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HETEROARM H-SHAPED TERPOLYMERS THROUGH CLICK REACTION

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CLICK REAKSİYONU ARACILIĞIYLA FARKLI KOLLU H-TİPİ TERPOLİMER SENTEZİ

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LIST of SYMBOLS

ATRP	**:** Atom Transfer Radical Polymerization
NMP	**:** Nitroxide Mediated Polymerization
RAFT	**:** Reversible Addition-Fragmentation Chain Transfer Polymerization
PPT	**:** Postpolymerization Transformation
St	**:** Styrene
MMA	**:** Methyl methacrylate
***t*BA**	**:** *tert*-butylacrylate
PEG	**:** Poly(ethylene glycol)
R_m and R_n	**:** Propagating Radical
P_n and P_m	**:** Terminated Macromolecules
LFRP	**:** Living Free Radical Polymerization
CTA	**:** Chain Transfer Agent
TEMPO	**:** 2, 2, 6, 6- Tetramethylpiperidinoxy
PDI	**:** Polydispersity
PRE	**:** Persistent Radical Effect
M_t^n	**:** Transition metal
L	**:** Ligand
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
***p*-TSA**	**:** Paratoluensulfonic acid
DMAP	**:** 4-dimethylaminopyridine
DCC	**:** *N,N*-dicyclohexylcarbodiimide
BPO	**:** Benzoyl peroxide
DPTS	**:** 4-dimethylamino pyridinium-4-toluene sulfonate
PMDETA	**:** *N,N,N',N'',N''* - pentamethyldiethylenetriamine
FPT	**:** Freeze-pump-thaw
GPC	**:** Gel Permeation Chromotography
UV	**:** Ultra Violet Spectrophotometer
NMR	**:** Nuclear Magnetic Resonance Spectroscopy
DSC	**:** Differential Scanning Calorimetry
AFM	**:** Atomic Force Microscopy

HETEROARM H-SHAPED TERPOLYMERS THROUGH CLICK REACTION

SUMMARY

H type polymers show unique morphologies and very interesting rheological properties of entangled polymer melts and solutions because they have special structure. Therefore, the syntheses of H-shaped copolymers have become attractive research projects, and several H-shaped copolymers have been prepared in recent years.

The synthesis of well-defined polymers is usually achieved by a living polymerization technique. Controlled/ "Living" Radical Polymerization processes have proven to be versatile for the synthesis of polymers with well-defined structures and complex architectures. Among the CRP processes, Atom Transfer Radical Polymerization (ATRP) and Nitroxide Mediated Polymerization (NMP), are the most efficient methods for the synthesis of special polymers with complex architectures. Both, ATRP and NMP methods based on the fast equilibrium between active and dormant chains, actually it is the main effect to obtain controlled structure.One of the advantageous of controlled radical polymerization techniques such as ATRP and NMP is that the molecular weight and the chain end functionality can be controlled. The wide range of functionality can be introduce into the polymer chain and this leads to the synthesis of well-defined copolymers by a sequential two-step or one pot method without any transformation or protection of initiating sites.

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 reactionsClick 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, we prepared a novel H type terpolymer with an alkyne, TEMPO, and tertiary bromide function via combination of atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP) routes, and click reaction. For this purpose, first, mikto-functional initiator, **7**, with tertiary bromide (for ATRP), 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) (for NMP), and alkyne (for click reaction) functionalities was synthesized. The initiator **7** thus obtained was used in the subsequent living radical polymerization routes such as ATRP of MMA and NMP of St, and click reaction of alkyne and azide groups respectively, in order to give H type terpolymer, (PS)(PMMA)-P*t*BA-(PMMA)(PS) and (PS)(PMMA)-PEG-(PMMA)(PS) with controlled molecular weight and low polydispersity (M_w/M_n=1.33, 1.16). GPC traces, ^{1}H-NMR, DSC, and AFM investigations show that both initiator and polymerization were carried out successfully.

CLICK REAKSİYONU ARACILIĞIYLA FARKLI KOLLU H-TİPİ TERPOLİMER SENTEZİ

ÖZET

H-tipi polimerler özel yapılarından dolayı eşsiz morfolojik ve ilgi çekici reolojik özelliklere sahiptirler. Bu nedenledir ki H-tipi polimerler araştırma projeleri için çok ilgi çekici duruma gelmiştir. Son zamanlarda çeşitli H-tipi polimerler hazırlanmıştır. Yıldız polimerler araştırmalarda üç boyutlu ve çok dallanmış yapılarından dolayı yıllardır ilgi çekmektedirler.

Kontrollü/ "Yaşayan" Polimerizasyon yöntemlerinin iyi tanımlanmış ve kompleks yapılı polimerlerin sentezinde birçok açıdan faydalar sağladığı bilinmektedir. Kontrollü/ "Yaşayan" Radikal Polimerizasyon yöntemlerinin arasında Atom Transfer Radikal Polimerizasyonu (ATRP) ve Nitroksit Ortamlı Radikal Polimerizasyonu (NMP) kompleks yapılı polimerlerin sentezinde en etkili yöntemlerdir. ATRP ve NMP metotlarının her ikisi de aktif ve kararlı zincirler arasındaki hızlı dinamik dengeye dayanır ki kontrolü de sağlayan aslında budur. ATRP ve NMP gibi kontrollü polimerizasyon tekniklerinin bir avantajı da elde edilen polimerin molekül ağırlığının ve zincir uç grubu fonksiyonalitesinin kontrol edilebilir olmasıdır. Bu teknikler sayesinde polimer uç gruplarına çok çeşitli fonksiyonellikler kazandırılabilir bu da herhangi bir transformasyon reaksiyonu gerektirmeden iyi tanımlı polimerlerin eldesine izin verir.

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

Bu çalışmada, sırasıyla Nitroksit Ortamlı Radikal Polimerizasyon (NMP), Atom Transfer Radikal Polimerizasyon (ATRP) yöntemleri ve click reaksiyonunu kullanarak farklı kollu H-tipi terpolimer hazırlandı. Bu amaç için, ilk olarak yapısında tersiyer bromür (ATRP için) ve 2,2,6,6-tetrametilpiperidin-1-iloksi (TEMPO) (NMP için) ve alkin (Click reaksiyonu için) fonksiyonu içeren farklı kollu 3 fonksiyonlu başlatıcı, **7**, sentezlendi. Başlatıcı **7**, stirenin Nitroksit Ortamlı Radikal Polimerizasyonu, metil metakrilatın Atom Transfer Radikal Polimerizasyonu gibi yaşayan radikal polimerizasyonları ve alkin-azid fonksiyonlarının click reaksiyonu ile kontrollü molekül ağırlığına ve düşük molekül ağırlığı dağılımına (M_w/M_n=1.33, 1.16) sahip (PS)(PMMA)-P*t*BA-(PMMA)(PS) ve (PS)(PMMA)-PEG-(PMMA)(PS) olmak üzere 2 çeşit farklı kollu H-tipi polimer elde etmek için kullanıldı. GPC, ^{1}H-NMR, DSC ve AFM analizlerinden elde edilen sonuçlar hem başlatıcı hem de H-tipi terpolimer sentezinin başarılı bir şekilde gerçekleştiğini göstermiştir.

1. INTRODUCTION

H-shaped polymers defined as two side chains attached to the each end of a polymer backbone (main chain) were generally prepared through anionic polymerization route starting from chlorosilane or aromatic diolefins as coupling agents [1–5]. Thus, numerous H-shaped polymers such as polystyrene (PS) backbone and side chains [1], $(PS)_2$-PS-$(PS)_2$, polyisoprene (PI) backbone and side chains [3], $(PI)_2$-PI-$(PI)_2$, PI backbone and PS side chains [2,4], $(PS)_2$-PI-$(PS)_2$, and polybutadiene (PB) backbone and side chains [5], $(PB)_2$-PB-$(PB)_2$, were successfully prepared. Because of its architectural difference, H-shaped polymers show different rheological properties, micellar properties, and self assembled structures when compared with other linear or branched block copolymers. H-shaped polymers are important as model materials in understanding the rheology of branched polymers such as LDPE [6–8]. H-shaped copolymers form micelles with lower aggregation numbers which results in smaller micellar structures compared to linear block copolymers [9,10]. The selfassembly of H-shaped block copolymers show a variety of morphologies depending on the preparation conditions [11]. The synthesis of H-shaped poly- mers having various chemical structures is thus important to thoroughly understand the above-mentioned physical properties. The ionic polymerizations (anionic or cationic) were the only living systems available until recently. These systems provide the polymers with the controlled molecular weight, well-defined chain ends, and low polydispersity. In recent years, the use of the living radical polymerization (LRP) techniques for the synthesis of complex macromolecules has fast increased because of the variety of applicable monomers and more tolerant experimental conditions than the living ionic polymerization routes require. The reversible addition fragmentation chain transfer [12] (RAFT) polymerization, the nitroxide-mediated free radical polymerization [13] (NMP), and the metal mediated living radical polymerization often called atom transfer radical polymerization [14–16] (ATRP) are versatile methods for the living radical polymerizations. Although a remarkable development in all LRP processes, there are still some disadvantages such as removal of transition metal catalyst for the

purification of polymer (particularly in ATRP), low yield, and relatively higher polydispersity index. ATRP route was effectively employed for the synthesis of H-shaped copolymer, PS_2-poly(ethyleneglycol)-PS_2, $(PS)_2$-PEG-$(PS)_2$, where PEG and PS represent main and side chains, respectively [17,18]. Furthermore, via combination of ATRP and anionic polymerization routes, asymmetric H-shaped $(PS)_2$-PEG-(poly(methyl methacrylate)$_2$) $(PMMA)_2$ has been prepared [19] Recently, Sharpless and coworkers used Cu(I) as a catalyst in conjunction with a base in Huisgen's 1,3-dipolar cycloadditions [20], [3 + 2] system, between azides and alkynes or nitriles, and termed them click reactions [21,22]. Later, click chemistry strategy was successfully applied to macromolecular chemistry, affording polymeric materials varying from the block copolymers [23] to the complex macromolecular [24–38] structures.

Click reactions permit C-C (or C-N) formation in a quantitative yield without side reaction and requirement for additional purification step.

The aim of this study was to investigate the efficiency of the click reaction strategy for the preparation of H-shaped polymer that has two thermodynamically incompatible arms (PS and PMMA) on either side of the central unit (P*t*BA or PEG). Using this strategy, diazide end-functionalized P*t*BA or PEG (main chain) and PS-*b*-PMMA copolymer (side chains) with an alkyne functional group at the junction point were linked to give (PS)(PMMA)-P*t*BA-(PMMA)(PS) and (PS)(PMMA)-PEG-(PMMA)(PS) heteroarm H-shaped terpolymer.

2. THEORITICAL PART

2.1. Conventional Free Radical Polymerizations

Conventional free radical polymerization (FRP) has many advantages over other polymerization processes. First, FRP does not require stringent process conditions and can be used for the (co)polymerization of a wide range of vinyl monomers. Nearly 50% of all commercial synthetic polymers are prepared using radical chemistry, providing a spectrum of materials for a range of markets [39]. However, the major limitation of FRP is poor control over some of the key elements of the process that would allow the preparation of well-defined polymers with controlled molecular weight, polydispersity, composition, chain architecture, and site-specific functionality.

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

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

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

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

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

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

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

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

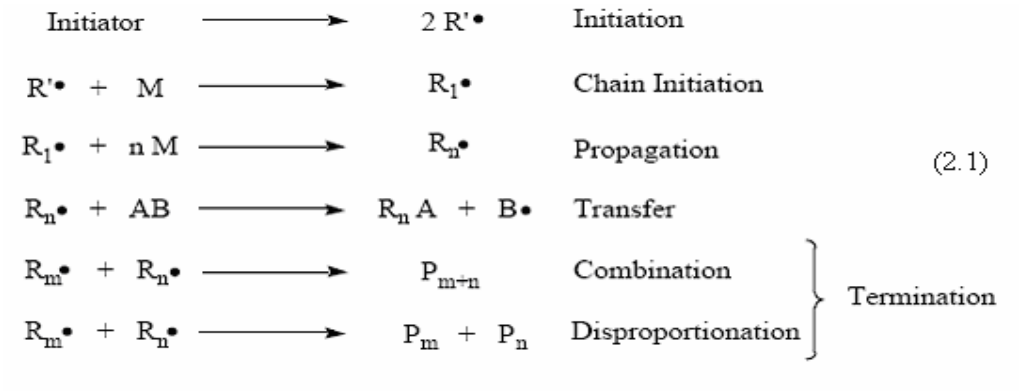


Figure 2.1. General Free Radical Polymerization Mechanism

2.2. Conventional Living Polymerizations

Living polymerizations are characterized by chain growth that matures linearly with time. Inherent in this definition are two characteristics of ionic polymerizations that both liken and distinguish ionic routes from the aforementioned free radical route. In order to grow linearly with time, ionic polymerizations must proceed by a chain mechanism in which subsequent monomer molecules add to a single active site; furthermore, addition must occur without interruption throughout the life of the active site. Thus, the chain transfer mechanisms described above must be absent. Living polymerizations may include slow initiation, reversible formation of species with various activities and lifetimes, reversible formation of inactive (dormant) species, and/or reversible transfer [40]. Living polymerizations must not include irreversible deactivation and irreversible transfer.

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

2.3. Controlled/ ''Living" Free Radical Polymerizations

Living polymerization was first defined by Szwarc [41] as a chain growth process without chain breaking reactions (transfer and termination). Such a polymerization provides end-group control and enables the synthesis of block copolymers by sequential monomer addition. However, it does not necessarily provide polymers with molecular weight (MW) control and narrow molecular weight distribution (MWD). Additional prerequisites to achieve these goals include that the initiator should be consumed at early stages of polymerization and that the exchange between species of various reactivities should be at least as fast as propagation [42-44]. It has been suggested to use a term controlled polymerization if these additional criteria are met [45]. This term was proposed for systems, which provide control of MW and MWD but in which chain breaking reactions continue to occur as in RP. However, the term controlled does not specify which features are controlled and which are not controlled. Another option would be to use the term ''living'' polymerization (with

quotation marks) or ‘‘apparently living,’’ which could indicate a process of preparing well-defined polymers under conditions in which chain breaking reactions undoubtedly occur, as in radical polymerization [46,47].

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

Living polymerization is defined as a polymerization that undergoes neither termination nor transfer. A plot of molecular weight vs conversion is therefore linear, as seen in Scheme (2.2), and the polymer chains all grow at the same rate, decreasing the polydispersity. The propagating center at 100 % conversion still exists and can be further reacted, which can allow novel block, graft, star, or hyperbranched copolymers to be synthesized. Living polymerizations have been realized in anionic processes where transfer and termination are easy to suppress. Due to the favorable coupling of two radical propagating centers and various radical chain transfer reactions, the design and control of a living radical processes is inherently a much more challenging task. The living process of radical polymerization involves the equilibration of growing free radicals and various types of dormant species. By tying up a great deal of the reactive centers as dormant species, the concentration of free radicals decreases substantially and therefore suppresses the transfer and termination steps. These reactions are also denoted as controlled /living polymerizations rather than as true living polymerizations because transfer and termination are decreased but not eliminated. Three processes, NMP, ATRP, and RAFT, will now be introduced [48].

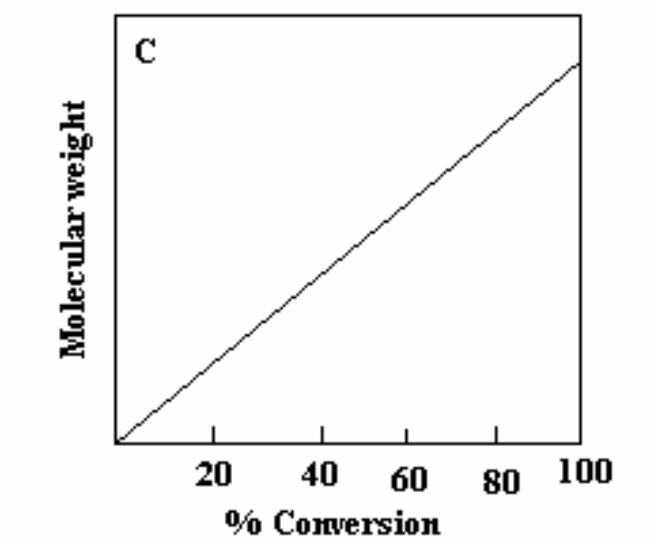


Figure 2.2. Molecular weight vs conversion graph of a typical living polymerization

Living free radical polymerizations, although only about a decade old, have attained a tremendous following in polymer chemistry. The development of this process has been a long-standing goal because of the desire to combine the undemanding and industrial friendly nature of radical polymerizations with the power to control polydispersities, architectures, and molecular weights that living processes afford. A great deal of effort has been made to develop and understand different living free radical polymerization (LFRP) methods. The methods at the forefront fall into one of three categories: nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition fragmentation chain transfer (RAFT) [48].

2.3.1. Nitroxide-Mediated Living Free Radical (NMP)

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

process. Shortly thereafter, it was shown that low molecular weight alkoxyamines such as styryl-TEMPO can be used as initiators/regulators for the controlled living radical polymerization of styrene [49]. Although NMP is one of the simplest methods of living free radical polymerization (LFRP), it has many disadvantages. Many monomers will not polymerize because of the stability of the dormant alkoxyamine that forms. Also, since the reaction is kinetically slow, high temperatures and bulk solutions are often required. Also, the alkoxyamine end groups are difficult to transform and require radical chemistry [50].

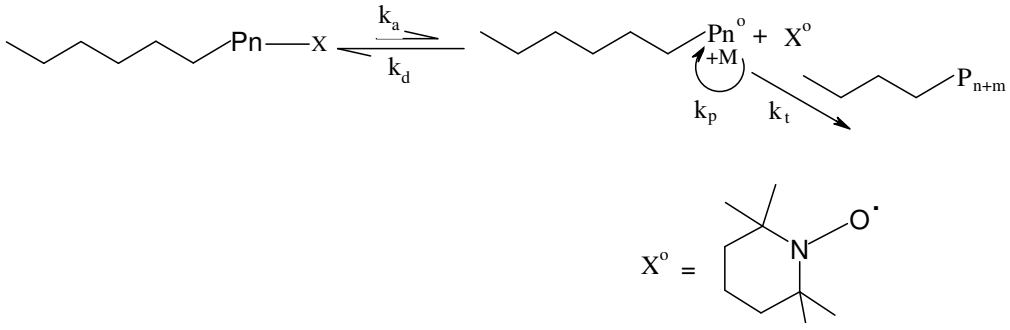


Figure 2.3. Mechanism for nitroxide-mediated living free radical polymerization

The key to the success is a reversible thermal C═O bond cleavage of a polymeric alkoxyamine to generate the corresponding polymeric radical and a nitroxide. Monomer insertion with subsequent nitroxide trapping leads to chain-extended polymeric alkoxyamine. The whole process is controlled by the so called persistent radical effect (PRE) [51]. The PRE is a general principle that explains the highly specific formation of the cross-coupling product (R_1–R_2) between two radicals R_1 and R_2 when one species is persistent (in NMP the nitroxide) and the other transient (in NMP the polymeric radical), and the two radicals are formed at equal rates (guaranteed in NMP by thermal C═O bond homolysis). The initial buildup in concentration of the persistent nitroxide, caused by the self termination of the transient polymeric radical, steers the reaction subsequently to follow a single pathway, namely the coupling of the nitroxide with the polymeric radical. First, nitroxide mediated polymerizations of styrene were conducted using conventional free radical initiators in the presence of free nitroxide and monomer [52]. In general better results are obtained using preformed alkoxyamines. Defined concentration of the initiator allows a better control of the targeted molecular weight using this approach. Based on the mechanism depicted in Scheme (2.3), it is obvious that the

equilibrium constant *K* between the dormant alkoxyamine and the polymeric radical and nitroxide is a key parameter of the polymerization process. The equilibrium constant *K* is defined as *k*a/*k*d (*k*a = rate constant for alkoxyamine C═O bond homolysis; *k*d = rate constant for trapping of the polymeric radical with the given nitroxide). Various parameters such as steric effects, H-bonding and polar effects influence the *K*-value [53]. Since the first TEMPO-mediated polymerizations many nitroxides and their corresponding alkoxyamines have been prepared and tested in NMP. Due to space limitation we cannot give an overview of all alkoxyamines tested so far [54].

The most popular nitroxide used for NMP in the past has been TEMPO. However, TEMPO is limited in the range of monomers which are compatible to polymerize by NMP, mostly due to the stability of the radical. Hawker et. al. recently discovered that by replacing the α-tertiary carbon atom with a secondary carbon atom, the stability of the nitroxide radical decreased which lead to an increased effectiveness in polymerization for many monomers in which TEMPO was uneffective. While TEMPO and TEMPO derivatives are only useful for styrene polymerizations, the new derivatives permit the polymerization of acrylates, acrylamides, 1,3-dienes, and acrylonitrile based monomers with very accurate control of molecular weights and low polydispersities. Another family of nitroxides that have shown to have the same success are phosphonate derivatives designed by Gnanou et.al [55].

The chain end functionalization of polymers synthesized by NMP is a significant problem because dormant chains containing alkoxyamines can regenerate terminal radicals which can depolymerize at high temperatures. A very interesting chain end functionalization process has also been discovered by Hawker et. al. which involves the controlled monoaddition of maleic anhydride or maleimide derivatives to the alkoxyamine chain end. The alkoxyamine can then be easily eliminated and other functional groups can be introduced. This process relies on the resistance of maleic anhydride or maleimide derivatives to homopolymerize and the ability of the precurser to reform the olefin by elimination of the hydroxylamine [56].

2.3.2. Atom Transfer Radical Polymerization

Atom transfer radical polymerization (ATRP) is a living radical polymerization process utilizing transition-metal complexes as catalysts to mediate the propagation

of the polymerization. It is a very versatile process and can synthesize a wide spectrum of polymers with controlled structures. Atom transfer radical polymerization (ATRP) is one of the most convenient methods to synthesize well-defined low molecular weight polymers [57]. A general mechanism for ATRP is given below.

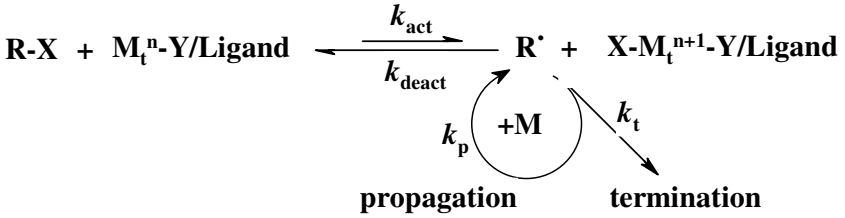


Figure 2.4. General Mechanism for ATRP

Firstly, initiation should be fast, providing a constant concentration of growing polymer chains. Secondly, because of the persistent radical effect, the majority of the growing polymer chains are dormant species that still presence the ability to grow because a dynamic equilibrium between dormant species. By keeping the concentration of active species of propagating radicals sufficiently low through the polymer, termination is suppressed. ATRP is a radical process that full fills these requirements by using a transition metal in combination with a suitable ligand [58].

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

ATRP can be used on a large number of monomers and requires ambient reaction conditions. The reaction is uneffected by the precence of O_2 and other inhibitors. Also, the alkyl halide end groups can be easily transformed by S_N^1, S_N^2, or radical chemistry. The major drawback to ATRP is that a transition metal catalyst which is used must be removed which after polymerization and possibly recycled. Future work in this field includes the removal and recycling of the catalyst as well as the design of catalysts that react with a larger range of monomers [48].

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

This process occurs with a rate constant of activation, k_{act}, and deactivation, k_{deact}. Polymer chains grow by the addition of the intermediate radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation k_p. Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination.

Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5 % of the total growing polymer chains terminate during the initial, short, nonstationary stage of polymerization. This process generates oxidized metal complexes, $X\text{-}M_t^{n+1}$, as persistent radicals to reduce the stationary concentration of termination [59]. Polydispersities in ATRP decrease with conversion, with the rate constant of deactivation, k_{deact}, and also with the concentration of deactivator. The molecular conversion and the amount of initiator used, $DP = \Delta[M]/[I]_0$; polydispersities are low, $M_w / M_n < 1{,}3$ [60].

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

ATRP has been successfully used in living polymerizations of a wide range of monomers, such as styrenic monomers, acrylates, methacrylates, (meth)acrylamides, acrylnitrile and vinyl chloride in bulk, solution using organics or water as solvents, and emulsion, supercritical carbon dioxide, producing polymers with well-controlled molecular weights and structures. For example, polystyrene with polydispersity as

narrow as those of PS standards synthesized by living anionic polymerization was obtained by copper-catalyzed ATRP [61].

The amount of the initiator in the ATRP determines the final molecular weight of the polymer at full monomer conversion. Multifunctional initiators may provide chain growth in several directions. The main role of the initiator is to determine the number of growing polymer chains. If initiation is fast and transfer and termination negligible, then the number of growing chains is constant and equal to the initial initiator concentration. The theoretical molecular weight or degree of polymerization (DP) increases reciprocally with the initial concentration of initiator in a living polymerization.

$$\mathbf{DP = [M]_0 / [I]_0 \times Conversion}$$

Figure 2.5. Degree of polymerization

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

Initiation should be fast and quantitative with a good initiator. In general haloganated alkanes, benzylic halides, α-haloesters, α-haloketones, α-halonitriles and sulfonyl halides are used as ATRP initiators [62].

The most frequently used initiator types used in the atom transfer radical polymerization systems are, 1-Bromo-1-phenyl ethane (Styrene), 1-Chloro-1-phenyl ethane (Styrene), Ethyl-2-bromo propionate (Methyl methacrylate) and Ethyl-2-bromo isobutyrate (Methyl methacrylate). Two parameters are important for a successful ATRP initiating system; first, initiation should be fast in comparison with propagation. Second, the probability of side reactions should be minimized [62].

Transition metal catalysts are the key to ATRP since they determine the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. The main effect of the ligand is to solubilize the transition-metal salt in organic media and to regulate the proper reactivity and dynamic halogen exchange between the metal center and the dormant species or persistent radical. Ligands, typically amines or phosphines, are used to increase the solubility of the

complex transition metal salts in the solution and to tune the reactivity of the metal towards halogen abstraction. Linear amines with ethylene linkage like tetramethylethylenediamine (TMEDA), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA), and 1,1,4,7,10,10 hexamethyltriethylenetetramine (HMTETA) were synthesized and examined for ATRP as ligands [63]. Reasons for examining of these type of ligands are, they are not expensive, due to the absence of the extensive π-bonding in the simple amines, the subsequent copper complexes are less colored and since the coordination complexes between copper and simple amines tend to have lower redox potentials than the copper-bpy complex, the employment of simple amines as the ligand in ATRP may lead to faster polymerization rates.

Catalyst is the most important component of ATRP. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst. First, the metal center must have at least two readily accessible oxidation states separated by one electron. Second, the metal center should have reasonable affinity toward a halogen. Third, the coordination sphere around the metal should be expandable upon oxidation to selectively accommodate a (pseudo)-halogen. Fourth, the ligand should complex the metal relatively strong.

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

ATRP can be carried out either in bulk, in solution or in a heterogeneous system (e.g., emulsion, suspension). Various solvents such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide and many others have been used for different monomers. A solvent is sometimes necessary especially when the obtained polymer is insoluble in its monomer [64].

2.3.3. Reversible-Addition Fragmentation Chain Transfer (RAFT)

The most recent report of a controlled/"living" free radical polymerization has been reported by Haddleton and co-workers as well as Thang et al. Reversible addition-fragmentation chain transfer (RAFT) is achieved by performing a free radical polymerization in the presence of dithio compounds, which act as efficient reversible

addition-fragmentation chain transfer agents. Much like the first two routes, the rapid switching mechanism between dormant and active chain ends affords living polymerization character [65].

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

The greatest advantage to RAFT is the incredible range of polymerizable monomers. As long as the monomer can undergo radical polymerization, the process will most likey be compatible with RAFT. However, there are many major drawback that arise when using this process. The dithio end groups left on the polymer give rise to toxicity, color, and odor and their removal or displacement requires radical chemistry. Also, the RAFT agents are expensive and not commercially available. Another drawback is that the process requires an initiator, which can cause undesired end groups and produce too many new chains which can lead to increased termination rates [48].

2.4. ABC terpolymers

In recent years ternary triblock terpolymers have attracted increasing interest owing to their rich variety of bulk morphologies [66].

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

Following the intense interest in the study of diblock and ABA triblock copolymers, the polymer community starts now to focus on a new type of block copolymers, that of ABC triblock copolymers comprising three blocks, each made of a different monomer repeat unit [67]. In bulk, four different ordered structures can be obtained (alternating lamellae, cylinders, body-centered cubic arrays of spheres and gyroid)

depending on the copolymer composition and architecture. Considerably less extended is the work dedicated to the synthesis, solution and bulk properties of triblock terpolymers of the ABC type [68].

Linear ABC triblock terpolymers represent a relatively new class of polymeric materials with an increasing interest for their properties in the bulk and in solution. The three chemically different components of these materials, each placed in a separate block, can confer to the terpolymer three different functions. Another similar, but more novel, and equally interesting class of polymeric materials is that of ABC heteroarm or miktoarm star terpolymers, bearing three arms, each of which is a different homopolymer [69].

The presence of three different monomers placed in different blocks confers to these polymers, three rather than two functions [67]. It is well known that the addition of a third block leads to a much richer variety of phases (over 30 phases have been identified to date in bulk). These materials have the potential to generate a variety of well controlled multiphase microdomain structures with nanosized structural units in bulk and thin films and to provide supramolecular structures in solution with a mesoscopic length scale. Therefore, numerous applications such as multifunctional sensors, multiselective catalysts for sequential or simultaneous chemical reactions, separation membranes, filters, etc., are possible [68].

The purpose of this investigation was to further extend the synthetic work on three-component polymers and prepare a new structure of star terpolymers whose arms are not different homopolymers but ABC triblock terpolymers. A combination of two hydrophilic and one hydrophobic monomers was chosen, leading to water-soluble, amphiphilic materials [69].

ABC triblock copolymers comprised mostly of diene-, styrene-, methacrylate-, or pyridine-based monomers have been studied extensively. These well-defined structures have elicited fascination not only for theoreticians modeling phase behavior but also in the physical realm for studying morphological transitions. The phase behavior of these systems is governed by the Flory interaction parameter between two domains, χ, and is strongly influenced by the weight fraction of the various blocks present in the copolymer. The morphological possibilities for these copolymers can range from a basic lamellar structure to highly complex core-shell

gyroid morphology and even to a unique knitting pattern. Blending these types of block copolymers with other copolymers enables additional manipulation of the morphological patterns. Until now, however, the monomers comprising the ABC triblock copolymers have been limited to those that can be polymerized either anionically or by group transfer polymerization. Recently, examples of inorganic/organic hybrid ABC triblock copolymers synthesized by combining living anionic ring-opening polymerization with atom transfer radical polymerization (ATRP) have been presented, in addition to ABC triblock copolymers synthesized wholly by ATRP or through reversible addition fragmentation chain transfer (RAFT). Kelly and Matyjaszewski demonstrated that ABC triblock copolymers of various chain architectures and monomer combinations can be successfully prepared using ATRP methods [70].

The key to the controlled synthesis of block copolymers in ATRP is to maintain high chain end functionality, i.e., limit termination and side reactions, and to balance the reactivity of the end group with that of the monomer, i.e., avoid slow initiation. While the latter consideration is not as problematic as it is in anionic or carbocationic polymerizations and can be overcome through a careful choice of the block order, radical termination cannot be completely avoided due to the nature of the polymerization process. It can be limited, however, through the careful choice of the polymerization conditions and through adjustment of the equilibrium between the active and dormant species, often by adding a "persistent radical" in the form of a higher oxidation state metal. Kelly and Matyjaszewski's report focuses on the preparation of copolymers using these approaches to obtain well-defined multiblock copolymers. Several different catalyst systems, based predominantly on linear amine ligands, as well as different synthetic methodologies (i.e., the halogen exchange technique) were utilized to successfully prepare these copolymers [70].

Recently, the co-terpolymerization reactions, involving two or three monomers for the synthesis of synthetic polymers, have been commonly used. The properties of available polymers can also be changed by these reactions and novel polymers can be obtained by co-terpolymerization reactions. Thus, several useful terpolymers have been synthesized and used for various purposes [71].

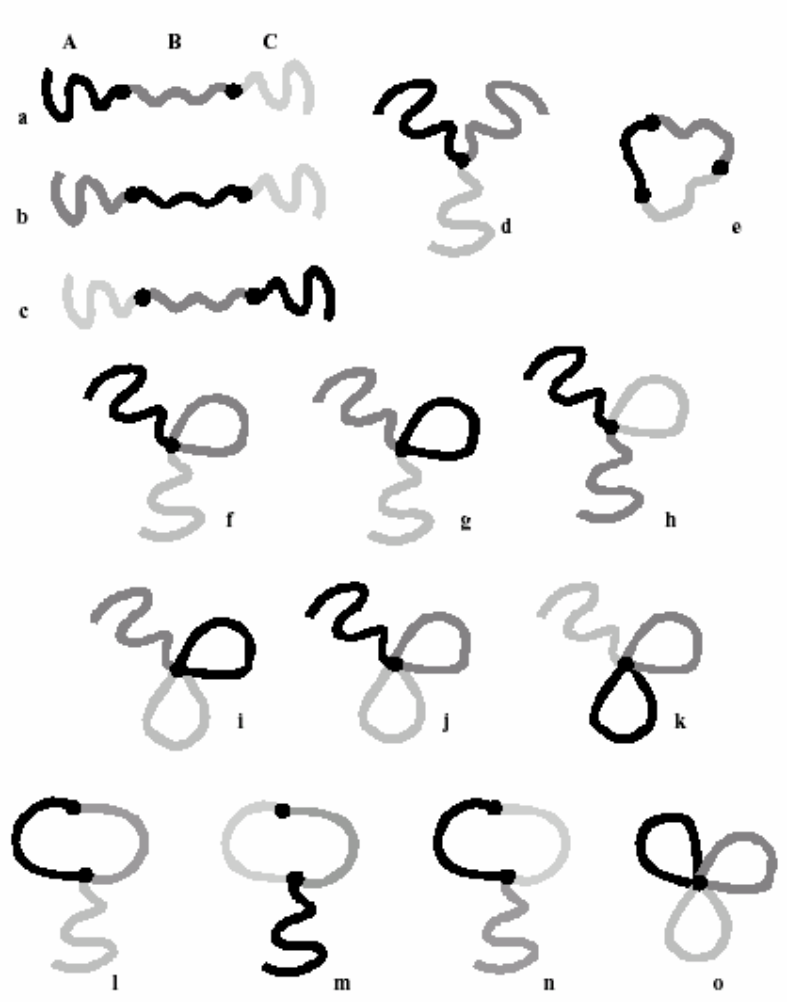


Figure 2.6. Schematic presentation of all possible arrangements for an ABC terpolymer. (a–c) Linear triblock terpolymer, ABC, BAC, CBA, respectively. (d) Miktoarm star terpolymer, (e) Cyclic terpolymer. (f–h) One of the chains is cyclic (starts and ends at the junction point) and the other two linear.(i-k) One chain is linear and the two are cyclic. (l) All chains are cyclic.

As an important illustration, interesting results have been recently obtained with SBM Nanostrengthw block terpolymers produced on an industrial scale. These triblocks copolymers combine polystyrene (PS), 1–4 polybutadiene (PBu) and polymethylmethacrylate (PMMA) segments. These engineering polymers can, for instance, be used as additives, allowing a much better solubility between incompatible commodity or technical plastics and fine tuning between toughness and stiffness of the host matrix. Detailed characterization of these new block copolymers obtained both by controlled radical polymerization and anionic polymerization represents a real challenge due to their increasing complexity [68].

2.5. Click Chemistry

Although demand for new chemical materials and biologically active molecules continues to grow, chemists have hardly begun to explore the vast pool of potentially active compounds. The emerging field of "click chemistry," a newly identified classification for a set of powerful and selective reactions that form heteroatom links, offers a unique approach to this problem [72]. "Click chemistry" is a term used to describe several classes of chemical transformations that share a number of important properties which include very high efficiency, in terms of both conversion and selectivity under very mild reaction conditions, and a simple workup [73]. It works well in conjunction with structure based design and combinatorial chemistry techniques, and, through the choice of appropriate building blocks, can provide derivatives or mimics of 'traditional' pharmacophores, drugs and natural products. However, the real power of click chemistry lies in its ability to generate novel structures that might not necessarily resemble known pharmacophores [74].

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

• Cycloaddition reactions, especially from the 1,3-dipolar family, but also hetero-Diels-Alder (DA) reactions.

• Nucleophilic ring-opening reactions, especially of strained heterocyclic electrophiles, such as epoxides, aziridines, cyclic sulfates, cyclic sulfamidates, aziridinium ions and episulfonium ions.

• Carbonyl chemistry of the non-aldol type (e.g. the formation of oxime ethers, hydrazones and aromatic heterocycles).

• Addition to carbon–carbon multiple bonds; particularly oxidation reactions, such as epoxidation, dihydroxylation, aziridination, and nitrosyl and sulfenyl halide additions, but also certain Michael addition reactions [74].

Huisgen's 1,3-dipolar cycloaddition of alkynes and azides yielding triazoles is, undoubtedly, the premier example of a click reaction [74]. Recently, DA reaction based on the macromolecular chemistry has attracted much attention, particularly for providing new materials. As an alternative route, recently, 1,3-dipolar cycloadditions, such as reactions between azides and alkynes or nitriles, have been

applied to macromolecular chemistry, offering molecules ranging from the block copolymers to the complexed macromolecular structures [75].

Sharpless and co-workers have identified a number of reactions that meet the criteria for click chemistry, arguably the most powerful of which discovered to date is the Cu(I)-catalyzed variant of the Huisgen 1,3-dipolar cycloaddition of azides and alkynes to afford 1,2,3-triazoles [72]. Because of Cu(I)-catalyzed variant of the Huisgen 1,3-dipolar cycloaddition of azides and alkynes reactions' quantitative yields, mild reaction condition, and tolerance of a wide range of functional groups, it is very suitable for the synthesis of polymers with various topologies and for polymer modification [76]. Because of these properties of Huisgen 1,3-dipolar cycloaddition, reaction is very practical. Moreover, the formed 1,2,3-triazole is chemically very stable[77].

In recent years, triazole forming reactions have received much attention and new conditions were developed for the 1,3-dipolar cycloaddition reaction between alkynes and azides [78]. 1,2,3-triazole formation is a highly efficient reaction without any significant side products and is currently referred to as a click reaction [79].

Huisgen 1,3-dipolar cycloadditions are exergonic fusion processes that unite two unsaturated reactants and provide fast access to an enormous variety of five-membered heterocycles. The cycloaddition of azides and alkynes to give triazoles is arguably the most useful member of this family [80].

The copper(I)-catalyzed 1,2,3-triazole formation from azides and terminal acetylenes is a particularly powerful linking reaction, due to its high degree of dependability, complete specificity, and the bio-compatibility of the reactants. With the ~10^6-fold rate acceleration of the copper(I)-catalyzed variant of Huisgen's 1,3-dipolar cycloaddition reaction, the generation of screening libraries has reached a new level of simplicity. Two subunits are reliably joined together by formation of a 1,4-disubstituted 1,2,3-triazole linkage. This ligation process works best in aqueous media without requiring protecting groups for any of the most common functional groups, enabling compound screening straight from the reaction mixtures (i.e. without prior purification) [74].

Azides usually make fleeting appearances in organic synthesis: they serve as one of the most reliable means to introduce a nitrogen substituent through the reaction

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

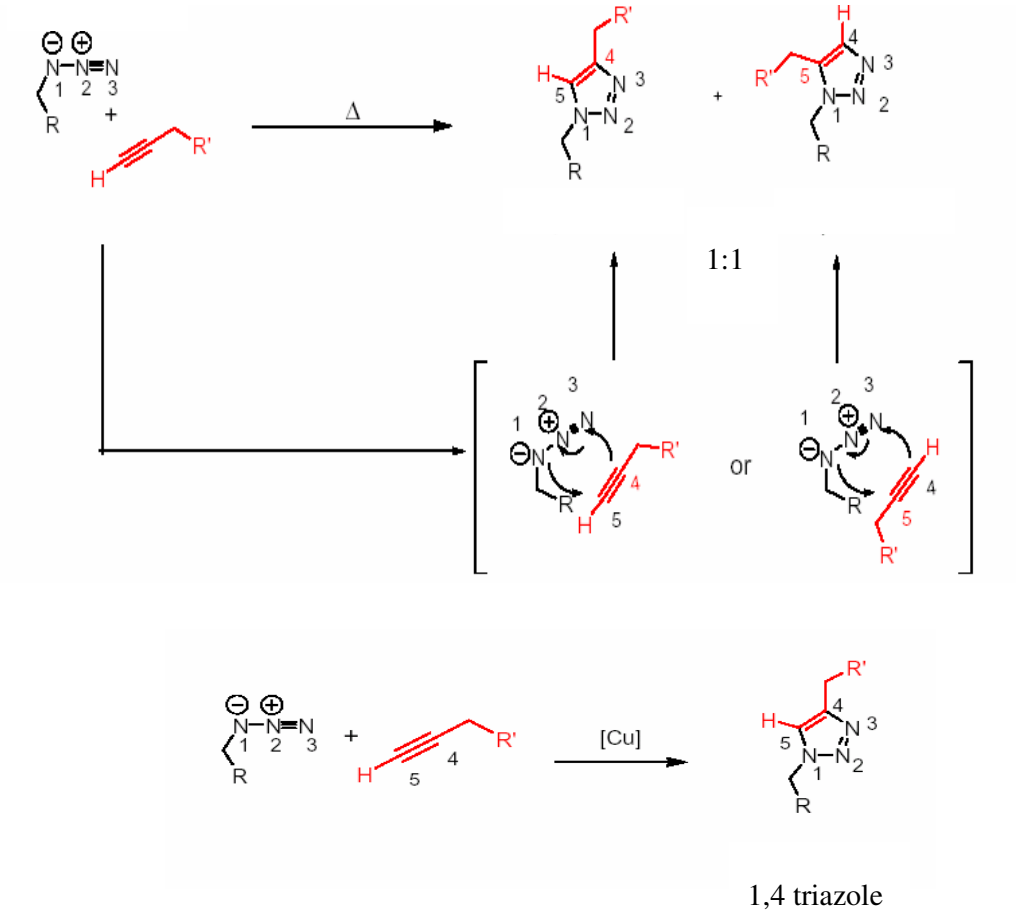


Figure 2.7. Regioselectivity mechanism of triazole forming cycloaddition

Since efforts to control this 1,4- versus 1,5-regioselectivity problem have so far met with varying success, it was found that copper(I)-catalyzed reaction sequence which regiospecifically unites azides and terminal acetylenes to give only 1,4-disubstituted 1,2,3-triazoles. The process is experimentally simple and appears to have enormous scope [80].

Since the initial discovery of Cu(I)-catalyzed alkyne–azide coupling, numerous successful examples have been recorded in the literature, but as of yet, no systematic study of optimal conditions has been reported. Further, conditions have varied widely, particularly with respect to generation of the active Cu(I) species. Sources of Cu(I) include Cu(I) salts, most commonly copper iodide, in-situ reduction of Cu(II) salts, particularly Cu(II) sulfate, and comproportionation of Cu(0) and Cu(II). Recent reports suggest that nitrogen-based ligands can stabilize the Cu(I) oxidation state under aerobic, aqueous conditions and promote the desired transformation. Steric factors and electronic effects may also play a role in the success of this click chemistry [72].

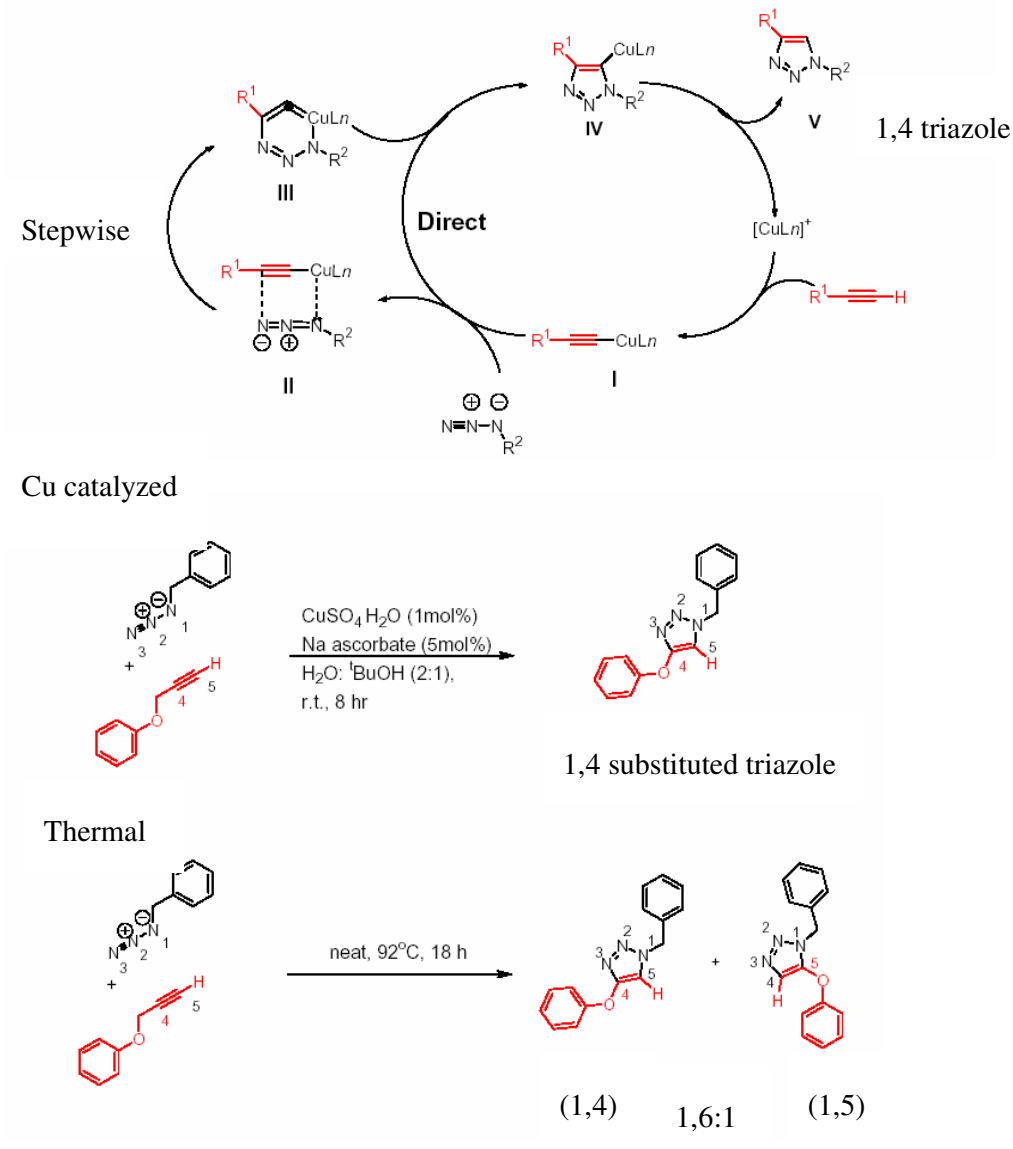


Figure 2.8. Proposed catalytic cycle for the Cu(I)-catalyzed ligation

The process exhibits broad scope and provides 1,4-disubstituted 1,2,3-triazole products in excellent yields and near perfect regioselectivity [80].

This ligation process has proven useful for the synthesis of novel polymers and materials in many laboratories, and its unique characteristics make it an ideal reaction for model network crosslinking. Johnson et al. therefore envisioned an azide telechelic macromonomer and a multifunctional small molecule alkyne, the former with a cleavable functionality at its center, as fulfilling the requirements for a degradable model network. Organic azides are most often made from alkyl halides, and several groups have reported the quantitative postpolymerization transformation (PPT) of polymeric halides to azides for the copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction by treatment with sodium azide in DMF. Atom transfer radical polymerization (ATRP) of various styrenic, acrylic, and methacrylic monomers from halide initiators is well-known to provide polymers of low polydispersity possessing alkyl halide end groups. Therefore, by a sequence of ATRP from a degradable halide-containing initiator, PPT, and CuAAC, one can conveniently prepare model networks of different macromonomer structure (e.g., star polymers, block copolymers) and incorporate a wide variety of functional groups [81].

Some click reactions have already been successfully used in polymer and materials chemistry. The efficient preparation of well-defined polymeric tetrazoles, or dendrimers, amphiphilic block copolymers, cross-linked block copolymer vesicles, and adhesives with triazole units has been reported. Click reactions were also used in the synthesis of functionalized poly(oxynorbornenes) and block copolymers and are a convenient alternative to other coupling reactions applied to polymers prepared by ATRP (such as atom transfer radical coupling or reversible thiol oxidative coupling) for the preparation of high molecular weight polymeric materials [82].

The halogen end group can be converted to other functional groups using standard organic procedures. However, the transformation is preferably carried out under mild conditions, as the substitution must be as free of side reactions as possible and the yield of the transformation reaction must be quantitative. With ATRP, the alkyl group of the alkyl halide initiator remains at one end of the produced polymer chain, a halogen atom is quantitatively transferred to the other end of the chain. By replacement of the halogen end group, several functional groups can be introduced at

the polymer chain end [83]. The functionalized polymers can find many applications, for example as macromonomers, telechelics or other specialty polymers [84]. An interesting functional group transformation is the one to azide end groups. Azide groups can produce nitrenes on thermolysis or photolysis, or can be converted to other functionalities such as amines, nitriles, isocyanates, etc [83].

In addition, click strategies have been used as an approach to synthetic cyclodextrins and the decoration of cyclic peptides by glycosylation. Synthetic glycochemicals have attracted increasing interest as carbohydrates are involved in a number of important biological processes involving highly specific events in cell-cell recognition, cell-protein interactions, and the targeting of hormones, antibodies, and toxins. Sugars are information-rich molecules, and an increasingly large number of known lectins are able to recognize subtle variations of oligosaccharide structure and act as decoders for this carbohydrate-encoded information. Gaining insight into the factors that control these phenomena may open the way for the development of new antiinfective, anti-inflammatory, and anticancer therapeutics and agents [73].

Due to their biological activity of click reactions as anti-HIV and antimicrobial agents, as well as selective β_3 adrenergic receptor agonist, new methods for the regio- and/or stereoselective synthesis of both 1,2,3 triazoles and 1,2,3,4-tetrazoles should be highly valuable [84].

2.6. H-Shaped Polymers

Through controlling the molecular architecture, block copolymers can be tuned to self-assemble into periodic structures of an astounding variety. A lot of work has been devoted to studies on block copolymers of different architectures because they may self-organize and undergo phase separation, leading to various morphologies and interesting properties. However, most of the works focused on linear block and star block copolymers. With the development of synthetic methods, block copolymers with more complex architectures, such as H-shaped, π-shaped, comb, centipede, and barbwire shape, were synthesized [85].

Three-arm star polymers represent the simplest example for branched polymers. The next complex structure is the H-polymer, where two sidearms are attached to the backbone chain. These polymers play an important role as model materials in

rheology, for example to understand the processing behavior of branched polymers [86].

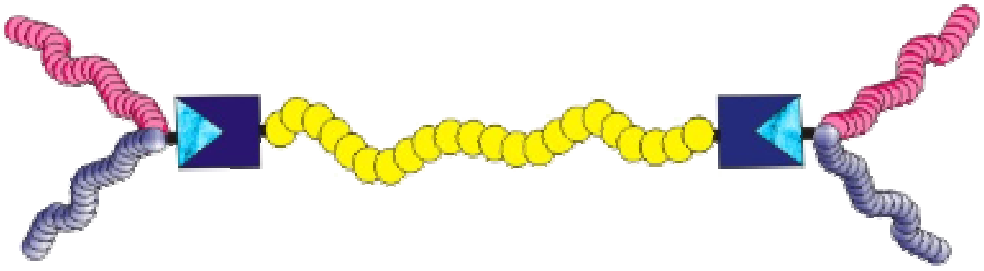


Figure 2.9. H-shaped polymer

In recent years several publications appeared reporting the synthesis of H-polymers or super H-polymers. In the latter case three arms are attached to each end of the cross-bar chain instead of two as for the H-shaped polymers. The synthetic procedures, however, are similar for both structures [86].

The first H-shaped polymer was synthesized from styrene by Roovers and Toporowski using anionic polymerization; two molecules of poly(styryllithium) were reacted with one molecule of methyltrichlorosilane, and the resulting $(PS)_2Si(CH_3)Cl$ was subsequently condensed with α,ω-difunctional poly(styryllithium) [87].

Numerous H-shaped polymers such as polystyrene (PS) backbone and side chains, [1]. $(PS)_2$-PS-$(PS)_2$, polyisoprene (PI) backbone and side chains [3], $(PI)_2$-PI-$(PI)_2$, PI backbone and PS side chains [2,4], $(PS)_2$-PI-$(PS)_2$, and polybutadiene (PB) backbone and side chains [5], $(PB)_2$-PB-$(PB)_2$, were successfully prepared. Because of its architectural difference, H-shaped polymers show different rheological properties, micellar properties, and self assembled structures when compared with other linear or branched block copolymers. H-shaped polymers are important as model materials in understanding the rheology of branched polymers such as LDPE [6-8]. H-shaped copolymers form micelles with lower aggregation numbers which results in smaller micellar structures compared to linear block copolymers [9,10]. The self-assembly of H-shaped block copolymers show a variety of morphologies depending on the preparation conditions [11]. Therefore, the synthesis of H-shaped copolymers have become attractive research projects, and several H-shaped copolymers have been prepared in recent years [88].

The synthetic strategies of these copolymers are based on anionic polymerization, and there are two general synthetic routes. One is anionic polymerization together with chlorosilane as coupling agent. Another method is repeating the reactions of living anionic polymer chain with aromatic diolefin or polymer capped with aromatic olefin. Due to the limited numbers of vinyl monomers applied in the living anionic polymerization, until now, H-shaped polymers were prepared from only a few kinds of polymers, such as polystyrene (PSt), polyisoprene (PI) and polybutadiene (PBD). In addition, after each reaction of living polymer chain with linking agents, trouble some purification for removing contaminants from the crude products is necessary, because the coupling reactions cannot go to completion and side reactions may occur. Therefore, finding a new, convenient, and more versatile synthetic strategy is challenging.

In the research program on star-shaped copolymers, Yu-gang Li et al. synthesized a series of star-shaped polymers by controlled radical polymerization using multifunctional initiators or by the combination of controlled radical and ring-opening polymerizations. In the latter case, the synthetic strategy is based on a heterofunctional macroinitiator bearing two chemically different functional groups that are able to initiate independently two different kinds of polymerizations. Thus, they try to extend the synthetic strategies to prepare H-shaped copolymers. Compared to anionic polymerization, the controlled radical polymerizations are more versatile in monomers, and they are easier to operate. They reported for the first time the synthesis of the H shaped copolymer $(PSt)_2PEG(PSt)_2$ by atom transfer radical polymerization (ATRP) using multifunctional macroinitiator [88].

3. EXPERIMENTAL WORK

3.1. Materials

St (99%, Merck), *t*BA (99%, Aldrich), *tert*-butylacrylate (*t*BA, 99%, Aldrich) and methyl methacrylate (MMA, 99%, Acros) were passed through a basic alumina column to remove the inhibitor and then distilled over CaH_2 *in vacuo* before use. *N,N,N',N'',N''*-Pentamethyldiethylenetriamine (PMDETA, Aldrich) was distilled over NaOH before use. Poly(ethylene glycol) (PEG) (M_n = 6000, Acros) with dihydroxy end group was dried over anhydrous toluene by azeotropic distillation. Tetrahydrofuran (THF, 99.8%, J.T. Baker) was dried and distilled over $LiAlH_4$. Other solvents were purified by conventional procedures. All other reagents were purchased from Aldrich and used as received. 2-(2-bromo-2-methyl-propionyloxymethyl)-3-hydroxy-2-methylpropionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester [89], **1**, and 1,2-bis (bromoisobutyrl-oxy)ethane [90], difunctional initiator, were synthesized according to the literature procedures.

3.2. Synthesis of Initiator

3.2.1. Synthesis of benzoic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperin-1-yloxy)-ethyl ester [1]

In a 500 mL of two-necked round bottom flask, equipped with a magnetic stirrer, TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) (6 g, 19.2 mmol) and BPO (9.4 g, 38.8 mmol) were dissolved in 600 mL of freshly distilled Styrene, then flask conducted three times evacuation and subsequent nitrogen purging. The solution was kept for 30 minutes stirring at 90 ^oC in an oil bath. After that period more styrene removed via back distillation and flask dissolved in 200 mL of ethyl acetate then extracted two portions (100 mL) of NaOH (1%). The combined organic phase was dried with Na_2SO_4 and solvent evaporated. The crude product purified by column chromatography over silica gel eluting just with dichloromethane, and the product

fully purified by recrystallization from cold hexane concentrated to yield 4.2 g (11 mmol, 58 %) as white needles.

3.2.2. Synthesis of 2-phenyl-2-(2,2,6,6-tetramethyl-piperin-1-yloxy)-ethanol [2]

Product **1** (4.2 g, 11 mmol) was dissolved in 70 mL of absolute ethanol and 17 mL of 2 N KOH and kept for 5 h to reflux. Then the product is extracted with water and dichloromethane (1:1). The combined liquid phase is again extracted with dichloromethane and combined organic phase dried with Na_2SO_4, evaporation of the solvent yielded 3.3 g (12 mmol, 96%) as yellow viscous liquid without further purification.

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

The 2,2-bis(hydroxymethyl)propanoic acid (4 g, 29.84 mmol) along with *p*-TSA (0.112g, 0.58 mmol), and 2,2-dimethoxypropane (5.6 mL, 44.8 mmol) dissolved in 20 mL of dry acetone , and stirred 2 h at room temperature. In the vicinity of 2 h, while stirring continued the reaction mixture was neutralized with 3 mL of totally NH_4OH (25%), and absolute ethanol (1:1), filtered off by-products and subsequent dilution with dichloromethane (50 mL) , and once extracted with distilled water (20 mL). The organic phase dried with Na_2SO_4, concentrated to yield 3.9 g (22.4 mmol, 75%) as white solid after evaporation of the solvent.

3.2.4. Synthesis of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid 2-phenyl-2-(2,2,6,6-trimethyl-piperidin-1-yloxy)-ethyl ester [4]

Compound **2** (3.3 g, 12 mmol) was dissolved in 20 mL of dry dichloromethane along with compound **3** (2.19 g, 12.6 mmol), and DPTS (0.561 g, 1.7 mmol) were added in that order, after stirring 5 minutes at room temperature DCC (3.198 g, 15.5 mmol) dissolved in 10 mL CH_2Cl_2 was added. Reaction mixture was then left overnight at room temperature to stir. After filtration off the urea byproduct, the solvent removed, and the remaining product was purified by column chromatography over silica gel eluting with hexane/ethylacetate (9:1). Solvent was removed in vacuum to give the yield 3.16 g (7.3 mmol, 62%) as pale yellow.

3.2.5. Synthesis of 3-hydroxy-2-hydroxymethyl-2-methyl-propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester [5]

Compound **4** (3.16 g, 7.3 mmol) was dissolved in 12 mL of THF and 12 mL of 1 M HCl. The reaction mixture was then stirred for 2h at room temperature. The precipitated product was filtered off, after removing of THF in vacuum, the reaction mixture extracted with 160 mL of CH_2Cl_2, and same 40 ml distilled water. The combined organic phase dried with Na_2SO_4, evaporation of the solvent concentrated, added hexane and kept in deep freeze an overnight and then solvent was removed to yield 2.5 g (6.3 mmol, 89%) as white solid.

3.2.6. Synthesis of 2-(2-bromo-2-methyl-propionyloxymethyl)-3-hydroxy-2-methyl propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester [6]

Compound **5** (2.5g, 6.3 mmol) was dissolved in 20 mL of CH_2Cl_2, and Et_3N (2 mL, 13.8 mmol) was added. The reaction mixture was cooled to 0 ^oC. Isobutrylbromide was added dropwise within 30 minutes. The reaction mixture was stirred 4 h at room temperature. After filtration off little byproduct, the mixture extracted with CH_2Cl_2, and saturated aq. $NaHCO_3$. The water phase again extracted with CH_2Cl_2, and combined organic phase dried with Na_2SO_4. The solution was concentrated, and the crude product was purified by column chromatography over silica gel eluting with hexane/ethylacetate (10:1) to give the yield 1.15 g (2.12 mmol, 72%) as pale yellow.

3.2.7. Synthesis of pen-4-ynoic acid 3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)-ethoxycarbonyl]-propyl ester [7]

6 (0.85 g, 1.56 mmol) was dissolved in 15 mL of dichloromethane. To this solution, DMAP (0.190 g, 1.56 mmol) and 4-pentynoic acid (0.199 g, 2.03 mmol) were added in that order. After stirring 5 minutes at room temperature, DCC (0.48g, 2.34 mmol) dissolved in 10 mL CH_2Cl_2 was added to the reaction medium. The reaction mixture was then left overnight at room temperature to stir. After filtration off the byproduct urea the solvent was removed, and the remaining product was purified by column chromatography over silica gel eluting with hexane/ ethylacetate (4:1) yielding **7** (0.765 g; 90%). ^1H NMR ($CDCl_3$) 7.32-7.26 (m, 5H, Ar*H*), 4.94 and 4.91 (dd, 1H, ArC*H*), 4.57 and 4.52 (dd, 1H, ArCHC*H*H), 4.42 and 4.37 (dd, 1H, ArCHCH*H*),

4.18-4.11 (m, 4H, CH_2OC=O), 2.45-2.40 (m, 4H, C=OCH_2CH_2C≡CH), 1.95 (t, 1H, HC≡C-CH_2), 1.83 (6H, CBr(CH_3)$_2$), 1.58-0.74 (m, 21H). Anal. Calc. for $C_{31}H_{44}NO_7Br$: C, 59.80 %; H, 7.12 %; N, 2.25 %. Found: C, 59.75 %; H, 7.06 %; N, 2.20 %.

3.3. Preparation of polystyrene macroinitiator by NMP of St

PS macroinitiator was prepared using NMP of St (2 mL, 17.4 mmol) in the presence of 7 (0.054 g, 0.087 mmol). The reaction mixture was degassed by three freeze-pump-thaw (FPT) cycles and left in *vacuo*. The tube was then placed in an oil bath thermostated at 125 ^oC for 17 h. The polymerization mixture was diluted with THF, and precipitated in methanol. The obtained polymer was dried for 24 h in a vacuum oven at 25 ^oC ($M_{n,GPC}$ = 9800; $M_{n,theo}$ = 9300; $M_{n,NMR}$ = 10000; M_w/M_n = 1.2).

3.4. Preparation of polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) by ATRP of MMA

The synthesis of PS-*b*-PMMA was accomplished by the ATRP of MMA in toluene with CuCl/PMDETA as a catalyst and the previously obtained PS as a macroinitiator. To a Schlenk tube equipped with a magnetic stirring bar, the degassed MMA (1 mL, 9.35 mmol), PMDETA (6.5 μL, 0.031 mmol), CuCl (3 mg, 0.031 mmol), toluene (1 mL) and PS macroinitiator (0.31 g, 0.031 mmol) were added in that order. The polymerization was carried out at 60 ^oC under degassed conditions for 1 h. After the polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove metal salt. The polymerization mixture was diluted with THF and precipitated in methanol. The obtained block copolymer was dried for 24 h in a vacuum oven at 25 ^oC ($M_{n,GPC}$ =17000; $M_{n,NMR}$ = 17800; $M_{n,theo}$ = 16000; M_w/M_n = 1.17).

3.5. Synthesis of diazide end-functionalized P*t*BA (N_3-P*t*BA-N_3)

3.5.1. Preparation of difunctional initiator [8]

Ethylene glycol (0.5g, 8 mmol), DMAP (0.492g, 4 mmol) was dissolved in 20 mL of CH_2Cl_2, and Et_3N (3.347 mL, 23mmol) was added into two neckled reaction baloon. The reaction mixture was cooled to 0 ^oC. 3 mL of 2-bromoisobutryl which is

dissolved in CH_2Cl_2 was added dropwise. After addition, first, the reaction mixture was stirred 30 min. at 0 ^oC. 30 min. later, the reaction mixture was stirred 24 h at room temperature. After filtration off little byproduct, the mixture extracted with 0.5M HCl and CH_2Cl_2, and organic phase again extracted with distilled water. Organic phase dried with $Na_2SO_{4.,}$ solvent is evaporated. Solid product is crystallized with distilled hexane, and ethylacetate was added to give yield 0,475g (1,448 mmol, 95%).

3.5.2. Preparation of dibromo end-functionalized P*t*BA (Br-P*t*BA-Br) by ATRP of *t*BA [9]

Dibromo end-functionalized P*t*BA was prepared by the ATRP of *t*BA in bulk with CuBr/PMDETA as catalyst and difunctional initiator. To a Schlenk tube equipped with a magnetic stirring bar, the degassed *t*BA, (10 mL, 68.27 mmol), ligand, (PMDETA, 95 μL, 0.455 mmol), CuBr (65 mg, 0.455 mmol) and difunctional initiator (0.081 g, 0.227 mmol) were added in the order mentioned. The polymerization was carried out at 80 ^oC under degassed conditions for 20 min. After the polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove metal salt. The excess of THF and the unreacted monomer were evaporated under reduced pressure. The resulting polymer was dissolved in THF and precipitated into excess amount of cold methanol/water (80/20; v/v). After decantation, the polymer was dissolved in CH_2Cl_2, extracted with water and dried over Na_2SO_4. Finally, the organic phase was evaporated to give dibromo end-functionalized P*t*BA ($M_{n,GPC}$ = 5100; $M_{n,theo}$ = 4970; $M_{n,NMR}$ = 4300; M_w/M_n = 1.29).

3.5.3. Preparation of diazide end-functionalized P*t*BA (N_3-P*t*BA-N_3) [10]

To a solution of dibromo end-functionalized P*t*BA (Br-P*t*BA-Br) (0.761 g, 0.177 mmol) in dimethylformamide (DMF) (10 mL), NaN_3 (0.2 g, 3 mmol) was added. After stirring the reaction mixture for overnight at room temperature, CH_2Cl_2 and water were added and the organic layer was extracted for another three times with water and dried over Na_2SO_4. The purification procedure was the same as described for the preparation of Br-P*t*BA-Br. After purification, the presence of azide end-groups of N_3-P*t*BA-N_3 was confirmed by FT-IR (cm^{-1}): 2109 (s) (azide stretching).

3.6. Synthesis of azide end-fuctionalized PEG (N_3-PEG-N_3)

3.6.1. Preparation of ditosylated-PEG (TsO-PEG-OTs) [11]

PEG (M_n = 6000 g/mol) (3 g, 0.5 mmol) with dihydroxyl end group is dissolved in 5 mL of dichloromethane. To this solution, added was DMAP (0.0305 g, 0.25 mmol), triethylamine (0.416 mL, 3 mmol) and toluene-4-sulfonyl chloride (tosyl chloride) (0.572 g, 3 mmol). Reaction mixture was then left overnight at room temperature to stir. It was first extracted with cold 4 M HCl then with distilled water and dried over Na_2SO_4. The organic phase was evaporated to 1/4 of its volume and precipitated into diethyl ether. The product was obtained as white solid, 2.93 g (0.46 mmol, 97.6 %).

3.6.2.Preparation of azide end-fuctionalized PEG (N_3-PEG-N_3) [12]

Thus obtained ditosylated-PEG (2.93 g, 0.46 mmol) was dissolved in DMF (15 mL) and sodium azide (NaN_3) (0.299 g, 4.6 mmol) was added to this solution. After stirring the reaction mixture overnight at room temperature, dichloromethane and water were added and the organic layer was extracted for another three times with water and dried over Na_2SO_4. The polymer was precipitated in diethylether. The obtained N_3-PEG-N_3 was dried for 24 h in a vacuum oven at 25 ^oC. The yield was 2.80 g (95.5 %).

3.7. Synthesis of H type terpolymer

3.7.1. Click reaction between PS-*b*-PMMA and N_3-P*t*BA-N_3

Alkyne functionalized PS-*b*-PMMA copolymer (0.19 g, 0.01 mmol) and N_3-P*t*BA-N_3 (0.0221 g, 0.005 mmol) were dissolved in nitrogen-purged DMF (5 mL) in a Schlenk tube equipped with magnetic stirring bar. CuBr (3.5 mg, 0.025 mmol) and PMDETA (5.2 µL, 0.025 mmol) were added and the reaction mixture was degassed by three FPT cycles and left in argon and stirred at room temperature for 24 h. Reaction mixture was passed through alumina column to remove copper salt, precipitated into methanol and dried in vacuum oven at 25 ^oC ($M_{n,GPC}$ = 32000; M_w/M_n =1.33).

3.7.2. Click reaction between PS-*b*-PMMA and N_3-PEG-N_3

Alkyne functionalized PS-*b*-PMMA copolymer (0.15 g, 0.008 mmol) and N_3-PEG-N_3 (0.025 g, 0.004 mmol) were dissolved in 5 mL of nitrogen-purged DMF in a

Schlenk tube. CuBr (0.003 g, 0.02 mmol) and PMDETA (4.4 μL, 0.02 mmol) were added and the reaction mixture was degassed by three FPT cycles and left in argon and stirred at room temperature for 24 h. The purification step was the same as described above ($M_{n,GPC}$ = 22000; M_w/M_n = 1.16).

3.8. Preparation of samples for AFM

Solutions of polymers were prepared in toluene at a concentration of 5 mg/mL. Films were spin-coated at 2000 rpm for 1 min from these solutions on oxidized silicon substrates. Spin-coated films were kept in vacuum oven at low temperatures for solvent evaporation.

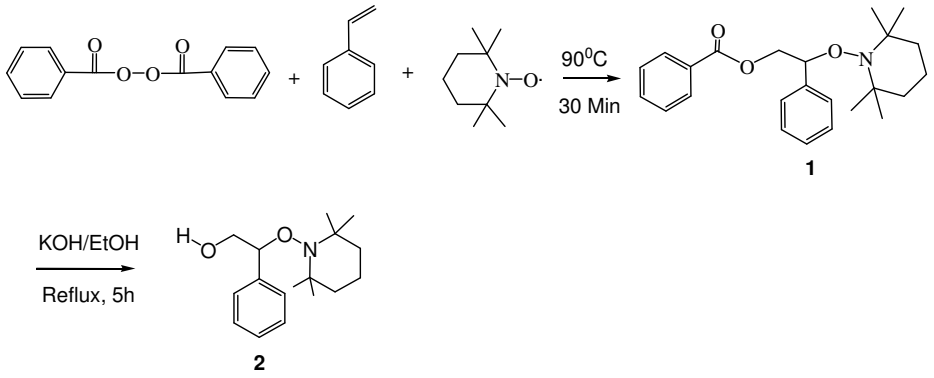
3.9. Characterization

^{1}H NMR spectra was recorded on a Bruker NMR Spectrometer (250 MHz) in $CDCl_3$. Gel permeation chromatography measurements were obtained from an Agilent instrument (Model 1100) consisting of a pump, a refractive index (RI) detector, and four Waters Styragel columns (HR 5E, HR 4E, HR 3, and HR 2). THF was used as eluent at a flow rate of 0.3 mL/min at 30 ^oC. Toluene was as an internal standard. Data analyses were performed with PL Caliber Software. The molecular weight of the polymers was calculated on the basis of linear polystyrene standards (Polymer Laboratories). Differential Scanning Calorimetry (DSC) was measured on a DSC Q100 (TA Instruments) at a heating rate of 10 ^oC/ min under nitrogen atmosphere. All data were collected from a second heating cycle and the glass transition temperatures (T_g) were calculated as a midpoint of thermogram. NT-MDT Solver P47 Atomic Force Microscopy (AFM) was used in tapping mode for morphological characterization. Ultra sharp Si cantilevers having force constant of 48 N/m were used.

4. RESULTS and DISCUSSION

4.1. Synthesis of Initiator

The initiator synthesis was carried out as follows: First of all, the synthesis of benzoic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester **(1)** was carried out by heating styrene in the presence of benzoyl peroxide and TEMPO for 30 minutes. The hydrolysis of ester was then carried out to give the 2-phenyl-2-(2, 2, 6, 6-tetramethyl-piperidin-1-yloxy)-ethanol **(2)**. The characteristic peak of aromatic protons adjacent to ester group at δ 7.9 ppm completely disappeared after hydrolysis. Moreover, the new signals appeared at δ 5.9 ppm of –O*H* and the shifts of the –CH_2 and –C*H* protons adjacent to hydroxyl and aromatic group, respectively, clearly confirm the successful hydrolysis. The ^{1}H NMR spectra of the corresponding ester and alcohol precursors are presented in Figures 4.1. and 4.2., respectively.



(4.1)

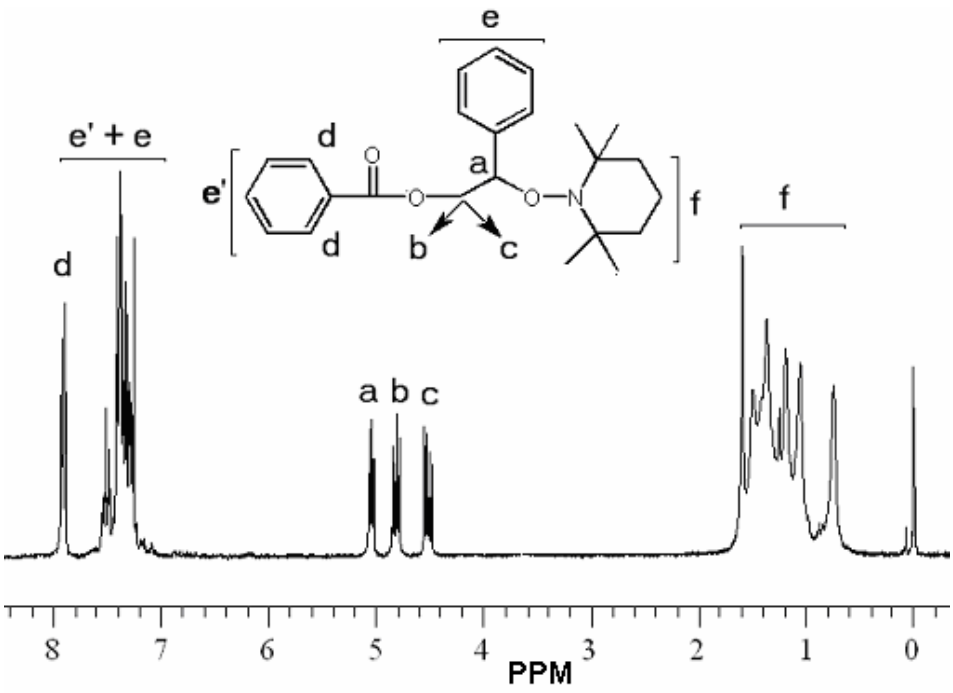


Figure 4.1. The ^{1}H NMR spectrum of benzoic acid 2-phenyl-2-(2, 2, 6, 6-tetramethyl-piperin-1-yloxy)-ethyl in $CDCl_3$.

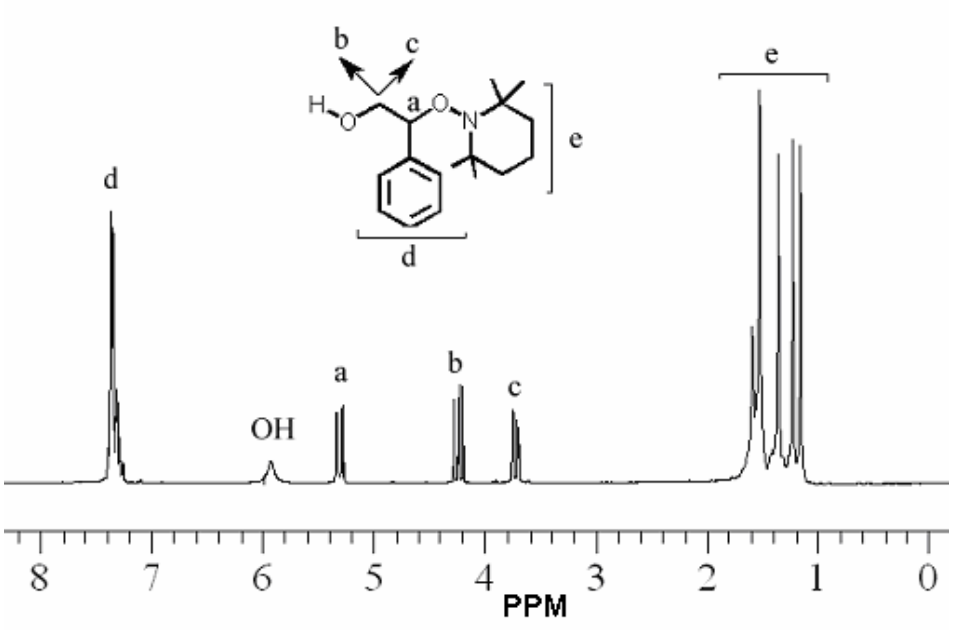
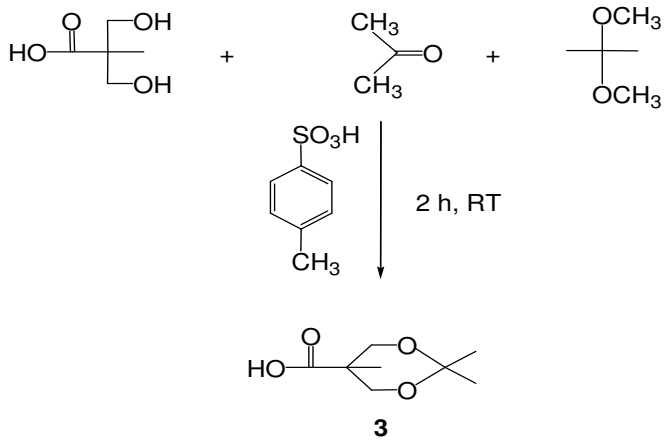


Figure 4.2. The ^{1}H NMR spectrum of 2-phenyl-2-(2, 2, 6, 6-tetramethyl-piperin-1-yloxy)-ethanol in $CDCl_3$.

In order to convert the hydroxyl functionality at compound **2** into two hydroxyl functionalities, successive protection, esterification and deprotection reactions were

realized. For this purpose, the hydroxyl protected acidic compound, **3**, was synthesized according to the following reaction.

In this reaction, 2, 2-bis (hydroxymethyl)-propanoic acid was reacted with excess amount of dry acetone using *p*-toluene sulfonic acid as catalyst. Additionally, 2,2-dimethoxy-propane was deliberately used to provide acetone during the reaction. The ^{1}H NMR spectrum of the compound, **(3)**, is shown in Figure 4.3.



3 (4.2)

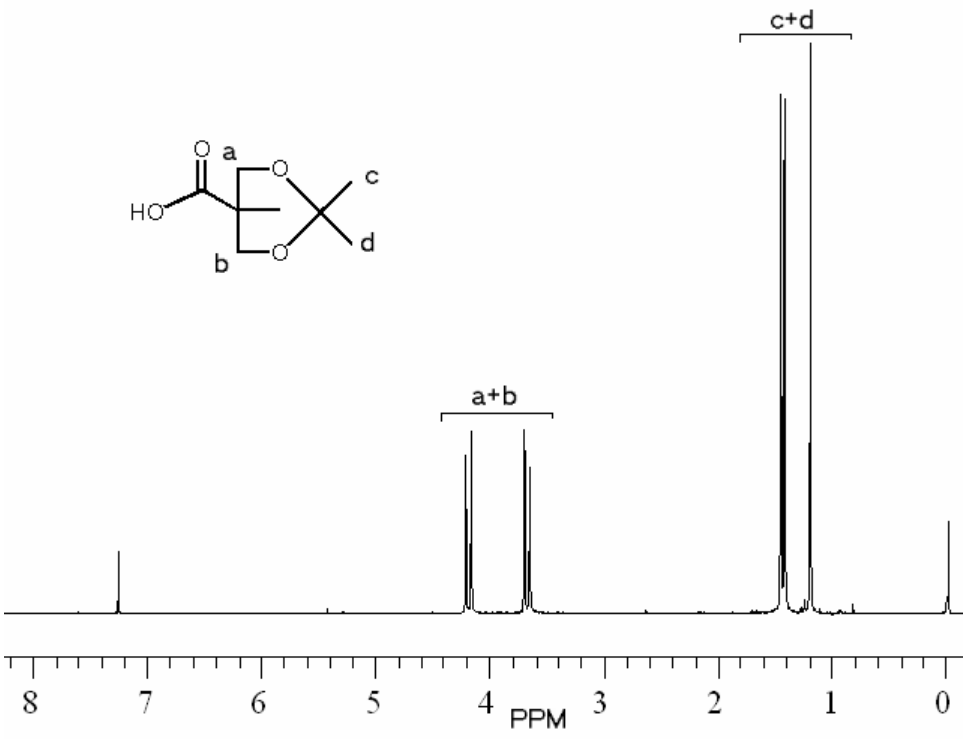
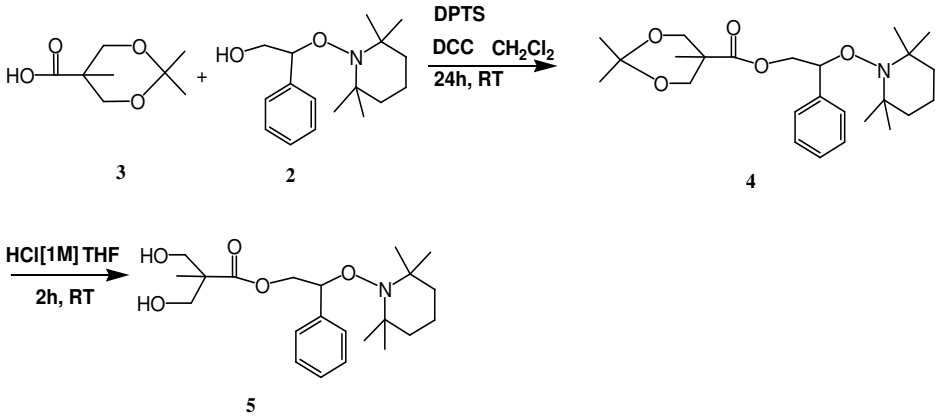


Figure 4.3. The ^{1}H NMR spectrum of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid in $CDCl_3$.

Subsequent esterification reaction between alcohol and hydroxyl protected acid was carried out using catalytic amount of DPTS (dimethylamino-4-toluene-sulfonate). Although this procedure was reported to be a suitable method for the esterification reaction [53], the main drawback of this system is related to the difficulties arising from the removal of formed urea by product. However, this was overcomed by further precipitation followed by filtration method. The ^{1}H NMR spectrum of the compound, **(4),** is shown in Figure 4.4.



(4.3)

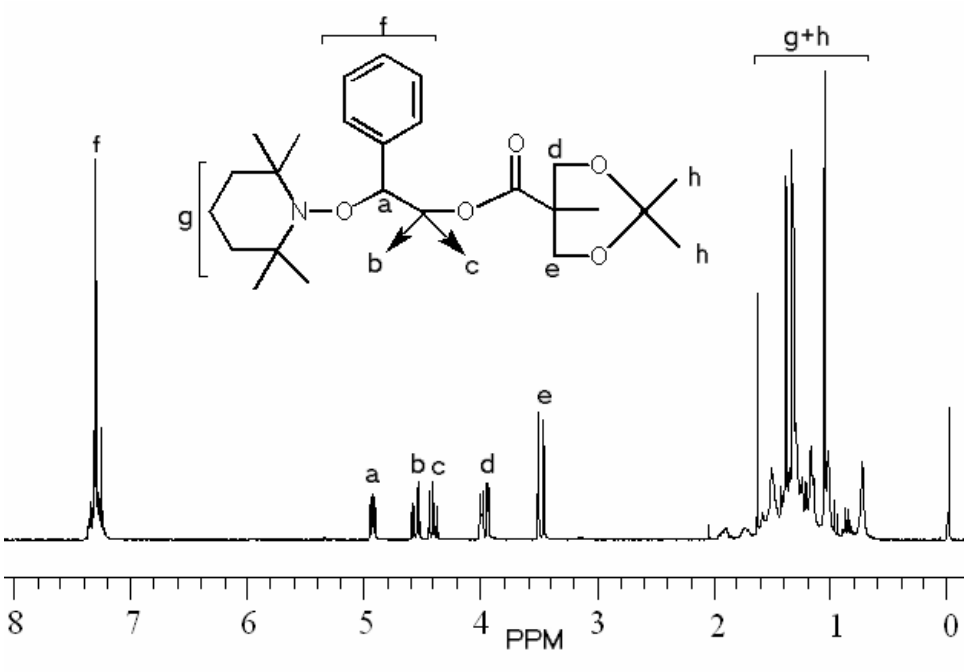


Figure 4.4. The ^{1}H NMR spectrum of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid 2-phenyl-2-(2,2,6-trimethyl-piperidin-1-yloxy)-ethyl ester in $CDCl_3$.

Finally, deprotection step was easily achieved by acidic hydrolysis using 1 M HCl and THF at room temperature. ^{1}H NMR spectrum of the desired compound, **(5),** is

shown in Figure 4.5. From the NMR spectrum -O*H* protons (e-e') at δ 2.7 ppm suggests that deprotection step was carried out successfully.

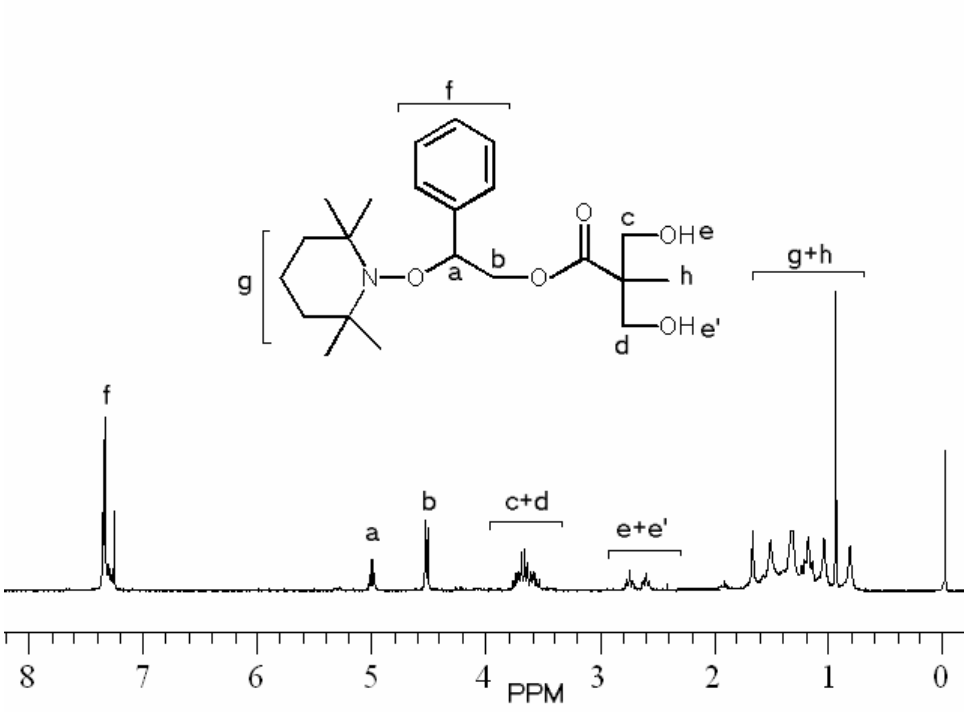
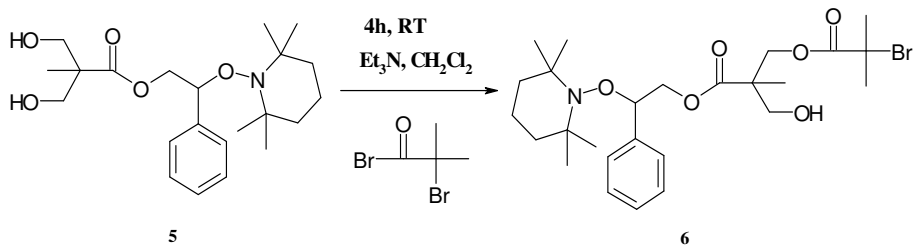


Figure 4.5. The ^{1}H NMR spectrum of 3-hydroxy-2-hydroxymethyl-2-methyl-propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester in $CDCl_3$.

In order to introduce ATRP functionality into the synthesis, second esterification reaction was achieved. In this connection, it should be pointed out that at this step severe reaction conditions may cause the hydrolysis of the ester groups present in the structure. Therefore, the esterification process was performed at room temparature and 2-bromoisobutryl bromide was added in a dropwise manner. The ^{1}H NMR spectrum of the compound **6** showed that the –O*H* protons of compound **5** at δ 2.7 ppm completely removed. Moreover, the new –O*H* proton at δ 2.2 ppm belongs to –CH_2 group, the shift of the -CH_2 protons adjacent to ATRP functionality to δ 4.1 ppm and the –CH_3 protons on ATRP functionality at δ 1.89 ppm indicate that esterification reaction was carried out successfully. The ^{1}H NMR spectrum of the resulting compound, **(6),** is shown in Figure 4.6.



(4.4)

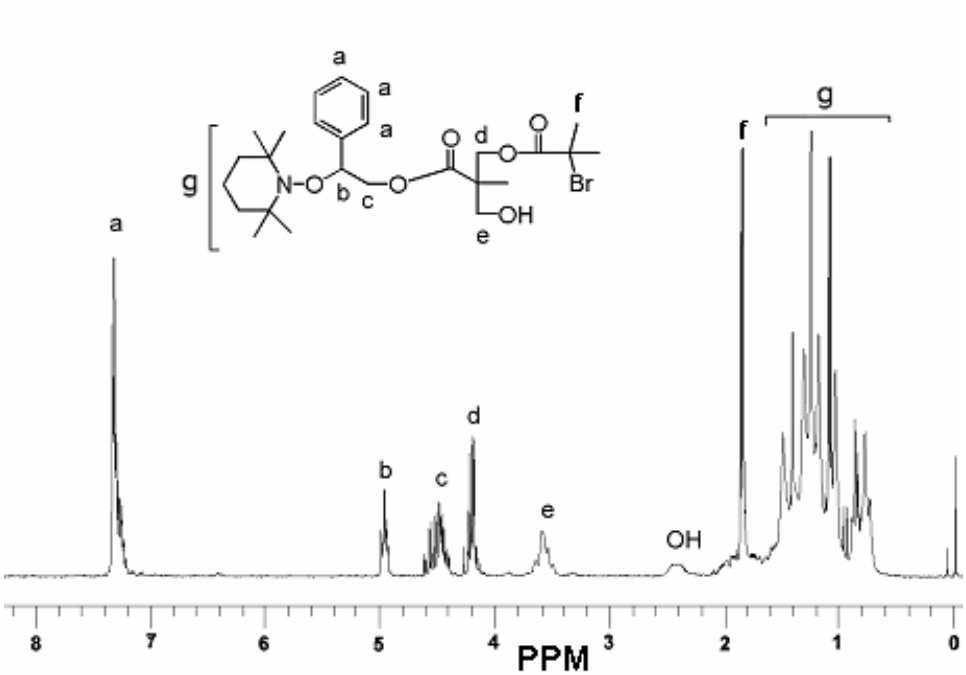
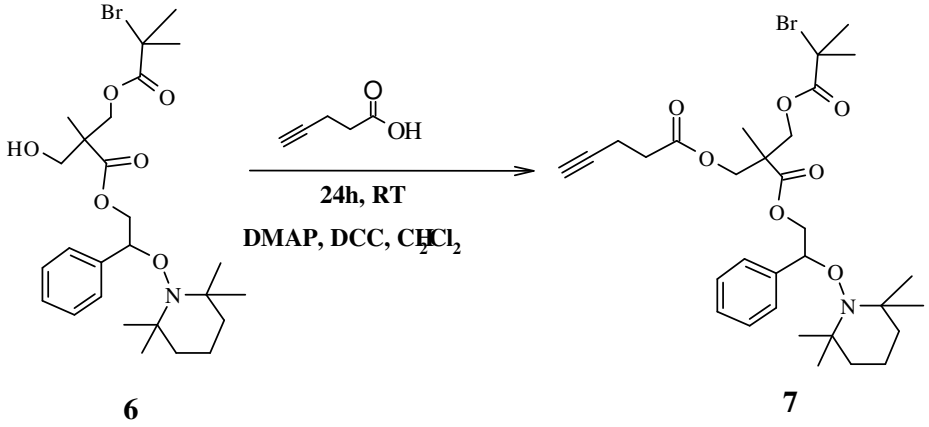


Figure 4.6. The ^{1}H NMR spectrum of 2-(2-bromo-2-methyl-propionyloxymethyl)-3-hydroxy-2-methyl propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester in $CDCl_3$.

4.2. Synthesis of Polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) Macroinitiator

For this purpose, first of all 7 containing proper initiating functionalities for ATRP (*tert*-bromide) and NMP (2,2,6,6-tetramethyl-piperidin-1-yloxy, TEMPO) was prepared from 6 and 4-pentynoic acid. The ^{1}H NMR spectrum of the compound 7 showed that a broad peak of -C*H*$_2$OH at δ 3.6 ppm disappeared and a corresponding ester (C*H*$_2$OC=O) signal came out at around δ 4.10 ppm together with another CH_2 ester linkage of 7. Furthermore, from the spectrum, C*H*$_2$-C*H* protons adjacent to TEMPO, *H*C≡C- hydrogen of alkyne, and CH_3 protons of *tert*–bromide functionality could easily be detected at δ 4.93-4.36, δ 1.95, and δ 1.83 ppm, respectively. Thus obtained 7 was used as an initiator for NMP of St at 125 ^{o}C. The theoretical number-

average molecular weight ($M_{n,theo}$) of PS precursor was calculated by using following equation: $M_{n,theo}$ = ($[M]_o/[I]_o$) X conversion X 104 + MW of **7** (622.6). The number average molecular weight calculated by GPC ($M_{n,GPC}$) was consistent with that of $M_{n,theo}$ (Table 4.1.). The ^{1}H NMR spectrum of the compound, **(7),** is shown in Figure 4.7.



6 **7** (4.5)

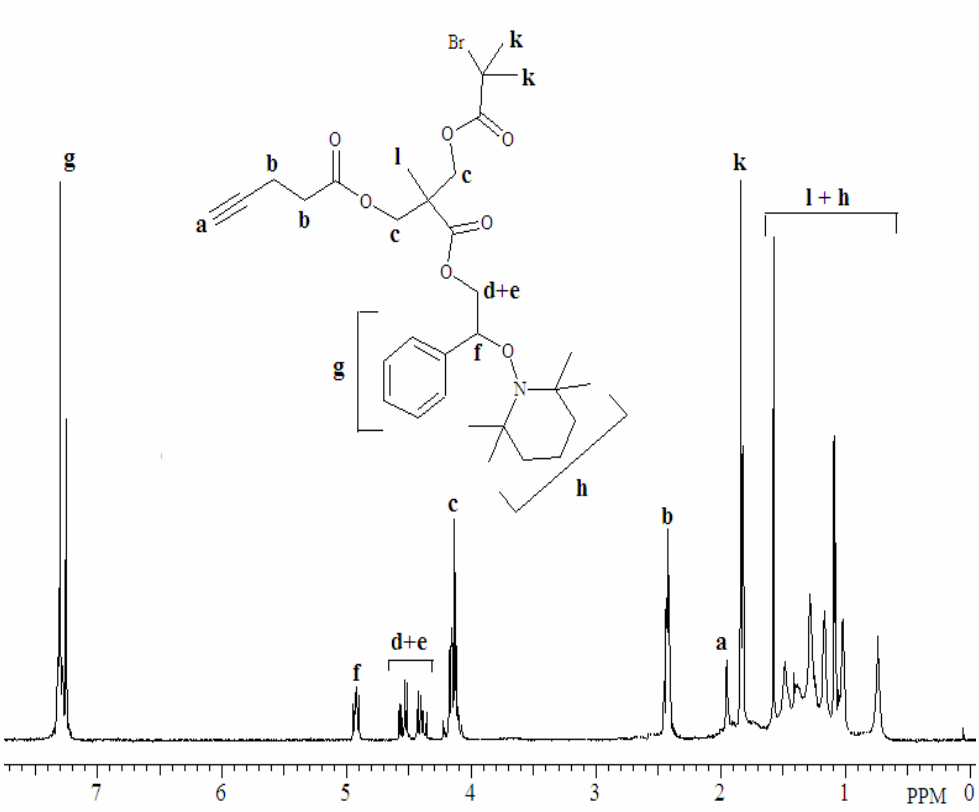


Figure 4.7. The ^{1}H NMR spectrum of 4-pentynoic acid 3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy) ethoxycarbonyl]-propyl ester in $CDCl_3$.

Then PS precursor containing *tert*-bromide functionality was used as a macroinitiator in ATRP of MMA in the presence of CuBr/PMDETA as a catalyst in toluene at 60 ^{o}C. $M_{n,theo}$ of PS-PMMA copolymer was calculated according to $M_{n,theo} = ([M]_o/[I]_o)$ X conversion X 100.12 + $M_{n,NMR}$ of PS precursor, and the molecular weight of the resulting copolymer ($M_{n,NMR}$) was determined accordingly from the integration of the signals at δ 3.6 and δ 6.2-7.5 ppm related to OCH_3 of PMMA and aromatic protons of PS segments, respectively. The theoretical, NMR and GPC molecular weights are in fairly good agreement (Table 4.1.).

Table 4.1. Polymers obtained from the living radical polymerizations.

Entry	Monomer	$[M]_o$ (mol.L^{-1})	$[M]_o/[I]_o$	Initiator	Time (h)	Conv. (%)	$M_{n,theo}$	$M_{n,GPC}$[e]	$M_{n,NMR}$	M_w/M_n
PS[a]	St	8.73	200	**7**	17	41	9300	9800	10000	1.20
PS-PMMA[b]	MMA	4.67	300	PS	1	20	16000	17000	17800	1.17
Br-P*t*BA-Br[c]	*t*BA	6.83	300	DFI[d]	0.33	12	5000	5200	4300	1.29

[a]$[M]_o:[I]_o$ = 200; polymerization was carried out in bulk at 125 °C.

[b]$[M]_o:[I]_o$: $[PMDETA]_o$: $[CuCl]_o$ = 300:1:1:1; polymerization was carried out in toluene at 60 °C.

[c]$[M]_o:[I]_o$: $[PMDETA]_o$: $[CuBr]_o$ = 300:1:2:2; polymerization was carried out at 80 °C.

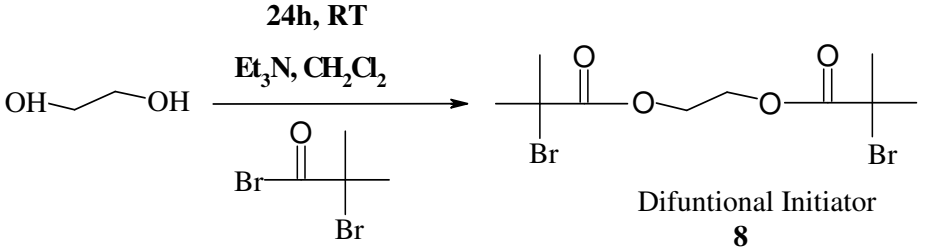
[d]DFI = difunctional initiator.

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

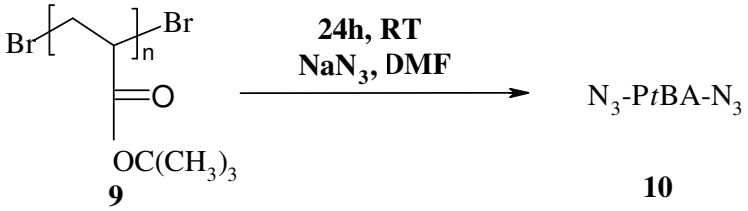
4.3. Synthesis of diazide end-functionalized P*t*BA and PEG

Br-P*t*BA-Br precursor was obtained from ATRP of *t*BA by using difunctional initiator **(8),** in the presence of PMDETA/CuBr catalyst system in bulk at 80 ^{o}C. $M_{n,NMR}$ was calculated by comparison of the integrals of the C*H* units of the P*t*BA at δ 2.2 ppm and that of the OCH_2CH_2O of the initiator fragment at δ 4.2 ppm. $M_{n,theo}$, $M_{n,NMR}$ and $M_{n,GPC}$ values of Br-P*t*BA-Br **(9),** are in good agreement (Table 4.1.). Br-P*t*BA-Br precursor was then converted quantitatively to diazide form in the presence of NaN_3 in DMF. The formation of N_3-P*t*BA-N_3 precursor, **10**, was monitored by ^{1}H NMR spectroscopy following the disappearing signal of the C*H*-Br end group at around δ 4.1 ppm and the appearing of the new C*H*-N_3 at δ 3.7-3.6 ppm. It should be noted that $M_{n,GPC}$ of N_3-P*t*BA-N_3 is calculated as 5250 and close to that of Br-P*t*BA-Br.

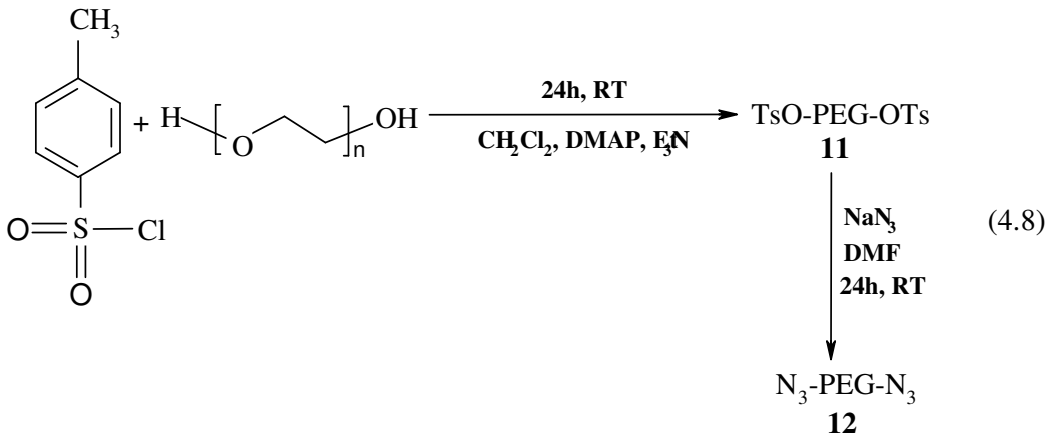
Moreover, dihydroxyl-end functionalized PEG was first tosylated and then converted to diazide form by reacting NaN_3 in DMF. The structure of N_3-PEG-N_3, **12,** was confirmed ^{1}H NMR spectroscopy. The signals originating from the CH_2O end group of the PEG at 4.1 ppm shifted to main peak of PEG at 3.6 ppm upon the azide formation. Additionally, the Ar*H* δ 7.8-7.3 ppm and CH_3 δ 2.4 ppm of the tosyl group disappeared from the spectrum.



(4.6)



(4.7)



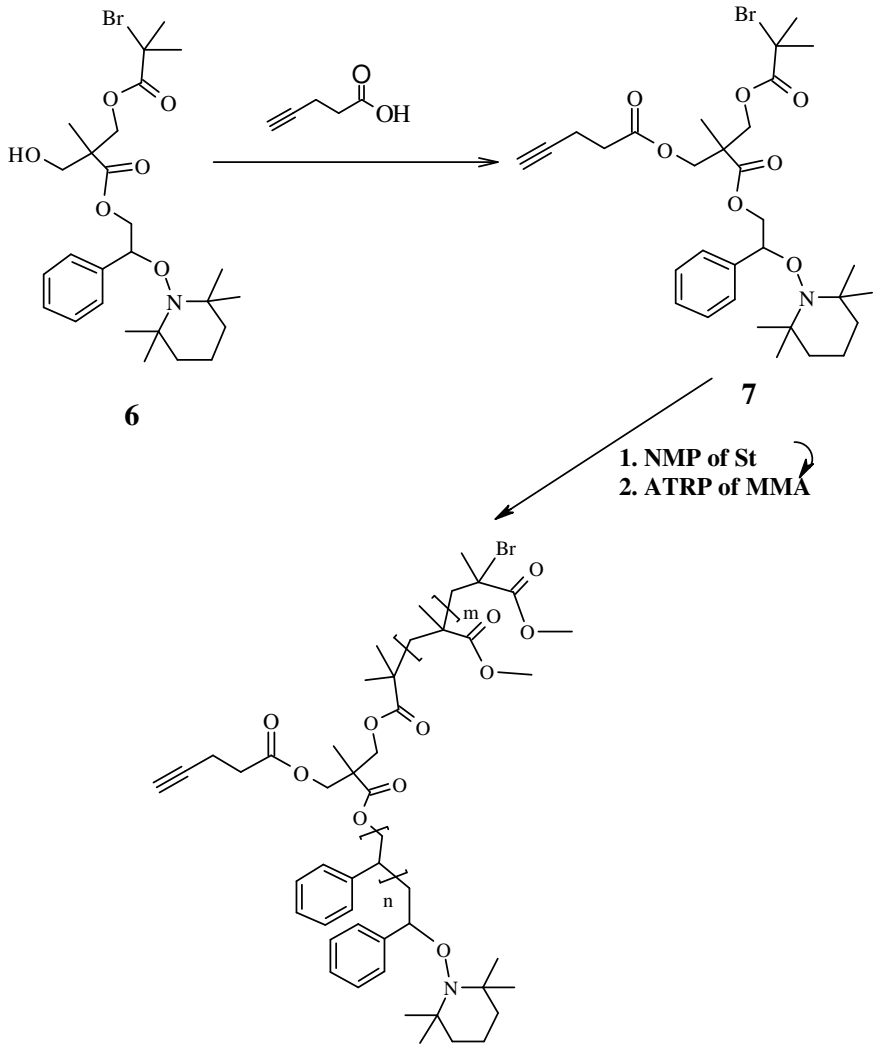
(4.8)

4.4. Synthesis of H-shaped terpolymers through click reactions

The "click" reactions between PS-PMMA copolymer with alkyne functionality and diazide end-functionalized P*t*BA or PEG afforded the corresponding H-shaped heteroarm terpolymers.

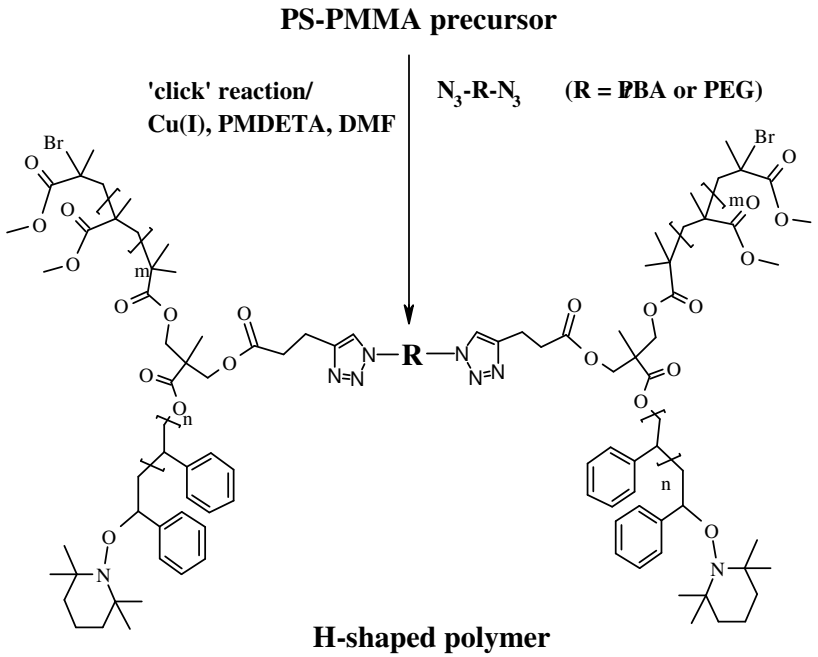
As given in the Experimental, we used an exact equivalent of alkyne per azide function in both click reactions, since the separation of the unreacted PS-PMMA precursor would cause a problem. The formation of H-shaped heteroarm terpolymers were confirmed by NMR and GPC measurements.

^{1}H NMR spectrum of (PS)(PMMA)-P*t*BA-(PMMA)(PS) H-shaped polymer displayed characteristic signals at δ 6.2-7.5, 3.6 and 1.4 ppm assignable to the Ar*H* of the PS, the OCH_3 of the PMMA and the C(CH_3)$_3$ of the P*t*BA segments, respectively (Fig.4.8.). The presence of a characteristic peak of the P*t*BA segment confirms the click reaction, due to the solubility of the unbound P*t*BA in MeOH during the recovery of H-shaped polymer.



(4.9)

PS-PMMA precursor



(4.10)

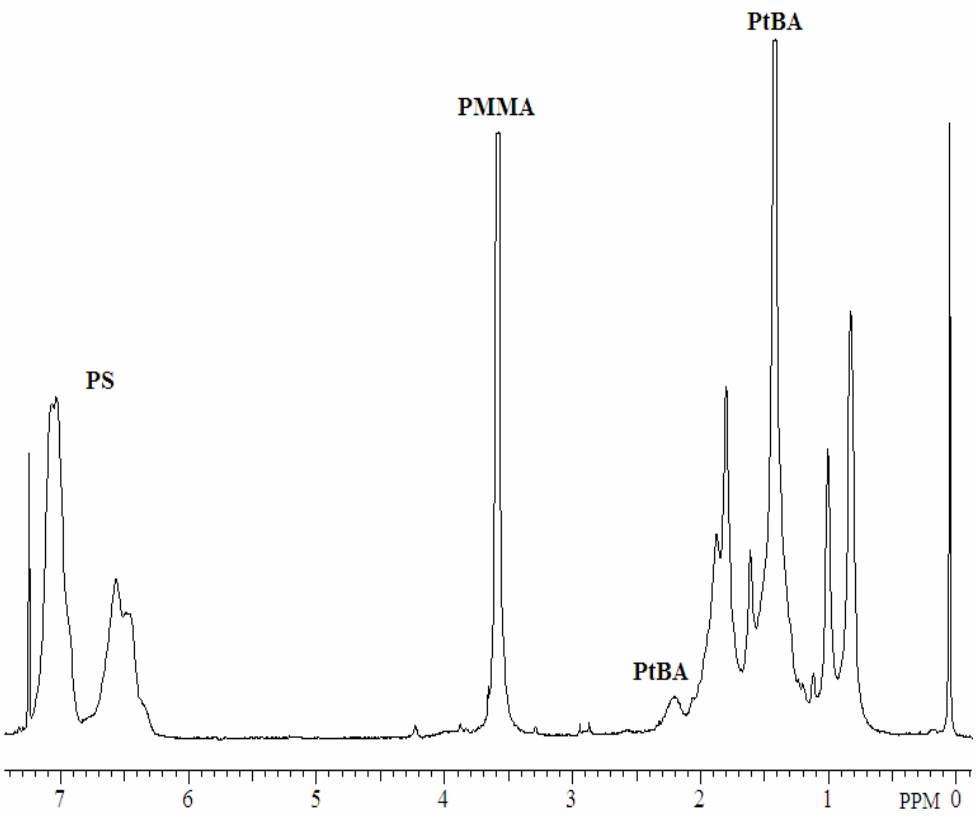


Figure 4.8. The ^{1}H NMR spectrum of (PS)(PMMA)-P*t*BA-(PMMA)(PS) H-shaped polymer in $CDCl_3$.

Moreover, an analysis on the integration values of the segments (PtBA and PS-PMMA) obtained from the spectrum of the H-shaped polymer displayed that click reaction was occurred quantitatively between PS-PMMA and P*t*BA precursors (Table 4.2.).

Here, $M_{n,theo}$ of the H-shaped polymer is calculated according to the equation: $M_{n,theo}$ = $M_{n,NMR}$ of P*t*BA + 2 X $M_{n,NMR}$ of PS-PMMA. Moreover, $M_{n,NMR}$ is derived from the ^{1}H NMR spectrum of the H-shaped polymer taking into account the ratio of the integrated values of the main chain (P*t*BA) to the side chain (PS and PMMA).

^{1}H NMR spectrum of (PS)(PMMA)-PEG-(PMMA)(PS) H-shaped polymer showed a characteristic peak of PEG at 3.63 ppm affording the incorporation of PEG into PMMA-PS copolymer due to the solubility of the unbound PEG precursor in MeOH as precipitation solvent. A quantitative analysis of the corresponding segments also indicated that $M_{n,theo}$ of H-shaped polymer was rather close to that of $M_{n,NMR}$ (Table 4.2.).

Table 4.2. H-shaped polymers obtained from click reactions

H-shaped polymers	Precursors	$M_{n,theo}$[c]	$M_{n,NMR}$[d]	$M_{n,GPC}$[e]	M_w/M_n[e]
(PS)(PMMA)-P*t*BA-(PMMA)(PS)	N_3-P*t*BA-N_3 + PS-PMMA[a]	39900	34800	32000	1.33
(PS)(PMMA)-PEG-(PMMA)(PS)	N_3-PEG-N_3 + PS-PMMA[b]	41600	36500	22000	1.16

[a]$[N_3\text{-P}t\text{BA-}N_3]_o$/ $[\text{PS-}b\text{-PMMA}]_o$ / $[\text{CuBr}]_o$/$[\text{PMDETA}]_o$= 1/2/5/5, the click reaction was carried out in DMF at 25°C.

[b]$[N_3\text{-PEG-}N_3]_o$ / $[\text{PS-}b\text{-PMMA}]_o$ / $[\text{CuBr}]_o$/$[\text{PMDETA}]_o$= 1/2/5/5, the click reaction was carried out in DMF at 25°C.

[c]$M_{n,theo} = M_{n,NMR}$ (P*t*BA) + 2 X $M_{n,NMR}$ (PS-PMMA).

[d]Calculated from ^{1}H NMR spectrum of the H-shaped polymer taking into consideration the ratio of the integrated values of the main chain (P*t*BA or PEG) to that of the side chain (PS and PMMA).

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

From GPC analysis, it was clearly observed that traces for both PMMA-PS and P*t*BA segments disappeared and a new monomodal trace in the higher molecular weight region appeared revealing the incorporation of the P*t*BA segment into the H-shaped polymer (Fig. 4.9.).

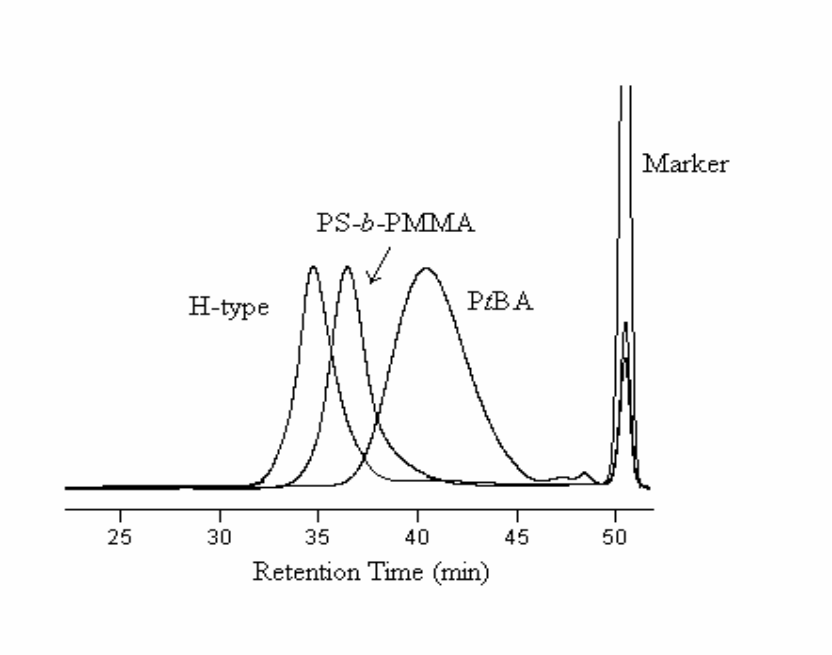


Figure 4.9. GPC traces of (PS)*b*(PMMA), P*t*BA and (PS)(PMMA)-P*t*BA-(PMMA)(PS) H-shaped polymer

Figure 4.10. showed the evolution of GPC traces. A clear shift to the higher molecular weight region was observed. A GPC trace of (PS)(PMMA)-PEG-(PMMA)(PS) H-shaped polymer is monomodal and displays almost no tail in the lower molecular weight region indicating an efficient click reaction between PEG and PS-PMMA precursors.

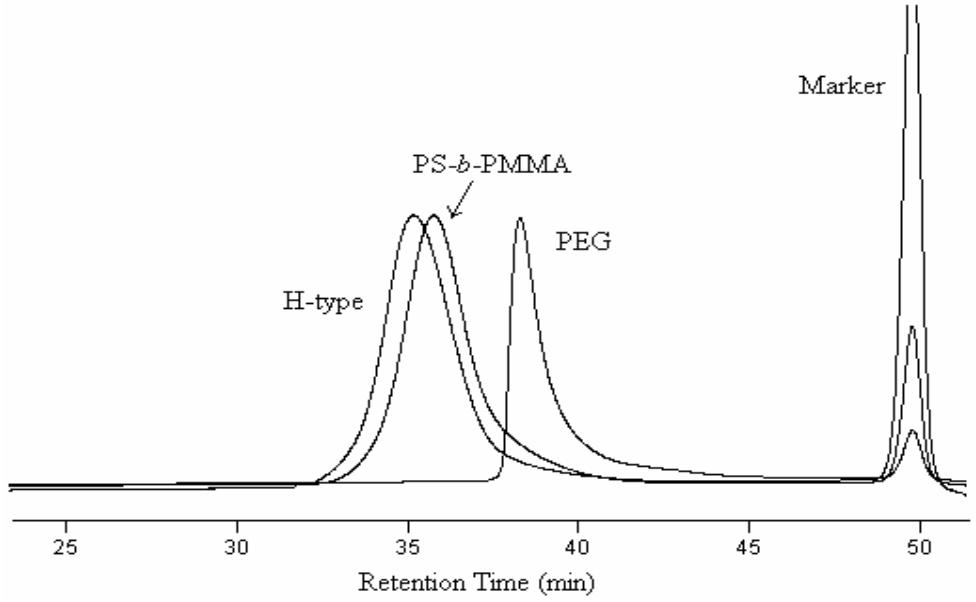


Figure 4.10. GPC traces of (PS)*b*(PMMA), PEG and (PS)(PMMA)-PEG-(PMMA)(PS) H-shaped polymer

Thermal properties of H shaped polymers were probed by DSC. (PS)(PMMA)-PEG-(PMMA)(PS) H-shaped polymer showed a T_m = 22 and T_g = 88 ^oC, corresponding to the PEG and PS/PMMA precursors, respectively. However, a T_g for PEG segment is not apparent from DSC analysis. For the case of (PS)(PMMA)-P*t*BA-(PMMA)(PS) H-shaped polymer, two T_gs are evident: one at 45 ^oC corresponding to P*t*BA and at 100 ^oC corresponding to PS/PMMA precursors.

AFM investigations confirmed the phase separation between PS and PMMA blocks in the polymers and showed different morphologies for the two H-type polymers. Fig. 4.11. shows the AFM height pictures (Fig. 4.11a-4.11c) and phase pictures (Fig. 4.11d-4.11f), respectively, for PS-*b*-PMMA, (PS)(PMMA)-PEG-(PMMA)(PS) and (PS)(PMMA)-P*t*BA-(PMMA)(PS). AFM height picture of PS-*b*-PMMA diblock copolymer (Fig. 4.11a) showed 2-3 nm height irregularly distributed surface undulations. The corresponding phase picture (Fig. 4.11d) shows a clear phase contrast between the lower and higher parts on the surface. The lower parts are bright in the phase picture and the higher parts are dark. This indicates a clear phase separation between the PS and PMMA blocks such that the lower surface energy PS block stays higher on the surface. In fact, annealing this film above the glass transition temperatures of both blocks (~100 ^oC) allowed PS to cover the top surface resulting in a smooth surface in height picture and a uniform phase in phase picture.

The height and phase picture of the H-type polymer (PS)(PMMA)-P*t*BA-(PMMA)(PS) (Fig. 4.11c and Fig. 4.11f, respectively) showed similar features to those of PS-*b*-PMMA. The height difference between the lower and higher parts was 2-3 nm and appeared bright and dark, respectively, in phase picture. The size of the higher regions was larger than that of PS-*b*-PMMA. This may be due to the increased density of PS blocks in the H-type polymer as two PS-*b*-PMMA chains were attached to a central P*t*BA block. The surface morphology of (PS)(PMMA)-PEG-(PMMA)(PS) was significantly different than (PS)(PMMA)-P*t*BA-(PMMA)(PS). A very smooth surface is seen in the height picture of Fig. 4.11b. But the phase picture of Fig. 4.11e shows ordered regions of rods that extend from lower right corner to upper left corner of the picture. The average width of these rods is approximately 30 nm. We attribute the observed rods to the self assembly of (PS)(PMMA)-PEG-(PMMA)(PS) into cylinders in which the central PEG blocks form the core of the cylinder with the PS and PMMA blocks on the shell. The phase picture of Fig. 4.11e shows the organization of the PS and PMMA blocks in the shell on the top surface. Our investigations of the detailed structure of this morphology have been continuing. The driving force for the morphology of ordered cylinders is the strong phase separation between the central PEG block and PS and PMMA. The tendency of PEG to crystallize may also contribute to the morphology formation. In the case of (PS)(PMMA)-P*t*BA-(PMMA)(PS), the three $-CH_3$ in the side group of P*t*BA may be preventing the strong segregation with the PS groups and hindering the formation of such an ordered morphology.

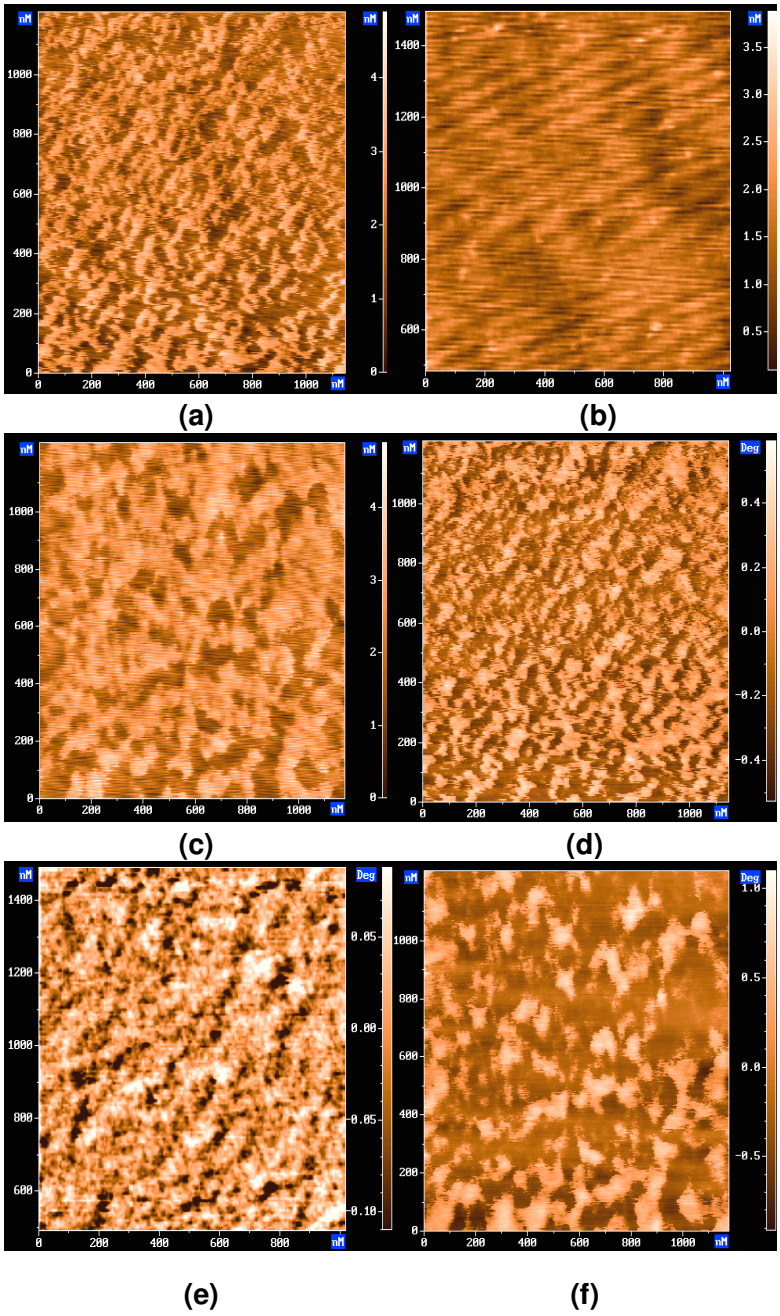


Figure 4.11. AFM images of (PS)-*b*-(PMMA), (PS)(PMMA)-P*t*BA-(PMMA)(PS) and (PS)(PMMA)-PEG-(PMMA)(PS) polymers

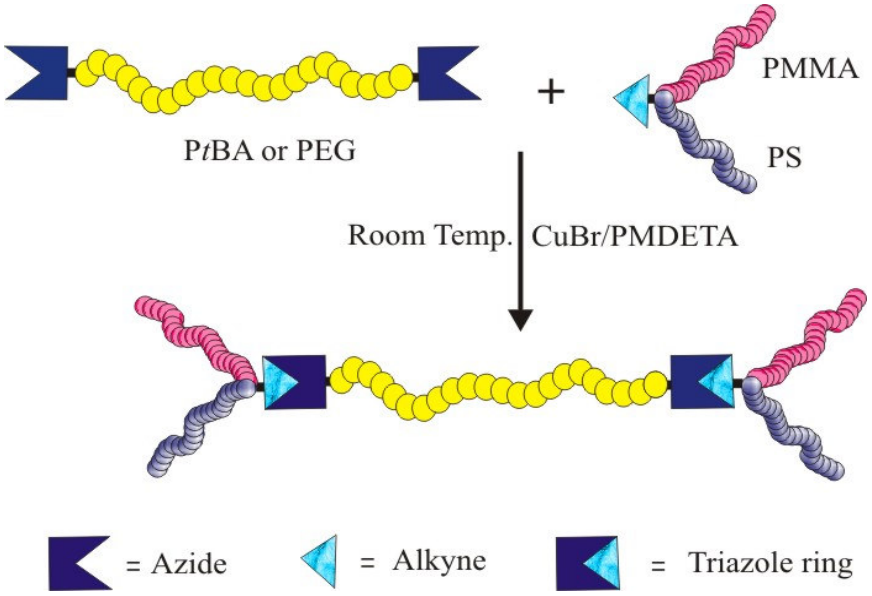


Figure 4.11. Schematic presentation of H-shaped terpolymers through click reaction

CONCLUSION

In conclusion using click chemistry strategy, two types of H shaped polymer containing PEG or P*t*BA as a main chain and PS-PMMA as side chains was successfully prepared. For this purpose, first, trifunctional initiator, pen-4-ynoic acid3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)-ethoxycarbonyl]-propyl ester **7**, with tertiary bromide (for ATRP) and 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) (for NMP) functionalities and an alkyne moiety was synthesized. The initiator **7,** thus obtained was used in the subsequent living radical polymerization routes such as ATRP of MMA and NMP of St, respectively, in order to give (PMMA)-(PSt) copolymer with controlled molecular weight and low polydispersity ($M_{n,GPC}$ =17000; $M_{n,NMR}$ = 17800; $M_{n,theo}$ = 16000; M_w/M_n = 1.17). Second, the click reaction between alkyne functionalized (PMMA)-(PSt) copolymer and di-azide end functionalized P*t*BA and PEG afforded the corresponding H-shaped heteroarm terpolymers.

In this study, an H-shaped polymer was synthesized that has two thermodynamically incompatible arms (PS and PMMA) on either side of the central unit (PtBA or PEG) by using click chemistry. Both NMR and GPC analyses confirmed the H-shaped structures. GPC traces of H-shaped polymers displayed monomodal behavior and narrow molecular weight distribution. Moreover, the H-shaped structures were analyzed by AFM measurements.

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