

İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

**DENDRIMER TYPE MULTIARM STAR BLOCK COPOLYMERS VIA
DIELS-ALDER CLICK REACTION**

M.Sc. Thesis by

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Department : Polymer Science & Technology

Programme : Polymer Science & Technology

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M.Sc. Thesis by

Ceyda ÖNEN

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Supervisor (Chairman) : Prof. Dr. Gürkan HIZAL (ITU)

Members of the Examining Committee : Prof. Dr. H. Ayşen ÖNEN (ITU)

Members of the Examining Committee : Assis. Prof. Dr. Amitav SANYAL (BU)

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**DIELS-ALDER CLİCK KİMYASI İLE DENDRİMERİK YILDIZ BLOK
KOPOLİMER SENTEZİ**

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Ceyda ÖNEN

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Tez Danışmanı : Prof. Dr. Gürkan HIZAL (İTÜ)
Diğer Jüri Üyeleri : Prof. Dr. H. Ayşen ÖNEN (İTÜ)
Diğer Jüri Üyeleri : Yrd. Doç. Dr. Amitav SANYAL (BÜ)

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Ceyda ÖNEN
Chemist, M. Sc.

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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
PS	: Polystyrene
PMMA	: Poly(methyl metacrylate)
CDCl₃	: Kloroform
R_n 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
RI	: Refractive Index
LS	: Light Scattering
PRE	: Persistent Radical Effect
M_tⁿ	: 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	: <i>N,N,N',N'',N'''</i> - pentamethyldiethylenetriamine
GPC	: Gel Permeation Chromotography
NMR	: Nuclear Magnetic Resonance Spectroscopy
UV-Vis.	: Ultra Violet-Visible Spectroscopy
TD-SEC	: Viscotek Triple Detection

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DENDRIMER TYPE MULTIARM STAR BLOCK COPOLYMERS VIA DIELS-ALDER CLICK REACTION

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. 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, two types of dendrimer type multiarm star block copolymers: (polystyrene)_n-poly(divinylbenzene)-poly((methylmethacrylate)₂)_m, ((PMMA)₂)_m-(PS)_n-polyDVB and (polystyrene)_n-poly(divinylbenzene)-poly((methylmethacrylate)₄)_m, ((PMMA)₄)_m-(PS)_n-polyDVB were successfully prepared via a combination of cross-linking and Diels–Alder click reactions based on “arm-first” methodology. For this purpose, multiarm star polymer with anthracene functionality as reactive periphery groups was prepared by a cross-linking reaction of divinyl benzene using α -anthracene end functionalized polystyrene (PS-Anth) as a macroinitiator. Thus, obtained multiarm star polymer was then reacted with furan protected maleimide-end functionalized polymers: (PMMA)₂-MI or (PMMA)₄-MI at reflux temperature of toluene for 48 h resulting in the corresponding multiarm star block copolymers via Diels–Alder click reaction. The multiarm star and multiarm star block copolymers were characterized by using ¹H NMR, SEC, Viscotek triple detection SEC (TD-SEC).

DIELS-ALDER CLİCK KİMYASI İLE DENDRİMERİK YILDIZ BLOK KOPOLİMERLERİN 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 fonksiyonlitesine 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 monomere uygulanabilir olması nedeniyle hızlı bir şekilde arttı. 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 siklokatalmalarda ([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, iki farklı dendrimerik multiarm star blok kopolimer: (polistiren)_n-poli(divinilbenzen)-poli(metilmetakrilat)_m, ((PMMA)₂)_m-(PS)_n-polyDVB ve (polistiren)_n-poli(divinilbenzen)-poli(metilmetakrilat)_m, ((PMMA)₄)_m-(PS)_n-polyDVB- 'arm-first' methoduna dayanan çapraz bağlanma ve Diels-Alder click reaksiyonu ile başarılı olarak hazırlandı. Burada, antrasen fonksiyonlu polistiren ile divinilbenzenin çaprazlama reaksiyonu, dendrimer multiarm star polimer ile antrasen fonksiyonlu reaktif çevreli gruplar hazırlandı. Böylece, multiarm star polimer elde edildi daha sonra furan korumalı maleimit sonlu polimerler ile reaksiyona sokuldu.: (PMMA)₂-MI ya da (PMMA)₄-MI toluenin reflüks sıcaklığı ile 48 saat için multiarm star blok kopolimerlerin Diels-Alder click reaksiyonu sonuçlandı. Multiarm star ve multiarm star blok kopolimerler ¹H NMR ve vizkotek üçlü dedektör sistemi ile karakterize edildi.

1. INTRODUCTION

Star and multiarm star polymers are the simplest branched macromolecules, in which multiple linear arms emanate from a single core. During the last decade, star polymers have gained much interest because of interesting properties in bulk state and in solution because of their compactness and high functionality compared to those of linear analogues of the same molecular weight.[1-2] Until last decade, the living anionic [3-4] and cationic polymerizations [5-6] were the known techniques for the synthesis of star polymers with the well-defined arms. With the recent advances in living radical polymerizations (LRPs), [7-8] the synthesis of polymers having complex architectures and predetermined chemical compositions became possible and received increased attention because of the variety of applicable monomers and greater tolerance to experimental conditions in comparison with living ionic polymerization routes. Star polymers have been mainly synthesized using a “core-first” or an “arm-first” methodology. In the “core first” method, a multifunctional initiator (the core) is used to initiate the CRP of monomer to obtain multiarm star polymers. [9-10] For the “arms first” method, the terminally reactive linear arms are synthesized first and then the core is produced either by the reaction of the arms using multifunctional coupling agent (coupling onto) [11-12] or by a cross-linking reaction of the arms with difunctional monomers through propagation. Although [13-14] these methodologies provide a powerful tool to produce star polymers, a number of challenges remain regarding the structural homogeneity, purity and molecular weight distribution of star molecules. The star-star coupling is the main reason for the observed broad molecular weight distribution in the “core first” method, because of the large amounts of initiating sites and high probability of radical-radical recombination. Therefore, the polymerization is usually limited to low monomer conversion (<20%).[15] Recently, 4- and 8- arm star poly(methyl acrylate)_s (PMA)_s with the ultrahigh molecular weights (i.e., Mn up to 1.000.000 at 90% conversion) were prepared by Percec and Coworkers using a multifunctional initiator via Single-Electron Transfer mediated Living Radical

Polymerization (SET-LRP) without the star-star coupling reaction. [16] However, this methodology has not been employed to synthesize multiarm star block copolymers up till now. Moreover, the poor structural homogeneity and broad molecular weight distribution arise from the result of a random distribution of arms per molecule during the cross-linking reaction of the arms in the “arm first” method. Furthermore, the coupling onto method necessitates a highly efficient organic reaction otherwise tedious purification steps should be carried out to remove polymeric precursors from the resulting star polymers. Fortunately, recently developed “click reactions” [17-18] has emerged as a powerful tool to synthesize polymeric materials varying from the block copolymers [19-20] to the complex macromolecular structures [21-22] because of its quantitative yield, mild reaction conditions and tolerance of numerous functional groups. In these reactions Cu(I)-catalyzed [3 + 2] Huisgen cycloaddition reaction between an azide and an alkyne and the Diels-Alder reaction, [4 + 2] cycloaddition, generally consists of a coupling of a diene and a dienophile by intra- or intermolecular reaction [23] are the most encountered routes.

1.1 Purpose of the Thesis

In this thesis, we report a simple approach for the synthesis of dendrimer type multiarm star block copolymers based on the “arm first” method. First, an anthracene end functionalized polystyrene (PS-Anth) and two different type dendrimer types poly(methyl methacrylate) (PMMA) were synthesized. (PMMA)₂-MI (two arms) and (PMMA)₄-MI (four arms) were prepared by atom transfer radical polymerization. This work has never been tried with Diels-Alder (DA) click reactions. It is different from another multiarm star working. Second, multiarm star polymer with anthracene functionality as reactive periphery group was synthesized by a cross-linking reaction of divinyl benzene using PS-Anth as a macroinitiator. Subsequently, the formation of dendrimer multiarm star block copolymers were achieved via DA click reaction between the reactive core and maleimide-end functionalized polymers G1 and G2.

2. THEORETICAL PART

2.1. Typical features of radical polymerization (RP)

It should be mentioned that Michael Szwarc not only contributed to the development of anionic polymerization but was also involved throughout the 1950s in detailed studies of radical processes [24–25]. Indeed, while living anionic vinyl polymerization was being discovered and developed, conventional radical polymerization was already flourishing. Many new products were commercialized, and a comprehensive theory of radical polymerization was developed [26–27], including a precise characterization of the active species involved, a detailed mechanistic description of all elementary reactions, kinetic and thermodynamic parameters for the relevant rate constants, and a structure–reactivity correlation. These studies included Szwarc’s quantitative evaluation of bond dissociation energies and his investigation of the dynamics of radical exchange via a so-called methyl transfer process [28–29]. He also studied carbon–halogen bond dissociation energies [24,30], of particular relevance to atom transfer radical polymerization (ATRP). There were some attempts during this time to control the overall radical polymerization rate (via retardation/inhibition) [31,32] and molecular weights (with transfer/telomerization) [33], but free radical polymerization essentially could not control MW or MWD and could not yield block copolymers due to the very short lifetime of the growing chains (~1 s).

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

1. *Initiation*. In this first step, a reactive site is formed, thereby “initiating” the polymerization.
2. *Propagation*. Once an initiator activates the polymerization, monomer molecules are added one by one to the active chain end in the propagation step. The reactive site is regenerated after each addition of monomer.

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

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

The free radical chain process is demonstrated schematically below (2.1): R' represents a free radical capable of initiating propagation; M denotes a molecule of monomer; R_m and R_n refer to propagating radical chains with degrees of polymerization of *m* and *n*, respectively; AB is a chain transfer agent; and P_n + P_m represent terminated macromolecules.

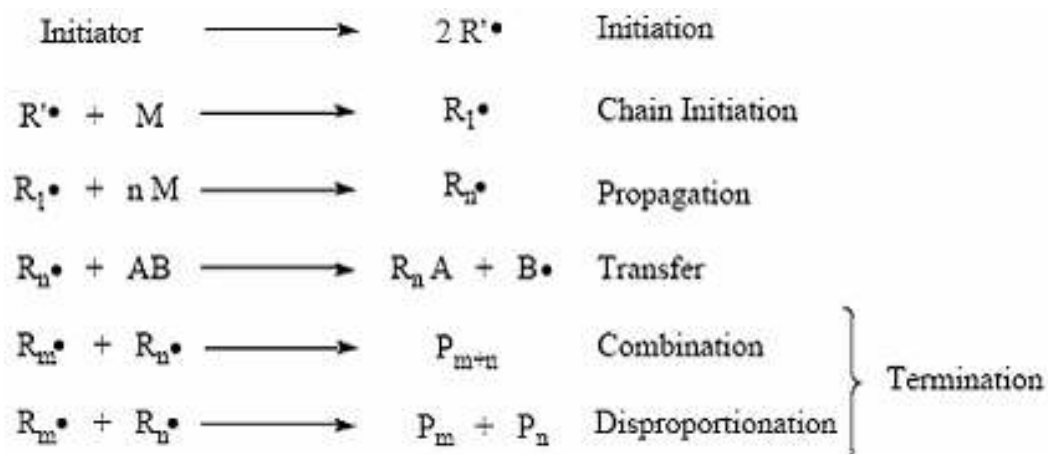


Figure 2.1 : General Free Radical Polymerization Mechanism

The active species in RP are organic (free) radicals. They are typically sp² hybridized intermediates and therefore show poor stereoselectivity. However, polymers formed by RP do show good regio- and chemoselectivity, as evidenced by the high degree of head-to-tail structures in the chain and the formation of high MW polymers, respectively. Radicals can be stabilized by resonance and to a lesser degree by polar effects. They can be electrophilic or nucleophilic and in some instances possess a moderate tendency to alternate during copolymerization. RP, like any chain polymerization, is comprised of four elementary reactions: initiation, propagation, transfer, and termination. Under steady state conditions, the initiation rate is the same

as the rate of termination (i.e., ~1000 times slower than the propagation rate). Such a slow initiation can be accomplished by using radical initiators with appropriately long half lifetimes (e.g., ~10 h). At the end of a polymerization, unreacted initiator is often left in the reaction mixture. The chain building reaction of propagation occurs by radical addition to the less substituted C atom in a monomer (resulting in head-to-tail polymers) with rate constants $k_p \sim 10^3 \text{ M}^{-1} \text{ s}^{-1}$ (k_p for acrylates $>10^4 \text{ M}^{-1} \text{ s}^{-1}$ and for butadiene $<10^2 \text{ M}^{-1} \text{ s}^{-1}$). In contrast to carbocationic polymerization, transfer is not the main chain breaking reaction in RP, and high MW polymers can be formed from most monomers. Transfer has a higher activation energy than propagation and becomes more important at higher temperatures. The bimolecular radical coupling/disproportionation termination reactions are very fast, essentially diffusion controlled ($k_t >10^8 \text{ M}^{-1} \text{ s}^{-1}$), in contrast to ionic polymerization where electrostatic repulsion prevents a reaction between two cations or two anions. In order to grow long chains in RP, the termination rate (not rate constant) must be much slower than propagation. Since termination is a 2nd-order reaction with respect to radical concentration while propagation is 1st-order, the rate of termination becomes slower than that of propagation at very low radical concentrations. Consequently, the radical concentration must be in the range of ppm or even ppb. Because the average life of a propagating chain is ~1 s, which constitutes ~1000 acts of propagation with a frequency ~1 ms, the life of a propagating chain is too short for any synthetic manipulation, end functionalization, or addition of a second monomer to make a block copolymer. The overall kinetics can be described by Eq. (1), where the rate of polymerization is a function of the efficiency of initiation (f) and the rate constants of radical initiator decomposition (k_d), propagation (k_p) and termination (k_t) according to

$$R_p = k_p [M] (f k_d [I]_0 / k_t)^{1/2} \quad (2.1)$$

The propagation rate scales with a square root of the radical initiator concentration and its efficiency of initiation (typically in the range of 50–80%). Molecular weights depend on the termination (= initiation) rate as well as the rate of transfer. When the contribution of transfer can be neglected, the degree of polymerization depends reciprocally on the square root of radical initiator concentration, as shown in

$$DP_n = k_p [M] (f_{kd} [I]_0 / k_t)^{-1/2} \quad (2.2)$$

Conventional RP can be carried out in bulk monomer, in solution, and also in dispersed media (suspension, emulsion, miniemulsion, microemulsion and inverse emulsion). Solvents should not contain easily abstractable atoms or groups, unless low MW polymers are desired. The range of reaction temperatures is quite large (-100 to > 200 °C). Monomers are sufficiently reactive when the generated radicals are stabilized by resonance or polar effects (styrenes, (meth)acrylates, (meth)acrylamides, acrylonitrile, vinyl acetate, vinyl chloride and other halogenated alkenes). Due to its lower reactivity, ethylene polymerization requires high temperatures. However, it is accompanied by transfer under these conditions that leads to (hyper)branched polymers. Initiators are typically peroxides, diazenes, redox systems and high-energy sources which slowly produce initiating radicals ($k_d \sim 10^{-5} \text{ s}^{-1}$). The industrial significance of conventional RP is evident in the fact that it accounts for the production of ~50% of all commercial polymers. Low density polyethylene, poly(vinyl chloride), polystyrene and its copolymers (with acrylonitrile, butadiene, etc.), polyacrylates, polyacrylamides, poly(vinyl acetate), poly(vinyl alcohol) and fluorinated polymers comprise the most important of these materials. However, no pure block copolymers and essentially no polymers with controlled architecture can be produced by conventional RP.

2.2. New Controlled/Living Radical Polymerization (CRP)

Weak intramolecular interactions among polymer chains can be exploited to form organized nanostructured materials, provided the polymers have uniform dimensions, topologies, compositions and functionalities. Following developments in anionic polymerization by Michael Szwarc, precise control over polymeric structural parameters prepared by RP has given rise to a virtually unlimited number of new polymeric materials. The improved macroscopic properties of many of these polymers are a direct result of comprehensive structure–property investigations as well as guidelines based on theoretical and empirical predictions, as will be discussed. Such precise macromolecular synthesis employs concepts of living polymerization, in which the contribution of chain breaking reactions is minimized and the apparent simultaneous growth of all chains can be achieved via nearly instantaneous initiation. A combination of fast initiation and an absence of

termination seemingly conflicts with the fundamental principles of RP, which proceeds via slow initiation and in which all chains are essentially dead at any given instant. However, the development of several controlled/living radical systems utilizing an intermittent formation of active propagating species has recently been realized concurrent with similar developments in anionic, cationic, coordination and ring-opening polymerization systems (cf. other reviews in this and other accompanying special issues).

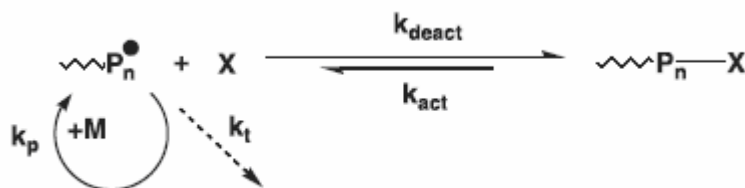


Figure 2.2 : Deactivation/Activation Process

The establishment of a dynamic equilibrium between propagating radicals and various dormant species is central to all CRP systems [34,35]. Radicals may either be reversibly trapped in a deactivation/activation process according to Figure 2.2, or they can be involved in a “reversible transfer”, degenerative exchange process (Figure 2.3).

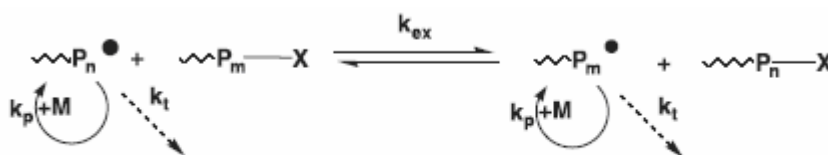


Figure 2.3 : Degenerative Exchange Process

The former approach relies on the persistent radical effect (PRE) [35–36]. The PRE is a peculiar kinetic feature which provides a self-regulating effect in certain CRP systems. Propagating radicals P_n^* are rapidly trapped in the deactivation process (with a rate constant of deactivation, k_{deact}) by species X, which is typically a stable radical such as a nitroxide [37,38] or an organometallic species such as a cobalt porphyrin [39]. The dormant species are activated (with a rate constant k_{act}) either spontaneously/thermally, in the presence of light, or with an appropriate catalyst (as in ATRP) to reform the growing centers. Radicals can propagate (k_p) but also

terminate (k_t). However, persistent radicals (X) cannot terminate with each other but only (reversibly) cross-couple with the growing species (k_{deact}). Thus, every act of radical–radical termination is accompanied by the irreversible accumulation of X. Its concentration progressively increases with time, following a peculiar 1/3 power law (vide infra). Consequently, the concentration of radicals as well as the probability of termination decreases with time. The growing radicals then predominantly react with X, which is present at 41000 times higher concentration, rather than with themselves.

In systems obeying the PRE, a steady state of growing radicals is established through the activation–deactivation process rather than initiation–termination as in conventional RP. These systems include stable free radical polymerization (SFRP), or more precisely, nitroxide mediated polymerization (NMP) and cobalt mediated radical polymerization (CMRP). Such techniques require a stoichiometric amount of mediating species, as all dormant chains are capped by the trapping agent. ATRP also operates via the PRE. However, in this catalytic process employing atom (or group) transfer between growing chains and a redox active catalyst, the amount of transition metal catalyst can often be substoichiometric. By contrast, systems employing degenerative transfer are not based on the PRE. Such systems follow typical RP kinetics with slow initiation and fast termination. The concentration of transfer agent is much larger than that of radical initiators. Thus, the transfer agent plays the role of the dormant species. Monomer is consumed by a very small concentration of radicals which can terminate but also degeneratively exchange with the dormant species. Fast exchange among active and dormant species is required for good control over molecular weight, polydispersity and chain architecture in all CRP systems. A growing species should ideally react only with a few monomer units (within a few milliseconds) before it is deactivated to the dormant state (where it remains for several seconds). The lifetime of a chain in the active state in a CRP process is comparable to the lifetime of a propagating chain in conventional RP. However, because the whole propagation process may take E1 d in CRP, there exists transfer agent is much larger than that of radical initiators. Thus, the transfer agent plays the role of the dormant species. Monomer is consumed by a very small concentration of radicals which can terminate but also degeneratively exchange with the dormant species. Fast exchange among active and dormant species is required for good control over molecular weight, polydispersity and chain architecture in all CRP

systems. A growing species should ideally react only with a few monomer units (within a few milliseconds) before it is deactivated to the dormant state (where it remains for several seconds). The lifetime of a chain in the active state in a CRP process is comparable to the lifetime of a propagating chain in conventional RP. However, because the whole propagation process may take E1 d in CRP, there exists the opportunity to carry out various synthetic procedures, including chain-end functionalization or chain extension [40].

2.3. Similarities and Differences Between RP and CRP

CRP and RP proceed via the same radical mechanism, exhibit similar chemo-, regio- and stereo-selectivities, and can polymerize a similar range of monomers. However, several important differences between CRP and RP exist as summarized below.

1. The lifetime of growing chains is extended from E1 s in RP to more than 1 h in CRP through the participation of dormant species and intermittent reversible activation.
2. Initiation is slow and free radical initiator is often left unconsumed at the end of a conventional RP. In most CRP systems, initiation is very fast and near instantaneous growth of all chains can be achieved, which ultimately enables control over chain architecture.
3. Nearly all chains are dead in RP, whereas in CRP the proportion of dead chains is usually <10%.
4. Polymerization in CRP is often slower than in RP. However, the rates may be comparable in certain cases (e.g., when the targeted MW in CRP is relatively low).
5. A steady state radical concentration is established in RP with similar rates of initiation and termination, whereas in CRP systems based on the PRE, a steady radical concentration is reached by balancing the rates of activation and deactivation.
6. Termination usually occurs between long chains and constantly generated new chains in RP. In CRP systems based on the PRE, all chains are short at the early stages of the reaction and become progressively longer; thus, the termination rate significantly decreases with time. In DT processes, new chains are constantly

generated by a small amount of conventional initiator, and therefore termination is more likely throughout the reaction.[41,42]

2.4. Synthesis of Star-Shaped Polymers

2.4.1. Introduction

Elucidation of structure-property relationships remains an ongoing field of study in polymer science. The introduction of long chain branching is known to affect polymer physical properties and processability as a result of changing the melt, solution, and solid-state properties of polymers [43]. It has been shown that branching results in a more compact structure in comparison to linear polymers of similar molecular weight, due to their high segment density, which alters the crystalline, mechanical, and viscoelastic properties of the polymer. While it is well-known that long chain branching greatly influences polymer physical properties, a fundamental understanding of structure-property relationships remains difficult due to the complexity of branched polymer structures. A branched polymer structure was described as a nonlinear polymer with multiple backbone chains radiating from junction points [44]. Star-shaped macromolecules constitute the simplest form of branched macromolecules, comprising only one branch point, and as such, have received significant attention in the elucidation of structure property relationships [45]. Although star polymers constitute the simplest branched structure, their synthesis remains challenging, and star polymers are often difficult to synthesize in a well-controlled manner. Due to the complex nature of these macromolecules, controlled polymerization techniques, such as anionic, cationic, living free radical, and group transfer (GTP) polymerization have typically been used to obtain well-defined star-shaped macromolecules. Star polymers are typically synthesized using either a core-first approach, or an arm-first approach. In the core-first synthetic method, a multifunctional initiator is used and the number of arms is proportional to the number of functionalities on the initiator (Fig. 2.4) [46].

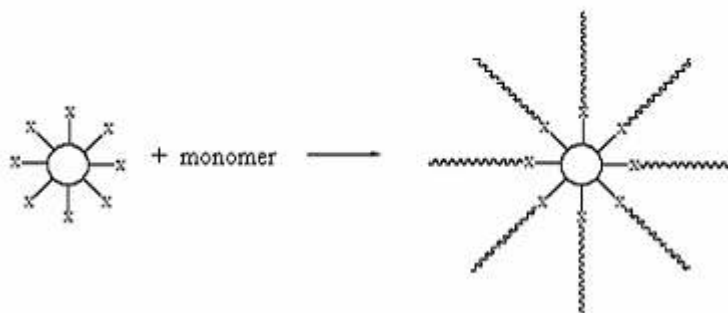


Figure 2.4 : The core-first synthetic method

Using the core-first method, well-defined star-shaped macromolecules can be synthesized as long as initiation is rapid relative to propagation. While this approach was used in the first cationic synthesis of star-shaped polymers, containing three or four arms, it tends to yield polymers with broadened molecular weight distributions [40]. In the arm-first synthetic method, linear arm polymers are synthesized and then coupled using a multifunctional linking agent or divinyl compound. In this case, the number of arms depends on the linking efficiency of the arm polymer to the multifunctional core and an alternative method is used to determine the number of arms (Fig. 2.5). This approach is typically used in both living anionic and cationic syntheses of star-shaped polymers [47].

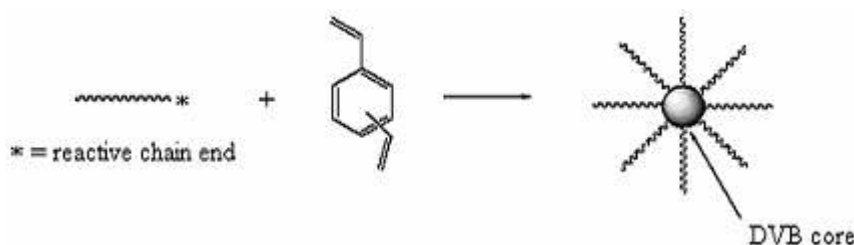


Figure 2.5 : The arm-first synthetic method

As discussed previously, living anionic chain ends are very reactive and are used in a variety of chain end functionalization strategy. This characteristic of living chain ends makes living anionic polymerization ideal for the synthesis of complex architectures using chain end coupling reactions. The synthesis of star-shaped polymers using living anionic polymerization has been achieved using a variety of linking agents. Typical linking reagents for coupling of living anionic chain ends are chlorosilanes and their derivatives. However, these types of endcapping reagents are limited in their utility by the necessity for equal reactivity and accessibility of all reactive sites on the linking agent. Use of both silicon tetrachloride and

chloromethylated benzenes have been hampered by these limiting factors. Other linking agents are dimethyl phthalate, trisallyloxytriazines, and divinylbenzene. In some cases, the number of arms using the arm first approach is controlled by the number of functionalities on the linking agent, such as trichloromethylsilane or tetrachlorosilane.

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

More recently, several of the techniques discussed above have been used in conjunction with one another to synthesize novel macromolecular architectures. For example, Muller et al. reported the use of both cationic and anionic polymerization to synthesize star-shaped block copolymers [48]. The polymerization of isobutylene was initiated using 1,3,5-tricumylchloride and terminated using diphenylethylene and methanol to yield a diphenylethylene methoxy group. This group was then transformed into an initiator for the anionic polymerization of methyl methacrylate using a K/Na alloy.

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

convergent coupling of arm polymers to synthesize dendritically branched polystyrene.

2.4.2. Synthesis of Functional Star Shaped Polymers

Chain-end functionalization is an additional challenge in the synthesis and characterization of complex polymer architectures. As discussed previously, living anionic polymerization methodologies are typically used to synthesize star-shaped macromolecules due to the controlled nature of these reactions. Functionalized alkyllithium initiators provide quantitative chain end functionalization and are an attractive alternative to electrophilic terminating reagents for the synthesis of chain-end functionalized polymers. Functionalized initiators facilitate the synthesis of telechelic and heterotelechelic polymers, functionalized block polymers, and star-shaped polymers with functional groups on each arm terminus [49]. The use of the functional initiator 3-(*t*-butyldimethylsilyloxy)-1-propyllithium (*t*BDMSPrLi) was reported in the synthesis of a variety of polymers with various architectures, such as polyisoprene, polybutadiene, poly(methyl methacrylate), and poly(1,3-cyclohexadiene), to yield hydroxyl chain end functionalized polymers. While living anionic polymerization using functional initiation has proven an excellent pathway to chain-end functional polymers, other researchers have reported various methodologies for the preparation of star-shaped macromolecules with diverse chain-end functionalities.

Hedrick et al. reported the core-first synthesis of star-shaped poly(ϵ -caprolactone) hydroxyl terminated macroinitiators with six arms using ring opening polymerization and the subsequent transformation into ATRP initiators [50]. The macroinitiators were then used to polymerize several monomers, including methyl methacrylate, hydroxyethyl methacrylate, or ethylene oxide. There are several parameters in an ATRP that should be controlled carefully in order to maximize the yield of stars and prevent star-star coupling reactions. Some detailed studies have been carried out on the coupling of monofunctional polystyrenes and polyacrylates with DVB and di(meth)acrylates to prepare star polymers and the following guidelines have been developed:

- The ratio of difunctional reagent to growing chains seems to be optimal in the range of 10-20.
- Monomer conversion (or reaction time) has to be carefully controlled and stopped before star-star coupling occurs.
- Higher yields of stars are observed for polyacrylates than for polystyrenes. This may be attributed to a higher proportion of terminated chains in styrene polymerization.
- The choice of the difunctional reagent is important and reactivity should be similar to, or lower than that of the arm-building monomers.
- Halogen exchange slightly improves efficiency of star formation.
- Solvent, temperature, catalyst concentration should be also optimized [51].

In a similar fashion, using living cationic polymerization, Gnanou and coworkers synthesized star-shaped polystyrenes and used functional group transformation to transform the chain-end functionality to either hydroxyl or amino at the periphery. The hydroxyl terminated samples were also utilized as macroinitiators for ethylene oxide polymerization. In several cases, ATRP was used in acrylic polymerizations to yield polymers with hydroxyl, epoxy, amino, bromide, or cyano functionalized star polymers.

Utilizing a different approach, Hirao et al. have introduced functionality to star polymers using living anionic polymerization in conjunction with functionalized diphenylethylene (DPE) derivatives and organic functional group transformations [46]. Using this approach, functionality was introduced at the α -terminus, at block junctions, or at the core. Quirk et al. pioneered this work and Hirao et al. based their research on this work [52]. Fréchet and Hawker et al. have also reported the use of nitroxide mediated polymerization in the synthesis of functionalized star polymers [53]. They reported the synthesis of a series of compounds, ranging from simple to complex, and have focused on homo, block, and random copolymers with both apolar and polar vinylic repeat units and functional group integration in diverse positions. Ishizu et al. have also reported on the functionalization of polyisoprene star polymers with p-chloro styrene to yield a periphery of reactive styrene groups, capable of forming a crosslinked network [54]. While both functional polymers and

star-shaped polymers are prevalent in the literature, the combination of well-defined thermoreversible chain end interactions, such as multiple hydrogen bonding interactions, and star-shaped macromolecules is limited. Hadjichristidis et al. studied the synthesis and characterization of well-defined linear and star-shaped polystyrenes, polyisoprenes, and polybutadienes bearing both sulfo- and phospho-zwitterionic groups, which have a thermoreversible nature [45]. While these studies have made great strides in delineating structure-property relationships for these materials, the reversible interaction is ionic and it is anticipated that their behavior will significantly differ from a multiple hydrogen bonding interaction. Meijer et al. have recently reported the synthesis of model low molar mass poly (ethylene oxide-*co*-propylene oxide) three arm star polymers bearing pendant quadruple hydrogen bonding functionalities [55]. These polymers were compared with three arm star polymers bearing urea chain ends, non-functional chain ends, and with a chemically crosslinked network and the influence of chain end functionality was studied. However, due to the hydrophilic nature of the parent polymer, the effect of atmospheric moisture on the polymer physical properties was not excluded. The introduction of thermally reversible interactions at the chain ends of star-shaped polymers is only one of the interesting families to which chain end functionalized polymers serve as a precursor. Organic functional groups, such as hydroxyl and amino serve as stepping stones to diverse and rich functionalization strategies.

2.5. Synthesis of Star Polymers by the ‘arm-first’ method

The three most popular CRP techniques, e.g., ATRP, NMP and RAFT polymerization, have been applied to the synthesis of star polymers with a cross-linked core by cross-linking reactive linear chains using a divinyl cross-linker. Since the formation of linear chains (arm precursors) by polymerization of monovinyl monomer is essentially complete before the formation of the cross-linked core via polymerization of cross-linker, this method is strategically termed as the “arm-first” route for the synthesis of star polymers. The “arm-first” method was first developed in the context of anionic polymerization [56,57]. This approach has been later extensively employed using different CRP methods for the synthesis of various

functional star polymers, because of the easy experimental setup and broad range of monomers in CRP. The addition of a cross-linker to a solution containing linear macroinitiator (MI) with reactivatable chain-end initiating site initially generates pendant vinyl groups during the polymerization of cross-linker from the linear chain. The highly cross-linked core is formed through inter molecular reactions between the chain-end radicals and the pendant double bonds. It produces a star polymer with a statistical distribution of the number of incorporated arms. Furthermore, star–star coupling reactions concomitantly occur, increasing the star molecular weights and leading to a broader MWD for the obtained star molecules. The average number of arms attached to a star core depends on several experimental parameters, including the degree of polymerization (DP) and composition of the arm precursor, the chemical nature of cross-linker, the amount and the addition moment of cross-linker. Incomplete incorporation of linear arm precursors into the formed star is a common problem in this “arm-first” method, which could be explained by the loss of chain-end initiating sites or a buildup of steric hindrance around the core, as the coupling reactions proceed [58].

2.5.1. Synthesis of Star Polymers with a Cross-linked Core by NMP

Stable free radical polymerization, specifically NMP, was also applied to the synthesis of star polymers with a cross-linked core by the “arm-first” approach. Solomon and coworkers [59] first reported the synthesis of poly(4-tert-butylstyrene) star polymers by employing tetramethyl piperidyl-N-oxyl (TEMPO) as the persistent stable radical to mediate the NMP of 4-tert-butylstyrene and subsequent cross-linking reaction using DVB as cross-linker. In the early stages of NMP, linear polySt MI was most frequently used for the synthesis of (polySt)_n-polyDVB star polymers with a cross-linked core due to the lack of powerful nitroxide mediating radicals for the polymerization of acrylate and methacrylate monomers. However, the optional ratios of polySt MI to DVB for obtaining high star yield significantly varied in different reports due to their applied conditions. Pasquale and Long [43] observed that in order to obtain efficient star formation (star yield ~70%, $M_w/M_n \sim 3.0$) with a polySt MI ($M_n = 19,300$ g/mol) and m-xylene as solvent, a high molar ratio of $[DVB]_0/[polyStMI]_0 = 68$ (1/2 by weight) was required. In contrast, Hadjichristidis and coworkers [60] employed a much lower molar ratio of $[DVB]_0/[polyStMI]_0 = 13$ with a polySt MI ($M_n = 10,000$ g/mol) to obtain a (polySt)_n-

polyDVB star polymer in 75% star yield and polydispersity $M_w/M_n = 1.56$ by using benzene as solvent at 125 °C. Use of a glycol-conjugated TEMPO-based alkoxyamine or St-derived functional comonomer synthesized polySt star polymers carrying functionalities in the core [61] and at the periphery [62], respectively.

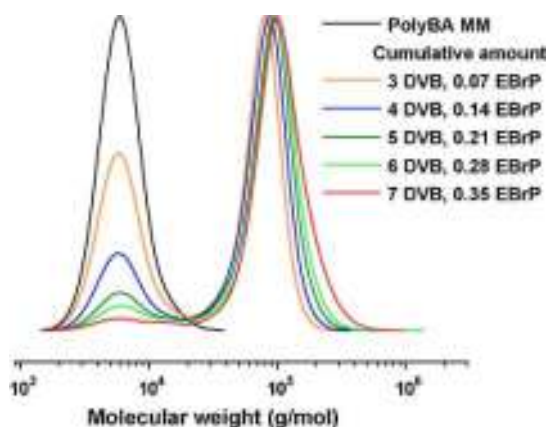


Figure 2.6 : Influence of several-step addition of DVB and EBrP on GPC traces of $(\text{polyBA})_n$ -polyDVB star polymers in the MM method; experimental conditions: $[\text{polyBAMM}_b(\text{DP}=42)]_o/[\text{EBrP}]_o/[\text{DVB}]_o/[\text{CuBr}]_o/[\text{Me}_6\text{TREN}]_o = 1/(0.07+0.07 \times 4)/(3+1 \times 4)/0.2/0.2$, $[\text{MM}]_o = 0.06\text{M}$, in anisole at 80 °C [49].

Initially, the strong covalent bond in a TEMPO-based alkoxyamine impeded the structural control of the star polymers and limited composition of the arms to polySt and its derivatives. With the development of a more active second-generation α -hydrido-based alkoxyamine, Hawker expanded utility of NMP to allow the synthesis of a series of star polymers with a cross-linked core and a variety of arm compositions by using different monomers, including St, acrylate, vinyl pyridine, methacrylate and acrylamide [63,64]. Furthermore, they used combinatorial techniques for high throughput star synthesis and screened the key experimental parameters to optimize control over star structures. Functional groups could be introduced onto star periphery and along the arms by using functionalized alkoxyamines and functional monomers, respectively.

2.5.2. Synthesis of Star Polymers with a Cross-linked Core by RAFT

Compared to the broad application of ATRP and NMP for the synthesis of functional star polymers using the “arm-first” method, only limited success has been obtained with RAFT polymerizations. Moad first proposed the possibility of using the “arm-first” method in RAFT polymerization for the synthesis of star polymers with a

cross-linked core [65]. The first experimental proof of the synthesis of star polymers with a cross-linked core by RAFT was reported by Davis and coworkers [66] although the synthesized (polySt)_n-polyDVB star polymers were poorly controlled with low star yield and high polydispersity. Zheng and Pan [67] reported the synthesis of (polySt)_n-polyDVB star polymers containing a cross-linked nodule by using benzyl dithiobenzoate as RAFT agent. The use of a comonomer during the core formation process and the appropriate selection of solvent, could favor micelle formation during the cross-linking of linear MIs, which improved both star formation and star yield [68,69].

2.5.3. Synthesis of Star Polymers with a Cross-linked Core by ATRP

2.5.3.1. Linear Macroinitiator as Arm Precursor (MI method)

The first synthesis of star polymers with a cross-linked core by ATRP was reported in 1999. Polystyrene-based linear MIs containing bromine chain-end functionality were crosslinked by using various divinyl cross-linkers in anisole at 110 °C [70]. The structure of the resulting star polymer could be denoted as (polySt)_n-polyX, where polyX represents the core of the star polymer and n is the average number of polySt arms per star molecule. The use of divinylbenzene led to the formation of star polymers with the best controlled structure, as compared to other cross-linkers, such as ethylene glycol diacrylate and ethylene glycol dimethacrylate. A molar ratio of DVB to polySt MI between 5 and 15 was found optimal for the formation of stars with fairly high star yield but the star product was contaminated with residual linear chains and exhibited broad MWD due to star–star coupling reactions. Following a similar route, chain-end functionalized (polytBA)_n-polyDVB star polymers were synthesized through the use of functional ATRP initiators for the synthesis of linear poly(tert-butyl acrylate) MIs [71]. Various functional groups, e.g., epoxy, amino, cyano or bromo, were introduced into the chain end of each arm, the periphery of the formed star. The prepared (polytBA)_n-polyDVB star polymers could subsequently be functionalized by hydrolysis of the tert-butyl groups to prepare (polyAA)_n-polyDVB stars with polyelectrolyte arms (AA: acrylic acid) [72]. Instead of isolating and purifying the linear polytBA MIs, cross-linker could be added to the polymerizing system at certain tBA conversion to produce higher yield star polymers with a cross-linked core in a one-pot reaction (Scheme 7) [73]. The timing of addition of the

subsequent DVB at different tBA conversions significantly affected the structure of star polymers formed in these reactions. For instance, by keeping the initial molar ratio of $[tBA]_0/[EBrP]_0 = 50/1$ constant, earlier addition of DVB resulted in formation of a shorter polytBA arm precursor and consequently more tBA monomer remained for copolymerization with DVB. This produced star polymers with looser core, more arms per star molecule, and broader MWD. Sawamoto also applied the “arm-first” approach to the synthesis of star polymers containing polymethacrylate arms using ruthenium (Ru)-based catalyst complexes and various divinyl cross-linkers, such as dimethacrylate- and dimethacrylamide-based compounds [74–76]. In addition to investigating the influence of experimental parameters on the structures of the star polymers, they reported the synthesis of functionalized star polymers by introducing various functionalities into the star core [77,78] and the star periphery [79]. After this pioneering work on the synthesis of star polymers with a cross-linked core by using ATRP, recent developments in this area mainly focused on two aspects [80–82]:(1) exploration of new synthetic methodologies to achieve better structural control over the topology of the star polymers and (2) introduction of various site.

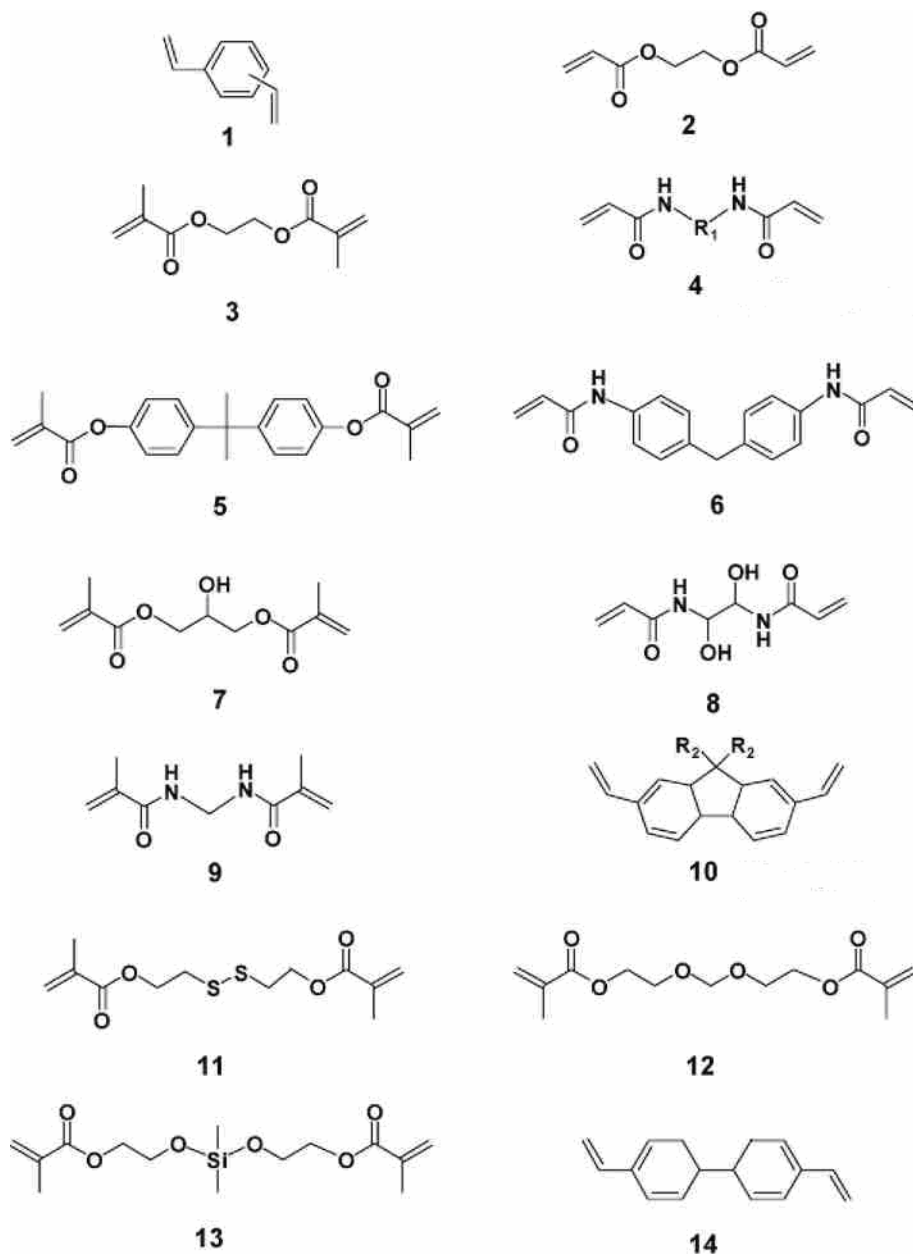


Figure 2.7 : Various divinyl cross-linkers used for star synthesis in CRPs.

Functionalities (e.g., targeting, imaging and biocompatible groups) into the star core, arm and periphery. For example, use of a functional cross-linker and/or functional comonomer in the star core formation step demonstrated the ease of successfully encapsulating functional groups into the star core, such as fullerene [83], and fluorophore [84,85]. Core degradable star polymers were synthesized by using degradable cross-linker containing disulfide group, [86], acetal group, [87,88], or siloxane group, [89], as the linker. When a functional initiator was used to synthesize the linear MI, various types of functionalities were introduced onto the star periphery. Examples include dendron groups [90], benzophenone groups [91], and

oligomeric poly(ethylene oxide) (PEO) [92]. Moreover, the choice of functional monomers provides an unparalleled number of options to introduce a variety of functional groups into the star arms, which can tune the star property to satisfy the requirements of many specific applications. Polyester-based polymers have attracted significant attention because of the facile hydrolytic degradation of the ester linkage. In particular, poly(ϵ -caprolactone) (PCL) is a biodegradable and biocompatible material with the degraded product being capable of absorption by the body with minimal tissue reaction [93]. The incorporation of PCL arms into star polymers with

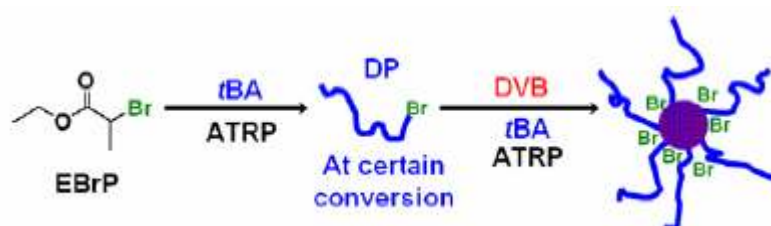


Figure 2.8 : Synthesis of $(\text{polytBA})_n\text{-poly(DVB-co-tBA)}$ star polymers via

ATRP using the “arm-first” method in a one-pot process [73]. Reproduced with permission from American Chemical Society. a cross-linked core has been achieved through chain-end functionalization of linear PCL with an alkyl halide group, followed by chain extension with divinyl cross-linker using ATRP [94,95]. The alkyl halide functionalized PCL MI could be alternatively synthesized by using a halogen-containing alcohol to initiate the anionic ring-opening polymerization (ROP) of ϵ -caprolactone monomer [96]. It is interesting to note that cross-linking a monofunctional linear MI generates star polymers with a cross-linked core, while cross-linking a difunctional linear MI could produce a dumbbell-structured nanoobject [97] or model network [98,99], depending on the solvent quality and the ratio of monovinyl monomer to divinyl cross-linker during the core formation process.

2.5.3.2. Linear Macromonomer as arm precursor (MM method)

A major drawback to star synthesis using linear MI as the arm precursor is that the star polymers usually have a broad MWD due to the significant level of star–star coupling reactions. Furthermore, caution has to be taken in order to avoid macroscopic gelation when too much star–star coupling occurs. Star–star coupling reactions can be decreased by using less divinyl cross-linker, e.g., lower molar ratio

of cross-linker to arm precursor, and/or conducting the reaction under dilute solution conditions, although the molecular weight and the yield of the obtained star molecules decrease significantly [70,76]. Moreover, the final star product formed via cross-linking the linear MIs is often contaminated by the presence of residual unincorporated linear polymers. This requires an extra purification step in order to obtain a star polymer with higher purity and narrower MWD. As noted above, star–star coupling reactions can occur via two possible routes: a radical–radical reaction or a radical-pendant vinyl group reaction between two star molecules. Since both reactions require the participation of radicals within the star core, a rational experimental design to decrease the molar ratio of initiating sites to arms per star could reduce the star–star coupling process and increase star uniformity. However, when linear MIs are used as arm precursors, both initiating sites (dormant form of radicals) and arms in the star molecule originate from the MIs, resulting, by default, in an identical number of arms and initiation sites in each star [73,100]. A recently developed strategy used linear MM, instead of MI, as the arm precursor for the synthesis of low polydispersity star polymers [101]. The biggest advantage of using a linear MM is that the number of initiating sites and arms can be independently controlled, since they are derived separately from the initiator and the MM. The incorporation of linear MM into the star molecule only increases the averaged number of arms per star, rather than changing the number of initiating sites. The number of initiating sites in the star core could be decreased, simply by decreasing the molar ratio of low-molar-mass initiator to MM. This effectively limits the extent of star–star coupling reactions and results in star polymers with low polydispersity. When star polymers are formed via copolymerization of linear MM and divinyl cross-linker using a low-molar-mass ATRP initiator, the residue of the initiator is incorporated into the star core segment. Therefore, different functional groups could be readily introduced into the star core through use of functional ATRP initiators [102]. Compared to the strategy of using a functional comonomer to introduce star core functionality in the MI method, the use of functional initiator does not lead to a higher polydispersity of the obtained star polymers. For instance, a pyrene-containing ATRP initiator (Py-Br) was used for the copolymerization of poly(*n*-butyl acrylate) (polyBA) MM and DVB. The core-functionalized star polymers showed strong UV absorption between 330 and 360 nm and high pyrene encapsulation efficiency (ca. 80%). When PEO methyl ether methacrylate MM was used for star

synthesis via ATRcP with EGDMA, amphiphilic (PEO)_n-polyEGDMA_(pyrene) star polymers with a hydrophobic core and hydrophilic PEO arms were synthesized. The functional stars showed high solubility in water and strong UV absorption due to the incorporation of pyrene groups into the star core. The incorporation of linearMMsinto the preformed star polymer increased the star yield but kept a low polydispersity of the resulted stars. The star polymer continued to growuntil the corewas fully covered by the linear arms and reached a steric saturation state, when further star growth stopped. Addition of another batch of cross-linker and ATRP initiator at this stage introducedmore pendant vinyl groups and initiating sites to the star core, expanding its size and functionality. This expansion decreased core congestion and made further incorporation of linear chain into star polymer possible. With appropriate amounts of additional cross-linker and ATRP initiator, it is possible to conduct star-linear MM reactions with limited star–star reactions. Therefore, the newly added cross-linker and ATRP initiator increased the star yield and star molecular weight while avoiding broadening of MWD. Star-linear MM reactions stopped when the star polymer reached its new saturated size, but the addition of a second batch of cross-linker and ATRP initiator expanded the core and allowed further star growth. This process could be repeated until the star yield essentially reaches 100% incorporation of the initially added MM [101]. This novel MM method could be extended as a general method to conventional RP [103,104] and other CRP techniques for the synthesis of star polymers with high star yield, high molecular weight and low polydispersity, although the synthesis of linear MMs [105–109] is not as straightforward or as easy as the synthesis of linear MIs.

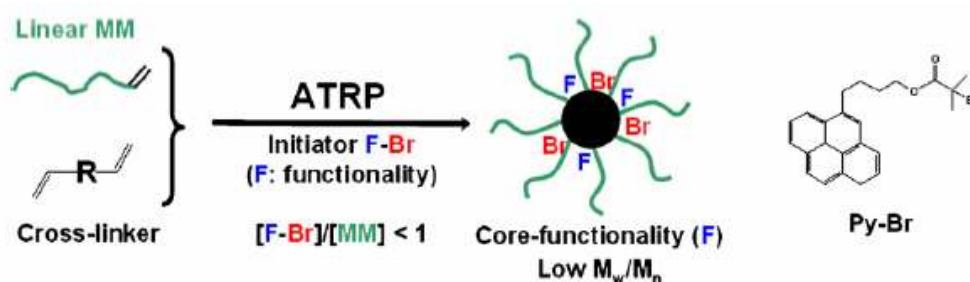


Figure 2.9 : Synthesis of core-functionalized star polymers via ATRP using MM method [102]. Reproduced with permission from American Chemical Society.

2.6 Click Chemistry

Click chemistry is a concept introduced by K. Barry Sharpless in 2001 and describes chemistry tailored to generate substances quickly and reliably by joining small units together as nature does.

Following nature's lead, the purpose is to generate substances by joining small units together with heteroatom links (C–X–C). The term “click chemistry”, the foundation of this approach, is defined a set of stringent criteria that a process must meet to be useful in this context.

A chemical transformation that is part of click chemistry obeys the following criteria:

- application modular and wide in scope
- obtains high chemical yield
- generates inoffensive byproducts
- is stereospecific
- simple reaction conditions
- has readily available starting materials and reagents
- no solvent involved or a benign solvent (preferably water)
- easy product isolation by crystallisation or distillation but not preparative chromatography
- physiologically stable
- large thermodynamic driving force > 84 kJ/mol for a fast reaction with a single reaction product. A distinct exothermic reaction makes a reactant "spring loaded".
- high atom economy

Chemical reactions that fit the bill are:

- cycloaddition reactions, particularly the Huisgen 1,3-dipolar cycloaddition (and the Cu(I) catalyzed azide-alkyne cycloaddition) as well as Diels-Alder reactions

- nucleophilic substitution especially to small strained rings like epoxy and aziridine compounds (ring opening reactions)
- carbonyl-chemistry-like formation of ureas and amides but reactions of the non-aldol type due to low thermodynamic driving force.
- addition reactions to carbon - carbon double bonds like epoxidation and dihydroxylation [103].

2.7 Diels-Alder Reactions

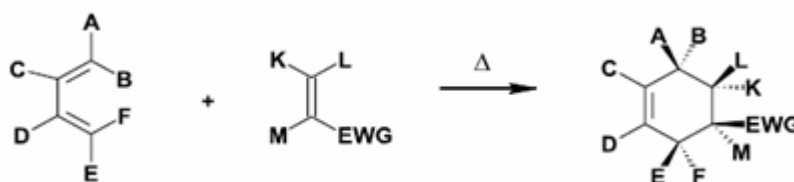
2.7.1 General features

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 [104].

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 [105].

The original version of the Diels-Alder reaction (Figure 2.10) 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. 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 [106] 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.



A — F and K — M: substituents; EWG: electron withdrawing group

Figure 2.10 : The original version of the diels-alder reaction

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 [107].

2.7.2 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 2.11) 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.

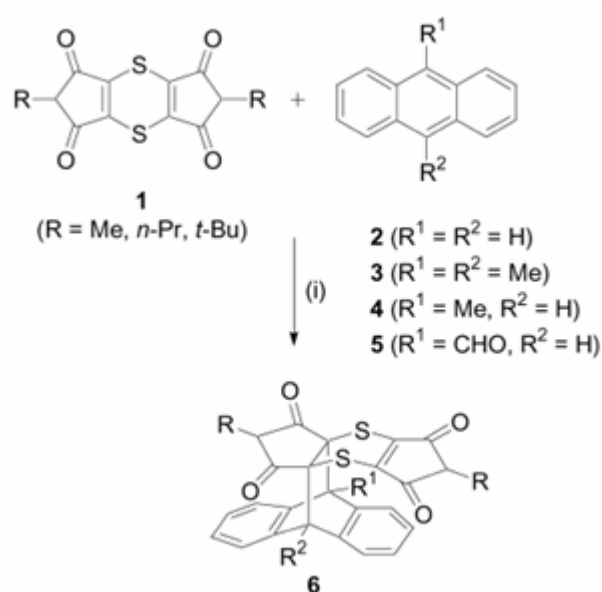


Figure 2.11 : Reagents and conditions: (i) C_6H_6 , Δ .

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 stabilisation 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-hydroxymethylantracene 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 [108].

3. EXPERIMENTAL

3.1 Materials

Styrene (St, 99%, Acros), methyl methacrylate (MMA, 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, and 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 a Agilent 1200 model 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) ($\lambda=670$ 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, $M_w/M_n=1.02$, $[\eta] = 0.519$ dL/g at 35 °C in THF, $dn/dc = 0.185$ mL/g) provided by Viscotek company. Typical sample concentrations for SEC-analysis were in the range of 2–8 mg/ml depending on molecular weight and filtered through 0.2 μ m pore-size PTFE membrane filter. Injection volume of the sample solutions were 50 μ L. Data analyses were performed with Omni-Sec version 4.5 software from Viscotek Company. DVB conversion was determined using the Agilent 6890 N gas chromatograph, equipped with an FID detector using a wide-bore capillary column (HP5, 30 m x 0.32 mm x 0.25 μ m, J and W Scientific). Injector and detector were kept constant at 280 and 285 °C, respectively. The ^1H spectra were recorded on a Bruker NMR Spectrometer (250 MHz) in CDCl_3 . UV spectra were recorded on a Shimadzu UV-1601 spectrophotometer in CH_2Cl_2 .

3.3 Synthesis of G1 and G2 Initiators

G1 and G2 initiators were provided by Sanyel Group at Bosphorus University Chemistry Department.

3.4 Synthesis of 9-anthrylmethyl 2-bromo-2-methyl propanoate (1)

To a round bottom flask were added 9-anthracene methanol (1.5 g, 7.18 mmol), triethylamine (1.2 mL, 8.6 mmol), DMAP (0.175 g, 1.436 mmol), and 20 ml of dry THF. To the reaction mixture, stirred at 0 °C under nitrogen was added drop-wise 2-bromo isobutyl bromide (1.82 g, 7.89 mmol) in 10 ml of dry THF over a period of 30 min. The reaction mixture was stirred at room temperature overnight. The salt was removed by filtration and after THF evaporation, crude product was extracted with CH_2Cl_2 and dilute NaHCO_3 aqueous solution for two times. The water phase again extracted with CH_2Cl_2 , and combined organic phase dried with Na_2SO_4 over anhydrous sodium sulfate (Na_2SO_4). CH_2Cl_2 was removed and the crude product was purified by column chromatography over silica gel eluting with hexane/ethylacetate (9:1) to give as solid yellow 1.78 g (4.97 mmol, %70) as yellow solid. (Yield: 1.78 g, 70 %). ^1H NMR (CDCl_3 , O). 7.43-8.52 (m, 9 ArH of anthracene) 6.21 (s, 2H, $\text{CH}_2\text{-O}$), 1.87 (s, (CH_3)₂-C-Br).

3.5 Preparation of PS with a-anthracene-End Functionality

PS-Anth was prepared by ATRP of St. St (20.0 mL, 174 mmol), PMDETA (0.181 mL, 0.87 mmol), CuBr (0.124 g, 0.87 mmol) and Ant-Br (0.31 g, 0.87 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 °C for 30 min. The darkgreen polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated in methanol. The polymer was dried for 24 h in a vacuum oven at 50 °C. ¹H NMR (CDCl₃, d) 8.4 (bs, ¹H, ArH of anthracene), 8.3 (bs, 2H, ArH of anthracene), 7.9 (bs, 2H, ArH of anthracene), 7.5 (bs, 4H, ArH of anthracene), 7.5–6.5 (ArH of PS), 5.8(CH₂-anthracene), 4.4 (CH(Ph)-Br), 0.6–2.2 (aliphatic protons of PS).

$[M]_0/[I]_0 = 200$; $[I]_0:[CuBr]:[PMDETA]=1:1:1$; conversion = 23%. $M_{n,theo} = 5200$, $M_{n,NMR} = 5400$, $M_{n,GPC} = 5400$, $M_w/M_n = 1.08$

3.6 Synthesis of Furan Protected Maleimide-End Functionalized PMMA using G1 as an initiator

(PMMA)₂-MI was prepared by ATRP of MMA. MMA (5.00 mL, 46.7 mmol), PMDETA (0.976 mL, 0.468 mmol), CuCl (0.0463g, 0.468 mmol), toluene (5 mL), and 3 (0.148 g, 0.234 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 40 °C for 75 minutes. 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 h in a vacuum oven at 25 °C. ¹H-NMR (CDCl₃, d) 6.5 (s, 2H, vinyl protons), 5.3 (s, 2H, CHCH=CHCH, bridge-head protons), 4.1 (m, 4H, CH₂ OC=O), 4.0–3.2 (m, OCH₃ of PMMA and NCH₂ CH₂ CH₂ OC=O), 2.9 (s, 2H, CH₂ NC=OCHA CH, bridge protons), 2.5–0.5 (m, CH₂ and CH₃ protons of PMMA).

$[M]_0/[I]_0 = 200$; $[I]_0:[CuBr]:[PMDETA]=1:1:1$; conversion = 19 %. $M_{n,theo} = 4500$, $M_{n,NMR} = 4600$, $M_{n,GPC} = 5900$, $M_w/M_n = 1.19$

3.7 Synthesis of Furan Protected Maleimide-End Functionalized PMMA using G2 as an initiator

(PMMA)₄-MI was prepared by ATRP of MMA. MMA (3.00 mL, 28 mmol), PMDETA (0.077 mL, 0.373 mmol), CuCl (0.0435g, 0.373 mmol), toluene (3 mL), and 4 (0.11 g, 0.093 mmol) were added in a 10 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 °C for 2 hours. 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 h in a vacuum oven at 25 °C. ¹H -NMR(CDCl₃, d) 6.5 (s, 2H, vinyl protons), 5.3 (s, 2H, CHCH=CHCH, bridge-head protons), 4.1 (m, 4H, CH₂ OC=O), 4.0–3.2 (m, OCH₃ of PMMA and NCH₂ CH₂ CH₂ OC=O), 2.9 (s, 2H, CH₂ NC=OCHA CH, bridge protons), 2.5–0.5 (m, CH₂ and CH₃ protons of PMMA).

[M]₀/[I]₀= 300; [I]₀:[CuBr]:[PMDETA]=1:1:1; conversion = 35 %. $M_{n,theo} = 8300$, $M_{n,NMR} = 7900$, $M_{n,GPC} = 10000$, $M_w/M_n = 1.18$

3.8 Synthesis of Multiarm Anthracene-End Functionalized (PS)_n-polyDVB Star Polymer (Core)

PS-Anth macroinitiator (3g, 0.0674 mmol), anisole (28.0 mL), PMDETA (14.1 μL, 0.0674mmol), DVB (1440 μL, 10.1 mmol), and CuBr (96.7 mg, 0.0674 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 °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. The reaction was stopped after 14 h 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 (1/1 v/v). Finally, the polymer was dried under vacuum at 30 °C for 24 h.

3.9 Synthesis of Dendrimeric Modified Multiarm (PS)_n-polyDVB-((PMMA)₂)_m Star Block Copolymer via Diels–Alder Click Reaction

A solution of (PMMA)₂-MI using G1 as initiator (0.409 g, 0.069 mmol) in 20 mL of toluene was added to a 10 mL solution of multiarm anthracene-end functionalized (PS)_n-polyDVB (0.25 g 0.00115 μmol) star polymer in toluene in a Schlenk tube. The mixture was bubbled with nitrogen for 30 min and refluxed for 48 h at 110 °C in the dark, and then toluene was evaporated under vacuum. The crude product was dissolved in THF and precipitated into methanol and diethyl ether. This procedure was repeated different three times. Firstly;the crude product was precipitated into 1/1 methanol/diethyl ether and then 1/2 methanol/diethyl ether finally only methanol. The obtained white product was dried in a vacuum oven at 25 °C for 24 h.

3.10 Synthesis of Dendrimeric Modified Multiarm (PS)_n-polyDVB-((PMMA)₄)_m Star Block Copolymer via Diels–Alder Click Reaction

A solution of (PMMA)₄-MI using G2 as initiator (0.798 g, 0.052 mmol) in 20 mL of toluene was added to a 10 mL solution of multiarm anthracene-end functionalized (PS)_n-polyDVB (0.25 g 0.00115 μmol) star polymer in toluene in a Schlenk tube. The mixture was bubbled with nitrogen for 30 min and refluxed for 48 h at 110 °C in the dark, and then toluene was evaporated under vacuum. The crude product was dissolved in THF and precipitated into methanol and diethyl ether. This procedure was repeated different three times. Firstly;the crude product was precipitated into 1/1 methanol/diethyl ether and then 2/3 methanol/diethyl ether finally 1/4 methanol/diethyl ether. The obtained white product was dried in a vacuum oven at 25 °C for 24 h.

4. RESULTS AND DISCUSSION

4.1. Synthesis of Initiators

First of all, the synthesis of 9-anthryl 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, Et₃N and as a solvent THF for 24 h at room temperature.

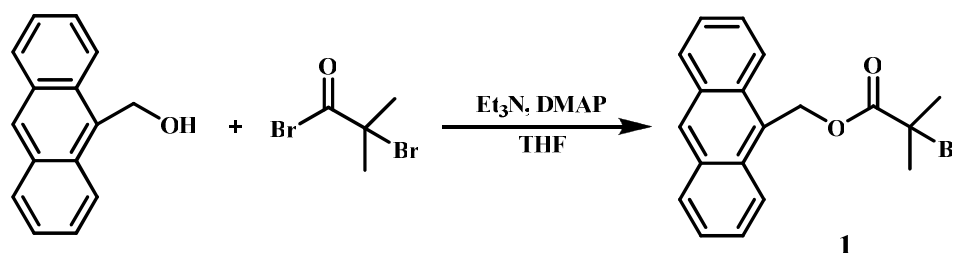


Figure 4.1 : Synthesis of 9-anthryl methyl 2-bromo-2-methyl propanoate, **1**.

In this reaction the excess of 2-bromo-2-methylpropanoyl bromide was used to achieve complete bromination and DMAP was used as a catalyst. The existence of HBr was captured by Et₃N as a salt in the solution. The synthesized initiator was characterized by using ¹H NMR. The protons between 8.6-7.3 ppm belong to anthracene's aromatic protons, 1.9 ppm belongs to methyl protons of initiator as can be seen Figure 4.2.

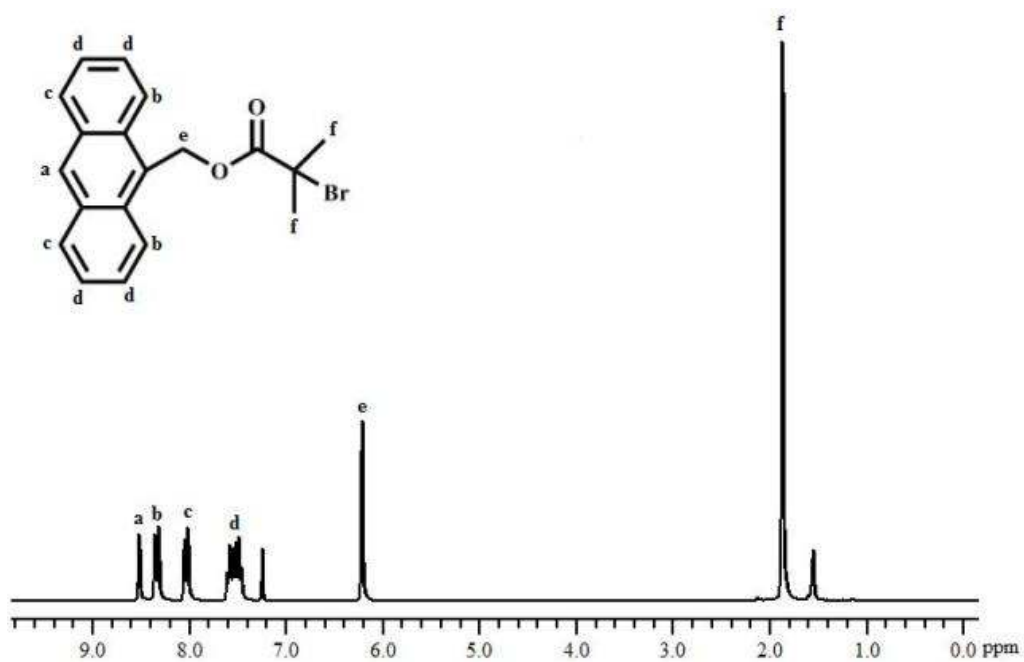


Figure 4.2 : The ^1H NMR Spectrum of 9-anthryl methyl 2-bromo-2-methyl propanoate in CDCl_3 .

Secondly, dendritic type initiators were provided by Sanyel Group at Bosphorus University Chemistry Department, The ^1H NMR spectra of the initiators G1 and G2 can be seen in Figure 4.3 and 4.4.

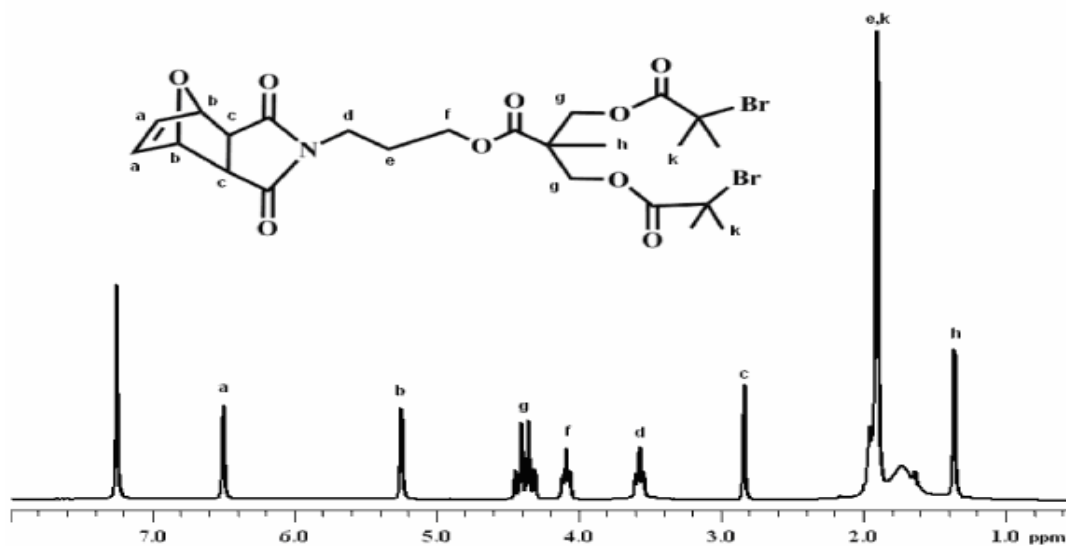


Figure 4.3 : The ^1H NMR spectrum of G1 initiator in CDCl_3

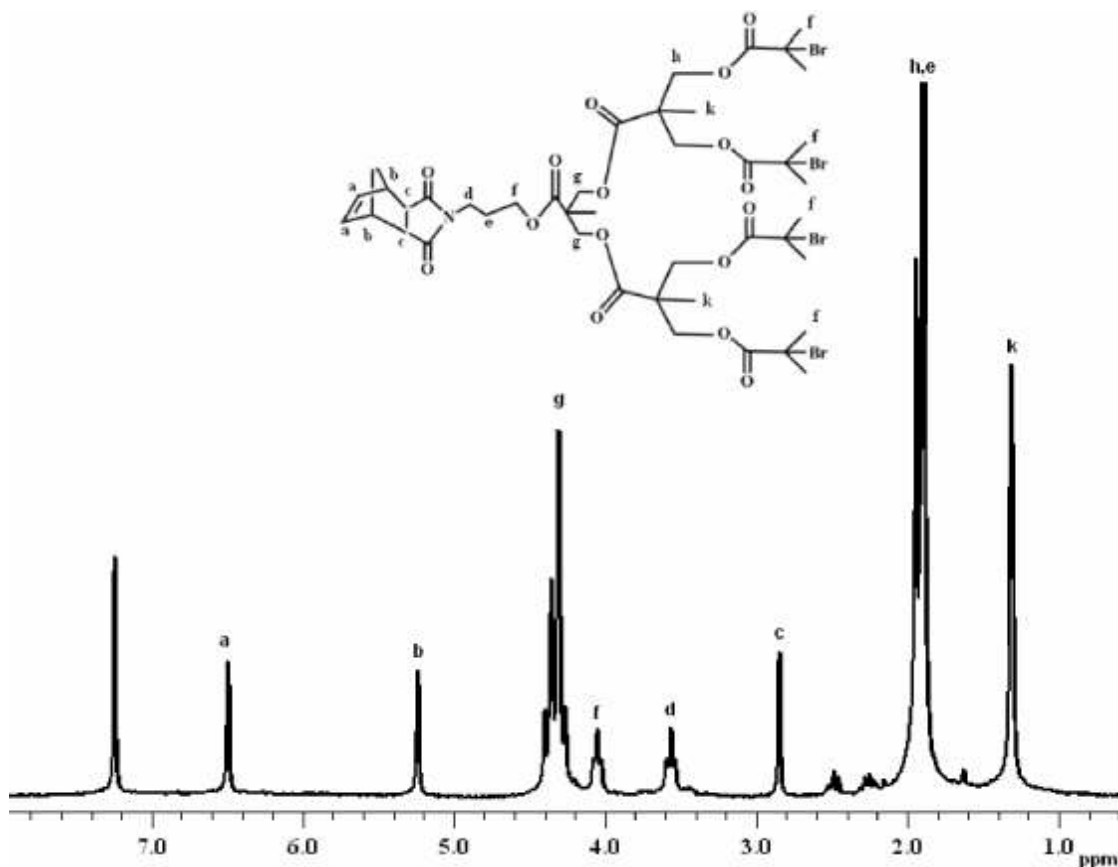


Figure 4.4 : The ^1H NMR spectrum of G2 initiator in CDCl_3

From ^1H NMR spectra, it is clearly be seen that the vinyl protons of the initiators at 6.45 ppm, the bridgehead protons 5.25 ppm and the bridge protons 2.8 ppm can be detected. The ester methylene protons next to oxygen can be seen at 4.4 ppm.

4.2. Synthesis of Polymers

First of all, the synthesis of PS-Anth macroinitiator was prepared by ATRP of St using $\text{CuBr}/\text{PMDETA}$ as a catalyst and 9-anthryl methyl 2-bromo-2-methyl propanoate (**1**) as an initiator.

The observed low polydispersity ($M_w/M_n = 1.08$) and a good correlation between the theoretical and experimental molecular weights of the macroinitiator indicate a controlled polymerization condition and high initiation efficiency.

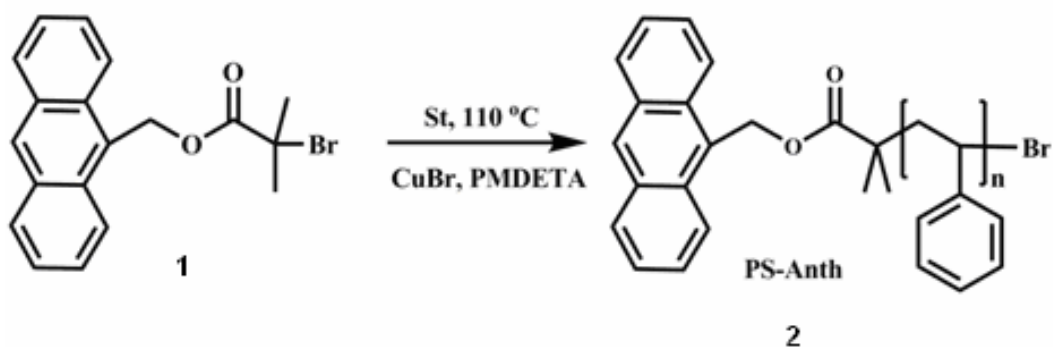


Figure 4.5 : Synthesis of PS with Anthracene-End Functionality

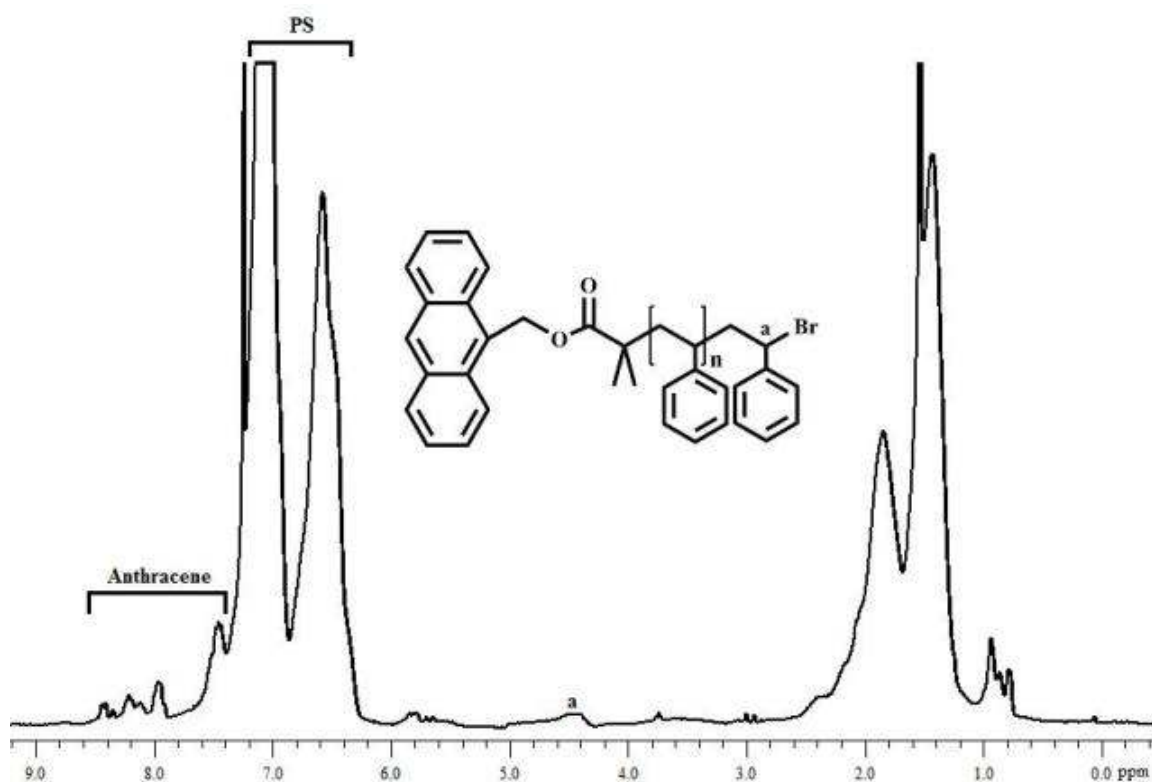


Figure 4.6 : The ^1H NMR spectrum of PS-Anth in CDCl_3

The polymerization was stopped at low monomer conversion (23%) to ensure a high degree of bromine chain-end functionality. The ^1H NMR number-average molecular weight ($M_{n,\text{NMR}}$) of the polymer was calculated from a ratio of the integrals of the aromatic protons of PS at 7.5-6.0 ppm and that of two protons of anthracene-end group at 7.9 ppm.

Secondly, synthesis of furan protected maleimide-end functionalized PMMA using G1 and G2 successfully as an initiator; α -furan protected maleimide-end functionalized $(\text{PMMA})_2\text{-MI}$ and $(\text{PMMA})_4\text{-MI}$ were prepared by ATRP (with

Figure 4.7 and Figure 4.9) of MMA using CuCl/PMDETA as a catalyst and G1 (3) and G2 (4) as a functional initiator.

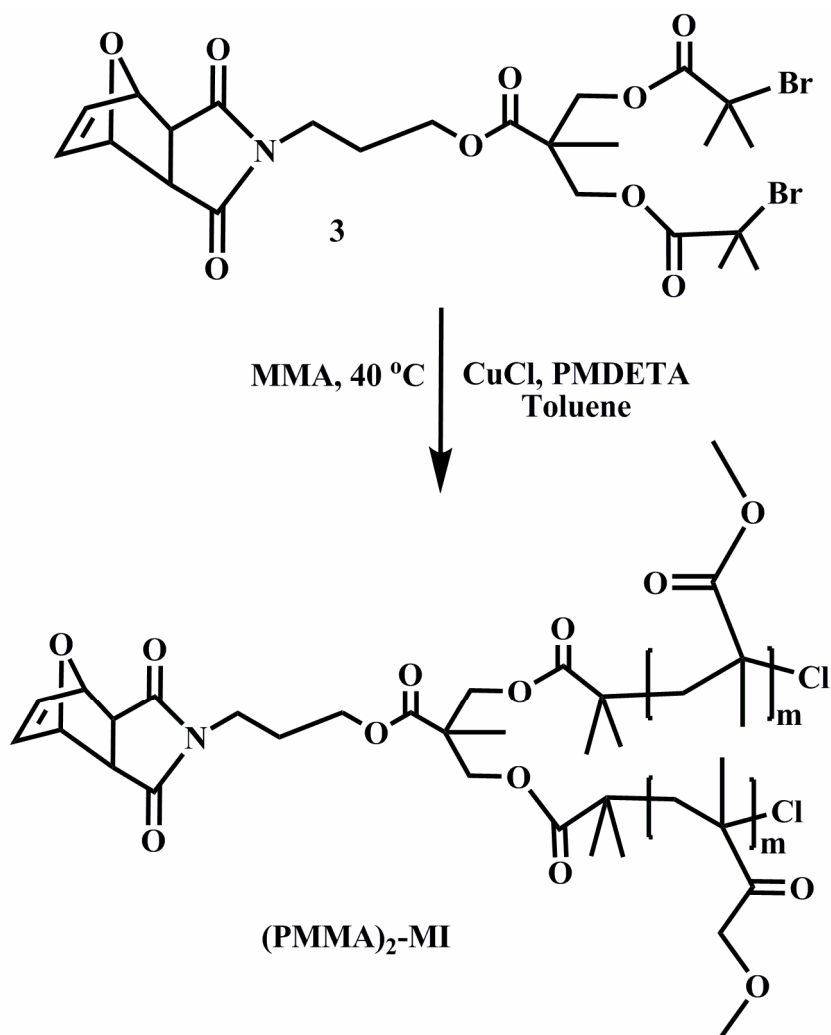


Figure 4.7 : Furan protected maleimide-end functionalized (PMMA)₂-MI via ATRP of MMA in the presence of **3** as an initiator, CuCl/PMDETA as a catalyst system at 40 °C.

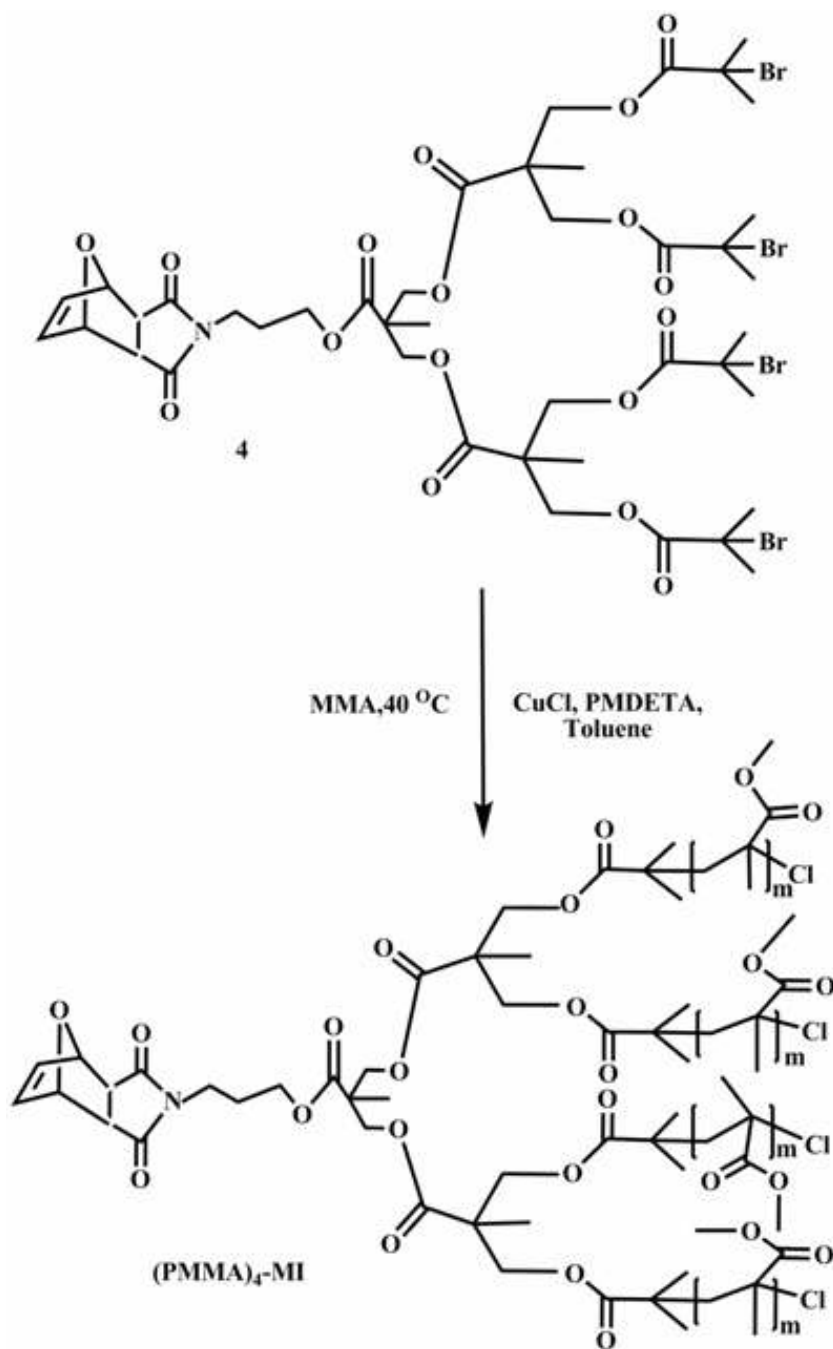


Figure 4.8 : Furan protected maleimide-end functionalized $(\text{PMMA})_4\text{-MI}$ via ATRP of MMA in the presence of 4 as an initiator, CuCl/PMDETA as a catalyst system at $40\text{ }^\circ\text{C}$.

The polymerization conditions and the results of ^1H NMR and TD-SEC analysis are given in Table 4.1; as can be seen in the table theoretical results are closer to ^1H NMR results. But $M_{n,\text{GPC}}$ results with TD-SEC is different from $M_{n,\text{theo}}$ and $M_{n,\text{NMR}}$, due to the low initiation efficiency at this reaction temperature ($40\text{ }^\circ\text{C}$).

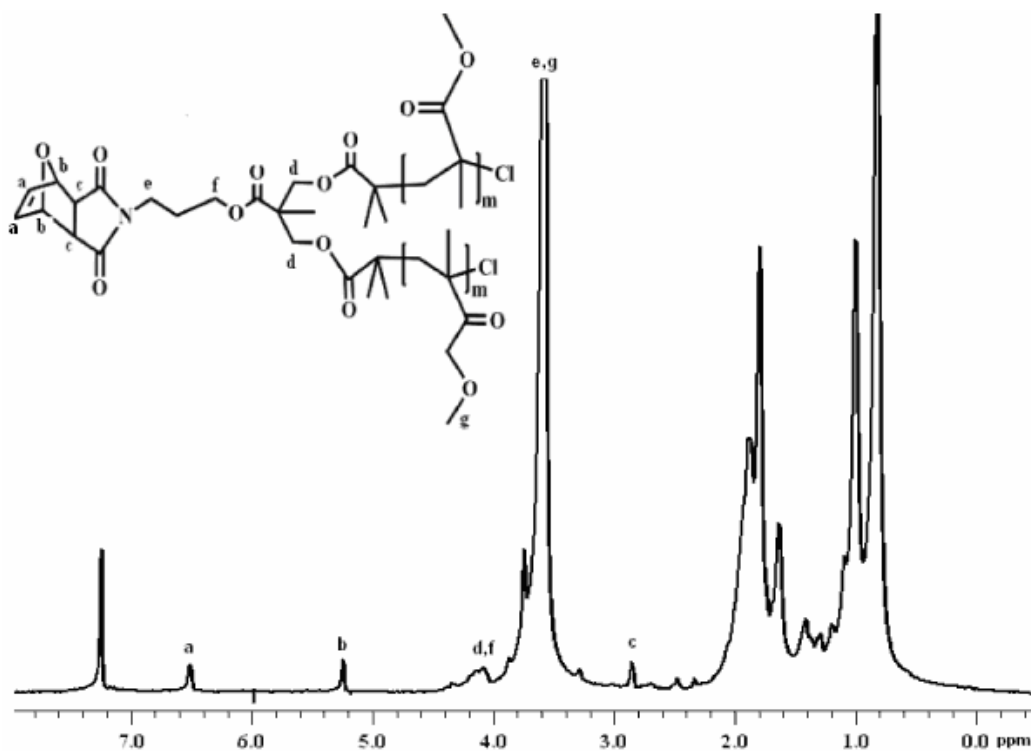


Figure 4.9 : The ^1H NMR spectrum of $(\text{PMMA})_2\text{-MI}$ in CDCl_3

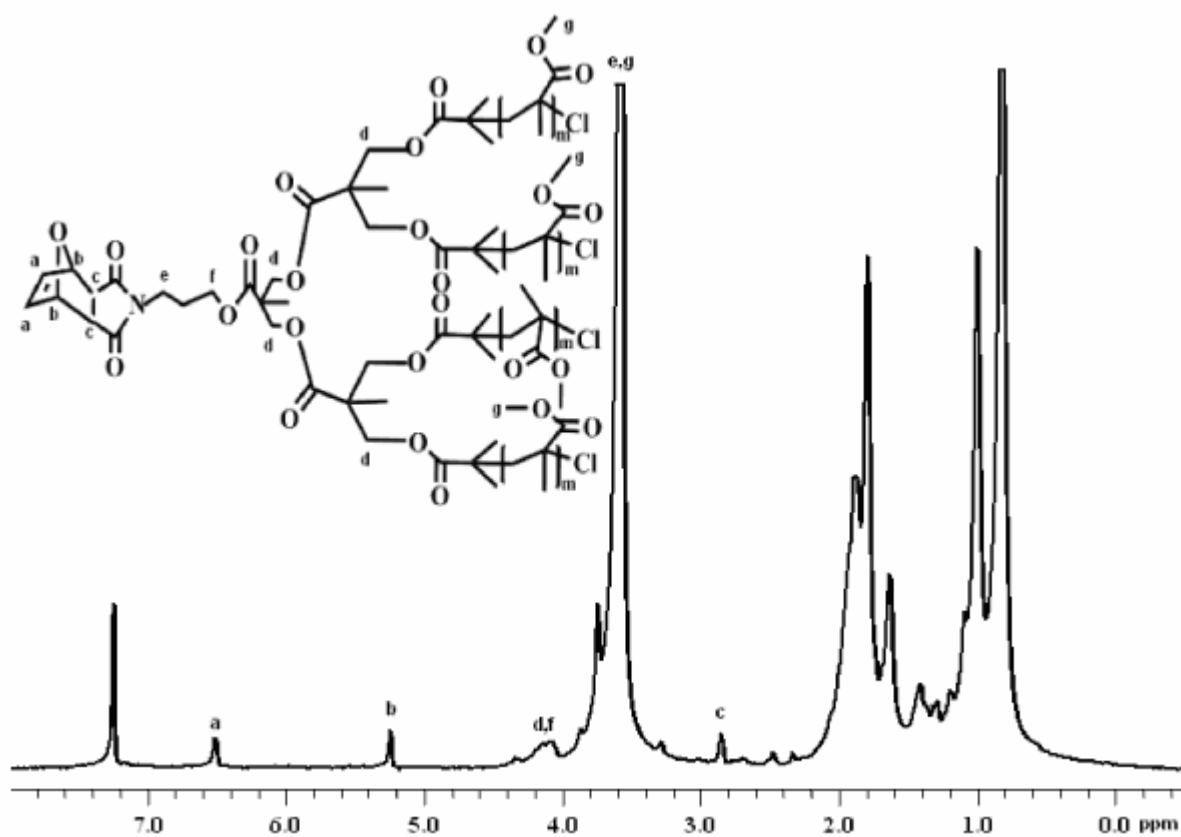


Figure 4.10 : The ^1H NMR spectrum of $(\text{PMMA})_4\text{-MI}$ in CDCl_3

It is obvious from ^1H NMR spectra; the vinyl protons of the polymers can be seen at 6.45 ppm, the bridgehead protons are at 5.3 ppm singlet. ($\text{CH}_2\text{OC}=\text{O}$) is at the 4.1 ppm multiplet and the characteristic peaks of PMMA (OCH_3) at 3.9 ppm. The bridge protons are at 2.9 ppm singlet. As a result of this, the polymerization was achieved successfully. The $M_{n,\text{NMR}}$ of the polymers were calculated from a ratio of the integrals of the vinyl protons at 6.45 ppm and that of three protons of PMMA (OCH_3) backbone at 3.58 ppm.

Table 4.1: Polymers obtained from the living radical polymerizations.

Entry	Polymer	$[M]_0/[I]_0$	[I]	Time (min)	Conv. (%)	GPC ^c		TD-GPC ^e		$M_{n, \text{theo}}$	$M_{n, \text{NMR}}$	$M_{n, \text{UV}}$
						M_n	M_w/M_n	M_n	M_w			
						(g/mol)		(g/mol)	(g/mol)			
1	PS-Anth ^a	200	1	30	23	5350	1.09	5600	6100	5150	5370	5300
2	(PMMA) ₂ -MI ^b	200	2	75	19	5900	1.19	6400	7900	4440	4650	-
3	(PMMA) ₄ -MI ^c	300	3	120	35	7850	1.18	12050	15100	8300	10050	-

^a $[M]_0:[I]_0 = 200$, polymerization was carried out in bulk at 110 °C.

^b $[M]_0:[I]_0 : [PMDETA]_0 : [CuCl]_0 = 200:1:1:1$; polymerization was carried out in toluene at 40 °C.

^c $[M]_0:[I]_0 : [PMDETA]_0 : [CuCl]_0 = 300:1:1:1$; polymerization was carried out in toluene at 40 °C.

^dMolecular weights were calculated according to linear PS standards.

^e GPC in THF with triple detector system.

4.3 Synthesis of Multiarm Anthracene-End Functionalized (PS)_n-polyDVB Star Polymer (Core)

Multiarm anthracene-end functionalized (PS)_n-polyDVB star polymer was obtained using PS-Anth as macroinitiator and DVB as cross-linker in ATRP conditions at 110 °C. It was demonstrated that soluble star polymers could be obtained when a suitable molar ratio of DVB to macroinitiator was used. The DVB conversion was followed by GC analysis and the polymerization was stopped after 10 h at 91 % conversion.

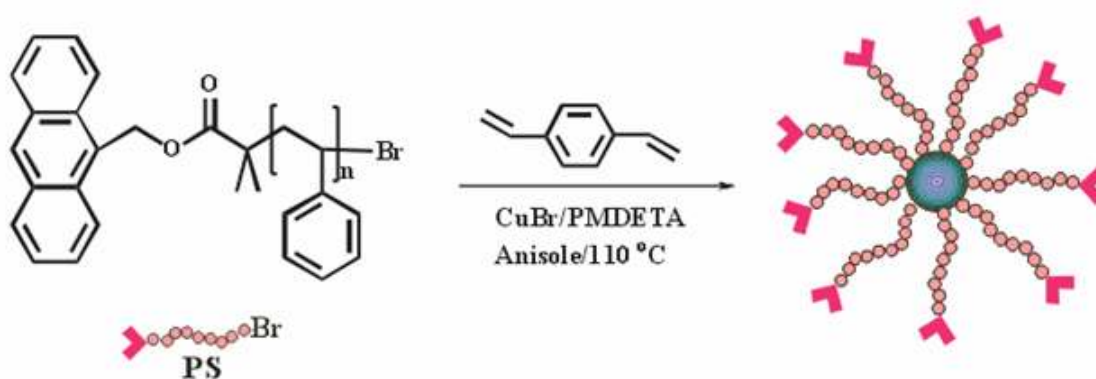


Figure 4.11 : Synthesis of core with DVB and CuBr/PMDETA as a catalyst system at 110 °C.

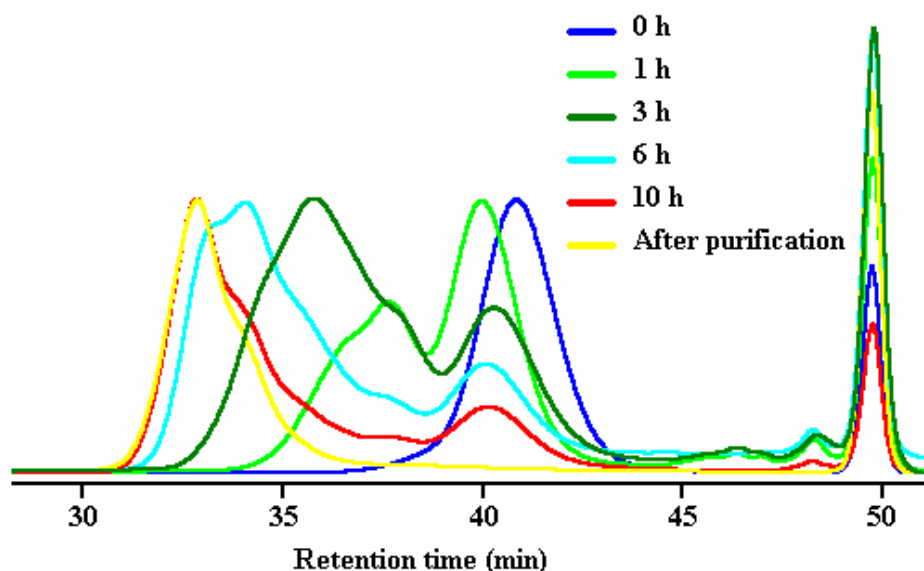


Figure 4.12 : SEC traces during the synthesis of anthracene end functionalized (PS)_n-polyDVB multiarm star polymer. Experimental conditions: [DVB]/15 = [PS-Ant] = [CuBr] = [PMDETA] = 0.023 M in anisole at 110 °C. GPC conditions: RI detector, relative to linear PS standards.

Figure 4.12 shows a series of conventional SEC curves of the reaction products at a given polymerization time and the purified multiarm star polymer. It was observed that the peak corresponding to the star polymer was shifted to the higher molecular weight region of the chromatogram and the RI signal corresponding to the PS macroinitiator also decreased with the extent of cross-linking reaction. These results clearly indicate that the formation of the multiarm star polymer, it was dissolved in THF and reprecipitated in methanol/diethyl ether mixture (1/1 v/v) to remove unreacted PS-Anth. The effectiveness of the purification procedure was confirmed by a complete disappearance of PS-Anth peak in an overlaid NMR chromatogram of purified sample in Figure 4.13.

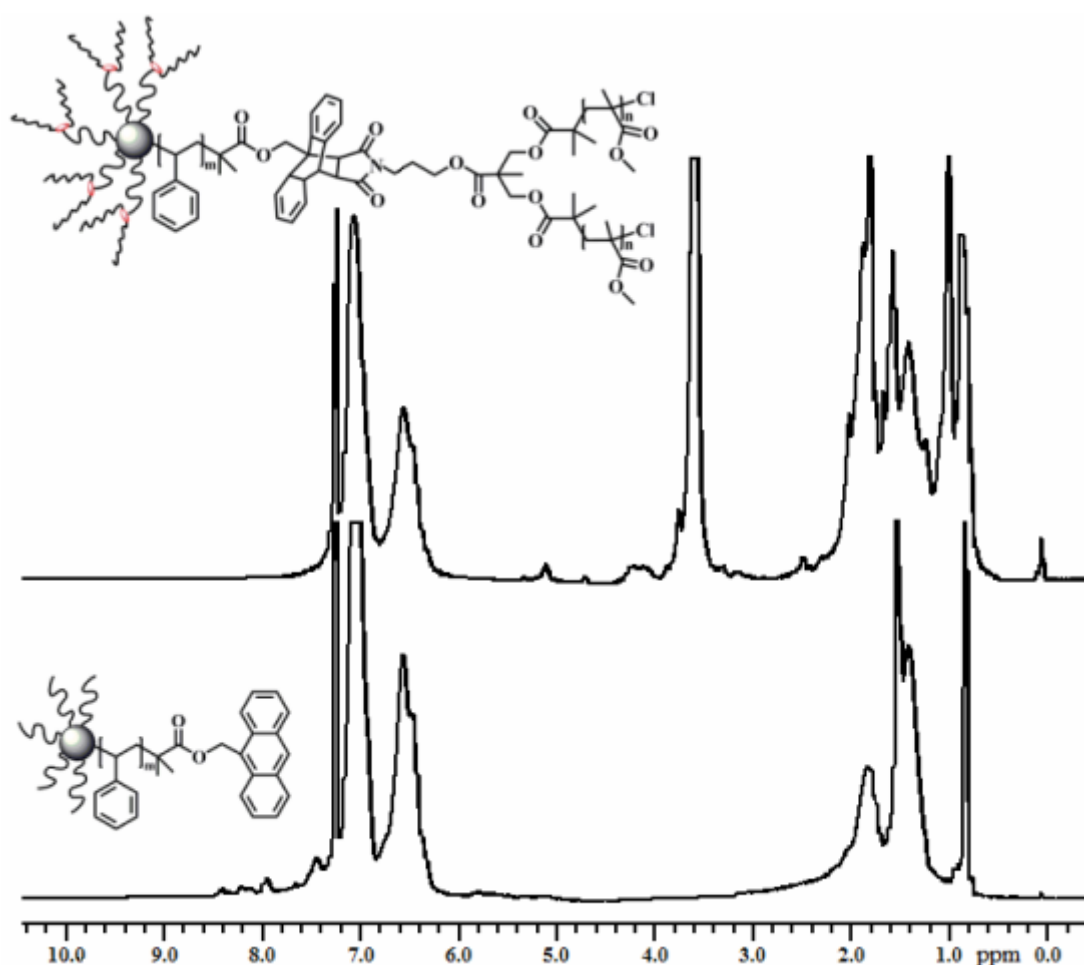


Figure 4.13 : Comparison of the ^1H NMR spectrum of $(\text{PS})_n$ -polyDVB multiarm star polymer (bottom) with $((\text{PMMA})_m)_2$ - $(\text{PS})_n$ -polyDVB multiarm star polymer (top).

The molecular weight values (M_n , M_w , M_p) of $(\text{PS})_n$ -polyDVB star polymer obtained using conventional SEC and Viscotek triple detection SEC (TD-SEC). 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 (f) of $(PS)_n$ -polyDVB star polymer was calculated using the following equation based on the absolute molecular weights (M_w) of multiarm star polymer.

$$f = \frac{WF_{arm} \times M_{w, star}}{M_{w, arm}} \quad (4.1)$$

$$= \frac{M_{w, star}}{M_{w, arm} + M_{DVB} \times conv_{DVB} \times [DVB]/[Si-p-PS]}$$

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-Anth 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, $[DVB]/[PS-Anth]$ is a feed molar ratio of the DVB to PS-Anth before cross-linking polymerization. The conversion of DVB ($conv_{DVB}$) was determined by GC. 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 eq 4.2.

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

where $[\eta]_{\text{star}}$ and $[\eta]_{\text{linear}}$ are the intrinsic viscosities of star polymer and the linear polymer with the same molecular weight and the composition, respectively. It is also shown that in regular (equal arm length) star polymers, g' is related with the number of arms, f as follows¹:

$$\log g' = 0.36 - 0.8 \log fg \quad (4.3)$$

Mark-Houwink-Sakurada (MHS) parameters k and a 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 $[\eta]_{\text{linear}}$ was calculated to have 1.011 dL/g for a specified molecular weight ($M_w = 216950$) of linear PS. Moreover, the $[\eta]_{\text{star}}$ of (PS)_n-polyDVB star polymer was measured to have 0.1452 dL/g by viscometer detector in TD-SEC. The number of arms, f was calculated to be 28 using eqs 4.2 and 4.3 and well agreed with that obtained from eq 4.1. All data were given in Table 4.2.

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

Entry	Polymer	GPC			TD-GPC						
		M_n (g/mol)	M_w/M_n	DA ef. (%)	M_n (g/mol)	M_w (g/mol)	dn/dc (mL/g)	$[\eta]$ (dL/g)	Rh (nm)	f^b	f^{xc}
4	(PS) _n -polyDVB ^a	55650	1,29	-	159450	216950	0.185	0.14	7.65	28	26
5	((PMMA) ₂) _m -(PS) _n -polyDVB	88800	1,29	96	266800	357050	0.141 ^d	0.17	9.68		
6	((PMMA) ₄) _m -(PS) _n -polyDVB	131200	1,31	88	414800	546100	0.122 ^d	0.18	11.24		

^a [DVB]/15 = [CuBr] = [PMDETA] = 0.07 M in anisole at 110 °C. ^bNumber of arms in multi arm star polymer, calculated according to Equation 1. ^cCalculated according to Equation. 4.2 and 4.3. ^fCalculated according to Equation 4.4.

4.4 Synthesis of Multiarm ((PMMA)₂)_n-(PS)_m-polyDVB and ((PMMA)₄)_n-(PS)_m-polyDVB Dendrimer Type Star Block Copolymers via Diels–Alder Click Reaction

The obtained multiarm anthracene-end functionalized (PS)_n-polyDVB star polymer was then reacted with (PMMA)₂-MI and (PMMA)₄-MI to give multiarm star block copolymers via Diels-Alder click reaction. The polymers with maleimide end functionality were used in a slight excess with respect to the concentration of anthracene in (PS)_n-polyDVB determined by UV. DA click reactions were performed at toluene reflux temperature for 24 h. The reaction was monitored by UV spectroscopy after the decrease in absorbance of anthracene between 300 and 400 nm in the reaction medium (Figure 4.14 and 4.17). DA efficiency was calculated by following anthracene $\text{Conv.}\% = (1 - A_t/A_0)$, where A_0 and A_t are initial and final absorbance values of anthracene, respectively. The efficiencies were found to be 96 and 88% for multiarm ((PMMA)₂)_m-(PS)_n-polyDVB and ((PMMA)₄)_m-(PS)_n-polyDVB star block copolymers, respectively. G1's conversion is higher than G2 through G1 has two end of groups G2 four. Steric hindrance is very important for conversion. The unreacted (PMMA)₂-MI and (PMMA)₄-MI were removed by precipitation into methanol /diethyl ether after the DA click reaction and thus, the purified multiarm star block copolymers were obtained.

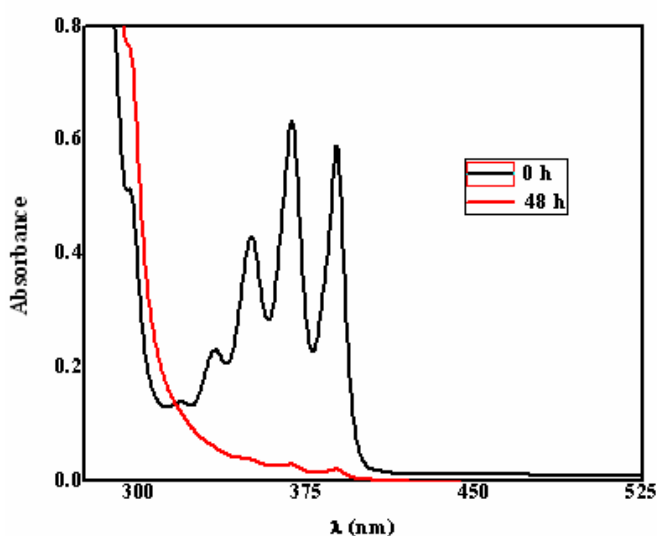


Figure 4.14 : UV spectra of multi arm anthracene-end functionalized (PS)_n-polyDVB star polymer during the synthesis of multiarm ((PMMA)₂)_m-(PS)_n-polyDVB star block copolymer 2.27×10^{-6} mol/L in CH₂ Cl₂.

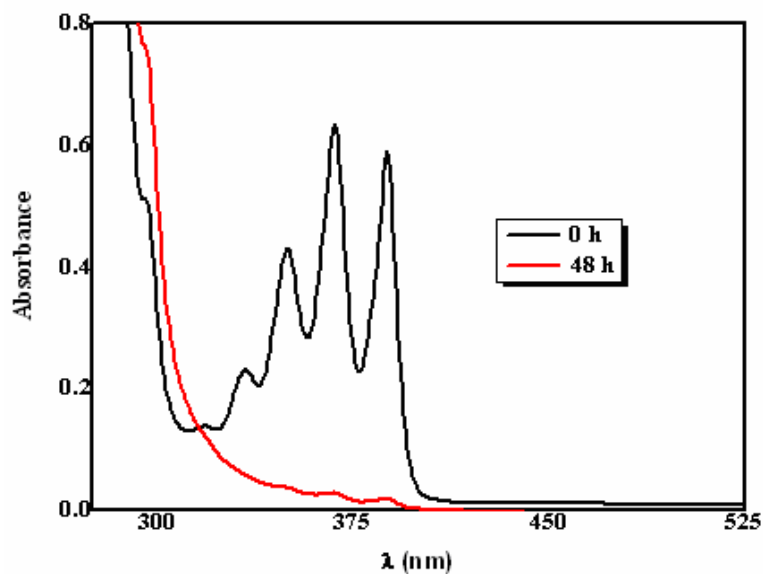


Figure 4.15 : UV spectra of multi arm anthracene-end functionalized (PS)_n-polyDVB star polymer during the synthesis of multiarm ((PMMA)₄)_m-(PS)_n-polyDVB star block copolymer 2.27×10^{-6} mol/L in CH₂ Cl₂.

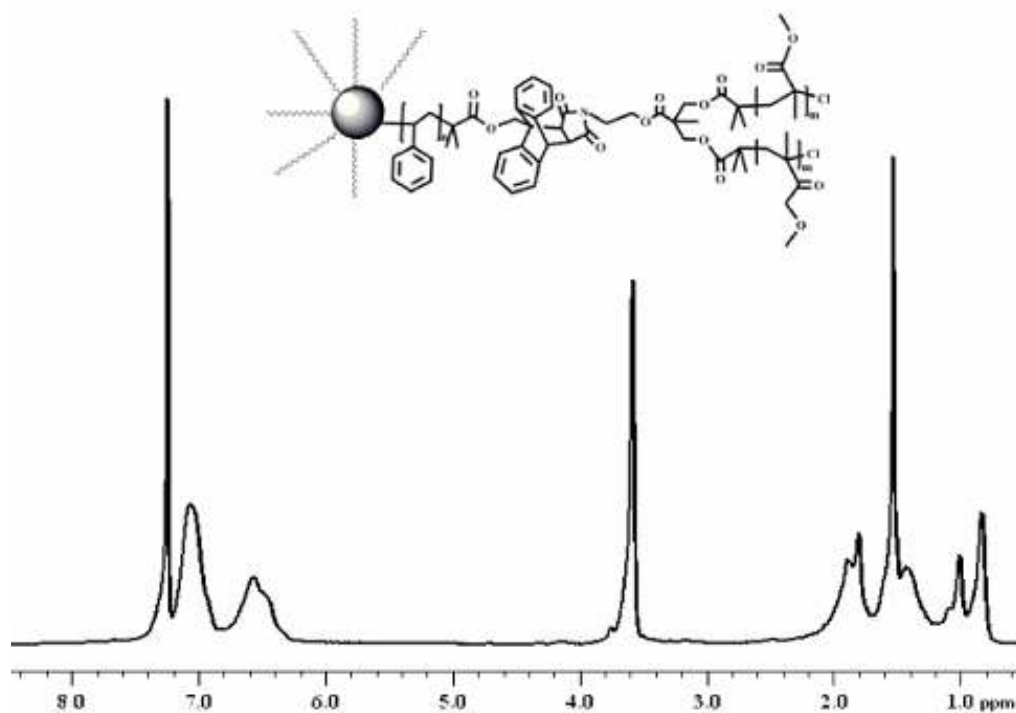


Figure 4.16 : ¹H NMR spectrum of multiarm ((PMMA)₂)_m-(PS)_n-polyDVB star block copolymer in CDCl₃.

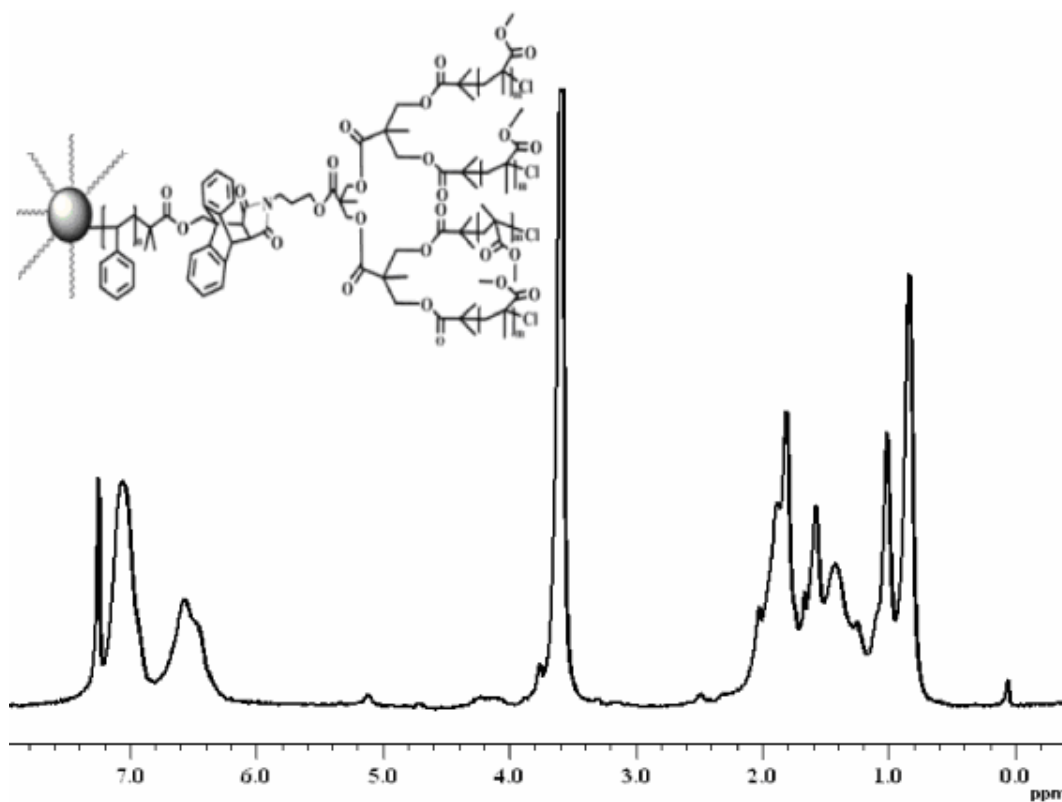


Figure 4.17 : ^1H NMR spectrum of multiarm $((\text{PMMA})_4)_m\text{-(PS)}_n\text{-polyDVB}$ star block copolymer in CDCl_3 .

The resulting multiarm star block copolymers were then confirmed by ^1H NMR and SEC. From ^1H NMR spectra of both dendrimetric multiarm star block copolymers, it was detected that characteristic peaks of anthracene (8.5–7.4 ppm) completely disappeared as a result of DA cycloaddition. New signals corresponding to CH_2 protons adjacent to anthracene ring at 5.3 ppm and a bridge-head proton of cycloadduct (CH) at 4.7 ppm were primarily observed (Figure 4.15 and 4.18). However, in the case of multiarm $((\text{PMMA})_2)_m\text{-(PS)}_n\text{-polyDVB}$ and $((\text{PMMA})_4)_m\text{-(PS)}_n\text{-polyDVB}$ star block copolymer, only two bridge protons at 3.3 ppm could be detected because of the overlapping OCH_3 protons of MMA.

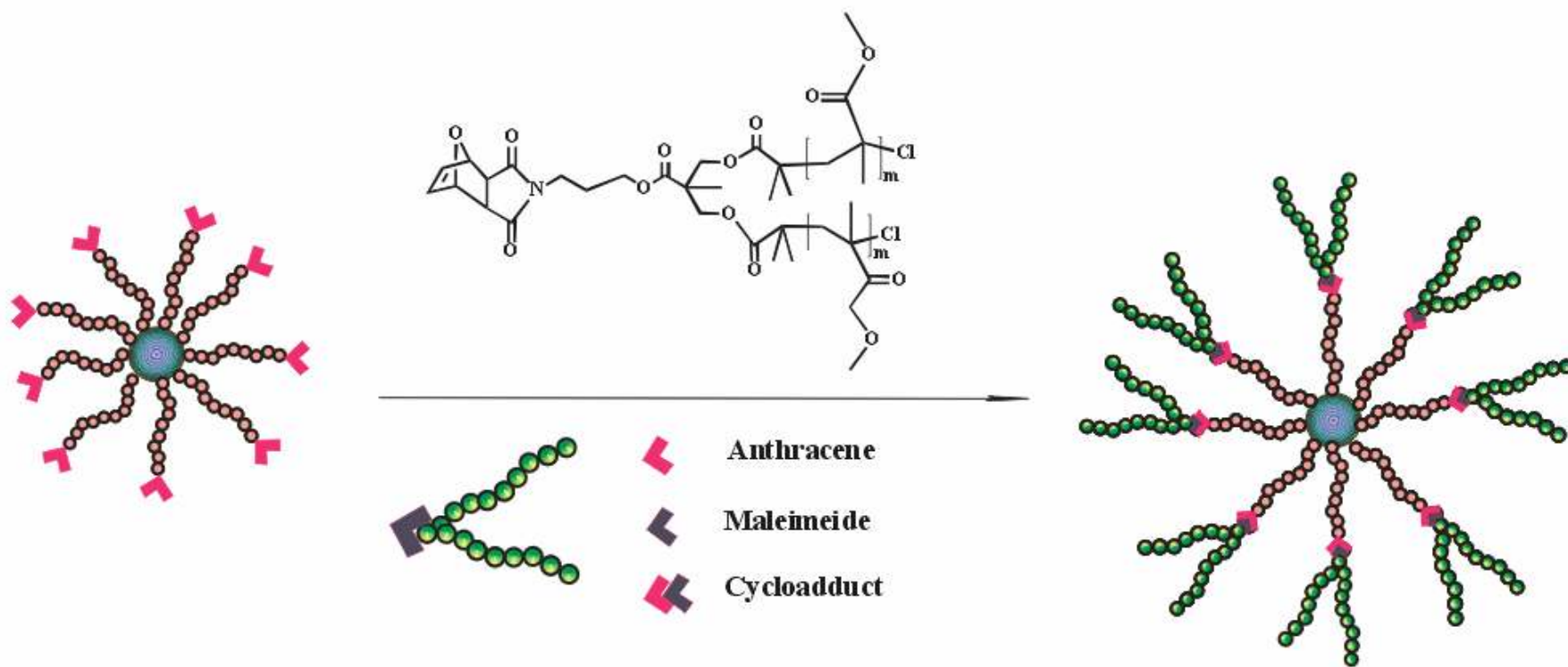


Figure 4.18 : The overall representation of the synthesis of multiarm star block copolymers $((\text{PMMA})_2)_m\text{-(PS)}_n\text{-polyDVB}$.

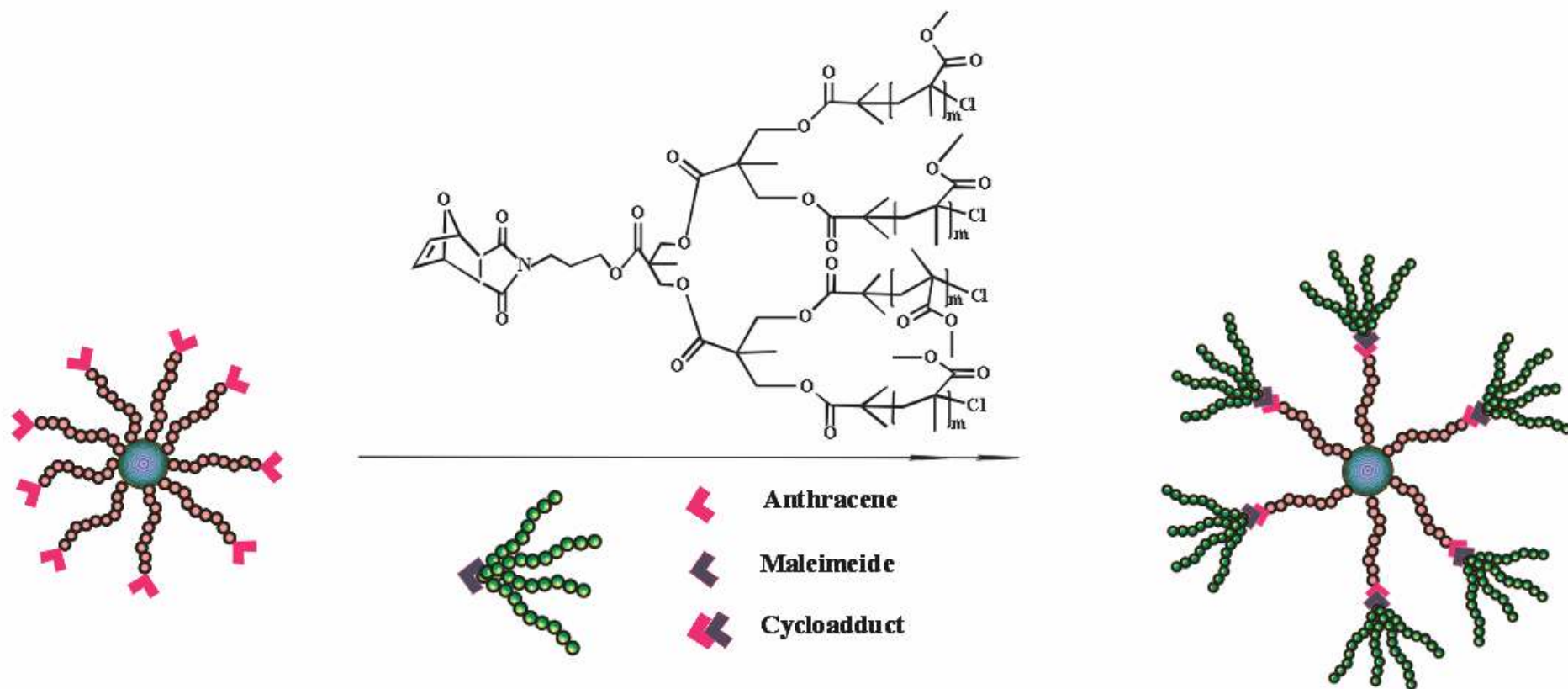


Figure 4.19 : The overall representation of the synthesis of multiarm star block copolymers ((PMMA)_{4m}-(PS)_n-polyDVB).

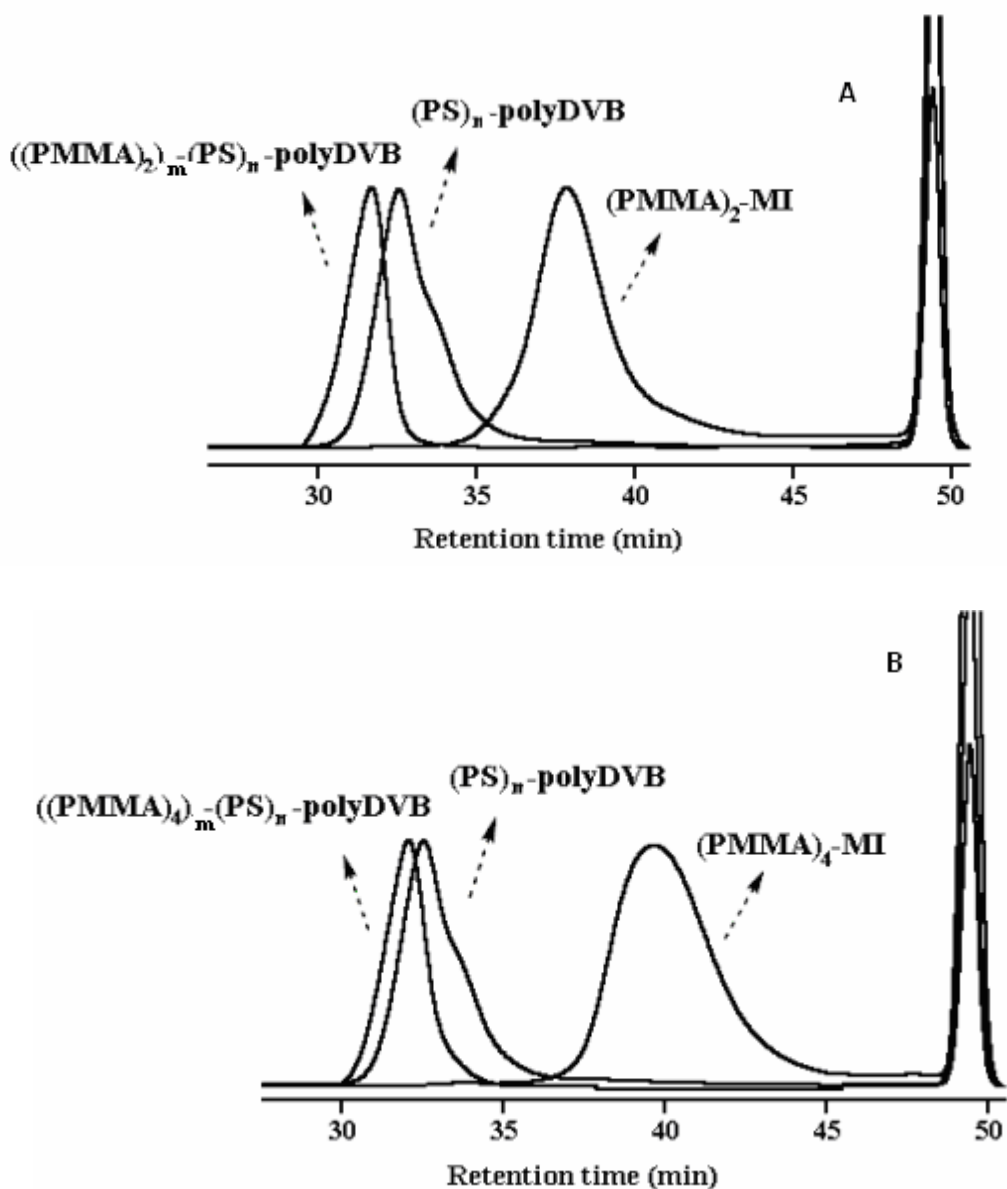


Figure 4.20 : The evolution of SEC traces: **a)** $(PMMA)_2$ -MI, multiarm anthracene-end functionalized $(PS)_n$ -polyDVB star polymer and multiarm $((PMMA)_2)_m$ - $(PS)_n$ -polyDVB star block copolymer **b)** $(PMMA)_4$ -MI, multiarm anthracene-end functionalized $(PS)_n$ -polyDVB star polymer and multiarm $((PMMA)_4)_m$ - $(PS)_n$ -polyDVB star block copolymer.

The evolution of SEC traces of multiarm anthracene-end functionalized $(PS)_n$ -polyDVB star polymer, $(PMMA)_2$ -MI and $(PMMA)_4$ -MI dendrimer polymers, and target multiarm star block copolymers are shown in Figure 4.20 a and b. The obtained multiarm $((PMMA)_2)_m$ - $(PS)_n$ -polyDVB and $((PMMA)_4)_m$ - $(PS)_n$ -polyDVB star block copolymers had higher hydrodynamic volume than that of multiarm

anthracene-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 multiarm 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 eq.4.4.

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

where x and y are weight fractions of PS and PMMA blocks from ¹H NMR according to the backbone protons. The weight fractions of PS and PMMA blocks in ((PMMA)₂)_m-(PS)_n-polyDVB and ((PMMA)₄)_m-(PS)_n-polyDVB are determined to be 0.64 and 0.36, respectively. For ((PMMA)₂)_m-(PS)_n-polyDVB and ((PMMA)₄)_m-(PS)_n-polyDVB 0.56 and 0.44 were found for weight fractions of PS and PMMA blocks, respectively. Using eq 4.4, dn/dc values are derived to have 0.14 and 0.12 mL/g for ((PMMA)₂)_m-(PS)_n-polyDVB and ((PMMA)₄)_m-(PS)_n-polyDVB dendrimetric type multiarm 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. Again the molecular weights of multiarm star block copolymers are inconsistent with those from conventional SEC because of the hydrodynamic volume difference between multiarm star block copolymers and linear PS standards. This methodology affords the molecular weight of multiarm star block copolymers up to around 800,000 without any star-star coupling reaction.

5. CONCLUSION

A combination of the cross-linking and highly efficient Diels-Alder click reactions is employed for the preparation of well-defined $((\text{PMMA})_2)_m\text{-(PS)}_n\text{-polyDVB}$ and $((\text{PMMA})_4)_m\text{-(PS)}_n\text{-polyDVB}$ initiator dendrimetric type multiarm star block copolymers based on ‘arm-first’ methodology. After cross-linking reaction, the average number of arms of $(\text{PS})_n\text{-polyDVB}$ multiarm star polymer is founded to be 28 and 26 using two different calculation methods. This result gives a proof of fort he well-defined structure and low degree of heterogeneity of the multiarm star polymer. Diels-Alder click reaction enables us to introduce the second block with precisely controlled in chain length into the multiarm star block copolymers. Moreover, the methodology reported herein can also provide a synthetic pathway for the introduction of various blocks obtained from different polymerization routes (ROP, ROMP etc.) into the multiarm star block copolymers. To the best of our knowledge, the dendrimetric type multiarm star block copolymers were successfully synthesized by our group.

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AUTOBIOGRAPHY



Candidate's full name: Ceyda ÖNEN

Place and date of birth: Fatih/İSTANBUL, 22.08.1985

Permanent Address: Cumhuriyet Mah. Murat Sok.Özkan Sitesi B Blok
No:23/7 Kartal/İSTANBUL

**Universities and
Colleges attended:**

Çemberlitaş Anadolu Lisesi

1999-2003

Marmara Üniversitesi – Fen-Edebiyat Fakültesi-Kimya

2003-2007

İstanbul Teknik Üniversitesi – Fen Bilimleri Enstitüsü

Polymer Science & Technology Master Programme

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