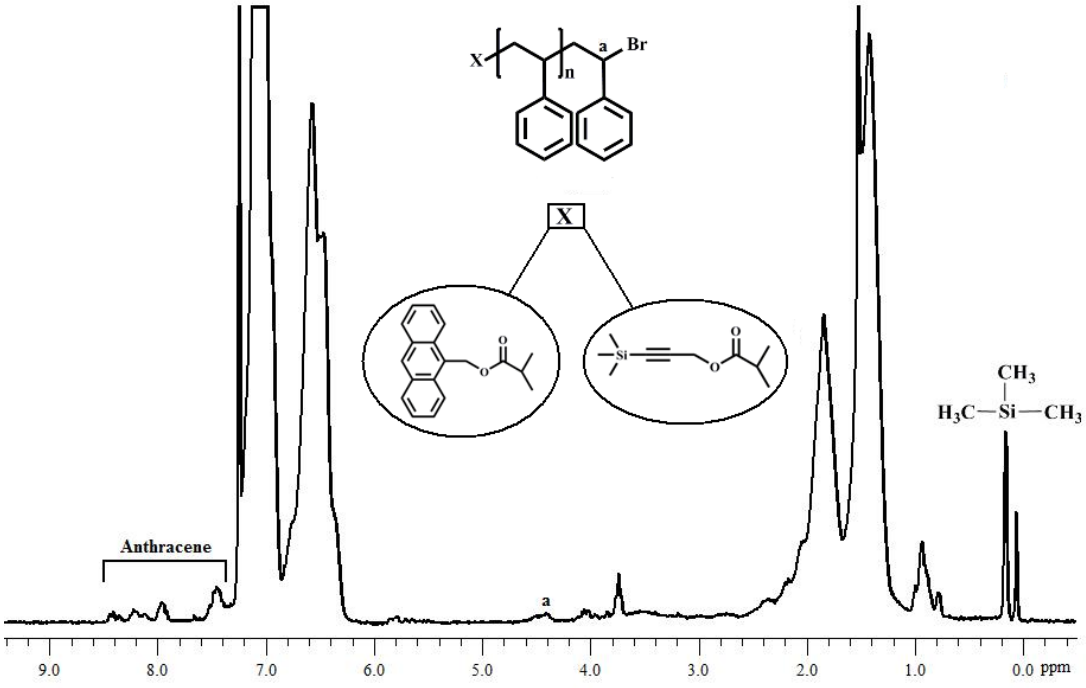

Figure 4.8 : ^{1}H NMR spectrum of α-silyl protected alkyne- and α-anthracene-end-capped PS Macroinitiator, **6**, in $CDCl_3$.

Furthermore, calculations from ^{1}H NMR spectrum showed that 53% of the arms of polystyrene consisted of α-silyl protected alkyne-end-capped and 47% of the arms of polystyrene consisted of α-anthracene-end-capped. This showed successful polymerization of the styrene via using two different types of initiator which were **1**, and **2**. Because we started equal moles of initiators and we expect **6** to have nearly equal amounts of anthracene and trimethyl silyl end caps on polymer. And what we expect was happened. As a result of this, chains grew nearly in the same rate and had nearly the same chain lengths. Because polydispersity index, which was 1.10, also proved our results. Conditions are given in Table 4.1.

4.3. Synthesis of Alkyne- and Anthracene-end-capped $(PS)_n$-polyDVB Multiarm Star Polymer (Core)

After the preparation of the macroinitiator **6**, multi arm star polymer was produced. For this purpose DVB, PMDETA, and CuBr was used and star polymer with α-silyl protected alkyne- and α-anthracene-end-capped arms was produced. Figure 4.9 also showed changes of molecular weight of multi arm star polymer during the reaction.

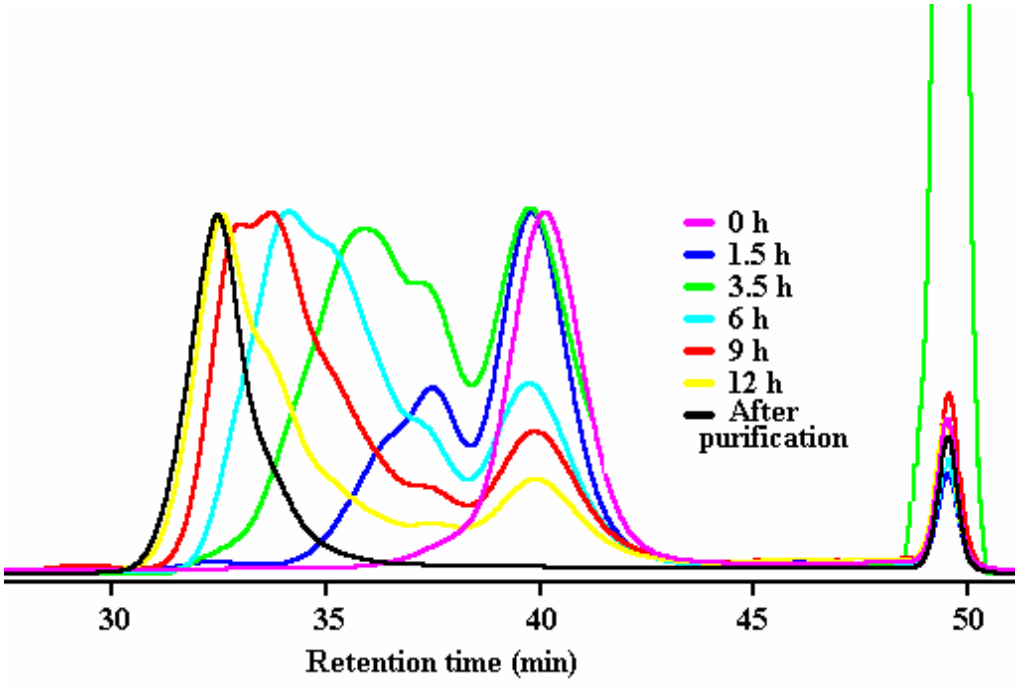

Figure 4.9 : GPC traces during the synthesis of $(PS)_n$-polyDVB multi-arm star polymer. Experimental conditions: [DVB]/15 = [**6**] = [CuBr] = [PMDETA] = 0.023 M in anisole at 110 °C. GPC conditions: RI detector, relative to linear PS standards.

As seen in GPC chromatogram of multi arm star polymer, the reaction was stopped at 12th hour via exposuring to air and diluting by THF with 94% DVB conversion. And polymer was precipitated in methanol/diethyl ether mixture to remove unreacted polystyrenes. We can see unreacted polystyrenes as a second peak after 35 minute (Fig. 4.9).

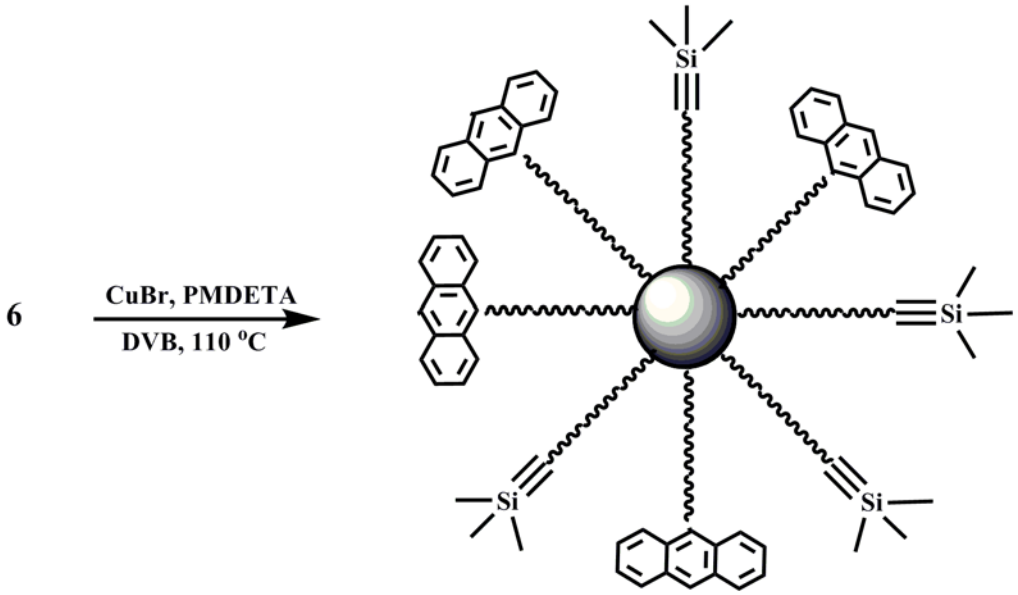

Figure 4.10 : Synthesis of α-silyl protected alkyne- and α-anthracene-end-capped $(PS)_n$-polyDVB multiarm star polymer, before hydrolysis.

Subsequently, this is followed by the hydrolysis of the multi arm star polymer. So, trimethyl silyl and anthracene end functional multi arm star polymer was dissolved and was hydrolyzed by TBAF for 3 hour. And now, our final product is produced with alkyne and anthracene end functionality, **7**.

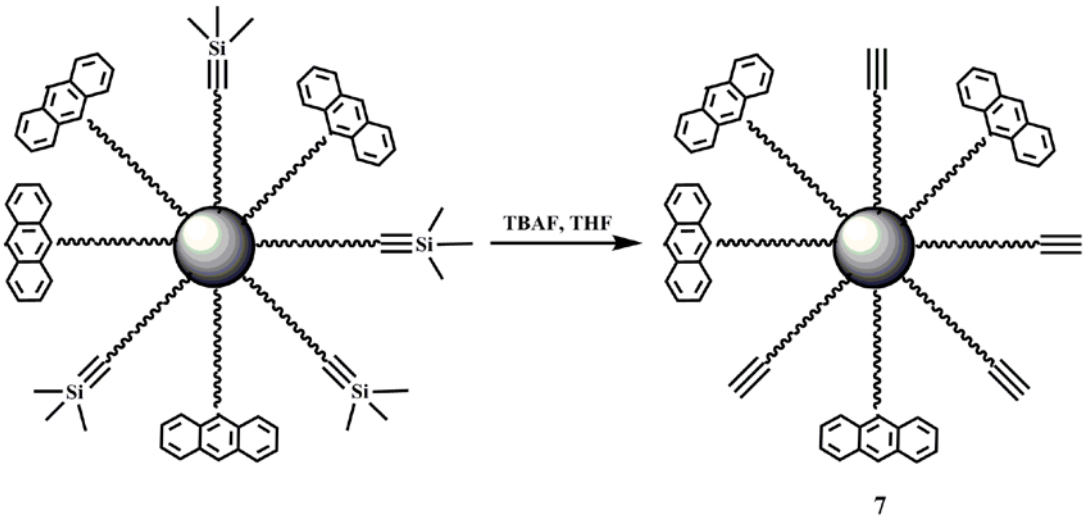

Figure 4.11 : Alkyne and anthracene-end-capped multi arm star polymer, **7**.

And here is the ^{1}H NMR spectrum of multi arm star polymer.

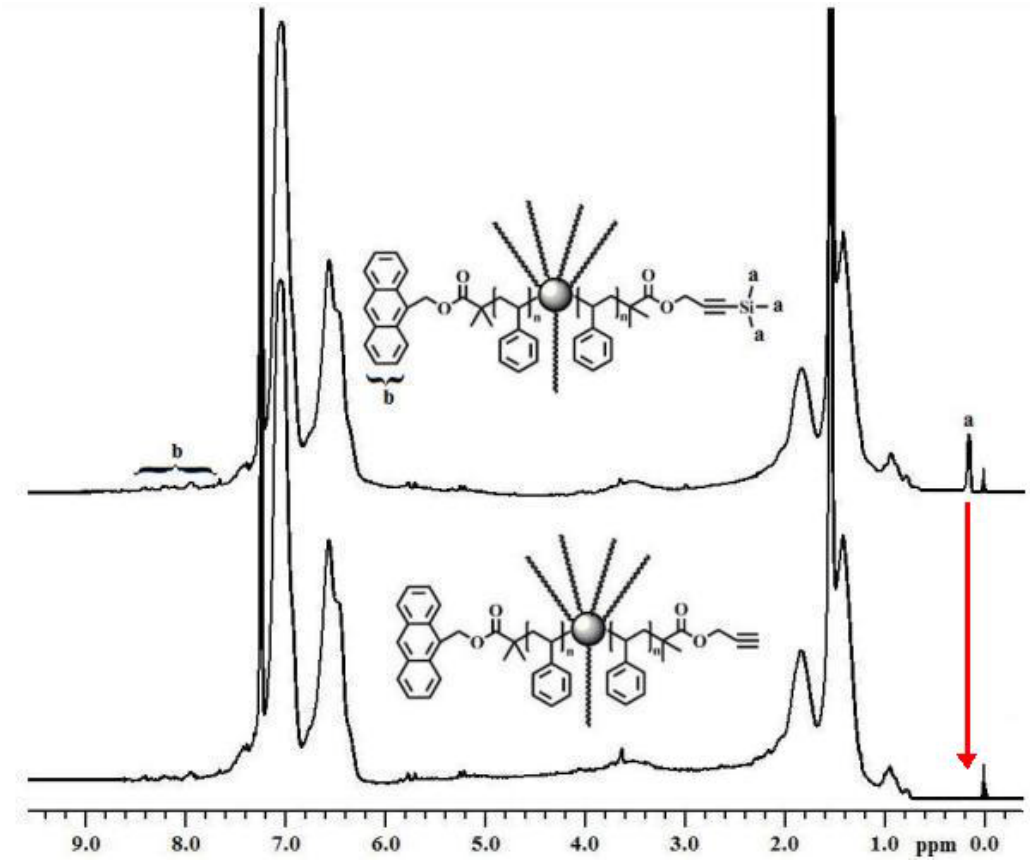

Figure 4.12 : Comparison of the ^{1}H NMR Spectrum of star polymer before and after hydrolysis.

And ^{1}H NMR spectrum showed that our hydrolysis was completely achieved (Figure 4.12). Because before hydrolysis we expected to losing sharp singlet peak of –Si(C*H*$_3$)$_3$ at 0.165 ppm. And ^{1}H NMR spectrum proves that after hydrolysis trimethyl silyl peak is completely. Quantitative yield was also so successful (99%).

4.4. Click Reaction of the Multi Arm Star Polymer, 7, with P*t*BA-N_3

In this case, previously prepared P*t*BA-N_3 was reacted with the star polymer in the presence of the CuBr and PMDETA as catalysts. After precipitation and purification processes first step was completed and the resulted polymer structure was shown in Figure 4.13.

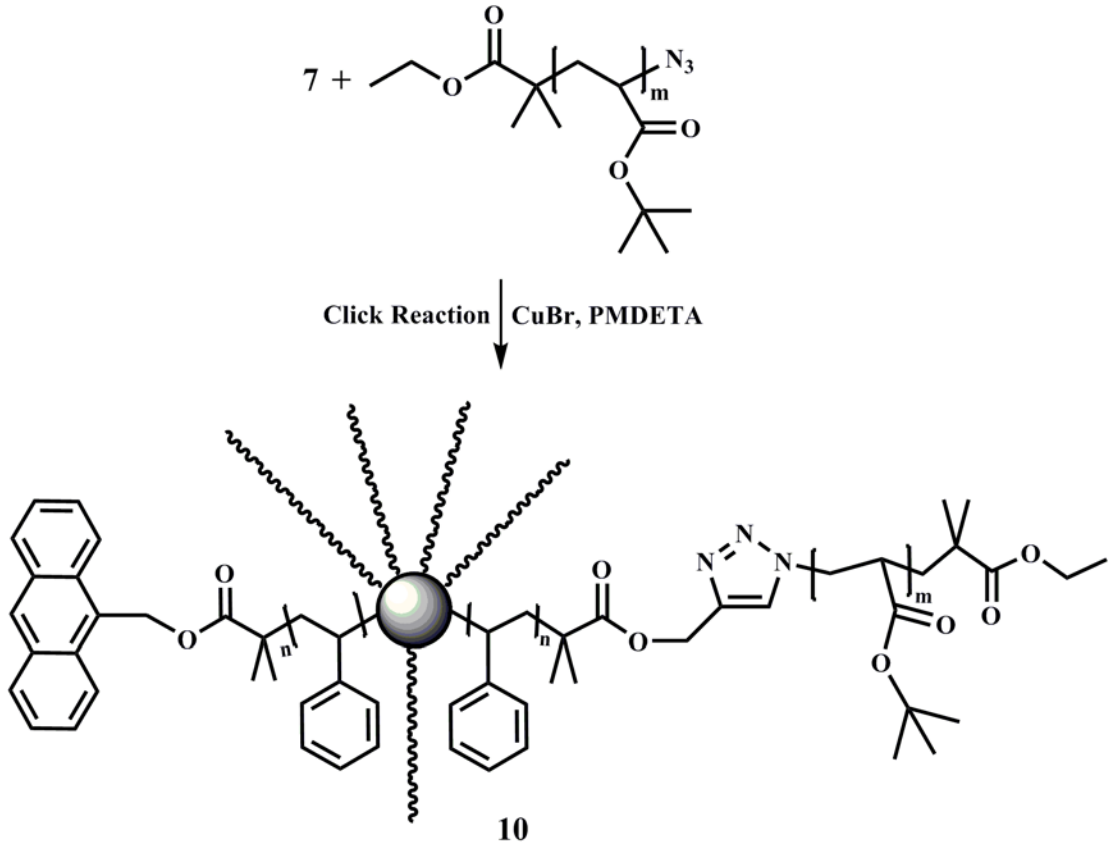

Figure 4.13 : Click reaction of multi arm star polymer, **7**, with **9**.

Table 4.1 : Polymers obtained from the living radical polymerizations.

Polymers	**$[M]_0$ (mol.L^{-1})**	**$[M]_0/[I]_0$**	**Initiator**	**Time (min.)**	**Conv. (%)**	**$M_{n,theo.}$**	**$M_{n,GPC}$[d]**	**$M_{n,NMR}$**	**M_w/M_n**
PS[a]	8.75	200	**1** and **2**	40	23	5100	5400	6030	1.10
P*t*BA-Br[b]	6.86	100	**EIBr**[*]	30	25	3400	3500	5100	1.16
PMMA-MI[c]	9.39	200	**5**	240	56	2800	3900	3000	1.17

[a]$[M]_0:[I]_0$ = 200, $[I]_0$= 0.5 mol **1** + 0.5 mol **2**; polymerization was carried out in bulk at 110 °C.

[b]$[M]_0:[I]_0$: $[PMDETA]_0$: $[CuBr]_0$ = 100:1:1:1; polymerization was carried out in ethylene carbonate at 80 °C.

[c]$[M]_0:[I]_0$: $[PMDETA]_0$: $[CuCl]_0$ = 50:1:1:1; polymerization was carried out in toluene at 40 ^{o}C.

[d]Molecular weigths were calculated according to linear PS standards.

*****Ethyl 2-bromo-2-methylpropanoate.

Also ^{1}H NMR spectra of the resulted polymer, **10**, is shown in Figure 4.14. Before Click reaction at 0.165 ppm there was –Si(C*H*$_3$)$_3$ peak but after the successful hydrolyzation and Click reaction this peak collapsed and lost. So the reaction was completely done. Except the peaks that were arranged in Figure 4.12 there is a new peak forms between 2.1-2.4 ppm which belongs to P*t*BA polymer chain that is just joined to multi arm star polymer. And it is the 9 *H* of ester peak of (CH$_3$)$_3$C-O that is specific to *t*BA unit presented on polymer structure.

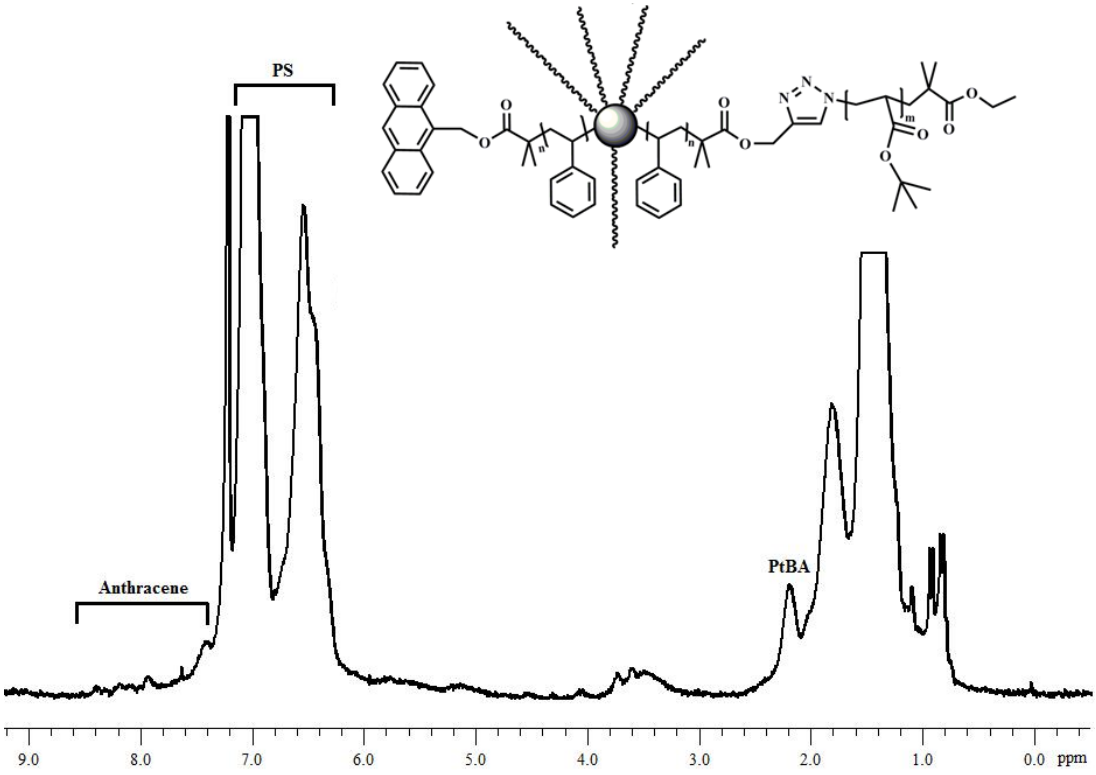

Figure 4.14 : ^{1}H NMR spectrum of **10** in CDCl$_3$.

Also GPC chromatogram showed us that the reaction was completed. Because when reaction finished, we didn't see red line again. On the other hand, blue line was the multi arm star polymer, **7**. So after the click reaction there was a little deviation on the left hand side, which was shown in turquoise blue color and this showed us that there is a little change in the molecular weight of the star polymer. We can understand this by looking retention time of the polymer on GPC chromatogram. **10** comes from the column of GPC before **7**. So its molecular weight is greater than **7**. As a result of this, the reaction was also completed according to the GPC chromatogram (Fig. 4.15). This little change on GPC chromatogram is because results were taken from traditional GPC, according to linear PS standars. So deviation is small. But when the results were taken by TD-SEC, absolute molecular

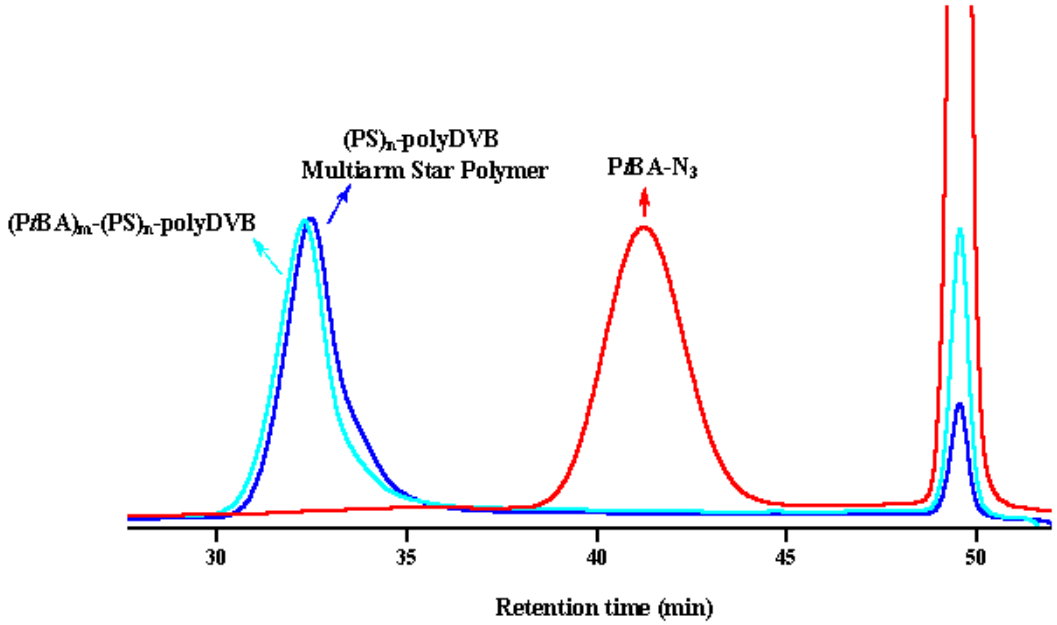

Figure 4.15 : GPC chromatogram of the polymers for comparison of **10**, **7**, and **9** according to their molecular weights.

weights were calculated. This is because of making calculations according to hydrodynamic volume of the star polymers. By this case, deviation is high. These results were anyway given in Table 4.2 which will be discussed later.

4.5. Diels-Alder Click Reaction of the Multi Miktoarm Star Polymer, 10, with PMMA-MI

In the final step of the polymerization, the previously synthesized multi miktoarm star block polymer, **10**, was reacted with the furan protected maleimide end functionalized PMMA (PMMA-MI), **11**, in toluene at reflux temperature for 48 hour in dark. Anthracene functional bearing groups are generally reacted in the dark because anthracene is sensitive to UV light from positions 9 and 10. To prevent anyside reactions reaction was taken place in the dark. By the effect of heat, furan undergoes de-protection and leaves from the maleimide PMMA as a byproduct. Now furan protected maleimide end functionalized PMMA converts to just maleimide end functionalized PMMA. Then anthracene reacts with maleimide to give Diels-Alder click reaction as [4+2] cycloaddition. By this multi miktoarm star block copolymer was obtained. After the precipitation and purification of the multi miktoarm star block copolymer, our final product, **12**, was obtained as reaction scheme shown in Figure 4.16.

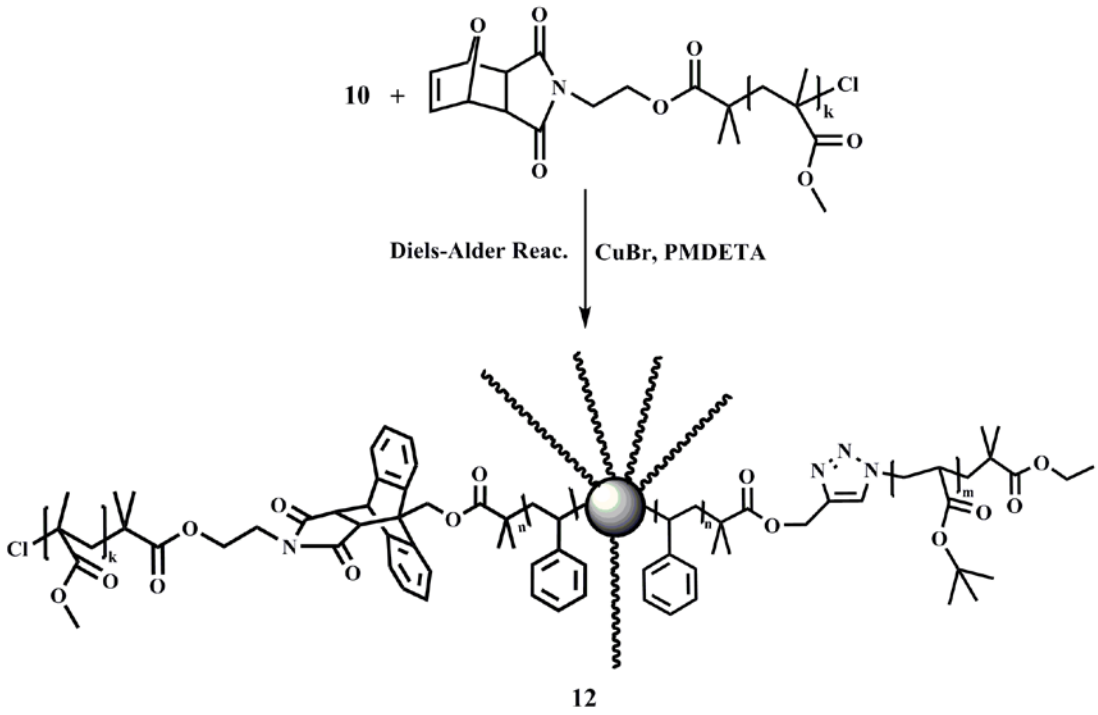

Figure 4.16 : Diels-Alder click reaction of **10** with PMMA-MI.

And ^{1}H NMR spectrum also shows the efficiency of the DA click reaction. After the reaction was completed, we expected to losing sharp peak of anthracene at between 7.96 – 8.41 ppm. This was the evidence of the reaction was carried out succesfully. Figure 4.17 shows ^{1}H NMR spectrum of $(PMMA)_k$-(P*t*BA)$_m$-$(PS)_n$-polyDVB multi miktoarm star block copolymer.

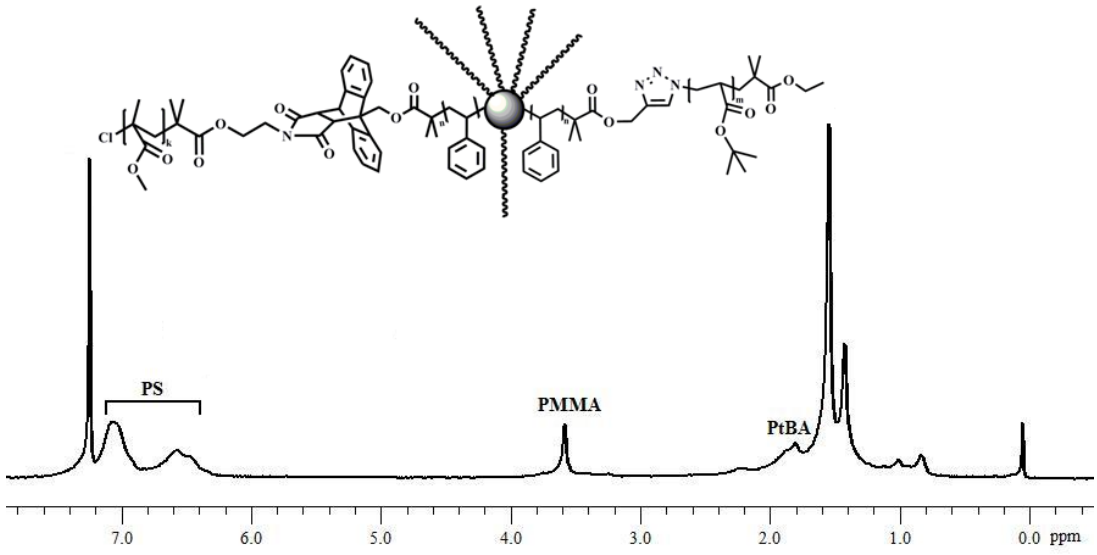

Figure 4.17 : ^{1}H NMR Spectrum of the multi miktoarm star block copolymer, **12**, through double click reactions in $CDCl_3$.

Diels-Alder click reaction efficiency was also monitored by UV spectroscopy after the decrease in absorbance of anthracene between 300 and 400 nm in the reaction medium (Figure 4.18). Diels–Alder efficiency was calculated by following anthracene Conv. % = $(1 - A_t/A_0)$, where A_0 and A_t are initial and final absorbance values of anthracene, respectively. The efficiency was found to be 95%.

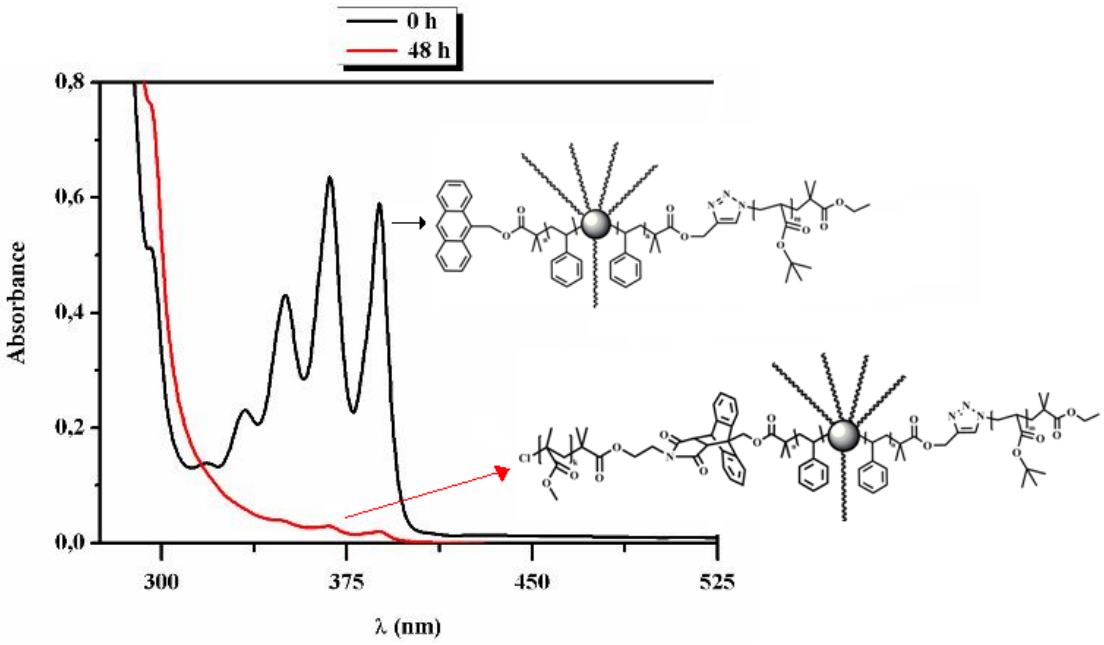

Figure 4.18 : UV spectrum of **10** and **12** in in CH_2Cl_2. *Black Line* is the UV spectrum of **10**. *Red Line* shows UV spectrum of **12** after 48 hour between the reactions of **10** with PMMA-MI, **11**.

The molecular weight values (M_n, M_w, M_p) of all the star polymers were characterized using conventional SEC and Viscotek triple detection SEC (TD-SEC) instruments and the results are given in Table 4.2. The molecular weight values of $(PS)_n$-polyDVB star polymer obtained are given in Table 4.2. It should be noted that there is a discrepancy between the molecular weight values obtained by conventional SEC and TD-SEC. This is expected that because star polymers have more compact structure than linear polymer of equivalent molecular weight and composition resulting in smaller hydrodynamic volume. Thus, apparent molecular weight of star polymers is underestimated by conventional SEC. Refractive index (RI), light scattering (LS) and differential viscometer detectors in TD-SEC instrument provides more advanced and accurate technique to measure the absolute molecular weight of

star polymer, if refractive index increment (dn/dc) value of the analyzed polymer is known. Although, dn/dc value of linear PS is available, an attempt has been made to clarify the effect of cross-linked DVB core on dn/dc value of multi arm PS star polymer. Therefore, the dn/dc of $(PS)_n$-polyDVB was measured by TD-SEC instrument and found to be 0.185 mL/g in THF at 35 °C, which is equal to that of linear PS. The weight average arm number ($\boldsymbol{f}$) of $(PS)_n$-polyDVB star polymer was calculated using the following equation based on the absolute molecular weights (M_w) of multi arm star polymer.

$$f = \frac{WF_{arm} \times M_{w,star}}{M_{w,arm}} = \frac{M_{w,star}}{M_{w,arm} + M_{DVB} \times conv_{DVB} \times [DVB]/[PS]} \quad \textbf{(4.1)}$$

where WF_{arm} is the weight fraction of PS arm in the star polymer, $M_{w,\,star}$ and $M_{w,\,arm}$ are the absolute molecular weights of the $(PS)_n$-polyDVB star and PS arm, respectively, obtained from TD-SEC instrument introducing the predetermined dn/dc value of PS to OmniSEC software, M_{DVB} is the molecular weight of DVB, [DVB]/[PS] is a feed molar ratio of the DVB to PS before cross-linking polymerization. The conversion of DVB ($conv_{DVB}$) was determined by GC. Thus, the weight average arm number ($\boldsymbol{f}$) of per molecule of $(PS)_n$-polyDVB star was calculated to be 33 and listed in Table 4.2. It is generally accepted that the intrinsic viscosity comparison of star polymer and its linear counterpart provides the most convenient method to elucidate the structure of star polymers, where g' is the contraction factor as given in Equation 4.2.

$$g' = [\eta]_{star} / [\eta]_{linear} \; (M = \text{constant}) \quad \textbf{(4.2)}$$

where $[\eta]_{star}$ and $[\eta]_{linear}$ are the intrinsic viscosities of star polymer and the linear polymer with the same molecular weight and the composition, respectively [118]. It is also shown that in regular (equal arm length) star polymers, g' is related with the number of arms, $\boldsymbol{f}$ as follows [116]:

$$\log g' = 0{,}36 - 0{,}8 \log f \quad \textbf{(4.3)}$$

Mark-Houwink-Sakurada (MHS) parameters k and α for linear PS were determined to be 1.44×10^{-4} dL/g and 0.707, respectively, in THF at 35 °C using a series of linear narrow PS standards by TD-SEC. Then, using these parameters $[\eta]_{linear}$ was calculated to have 0.948 dL/g for a specified molecular weight (M_w = 250460) of

linear PS. Moreover, the $[\eta]_{star}$ of $(PS)_n$-polyDVB star polymer was measured to have 0.156 dL/g by viscometer detector in TD-SEC. The number of arms, ***f*** was calculated to be 27 using equations 4.2 and 4.3 and well agreed with that obtained from Equation 4.1. The obtained multi miktoarm $(PMMA)_k$-(P*t*BA)$_m$-$(PS)_n$-polyDVB star block copolymers had higher hydrodynamic volume than that of multi arm anthracene and alkyne end functionalized $(PS)_n$-polyDVB star polymer, which manifested itself in a clear shift to higher molecular weight region. To determine the absolute molecular weight of the multi miktoarm star block copolymers, dn/dc value of the polymer-solvent combination is required. It is shown that dn/dc value correlates linearly with composition of block copolymer in Equation 4.4 [117].

$$(dn/dc)_{block\ copolymer} = x(dn/dc)_{PS} + y(dn/dc)_{PtBA} + z(dn/dc)_{PMMA} \quad \textbf{(4.4)}$$

where *x*, *y* and *z* are weight fractions of PS, P*t*BA and PMMA blocks from ^{1}H NMR according to the backbone protons. The weight fractions of PS and P*t*BA blocks in (P*t*BA)$_m$-$(PS)_n$-polyDVB are determined to be 0.715 and 0.385, respectively. For $(PMMA)_k$-(P*t*BA)$_m$-$(PS)_n$-polyDVB, 0.12, 0.25 and 0.63 were found, respectively. Using Eqution 4.4, dn/dc values are derived to have 0.150 and 0.137 mL/g for (P*t*BA)$_m$-$(PS)_n$-polyDVB and $(PMMA)_k$-(P*t*BA)$_m$-$(PS)_n$-polyDVB multi miktoarm star block copolymers. Therefore, the absolute molecular weights and hydrodynamic radius (*Rh*) of the multiarm star block copolymers are obtained from TD-SEC instrument introducing the above dn/dc values into Omnisec software (Table 4.2). Again the molecular weights of multi miktoarm star block copolymers are inconsistent with those from conventional SEC because of the hydrodynamic volume difference between multi arm star block copolymers and linear PS standards. This methodology affords the molecular weight of multi arm star block copolymers up to around 800,000 without any star-star coupling reaction. All datas were given in Table 4.2.

Table 4.2 : The characterization of multiarm star and multi miktoarm star block copolymers.

Polymers	SEC[b]				TD-SEC[c]								
	M_n (g/mol)	M_w (g/mol)	M_p (g/mol)	M_w/M_n	M_n (g/mol)	M_w (g/mol)	M_p (g/mol)	$[\eta]$ (dL/g)	Rh (nm)	dn/dc (mL/g)	g'	f[d]	f[e]
$(PS)_n$-polyDVB[a]	62600	80600	76000	1.28	193800	250460	210270	0.155	8.28	0.185	0.166	33	27
$(PtBA)_m$-$(PS)_n$-PolyDVB	74430	98560	88700	1.32	282520	354740	279500	0.142	9.03	0.150[f]	-	-	-
$(PMMA)_k$-$(PtBA)_m$-$(PS)_n$-PolyDVB	86770	111900	95300	1.29	311630	406600	310160	0.177	10.1	0.137[f]	-	-	-

[a] [DVB]/15 = [**6**] = [CuBr] = [PMDETA] = 0.023 M in anisole at 110 °C.

[b]Calibrated on the basis of linear PS standards in THF at 30 °C.

[c]Calibrated on the basis of linear PS standards in THF at 35 °C.

[d]Number of arms in multi arm star polymer, calculated according to Equation 4.1.

[e]Calculated according to Equation 4.2 and 4.3.

[f]Calculated according to Equation 4.4.

On the other hand, our other evidence was GPC chromatogram which showed us that the reaction was completed. Because when reaction finished, we didn't see blue line again. On the other hand, turquoise blue colored line was **10**. So after the Diels-Alder click reaction by looking at the retention times, there was a little deviation on the left hand side, which was shown red color, and this showed us that there is a little change in the molecular weight of the multi miktoarm star block copolymer. The change in the molecular weight of the multi miktoarm star block copolymer, **10**, is the proof of the achievement of the reaction. Because new polymer chain PMMA is joined to multi miktoarm star block copolymer. If that was not the case, so no change in the molecular weight of **10** would be observed. The reason for the little deviation is the same as previously described in GPC chromatogram of **10.** As a result of this, the reaction was also completed according to the GPC chromatogram.

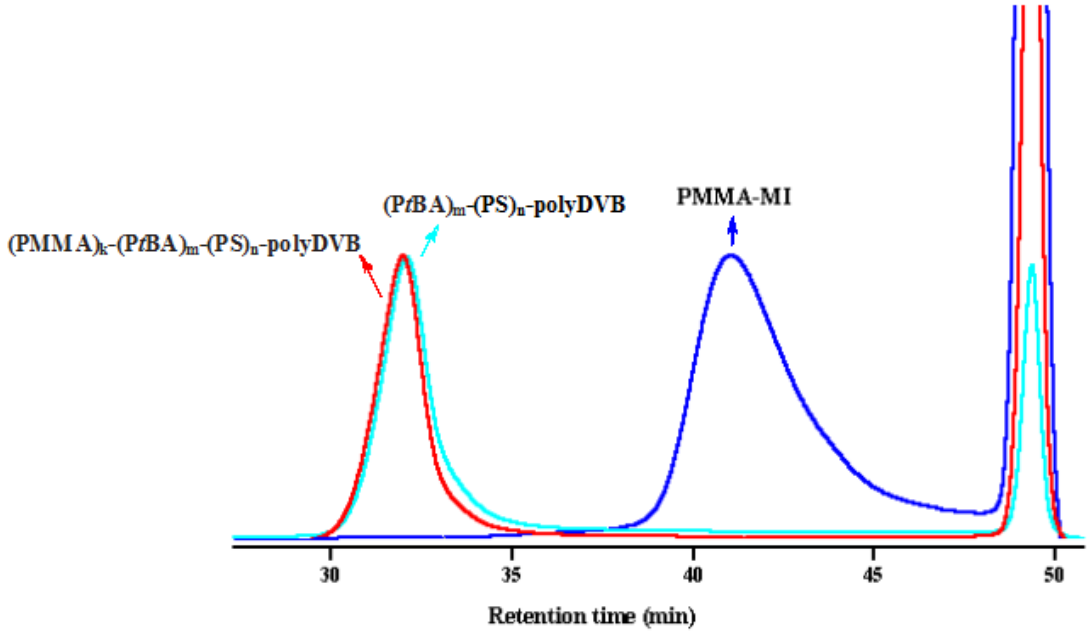

Figure 4.19 : GPC chromatogram of the polymers for comparison of **12**, **10**, and **11** according to their molecular weights.

Finally, we can show schematically all the steps of the synthesis of the multi miktoarm star block copolymer as shown in Figure 4.20. It also gives brief visual informations about arrangement order of the reactions. The means of the symbols are also given. In conclusion, our main goal from these syntheses was to synthesize multi miktoarm star block copolymer through Double Click reactions which were "Click" and Diels-Alder Click reactions.

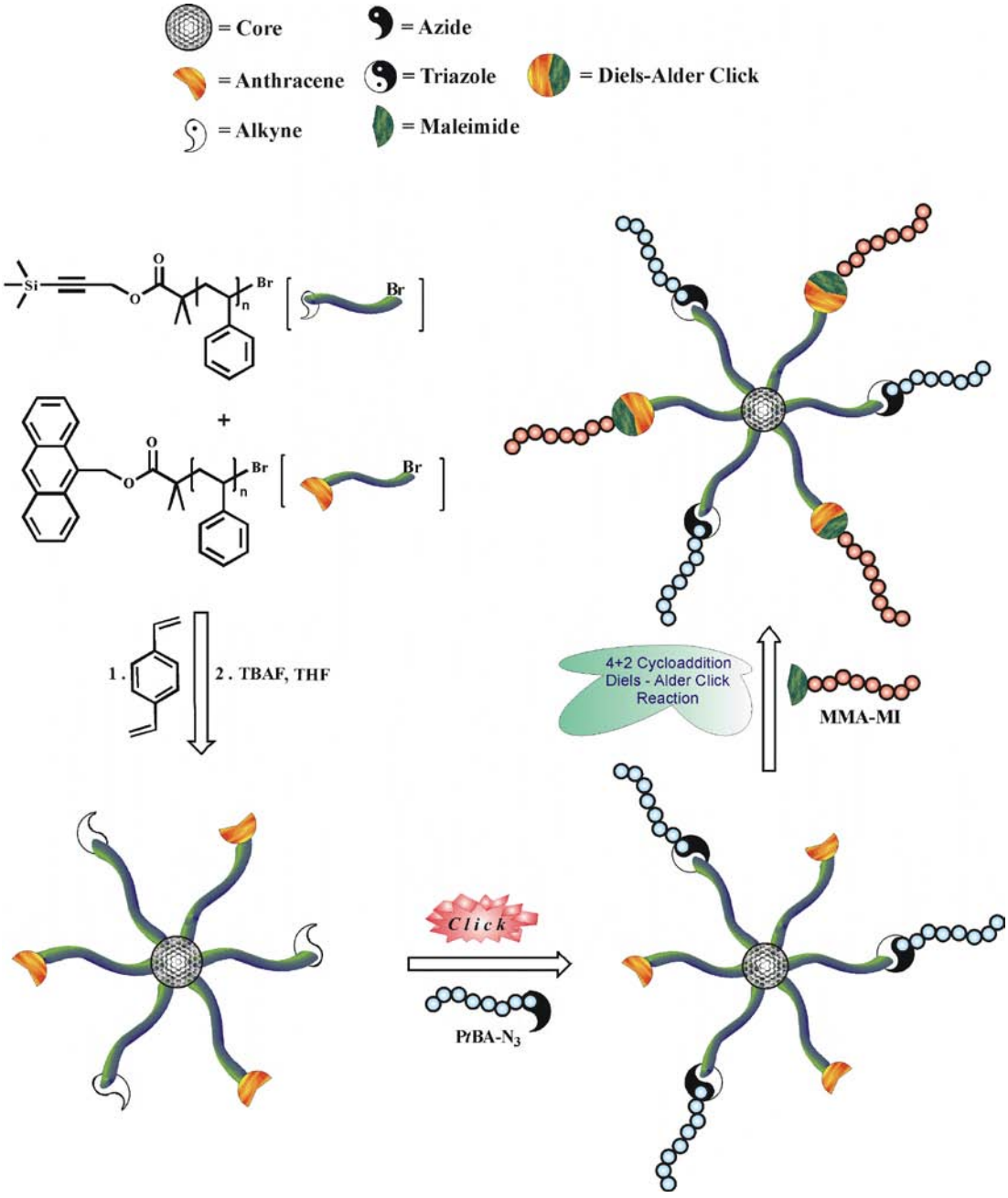

Figure 4.20 : Schematic presentation of synthesis of multi miktoarm star block copolymer through double click reactions.

5. CONCLUSION

In conclusion, a combination of the cross-linking, highly efficient Click and Diels–Alder click reactions are employed for the preparation of well-defined $(PMMA)_k$-$(PtBA)_m$-$(PS)_n$-polyDVB multi miktoarm star block copolymers based on ‘‘arm-first’’ methodology.

Firstly, by using double initiator, well defined PS is synthesized by ATRP method. In this synthesis both of the initiators **1** and **2** are added in equal moles. This is the one of the new experiment that has not been done before. The PDI we obtained by this method is also very low. After cross-linking reaction of PS, the average number of arms of $(PS)_n$-polyDVB multi arm star polymer, **7**, is found to be 33 using the given calculation methods. This result gives a proof for the well-defined structure and low degree of heterogeneity of the multi arm star polymer. Moreover by this method, we now combine two different functional group bearing arms into a one core by arm first method. This olaso is another innovation in multi miktoarm star block copolymer synthesis. This is followed by the synthesis and azidation of well defined P*t*BA, **9**, and synthesis of well defined maleimide end functionalized PMMA, **11**, for application of synthesis of multi miktoarm star block copolymers. So hydrolyzed multi arm star polymer, **7**, is firstly reacted with **9** by click reaction and secondly the resulted polymer, **10**, is reacted with **11** by Diels-Alder click reaction. Click and Diels-Alder click reaction enable us to introduce the second block with precisely controlled in chain length into the multi arm star polymer for the preparation of multi miktoarm star block copolymers.

In all steps the structures of well defined polymers and their molecular weights are proved by GPC, NMR and UV instruments. In every step, GPC and NMR are used. To follow the final action UV is used. By the collapse of the peaks the efficiency of the reaction is documented.

As a consequence, this study bears an important role in science world that a new route is followed by polymerizing arms of the star using two different initiators at the

same time and in the same reaction medium. Furthermore of this, two different functionality is brought to the ends of arms of multi arm star polymer. The most important parameter is that arms of multi miktoarm star polymer are initiated by equal amount of initiator and the resulted arms bear 47% anthracene functionality and 53% alkyne functionality. And this is what we expect. So by using Double Click reactions and a combination of ATRP method presents a versatile synthetic approach for obtaining well-defined miktoarm star polymers.

REFERENCES

[1] **Roovers, J.,** 1998. In Star and Hyperbranched Polymers; Mishra, M.; Kobayashi, K. S.; Eds. Marcel Dekker: New York, 285.

[2] **Matyjaszewski, K., Davis, T. P.,** 2002. Edds. *Handbook of Radical Polymerization*, Wiley: Hoboken, NJ.

[3] **Matyjaszewski, K.,** 2006. Ed. *Controlled/Living Radical Polymerization From Synthesis to Materials*; ACS Symposium Series No. 944; American Chemical Society: Washington, DC.

[4] **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.

[5] **Gao, H., Matyjaszewski, K.,** 2006. Synthesis of Star Polymers by a Combination of ATRP and "Click" Coupling Method, *Macromolecules*, **39**, 4960-4965.

[6] **Matyjaszewski, K., Gaynor, S.G.,** 2000**.** *In Applied Polymer Science*, p. 929 Craver, C. D., Carraher C. E., eds., Pergamon Press, Oxford.

[7] **Wang, J. S.; Matyjaszewski, K.,** 1995. Controlled/"Living" radical polymerization, atom radical polymerization in the presence of transition–metal complexes, *J. Am. Chem. Soc.*, **117**, 5614-5615.

[8] **Coessens, V.; Pintauer, T.; Matyjaszewski, K.,** 2001. Functional polymers by atom transfer radical polymerization, *Prog. Polym. Sci.*, **26**, 337-377.

[9] **Manetsch, R.; Krasinski, A.; Radic, Z.; Raushel, J.; Taylor, P.; Sharpless, K. B.; Kolb, H. C.,** 2004. In Situ Click Chemistry: Enzyme Inhibitors Made to Their Own Specifications, *J. Am. Chem. Soc.*, **126**, 12809-12818.

[10] **Huisgen, R.,** 1963. 1,3-Dipolar Cycloadditions. Past Future, *Angew. Chem., Int. Ed. Engl.*, **2**, 565-598.

[11] **Diaz, D. D.; Punna, S.; Holzer, P.; McPherson, A. K.; Sharpless, K. B.; Fokin, V. V.; Finn, M. G.,** 2004. Click Chemistry in Material Synthesis. 1. Adhsive Polymers from Copper-Catalyzed Azide-Alkyne Cycloaddition, *J Polym Sci Part A: Polym. Chem.*, **42**, 4392-4403.

[12] **Tornoe, C. W.; Christensen, C.; Meldal, M.,** 2002. Peptidotriazoles on Solid Phase: [1,2,3]-Triazoles by Regiospecific Copper(I)-Catalyzed 1,3-Dipolar Cycloadditions of Terminal Alkynes to Azides, *J. Org. Chem.*, **67**, 3057.

[13] **Diels, O.; Alder K.,** 1928**.** "Synthesen in der hydroaromatischen Reihe". *Justus Liebig's Annalen der Chemie*, **460**, 98-122.

[14] **Diels, O.; Alder, K.,** 1929**.** Synthesis in the hydroaromatic series, IV. Announcement: The rearrangement of malein acid anhydride on arylated diene, triene and fulvene, *Chem. Macromol. Symp*., Ber., **62**, 2081& 2087.

[15] **Kloeetzel, M. C.,** 1948**.** Organic Reactions, *Chemical Review*, **4**, 1-59.

[16] **Holmes, H. L.,** 1948**.** Organic Reactions, *Chemical Review*, **4**, 60-173.

[17] **Kagan, H. B.; Riant,** 1992. "Catalytic asymmetric Diels Alder reactions", *Chemical Reviews* 92 (5): 1007-1019.

[18] **Nicolaou, K. C.; Snyder, S. A.; Montagnon, T., Vassilikogiannakis, G.,** 2002. *"The Diels-Alder Reaction in Total Synthesis"*, Angew. Chem. Int. Ed. 2002, **41**, 1668-1698.

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

[20] **Nielsen, L. E.,** 1974. Mechanical Properties of Polymers and Composites, J. Macromol. Sci., chapter 5, **2**, Marcel Dekker: New York.

[21] **Szwarc, M.,** 1956. Block copolymers, *Nature*, **178**, 1168-1169.

[22] **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**, 359-360.

[23] **Matyjaszewski, K. and Lin, C. H.,** 1991. Naming of controlled, living polymerizations, *Makromol. Chem. Macromolecules Symp.*, **47**, 221-237.

[24] **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**, 1253-1266.

[25] **Matyjaszewski, K. and Müler, A. H. E.,** 1997. AHE naming of controlled, living, and "living" polymerizations, *Polym. Prepr*. **38 (1)**, 6-9.

[26] **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**, 5614-5615.

[27] **Matyjaszewski, K. and Sigwalt, P.,** 1994. Unified approach to living and non-living cationic polymerization of alkenes, *Polym. Int.* **35**, 1-26.

[28] **Durmaz, H., Dag, A., Hizal, A., Hizal, G., and Tunca, U.** 2009. One-Pot Synthesis of Star-Block Copolymers Using Double Click Reactions, *J. Polym Sci, Part A Polym. Chem. Ed.*, **46**, 7091-7100.

[29] **Hawker,** 1994. Molecular weight control by a "living" free-radical polymerization process, *C. J. J Am Chem Soc*, **116**, 11185-11186.

[30] **Odian,** 1991. G. Principles of polymerization, p 8, *John Wiley Sons Inc*, New York.

[31] **Fischer,** 1999. The persistent radical effect in controlled radical polymerizations, *H. J Polym Sci Part A: Polym Chem*, **37**, 1885-1901.

[32] **Andrea, R. S., Michael, K. G.,** 2004. Aqueous stable free radical polymerization process, *Journal of Polymer Science*, **22 (4)**, 309-312.

[33] **Marque,** 2003. Influence of the nitroxide structure on the homolysis rate constant of alkoxyamines: A taft-ingold analysis, *S. J Org Chem*, **68**, 7582-7590.

[34] **Hawker, C. J.; Bosman, A. W.,** 2001. New polymer synthesis by nitroxide mediated living radical polymerizations, *Harth, E. Chem Rev*, **101**, 3661-3688.

[35] **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 acrylic-phosphonylated nitroxide, *J. Am. Chem. Soc.*, **122**, 5929-5939.

[36] **Harth, E.; Hawker, C. J.; Fan, W.; Waymouth,** 2001. Chain end functionalization in nitroxide mediated "living" free radical polymerizations, *R. M. Macromolecules*, **34**, 3856-3862.

[37] **Grimaud, T.; Matyjaszewski, K.,** 1997. Controlled/"Living" radical polymerization of methyl metacrylate by atom transfer radical polymerization, *Macromolecules*, **30**, 2216.

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

[39] **Fischer, H.,** 1999. The persistent radical effect in controlled radical polymerizations, *J. Polym. Sci.*; *Part A*: *Polym. Chem.*, **37**, 1885-1901.

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

[41] **Youqing Shen, Huadong Tang,** 2004. Catalyst separation in atom transfer radical polymerization, *J. Am. Chem. Soc.*, **126**, 13908-13909.

[42] **Matyjaszewski, K.; Xia, J.,** 2001. Atom transfer radical polymerization, *Chem. Rev.*, **101**, 2921-2990.

[43] **Xia, J.; Matyjaszewski, K.,** 1997. Controlled/"Living" radical polymerization. Atom transfer radical polymerization using multidentate amine ligands, *Macromolecules*, **30**, 7697-7700.

[44] **Hamley, I. W.,** 1998. The Physics of block copolymers, *Oxford University Press*, Oxford.

[45] **a) Haddleton, D. M.; Topping, C.; Hastings, J. J.; Suddaby, K. G.,** 1996. Cobalt(II) in catalytic chain transfer polymerization (CCTP), *Macromeolecules*, **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**, 2071-2074.

[46] **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.

[47] **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 LivingRadical Polymerization, *J. Am. Chem. Soc.*, **128**, 4823-4830.

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

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

[50] **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.

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

[52] **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.

[53] **Hotha, S.; Anegundi, R. ; 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.

[54] **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.

[55] **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 Chemsitry, *J. Am. Chem. Soc.*, **128**, 6564-6565.

[56] **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.

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

[58] **Coessens, V., Matyjaszewski, K.,** 1999. End group transformation of polymers prepared by ATRP, substitution to azides, *J. M. S. – Pure Appl. Chem.*, **36**, 667-679.

[59] **Molten, G.; Buttero, P. D.,** 2005. 1,3-Dipolar cycloadditions of MeOPEG-bounded azides, *Tetrahedron*, **61**, 4983-4987.

[60] **Pindur, U.; Lutz, G.; Otto, C.,** 1993. *Chemical Review*, **93** , 741–761.

[61] **Yli-Kauhaluoma, J. T.; Ashley, C.; Lo H.; Tucker, L.; Wolfe, M. M.; Janda, K. D.,** 1995. *J. Am. Chem. Soc.*, **117**, 7041-7047.

[62] **Vaughan, W. R.; Andersen, K. S.;** 1956. *J. Org. Chem.*, **21**, 673-683.

[63] **Atherton, J. C. C.; Jones S.,** 2003**.** Diels-Alder Reactions of Anthracene, 9-Substituted Anthracenes and 9,10-Disubstituted Anthracenes, *Tetrahedron*, **59**, 9039-9057.

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

[65] **Roovers, J. E. L.,** 1985. Branched Polymers, *Encyclopedia of Polymer Science and Engineering*; Wiley, New York.

[66] **Eschwey, H., Hallensleben, M. L., and Burchard, W.,** 1973. Preparation and Some Properties of Star-Shaped Polymers with more than Hundred Side Chains, *Makromol. Chem.*, **173 (1),** 235-239.

[67] **Cloutet, E., Fillaut, J., Gnanou, Y., and Astruc, D.,** 1994. Hexaarm Star-Shaped Polystyrenes by Core-First Method, *J. Chem. Soc., Chem Commun.*, **21**, 2433-2434.

[68] **Shohi, H., Sawamoto, M., and Higashimura, T.,** 1991. Tri-Armed Star Polymers by Living Cationic Polymerization. 1. Trifunctional Initiators for Living Polymerization of isobutyl vinyl ether, *Macromolecules,* **24 (17),** 4926-4931.

[69] **Angot, S., Taton, D., and Gnanou, Y.,** 2000. Amphiphilic Stars and Dendrimer-Like Architectures Based on Poly(ethylene oxide) and Polystyrene, *Macromolecules,* **33 (15),** 5418-5426.

[70] **Roovers, J., Zhou, L. L., Toporowski, P. M., Zwan, M., Iatrou, H., and Hadjichristidis N.,** 1993. Regular Star Polymers with 64 and 128 Arms. Models For Polymeric Micelles, *Macromolecules,* **26 (16),** 4324-4331.

[71] **Sunder, A., Krämer, M., Hanselmann, R., Mülhaupt, R., and Frey, H.,** 1999. Molecular Nanocapsules Based on Amphiphilic Hyperbranched Polyglycerols, *Angew. Chem. Int. Ed.,* **38 (23),** 3552-3555.

[72] **Claesson, H., Malstrom, E., Johansson, M., and Hult, A.,** 2002. Synthesis and Characterisation of Star Branched Polyesters with Dendritic Cores and The Effect of Structural Variations on Zero Shear Rate Viscosity, *Polymer,* **43 (12),** 3511-3518.

[73] **Gauthier, M., Tichagwa, L., Downey, J., and Gao, S.,** 1996. Arborescent Graft Copolymers: Highly Branched Macromolecules with a Core-Shell Morphology, *Macromolecules,* **29 (2),** 519-527.

[74] **Kanaoka, S., Omura. T., Sawamoto, M., and Higashimura, T.,** 1992. Star-Shaped Polymers by Living Cationic Polymerization. 3. Synthesis of Heteroarm Amphiphilic Star-Shaped Polymers of Vinyl Ethers with Hydroxyl or Carboxyl Pendant Groups, *Macromolecules,* **25 (24),** 6407-6413.

[75] **Okay, O., and Funke, W.,** 1990. Anionic Dispersion Polymerization of 1,4-divinylbenzene, *Macromolecules,* **23 (10),** 2623-2628.

[76] **Hadjichristidis, N., Pitsikalis, M., Pispas, S. and Iatrou, H.,** 2001. Polymers with Complex Architecture by Living Anionic Polymerization, *Chem. Rev.,* **101 (12),** 3747-3792.

[77] **Hadjichristidis, N.,** 1999**.** Synthesis of Miktoarm Star (μ-Star) Polymers, *J. Polym. Sci., Part A. Polym Chem.,* **37 (7),** 857-871.

[78] **Hadjichristidis, N., Pispas, S., Pitsikalis, M., Iatrou, H. and Vlahos, C.,** 1999. Asymmetric Star Polymers: Synthesis and Properties, *Adv. Polym. Sci.,* **142,** 71-127.

[79] **Schaefgen, J. R., Flory, P. J.,** 1948. Synthesis of Multichain Polymers and Investigation of their Viscosities, *J. Am. Chem. Soc.,* **70 (8),** 2709-2718.

[80] **Hsieh, H. L. and Quirk, R. P.** 1996. Star Polymers, in**,** *Anionic Polymerization, Principles and Practical Applications,* Marcel Dekker, New York, 333-368.

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

[82] **Nguyen, A. B., Hadjichristidis, N., and Fetters, L. J.,** 1986. Static Light Scattering Study of High-Molecular Weight 18-Arm Star Block Copolymers, *Macromolecules,* **19 (3),** 768-773.

[83] **Alward, D. B., Kinning, D. J., Thomas, E. L., and Fetters, L. J.,** 1986. Effect of Arm Number and Arm Molecular Weight on the Solid-State Morphology of Poly(styrene-isoprene) Star Block Copolymers, *Macromolecules,* **19 (1),** 215-224.

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

[85] **Matyjaszewski, K. and Xia, J.,** 2001. Atom Transfer Radical Polymerization, *Chem. Rev.,* **101 (9),** 2921-2990.

[86] **Kamigaito, M., Ando, T., and Sawamoto, M.,** 2001. Metal-Catalyzed Living Radical Polymerization, *Chem. Rev.,* **101 (12),** 3689-3745.

[87] **Hawker, C. J., Bosman, A.W., and Harth, E.,** 2001. New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations, *Chem. Rev.,* **101 (12),** 3661-3688.

[88] **Chiefari, J., Chong, Y. K., Ercole, F., Krstina, J., Jeffery, J., Le, T. P. T., Mayadunne, R. T. A., Meijs, G. F., Moad, C. L., Moad, G., Rizzardo, E., and Thang, S. H.,** 1998. Living Free-Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer: The RAFT Process, *Macromolecules,* **31 (16),** 5559-5562.

[89] **Chong, Y.K., Le, T.P.T., Moad, G., Rizzardo, E., and Thang, S.H.,** 1999. A More Versatile Route to Block Copolymers and Other Polymers of Complex Architecture by Living Radical Polymerization: The RAFT Process, *Macromolecules,* **32 (8),** 2071-2074.

[90] **Glaied, O., Delaite, C. and Dumas, P.,** 2006. Synthesis of A_2B Star Block Copolymers from a Heterotrifunctional Initiator, *J. Polym. Sci., Part A. Polym. Chem.,* **44 (6),** 1796-1806.

[91] **Tsoukatos, T., Pispas, S., and Hadjichristidis, N.,** 2001. Star-Branched Polystyrenes by Nitroxide Living Free-Radical Polymerization, *J. Polym. Sci. Part A. Polym. Chem.,* **39 (2),** 320-325.

[92] **Bosman, A.W., Vestberg, R., Heumann, A., Fréchet J. M. J., and Hawker, C.J.,** 2003. A Modular Approach toward Functionalized three-Dimensional macromolecules: From Synthetic Concepts to Practical Applications, *J. Am. Chem. Soc.,* **125 (3),** 715-728.

[93] **Bosman, A. W., Heumann, A., Klaerner, G., Benoit, D., Fréchet, J. M. J., and Hawker, C. J.,** 2001. High-Throughput Synthesis of Nanoscale Materials: Structural Optimization of Functionalized One-Step Star Polymers, *J. Am. Chem. Soc.,* **123 (26),** 6461-6462.

[94] **Baek, K.Y., Kamigaito, M., and Sawamoto, M.,** 2001. Star-Shaped Polymers by Metal-Catalyzed Living Radical Polymerization. 1. Design of Ru(II)-Based Systems and Divinyl Linking Agents, *Macromolecules* **34 (2),** 215-221.

[95] **Baek, K. Y., Kamigaito, M., and Sawamoto, M.,** 2001. Core-Functionalized Star Polymers by Transition Metal-Catalyzed Living Radical Polymerization. 1. Synthesis and Characterization of Star Polymers with PMMA Arms and Amide Cores, *Macromolecules* **34 (22),** 7629-7635.

[96] **Baek, K. Y., Kamigaito, M., Sawamoto, M.,** 2002. Core-Functionalized Star Polymers by Transition Metal-Catalyzed Living Radical Polymerization. 2. Selective Interaction with Protic Guests via Core Functionalities, *Macromolecules* **35 (5),** 1493-498.

[97] **Baek, K.Y., Kamigaito, M., and Sawamoto, M.,** 2002. Synthesis of star-shaped copolymers with methyl methacrylate and *n*-butyl methacrylate by metal-catalyzed living radical polymerization: Block and random copolymer arms and microgel cores, *J. Polym. Sci., Part A. Polym. Chem.,* **40 (5),** 633-641.

[98] **Baek, K.Y., Kamigaito, M., and Sawamoto, M.,** 2002. Star Poly(methyl methacrylate) with End-Functionalized Arm Chains by Ruthenium-Catalyzed Living Radical Polymerization, *J. Polym. Sci., Part A. Polym. Chem.,* **40 (12),** 1972-1982.

[99] **Baek, K.Y., Kamigaito, M., and Sawamoto, M.,** 2002. Star-Shaped Polymers by Ru(II)-Catalyzed Living Radical Polymerization. II. Effective Reaction Conditions and Characterization by Multi-Angle Laser Light Scattering/Size Exclusion Chromatography and Small-Angle X-Ray Scattering, *J. Polym. Sci., Part A. Polym. Chem.,* **40 (14),** 2245-2255.

[100] **Xia, J., Zhang, X., and Matyjaszewski, K.,** 1999. Synthesis of Star-Shaped Polystyrene by Atom Transfer Radical Polymerization Using an "Arm First" Approach, *Macromolecules,* **32 (13),** 4482-4484.

[101] **Zhang, X., Xia, J., and Matyjaszewski, K.,** 2000. End-Functional Poly(*tert*-butyl acrylate) Star Polymers by Controlled Radical Polymerization, *Macromolecules,* **33 (7),** 2340-2345.

[102] **Zheng, G., and Pan, C.,** 2005. Preparation of Star Polymers Based on Polystyrene or Poly(styrene-*b*-*N*-isopropyl acrylamide) and Divinylbenzene via Reversible Addition-Fragmentation Chain Transfer Polymerization, *Polymer,* **46 (8),** 2802-2810.

[103] **Francis, R., Lepoittevin, B., Taton, D., and Gnanou, Y.,** 2002. Toward an Easy Access to Asymmetric Stars and Miktoarm Stars by Atom Transfer Radical Polymerization, *Macromolecules,* **35 (24),** 9001-9008.

[104] **Matyjaszewski, K.,** 2003. The Synthesis of Functional Star Copolymers as an Illustration of the Importance of Controlling Polymer Structures in the Design of New Materials, *Polym. Int.* **52 (10),** 1559-1565.

[105] **Du, J., and Chen, Y.,** 2004. PCL Star Polymer, PCL-PS Heteroarm Star Polymer by ATRP, and Core-Carboxylated PS Star Polymer Thereof, *Macromolecules,* **37 (10),** 3588-3594.

[106] **Du J, and Chen Y.,** 2004. Preparation of Poly(ethylene oxide) Star Polymers and Poly(ethylene oxide)-Polystyrene Heteroarm Star Polymers by Atom Transfer Radical Polymerization, *J. Polym. Sci., Part A. Polym. Chem.,* **42 (9),** 2263-2271.

[107] **Wu, Y., Shi, Y., and Fu, Z.,** 2005. Synthesis of Heteroarm Star-Shaped $(Polystyrene)_n$–$[Poly(ethyl\ acrylate)]_m$ via Atom Transfer Radical Polymerization, *Polymer,* **46 (26),** 12722–12728.

[108] **Heise, A., Trollsås, M., Magbitang, T., Hedrick, J. L., Frank, C.W., and Miller, R.D.,** 2001. Star Polymers with Alternating Arms from Miktofunctional μ-Initiators Using Consecutive Atom Transfer Radical Polymerization and Ring-Opening Polymerization, *Macromolecules,* **34 (9),** 2798-2804.

[109] **Erdogan, T., Ozyurek, Z., Hizal, G., and Tunca, U.** 2004. Facile Synthesis of AB_2-Type Miktoarm Star Polymers through the Combination of Atom Transfer Radical Polymerization and Ring-Opening Polymerization, *J. Polym. Sci., Part A. Polym. Chem.,* **42 (10),** 2313-2320.

[110] **Celik, C., Hizal, G., and Tunca, U.,** 2003. Synthesis of Miktoarm Star Block Copolymers via a Combination of Atom Transfer Radical polymerization and Stable Free-Radical Polymerization, *J. Polym. Sci., Part A. Polym. Chem.,* **41 (16),** 2542-2548.

[111] **Durmaz, H., Karatas, F., Hızal, G., and Tunca, U.,** 2006. Preparation of ABC Miktoarm Star Terpolymer Containing Poly(ethylene glycol), Polystyrene, and Poly(*tert*-butylacrylate) Arms by Combining Diels–Alder Reaction, Atom Transfer Radical, and Stable Free Radical Polymerization Routes, *J. Polym. Sci., Part A. Polym. Chem.,* **44 (1),** 499-509.

[112] **Erdogan, T., Gungor, E., Durmaz, H. Hizal, G. and Tunca, U.,** 2006. Photoresponsive Poly(methyl methacrylate)$_2$–(Polystyrene)$_2$ Miktoarm Star Copolymer Containing an Azobenzene Moiety at the Core, *J. Polym. Sci., Part A. Polym. Chem.,* **44 (4),** 1396–1403.

[113] **Erdogan, M.; Hızal, G.; Tunca, U.; Hayrabetyan, D.; Pekcan, O.,** 2002. Molecular Weight Effect on Sweling of Polymer Gels in Homopolymer Solution; A Fluorescence Study, *Polymer Com.*, **43**, 1925.

[114] **Opsteen, J. A.; Van Hest, J. C. M.,** 2005. Modular synthesis of block copolymers via cycloaddition of terminal azide and alkyne functionalized polymers, *Chem. Commun*., **1**, 57-59.

[115] **Mantovani, G.; Lecolley, F.; Tao, L.; Haddleton, D. M.; Clerx, J.; Cornellisen, J. J. L. M.; Velonia, K. J.,** 2005. Design and synthesis of N-maleimido-functionalized hydrophilic polymers via copper-mediated living radical polymerization: A suitable alternative to PEGylation chemistry, *Am. Chem. Soc.*, **127**, 2966-2973.

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

[117] **Huglin, M. B.,** 1972. In Light Scattering From Polymer Solutions, Chapter 6; Huglin, M. B., Ed.; *Academic Press*: New York.

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