ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF PHOTORESPONSIVE A_2B_2 TYPE MIKTOARM STAR COPOLYMER CONTAINING AZOBENZENE MOIETY AT THE CORE

M. Sc. Thesis by

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Department : **Polymer Science and Technology**

Programme: **Polymer Science and Technology**

FEBRUARY 2006

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ÇEKİRDEĞİNDE AZOBENZEN BİRİMİ BULUNDURAN IŞIĞA DUYARLI A_2B_2 TİP FARKLI KOLLU STAR KOPOLİMER SENTEZİ

YÜKSEK LİSANS TEZİ

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LIST of SYMBOLS

ATRP	**:** Atom Transfer Radical Polymerization
NMP	**:** Nitroxide Mediated Polymerization
RAFT	**:** Reversible Addition-Fragmentation Chain Transfer Polymerization
St	**:** Styrene
MMA	**:** Methyl methacrylate
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
DVB	**:** Divinylbenzene
THF	**:** Tetrahydrofuran
DMAP	**:** 4-dimethylaminopyridine
DCC	**:** *N*,*N*-dicyclohexylcarbodiimide
BPO	**:** Benzoyl peroxide
DPTS	**:** 4-dimethylamino pyridinium-4-toluene sulfonate
PMDETA	**:** *N*,*N*,*N*′,*N*″,*N*‴- pentamethyldiethylenetriamine
GPC	**:** Gel Permeation Chromotography
UV	**:** Ultra Violet Spectrophotometer
NMR	**:** Nuclear Magnetic Resonance Spectroscopy

SYNTHESIS OF PHOTORESPONSIVE A_2B_2 TYPE MIKTOARM STAR COPOLYMER CONTAINING AN AZOBENZENE MOIETY AT THE CORE

SUMMARY

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

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

In this study, we prepared a novel miktoarm star copolymer with an azobenzene unit at the score via combination of atom transfer radical polymerization (ATRP) and nitroxide mediated polymerization (NMP) routes. For this purpose, first, mikto-functional initiator, **8**, with tertiary bromide (for ATRP) and 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) (for NMP) functionalities and an azobenzene moiety at the core was synthesized. The initiator **8** 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 A_2B_2 type miktoarm star copolymer, $(PMMA)_2$-$(PSt)_2$ with an azobenzene unit at the core with controlled molecular weight and low polydispersity ($M_w/M_n < 1.15$). The photoresponsive properties of **8** and $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer were investigated. GPC (Gel Permeation Chromatography) traces, ^{1}H-NMR and UV spectra showed that both initiator and polymerization were carried out successfully.

ÇEKİRDEĞİNDE AZOBENZEN YAPISI İÇEREN IŞIĞA DUYARLI A_2B_2 TİP FARKLI KOLLU YILDIZ KOPOLİMER SENTEZİ

ÖZET

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

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

Bu çalışmada, sırasıyla atom transfer radikal polimerizasyon (ATRP) ve nitroksit ortamlı radikal polimerizasyon (NMP) yöntemlerini kullanarak çekirdeğinde azobenzen birimi içeren yeni farklı kollu yıldız kopolimer hazırlandı. Bu amaç için, ilk olarak yapısında tersiyer bromür (ATRP için) ve 2,2,6,6-tetrametilpiperidin-1-iloksi (TEMPO) (NMP için) fonksiyonları ve çekirdeğinde azobenzen içeren farklı kollu fonksiyonlu başlatıcı, **8**, sentezlendi. Başlatıcı **8**, metil metakrilatın atom transfer radikal polimerizasyonu, stirenin nitroksit ortamlı radikal polimerizasyonu gibi yaşayan radikal polimerizasyonların uygulanmasıyla, çekirdeğinde azobenzen birimi bulunan, kontrollü molekül ağırlığına ve düşük molekül ağırlığı dağılımına (M_w/M_n < 1.15) sahip A_2B_2 tip $(PMMA)_2$-$(PSt)_2$ farklı kollu yıldız kopolimer oluşması için kullanıldı. Başlatıcının **(8)** ve $(PMMA)_2$-$(PSt)_2$ yıldız kopolimerin ışığa karşı duyarlılığı incelendi. GPC (Jel Geçirgenlik Kromatografisi), ^{1}H-NMR ve UV analizlerinden elde edilen sonuçlar hem başlatıcı sentezinin hem de polimerizasyonun başarılı bir şekilde gerçekleştiğini göstermiştir.

1. INTRODUCTION

Miktoarm star polymers have been synthesized on the basis of two general strategies [1,2]. The first involves the use of living anionic polymers to be consecutively reacted with an appropriate multifunctional core (chlorosilane compound) in a consecutive polymer reaction. The second is the reaction of the active chain with divinylbenzene (DVB). In this route, living polymer (derived from anionic polymerization) is added to DVB affording to the formation of a star polymer with active anionic sites on the polymer core. Subsequent anionic polymerization of another monomer results in the miktoarm star polymer.

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 controlled/living radical polymerization (CRP) techniques in 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 (RAFT) [3], the nitroxide-mediated free radical polymerization [4] (NMP), and the metal mediated controlled / living radical polymerization often called as atom transfer radical polymerization. [5-7] (ATRP) are versatile methods for the controlled/living radical polymerizations. However, the latter two cases turned out to be more extensive. In addition, living ring opening polymerization (ROP) technique has found a wide application in the polymerization of lactones and lactides [8].

Photoresponsive systems are currently attracting much attention because of their many possible optical applications [9]. Azo compounds and their derivatives provide such photoresponsive systems, which undergo conversion from trans- to cis-forms on irradiation with UV light (λ= 330 nm) in solution [10,11]. Back isomerization (cis to trans) can be carried out by various processes, e.g. thermal, or/and photochemical. Although extensive studies have been conducted on polymers with azobenzene units,

[10-16] there has been recently growing interest for azobenzene containing polymers obtained from the controlled/living radical polymerization techniques [17-21].

In this work, by combination of ATRP and NMP routes, we prepared a novel miktoarm star copolymer with an azobenzene unit at core. For this reason, first, mikto-functional initiator, (Azobenzene-4,4'-dicarboxylic acid bis-{3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethoxycarbonyl]-propyl} ester) (**8**), with tertiary bromide (for ATRP) and 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) (for NMP) functionalities and an azobenzene moiety at core was synthesized. The second, **8** thus obtained was employed in consecutive living radical polymerization routes such as ATRP of MMA and NMP of St, respectively, in order to give A_2B_2 type miktoarm star copolymer, $(PMMA)_2$-$(PSt)_2$ with an azobenzene unit at core. The photoresponsive properties of **8** and $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer were investigated.

2. THEORETICAL PART

2.1. Conventional Free Radical Polymerizations

Conventional free radical polymerization (FRP) has many advantages over other polymerization processes. First, FRP does not require stringent process conditions and can be used for the (co)polymerization of a wide range of vinyl monomers. Nearly 50% of all commercial synthetic polymers are prepared using radical chemistry, providing a spectrum of materials for a range of markets [22]. 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.

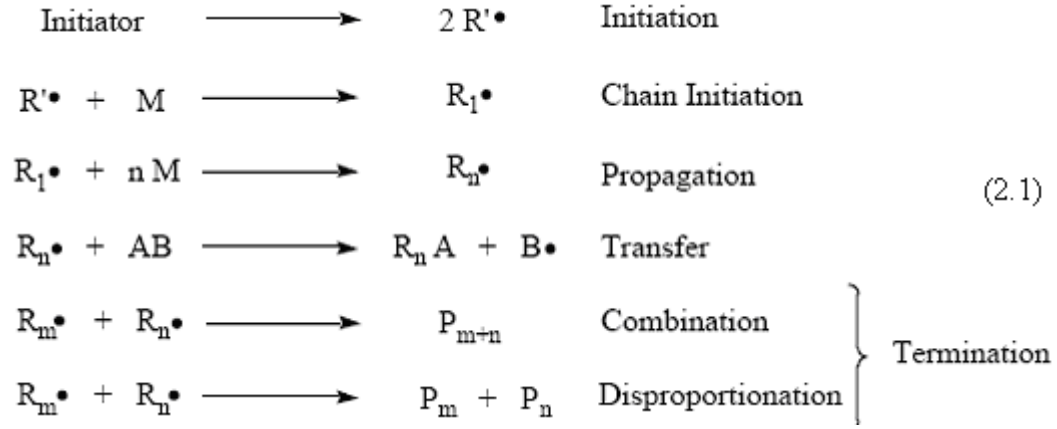
4. *Termination*. In this final step, eradication of active sites leads to "terminated," or inert, macromolecules. Termination occurs via coupling reactions of two active centers (referred to as combination), or atomic transfer between active chains (termed disproportionation).

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.

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 [23]. Living polymerizations must not include irreversible deactivation and irreversible transfer.

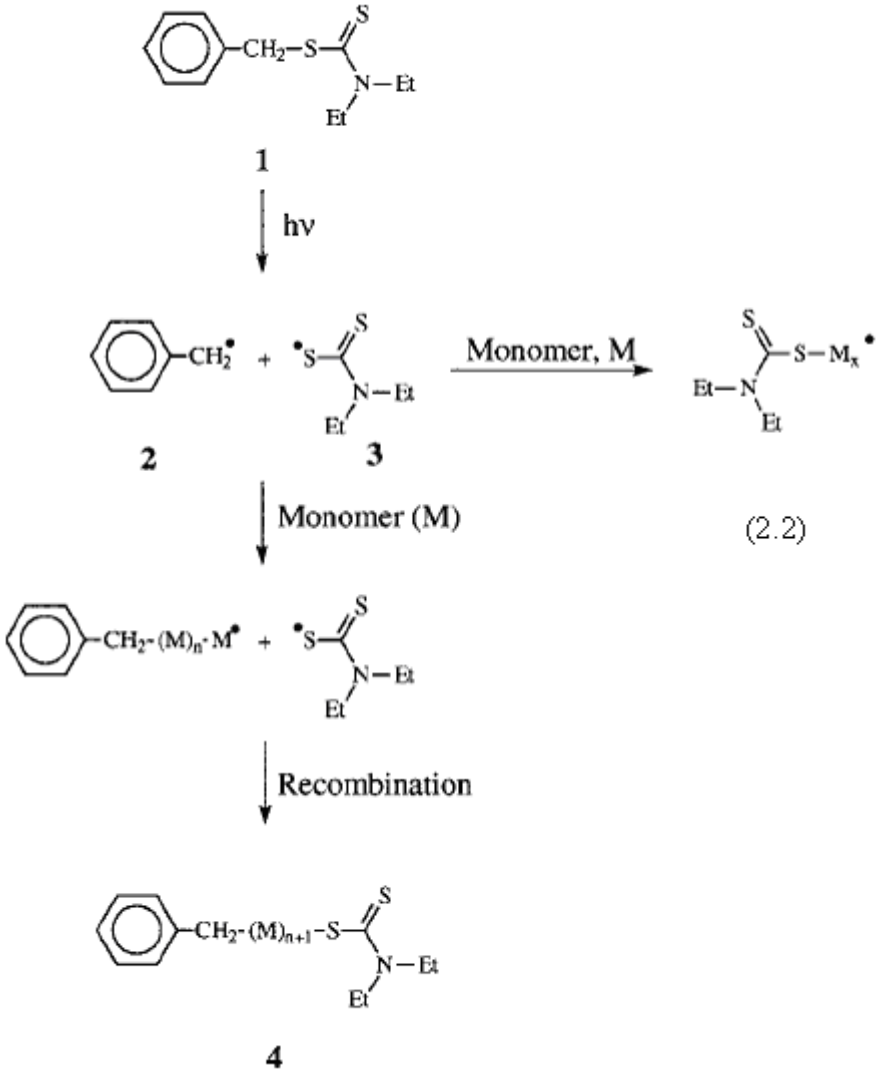
Classical living polymerizations occur by the formation of active ionic sites prior to any significant degree of polymerization. A well-suited initiator will completely and instantaneously dissociate into the initiating ions. Dependent on the solvent, polymerization may then proceed via solvent pairs 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

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 which are atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP), and reversible addition fragmentation chain transfer (RAFT) 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.

In 1982, Otsu et al. extended the idea of living polymerizations to free radical systems in the use of initiator-transfer agent-terminators, or iniferters [24]. Such

initiators act both as primary radicals to initiate polymerization (R'•, 2.1) and as radical chain terminators (R_m• or R_n•, 2.1), consequently permitting a near linear increase of molar mass with time and percent conversion [25]. However, the similarities between living anionic systems and Otsu's iniferter reaction end there. The iniferter mechanism yields radicals that can initiate new chains throughout the course of the reaction [26]. The iniferter systems also show significant loss of active end groups from the growing polymers [26b]. Consequently, these systems display relatively large polydispersities with a substantial amount of homopolymer being formed in conjunction with block copolymer [26a]. (2.2) mechanism of iniferter

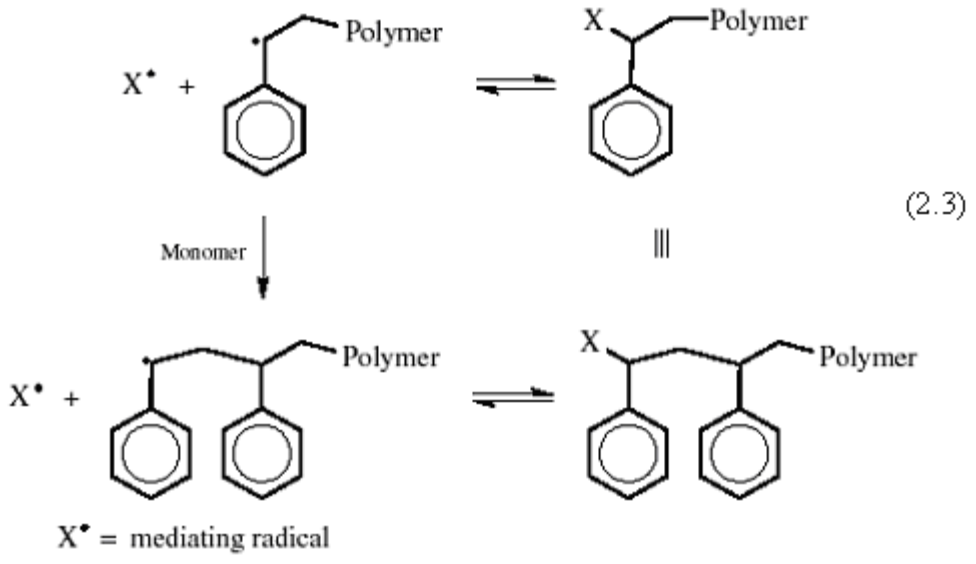


(2.2)

2.3.1. Nitroxide-Mediated Living Radical Polymerizations

This pioneering work was one of the seminal contributions that provided the basis for the development of living free radical polymerization (LFRP), and it is interesting to note the similarity between the iniferter mechanism outlined in Scheme 2.2 and the general outline of a living free-radical mechanism (2.3). In this general mechanism, the reversible termination of the growing polymeric chain is the key step for reducing the overall concentration of the propagating radical chain end. In the absence of other reactions leading to initiation of new polymer chains (i.e., no reaction of the mediating radical with the vinylic monomer), the concentration of reactive chain ends is extremely low, minimizing irreversible termination reactions, such as combination or disproportionation. All chains would be initiated only from the desired initiating species and growth should occur in a pseudoliving fashion, allowing a high degree of control over the entire polymerization process with well-defined polymers being obtained.

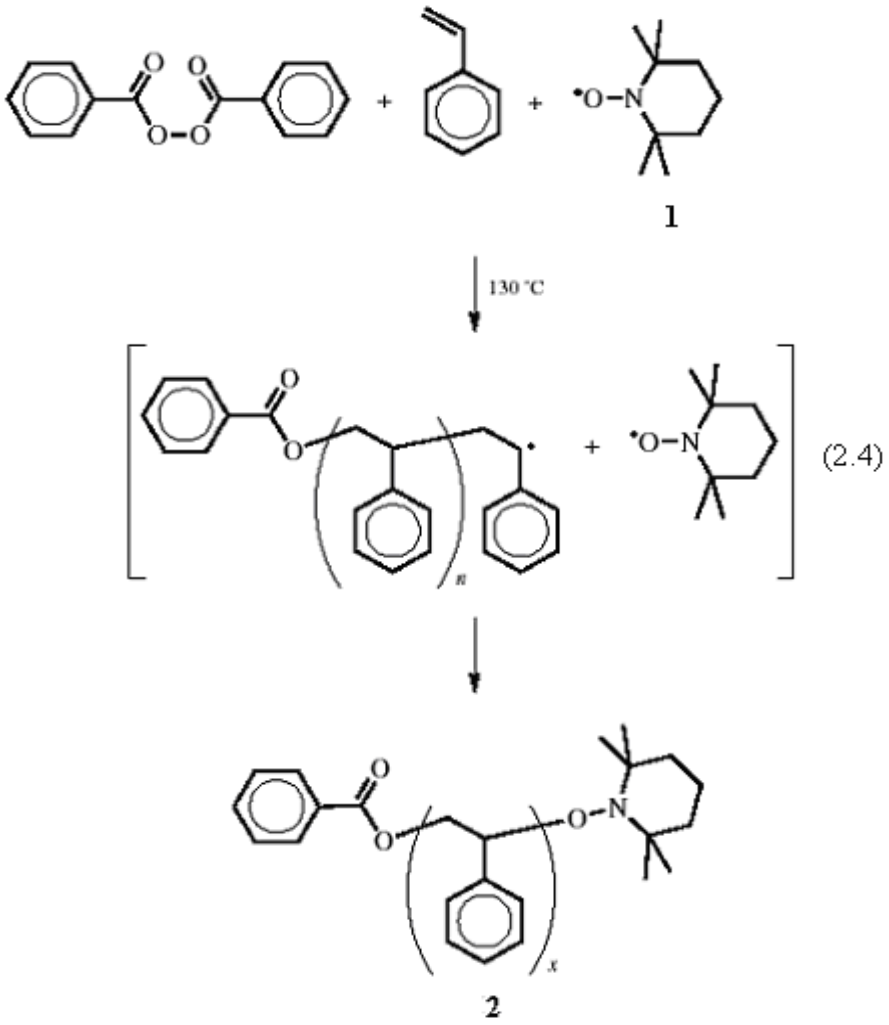
The identity of the mediating radical, $X^{\bullet}$, is critical to the success of living free radical procedures and a variety of different persistent, or stabilized radicals have been employed [27–31]. However the most widely studied and certainly most successful class of compounds are the nitroxides and their associated alkylated derivatives, alkoxyamines. Interestingly, the development of nitroxides as mediators for radical polymerization stems from pioneering work by Solomon, Rizzardo, and Moad into the nature of standard free-radical initiation mechanisms and the desire to efficiently trap carbon-centered free radicals [32].



(2.3)

2.3.1.1. Bimolecular Process

The second seminal contribution that proved conclusively that living free-radical polymerizations are a viable synthetic methodology was a report from the group of Georges at XEROX describing the preparation of low polydispersity polystyrene (PDI = 1.20) and the subsequent synthesis of polystyrene-based block copolymers [33]. The key feature of this work was the realization that, while nitroxides are polymerization inhibitors at low temperatures, hence their use by Solomon to trap polymerization intermediates, at elevated temperatures they may act as polymerization mediators, not inhibitors. By increasing the temperature to 130 ^{o}C and conducting the polymerizations in the bulk, a system consisting of benzoyl peroxide and a stable nitroxide, TEMPO **1**, in the molar ratio of 1.3 : 1, gave polystyrene derivatives, **2**, by a living process in which the molecular weight increased in a linear fashion with conversion (2.4). Even more startling were the polydispersity values for **2**, PDI =1.2, which were significantly lower than the theoretical lower limit for a free-radical process of 1.5 and the typical values of ~2.0 for free-radical systems.



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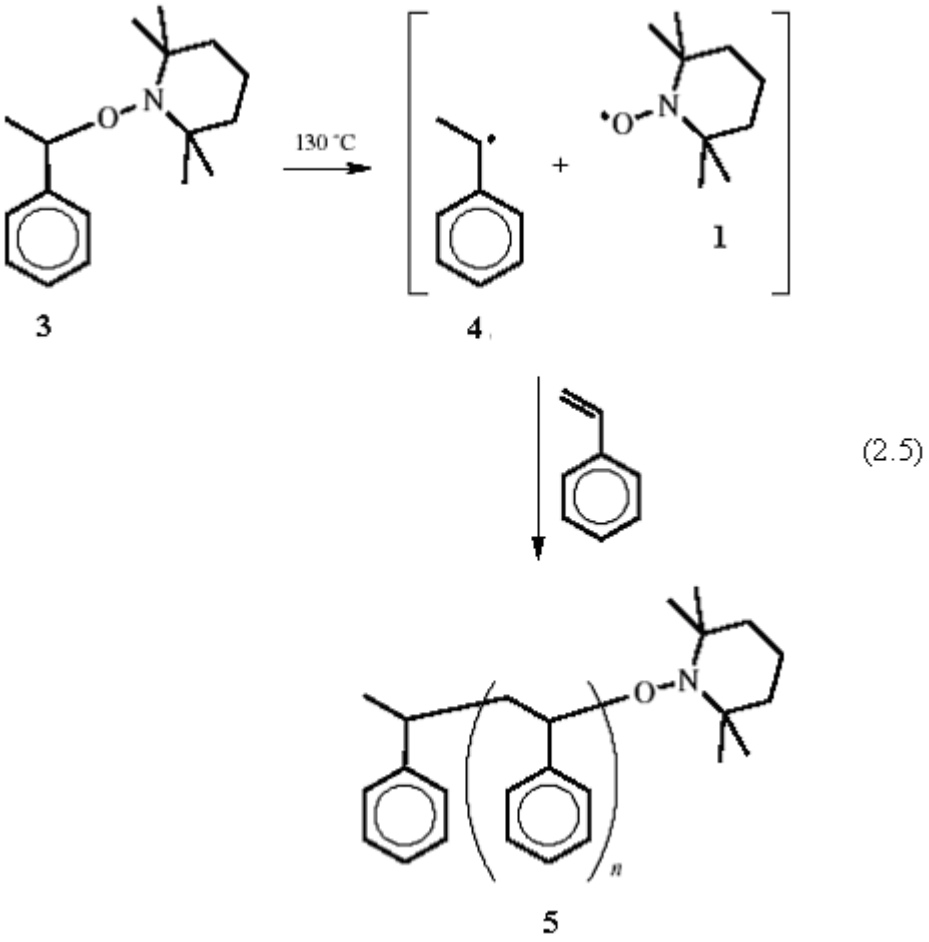
2

2.3.1.2. Unimolecular Initiators

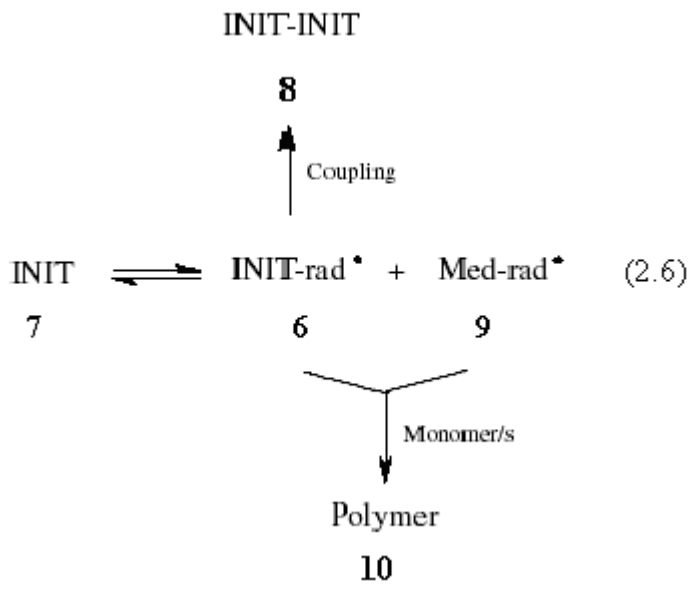
The structure of these initiators was based on the alkoxyamine functionality that is present at the chain end of the growing polymer during its dormant phase. The C-O bond of the small-molecule alkoxyamine derivative, **3**, is therefore expected to be thermalytically unstable and decompose on heating to give an initiating radical, namely, the a-methyl benzyl radical, **4**, as well as the mediating nitroxide radical, **1**, in the correct 1:1 stoichiometry (seen in 2.5). Following initiation the polymerization would proceed as described previous for the bimolecular case to give the polystyrene derivative, **5**. The advantage of the unimolecular initiator approach is that the structure of the polymers prepared can be controlled to a much greater extent. Since the number of initiating sites per polymerization is known, the molecular weight can be accurately controlled. The unimolecular initiator can also be functionalized to permit the controlled introduction of functional groups at the chain ends of the macromolecules.



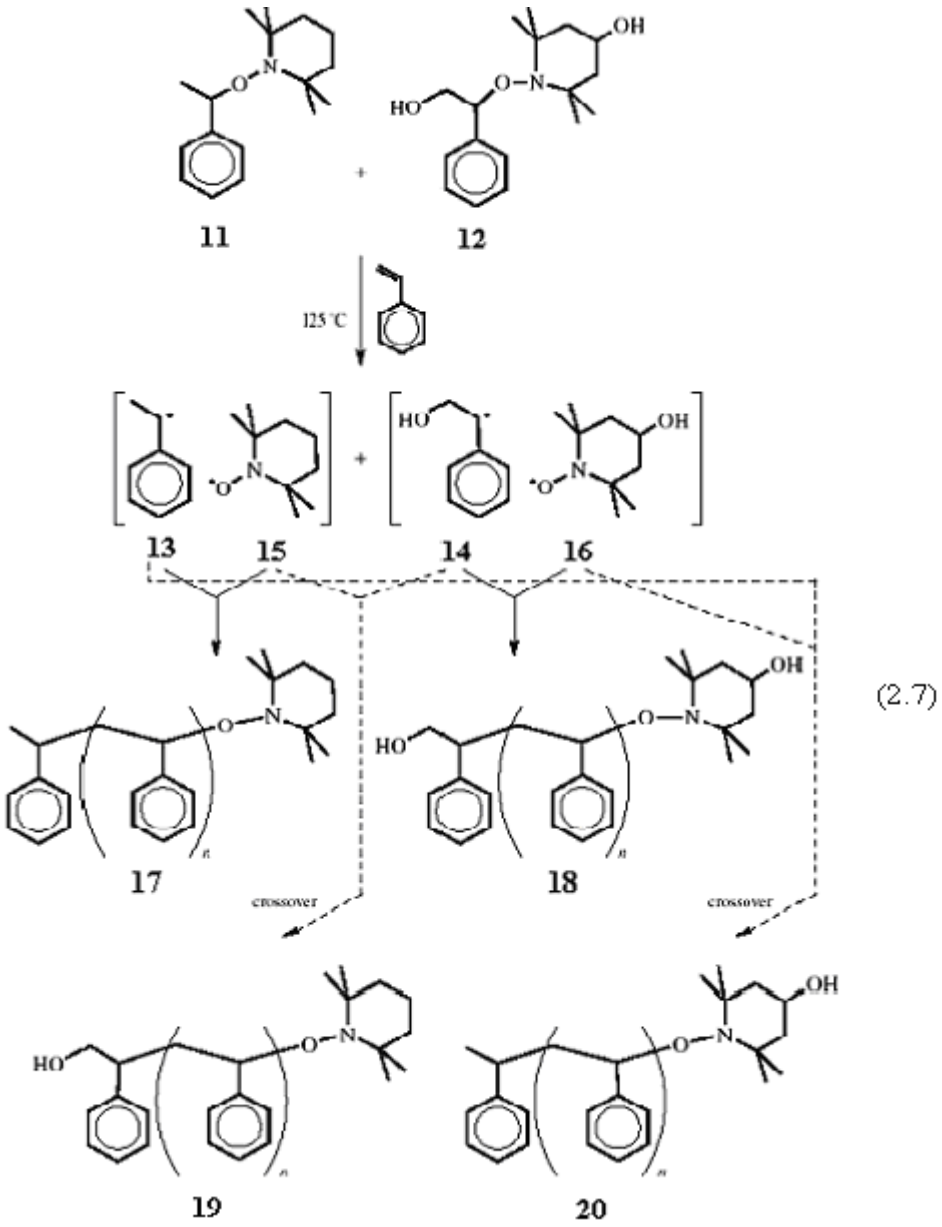
2.3.1.3. Mechanistic and Kinetic Features

The key kinetic feature of nitroxide mediated living free-radical polymerization is the operation of a special phenomenon, termed the persistent radical effect (PRE). Fischer has developed the analytic equations for the polymerizations rates and for the polydispersities of the resulting polymers that have been shown to effectively model LFRP [4, 34].

In the initial stages of the polymerization, a small fraction of the initiating radicals, 6, formed from decomposition of the initiator, **7**, undergo radical–radical coupling. This leads to a terminated molecule/oligomer, **8**, and the resulting removal of two initiating radicals from the system. At this early stage of the polymerization, this is a facile reaction since the diffusing radicals are sterically small and the reaction medium is not viscous. However, by nature, the mediating radical, or persistent radical, **9**, does not undergo coupling and so a small increase in the overall concentration of **9** relative to the propagating/initiating radical, **6**, occurs.



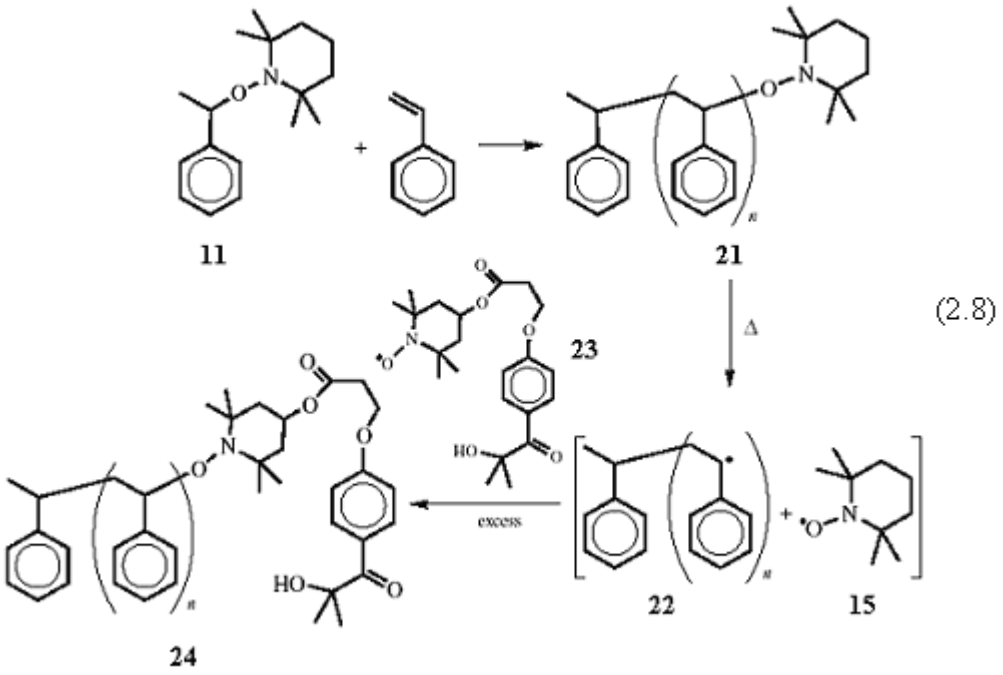
This increased level of **9** is self-limiting since a higher concentration leads to more efficient formation of the dormant chain end, **10**, and a decrease in the amount of radical–radical coupling (see 2.7) leading to the persistent radical effect (PRE) and to the eventual control over the polymerization process. The nature of the equilibrium between the dormant system, **10**, and the pair of radicals, **6** and **9**, has been probed and exploited by a number of groups. The exact nature of the radical pair, caged versus freely diffusing, was probed by a series of crossover experiments [35, 36].



(2.7)

The design of crossover experiments to probe the potential diffusion of the mediating radical from the propagating chain end during ‘‘living’’ free-radical polymerizations involves the use of two structurally similar alkoxyamines, which differ only in their substitution pattern. One derivative is unfunctionalized, **11**, while the other alkoxyamine, **12**, contains two hydroxy groups, one is attached to the TEMPO unit while the second is located at the beta-carbon atom of the ethylbenzene unit. If a 1:1 mixture of **11** and **12** is used to initiate the ‘‘living’’ free-radical polymerization of styrene, homolysis of the carbon–oxygen bond of **11** and **12** will lead to four radical species. Each radicals produced is chemically different and constitutes a pair of initiating, or propagating, radicals, **13** and **14**, and a pair of structurally similar mediating nitroxide radicals are produced, TEMPO, **15**, and 4-hydroxy-TEMPO, **16**.

If no escape of the mediating nitroxide radical from propagating chain end occurs, only two polystyrene derivatives will therefore be formed; **17** and **18**. In contrast, if radical crossover does occur and the mediating nitroxide radicals are free to diffuse to the polymerization medium, four polystyrenes having different substitution **17–20**, will be obtained. Significantly, the experimental result from these crossover experiments revealed a statistical mixture of all four products, even at low conversions, implying freely diffusing radicals (see 2.7). Turro [37] has elegantly taken advantage of this feature to develop a strategy for the facile preparation of chain-end functionalized macromolecules. In this approach a precursor polymer, **21**, is prepared from a standard unfunctionalized initiator, such as **11**, purified and then redissolved in a high-boiling-point solvent such as chlorobenzene and heated at 125^{o}C in the presence of a large excess of functionalized nitroxide, **23**. At this temperature the equilibrium between **22** and the two radicals is established and since the released nitroxide, **11**, is free to diffuse into the solution, exchange with the functionalized nitroxide, **23**, can occur leading to the desired chain end functionalized macromolecule, **24** (see 2.8).

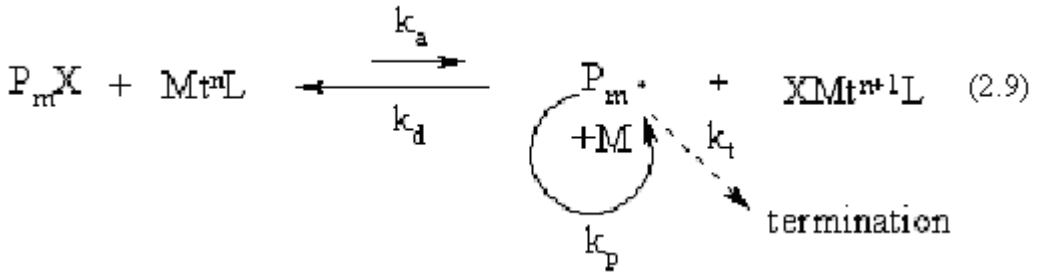


(2.8)

This strategy presents a number of advantages, reactive functional groups can be introduced under mild conditions, from the same precursor polymer a variety of differently tagged macromolecules can be prepared, and the same strategy can be applied to macromolecules of different architectures.

2.3.2. Atom Transfer Radical Polymerization (ATRP)

ATRP is one of the most versatile controlled radical polymerization method. This method utilizes a reversible halogen atom abstraction step in which a lower oxidation state metal (M_t^n complexed by ligands L) reacts with an alkylhalide (P_m-X) to generate a radical ($P_m^{\bullet}$) and a higher oxidation state metal complex ($XM_t^{n+1}L$). This radical then adds monomer to generate the polymer chain (k_p). The higher oxidation state metal can then deactivate the growing radical to generate a dormant chain and the lower oxidation state metal (k_d) as seen in (2.9). The molecular weight is controlled because both initiation and deactivation are fast, allowing for all the chains to begin growing at approximately the same time while maintaining a low concentration of active species. Termination cannot be totally avoided; however, the proportion of chains terminated compared to the number of propagating chains is small [38]. Several metal/ligand systems have been used to catalyze this process and a variety of monomers including styrene, methacrylates, and acrylonitrile have been successfully polymerized [39-40-3].



The rate of ATRP is internally first order in monomer, externally first order with respect to initiator and activator, Cu(I), and negative first order with respect to deactivator, XCu(II). The actual kinetics depends on many factors including the solubility of activator and deactivator, their possible interactions, and variation of their structures and reactivities with concentrations and composition of the reaction medium.

One of the most important parameters in ATRP is the dynamics of exchange, especially the relative rate of deactivation. If the deactivation process is slow in comparison with propagation, then a classic redox initiation process operates leading to conventional, and not controlled, radical polymerization. Polydispersities in ATRP decrease with conversion, with the rate constant of deactivation, k_d, and also with the concentration of deactivator, [XCu(II)]. They, however, increase with the

propagation rate constant, k_p, and the concentration of initiator, $[RX]_o$. This means that more uniform polymers are obtained at higher conversion, when the concentration of deactivator in solution is high and the concentration of initiator is low. Also, more uniform polymers are formed when deactivator is very reactive and monomer propagates slowly (styrene rather than acrylate) [41].

2.3.2.1. Monomers

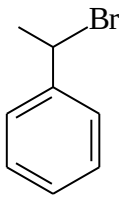
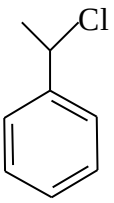
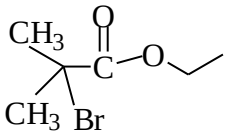
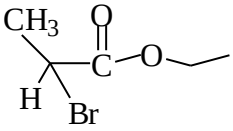
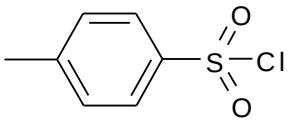
A variety of monomers have been successfully polymerized using ATRP. Typical monomers include styrenes (meth) acrylates, (meth) acrylamides, and acrylonitrile, which contain substituents that can stabilize the propagating radicals. Even under the same conditions using the same catalyst, each monomer has its own unique atom transfer equilibrium constant for its active and dormant species. In the absence of any side reactions other than radical termination by coupling or disproportionation, the magnitude of the equilibrium constant $(K_{eq}=k_{act}/k_{deact})$ determines the polymerization rate.

2.3.2.2. Initiators

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

In ATRP, alkylhalides (RX) are typically used as initiator and the rate of polymerization is first order with respect to the concentration of RX. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, must rapidly and selectively migrate between the growing chain and the transition metal complex. When X is either bromine or chlorine, the molecular weight control is the best. Flourine is not used because the C-F bond is too strong to undergo homolytic cleavage.

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

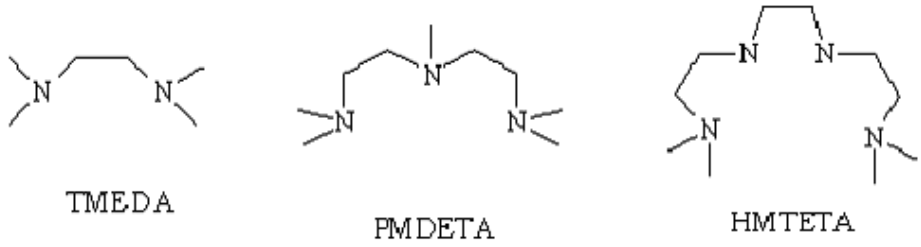
Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 Ethyl-2-bromo isobutyrate	Methyl methacrylate
 Ethyl-2-bromo propionate	Methylacrylate and other acrylates
 p-toluene sulphonyl chloride	Methyl methacrylate

2.3.2.3. Ligands

The main role of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential of the metal center for the atom transfer. There are several guidelines for an efficient ATRP catalyst. First fast and quantitative initiation ensures that all the polymer chains start to grow simultaneously. Second, the equilibrium between the alkylhalide and the transition metal is strongly shifted toward the dormant species side. This equilibrium position will render most of the growing polymer chains dormant and produce a low radical concentration. As a result, the contribution of radical termination reactions to the overall polymerization is minimized. Third fast deactivation of the active radicals by halogen transfer ensures that all polymer chains are growing at approximately the

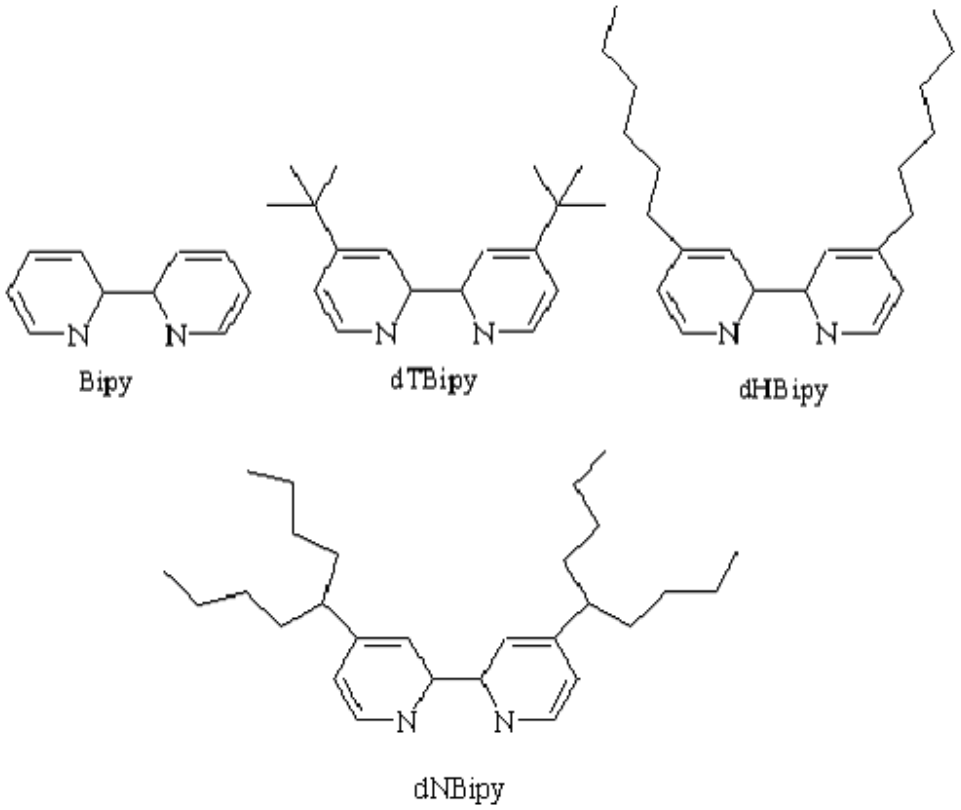
same rate, leading to a narrow molecular weight distribution. Fourth relatively fast activation of the dormant polymer chains provides a reasonable polymerization rate. Fifth, there should be no side reactions such as β-H abstraction or reduction/oxidation of the radicals.

Nitrogen based ligands:



(2.10)

Derivatives of 2,2-bipyridine:



(2.11)

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

2.3.2.4. Transition Metal Complexes

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

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

2.3.2.5. Solvents

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

2.3.2.6. Temperature and Reaction time

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

2.3.2.7. Molecular weight and molecular weight distribution

We can determine the average molecular weight of the polymer by the ratio of consumed monomer and the initiator as in a typical living polymerization

($DP_n=\Delta[M]/[I]_o$, DP=degree of polymerization) while there is a narrow molecular weight distribution ($1.0 < M_w/M_n < 1.5$).

The molecular weight distribution or polydispersity M_w / M_n is the index of the polymer chain distribution. In a well-controlled polymerization, M_w / M_n is usually less than 1.1. The polydispersity index in ATRP in the absence of chain termination and transfer is shown below.

$$\mathbf{M_w / M_n = 1 + [[RX]_o k_p / k_d [D]] . [(2/p) - 1]} \qquad (2.12)$$

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

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

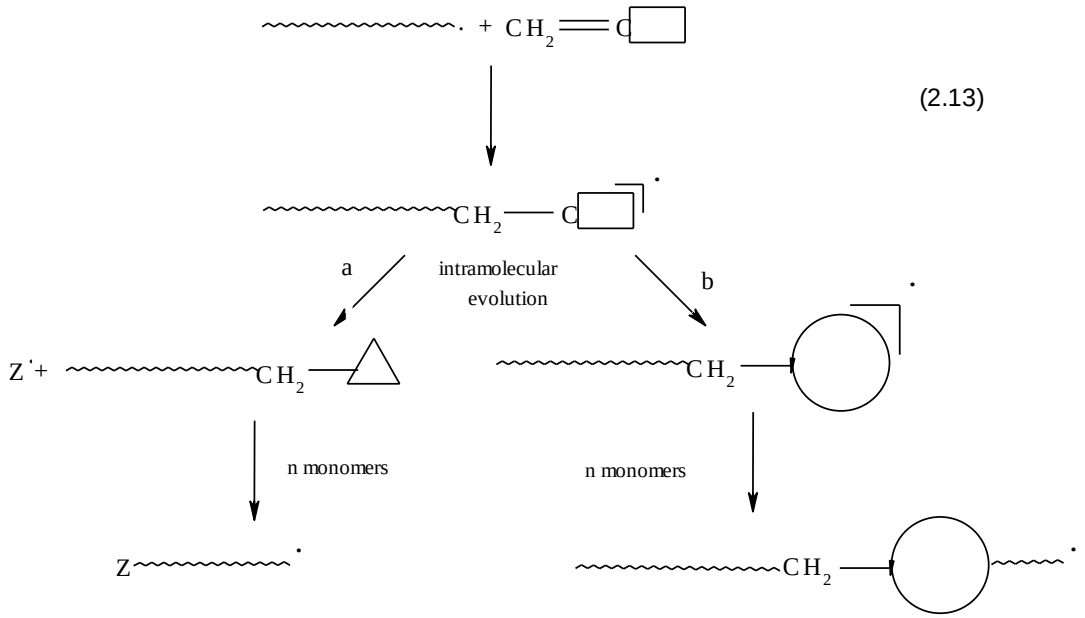
i) Polydispersities (molecular weigh distributions) decrease, if the catalyst deactivates the chains faster (smaller k_p / k_d)

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

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

2.3.3. Addition –Fragmentation Polymerization (RAFT)

An addition-fragmentation process is said to occur in free radical polymerization whenever a growing polymer chain reacts with a compound bearing both an activated site of unsaturation and a weak bond located somewhere else in the molecule. The intermediate radical formed by the addition of propagating radical on the transfer agent undergoes fragmentation involving the weak bond generating another radical which can enter the polymerization cycle. Such a process occurs with the formation of a functional group on the backbone of the polymer (which carried also radical, (2.13a) or at the end of the polymer chain (the radical resting another molecule (2.13b). The former case involves the use of an addition-fragmentation monomer and the latter the introduction of an addition-fragmentation chain transfer agent in the polymerization medium (2.13).



(2.13a) (2.13b)

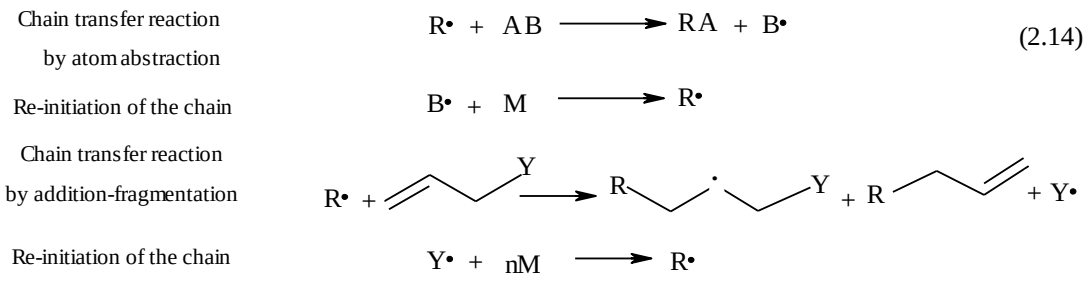
Many monomer and transfer agents based on these types of skeleton have already been developed. However the actual use of an addition-fragmentation chain transfer agent or of an addition-fragmentation monomer in industrial applications is still limited at the present time, because of various problems arising from their synthesis, polymerizability and properties, although such compounds could inherently be useful in most industrial applications.

The control of molar mass in free radical polymerization is usually achieved by the addition of a chain transfer agent in the polymerization medium. When a chain carrying radical is trapped by another specific compound XY to produce a radical Y• which is also reactive, this radical Y• can re-initiate a new radical chain. In this case XY is called a chain transfer agent. Two kinds of chain transfer agents can be distinguished according to their mode of action:

1. Atom or group transfer agents operating by an abstraction pathway (2.14). These additives are generally solvents such as CCl_4, mercaptans, substituted disulfides which react in the medium as atom donors to the growing macro radicals, thus terminating the polymer chain and generating, respectively a trichloromethyl a thiyl radical, able to re-initiate polymerization [42-43].

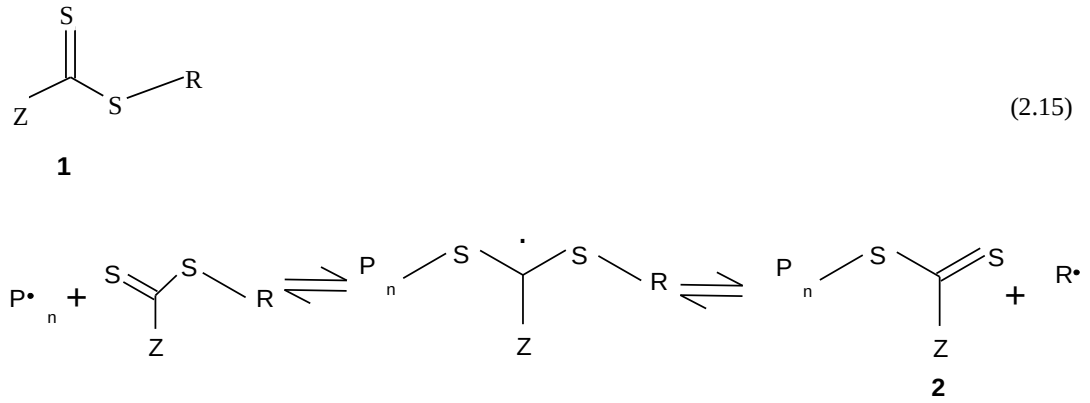
2. Addition-fragmentation chain transfer agents (2.14). The chain transfer agents which follow the addition-fragmentation mechanism are particular interest in organic

and polymer chemistry. Recently many studies have shown that allyl, acrylyl and allenyl transfer to alkyl halides represent powerful synthetic tolls to prepare sophisticated molecules. Such a process was also identified as an effective means for controlling the molar mass of vinyl polymers, avoiding the use of conventional chain transfer agents based on thioderivatives.

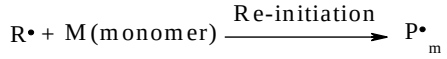


(2.14)

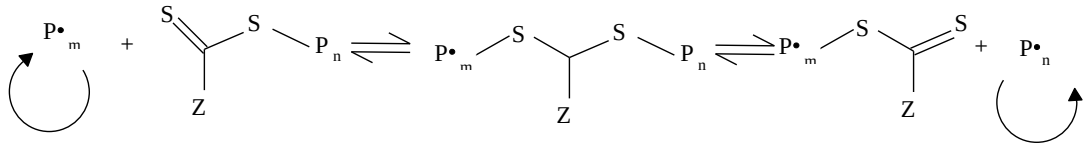
Thiocarbonylthio compounds of general structure 1 in (2.15) confer living characteristics to radical polymerization [44-45]. These reagents function by establishing a dynamic equilibrium between propagating radicals ($P_n^{\bullet}$) and dormant chains 2 in (2.15) by a mechanism of reversible addition –fragmentation chain transfer (raft) as shown in (2.15). RAFT agents 1 in (2.15) function effectively only when the substituent on sulfur (R) is good homolytic leaving group when compared to the polymer chain P_n. With appropriate choice of the RAFT agent 1 in (2.15) a wide range of polymers of predetermined M_W and narrow polydispersity can be prepared [44-45-46]. The versatility and convenience of this process offer distinct advantages over other forms of living radical polymerization [47-48].



(2.15)



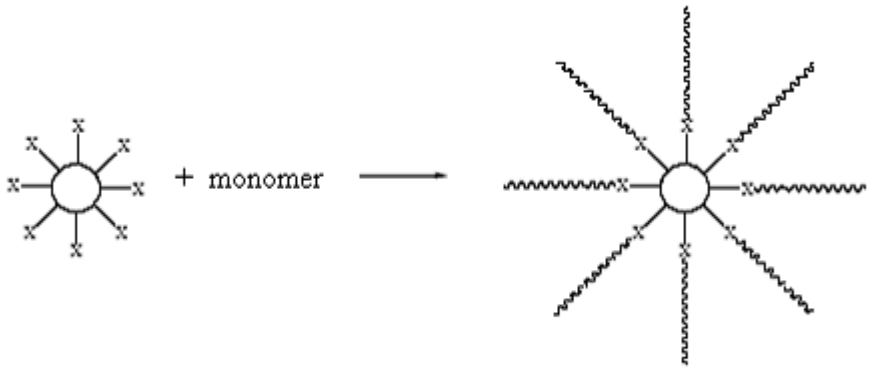
Equilibration



2.4 Synthesis of Star-Shaped Polymers

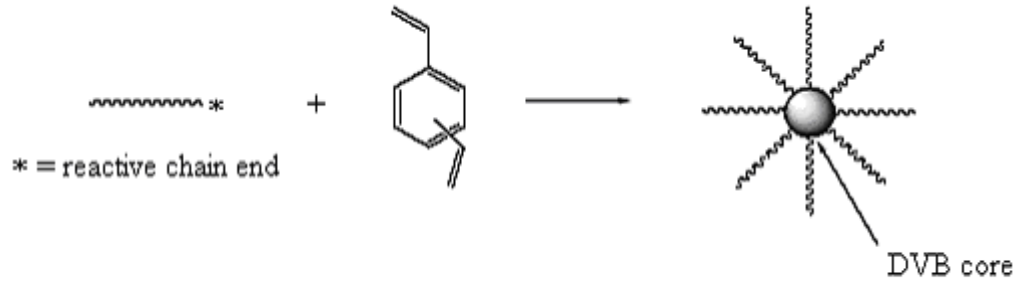
2.4.1 Introduction

Elucidation of structure-property relationships remains an ongoing field of study in polymer science. The introduction of long chain branching is known to affect polymer physical properties and processability as a result of changing the melt, solution, and solid-state properties of polymers [49]. It has been shown that branching results in a more compact structure in comparison to linear polymers of similar molecular weight, due to their high segment density, which alters the crystalline, mechanical, and viscoelastic properties of the polymer. While it is well-known that long chain branching greatly influences polymer physical properties, a fundamental understanding of structure-property relationships remains difficult due to the complexity of branched polymer structures. A branched polymer structure was described as a nonlinear polymer with multiple backbone chains radiating from junction points [50]. Star-shaped macromolecules constitute the simplest form of branched macromolecules, comprising only one branch point, and as such, have received significant attention in the elucidation of structure property relationships [1]. Although star polymers constitute the simplest branched structure, their synthesis remains challenging, and star polymers are often difficult to synthesize in a well-controlled manner. Due to the complex nature of these macromolecules, controlled polymerization techniques, such as anionic, cationic, living free radical, and group transfer (GTP) polymerization have typically been used to obtain well-defined star-shaped macromolecules. Star polymers are typically synthesized using either a core-first approach, or an arm-first approach. In the core-first synthetic method, a multifunctional initiator is used and the number of arms is proportional to the number of functionalities on the initiator (2.16) [51].



(2.16) Synthesis of star-shaped polymer using the core-first method.

Using the core-first method, well-defined star-shaped macromolecules can be synthesized as long as initiation is rapid relative to propagation. While this approach was used in the first cationic synthesis of star-shaped polymers, containing three or four arms, it tends to yield polymers with broadened molecular weight distributions [52]. In the arm-first synthetic method, linear arm polymers are synthesized and then coupled using a multifunctional linking agent or divinyl compound. In this case, the number of arms depends on the linking efficiency of the arm polymer to the multifunctional core and an alternative method is used to determine the number of arms (2.17). This approach is typically used in both living anionic and cationic syntheses of star-shaped polymers [53].



(2.17) Synthesis of star-shaped polymers using the arm-first method

As discussed previously, living anionic chain ends are very reactive and are used in a variety of chain end functionalization strategy. This characteristic of living chain ends makes living anionic polymerization ideal for the synthesis of complex architectures using chain end coupling reactions. The synthesis of star-shaped polymers using living anionic polymerization has been achieved using a variety of linking agents. Typical linking reagents for coupling of living anionic chain ends are chlorosilanes and their derivatives. However, these types of endcapping reagents are

limited in their utility by the necessity for equal reactivity and accessibility of all reactive sites on the linking agent. Use of both silicon tetrachloride and chloromethylated benzenes have been hampered by these limiting factors. Other linking agents are dimethyl phthalate, trisallyloxytriazines, and divinylbenzene. In some cases, the number of arms using the arm first approach is controlled by the number of functionalities on the linking agent, such as trichloromethylsilane or tetrachlorosilane.

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

More recently, several of the techniques discussed above have been used in conjunction with one another to synthesize novel macromolecular architectures. For example, Muller et al. reported the use of both cationic and anionic polymerization to synthesize star-shaped block copolymers [54]. The polymerization of isobutylene was initiated using 1,3,5-tricumylchloride and terminated using diphenylethylene and methanol to yield a diphenylethylene methoxy group. This group was then transformed into an initiator for the anionic polymerization of methyl methacrylate using a K/Na alloy.

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

bromomethylbenzene derivative in the synthesis of *t*-butyl methacrylate star-shaped macromolecules, hyperbranched cores, main chain functional graft sites, and convergent coupling of arm polymers to synthesize dendritically branched polystyrene.

2.4.2 Synthesis of Functional Star-Shaped Polymers:

Chain-end functionalization is an additional challenge in the synthesis and characterization of complex polymer architectures. As discussed previously, living anionic polymerization methodologies are typically used to synthesize star-shaped macromolecules due to the controlled nature of these reactions. Functionalized alkyllithium initiators provide quantitative chain end functionalization and are an attractive alternative to electrophilic terminating reagents for the synthesis of chain-end functionalized polymers. Functionalized initiators facilitate the synthesis of telechelic and heterotelechelic polymers, functionalized block polymers, and star-shaped polymers with functional groups on each arm terminus [55]. The use of the functional initiator 3-(*t*-butyldimethylsilyloxy)-1-propyllithium (*t*BDMSPrLi) was reported in the synthesis of a variety of polymers with various architectures, such as polyisoprene, polybutadiene, poly(methyl methacrylate), and poly(1,3-cyclohexadiene), to yield hydroxyl chain end functionalized polymers.

While living anionic polymerization using functional initiation has proven an excellent pathway to chain-end functional polymers, other researchers have reported various methodologies for the preparation of star-shaped macromolecules with diverse chain-end functionalities.

Hedrick et al. reported the core-first synthesis of star-shaped poly(ε-caprolactone) hydroxyl terminated macroinitators with six arms using ring opening polymerization and the subsequent transformation into ATRP initiators [56]. The macroinitiators were then used to polymerize several monomers, including methyl methacrylate, hydroxyethyl methacrylate, or ethylene oxide. There are several parameters in an ATRP that should be controlled carefully in order to maximize the yield of stars and prevent star-star coupling reactions. Some detailed studies have been carried out on the coupling of monofunctional polystyrenes and polyacrylates with DVB and di(meth)acrylates to prepare star polymers and the following guidelines have been developed:

- The ratio of difunctional reagent to growing chains seems to be optimal in the range of 10-20
- Monomer conversion (or reaction time) has to be carefully controlled and stopped before star-star coupling occurs.
- Higher yields of stars are observed for polyacrylates than for polystyrenes. This may be attributed to a higher proportion of terminated chains in styrene polymerization.
- The choice of the difunctional reagent is important and reactivity should be similar to, or lower than that of the arm-building monomers.
- Halogen exchange slightly improves efficiency of star formation.
- Solvent, temperature, catalyst concentration should be also optimized [57].

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

Utilizing a different approach, Hirao et al. have introduced functionality to star polymers using living anionic polymerization in conjunction with functionalized diphenylethylene (DPE) derivatives and organic functional group transformations [58]. Using this approach, functionality was introduced at the α-terminus, at block junctions, or at the core. Quirk et al. pioneered this work and Hirao et al. based their research on this work [59]. Fréchet and Hawker et al. have also reported the use of nitroxide mediated polymerization in the synthesis of functionalized star polymers [60]. They reported the synthesis of a series of compounds, ranging from simple to complex, and have focused on homo, block, and random copolymers with both apolar and polar vinylic repeat units and functional group integration in diverse positions. Ishizu et al. have also reported on the functionalization of polyisoprene star polymers with p-chloro styrene to yield a periphery of reactive styrene groups, capable of forming a crosslinked network [61]. While both functional polymers and star-shaped polymers are prevalent in the literature, the combination of well-defined

thermoreversible chain end interactions, such as multiple hydrogen bonding interactions, and star-shaped macromolecules is limited. Hadjichristidis et al. studied the synthesis and characterization of well-defined linear and star-shaped polystyrenes, polyisoprenes, and polybutadienes bearing both sulfo- and phosphoro-zwitterionic groups, which have a thermoreversible nature [1]. While these studies have made great strides in delineating structure-property relationships for these materials, the reversible interaction is ionic and it is anticipated that their behavior will significantly differ from a multiple hydrogen bonding interaction. Meijer et al. have recently reported the synthesis of model low molar mass poly (ethylene oxide-*co*-propylene oxide) three arm star polymers bearing pendant quadruple hydrogen bonding functionalities [62]. These polymers were compared with three arm star polymers bearing urea chain ends, non-functional chain ends, and with a chemically crosslinked network and the influence of chain end functionality was studied. However, due to the hydrophilic nature of the parent polymer, the effect of atmospheric moisture on the polymer physical properties was not excluded. The introduction of thermally reversible interactions at the chain ends of star-shaped polymers is only one of the interesting families to which chain end functionalized polymers serve as a precursor. Organic functional groups, such as hydroxyl and amino serve as stepping stones to diverse and rich functionalization strategies.

2.5. Photochemistry of Azobenzene-Containing Polymers

The need for materials better suited for the emerging technological applications has prompted the study of new polymers. In this respect, the preparation of systems containing azobenzene moieties appears to be very promising. Indeed, the photoinduced trans–cis isomerization of azobenzene chromophores can give rise to photochromic and optical dichroic effects [63]. These properties are attracting increasing attention because of their potential industrial applications [11]. Azobenzene containing polymers have been investigated for the preparation of holographic optical memories [64–66], the photo-controlled release of drugs [67], the preparation of polymeric dyes [68–70], and non-linear optical materials [71–74].

Photochemical reactions which occur in small molecules can also be induced to occur in macromolecules. Though, in macromolecular environments there are constraints which are not present on a small-molecule scale, the challenge is to apply fundamental principles to macromolecules which may coil, branch, or be chemically

cross-linked increasing the order of complexity. The free volume available to a reactive site or dissolved probe controls the course of photophysical and photochemical processes, for example. Likewise, molecular mobility plays an important role in determining the course of photochemical reactions in polymers and is related to the size of the molecule, the flexibility of the polymer chain, and whether the polymer is in solution or the solid state.

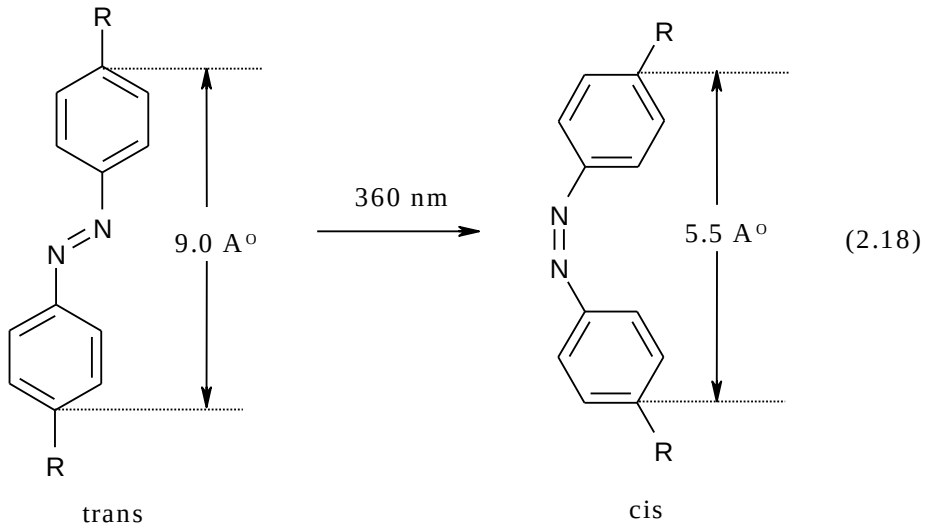
2.5.1. Photochemistry of Azobenzene: Cis- Trans Isomerism

Azobenzene and many of its derivatives are characterized by reversible transformations from the generally more stable trans form to the less stable cis form upon irradiation with UV or visible light to yield a photostationary composition that is wavelength and temperature dependent. Azobenzene is thus a textbook representative demonstrating the rotoresistant property of the N=N double bond [75-76], and spectroscopists and photochemists have long been aware of the inversion-rotation mechanistic dichotomy. Many theoretical and experimental papers deal with this subject [77-84]. The intense absorption at 330 nm due to the π-π^* transition of the trans isomer decreases during such an isomerization, while the absorption maximum due to the cis isomer at 450 nm which is due to the n-π* transition increases.

Thermal isomerism from the photogenerated cis to the trans form also occurs. The thermal isomerization follows first-order kinetics and the slope of a plot of log $(A_\alpha - A_t)$ against time gives the rate. Quantum yields are generally high for the isomerization of azobenzene and there are no competing reactions of significance. Therefore, the cis-trans isomerization of the azobenzene moiety represents virtually a model photochemical process in which one stereoisomer is favored thermally and the other stereoisomer is favored photochemically. The conversion of one isomer to the other is virtually quantitative. There is no known evidence of emission from the excited states of azobenzene either in the cis form or in the trans form, so the photochemical process is entirely efficient, at least to the extent that it can be experimentally traced.

Photoinduced isomerism of azobenzene also proceeds with large structural change as reflected in the dipole moment and change in geometry. The isomerization involves a decrease in the distance between the para carbon atoms in azobenzene from about 9.0

A° in the trans form to 5.5 A° in the cis form (2.18), and the local contraction may be even greater. Likewise, trans-azobenzene has no dipole moment while the dipole moment of the nonplanar cis compound is 3.0 D. These properties when manifested in polymers are useful probes of conformational dynamics of macromolecules by site-specific photolabeling, in estimating the free volume in cross-linked networks, and in designing photoreactive polymers responsive to external stimuli.



(2.18)

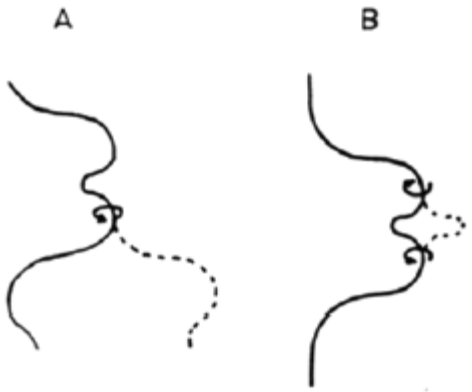
2.5.2. Macromolecular Photochemistry

Macromolecular photochemistry involving azobenzene moieties has progressed along two lines. Early [85-86] studies sought to clarify a physical problem. What is the nature of hindered rotation in long-chain molecules? What is the distribution of free volume in the glassy state? What is the flexibility of chain molecules? Later studies concentrated on the photochromic properties of the materials. Since azo labels can be selectively attached to the side chains, main chain, cross-links, or chain ends of the polymer as photochromic "probes", selective site labeling allowed one to identify motion associated with a specific location on the polymer chain. By varying the molecular structure and the polymeric system, as well as by inhibiting the motion of the polymer matrix, it was possible to construct materials having photochromic characteristics. In that the need for polymer materials is changing from structural materials to functional materials, the current trend is to employ the azobenzene moiety as a 'trigger" to induce morphological changes which can be light driven. The applications are as a chemical valve or as a light-induced porous filter of differing, and easily controlled, porosity. Chemical substances which exhibit photoinduced structural changes are candidates not only to become chemical condensers for the

storage of light energy but also to be used as mediators of light energy for chemical functions. The possibility thus arises that since conformations of azobenzene-containing polymers can be controlled by using photoinduced changes of the azobenzene moiety, they may provide light-controlled chemical functions. Expectedly, this would lead to the possibility of controlling the chemical functions by an 'on-off light switch"

2.5.3. Backbones: “Crankshaft-like Motion”

While conformational distribution in flexible chain molecules has been the subject of intense theoretical and experimental study ever since Kuhn’s pioneering work, [87] the dynamics of conformational transitions have become of interest only relatively. It is theorized that conformational transitions in the backbones of long polymer chains must involve two correlated hindered rotations (a so-called crankshaft-like motion) so as to avoid the need for a long chain segment to swing through the viscous solvent medium (2.19) [88]. If this model is correct, the free energy of activation should be substantially higher for hindered rotation in polymer backbones than for a similar process in a small molecule, resulting in a large decrease in the rate of conformational transition [88]. Zimmerman et al. [78] suggested that the photoisomerization of azobenzene involves a thermal reaction between the excited trans and cis states which is separated by a low-energy barrier. This concept was later confirmed by Fischer and Malkin; who showed that the temperature dependence of the quantum yield for the trans-cis photoisomerization led to an estimate of a 2-3 kcal/mol energy barrier separating the two excited states. Such a low value for the energy barrier between the trans and cis excited states of azobenzene makes the study of photoisomerization of azobenzene residues in the backbone of polymers and their analogues eminently suitable for the characterization of the general behavior of conformational transitions involving low-energy barriers.



(2.19). Schematic representation of conformational transition in a flexible chain molecule: **(A)** rotation around a single bond; **(B)** correlated rotation around double bonds.

2.5.4. Photoresponsive Polymers: Azobenzene as a "Trigger"

A photoresponsive synthetic polymer is a special polymer having photoreceptor chromophores which can transfer light energy into a change in the conformation of the polymer [89]. The light is stored at once in a chemical structure change of the chromophore and then transferred into the polymer chain, causing reversible conformational changes. The conformational change is expected to produce a concomitant change in physical and chemical properties of the polymer solutions and solids. The basic idea for controlling properties of polymers by photoirradiation is to use photoresponsive trigger molecules. Several examples of photostimulated physical property changes of photoresponsive polymers having azobenzene residues are described. Some of the physical and chemical properties which are reversibly controlled include (a) viscosity, (b) conductivity, (c) pH, (d) solubility, (e) wettability, and (f) mechanical properties.

3. EXPERIMENTAL WORK

3.1. Materials

Methyl methacrylate (MMA, 99% Aldrich), and styrene (St, 99% Aldrich) were passed through basic alumina column to remove inhibitors and then dried over CaH_2 and distilled under vacuum prior to use. *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (PMDETA, Aldrich) distilled over NaOH. Tetrahydrofuran (THF, 99.8%, J.T.Baker) was dried and distilled over lithium aluminium hydride. Dichloromethane was purchased from Aldrich and used after distillation over P_2O_5. 4-dimethylamino pyridinium-4-toluene sulfonate (DPTS) was prepared according to the literature procedure [90]. 2,2-bis(hydroxymethyl)propanoic acid (bis-MPA, 99% Acros), triethylamine (Et_3N, 99% Merck), 2-Bromoisobutryl bromide (99% Aldrich), 4-dimethylaminopyridine (DMAP, 99% Aldrich), *N*,*N*-dicyclohexylcarbodiimide (DCC, 99% Acros), 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO, 98% Acros), 2,2-dimethoxypropane (98% Acros), Benzoyl peroxide (BPO, 77% Fluka), 4-Nitrobenzoic acid (99% Acros), α-D glucose (99% Acros), Acetic acid (glacial 99-100% J.T.Baker), Thionyl chloride (99.5% Acros) absolute ethanol (99.5% J.T.Baker) were used as received.

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 (0.112, 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,-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 Azodibenzoyl Chloride [7]

3.2.7.1. Synthesis of trans-4,4'-dicarboxyazobenzene :

A solution of 13,1 g (78,3 mmol) 4-nitrobenzoic acid and 50,1 g (1,25 mol) NaOH in 225 ml water was heated at 50 °C then a hot solution of 100,4 g (0,56 mol) α-D glucose in 150 ml water was added under stirring over 1h. The stirring was continued for 2h at 50 °C and overnight at room temperature, then air was bubbled within the resulting solution for 12h. After addition of acedic acid to pH 6, the solid precipitate was filtered and dried to constant weight to give 10.5 g (99.5 %) of a brownish solid [91].

3.2.7.2. Preparation of Azodibenzoyl Chloride [7]

Charge 5 g (0.0185 mol) azodibenzoic acid, 25 ml (40.75 g ; 0.34 mol) thionyl chloride, and 0.076 ml triethylamine into a 100 ml round-bottom flask equipped with stirred and a reflux condenser with a drying tube. Reflux reaction mixture until a dark red solution is obtained, about 4h. (The off-gas hydrogen chloride must be trapped or scrubbed in a water trap.) Excess thionyl chloride is removed using a water pump at a temperature < 50 °C gives 5.6 g (90 %) of azodibenzoyl chloride. The acid chloride thus obtained is sufficiently pure for polymerization but can be further purified by recrystallization from dry hexane. (1g 16 %) [92]

3.2.8. Synthesis of Azobenzene-4,4'-dicarboxylic acid bis-{3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethoxycarbonyl]-propyl} ester [8]

The compound **6** (1.15 g, 2.12 mmol) is dissolved in 20 mL of dichloromethane. To this solution, added was DMAP (0.117 g, 0.96 mmol), triethylamine (0.3 mL, 2.16 mmol) in that order and the reaction mixture was stirred and cooled to 0 ^{o}C. Azodibenzoyl chloride **(7)** (0.295 g, 0.96 mmol) dissolved in 5 mL of dichloromethane was added drop-wise to the mixture. The reaction was continued overnight with stirring and then filtered. It was extracted with water and dried with Na_2SO_4. The organic phase was evaporated and the remaining product was purified by column chromatography over silica gel eluting once with ethylacetate /hexane (1:15) and then with (1:10) to give **8** as viscous red liquid (Yield: 0.67 g, 53 %). It was solidified upon storage. ^{1}H NMR ($CDCl_3$, δ) 8.06 (d, J = 8.4 Hz, 4H, Ar*H* of azobenzene), 7.95 (d, J = 8.4 Hz, 4H, ArH of azobenzene), 7.28-7.17 (m, 10H, Ar*H*), 4.94 (t, 2H, ArC*H*), 4.59 and 4.46 (m, 4H, ArCHC*HH*), 4.45-4.24 (m, 8H, C*H*$_2$OC=O), 1.84 (12H, CBr(C*H*$_3$)$_2$), 1.69-0.73 (m, 42H); ^{13}C NMR ($CDCl_3$, δ) 172.08, 170.99, 165.08, 155.08, 140.23, 131.96, 128.68, 123.83, 121.68, 83.07, 66.54, 66.06, 64.69, 60.11, 55.26, 46.64, 40.37, 38.87, 32.90, 31.18, 30.19, 29.65, 20.55, 17.08, 15.25. Anal. Calc. for $C_{66}H_{86}Br_2N_4O_{14}$: C, 60.09 %; H, 6.57 %; N, 4.25 %. Found: C, 59.38 %; H, 6.64 %; N, 4.13 %. MS (ESI): 1319.5 $(M+H)^+$, 1341.4 $(M+Na)^+$.

3.3. Preparation of $(PMMA)_2$ macroinitiator (P Ia) by ATRP of MMA:

$(PMMA)_2$ macroinitiator was prepared by ATRP of MMA using **8** as an initiator and copper chloride (CuCl) complexed by *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) as the catalyst at 60 ^oC. To a Schlenk tube equipped with a magnetic stirring bar, the degassed MMA, (1 mL, 9.35 X 10^{-3} mol), ligand, (PMDETA, 0.0195 mL, 9.34 X 10^{-5} mol), CuCl (0.0092 g, 9.34 X 10^{-5} mol) and initiator (0.061 g, 4.67 X 10^{-5} mol) in 1 mL of anisole were added in the order mentioned. The tube was degassed by three freeze-pump-thaw cycles, left *in vacuo* and placed in a thermostated oil bath at 60 ^oC for a given time 15 min. Subsequently the brown polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in a vacuum oven at 25 ^oC. The isolated PMMA macroinitiator (**P Ia**) had the predicted molecular weight and low polydispersity ($M_{n,GPC}$= 4500; M_w/M_n= 1.09). $[M]_o/[I]_o$ = 200; conv. 13%; $M_{n,theo}$ = 3920.

3.4. Preparation of $(PMMA)_2$-$(PS)_2$ miktoarm star copolymer (P IIa) by NMP of St:

$(PMMA)_2$-$(PS)_2$ miktoarm star copolymer was prepared using NMP of St (0.687 mL, 6 X 10^{-3} mol) in the presence of TEMPO functionalized $(PMMA)_2$ as a macroinitiator, **P Ia** (0.09 g, 2 X 10^{-5} mol). The reaction mixture was degassed by three freeze-pump-thaw cycles and left in *vacuo*. The tube was then placed in an oil bath thermostated at 125 ^oC for a given time 19.5 h (Table 1, Run **P IIa**). The polymerization mixture was diluted with THF, and precipitated in methanol. The obtained star polymer was dried for 24 h in a vacuum oven at 25 ^oC. $[M]_o/[I]_o$ = 300; conv. 11%; $M_{n,theo}$ = 7950; $M_{n,GPC}$ = 8380; M_w/M_n = 1.15.

3.5. Photoisomerization Study:

3.5.1. Photoisomerization experiment of initiator (8):

UV visible spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer in $CHCl_3$. Trans-cis photoisomerization experiments were carried out in a Schlenk tube equipped with a lateral quartz cell, using a merry-go-round type reactor equipped with 16 Philips 8W/06 lamps emitting light at $\lambda < 350$ nm. Trans to cis

photoisomerization of **8** was determined by using UV spectrophotometer. The miktofunctional initiator **8** dissolved in $CHCl_3$ and was prepared $2.5x10^{-5}$ M solution. And then this sample was irradiated with UV light (λ < 350 nm) by 10 s intervals (0-120 s). When this solution was kept in the dark for 2 days, the back isomerization (cis-to-trans) occurred. This process was also monitored by UV spectrophotometer.

3.5.2. Photoisomerization experiment of miktoarm star polymer:

$2.5x10^{-5}$ M solution of $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer was prepared in $CHCl_3$. A similar behavior was observed upon UV irradiation (λ < 350 nm) of $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer (**P IIa**) for 7h. Trans to cis isomerization was recorded using UV spectrophotometer. The back isomerization of **P IIa** (cis to trans) occurred when keeping it in the dark for 5 days. Trans to cis isomerization of miktoarm star copolymer (**P IIa**) was also observed in GPC traces.

3.6. Characterization

The ^1H and ^{13}C NMR spectra were recorded on a Bruker NMR Spectrometer (250 MHz for proton and 62.89 MHz for carbon) in $CDCl_3$. Mass spectrum was obtained on a Micromass Autospec instrument operating in ESI positive mode at 70 eV. Gel permeation chromatography measurements were obtained from an Agilent instrument (Model 1100) consisting of a pump, refractive index and UV detectors, 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. Butylide hydroxy toluene (BHT) 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) and the conversions were determined by gravimetrically. UV visible spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer in $CHCl_3$. Trans-cis photoisomerization experiments were carried out in a Schlenk tube equipped with a lateral quartz cell, using a merry-go-round type reactor equipped with 16 Philips 8W/06 lamps emitting light at λ < 350 nm.

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Charge 5 g (0.0185 mol) azodibenzoic acid, 25 ml (40.75 g ; 0.34 mol) thionyl chloride, and 0.076 ml triethylamine into a 100 ml round-bottom flask equipped with stirred and a reflux condenser with a drying tube. Reflux reaction mixture until a dark red solution is obtained, about 4h. (The off-gas hydrogen chloride must be trapped or scrubbed in a water trap.) Excess thionyl chloride is removed using a water pump at a temperature < 50 °C gives 5.6 g (90 %) of azodibenzoyl chloride. The acid chloride thus obtained is sufficiently pure for polymerization but can be further purified by recrystallization from dry hexane. (1g 16 %) [92]

3.2.8. Synthesis of Azobenzene-4,4'-dicarboxylic acid bis-{3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethoxycarbonyl]-propyl} ester [8]

The compound **6** (1.15 g, 2.12 mmol) is dissolved in 20 mL of dichloromethane. To this solution, added was DMAP (0.117 g, 0.96 mmol), triethylamine (0.3 mL, 2.16 mmol) in that order and the reaction mixture was stirred and cooled to 0 ^{o}C. Azodibenzoyl chloride **(7)** (0.295 g, 0.96 mmol) dissolved in 5 mL of dichloromethane was added drop-wise to the mixture. The reaction was continued overnight with stirring and then filtered. It was extracted with water and dried with Na_2SO_4. The organic phase was evaporated and the remaining product was purified by column chromatography over silica gel eluting once with ethylacetate /hexane (1:15) and then with (1:10) to give **8** as viscous red liquid (Yield: 0.67 g, 53 %). It was solidified upon storage. ^{1}H NMR ($CDCl_3$, δ) 8.06 (d, J = 8.4 Hz, 4H, Ar*H* of azobenzene), 7.95 (d, J = 8.4 Hz, 4H, ArH of azobenzene), 7.28-7.17 (m, 10H, Ar*H*), 4.94 (t, 2H, ArC*H*), 4.59 and 4.46 (m, 4H, ArCHC*HH*), 4.45-4.24 (m, 8H, C*H*$_2$OC=O), 1.84 (12H, CBr(C*H*$_3$)$_2$), 1.69-0.73 (m, 42H); ^{13}C NMR ($CDCl_3$, δ) 172.08, 170.99, 165.08, 155.08, 140.23, 131.96, 128.68, 123.83, 121.68, 83.07, 66.54, 66.06, 64.69, 60.11, 55.26, 46.64, 40.37, 38.87, 32.90, 31.18, 30.19, 29.65, 20.55, 17.08, 15.25. Anal. Calc. for $C_{66}H_{86}Br_2N_4O_{14}$: C, 60.09 %; H, 6.57 %; N, 4.25 %. Found: C, 59.38 %; H, 6.64 %; N, 4.13 %. MS (ESI): 1319.5 $(M+H)^+$, 1341.4 $(M+Na)^+$.

3.3. Preparation of $(PMMA)_2$ macroinitiator (P Ia) by ATRP of MMA:

$(PMMA)_2$ macroinitiator was prepared by ATRP of MMA using **8** as an initiator and copper chloride (CuCl) complexed by *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) as the catalyst at 60 ^oC. To a Schlenk tube equipped with a magnetic stirring bar, the degassed MMA, (1 mL, 9.35 X 10^{-3} mol), ligand, (PMDETA, 0.0195 mL, 9.34 X 10^{-5} mol), CuCl (0.0092 g, 9.34 X 10^{-5} mol) and initiator (0.061 g, 4.67 X 10^{-5} mol) in 1 mL of anisole were added in the order mentioned. The tube was degassed by three freeze-pump-thaw cycles, left *in vacuo* and placed in a thermostated oil bath at 60 ^oC for a given time 15 min. Subsequently the brown polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated in hexane. The polymer was dried for 24 h in a vacuum oven at 25 ^oC. The isolated PMMA macroinitiator (**P Ia**) had the predicted molecular weight and low polydispersity ($M_{n,GPC}$= 4500; M_w/M_n= 1.09). $[M]_o/[I]_o$ = 200; conv. 13%; $M_{n,theo}$ = 3920.

3.4. Preparation of $(PMMA)_2$-$(PS)_2$ miktoarm star copolymer (P IIa) by NMP of St:

$(PMMA)_2$-$(PS)_2$ miktoarm star copolymer was prepared using NMP of St (0.687 mL, 6 X 10^{-3} mol) in the presence of TEMPO functionalized $(PMMA)_2$ as a macroinitiator, **P Ia** (0.09 g, 2 X 10^{-5} mol). The reaction mixture was degassed by three freeze-pump-thaw cycles and left in *vacuo*. The tube was then placed in an oil bath thermostated at 125 ^oC for a given time 19.5 h (Table 1, Run **P IIa**). The polymerization mixture was diluted with THF, and precipitated in methanol. The obtained star polymer was dried for 24 h in a vacuum oven at 25 ^oC. $[M]_o/[I]_o$ = 300; conv. 11%; $M_{n,theo}$ = 7950; $M_{n,GPC}$ = 8380; M_w/M_n = 1.15.

3.5. Photoisomerization Study:

3.5.1. Photoisomerization experiment of initiator (8):

UV visible spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer in $CHCl_3$. Trans-cis photoisomerization experiments were carried out in a Schlenk tube equipped with a lateral quartz cell, using a merry-go-round type reactor equipped with 16 Philips 8W/06 lamps emitting light at $\lambda < 350$ nm. Trans to cis

photoisomerization of **8** was determined by using UV spectrophotometer. The miktofunctional initiator **8** dissolved in $CHCl_3$ and was prepared $2.5x10^{-5}$ M solution. And then this sample was irradiated with UV light (λ < 350 nm) by 10 s intervals (0-120 s). When this solution was kept in the dark for 2 days, the back isomerization (cis-to-trans) occurred. This process was also monitored by UV spectrophotometer.

3.5.2. Photoisomerization experiment of miktoarm star polymer:

$2.5x10^{-5}$ M solution of $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer was prepared in $CHCl_3$. A similar behavior was observed upon UV irradiation (λ < 350 nm) of $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer (**P IIa**) for 7h. Trans to cis isomerization was recorded using UV spectrophotometer. The back isomerization of **P IIa** (cis to trans) occurred when keeping it in the dark for 5 days. Trans to cis isomerization of miktoarm star copolymer (**P IIa**) was also observed in GPC traces.

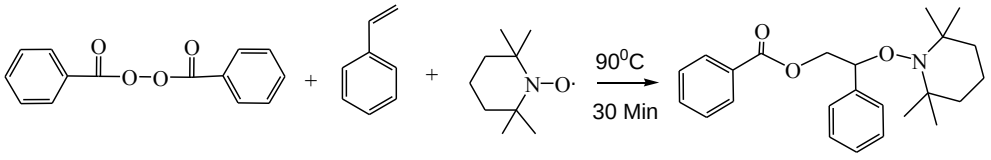
3.6. Characterization

The ^1H and ^{13}C NMR spectra were recorded on a Bruker NMR Spectrometer (250 MHz for proton and 62.89 MHz for carbon) in $CDCl_3$. Mass spectrum was obtained on a Micromass Autospec instrument operating in ESI positive mode at 70 eV. Gel permeation chromatography measurements were obtained from an Agilent instrument (Model 1100) consisting of a pump, refractive index and UV detectors, 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. Butylide hydroxy toluene (BHT) 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) and the conversions were determined by gravimetrically. UV visible spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer in $CHCl_3$. Trans-cis photoisomerization experiments were carried out in a Schlenk tube equipped with a lateral quartz cell, using a merry-go-round type reactor equipped with 16 Philips 8W/06 lamps emitting light at λ < 350 nm.

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 –OH and the shifts of the $–CH_2$ and –CH protons adjacent to hydroxyl and aromatic group, respectively, clearly confirm the successful hydrolysis. The ^1H NMR spectra of the corresponding ester and alcohol precursors are presented in Figures 1 and 2, respectively.



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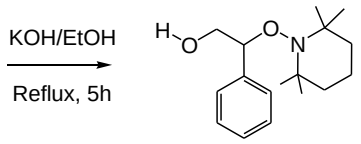

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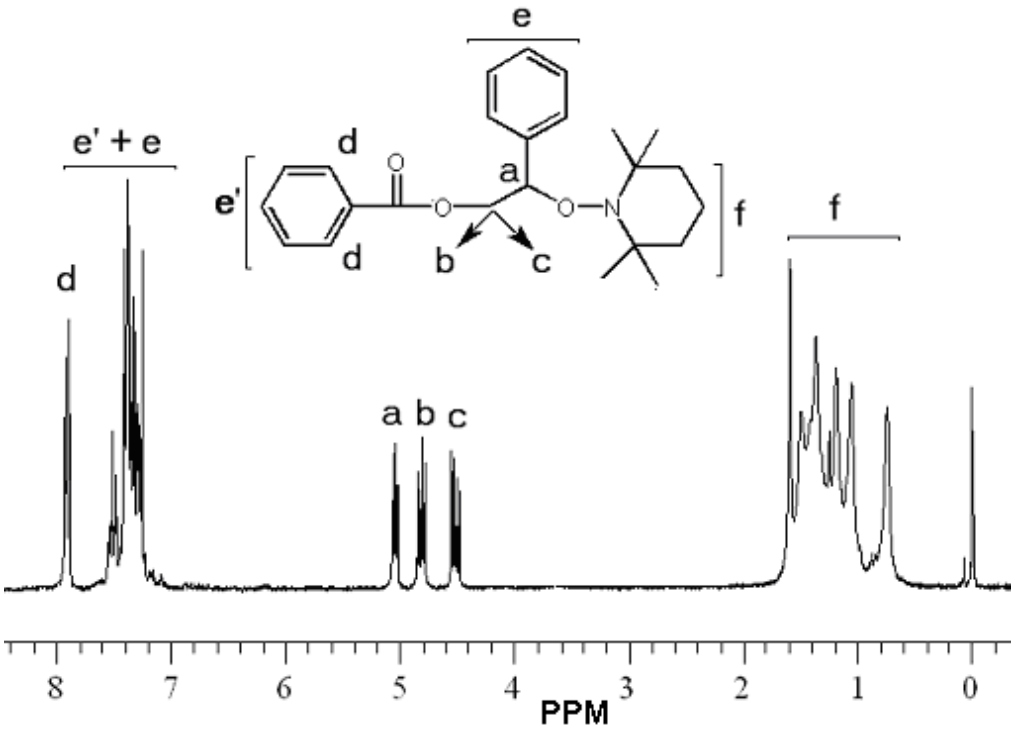


Figure 1. The ^{1}H NMR spectrum of benzoic acid 2-phenyl-2-(2, 2, 6, 6-tetramethyl-piperin-1-yloxy)-ethyl in $CDCl_3$.

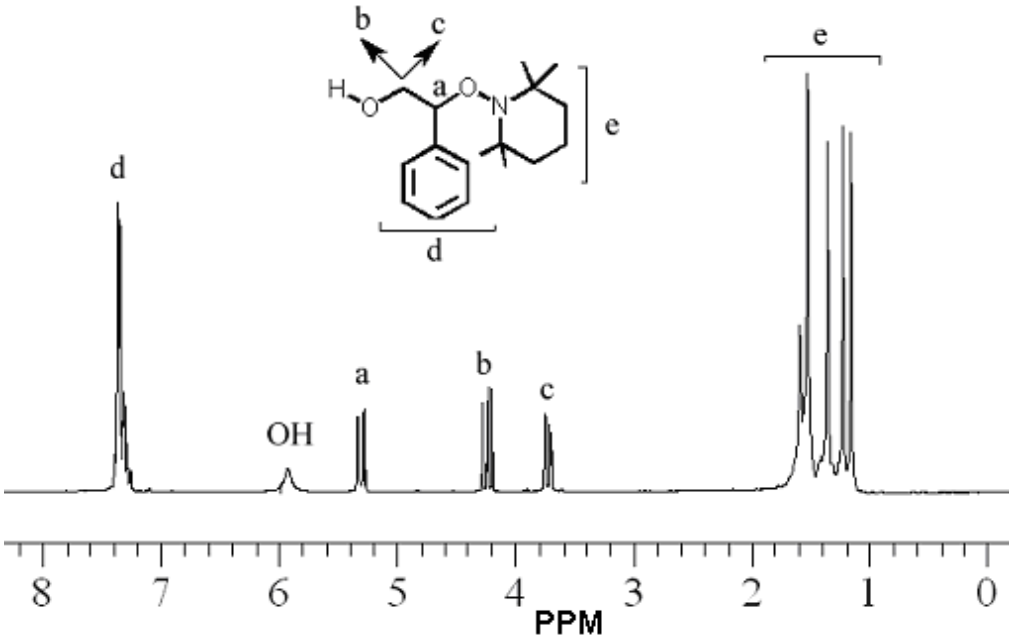
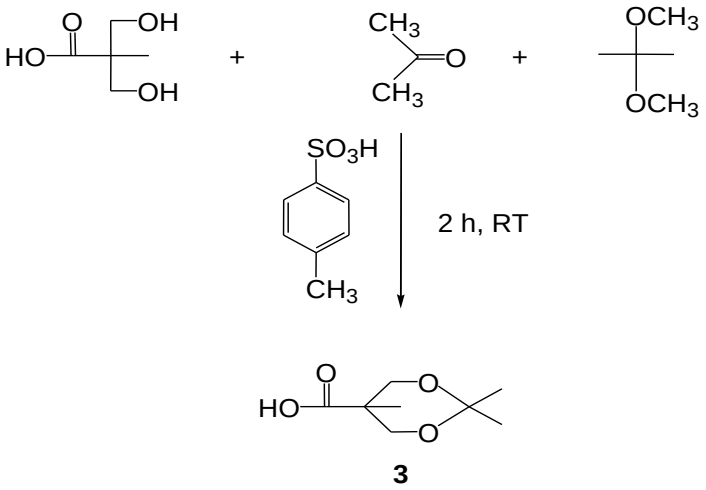


Figure 2. The ^{1}H NMR spectrum of 2-phenyl-2-(2, 2, 6, 6-tetramethyl-piperin-1-yloxy)-ethanol in $CDCl_3$.

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 3.



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3

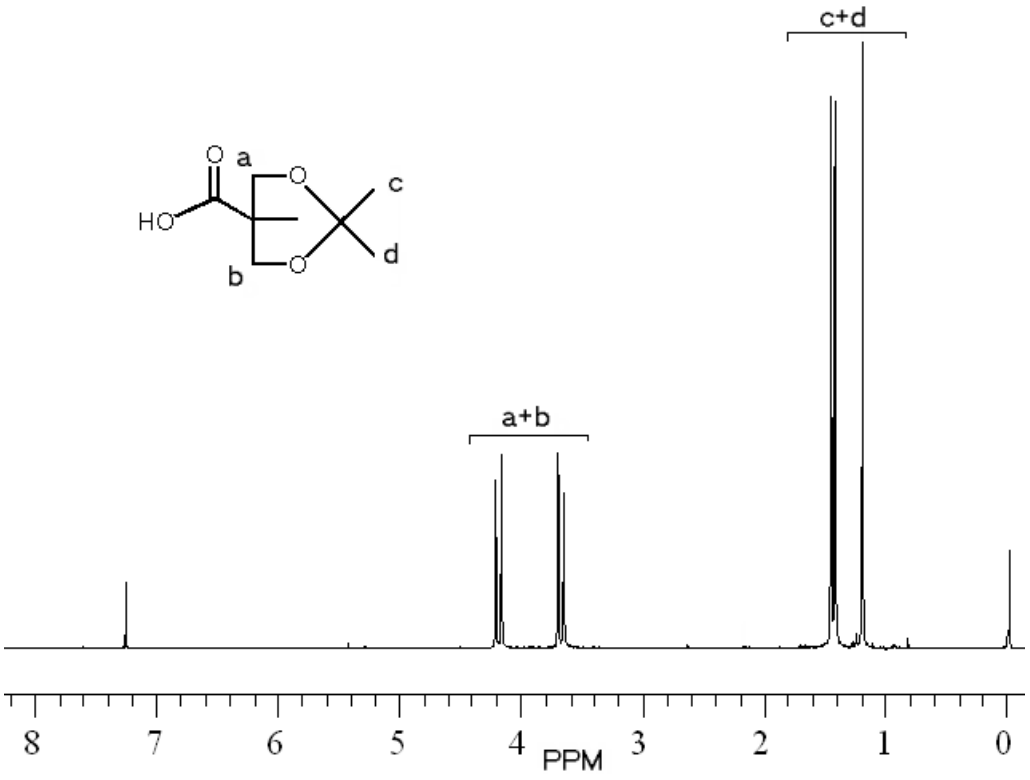


Figure 3. The ^{1}H NMR spectrum of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid in $CDCl_3$.

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.

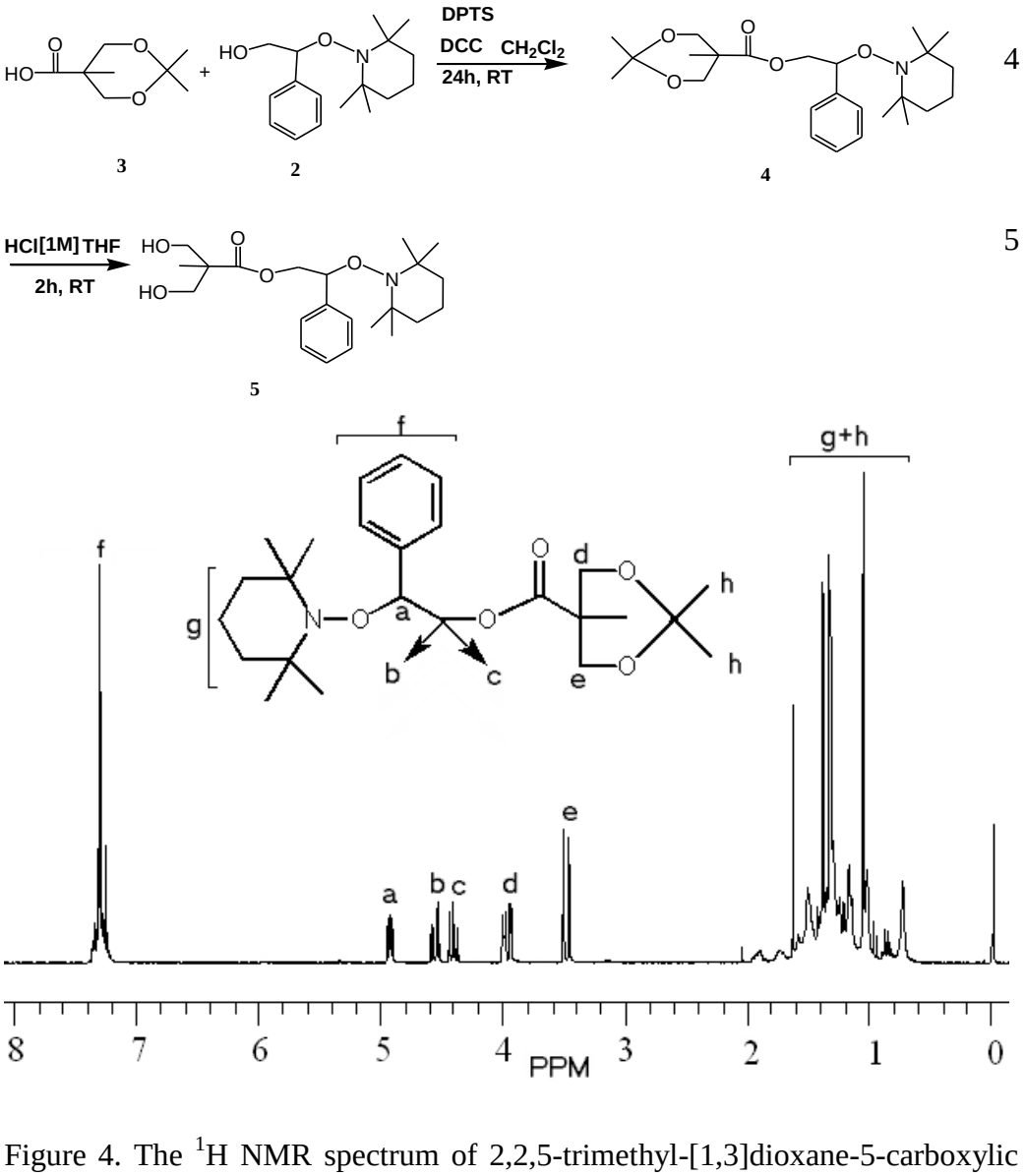


Figure 4. The ^{1}H NMR spectrum of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid 2-phenyl-2-(2,2,6-trimethyl-piperidin-1-yloxy)-ethyl ester in $CDCl_3$.

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 5. From the NMR spectrum -OH protons (e-e') at δ 2.7 ppm suggests that deprotection step was carried out successfully.

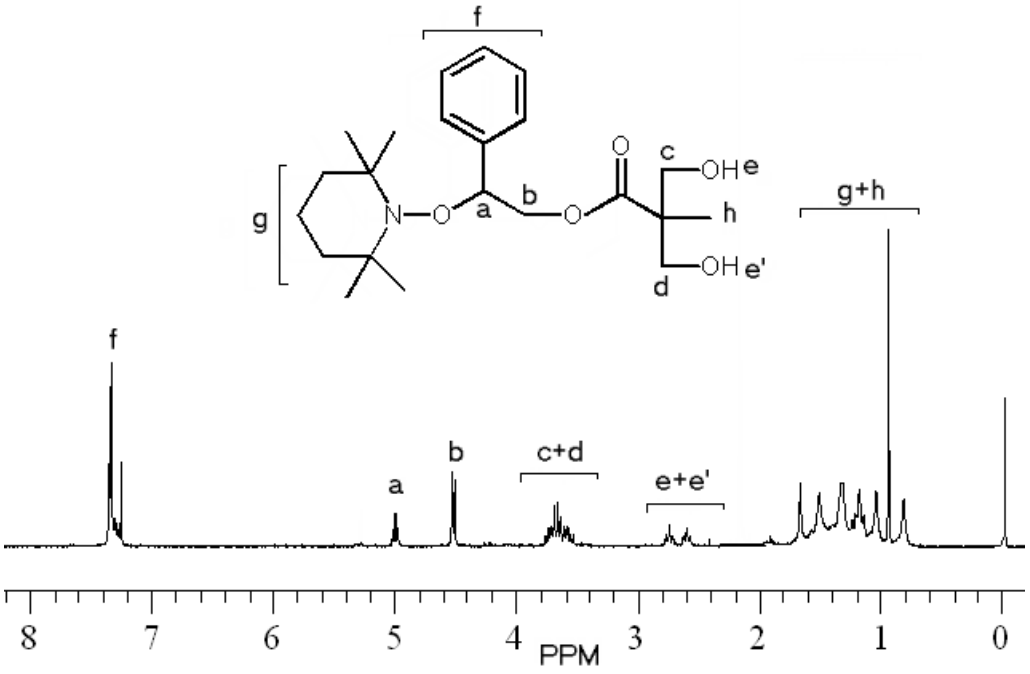
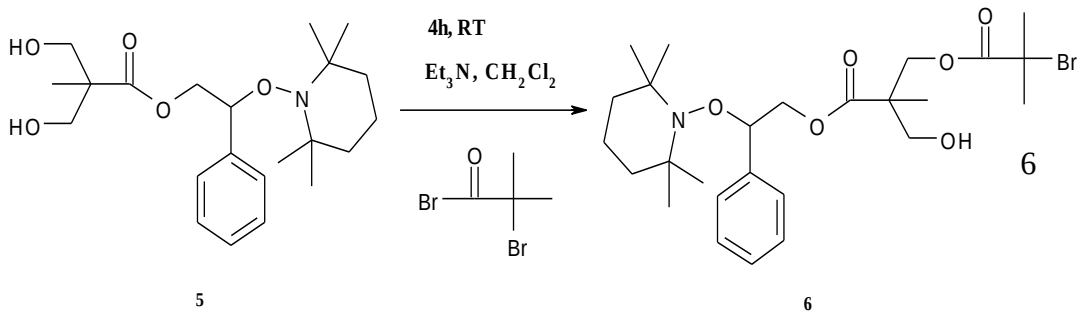


Figure 5. The ^{1}H NMR spectrum of 3-hydroxy-2-hydroxymethyl-2-methyl-propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester in $CDCl_3$.

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 ^{0}C and 2-bromoisobutryl bromide was added in a dropwise manner. The ^{1}H NMR spectrum of the compound 6 showed that the –OH protons of compound 5 at δ 2.7 ppm completely removed. Moreover, the new –OH 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 6.



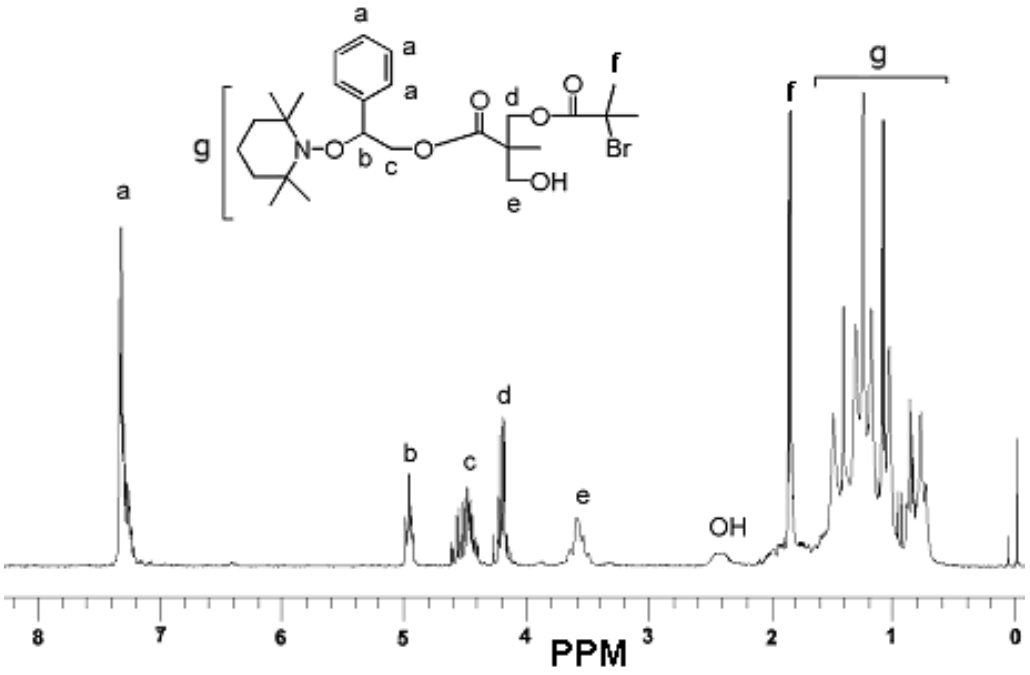
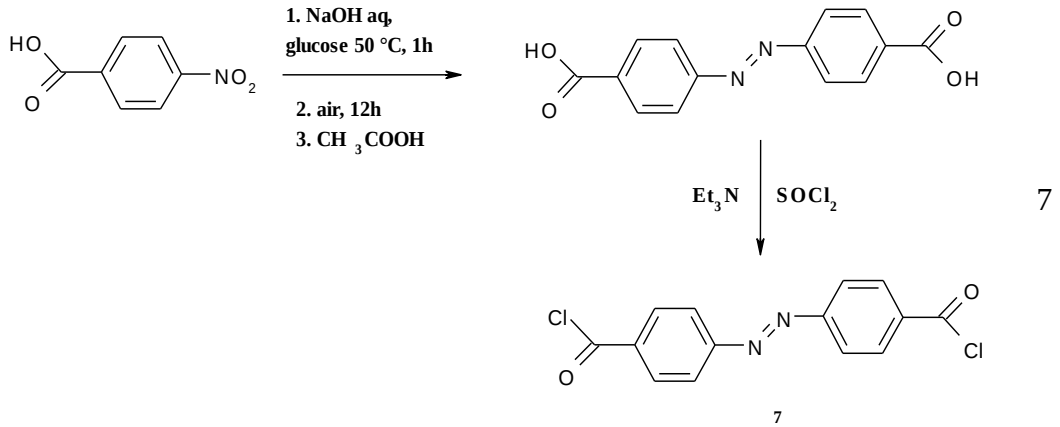


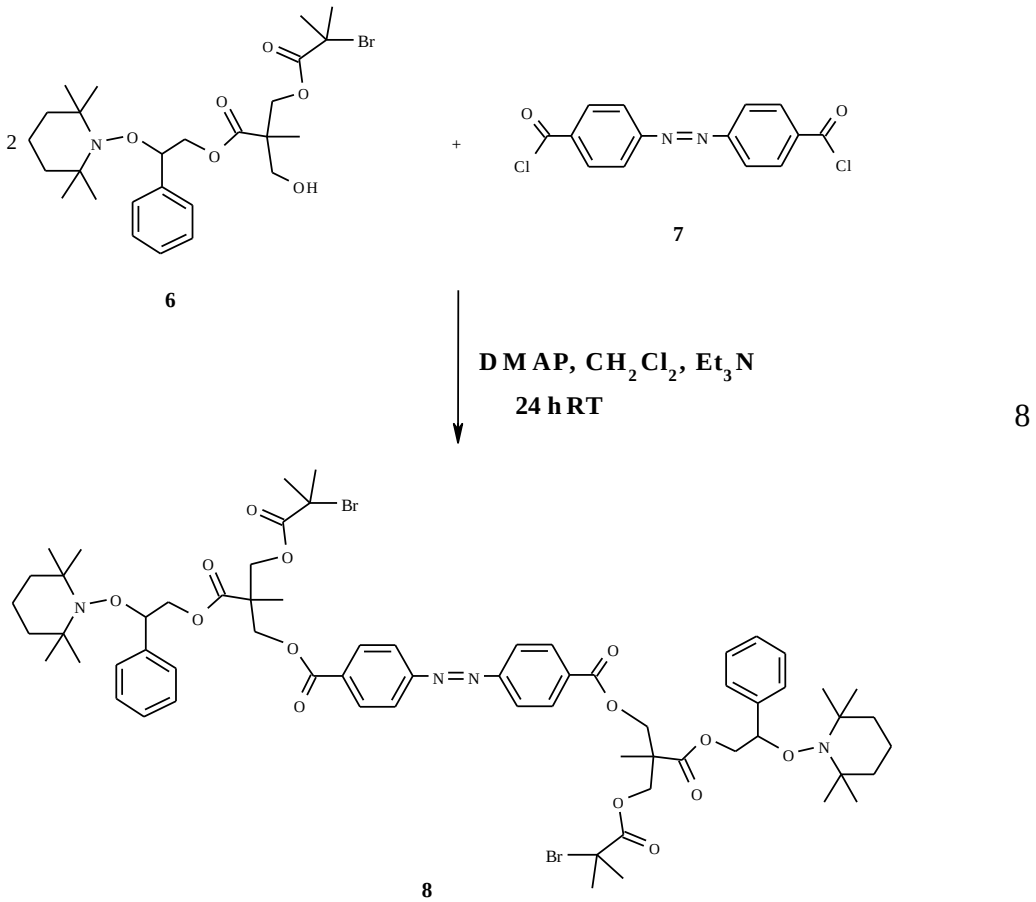
Figure 6. The ^{1}H NMR spectrum of 2-(2-bromo-2-methyl-propionyloxymethyl)-3-hydroxy-2-methyl propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester in $CDCl_3$.

4,4'-bis(chlorocarbonyl)azobenzene was used to carry out azobenzene functionality for initiator. To obtain 4,4'-bis(chlorocarbonyl)azobenzene first, trans-4,4'-dicarboxyazobenzene was prepared in 99.5% yield by glucose reduction of 4-nitrobenzoic acid followed by air oxidation [94,95]. Then, trans-4,4'-dicarboxyazobenzene reacted with thionyl chloride to obtain 4,4'-bis(chlorocarbonyl)azobenzene (**7**).



Finally, the miktofunctional initiator (Azobenzene-4,4'-dicarboxylic acid bis-{3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethoxycarbonyl]-propyl} ester) **8** containing azobenzene at core and both two tertiary bromide and TEMPO end functional groups was successfully

synthesized by reacting **6** with 4,4'-bis(chlorocarbonyl)azobenzene (**8**). Esterification reaction was monitored by ^{1}H NMR. The ^{1}H NMR spectrum of the compound **8** showed that a broad peak of -C*H*$_2$OH at 3.55 ppm is disappeared and a corresponding ester (C*H*$_2$OC=O) signal is detected at 4.09 ppm. Moreover, aromatic protons of azobenzene, C*H*$_2$C*H*- protons adjacent to TEMPO, and CH_3 protons of *tert*–bromide groups can be determined at 8.08-7.94, 4.93-4.36, and 1.81 ppm, respectively. The ^{1}H NMR spectrum of the compound, (**8),** is shown in Figure 7.



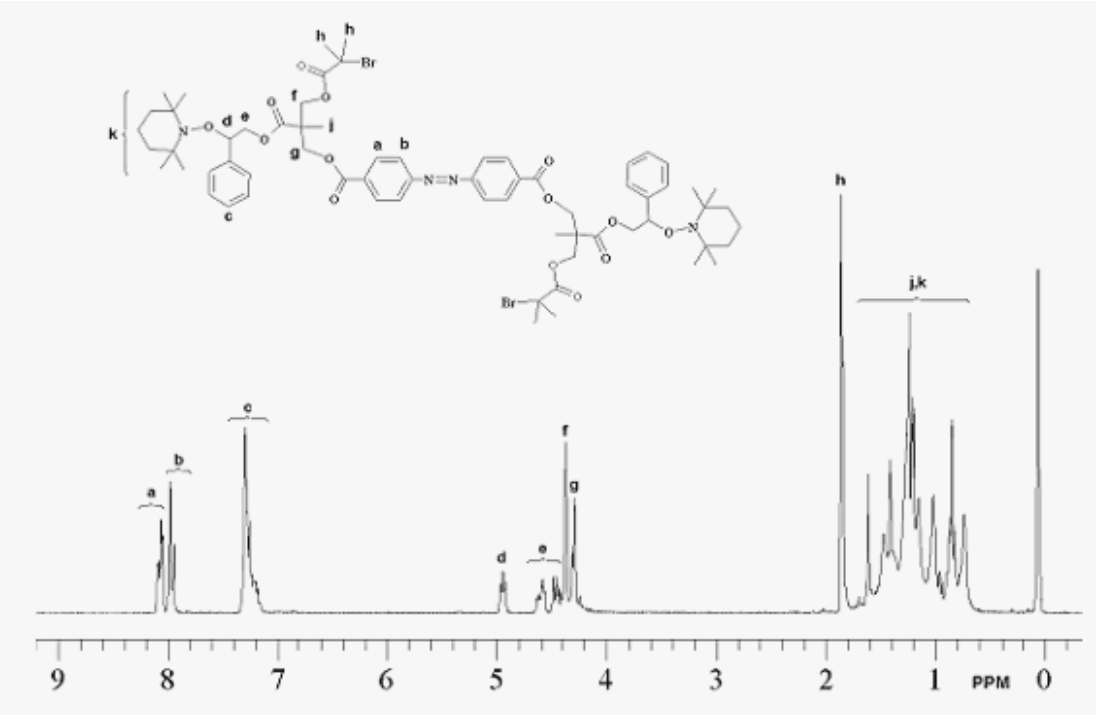


Figure 7. The ^{1}H NMR spectrum of (Azobenzene-4,4'-dicarboxylic acid bis-{3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethoxycarbonyl]-propyl} ester) in $CDCl_3$.

The obtained miktofunctional core including NMP and ATRP functionalities was then used for the synthesis of A_2B_2 type miktoarm star copolymers. First of all, PMMA macroinitiator was synthesized via ATRP method, and then NMP of St was carried out successively. The details for experimental conditions of polymerization are given in Table 1.

4.2. Synthesis of $(PMMA)_2$ Macroinitiator

For this purpose, first ATRP of MMA was accomplished using **8** as an initiator in the presence of CuCl/PMDETA complex system as a catalyst in anisole at 60 ^{o}C (Table 1). The characteristics of $(PMMA)_2$ macroinitiators (P Ia-c) were given in Table 1. The ^{1}H NMR spectrum of the $(PMMA)_2$ macroinitiator is shown in Figure 8.

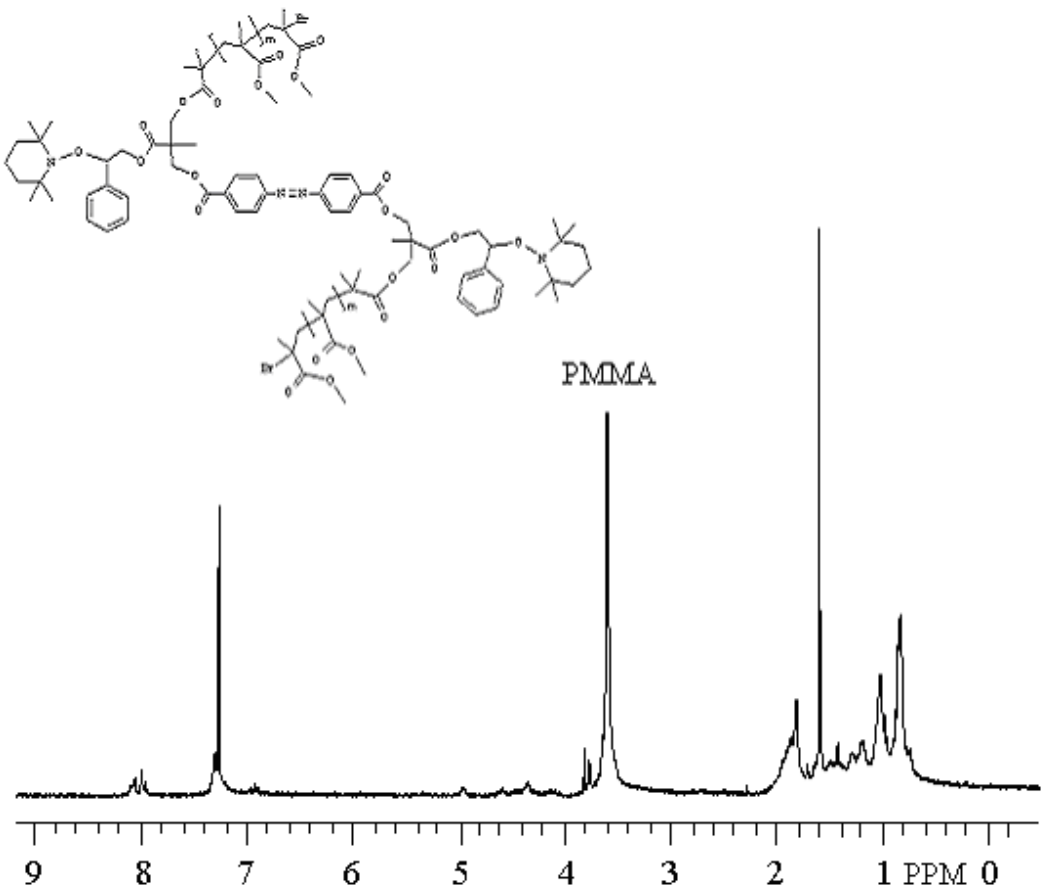


Figure 8. The ^{1}H NMR spectrum of $(PMMA)_2$ macroinitiator in $CDCl_3$.

4.3. Synthesis of $(PMMA)_2$-$(PSt)_2$ Miktoarm Star Copolymers

$(PMMA)_2$ macroinitiator containing two TEMPO moieties was then used for NMP of St at 125 ^{o}C in order to give $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer (P IIa and b) (Table 1). The signals of the aromatic group were assigned by means of ^{1}H NMR confirming the incorporation of the St block into the miktoarm star copolymer. The ^{1}H NMR spectra of the miktoarm star copolymer is shown in Figure 9.

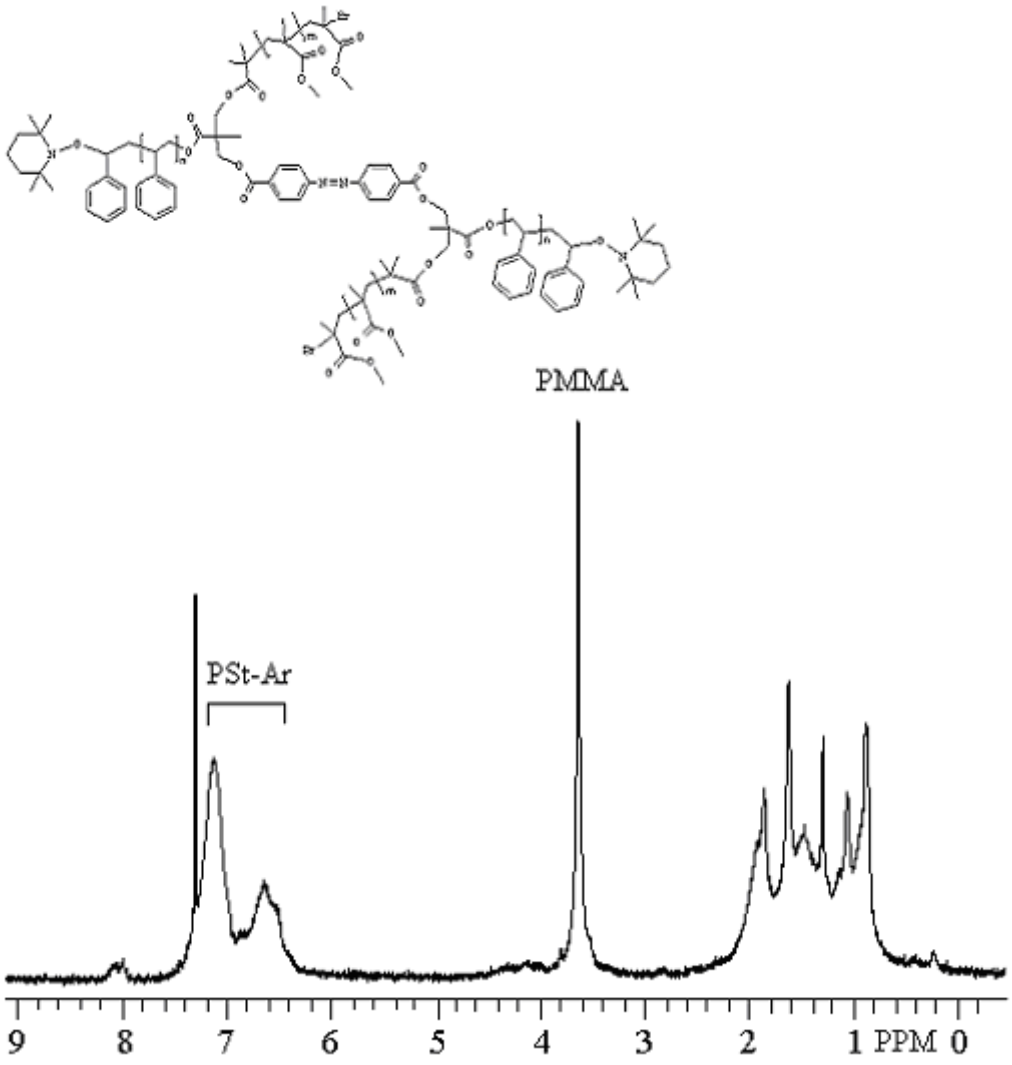
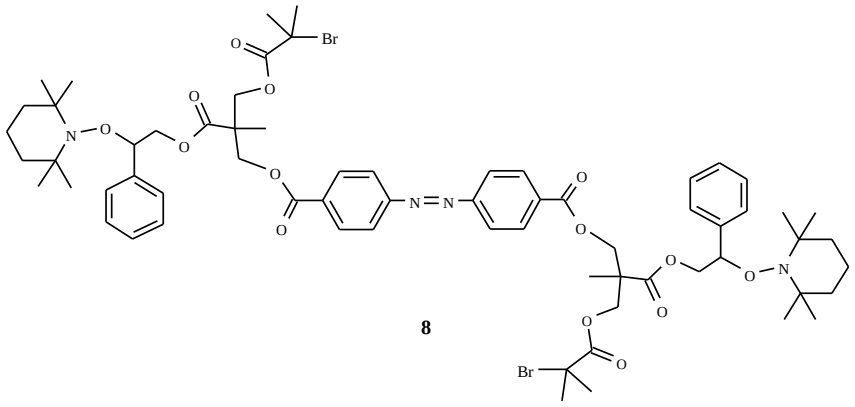


Figure 9. The ^{1}H NMR spectrum of $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer in $CDCl_3$.



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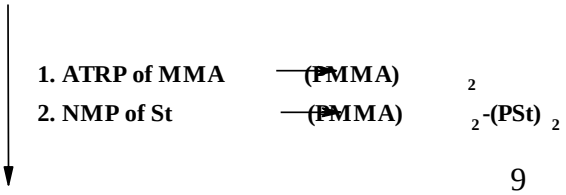

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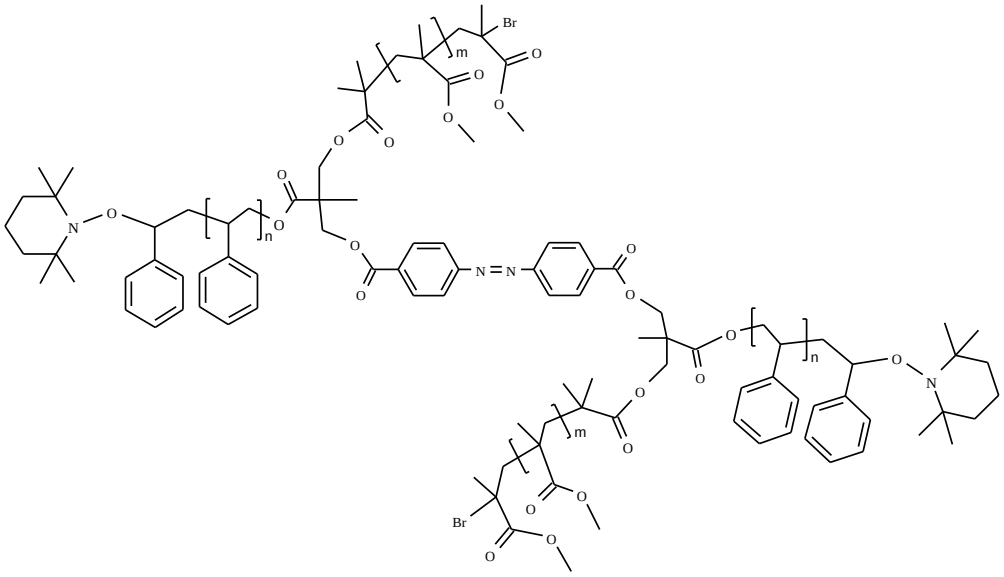


The average molecular weight increased with MMA conversion in ATRP, confirming the introduction of the PMMA blocks to the initiator **8** (Table 1, P Ia-c). In the case of miktoarm star copolymer, the disappearance of the PMMA precursor trace revealed that the all of the precursor chains having TEMPO moiety efficiently initiated the NMP of St (Fig. 10). Moreover, any peak in higher molecular weight region of the GPC traces was not observed indicating the absence of the star-star coupling reaction.

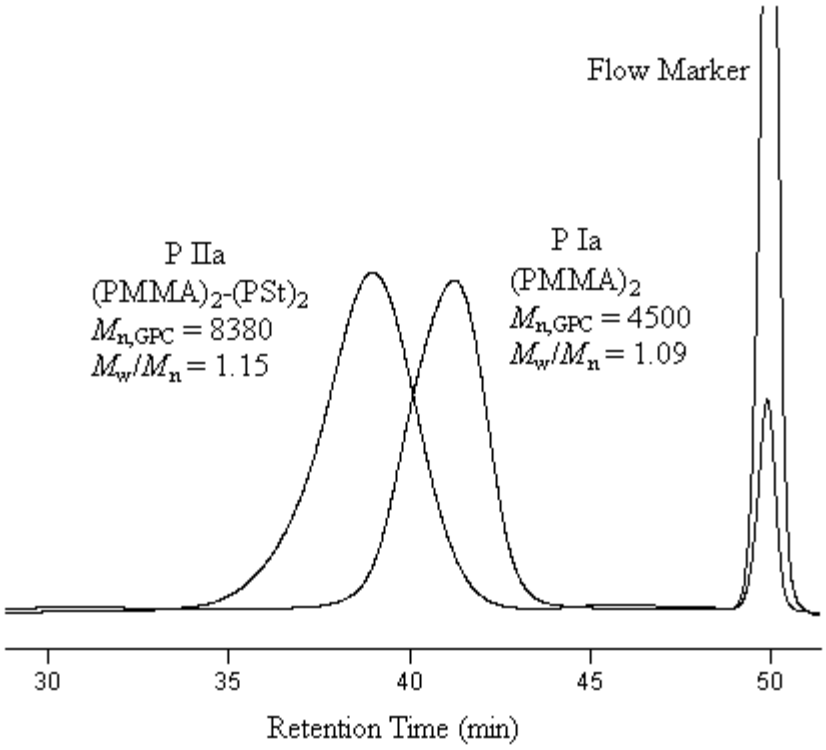


Figure 10. GPC traces of $(PMMA)_2$ precursor, P Ia and $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer, P IIa.

Table 1. The characteristics of photoresponsive $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer

Run	Monomer	Initiator	$[M]_o$ ($mol.L^{-1}$)	$[M]_o/[I]_o$	Time (h)	Conversion (%)	$M_{n,theo}$	$M_{n,GPC}$ [c]	M_w/M_n
P Ia[a]	MMA	8	4.68	200	0.25	13	3920	4500	1.09
P Ib[a]	MMA	8	4.68	200	0.5	30	7330	8230	1.13
P Ic[a]	MMA	8	4.68	200	1	38	8950	10700	1.12
P IIa[b]	St	P Ia	8.73	300	19.5	11	7950	8380	1.15
P IIb[b]	St	P Ic	8.73	300	16	8	13200	13900	1.14

8 = Miktofunctional initiator, P I = $(PMMA)_2$ macroinitiator, P II=$(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer respectively

[a] $[M]_o$: $[I]_o$ = 200 $[I]_o/[CuCl]_o/[PMDETA]_o$ = 1/ 2/ 2. The polymerization was carried out at 60 ^oC. MMA / Anisole = 1 (v/v)
$Mn_{,theo}$ = ($[M]_o/[I]_o$ x conversion % x (100.12) + 1319.25 ($MW_{initiator}$)

[b] $[M]_o$: $[I]_o$ =300 The polymerization was carried out at 125 ^oC in bulk.
$Mn_{,theo}$ = ($[M]_o/[I]_o$ x conversion % x (104.15) + $Mn_{,macroinitiator}$

[c] Calculated from GPC calibrated with linear polystyrene standards.

4.4. Photoresponsive Study:

The miktofunctional initiator **8** dissolved in $CHCl_3$ and was irradiated with UV light (λ < 350 nm) by 10 s intervals (0-120 s) (Fig. 11). During the irradiation, the absorption maximum at 330 nm corresponding to the π-π* transition of trans-azobenzene decreased and concurrently a weak band at 450 nm corresponding to n-π* transition of azobenzene moiety increased with time. Thus upon irradiation of these solutions with λ < 350 nm UV light, energetically preferred trans-form turned to the cis- (photochemical isomerization process).

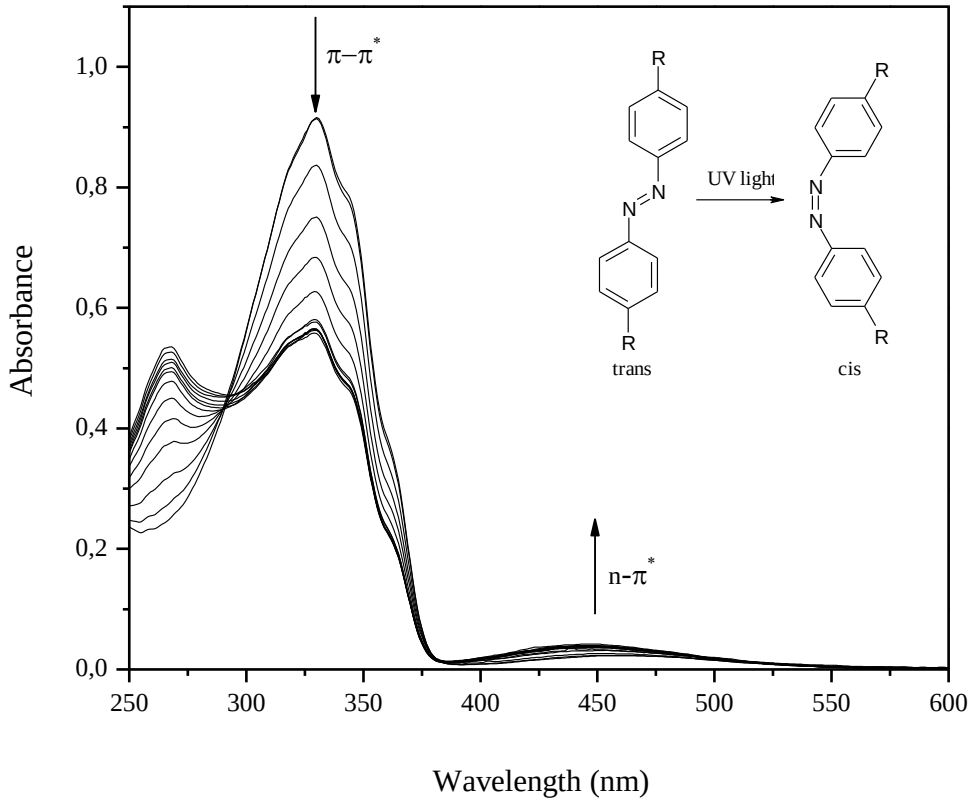


Figure 11. UV visible absorption changes of **8** in $CHCl_3$ (2.5 X 10^{-5} M) (trans-cis isomerization) under irradiation conditions (λ < 350 nm; 10 s interval; 0 to 120 s).

When this solution was kept in the dark, the back isomerization (cis-to-trans) occurred. This process was also monitored by UV spectrophotometer and evidenced by an increase in the absorbance at 330 nm and concurrently a decrease in absorbance at 450 nm with respect to time.

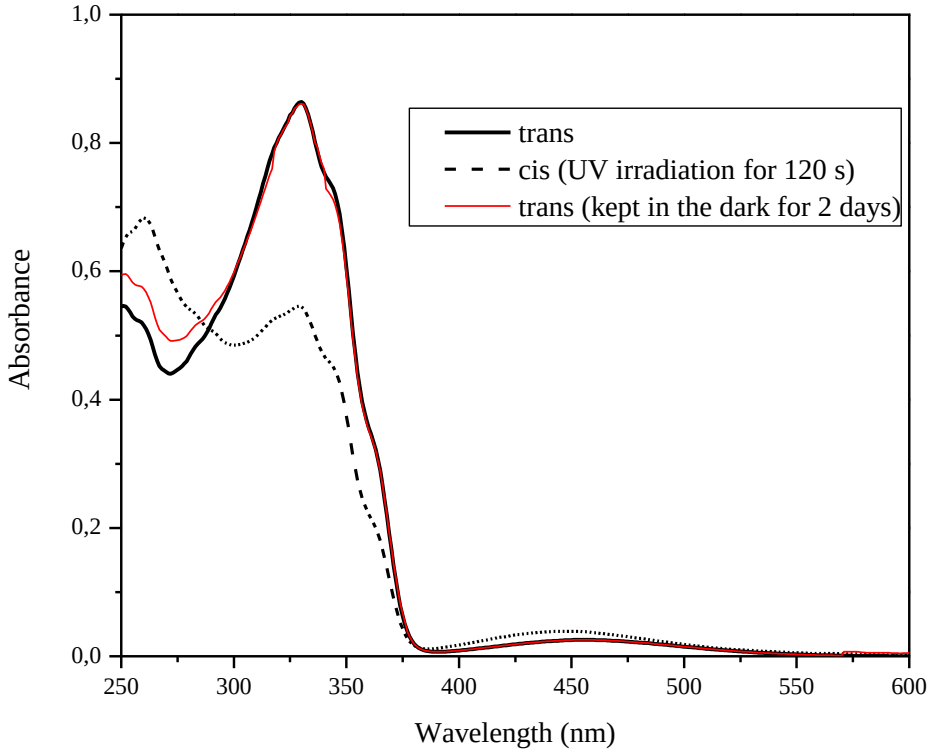


Figure 12. UV visible absorption changes of miktofunctional initiator, **8** in $CHCl_3$ (2.5 X 10^{-5} M); trans-cis isomerization occurred after 120 s irradiation at λ < 350 nm, followed by cis-trans back isomerization after 2 days in the dark**.**

A similar behavior was observed upon UV irradiation (λ < 350 nm) of $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer (**P IIa**) for 7h. (Fig.13).

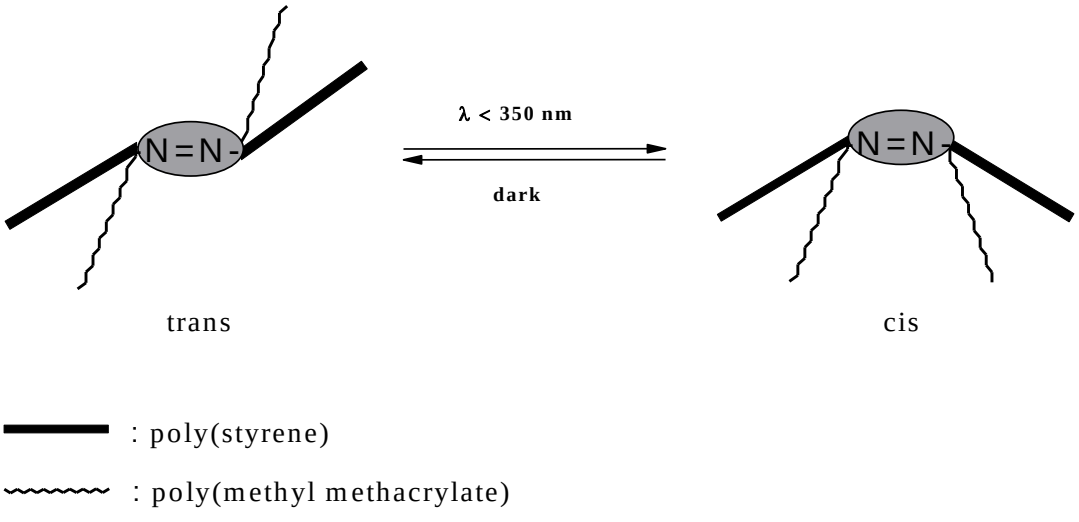


Figure 13. Trans to cis photoisomerization of $(PMMA)_2$-$(PSt)_2$ miktoarm star polymer

Trans to cis photoisomerization of $(PMMA)_2$-$(PSt)_2$ miktoarm star polymer (**P IIa)** was determined by using UV spectrophotometer (Fig. 14). However, it was obvious that trans-cis isomerization of **P IIa** was quite slow when compared with that of initiator **8**. The back

isomerization of **P IIa** (cis to trans) occurred when keeping it in the dark for 5 days (Fig. 14). Overall, these results were consistent with data obtained in the literature [12] and clearly demonstrated that $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer containing an azobenzene unit at the core displayed reversible isomerization by photochemical procedures.

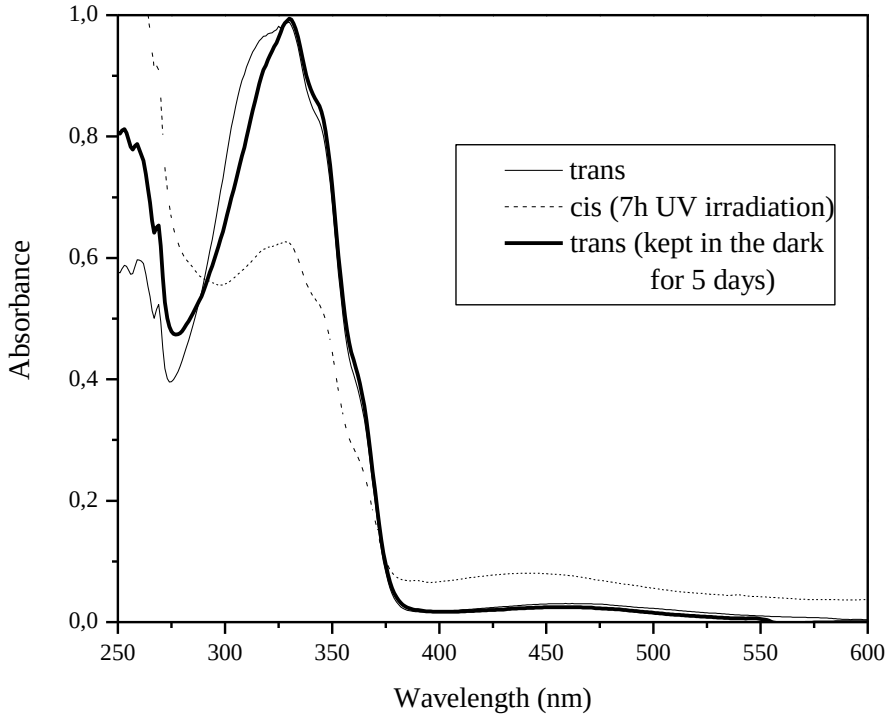


Figure 14**.** UV visible absorption changes of $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer, P IIa in $CHCl_3$ (2.5×10^{-5} M); trans-cis isomerization occurred after 7 h irradiation at $\lambda <$ 350 nm, followed by cis-trans back isomerization after 5 days in the dark.

Trans to cis isomerization of miktoarm star copolymer (**P IIa**) was also observed in GPC traces. As can be seen from Figure15, a peak of $(PMMA)_2$-$(PSt)_2$ miktoarm star (**P IIa**) in trans-form shifted slightly to lower molecular weight region (cis-form) when exposed to UV light ($\lambda < 350$ nm) for 7 h.

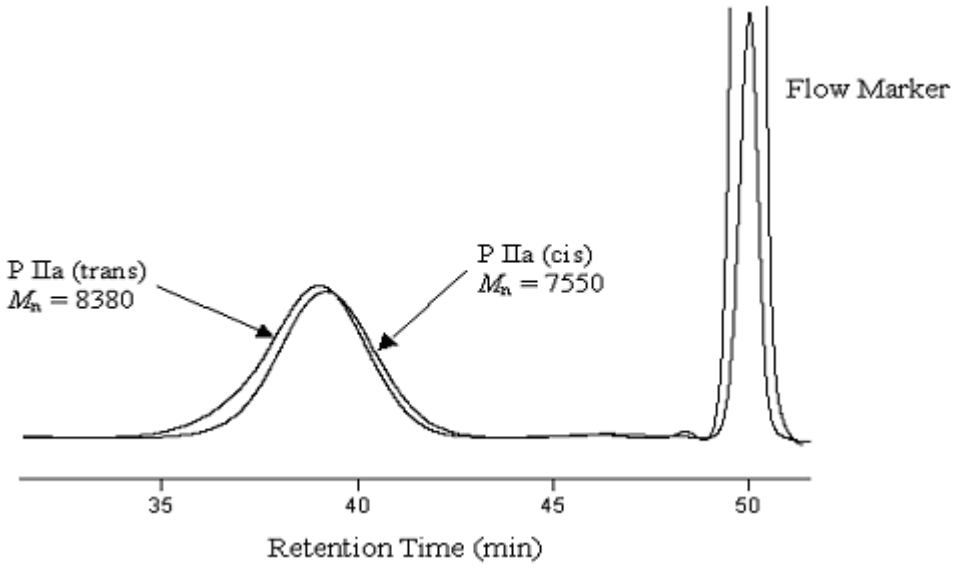


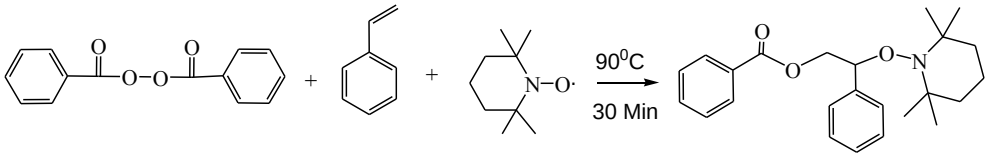
Figure 15. GPC traces of P IIa (trans) and P IIa (cis) after 7 h irradiation at λ < 350 nm.

This is for the reason that photoinduced trans to cis isomerization leads to a small change (contraction) in hydrodynamic volume of the miktoarm star polymer. A similar behavior was encountered remarkably for the aromatic polymers with azobenzene units in the main chain [10]. In this respect, the viscosity of the polymer solutions decreased on UV irradiation and returned slowly to the initial value in the dark indicating that the contraction of the hydrodynamic volume was certainly induced by the isomerization of the azobenzene units and that back isomerization expanded the chain conformation [10].

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 –OH and the shifts of the $–CH_2$ and –CH protons adjacent to hydroxyl and aromatic group, respectively, clearly confirm the successful hydrolysis. The ^1H NMR spectra of the corresponding ester and alcohol precursors are presented in Figures 1 and 2, respectively.



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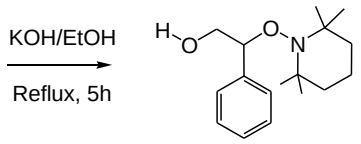

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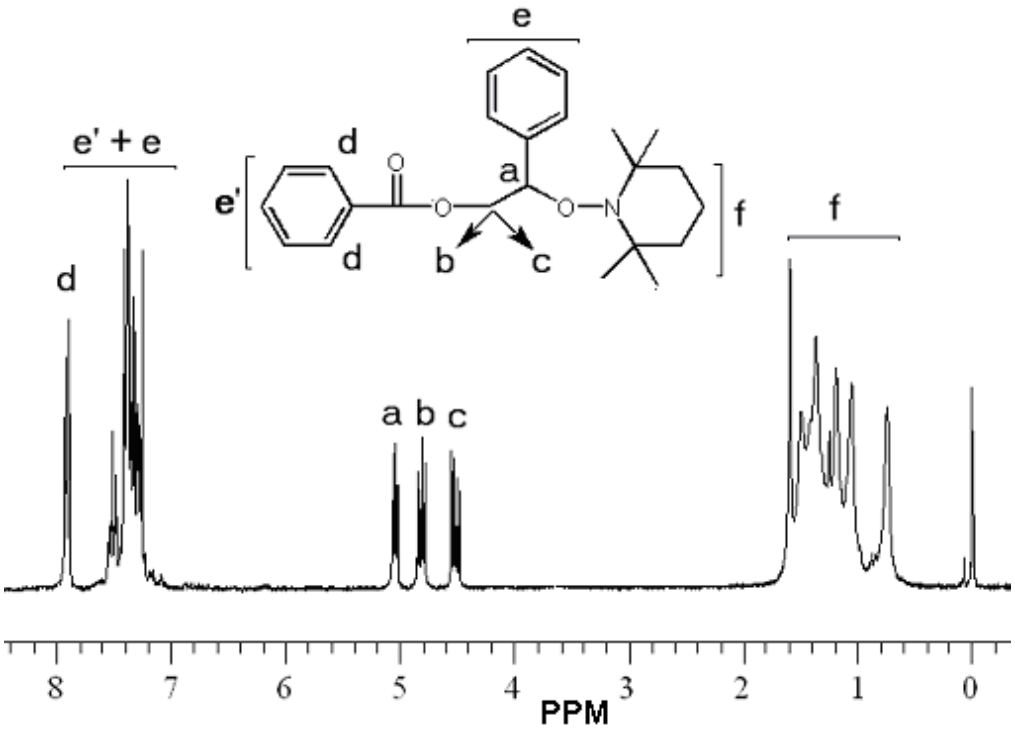


Figure 1. The ^{1}H NMR spectrum of benzoic acid 2-phenyl-2-(2, 2, 6, 6-tetramethyl-piperin-1-yloxy)-ethyl in $CDCl_3$.

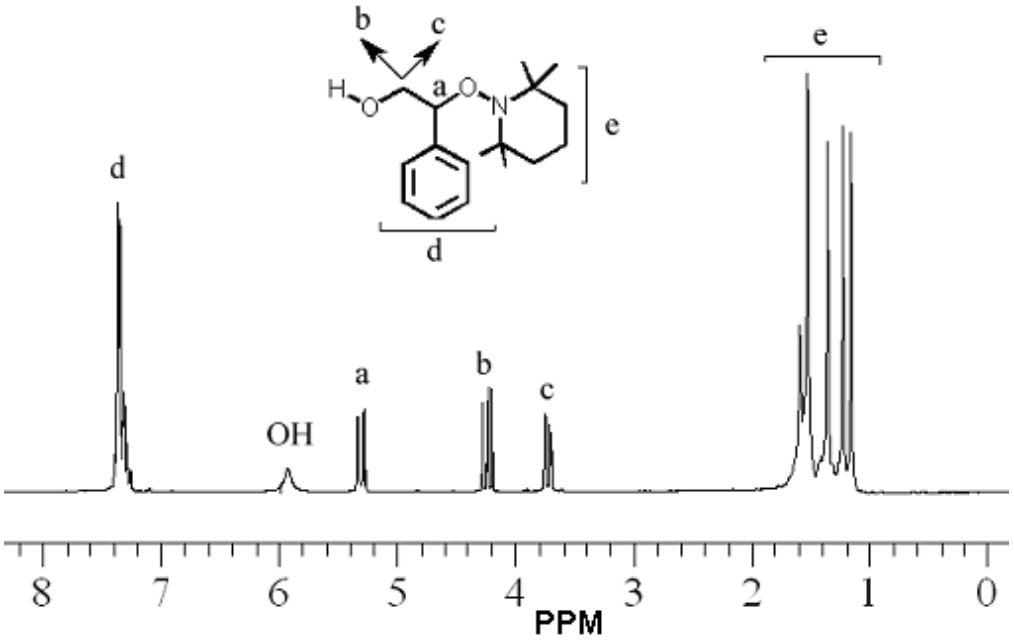
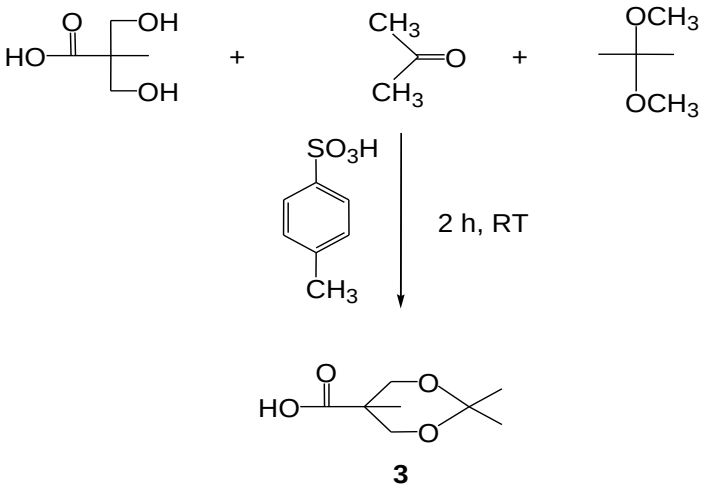


Figure 2. The ^{1}H NMR spectrum of 2-phenyl-2-(2, 2, 6, 6-tetramethyl-piperin-1-yloxy)-ethanol in $CDCl_3$.

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 3.



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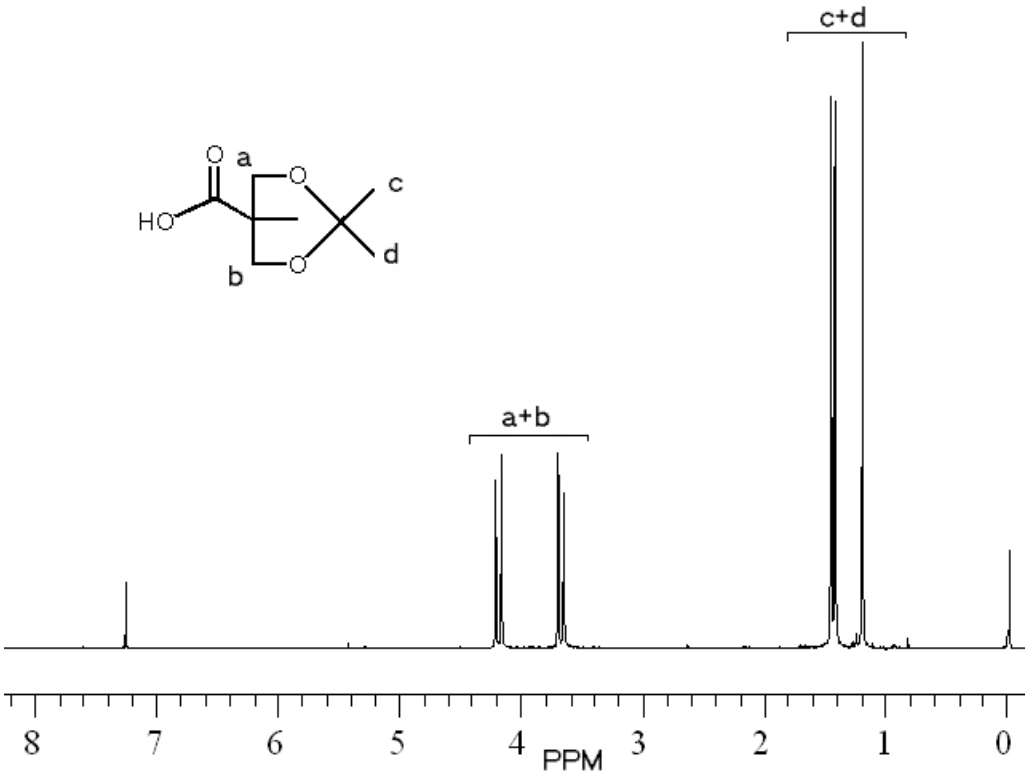


Figure 3. The ^{1}H NMR spectrum of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid in $CDCl_3$.

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.

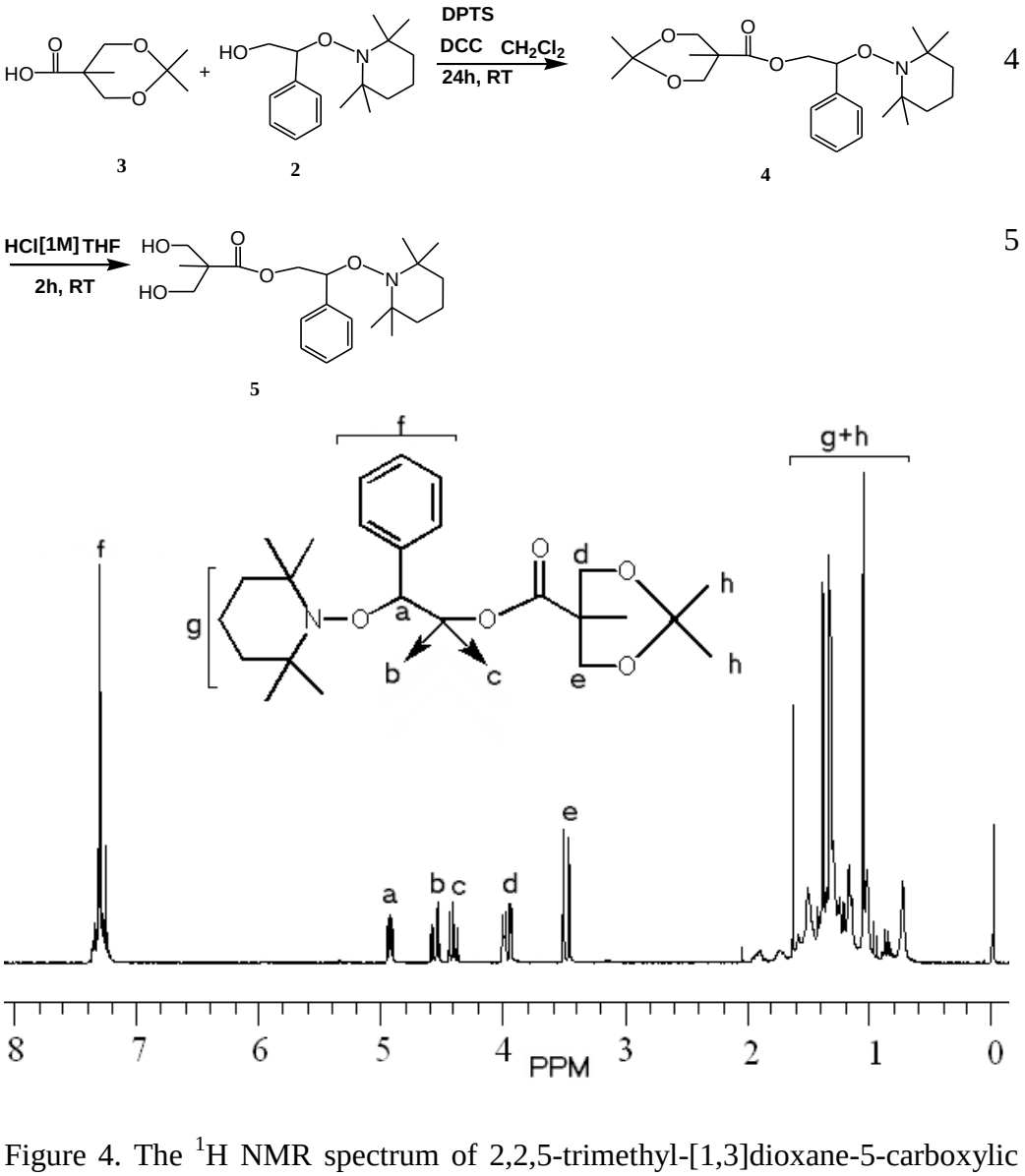


Figure 4. The ^{1}H NMR spectrum of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid 2-phenyl-2-(2,2,6-trimethyl-piperidin-1-yloxy)-ethyl ester in $CDCl_3$.

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 5. From the NMR spectrum -OH protons (e-e') at δ 2.7 ppm suggests that deprotection step was carried out successfully.

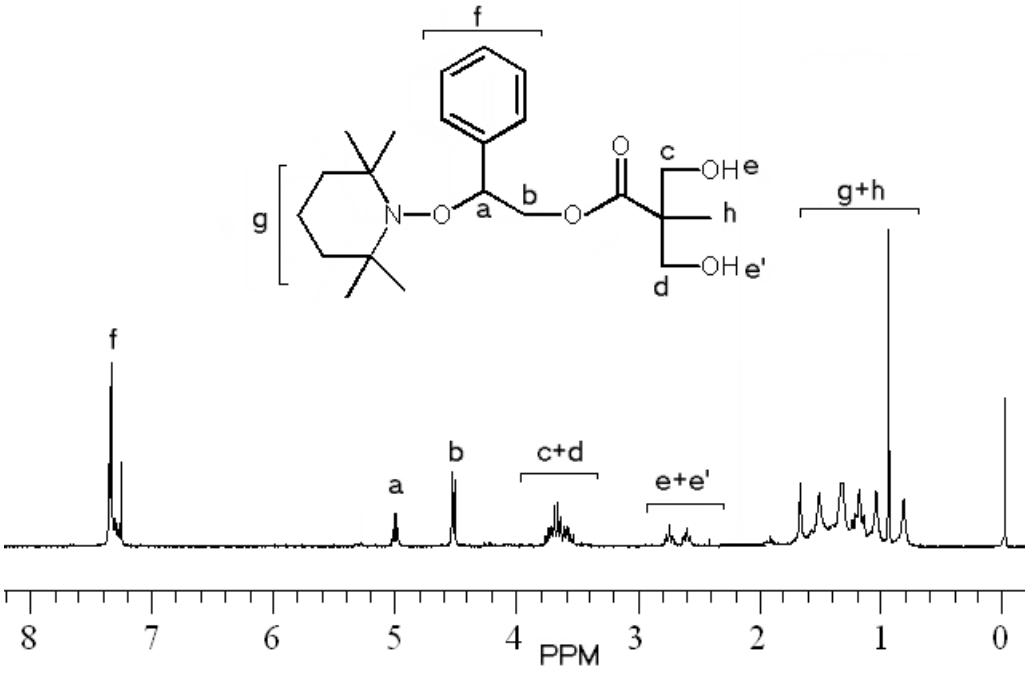
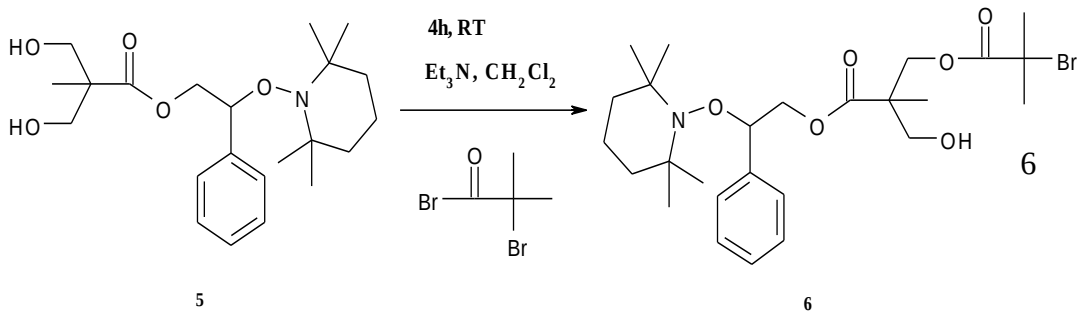


Figure 5. The ^{1}H NMR spectrum of 3-hydroxy-2-hydroxymethyl-2-methyl-propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester in $CDCl_3$.

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 ^{0}C and 2-bromoisobutryl bromide was added in a dropwise manner. The ^{1}H NMR spectrum of the compound 6 showed that the –OH protons of compound 5 at δ 2.7 ppm completely removed. Moreover, the new –OH 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 6.



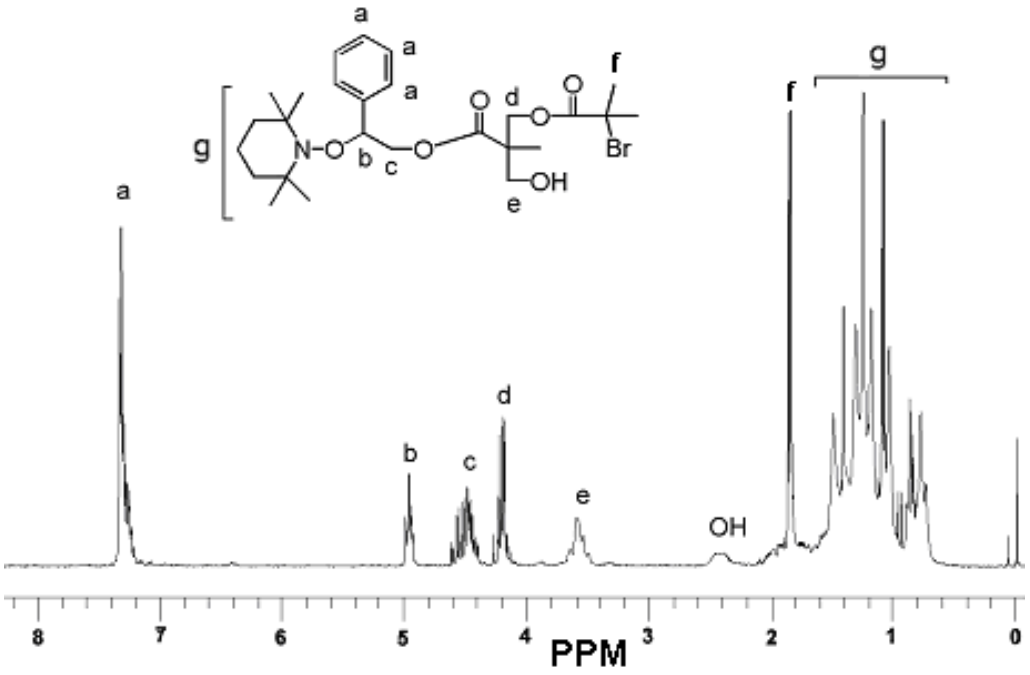
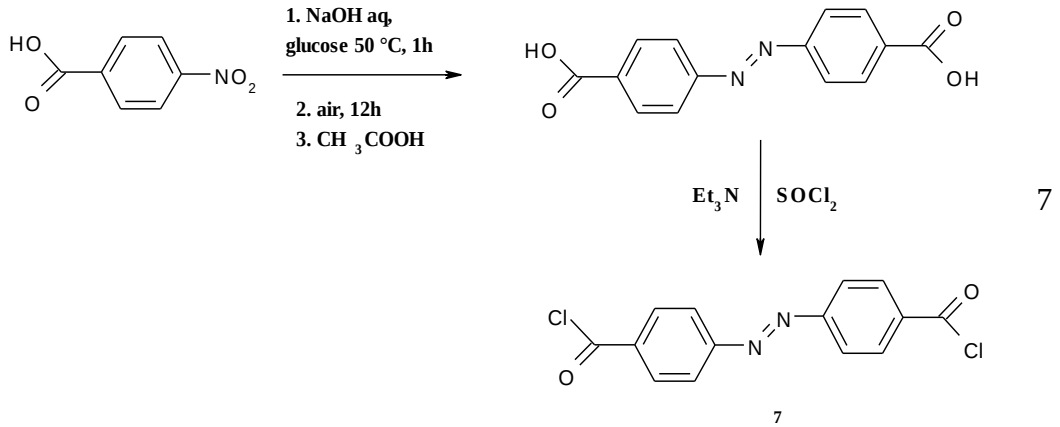


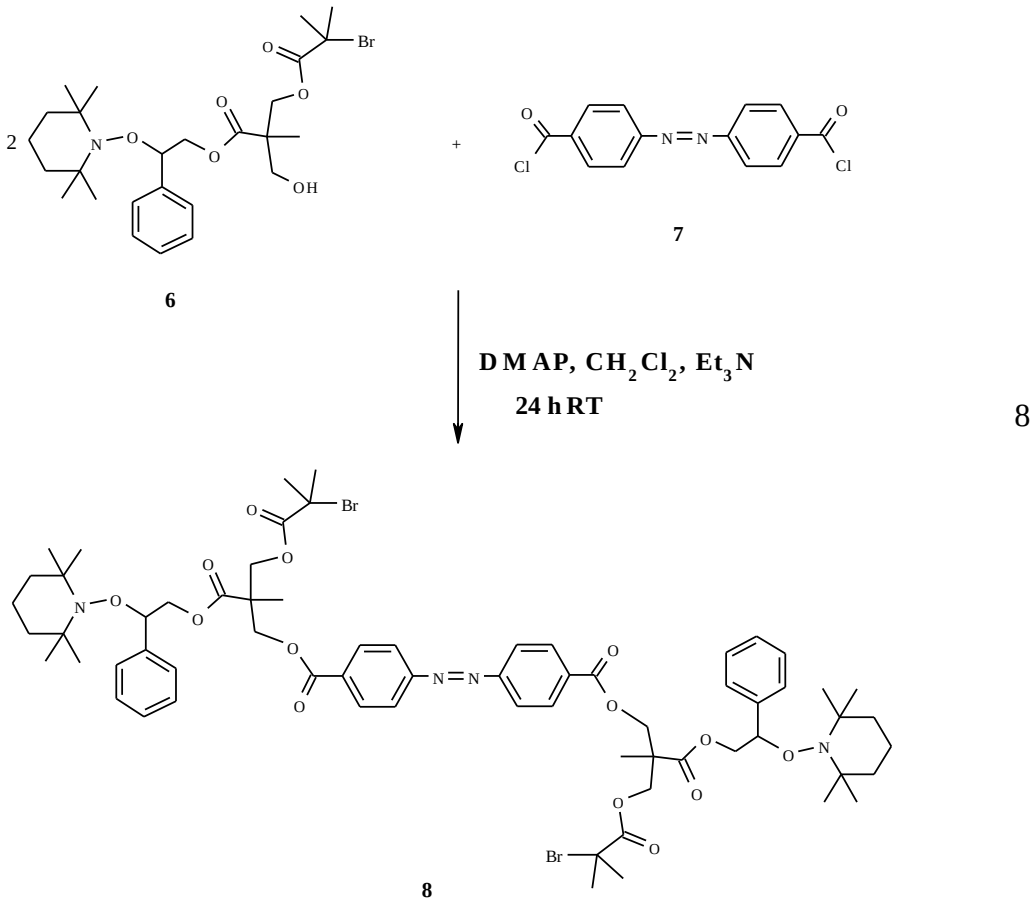
Figure 6. The ^{1}H NMR spectrum of 2-(2-bromo-2-methyl-propionyloxymethyl)-3-hydroxy-2-methyl propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester in $CDCl_3$.

4,4'-bis(chlorocarbonyl)azobenzene was used to carry out azobenzene functionality for initiator. To obtain 4,4'-bis(chlorocarbonyl)azobenzene first, trans-4,4'-dicarboxyazobenzene was prepared in 99.5% yield by glucose reduction of 4-nitrobenzoic acid followed by air oxidation [94,95]. Then, trans-4,4'-dicarboxyazobenzene reacted with thionyl chloride to obtain 4,4'-bis(chlorocarbonyl)azobenzene (**7**).



Finally, the miktofunctional initiator (Azobenzene-4,4'-dicarboxylic acid bis-{3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethoxycarbonyl]-propyl} ester) **8** containing azobenzene at core and both two tertiary bromide and TEMPO end functional groups was successfully

synthesized by reacting **6** with 4,4'-bis(chlorocarbonyl)azobenzene (**8**). Esterification reaction was monitored by ^{1}H NMR. The ^{1}H NMR spectrum of the compound **8** showed that a broad peak of -C*H*$_2$OH at 3.55 ppm is disappeared and a corresponding ester (C*H*$_2$OC=O) signal is detected at 4.09 ppm. Moreover, aromatic protons of azobenzene, C*H*$_2$C*H*- protons adjacent to TEMPO, and CH_3 protons of *tert*–bromide groups can be determined at 8.08-7.94, 4.93-4.36, and 1.81 ppm, respectively. The ^{1}H NMR spectrum of the compound, (**8),** is shown in Figure 7.



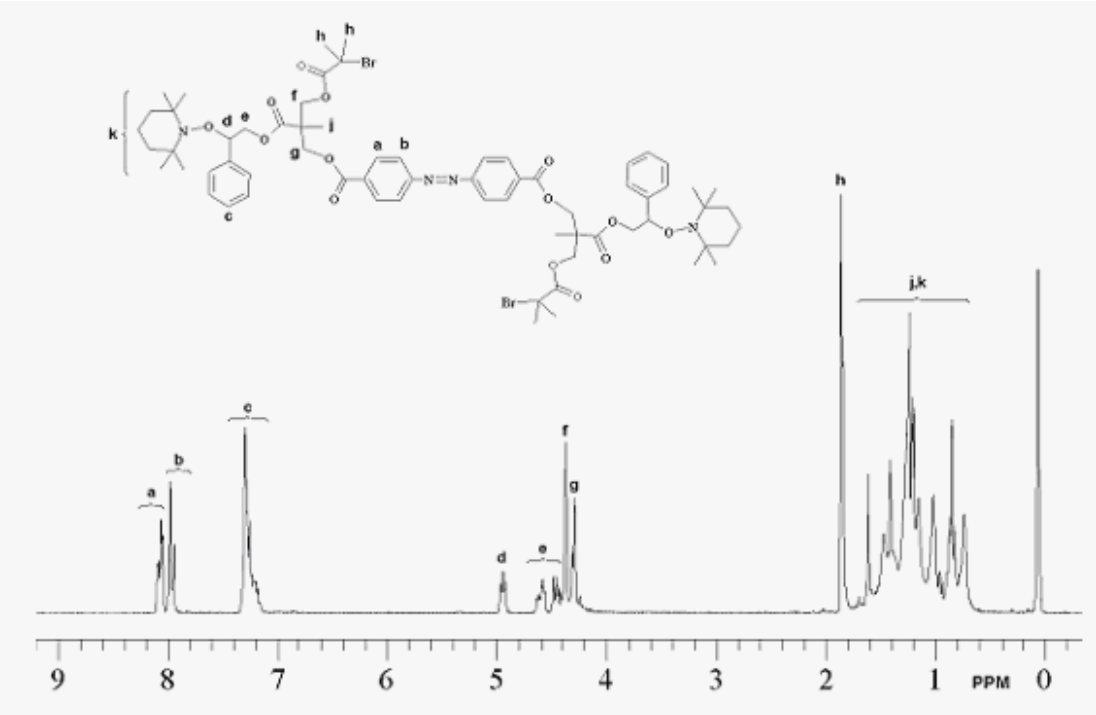


Figure 7. The ^{1}H NMR spectrum of (Azobenzene-4,4'-dicarboxylic acid bis-{3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethoxycarbonyl]-propyl} ester) in $CDCl_3$.

The obtained miktofunctional core including NMP and ATRP functionalities was then used for the synthesis of A_2B_2 type miktoarm star copolymers. First of all, PMMA macroinitiator was synthesized via ATRP method, and then NMP of St was carried out successively. The details for experimental conditions of polymerization are given in Table 1.

4.2. Synthesis of $(PMMA)_2$ Macroinitiator

For this purpose, first ATRP of MMA was accomplished using **8** as an initiator in the presence of CuCl/PMDETA complex system as a catalyst in anisole at 60 ^{o}C (Table 1). The characteristics of $(PMMA)_2$ macroinitiators (P Ia-c) were given in Table 1. The ^{1}H NMR spectrum of the $(PMMA)_2$ macroinitiator is shown in Figure 8.

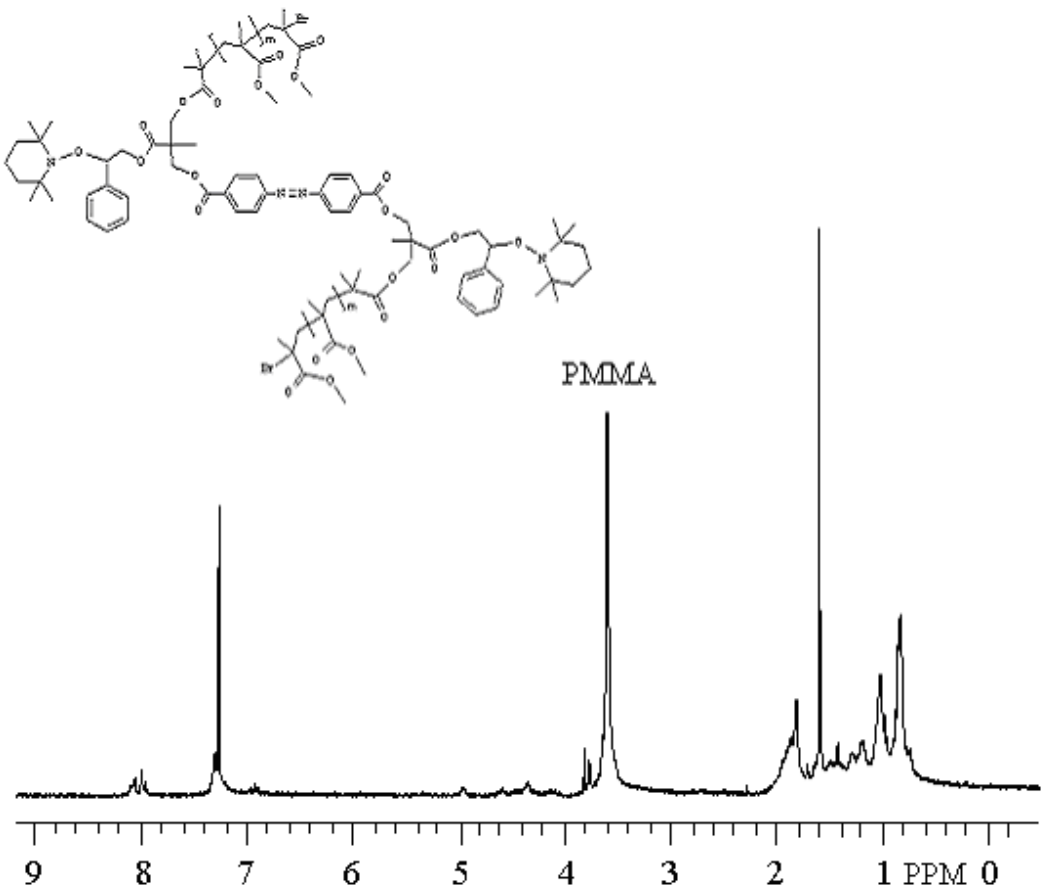


Figure 8. The ^{1}H NMR spectrum of $(PMMA)_2$ macroinitiator in $CDCl_3$.

4.3. Synthesis of $(PMMA)_2$-$(PSt)_2$ Miktoarm Star Copolymers

$(PMMA)_2$ macroinitiator containing two TEMPO moieties was then used for NMP of St at 125 ^{o}C in order to give $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer (P IIa and b) (Table 1). The signals of the aromatic group were assigned by means of ^{1}H NMR confirming the incorporation of the St block into the miktoarm star copolymer. The ^{1}H NMR spectra of the miktoarm star copolymer is shown in Figure 9.

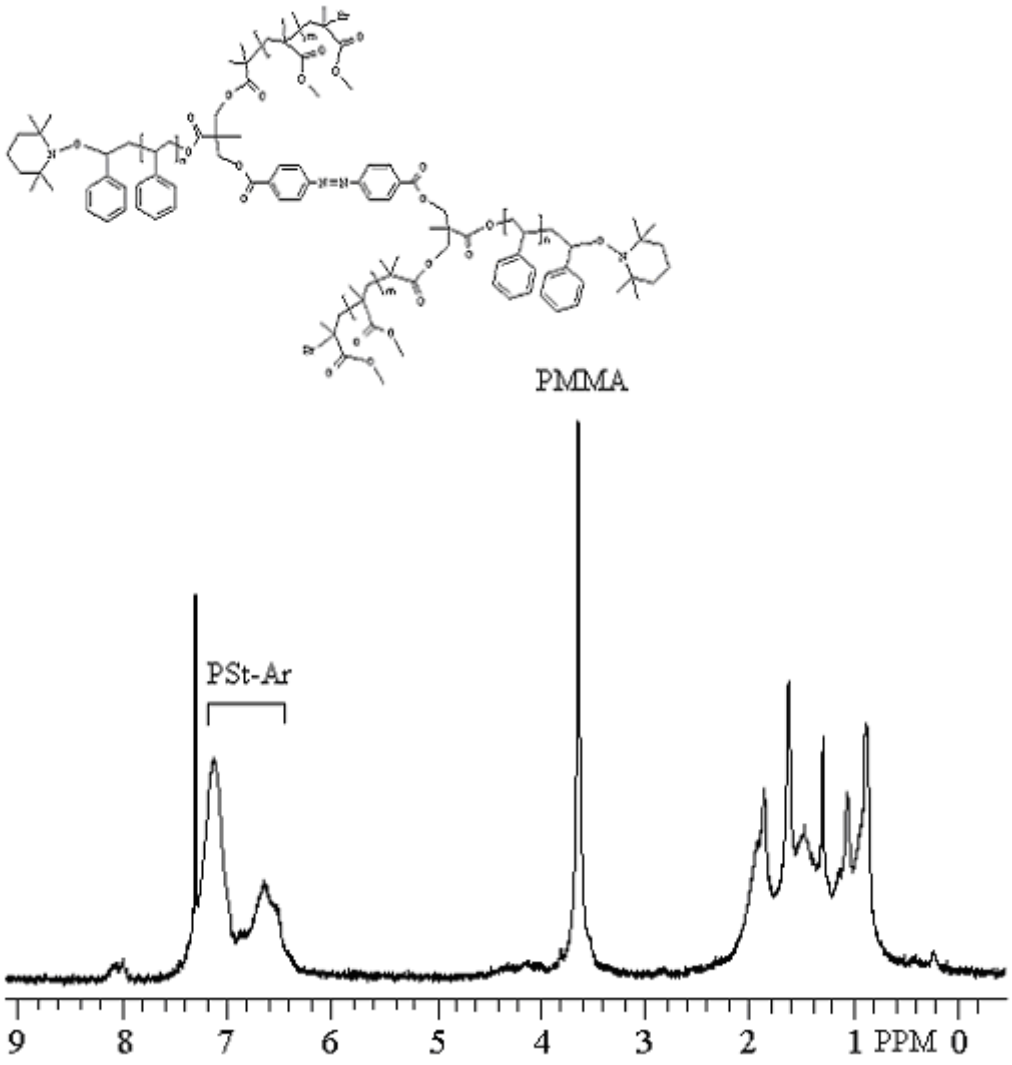
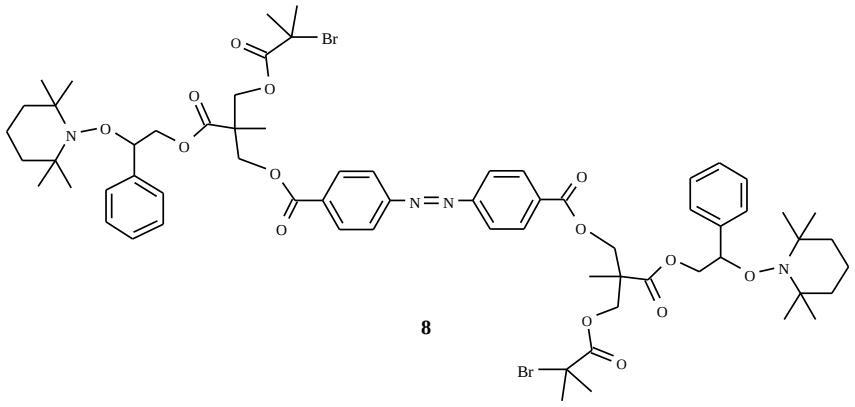


Figure 9. The ^{1}H NMR spectrum of $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer in $CDCl_3$.



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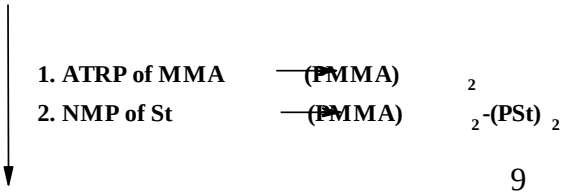

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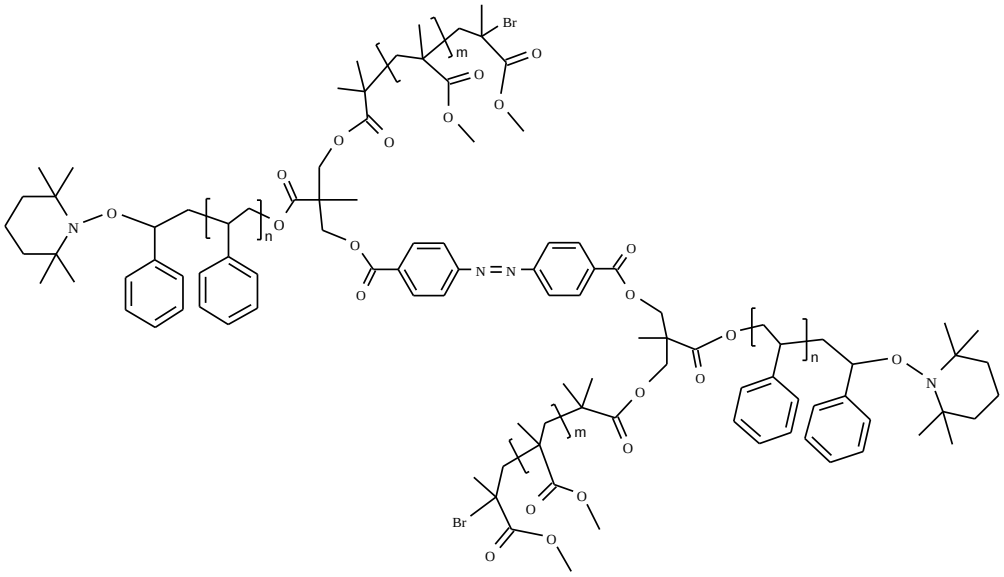

The average molecular weight increased with MMA conversion in ATRP, confirming the introduction of the PMMA blocks to the initiator **8** (Table 1, P Ia-c). In the case of miktoarm star copolymer, the disappearance of the PMMA precursor trace revealed that the all of the precursor chains having TEMPO moiety efficiently initiated the NMP of St (Fig. 10). Moreover, any peak in higher molecular weight region of the GPC traces was not observed indicating the absence of the star-star coupling reaction.

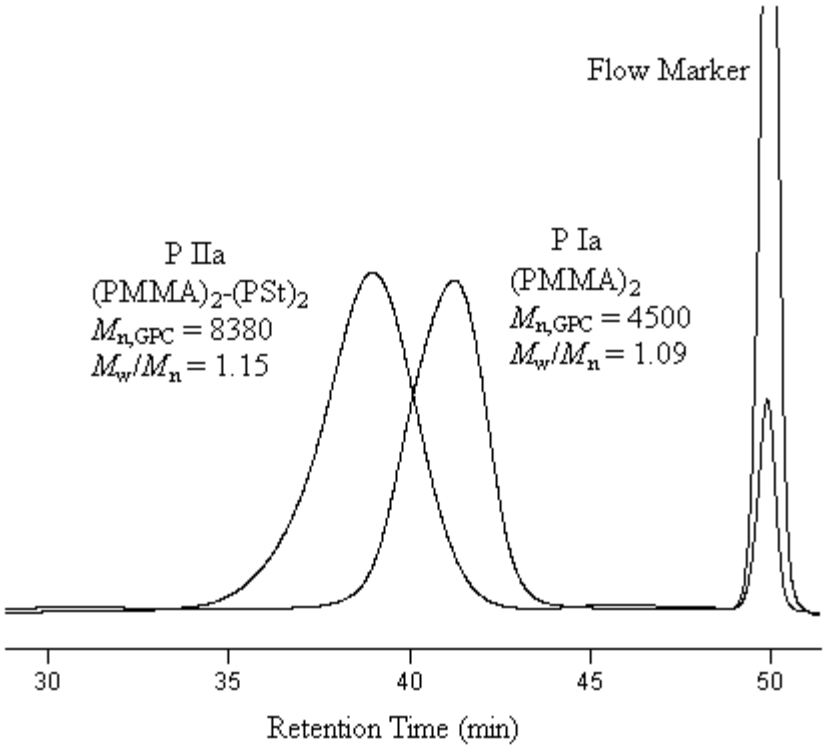

Figure 10. GPC traces of $(PMMA)_2$ precursor, P Ia and $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer, P IIa.

Table 1. The characteristics of photoresponsive $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer

Run	Monomer	Initiator	$[M]_o$ ($mol.L^{-1}$)	$[M]_o/[I]_o$	Time (h)	Conversion (%)	$M_{n,theo}$	$M_{n,GPC}$ [c]	M_w/M_n
P Ia[a]	MMA	8	4.68	200	0.25	13	3920	4500	1.09
P Ib[a]	MMA	8	4.68	200	0.5	30	7330	8230	1.13
P Ic[a]	MMA	8	4.68	200	1	38	8950	10700	1.12
P IIa[b]	St	P Ia	8.73	300	19.5	11	7950	8380	1.15
P IIb[b]	St	P Ic	8.73	300	16	8	13200	13900	1.14

8 = Miktofunctional initiator, P I = $(PMMA)_2$ macroinitiator, P II=$(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer respectively

[a] $[M]_o$: $[I]_o$ = 200 $[I]_o/[CuCl]_o/[PMDETA]_o$ = 1/ 2/ 2. The polymerization was carried out at 60 ^oC. MMA / Anisole = 1 (v/v)
$Mn_{,theo}$ = ($[M]_o/[I]_o$ x conversion % x (100.12) + 1319.25 ($MW_{initiator}$)

[b] $[M]_o$: $[I]_o$ =300 The polymerization was carried out at 125 ^oC in bulk.
$Mn_{,theo}$ = ($[M]_o/[I]_o$ x conversion % x (104.15) + $Mn_{,macroinitiator}$

[c] Calculated from GPC calibrated with linear polystyrene standards.

4.4. Photoresponsive Study:

The miktofunctional initiator **8** dissolved in $CHCl_3$ and was irradiated with UV light (λ < 350 nm) by 10 s intervals (0-120 s) (Fig. 11). During the irradiation, the absorption maximum at 330 nm corresponding to the π-π* transition of trans-azobenzene decreased and concurrently a weak band at 450 nm corresponding to n-π* transition of azobenzene moiety increased with time. Thus upon irradiation of these solutions with λ < 350 nm UV light, energetically preferred trans-form turned to the cis- (photochemical isomerization process).

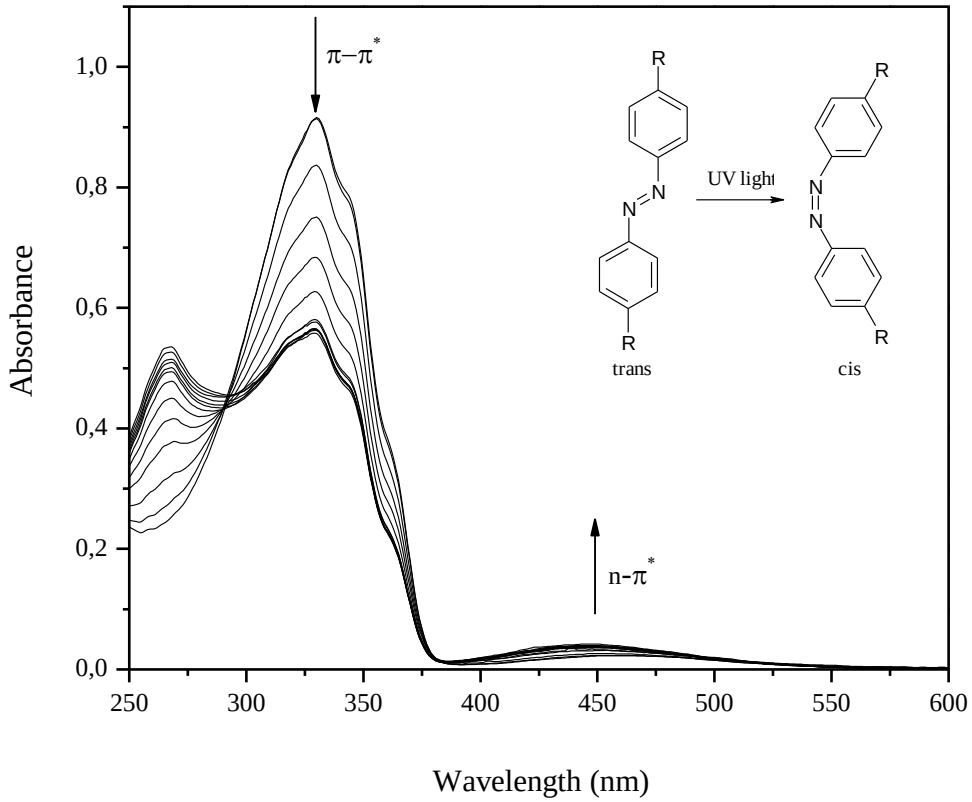

Figure 11. UV visible absorption changes of **8** in $CHCl_3$ (2.5 X 10^{-5} M) (trans-cis isomerization) under irradiation conditions (λ < 350 nm; 10 s interval; 0 to 120 s).

When this solution was kept in the dark, the back isomerization (cis-to-trans) occurred. This process was also monitored by UV spectrophotometer and evidenced by an increase in the absorbance at 330 nm and concurrently a decrease in absorbance at 450 nm with respect to time.

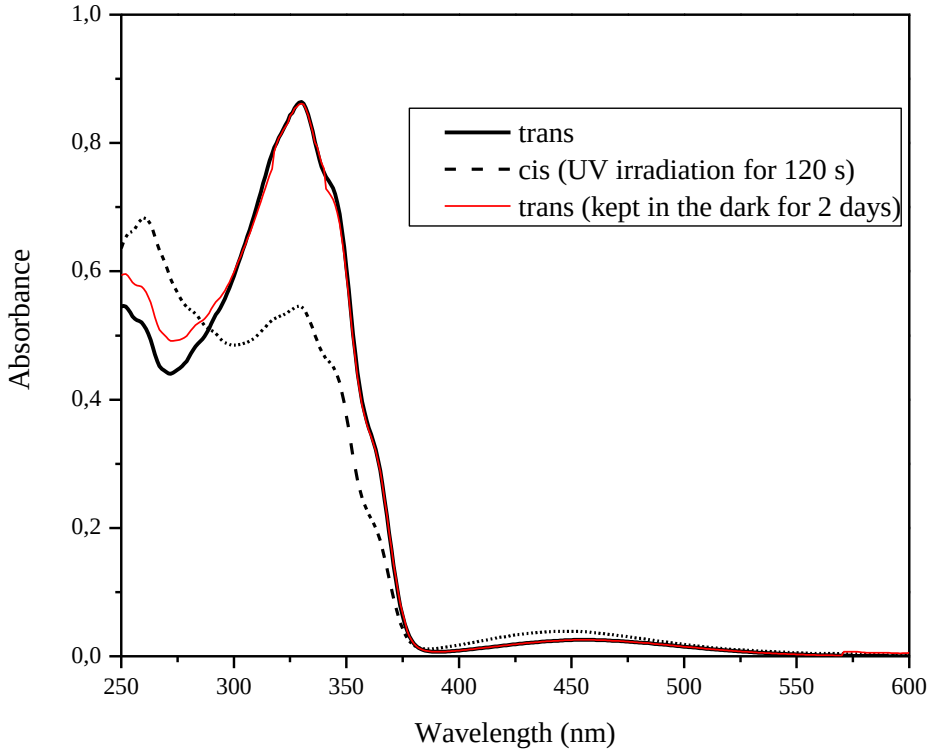

Figure 12. UV visible absorption changes of miktofunctional initiator, **8** in $CHCl_3$ (2.5 X 10^{-5} M); trans-cis isomerization occurred after 120 s irradiation at λ < 350 nm, followed by cis-trans back isomerization after 2 days in the dark**.**

A similar behavior was observed upon UV irradiation (λ < 350 nm) of $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer (**P IIa**) for 7h. (Fig.13).

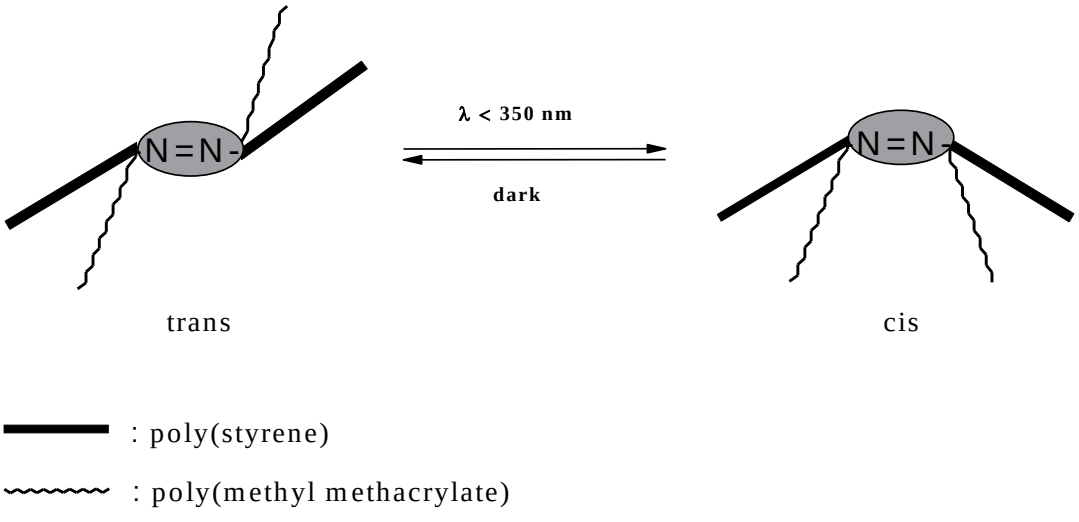

Figure 13. Trans to cis photoisomerization of $(PMMA)_2$-$(PSt)_2$ miktoarm star polymer

Trans to cis photoisomerization of $(PMMA)_2$-$(PSt)_2$ miktoarm star polymer (**P IIa)** was determined by using UV spectrophotometer (Fig. 14). However, it was obvious that trans-cis isomerization of **P IIa** was quite slow when compared with that of initiator **8**. The back

isomerization of **P IIa** (cis to trans) occurred when keeping it in the dark for 5 days (Fig. 14). Overall, these results were consistent with data obtained in the literature [12] and clearly demonstrated that $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer containing an azobenzene unit at the core displayed reversible isomerization by photochemical procedures.

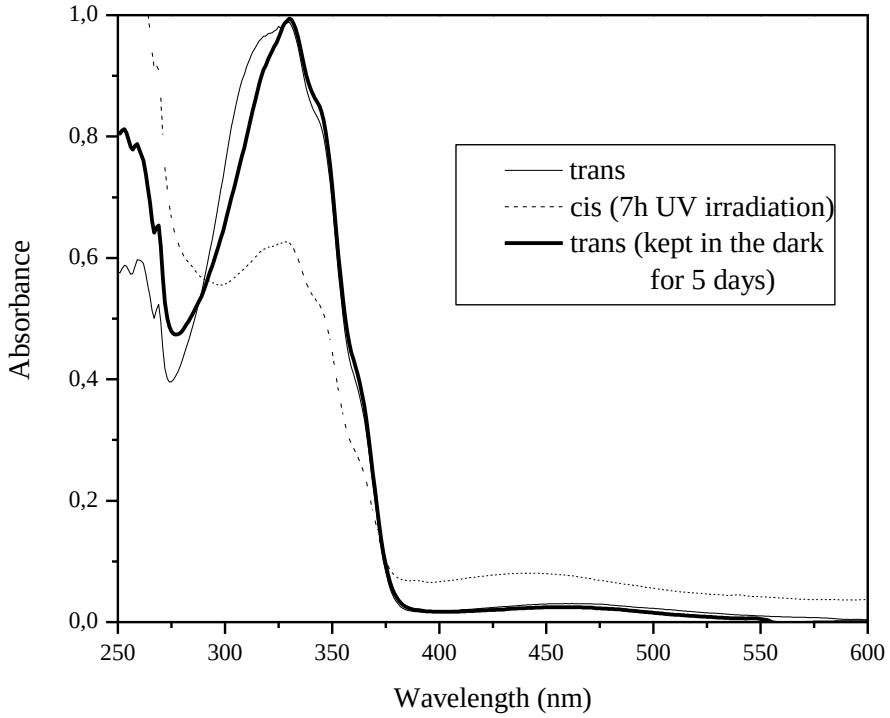

Figure 14**.** UV visible absorption changes of $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer, P IIa in $CHCl_3$ (2.5×10^{-5} M); trans-cis isomerization occurred after 7 h irradiation at $\lambda <$ 350 nm, followed by cis-trans back isomerization after 5 days in the dark.

Trans to cis isomerization of miktoarm star copolymer (**P IIa**) was also observed in GPC traces. As can be seen from Figure15, a peak of $(PMMA)_2$-$(PSt)_2$ miktoarm star (**P IIa**) in trans-form shifted slightly to lower molecular weight region (cis-form) when exposed to UV light ($\lambda < 350$ nm) for 7 h.

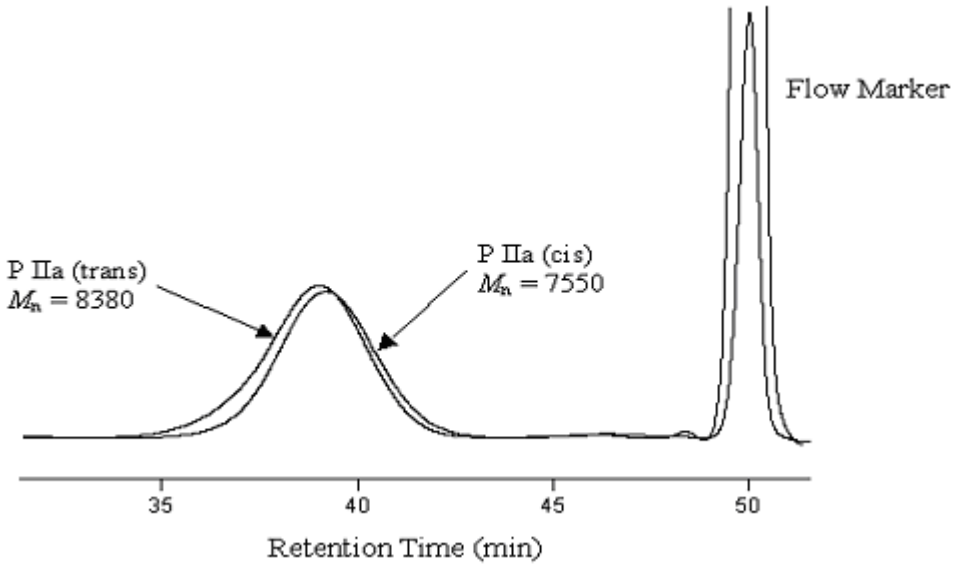

Figure 15. GPC traces of P IIa (trans) and P IIa (cis) after 7 h irradiation at λ < 350 nm.

This is for the reason that photoinduced trans to cis isomerization leads to a small change (contraction) in hydrodynamic volume of the miktoarm star polymer. A similar behavior was encountered remarkably for the aromatic polymers with azobenzene units in the main chain [10]. In this respect, the viscosity of the polymer solutions decreased on UV irradiation and returned slowly to the initial value in the dark indicating that the contraction of the hydrodynamic volume was certainly induced by the isomerization of the azobenzene units and that back isomerization expanded the chain conformation [10].

CONCLUSION

In conclusion a novel miktoarm star copolymer with an azobenzene unit at the core via combination of atom transfer radical polymerization (ATRP) and nitroxide-mediated free radical polymerization (NMP) routes was prepared. For this purpose, first, mikto-functional initiator, (Azobenzene-4,4'-dicarboxylic acid bis-{3-(2-bromo-2-methyl-propionyloxy)-2-methyl-2-[2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethoxycarbonyl]-propyl} ester) **(8)**, with tertiary bromide (for ATRP) and 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) (for NMP) functionalities and an azobenzene moiety at the core was synthesized. The initiator (**8)** 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 A_2B_2 type miktoarm star copolymer, $(PMMA)_2$-$(PSt)_2$ with an azobenzene unit at the core with controlled molecular weight and low polydispersity ($M_w/M_n < 1.15$).

The photoresponsive properties of **8** and $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer were investigated. Trans to cis and the back isomerization (cis to trans) of **8** and $(PMMA)_2$-$(PSt)_2$ miktoarm star copolymer were monitored by UV measurements. Trans to cis isomerization process of $(PMMA)_2$-$(PSt)_2$ was also observed in GPC traces. A peak of $(PMMA)_2$-$(PSt)_2$ (in trans-form) shifted to lower molecular weight region (cis-form) when irradiated at $\lambda < 350$ nm UV light, due to a change in hydrodynamic volume of polymers through isomerization process (configurational/ conformational changes).

In this study, by applying the most efficient CRP techniques containing ATRP and NMP, well-defined miktoarm star copolymers with various molecular weights and relatively narrow molecular weight distributions were synthesized.

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