İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF MIKTOARM STAR POLYMERS VIA COMBINATION OF CONTROLLED POLYMERIZATION SYSTEMS

Ph.D. Thesis by

Tuba ERDOĞAN BEDRİ

Department: Polymer Science and Technology

Programme: Polymer Science and Technology

SEPTEMBER 2006

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(515022003)

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Supervisor (Chairman): Prof. Dr. Ümit TUNCA

Members of the Examining Committee: Prof. Dr. Gürkan HIZAL (I.T.U)

Prof. Dr. Ersin SERHATLI (I.T.U)

Prof. Dr. Nergis ARSU (Y.T.U)

Prof. Dr. Duygu AVCI (B.U)

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September 2006 Tuba ERDOĞAN BEDRİ

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LIST of ABBREVIATIONS

ATRP	: Atom Transfer Radical Polymerization
ROP	: Ring-Opening Polymerization
NMP	: Nitroxide Mediated Radical Polymerization
SFRP	: Stable Free Radical Polymerization
CRP	: Controlled/"Living" Radical Polymerization
RAFT	: Reversible Addition-Fragmentation Chain Transfer Polymerization
PS	: Polystyrene
P*t*BA	: Poly(*tert*-butyl acrylate)
PMMA	: Poly(methyl methacrylate)
PCL	: Poly(ε-caprolactone)
PBA	: Poly(butyl acrylate)
PAA	: Poly(acrylic acid)
PMA	: Poly(methyl acrylate)
^{1}H-NMR	: Proton Nuclear Magnetic Resonance Spectroscopy
IR	: Infrared Spectrophotometer
GPC	: Gel Permeation Chromatography
SEC	: Size Exclusion Chromatography
DSC	: Differential Scanning Calorimetry
TGA	: Thermogravimetric Analyzer
MS	: Mass Spectrometer
UV	: Ultra Violet
UCC	: Universal Calibration Curve
DP	: Degree of Polymerization
PRE	: Persistent Radical Effect
ε-CL	: Epsilon Caprolactone
St	: Styrene
***t*BA**	: *tert*-butyl acrylate
MMA	: Methyl Methacrylate
Sn(Oct)$_2$	: Stannous Octoate
Al(O*i*-Pr)$_3$	: Aluminum (III) isopropoxide
bis-MPA	: 2,2-bis(hydroxymethyl)propanoic acid
DMAP	: 4-Dimethylaminopyridine
DPTS	: 4-Dimethylamino pyridinium-4-toluene sulfonate
DCC	: *N,N*-Dicyclohexylcarbodiimide
AIBN	: 2,2'-azobisisobutyronitrile
MWD	: Molecular Weight Distribution
FRP	: Free Radical Polymerization
PDI	: Polydispersity Index
Bipy	: 2,2'-Bipyridine
BPO	: Benzoyl peroxide

PMDETA	: *N,N,N',N'',N''*-Pentamethyldiethylenetriamine
Bipy	: 2,2'-Bipyridine
TMEDA	: *N,N,N',N'*-Tetramethylethylenediamine
HMTETA	: *N,N,N',N'',N''',N'''*-Hexamethyltriethylenetetraamine
Me_6-TREN	: Tris[2-(dimethylamino)ethyl]amine
DMF	: Dimethyl Formamide
P-X	: Dormant Species
THF	: Tetrahydrofuran
PLi	: Organolithium compounds
DVB	: Divinyl benzene
EGDM	: Ethylene glycol dimethacrylate
dTBipy, dHBipy	
dNBipy	: Substituted Bipyridines
TEMPO	: 2,2,6,6-Tetramethylpiperidinyl-1-oxy
DBN	: di-*tert*-butyl nitroxide
DEPN	: *N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide
PPh_3	: Triphenylphosphine
M_o	: Initial molar concentration of the monomer
I_o	: Initial molar concentration of the initiator
$M_{n,theo}$	: Theoretical molecular weight
$M_{initiator}$	: Molecular weights of the initiator
PTHF	: Polytetrahydrofuran
PCl_5	: Phosphorus penta chloride
Et_3N	: Triethylamine

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LIST of SYMBOLS

λ	: Wavelength
$R\cdot$	: Radical
$P\cdot$	: Propagating Radical
$X\cdot$	: Persistent Radical
I	: Initiator
M	: Monomer
M_n	: The number average molecular weight
M_w	: The weight average molecular weight
M_w/M_n	: The molecular weight distribution
$P_n\cdot$	: Propagating species
M_t^n	: Transition metal
R_p	: Rate of polymerization
k_{act}	: Pseudo-first-order activation rate constant
k_{deact}	: Pseudo-first-order deactivation rate constant
k_a	: Rate constant of activation
k_{da}	: Rate constant of deactivation
k_d	: Rate constant of dissociation
k_c	: Rate constant of combination
k_{ex}	: Degenerative chain transfer rate constant
k_p	: Rate constant of propagation
k_t	: Rate constant of termination

SYNTHESIS OF MIKTOARM STAR POLYMERS VIA COMBINATION OF CONTROLLED POLYMERIZATION SYSTEMS

SUMMARY

Complex macromolecular structures such as star polymers have been synthesized in the search for polymers with improved mechanical and thermal properties. Star polymers are branched polymers consisting of several linear chains linked to a central core. Among all branched structures, star polymers have been certainly the most investigated architectures, attracting much experimental and theoretical interest. Such species have been very useful in providing further insight into how branching affects the overall properties of polymers in solution or in melt. Some of the applications involving star polymers are the direct result of these structure-property relationships, these polymers being now commonly used as viscosity modifiers in paints and coatings or for their improved processability and mechanical properties compared to their linear analogues.

Star polymers containing chemically different arms are termed miktoarm or heteroarm star polymers. Miktoarm is the combination of Greek word miktos meaning ″mixed″, and "arm". Recently, miktoarm star polymers have gained much attention due to its unique properties arising from their arm segments differ in molecular weight and chemical composition. Compared with the corresponding linear block copolymers, miktoarm star polymers exhibit many interesting properties, such as unique phase separation behavior either in bulk or in solution, due to steric hindrance as a result of more than two different types of polymers being brought together at a single junction (core).

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, living polymerization techniques, such as anionic, cationic have typically been used to obtain well-defined star-shaped macromolecules.

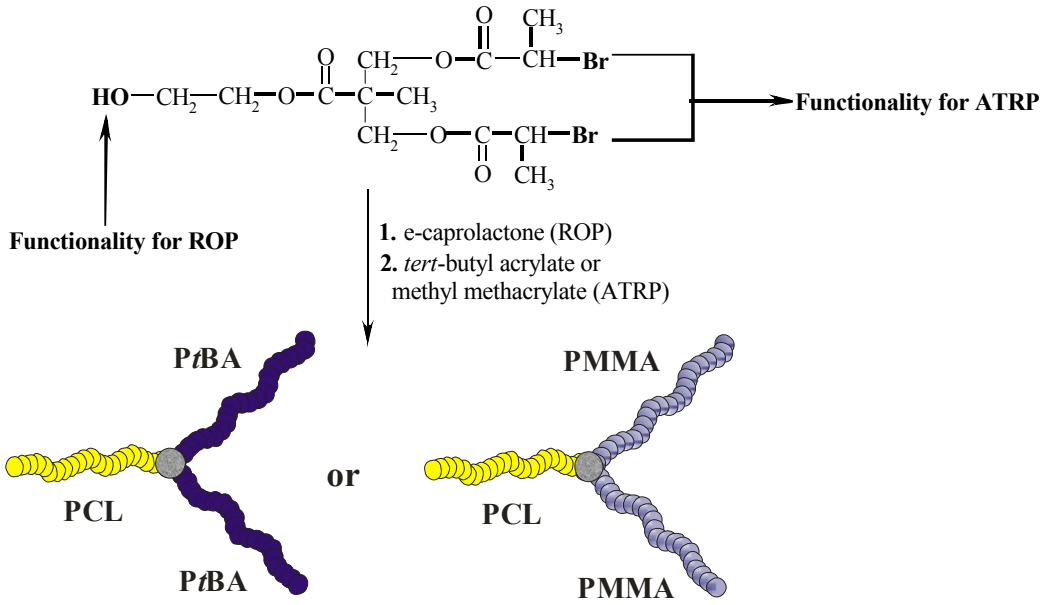
The early synthesis of miktoarm star polymers have been based on two general strategies. The first involves living anionic polymers being consecutively reacted with an appropriate multifunctional core (chlorosilane compound) in a consecutive polymer reaction. The second is the reaction of the active chain with divinylbenzene (DVB). In this route, a living polymer (derived from anionic polymerization) is added to DVB, and this leads to the formation of a star polymer with active anionic sites on the polymer core. The subsequent anionic polymerization of another monomer results in a miktoarm star polymer.

Living polymerization is a chain growth polymerization that proceeds in the absence of irreversible chain transfer and chain termination. Living polymerizations provide the maximum degree of control for synthesis of polymers with predictable, well-defined structures. For a long period of time, living ionic polymerization (anionic or cationic) was the dominant living polymerization method. However, in recent years there has been rapid growth in the area of growing controlled/"living" radical polymerizations (CRP), which have some advantages over anionic polymerization, in that they do not require rigorous experimental conditions.

CRP is a simple and robust method for the synthesis of complex macromolecular structures with low polydispersity and well-controlled architecture and functionality. Atom transfer radical polymerization (ATRP) and nitroxide-mediated radical polymerization (NMP) are the most widely used CRP methods. In addition, controlled ring-opening polymerization (ROP) has found wide applications in the polymerization of lactones and lactides.

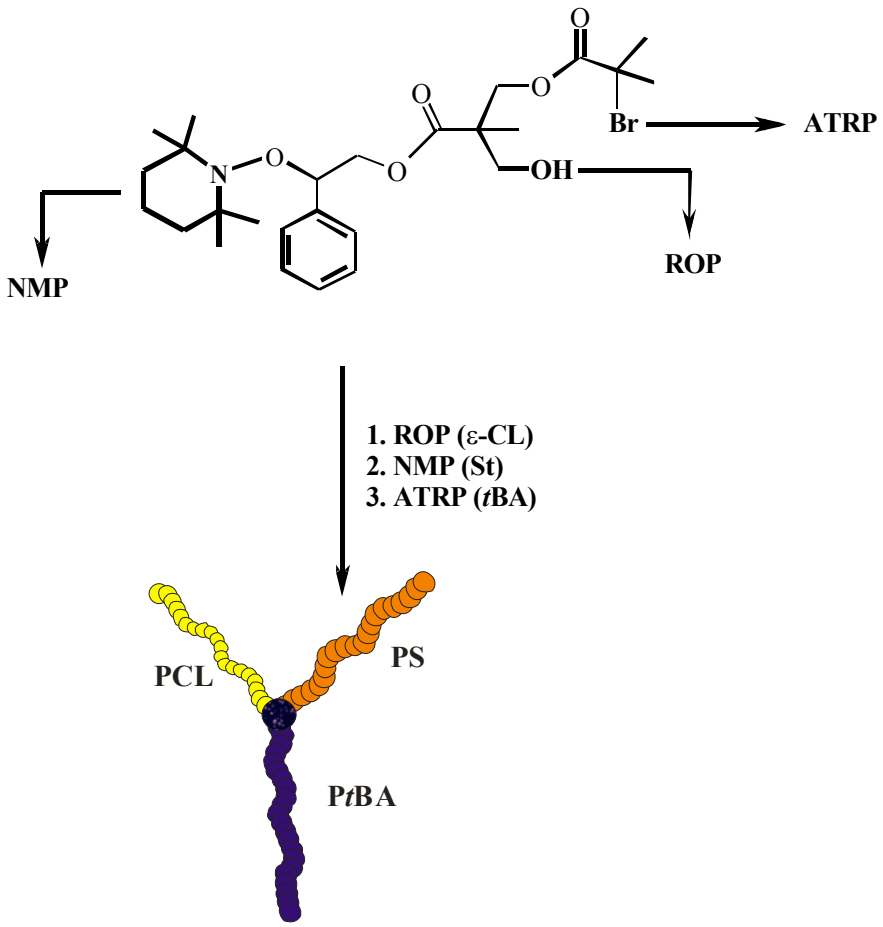
This thesis focused on the synthesis of well-defined miktoarm star polymers based on combination of controlled radical and nonradical polymerization systems by using a core-first approach employing miktofunctional initiators.

For this purpose, three novel miktofunctional initiators were synthesized. The first one,2-hydroxyethyl 3-[(2-bromopropanoyl)oxy]-2-{[(2bromopropanoyl)oxy]methyl} -2-methyl-propanoate, possessing one initiating site for ROP and two initiating sites for ATRP, was synthesized in a three-step reaction sequence. This initiator was first used in the ROP of ε-caprolactone (ε-CL), and this led to a corresponding polymer with secondary bromide end groups. The obtained poly(ε-caprolactone) (PCL) was then used as a macroinitiator for the ATRP of *tert*-butyl acrylate or methyl methacrylate, and this resulted in AB_2-type PCL–[poly(*tert*-butyl acrylate)]$_2$, PCL-(P*t*BA)$_2$ or PCL–[poly(methyl methacrylate)]$_2$, PCL-(PMMA)$_2$ miktoarm star polymers with controlled molecular weights and low polydispersities via the ROP–ATRP sequence. The formula of the initiator and illustration of AB_2-type miktoarm star polymers are shown in Scheme 1.



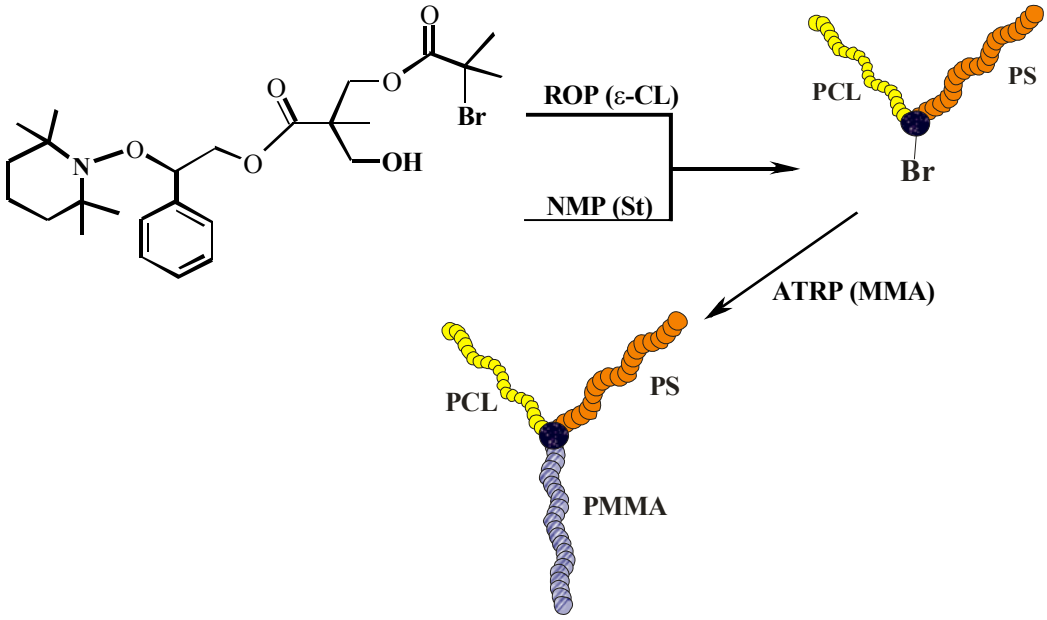
Scheme 1. Illustration of the miktofunctional initiator and AB_2 miktoarm star.

The ABC type miktoarm star polymer was prepared utilizing a "core-first" method via combination of ROP, NMP and ATRP. First, the ROP of ε-CL was carried out by using a miktofunctional initiator, 2-(2-Bromo-2-methylpropionyloxymethyl)-3-hydroxy-2-methyl-propionic acid 2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1yl oxy)-ethyl ester, at 110 °C. Second, previously obtained PCL was used as a macroinitiator for NMP of styrene. As a third step, this PCL-polystyrene (PS) precursor with a bromine functionality in the core was employed as a macroinitiator for ATRP of *t*BA in the presence of Cu(I)Br and pentamethyldiethylenetriamine (PMDETA) in order to give ABC type miktoarm star polymer (PCL-PS-P*t*BA) with controlled molecular weight and moderate polydispersity. The schematic representation of synthesized initiator and ABC type miktoarm star polymer are shown in Scheme 2. The thermal properties of obtained star polymers were also investigated by DSC and TGA analysis.



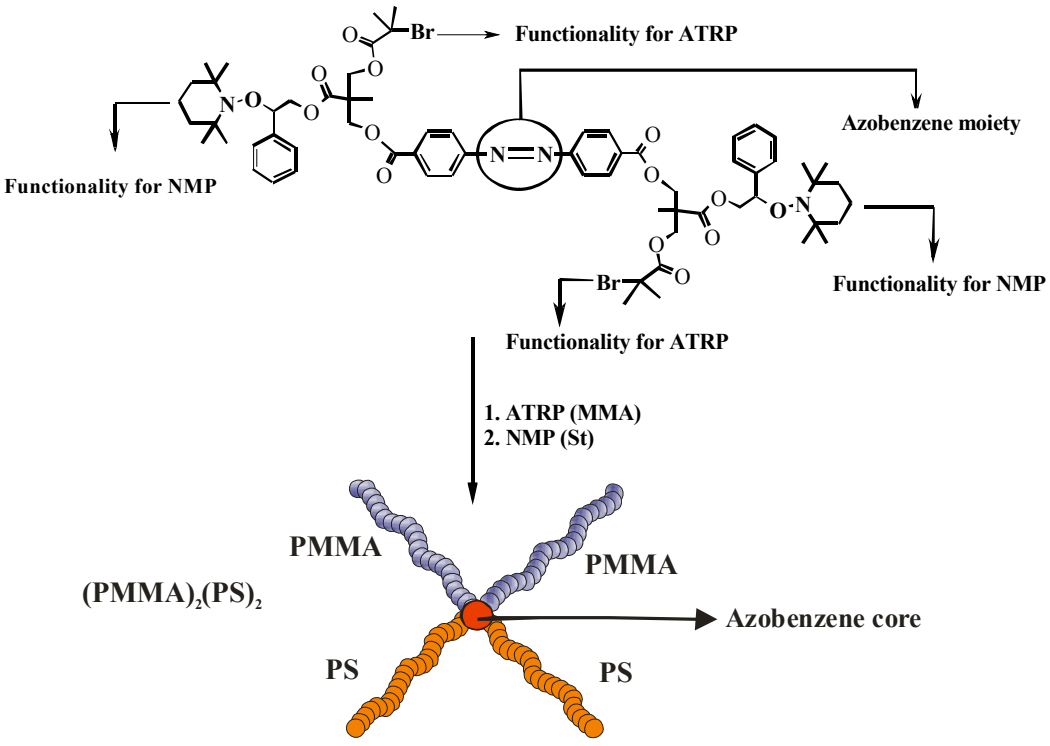
Scheme 2. Illustration of the miktofunctional initiator and ABC miktoarm star.

Since the above initiator contains a single primary alcohol functionality, which is the initiation center for ROP of ε-CL, as well as a secondary benzyl group linked to an alkoxyamine; the benzyl group is an efficient initiator for NMP of styrene, polymerization of a mixture of St and ε-CL initiated by corresponding initiator in the presence of $Sn(Oct)_2$ as ROP catalyst produces the block copolymer, PCL-*b*-PS. The obtained PCL-*b*-PS having tertiary bromide functionality was used as macroinitiator for ATRP of MMA to prepare PCL-PS-PMMA miktoarm star polymer (Scheme 3).



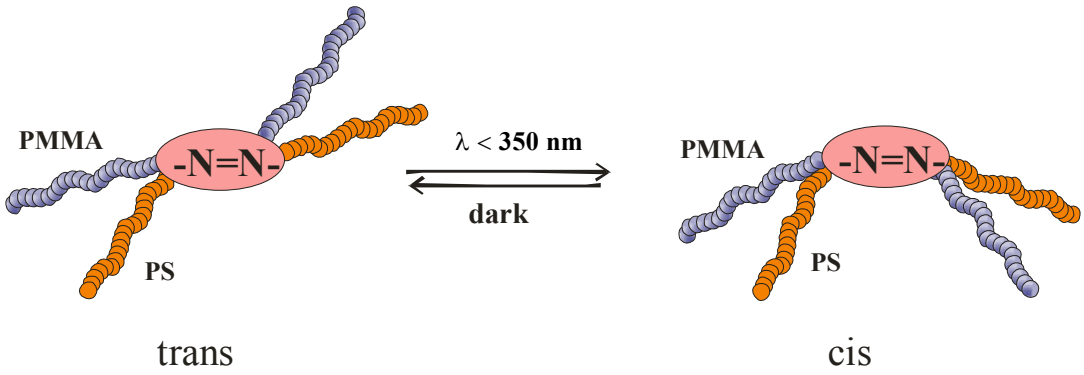
Scheme 3. Illustration of the miktofunctional initiator and ABC miktoarm star.

As a third one, a novel miktofunctional initiator with two tertiary bromide (for ATRP) and two 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) (for NMP) functionalities and an azobenzene moiety at the core was synthesized. The initiator thus obtained was used in the subsequent controlled/"living" radical polymerization routes such as ATRP of MMA and NMP of St, respectively, to give A_2B_2 type miktoarm star copolymer, $(PMMA)_2$-$(PS)_2$ with an azobenzene unit at the core with controlled molecular weight and low polydispersity. The idealized structures of the initiator and A_2B_2 type miktoarm star copolymer were shown in Scheme 4.



Scheme 4. Illustration of the miktofunctional initiator and A_2B_2 miktoarm star.

Furthermore, the photoresponsive properties of the miktofunctional intiator and $(PMMA)_2$-$(PS)_2$ miktoarm star copolymer were investigated by UV and GPC measurements (Scheme 5).



Scheme 5. Trans to cis photoisomerization process of A_2B_2 miktoarm star polymer

The structure of the novel miktofunctional initiators were elucidated by mass spectroscopy and ^1H (^{13}C)-NMR measurements and the star polymers were characterized by ^1H-NMR and GPC analysis.

KONTROLLÜ POLİMERİZASYON SİSTEMLERİYLE FARKLI KOLLU YILDIZ POLİMERLERİN SENTEZİ

ÖZET

Kompleks makromoleküler yapılar örneğin yıldız polimerler geliştirilmiş mekanik ve termal özelliğe sahip polimer araştırmaları için oldukça önem taşımaktadır. Yıldız polimerler birkaç lineer polimer zincirinin bir merkez çekirdeğe bağlı olduğu dallanmış yapılardır. Tüm dallanmış yapılar arasında, şüphesiz yıldız polimerler en çok araştırılan, deneysel ve teorik açıdan ilgi çeken yapılardır. Bu tür yapılar, dallanmanın polimerlerin çözelti veya eriyik haldeki tüm özelliklerini nasıl etkilediğini anlamak için oldukça elverişlidir. Yıldız polimerlerin bazı uygulamaları da işte bu yapı-özellik arasındaki ilişkinin sonucudur. Günümüzde, yıldız polimerler genellikle boya ve kaplamalarda viskozite ayarlayıcı olarak kullanılmaktadır.

Kimyasal olarak farklı kollara sahip yıldız polimerler miktokollu ya da farklı kollu yıldız polimer olarak adlandırılır. "Mikto" kökü Yunanca'dan gelmektedir ve "karışık" anlamına gelir. Son zamanlarda, farklı kollu yıldız polimerler sahip oldukları farklı molekül ağırlığı ve kimyasal kompozisyonda kollardan dolayı oldukça ilgi uyandırmaktadır. Lineer polimerlerle karşılaştırıldıklarında, farklı kollu yıldız polimerler oldukça ilginç özellikler göstermektedir. Bunun nedeni, katı halde ya da çözücü içinde sahip oldukları farklı kollardan dolayı gösterdikleri eşsiz faz ayrımı davranışlarıdır.

Her ne kadar yıldız polimerler en basit dallanmış yapıyı oluştursa da, kontrollü yaklaşımla sentezleri çoğu zaman güçtür. Bu tip makromoleküller kompleks yapılarından dolayı genellikle yaşayan polimerizasyon sistemleriyle (yaşayan anyonik, kaytonik polimerizasyon) sentezlenmektedir.

Farklı kollu yıldız polimerlerin sentezi iki genel stratejiye dayanmaktadır. Bunlardan ilki yaşayan anyonik polimerizasyonla sentezlenen polimerlerin uygun çok fonksiyonlu bir bileşikle tepkimeye uğratılmasıdır. İkincisi ise aktif polimer zincirlerinin divinil benzen (DVB) gibi çift fonksiyonlu bir bileşik ile tepkimeye sokulmasıdır. Bu yöntemde, anyonik polimerizasyonla sentezlenen yaşayan polimer DVB bileşiği ile tepkimeye sokulur, böylece çekirdeğinde aktif anyonik merkezler içeren yıldız polimer oluşturulur. Sonrasında faklı bir monomerin anyonik polimerizasyonu farklı kollu yıldız polimer ile sonuçlanır.

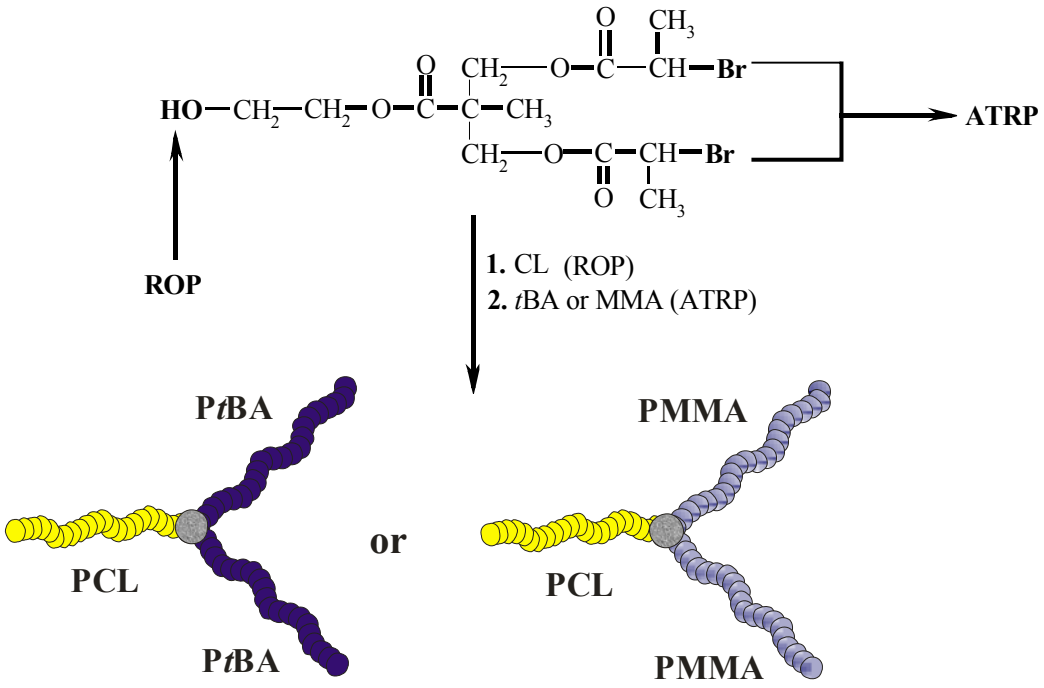
Yaşayan polimerizasyonlar geri dönüşümsüz zincir transferi veya zincir sonlanması olmaksızın ilerleyen zincir büyüme reaksiyonlarıdır. Polimerin sonuç molekül ağırlığı, dar bir molekül ağırlığı dağılımı sağlanarak, başlangıç monomer/başlatıcı oranı değiştirilerek ayarlanabilir. Şimdiye kadar yaşayan iyonik polimerizasyon yöntemleri en çok kullanılan yaşayan polimerizasyon yöntemleriydi. Fakat, son yıllarda

kontrollü/"yaşayan" polimerizasyon alanındaki gelişmeler iyonik polimerizasyon yöntemlerine karşı birçok üstünlük sağlamıştır. Bunlardan en önemlisi çok zor deneysel şartları gerektirmemesidir.

Kontrollü/"yaşayan" radikal polimerizasyon iyi tanımlanmış kompleks makromoleküler yapıların sentezi için oldukça basit ve etkili bir yöntemdir. Şüphesiz, atom transfer radikal polimerizasyon (ATRP) ve nitroksit ortamlı radikal polimerizasyon (NMP) en çok araştırılan kontrollü/"yaşayan" radikal polimerizasyon yöntemleridir. Öte yandan, kontrollü halka açılma polimerizasyonu, lakton ve laktidlerin polimerizasyonunda geniş uygulama alanı bulmuştur.

Bu çalışma, kontrollü polimerizasyon yöntemleri kullanılarak iyi tanımlanmış yapıya sahip farklı kollu yıldız polimerlerin sentezi üzerine yoğunlaşmıştır.

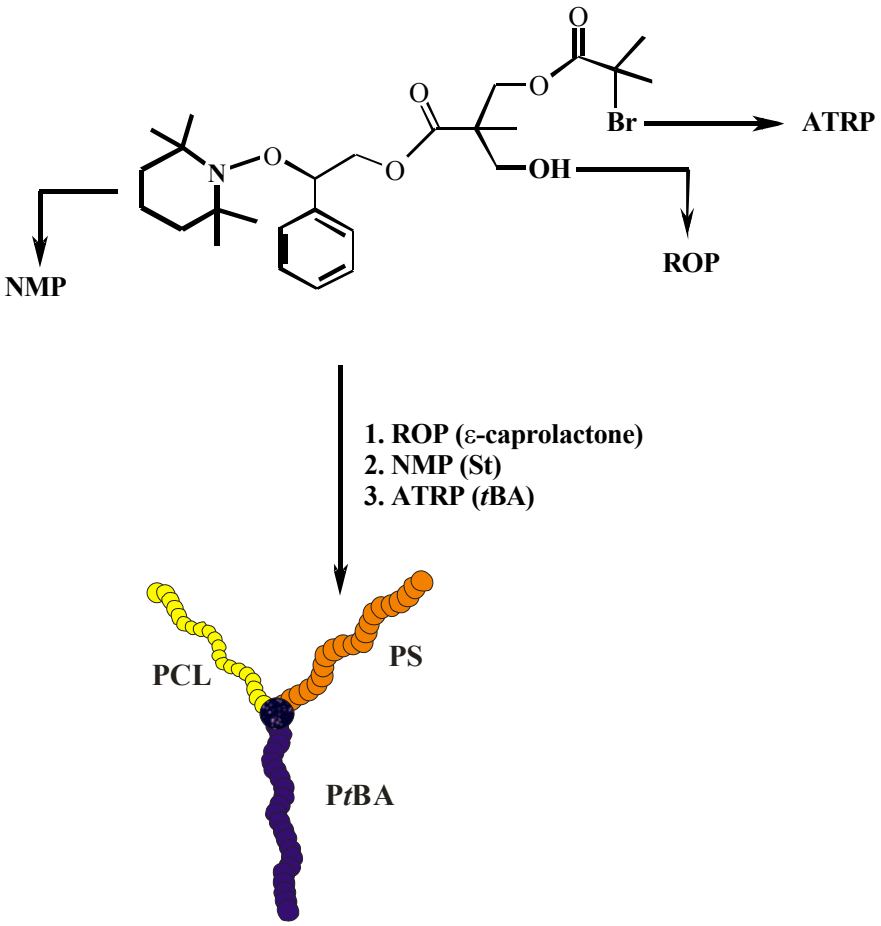
Bu amaçla, üç tane farklı fonksiyonlu başlatıcı sentezlenmiştir. İlki, 2-hidroksietil 3-[(2-bromopropanoyil)oksi]-2-{[(2-bromopropanoyil)oksi]metil}-2-metil-propanoat, ROP için bir fonksiyonel gruba ve ATRP için iki fonksiyonel gruba sahip üç fonksiyonlu başlatıcıdır. Bu başlatıcı ilk olarak kaprolaktonun (ε-CL) ROP'sinde kalay oktoat ($Sn(Oct)_2$) varlığında başlatıcı olarak kullanılmıştır. Elde edilen polikaprolakton (PCL) tersiyer-butil akrilatın (*t*BA) ya da metil metakrilatın (MMA) ATRP'sinde makrobaşlatıcı olarak kullanılmıştır. Sonuç olarak, düşük molekül ağırlığı dağılımına sahip AB_2- tipli PCL-(P*t*BA)$_2$ veya PCL-(PMMA)$_2$ farklı kollu yıldız polimerler hazırlanmıştır. Sentezlenen başlatıcının ve AB_2- tipli farklı kollu yıldız polimerlerin yapısı Şema 1'de gösterilmiştir.



Şema 1. ABC-tipli farklı kollu yıldız polimerin şematik gösterimi.

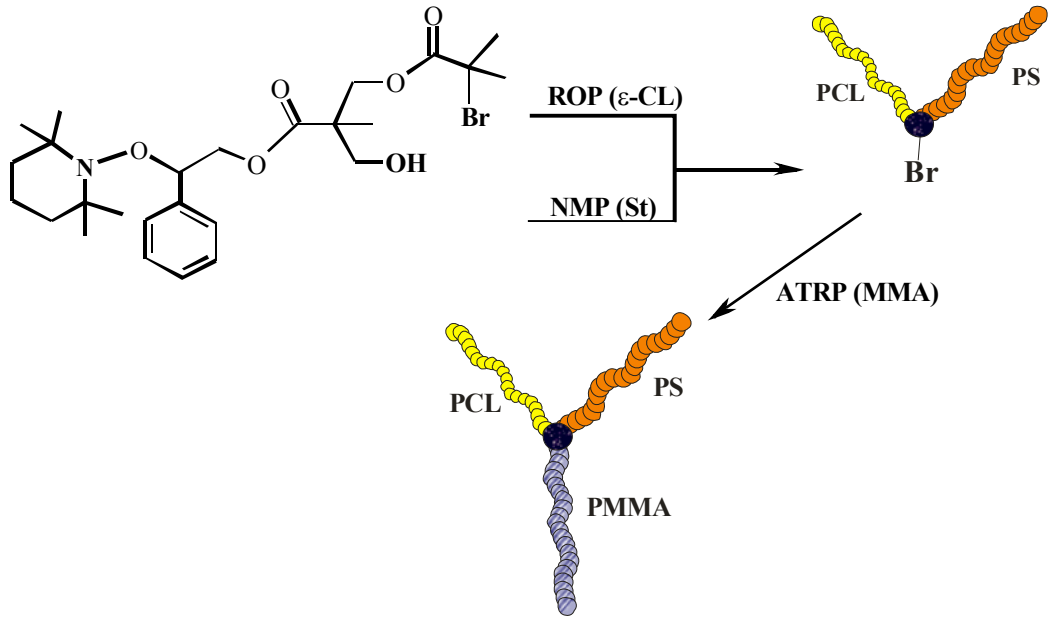
İkinci olarak, ATRP, NMP, ve ROP için uygun fonksiyonel gruba sahip yeni bir başlatıcı, 2-(2-bromo-2-metil-propiyoniloksimetil)- 3-hidroksil-2-metil-propiyonikasit 2-fenil-2-(2,2,6,6 tetrametilpiperidinil oksi)-etil ester, sentezlendi ABC- tipli farklı kollu yıldız polimerin eldesi için iki farklı yol izlendi. Birinci yaklaşımda, sentezlenen başlatıcı kalay oktoatın, $Sn(Oct)_2$ katalizör olduğu ε-CL'nin ROP' sinde kullanılarak PCL makrobaşlatıcısı elde edildi. Sentezlenen PCL stirenin

(St) NMP'sinde makrobaşlatıcı olarak kullanıldı ve polistiren(PS)-*blok*-PCL blok kopolimeri sentezlendi. Son olarak, uç grubunda ATRP için uygun tersiyer bromür fonksiyonel grubuna sahip PS-*blok*-PCL blok kopolimer, *t*BA'nın ATRP'sinde makrobaşlatıcı olarak kullanıldı ve nihayetinde PCL, PS ve P*t*BA kollarına sahip, düşük molekül ağırlığı dağılımlı ABC tipli farklı kollu yıldız polimer elde edildi (Şema 2).



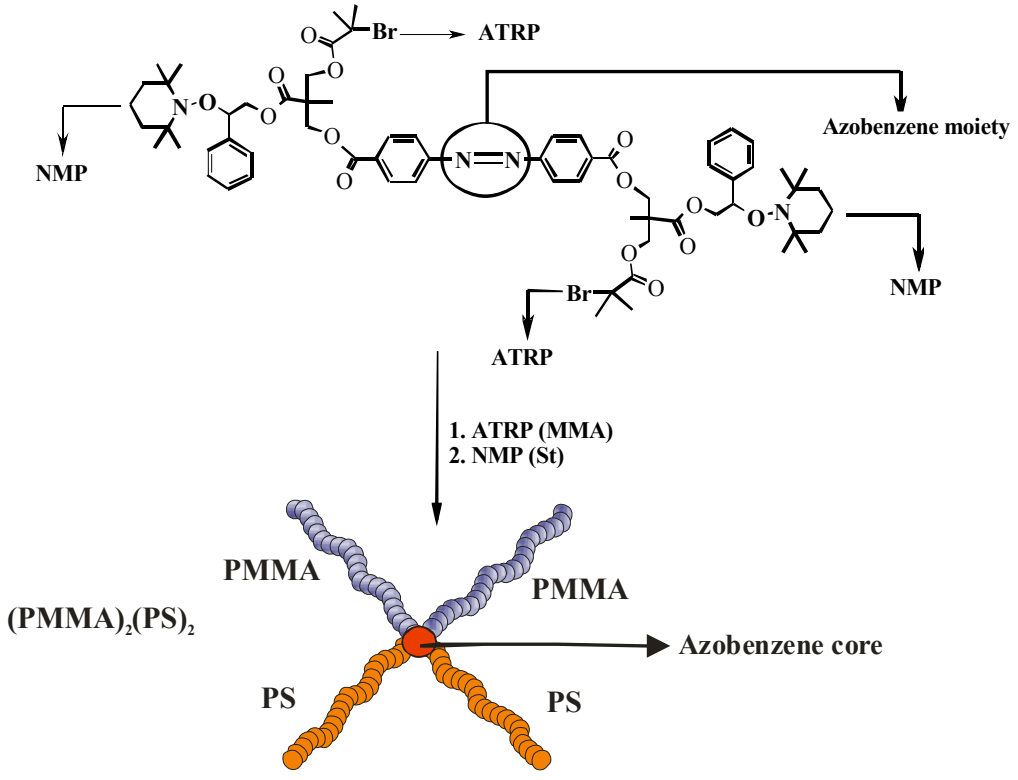
Şema 2. ABC-tipli farklı kollu yıldız polimerin şematik gösterimi.

İkinci yaklaşımda ise, ROP ve NMP yöntemleri aynı anda kullanılarak tek aşamada PS-*blok*-PCL blok kopolimeri sentezlendi ve MMA'nın ATRP'sinde makrobaşlatıcı olarak kullanıldı sonuç olarak PCL, PS ve PMMA kollarına sahip ABC tipli farklı kollu yıldız polimer elde edildi (Şema 3).



Şema 3. ABC-tipli farklı kollu yıldız polimerin şematik gösterimi.

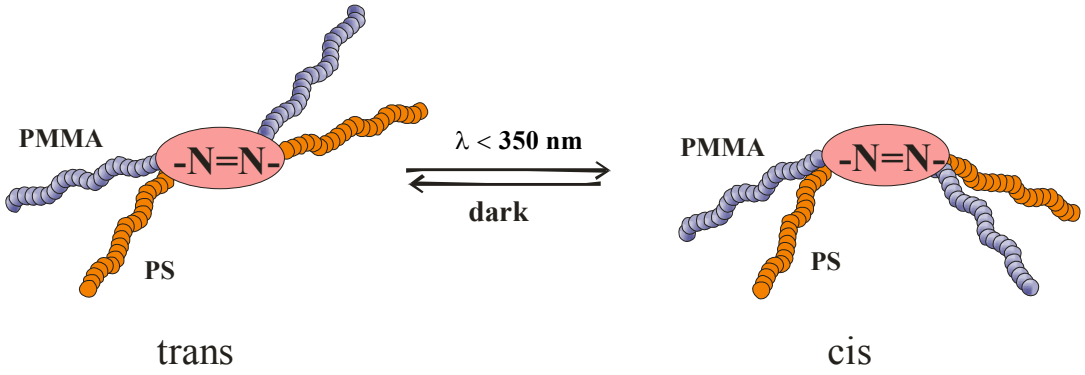
Üçüncü olarak ise, iki tersiyer bromür grubuna ve iki TEMPO fonksiyonuna sahip ve merkezinde azobenzen grubu içeren dört fonksiyonlu başlatıcı hazırlanmıştır. Bu başlatıcı öncelikle MMA'nın ATRP'sinde kullanıldı ve kontrollü molekül ağırlığına ve dar molekül ağırlığı dağılımına sahip $(PMMA)_2$ ön polimeri hazırlandı. Hazırlanan polimer stirenin NMP'sinde makrobaşlatıcı olarak kullanılarak merkezinde azobenzen grubu içeren A_2B_2-tipli $(PMMA)_2(PS)_2$ farklı kollu yıldız polimer elde edilmiştir (Şema 4).



Şema 4. A_2B_2-tipli farklı kollu yıldız polimerin şematik gösterimi.

Merkezinde azobenzene grubu içeren başlatıcı ve farklı kollu yıldız polimerin ışığa cevap verme (trans-cis isomerizasyon) özellikleri UV ve GPC ölçümleri ile incelenmiştir (Şema 5).

Sentezlenen başlatıcıların yapısı ^{1}H (^{13}C)-NMR, kütle spektroskopi ve yıldız polimerler ^{1}H-NMR, GPC, DSC ölçümleriyle karakterize edilmiştir.



Şema 5. Trans-cis isomerizasyon prosesi.

1. INTRODUCTION

It is well known that polymer properties are determined by the structure and molecular architecture. Major developments in the science and technology of polymeric materials have resulted from the preparation and characterization of polymers with well-defined structures [1, 2]. Well-defined structure provides low degrees of compositional heterogeneity to understand and predict polymer structure-property relationships.

The construction of polymeric materials with controlled compositions, topologies, and functionalities has been the enduring focus in current research [3-6]. Among them, star polymers with well-defined structures are of considerable interest in the understanding of the fundamental question of how macromolecular architecture can affect polymer properties. Star polymers are characterized as the simplest case of branched species where all chains of a given macromolecule are connected to a single nodule referred to as the core. The presence of a central core in these macromolecules has lead to new, often improved characteristics, compared with their linear polymer analogs. In particular, star polymers provide compact morphology, reduced solution viscosity, higher retention of properties under high temperature and high shear applications.

Miktoarm (mikto from the Greek word miktos meaning mixed) star polymers are a special class of nonlinear polymers where arms of different chemical nature and/or composition are linked to the same branch point [7]. Recently, miktoarm star polymers have received much attention because of their specific heterophase structures, in addition to branched architectures. These star polymers may possibly induce microdomain arrangements to form novel and interesting nanoscopic objects with suprastructures [8-13]. The availability of miktoarm stars has facilitated studies in many fields of polymer physics and particularly in block copolymer self-assembly in selective solvents, in bulk, or on surfaces [14].

The synthesis of star-shaped polymers is generally achieved by one of two approaches; the ‘‘arm-first route’’ in which the polymer arms are coupled to a multifunctional coupling agent and the ‘‘core-first route’’ based on a multifunctional core as initiator. However, well-defined miktoarm star polymers are generally much more difficult in synthesis than the corresponding regular stars with the same arms because two or more quantitative nature of reactions and the isolation of intermediate polymers during the synthesis are often required.

Previously, miktoarm star polymers have been prepared by living ionic procedures [6]. However, the synthetically demanding nature of this approach and its lack of compatibility with a variety of functional groups and stringent reaction conditions, such as high sensitivity to CO_2 and moisture have limited the applicability of this strategy.

In contrast, free radical polymerization is more tolerant to protic impurities and is capable of polymerizing a vast variety of vinyl monomers. However, because of slow initiation and fast radical-radical termination reactions, the resulting materials are polydisperse, and the control over molecular weight and functionality is very difficult. Controlled/“living” radical polymerization (CRP) combines the advantages of living ionic polymerization and conventional free radical polymerization. It can produce polymers with well-controlled structure and functionality under mild reaction conditions. Currently, there is no truly living radical polymerization process. The strategy to achieve system’s “livingness” is to temporarily and frequently shield radical active centers from termination and other side reactions while allowing monomer insertions. Mechanistically, the most distinguishable difference between controlled/“living” radical polymerization and conventional free radical polymerization is the presence of a reversible activation/deactivation process. This process is the key factor in determining the livingness and control of a radical process.

Controlled polymerization systems have attracted great attention in polymer science over the past decade for providing simple synthesis of well-defined polymers. The importance of these systems can be seen from the enormous number of scientific papers published every year in leading journals in the fields of polymer and material science. In the past 20 years, several controlled/“living” radical polymerization methods were discovered. Among them, nitroxide-mediated radical polymerization

[15] and atom transfer radical polymerization [3, 4] are the two most successful and promising CRP techniques for the synthesis of well-defined, low-polydispersity polymers and the fabrication of novel functional materials.

In addition, controlled ring-opening polymerization (ROP) has found wide applications in the polymerization of lactones and lactides.

One efficient method to prepare miktoarm star polymer is to employ the combination of several controlled/‘‘living’’ radical polymerization methods by employing miktofunctional initiators (multifunctional initiator having at least two different functional groups).

This thesis focused on the designation of novel miktofunctional initiators and their use in the synthesis of well-defined miktoarm star polymers by combination of controlled/“living” polymerization techniques. This approach enables to combine very different types of monomers into one polymeric structure by a one-pot or sequential two-step method.

2. THEORETICAL PART

2.1 Star Polymers

Polymer properties are influenced by their structure and topology. Therefore, the synthesis of complex macromolecular architectures to control polymer properties is an ongoing field of study in polymer science. Branching in polymers is a useful structural variable that can be used advantageously to modify polymer physical properties and the processing characteristics as a result of changing the melt, solution, and solid-state properties of polymers [16]. It has been shown that branching results in a more compact structure in comparison to linear polymers of similar molecular weight, due to their high segment density, which affects the crystalline, mechanical, and viscoelastic properties of the polymer. A branched polymer structure was described as a nonlinear polymer comprised of molecules with more than one backbone chain radiating from branch points (junction points; atoms or small group from which more than two long chains emanate) [17]. *Star polymers* constitute the simplest form of branched macromolecules where all the chains as arm segments of one molecule are linked to a centre, which is called the core (Fig. 2.1). The core of the star polymer can be composed of a multifunctional low molar mass compound [18-21], a dendrimer [22], a hyperbranched polymer [23, 24], an arborescent structure [25] and a crosslinked microgel [26, 27]. When the core is big

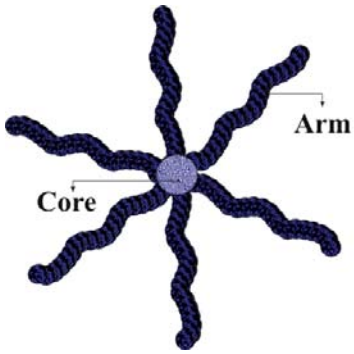


Figure 2.1 Illustration of a symmetric (regular) star polymer.

enough, the stars obtained are called core-shell structures. They exhibit interesting properties, especially when the chemical differentiation between internal and external parts occurs. There are two general types of star polymers:

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

(b) Asymmetric star polymers, which are a special class of stars that is characterized by an asymmetry factor compared to the classical symmetric stars, represented as A_nB_m. The following categories of asymmetric stars are defined in the literature [6, 7, 28]:

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

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

-stars with topological asymmetry: The arms of the star are block copolymers that may have the same molecular weight and composition but differ with respect to the polymeric block that is covalently attached to the core of the star. The schematic representation of these structures is depicted in Figure 2.2.

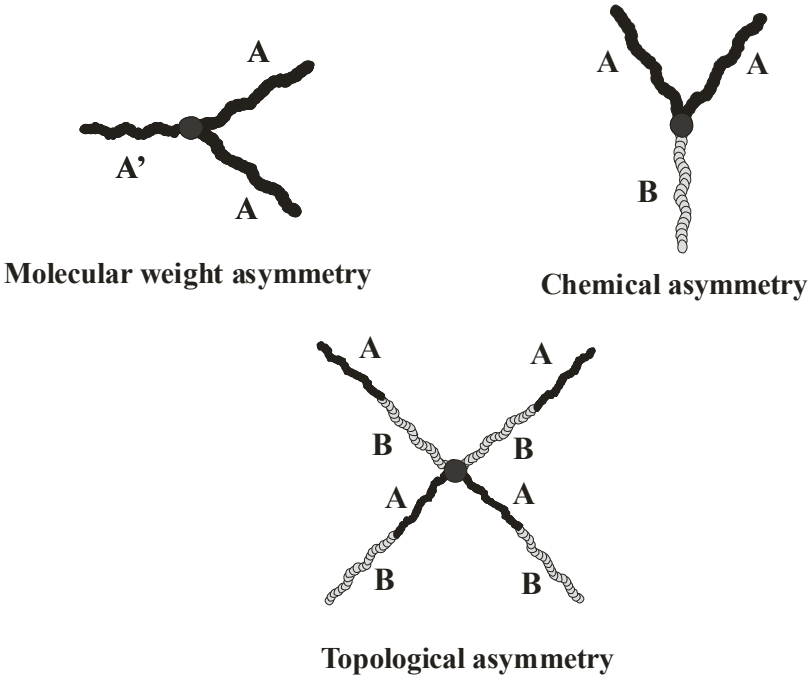


Figure 2.2 The schematic representation of asymmetric star structures.

2.1.1 Preparation of star polymers

Star polymers consist of a central core, from which a given number of chains radiate attracted the attention of scientists so as to they constitute the simplest form of branching. The earliest attempt to prepare a model star polymer was that by Schaefgen and Flory [29]. They were able to synthesize four- and eight-armed polyamide stars by condensation polymerization of with either a tetrafunctional acid (cyclohexanone tetrapropionic acid) or an octafunctional acid (dicyclohexanone octapropionic acid) as multifunctional reactants.

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

I. One polymer is formed for each initiator molecule, so that the number average molecular weight of polymers or block segments can be predicted from the reaction stoichiometry. Multifunctional initiators with functionality n can form stars with n arms.

II. If the rate of initiation is rapid or competitive with the rate of propagation, polymers (precursor arms) with narrow molecular weight distributions are formed [30].

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

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

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

Although a variety of mechanistic types of living chain reaction polymerization have been developed [31] such as cationic, group transfer, or living ring opening metathesis polymerization for the synthesis of star-shaped polymers, until recently anionic polymerization was one of the best methods to obtain well-defined star-

shaped macromolecules of predetermined branch molar mass. However, in recent years there has been rapid growth in the area of growing controlled/ "living" radical polymerizations (CRP), which have some advantages over anionic polymerization, in that they do not require rigorous experimental conditions and are applicable to a wide range of monomers. The detailed historical background regarding the basic concepts of CRP will be given in the following sections of this thesis. First, the general methods for the synthesis of star-shaped polymers will be described based on living anionic polymerization. There are three general synthetic methods for the preparation of star-shaped polymers. These methods have been based on two approaches: arm-first and core-first.

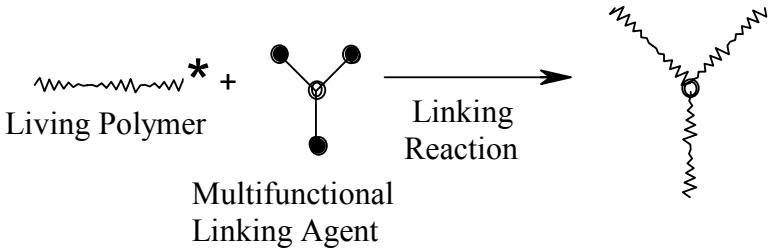
[1] end linking with multifunctional linking agent (arm-first)

[2] use of multifunctional initiators (core-first)

[3] use of difunctional monomers (arm-first)

2.1.1.1 End linking with multifunctional linking agent (arm-first method)

In the first method, referred to as the "arm-first" method, monofunctional living chains of known length and low polydispersity are used as precursor. Subsequently, the active sites located at chain end are reacted with a compound carrying a number of appropriate reactive functions, whereupon chemical links are formed. The number of arms corresponds to the functionality of the linking agent as shown in (2.1). The precursor chains become the star branches, and the linking agent becomes the core.



(2.1)

The main advantage of this method is that the arms of the resulting star polymer are well-defined because the precursor arms can be characterized independently from the star. Because of the well-defined arms, the number of arms can be readily determined by measuring the molecular weight of the star. In principle, a variety of well defined, star polymers with different numbers of arms can be prepared using this methodology by varying the functionality of the linking agents. Disadvantages of the method can be considered the sometimes long time required for the linking reaction

and the need to perform fractionation in order to obtain the pure star polymer, since in almost all cases a small excess of the living arm is used in order to ensure complete linking.

A wide variety of linking agents have been used for the preparation of star polymers via anionic polymerization [30]. The most important of those are chlorosilanes [32] and the chloromethyl [33] or bromomethyl benzene derivatives [34]. However, linking reactions involving polyfunctional alkyl halides are complicated by side reactions such as elimination and metal-halogen exchange that lead to compositional heterogeneity. In contrast, the linking reactions of living polymers with the chlorosilanes proceed without any side reactions. The most common example is the reaction of polymeric organolithium compounds (PLi) with multifunctional electrophilic species such as silicon tetrachloride ($SiCl_4$) as shown in 2.2.

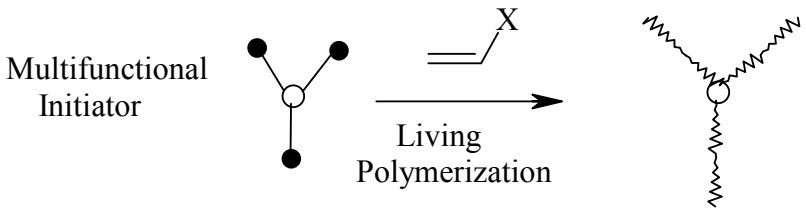
$$4PLi + SiCl_4 \longrightarrow SiP_4 + 4LiCl \qquad (2.2)$$

Although this linking reaction is not complicated by side reactions, the efficiency of the linking reaction depends on the steric requirements of the linking agent and the living macromolecular chain end. The linking efficiency can be improved by separating the Si-Cl groups by spacers, such as methylene groups, and/ or by end-capping the living chains with a few units of butadiene in order to reduce the steric hindrance and facilitate the linking reaction.

2.1.1.2 Use of multifunctional initiators (core-first method)

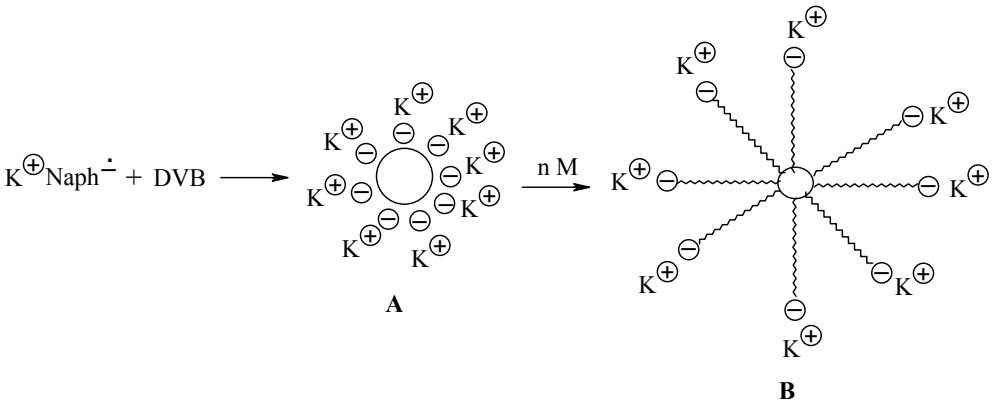
The “arm-first” methods are efficient at synthesizing well-defined star polymers. Difficulty arises, however, in the functionalization of the outer chain ends, which is only possible through the use of functional initiators to generate the precursor chains [35]. Living polymerization using homogeneous, multifunctional initiator of functionality *n* can, in principle, form a star-branched polymer with *n* arms (2.3) and low-degree of compositional heterogeneity among the arms. There are several requirements that a multifunctional initiator has to fulfill in order to produce star polymers with uniform arms, low molecular weight distribution, and controllable molecular weights. All the initiation sites must be equally reactive and have the same rate of initiation. Furthermore, the initiation rate must be higher than the propagation rate. Only a few multifunctional initiators satisfy these requirements. The high chain

segment density in a growing star-branched molecule exacerbates complications arising from chain end/chain end interactions such as aggregation of ionic species, oxidation-reduction reactions of organometallic centers, and bimolecular termination reactions. Complications often arise from the insolubility of these initiators, due to the strong aggregation effects. The steric hindrance effects, caused by the high segment density, causes excluded volume effects.



(2.3)

As a result of these problems, few well-defined multifunctional systems are available. The use of divinyl benzene (DVB) as a multifunctional initiator was first demonstrated by Burchard and co-workers [18]. DVB was first polymerized using butyllithium in benzene to form soluble microgels of high molecular weight. These microgels with their attendant anionic groups were used as multifunctional initiators to polymerize monomers such as styrene. This method has been extended by Rempp and coworkers [36, 37] as a general "core-first" method to prepare star polymers, as shown in (2.4).

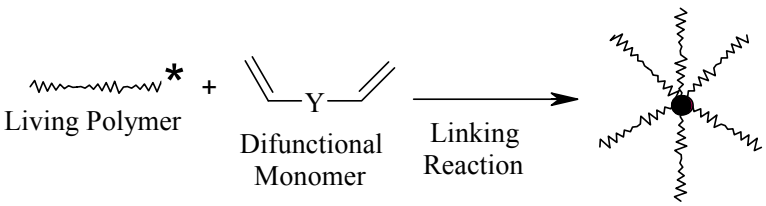


(2.4)

The "plurifunctional" metalorganic initiator (**A**) was prepared by potassium naphthalene-initiated polymerization of DVB in tetrahydrofuran (THF) at -40°C with [DVB]/[K^+] ratios of 0.5-3. Within the prescribed stoichiometric ratios, star polymers (**B**) with arm functionalities varying from 8 to 42 were reported. The polydispersities of resulting products were quite broad as expected for this type of process and were attributed primarily to a random distribution of core sizes and functionalities.

2.1.1.3 Use of difunctional monomers (arm-first method)

In this method, a living polymer precursor is used as initiator for the polymerization of a small amount of a suitable difunctional monomer, such as ethylene glycol dimethacrylate (EGDM) or DVB [38, 39]. Microgel nodules of tightly cross-linked polymer are formed upon the polymerization. These nodules serve as the branch point from which the arms emanate. The functionality of the stars prepared by this method can be determined by molecular weight measurements on the arms and the star product, but it is very difficult to predict and control the number of arms. The number of branches incorporated in the star structure is influenced by many parameters. The most important is the molar ratio of the difunctional monomer over the living polymer. The functionality of the star increases by increasing this ratio. Other parameters that influence the number of branches are the chemical nature



(2.5)

(polystyrene, polydiene etc.), the concentration and the molecular weight of the living polymer chain, the temperature and the time of the reaction, the rate of stirring, the composition of the isomers in the case of DVB (ratio of *meta*, *ortho*, and *para* isomers), etc. Another disadvantage of this procedure is that the final products are characterized by a distribution in the number of the arms incorporated into the star structure. Consequently, the number of the arms determined experimentally by molecular weight measurements is an average value. It is obvious that although this method is technologically very important and can be applied on an industrial scale, it is less suitable for the preparation of well-defined stars.

2.1.1.4 Synthesis of star-block copolymers

Star-block copolymers are star polymers in which each arm is a diblock (or a triblock) copolymer (Fig. 2.3). They can be prepared by all the methods described earlier. The best way involves the linking reaction of a living diblock copolymer, prepared by sequential anionic polymerization of the two monomers, with a suitable linking agent.

Using this method and chlorosilane linking agents, Fetters and collaborators synthesized star-block copolymers (polystyrene-*b*-polyisoprene)$_n$, where n=4, 8, 12, 18 [40, 41].

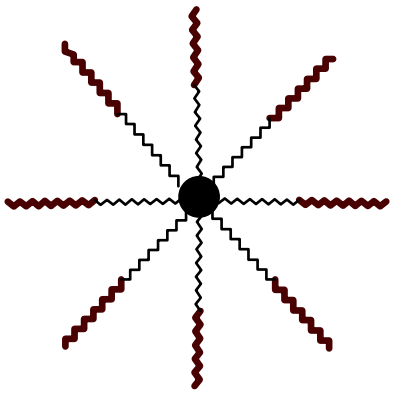


Figure 2.3 Schematic representation of star-block structure

2.1.2 Miktoarm star polymers

The term "miktoarm" has been attributed to star polymers with three or more arms, at least two of which are molecularly and chemically different (chemical asymmetry). Miktoarm is a combination of Greek miktos, meaning "mixed", and arm. This term was proposed by Hadjichristidis in 1992 [42] and was widely accepted by the other research groups all over the world. Although, the terms heteroarm star and A_nB_m-type star were also used for these types of star structures, miktoarm star (μ-star) will be used throughout this work to refer to star polymers with corresponding structure.

The most common examples of miktoarm stars are the A_2B, A_3B, A_2B_2, A_nB_n ($n > 2$) and ABC types. Other less common structures, like the ABCD, AB_5, and AB_2C_2 are also available (Fig. 2.4).

2.1.3 Synthesis of miktoarm star polymers by anionic polymerization

2.1.3.1 Chlorosilane method

The synthesis of AB_2 type miktoarm star polymer was first reported by Mays [43]. A and B represents polystyrene (PS) and polyisoprene (PI), respectively. The living PS chains were reacted with an excess of methyltrichlorosilane to produce the monosubstituted macromolecular linking agent (2.6). The steric hindrance of the living polystyryllithium and the excess of the silane led to the absence of any coupled byproduct.

The excess silane was removed and then a slight excess of the living PI chains was added to produce the miktoarm star $PS(PI)_2$. Excess PI was then removed by fractionation.

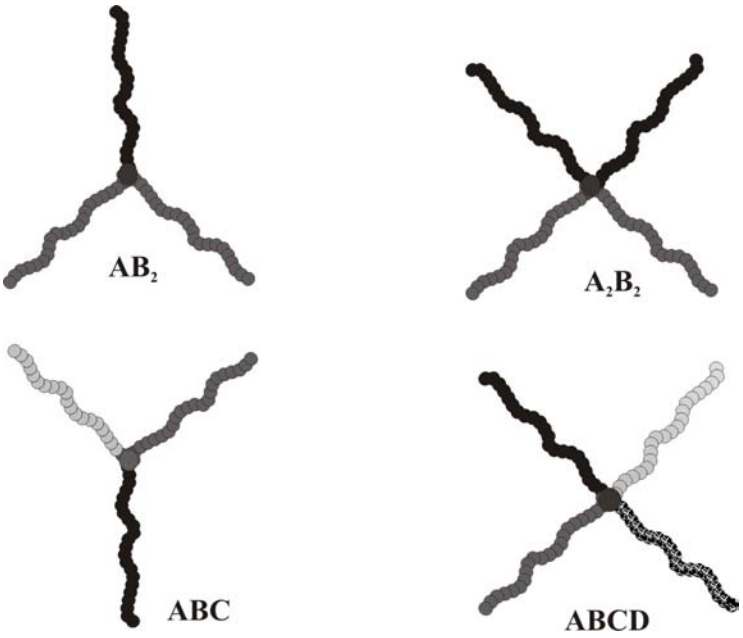


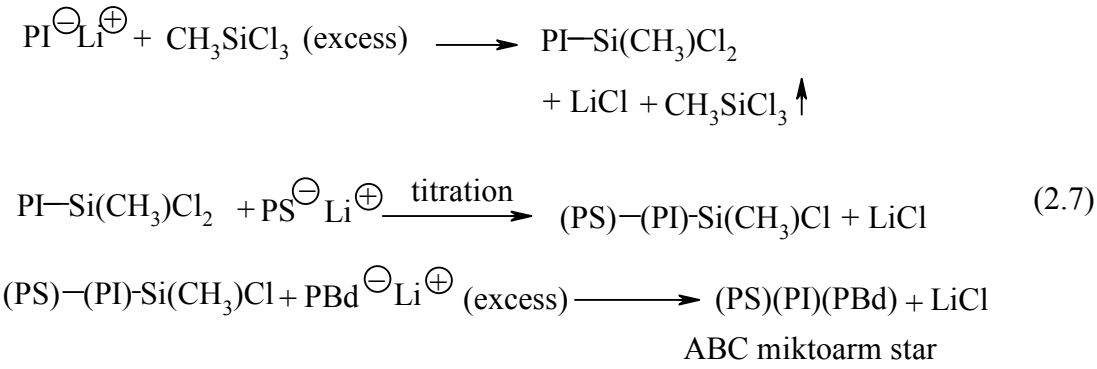
Figure 2.4 Illustration of miktoarm star polymers structures where each letter represents different polymeric arms.

$$\overset{A}{\sim\!\sim}Li + CH_3SiCl_3 \text{ (excess)} \longrightarrow \overset{A}{\sim\!\sim}Si(CH_3)Cl_2 + LiCl + CH_3SiCl_3\uparrow$$

$$\overset{A}{\sim\!\sim}Si(CH_3)Cl_2 + \overset{B}{\sim\!\sim}Li \longrightarrow AB_2 \qquad (2.6)$$

AB_2 miktoarm star

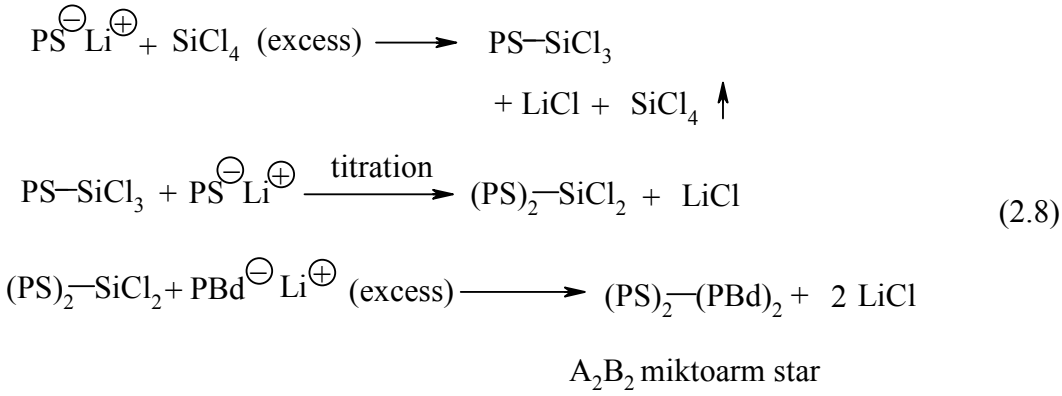
The method was further developed by Hadjichristidis and coworkers [44] to all possible combination of AB_2 μ-stars, where A, B is PS, PI or polybutadiene (PBd). Furthermore, they have prepared $PS(PI)_3$, AB_3 μ-stars [45]. ABC miktoarm stars containing PS, PI and PBd were synthesized by Hadjichristidis and coworkers [42] according to the procedure shown in 2.7. The first step involved the addition of living PI arms to excess $SiMeCl_3$, followed by elimination of the excess $SiMeCl_3$ and titration of PI-$Si(CH_3)Cl_2$ with the living PSLi arms. Finally, excess living PBd arms reacted with the resulting $(PI)(PS)Si(CH_3)Cl$ to give the miktoarm star (PS)(PI)(PBd).



(2.7)

More recently, Hadjichristidis et al. [46] prepared ABC miktoarm stars of PS, PI and PDMS with the same methodology. In a slightly modified procedure, the same group [47] prepared also ABC miktoarm stars of PS, PI and PMMA.

Another most common type of miktoarm star polymers is A_2B_2 type μ-stars. The synthesis of the PS_2PBd_2 stars was performed by Iatrou and Hadjichristidis [48] using the reaction sequence outlined in 2.8. The living PS chains reacted with a large excess of tetrachlorosilane ($SiCl_4$), which is the linking agent to produce the trichlorosilane endcapped PS (PS-$SiCl_3$). The excess silane was evaporated on the vacuum line. The second living PS arm was incorporated to the macromolecular chains were reacted with $SiCl_4$ in a molar ratio 2:1 for the formation of the two-arm product. The formation of the three-arm product is avoided by the increased steric hindrance of the living PS chain end. Subsequent addition of the living PI chains resulted in the formation of the desired miktoarm star.



(2.8)

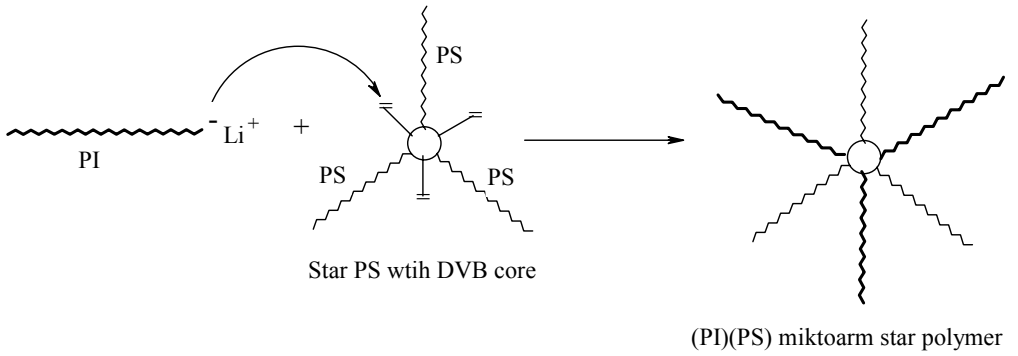
The less common structure of miktoarm star polymer is ABCD type μ-stars in which each letter represents a different block. Only two examples of the synthesis of ABCD miktoarm star are reported in the literature [48, 49]. The first one consists of four different arms, PS, PI, PBd, and poly(4-methylstyrene) (P4MeS). A step by step

incorporation of the branches was adopted. The synthetic procedure involved two titration steps. Therefore, the order of linking of the different branches plays an essential role in controlling the reaction sequence. The presence on the same nodules of chains exhibiting different chemical structures leads to original solution properties. The second example of ABCD miktoarm star polymer with four incompatible arms, PS, PI, poly(dimethylsiloxane) (PDMS) and poly(2-vinylpyridine) (P2VP) was synthesized more recently by Hadjichristidis [49]. Roovers et al. [50] have examined in detail the solution properties and compared the specific behaviour of these miktoarm star polymers to linear diblock copolymers.

2.1.3.2 Divinylbenzene method

The DVB method can be applied for the synthesis of miktoarm stars of the type A_nB_n. It is a three-step procedure starting from the synthesis of the living chains A. These living chains initiate the polymerization of a small quantity of DVB, leading to the formation of a living star polymer carrying within its core a number of active sites equal to the number of arms that have contributed to its formation. During the third step, these active sites are used to polymerize the monomer B, thus producing A_nB_n.type miktoarm star. This method for the synthesis of miktoarm stars was first disclosed by Funke [27, 51] and then extended and improved by Rempp et al [52].

Funke [27, 51] started from poly (*tert*-butylstyrene) of low molar mass made with *sec*-butyllithium in a cyclohexane solution. A small amount of DVB was then added to generate the living cores. Subsequently, second-generation branches of polydiene or polystyrene were grown from these living cores. Funke has studied the influence of the isomer of DVB and the diameter of the particles and has extended that reaction other difunctional monomers such as diisopropenylbenzenes. Recently, Taromi and coworkers [53] reported that star polymers obtained from living anionic PS chains and a small amount of divinyl benzene (DVB) would have many unreacted vinyl groups in the gel core, and that these vinyl groups could be attacked by carbonions of another kind of polymer chain, forming miktoarm star polymers with A_nB_m type. In his work, linear polyisoprene chains were used to attack the double bonds existing in the poly(divinyl benzene) cores of polystyrene star polymers, so that a miktoarm star polymer with polystyrene and polyisoprene arms was synthesized as shown in (2.9).



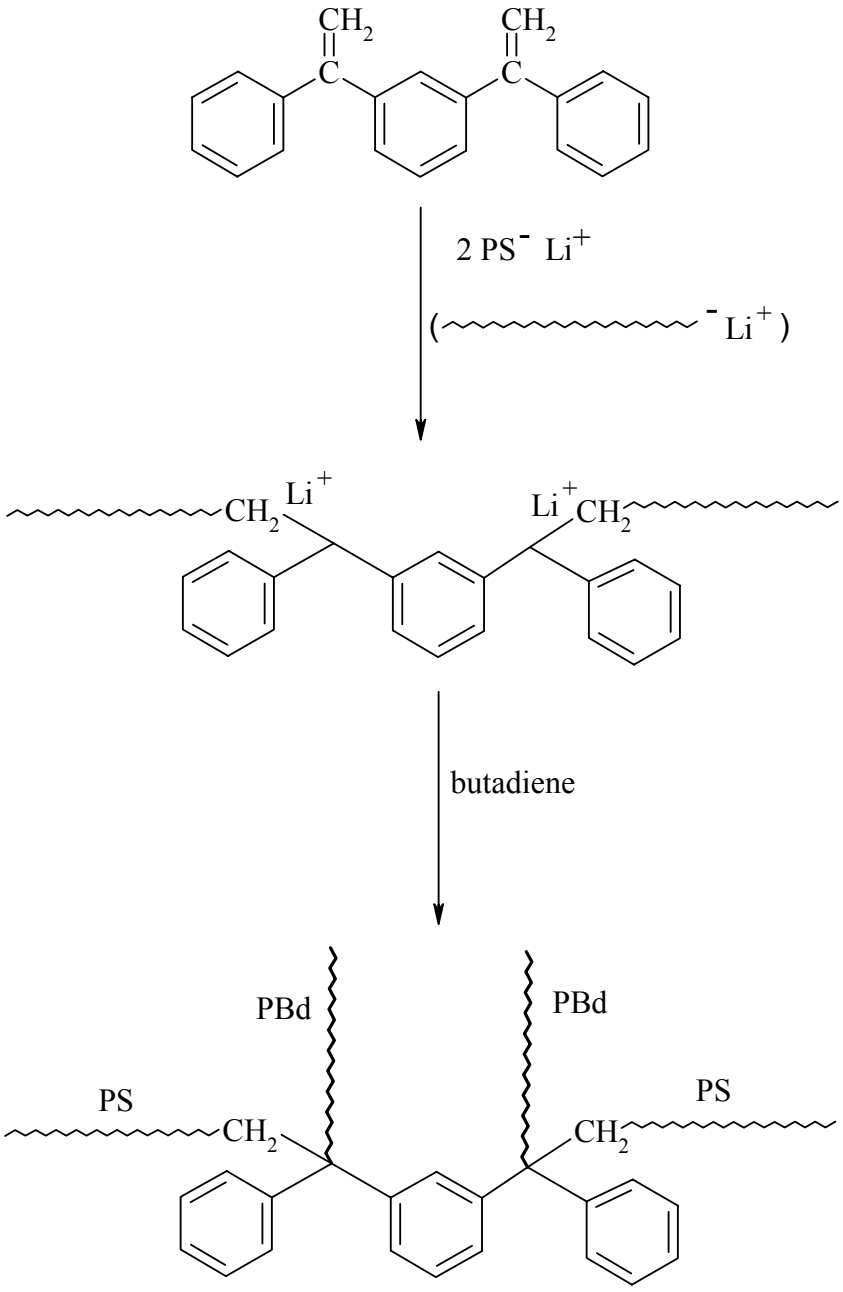
(2.9)

2.1.3.3 Diphenylethylene derivative method

The method developed by Quirk [30, 54] to prepare well-defined asymmetric star polymers is based on the use of 1,1-diphenylethylene derivatives that are nonhomopolymerizable monomers. This reaction involves first the synthesis of linear precursor with the active chain end coupled with 1,3-bis(1-phenylvinylbenzene) or 1,3-bis(1-phenylethenyl)benzene (MDDPE) to form a living dianion. When butadiene is added, polymerization of second branches occurs, yielding the desired miktoarm star polymer (2.10).

Dumas et al. [55] have applied dipenylethylene (DPE) methodology in the preparation of ABC type miktoarm star polymer exhibiting on the same nodules PS, PMMA, and poly(ethylene oxide) (PEO) or ε-caprolactone chains. Dumas et al. [56] also synthesized a series of (PS)(P*t*BuMA)(PEO) miktoarm star terpolymers where P*t*BuMa is poly(*tert*-butyl methacrylate) with the same methodology.

Hadjichiristidis [47] has also taken advantage of that coupling reaction with DPE derivatives to prepare ABC miktoarm star polymers exhibiting PMMA branches, since chlorosilane chemistry does not apply efficiently to the synthesis of star polymers containing PMMA branches (living PMMA does not react with chlorosilanes). In an extension of the methodology involving DPE derivatives, Hirao and collaborators [57, 58] reported the preparation of chain-end and in-chain functionalized polymers with a definite number of chloromethylphenyl or bromomethylphenyl groups as well as their utilization in the synthesis of miktoarm star polymers.



(2.10)

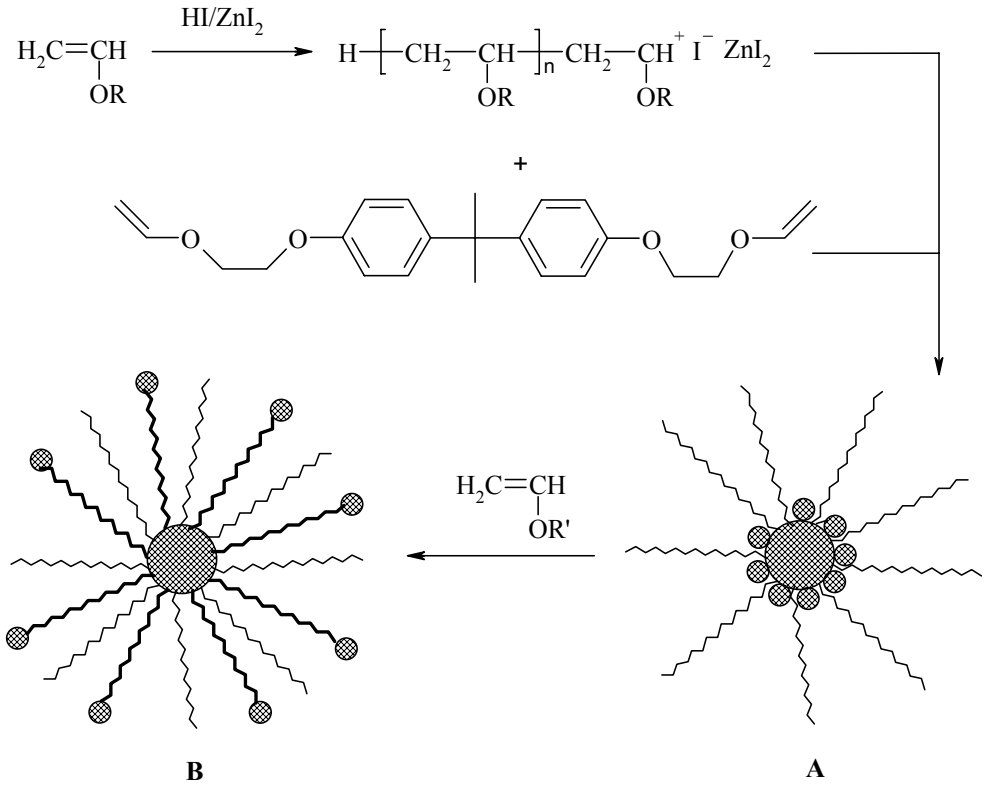
A_2B_2 miktoarm star polymer

2.1.4 Synthesis of miktoarm star polymers by living cationic polymerization

It was a major challenge to synthesize stars via cationic polymerizations until the discovery of living polymerization of isobutylene and vinyl ethers during the early 1980s.

Amphiphilic star polymers with heteroarms of vinyl ethers can be prepared on the basis of living cationic polymerization [59], where living polyvinyl ether chains,

produced with the hydrogen iodide/Lewis acid initiating system (HI/I_2, HI/ZnI_2, etc.), undergo linking reactions via a difunctional vinyl ether into a star-shaped polymer as illustrated in 2.11. The initially formed star polymer (first star; **A** in 2.11) may still carry living growing sites within its microgel core.



(2.11)

These "core" living sites may be used to initiate a second-phase living polymerization to grow new arms from the core to give a "second-star" polymer **B** where the number of arms per molecule is doubled from the star. When a second monomer differs from the first polymerized monomer, a miktoarm star polymer may be obtained where different arms are attached to a single core.

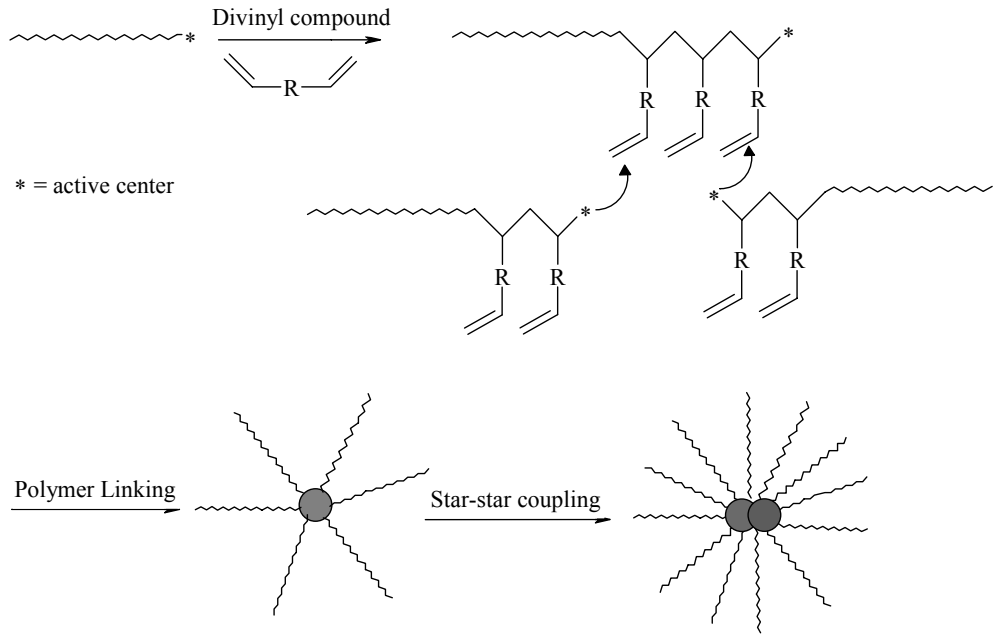
2.1.5 Synthesis of miktoarm star polymers by combination of controlled polymerization methods

It was a major challenge to synthesize well-defined complex macromolecular architectures such as block and graft copolymers and star polymers via radical polymerizations until the discovery of controlled/"living" radical polymerization (CRP) techniques. Although these architectures have been prepared mainly by truly living systems (anionic, cationic), the radical polymerization method is more convenient because it does not require strict purification of monomers and solvents,

and allows the presence of functional groups. The combination of various controlled polymerization techniques to produce novel polymer architectures is quite important because of the synthetic limitations of the pure living systems. CRP combines the advantages offered by truly living systems with the experimental easiness characterizing free radical processes.

The synthesis of miktoarm star polymers by controlled polymerization methods can be accomplished by those explained for the synthesis of miktoarm star polymers by anionic polymerization. Although miktoarm star polymers have been synthesized mainly by the anionic polymerization [7, 6, 28, 31], the recent development in the CRP [3-5, 60, 61] has brought about a drastic change in the synthetic methodology for miktoarm star polymers for the last 5 years [62-94]. They are essentially two approaches to synthesize star polymers by CRP methods: core-first and arm-first method [3-5, 60, 61]. The core first method exploits simultaneous growth from the multifunctional initiators to give star polymers with constant arm number and constant arm length as in living ionic polymerization.

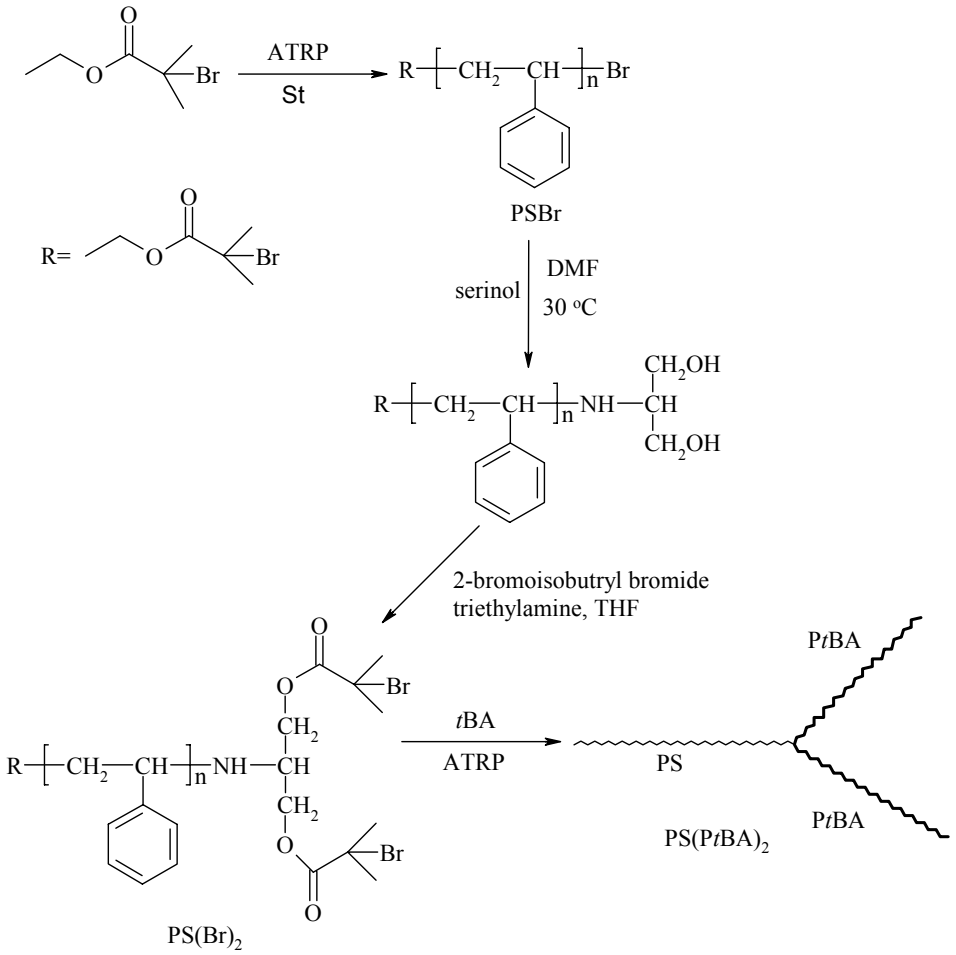
The arm-first approach involves the linking reaction of linear living polymers obtained by CRP with a divinyl compound. This gives a crosslinked gel core and a random distribution of the number of arms per polymer molecule [64, 95-105]. The mechanism of divinyl compound method is shown in 2.12. Firstly, a few units of divinyl reagents add to the reactive macroinitiators (arms) to form short block copolymers with hanging vinyl groups. Then, the reactive macroinitiator chain ends react with the hanging vinyl groups to form a microgel core or add to a sterically accessible star core. Finally, core–core coupling reaction can occur to form a higher-order star polymer. The star polymer thus obtained still carries a number of active sites within its microgel core, which is theoretically equal to the number of incorporated arms of the star polymer. These ‘core’ active sites can initiate the living polymerization of another monomer to grow new arms from the core, yielding a miktoarm star polymer with A_nB_n type. Using this method, miktoarm star polymers have been synthesized also by CRP methods [3, 4, 60, 61]. In the following, the readers can find a historical background for the preparation of miktoarm star polymers based on controlled polymerization methods and combination of those.



(2.12)

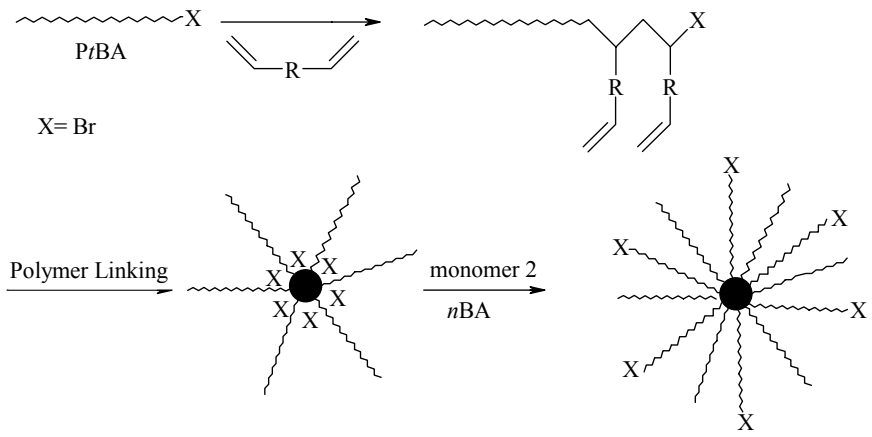
2.1.5.1 Synthesis of miktoarm star polymers by atom transfer radical polymerization (ATRP)

Gnanou and coworkers [69] synthesized AB_2 type miktoarm star polymers by combination of atom transfer radical polymerization (ATRP) and chemical modification of the termini of ATRP derived polymers (2.13). The first step involved the preparation of ω-bromo PS chains by ATRP using ethyl 2-bromoisobutyrate as initiator. Next, the bromo end groups of the resulting PS chains were derivatized into twice as many bromoisobutyrates in order to obtain ω,ω′-bis(bromo)-PS chains. The last step consisted of growing two poly(*tert*-butyl acrylate) (P*t*BA) blocks by ATRP, This methodology enabled to synthesize PS(P*t*BA)$_2$ stars with chemically different PS and P*t*BA arms. They further performed the selective cleavage of *tert*-butyl groups from PS(P*t*BA)$_2$ stars under acidic conditions. This resulted amphiphilic PS(PAA)$_2$ miktoarm stars carrying one hydrophobic PS branch and two ionizable poly(acrylic acid) (PAA) arms.



(2.13)

In 2003, Matyjaszewski reported the synthesis of miktoarm star polymer by arm-first approach using ATRP [106]. The coupling of living P*t*BA arms with DVB and subsequent growth of poly(n-butyl acrylate), PBA arms from the core gave multiarm $(P\textit{t}BA)_n$-$(PBA)_n$ miktoarm star polymer (2.14).

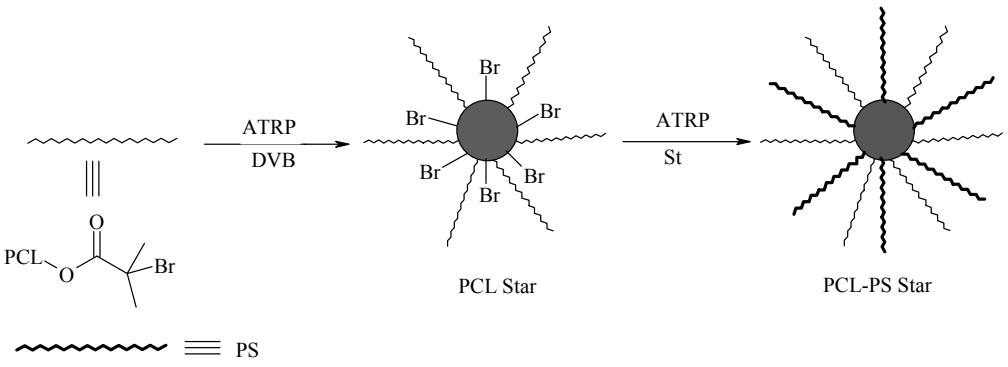


(2.14)

Using the same methodology, Chen and coworkers [76] prepared $(PCL)_n$-$(PS)_n$ miktoarm star polymer by ATRP. For this purpose, they first synthesized PCL star

polymer with a cross-linked microgel core by ATRP of DVB using mono-2-bromoisobutyryl PCL ester as a macroinitiator. Then $(PCL)_n$-$(PS)_n$ miktoarm star polymer was produced subsequently by grafting PS from the core of PCL star polymer in which the initiating groups were inherited from PCL star formation using ATRP as shown in 2.15.

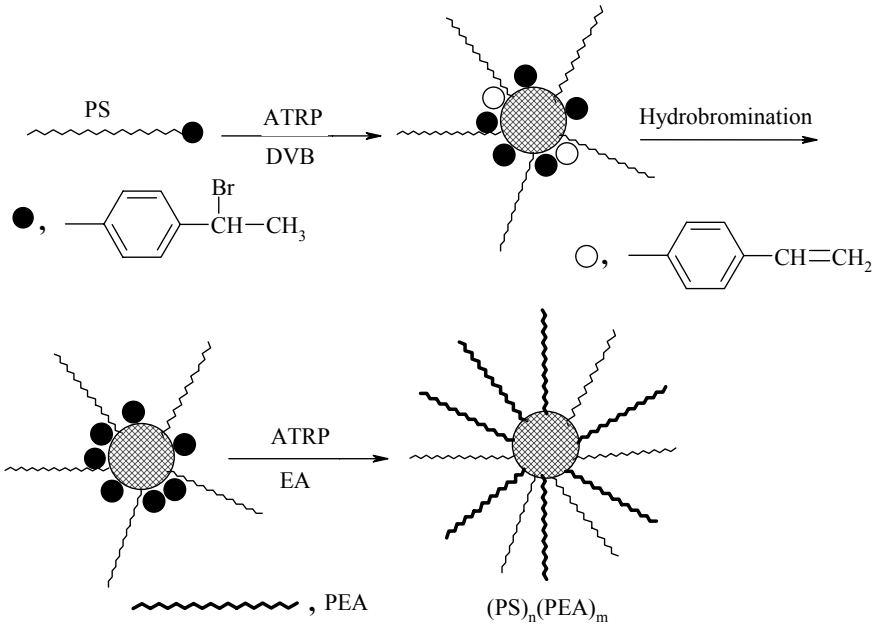
The same group also reported the synthesis of $(PEO)_n$-$(PS)_n$ miktoarm star polymer where PEO is poly(ethylene oxide) using the similar approach [77].



(2.15)

With a slightly different strategy, Wu et al. [78] have been prepared $(PS)_n$-$(PEA)_m$ miktoarm star polymer where PEA represents poly(ethyl acrylate) arms. In their work, star polystyrene PS, was first synthesized by the arm- first method via ATRP using a preformed PS macroinitiator in the presence of DVB. Then, the residual vinyl groups in the gel core were converted to 1-bromoethylbenzene groups by hydrobromination.

Lastly, miktoarm star polymer, $(PS)_n$-$(PEA)_m$, where the arm number of PEA was greater than that of PS, was prepared by ATRP of ethyl acrylate from 1-bromoethylbenzene initiating sites, obtained by both the addition of linear PS macrointiators to vinyl groups of DVB and by hydrobromination of residual vinyl groups (2.16).

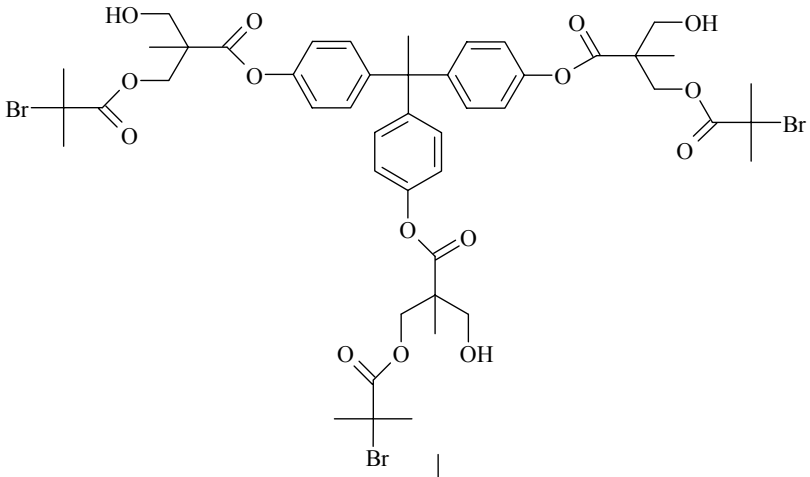


(2.16)

2.1.5.2 Synthesis of miktoarm star polymers by combination of ATRP and ring opening polymerization (ROP)

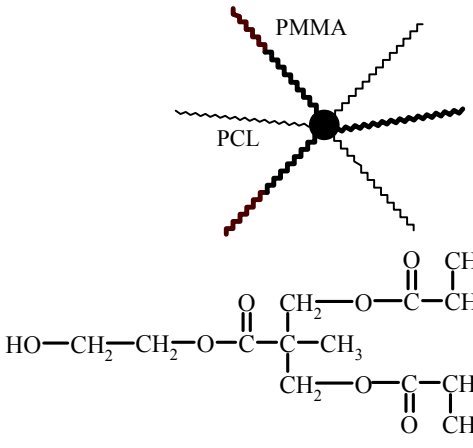
Hedrick and coworkers [65] reported the production of miktoarm star copolymers with alternating PCL and PMMA arms from miktofunctional initators using consecutive ATRP and living ring opening polymerization (ROP) via core-first approach. The key to this technique is the initiator molecule, since it determines the structure of the resulting copolymer. They employed a building block containing initiating sites for both ROP and ATRP (2.17). Coupling of this building block to a multifunctional core leads to a multiarm initator with initiating sites arranged in an alternating fashion for the synthesis of corresponding miktoarm star copolymer as illustrated in 2.17.

The same methodology can also be applied for the preparation of other types of miktoarm star structures such as AB_2 μ-stars by differentiation of the building block. Erdogan et al. [72] have reported the facile synthesis of AB_2 type miktoarm star copolymers with PCL and P*t*BA or PMMA arms by combination of ROP and ATRP processes. They employed a novel miktofunctional intiator (2.18) possessing one initiating site for ROP and two initiating sites for ATRP. The successive ROP and ATRP processes yield the desired AB_2 miktoarm star polymer (2.18).



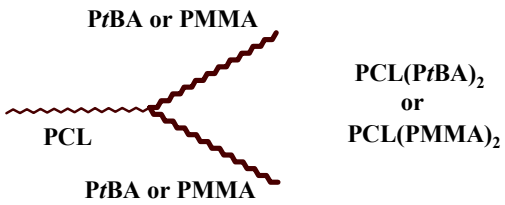
(2.17)

1. ROP (PCL)
2. ATRP (PMMA)



1. ROP (PCL)
2. ATRP (P*t*BA or PMMA)

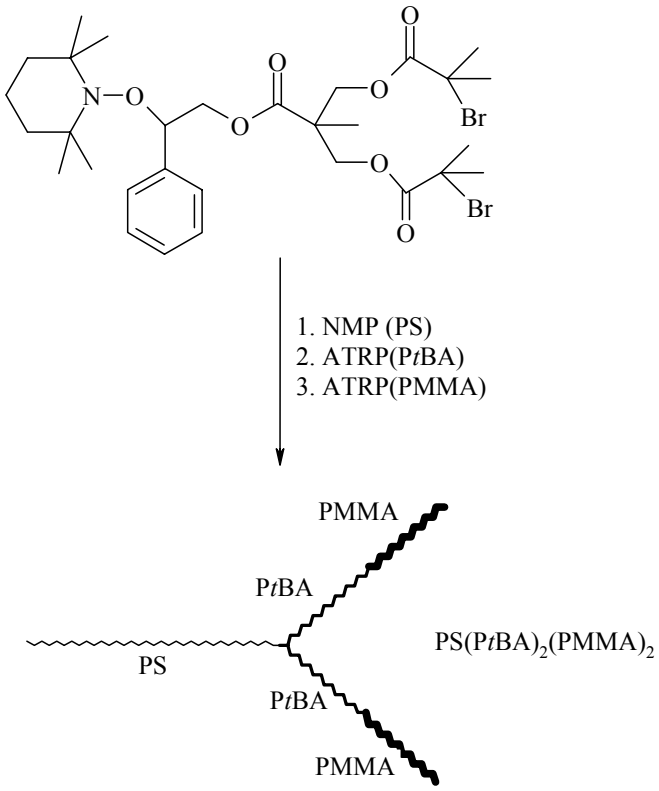
(2.18)



The details of this work will be represented in the results and discussions part of this thesis. The described core-first approach provides another level of control to the preparation of miktoarm star polymers by employing different miktofunctional initiators.

2.1.5.3 Synthesis of miktoarm star polymers by combination of ATRP and nitroxide-mediated radical polymerization (NMP)

Tunca et al. [71] synthesized miktoarm stars of the AB_2C_2 type, where A is PS, B P*t*BA and C is PMMA by using the trifunctional initiator. They used a combination of nitroxide mediated radical polymerization (NMP) and ATRP techniques and a three-step reaction sequence. In the first step, PS macroinitiator with dual ω-bromo functionality was obtained by NMP of styrene in bulk at 125 ºC. This precursor was subsequently used as the macroinitiator for the ATRP of *t*BA in the presence of copper bromide (CuBr) and pentamethyldiethylenetriamine (PMDETA) at 80 ºC, to produce the miktoarm star of the (PS)(P*t*BA)$_2$. This star was the macroinitiator for the subsequent polymerization of MMA, giving the (PS)(P*t*BA)$_2$(PMMA)$_2$ (2.19).

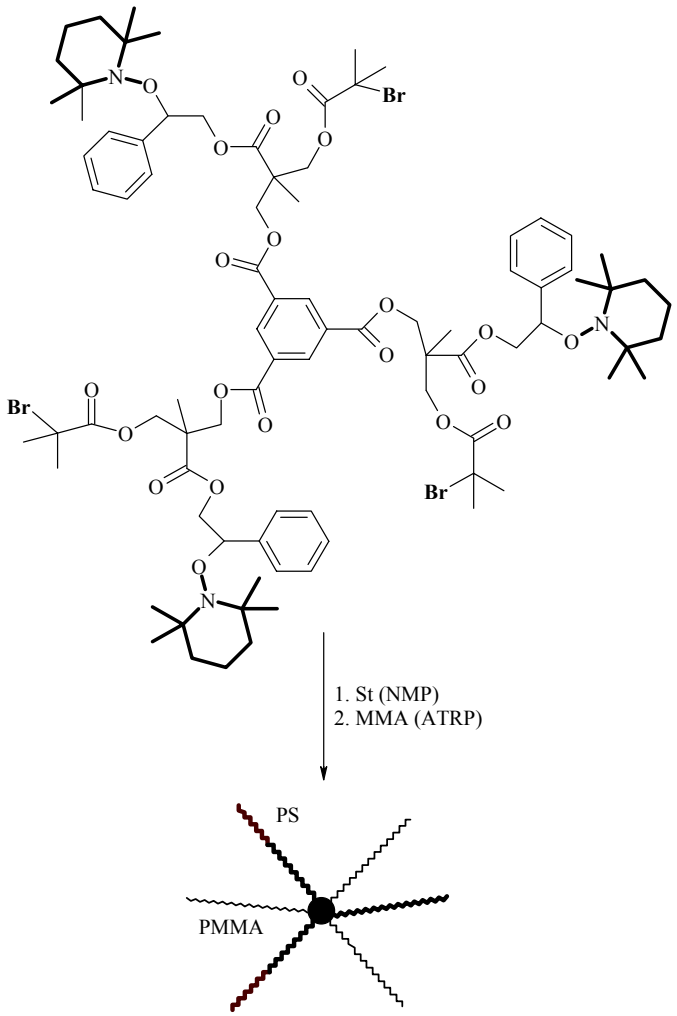


(2.19)

More recently, same group reported the preparation of A_3B_3 type $(PS)_3$-$(PMMA)_3$ miktoarm star polymers via combination of NMP and ATRP routes [92]. They synthesized a novel initiator having initiating sites for both NMP and ATRP and first used in the preparation of A_3 type PS macroinitiator by NMP. Next, using this macroinitiator, the synthesis of A_3B_3 type $(PS)_3$–$(PMMA)_3$ miktoarm star polymers was carried out by ATRP of MMA (2.20). As can be seen in the given studies, the

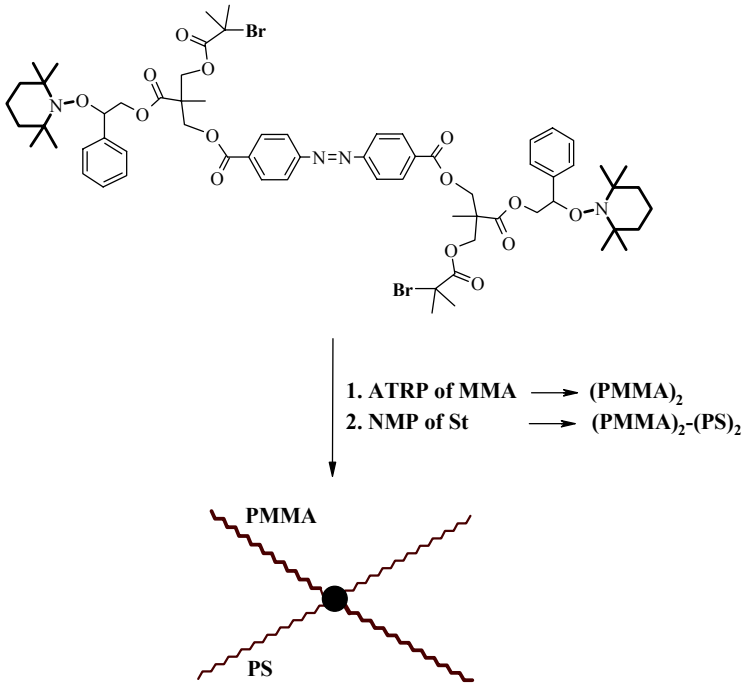
core-first approach does not need any chemical transformation of functional end-groups in order to obtain proper functionality for a succeeding polymerization step.

Using the same approach, Erdoğan et al. [93] prepared a novel miktoarm star copolymer with an azobenzene unit at the core (2.21). For this purpose, first, miktofunctional initiator, 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 thus obtained was used in ATRP of



(2.20)

MMA and NMP of St, respectively, to give A_2B_2 type miktoarm star copolymer, $(PMMA)_2$-$(PS)_2$ with an azobenzene unit at the core. The details of this work will be given in the results and discussions part of this thesis.

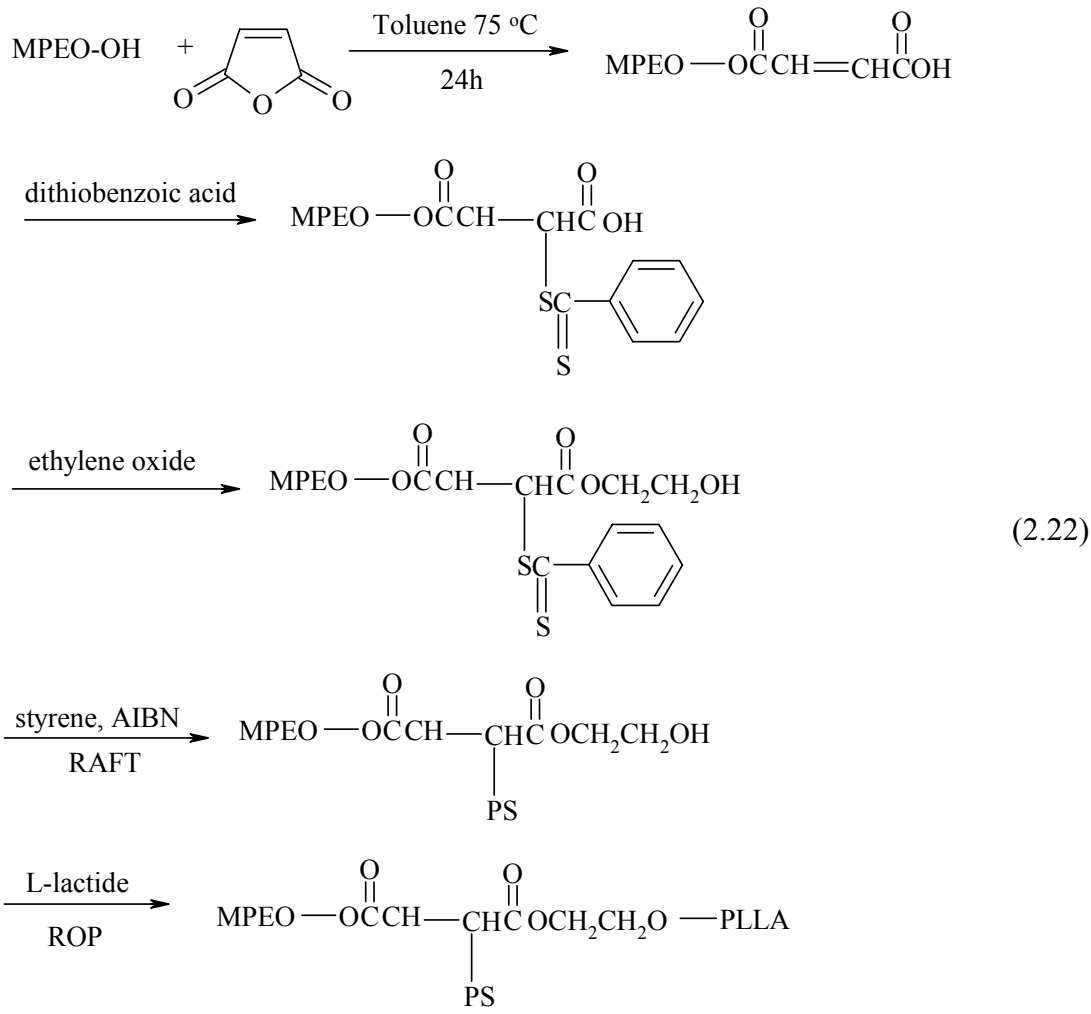


(2.21)

2.1.5.4 Synthesis of miktoarm star polymers by combination of reversible addition-fragmentation chain transfer (RAFT) polymerization and ROP

By combination of reversible addition-fragmentation chain transfer (RAFT) and ROP, Pan et al. [80] synthesized (poly(ethylene oxide) methyl ether)(polystyrene)(poly(L-lactide)((MPEO)(PS)(PLLA)), ABC miktoarm star terpolymers. The synthetic approach involved the reaction of the ω-functionalized hydroxyl group of the poly(ethyleneoxide) methyl ether with maleic anhydride under conditions where only one hydroxyl group could be esterified. The double bond of the maleic group was then reacted with dithiobenzoic acid, resulting a dithiobenzoic terminated MPEO. The second carboxyl group of the maleic anhydride was then reacted with ethylene oxide, leading to the corresponding ester with a free hydroxyl group. The dithiobenzoic group of the MPEO was used for the RAFT polymerization of styrene in THF, at 110 ºC, and 2,2'-azobisisobutyronitrile (AIBN) as the initiator. Finally, the hydroxyl group attached at the junction point of the diblock copolymer was used as the initiating site for the ROP of L-lactide, in the presence of Stannous octanoate, $Sn(Oct)_2$ in toluene at 115 ºC (2.22).

Furthermore, Pan et al. [70] by using a combination of RAFT and cationic ROP, synthesized a series of [poly(methyl methacrylate)][poly(1,3-dioxepane)](polystyrene), ABC miktoarm star polymers.

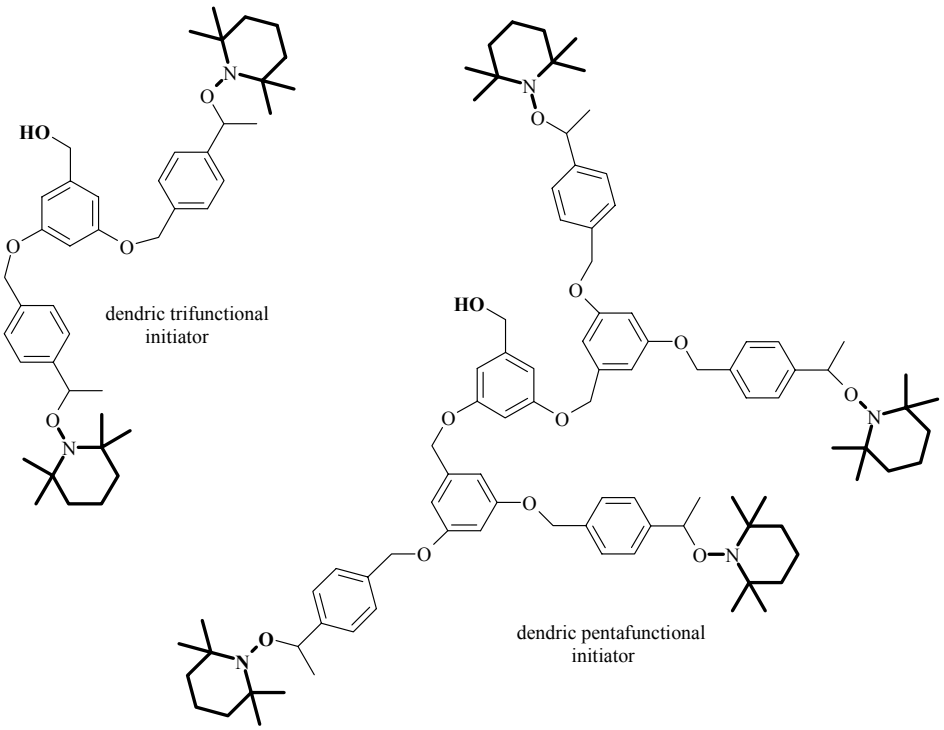


(2.22)

2.1.5.5 Synthesis of miktoarm star polymers by combination of ROP and NMP

The syntheses of well-defined AB_2 and AB_4 type miktarm star copolymers have been performed using dendric tri- and penta- functional initiators (2.23) via combination of ROP of ε-CL and NMP of styrene by Miura and coworkers [88, 89].

They first prepared two kinds of dendric initiators having one benzylic hydroxyl and two or four TEMPO-based alkoxyamine moieties. By using them, they performed ROP of ε-CL to give PCL macroinitiators carrying two or four alkoxyamine moieties. NMP of styrene from the preformed PCL macroinitiators gave corresponding miktoarm star polymer.



(2.23)

2.1.5.6 Synthesis of miktoarm star polymers by combination of ROP, NMP and ATRP

As can be defined previously, ABC miktoarm star polymers are molecules composed of three different polymer chains emanating from a central junction point. The synthesis of ABC miktoarm star polymers by combination of three different controlled polymerization methods either radical or nonradical provides a fundamentally synthetic methodology. Tunca [73] and Zhao [74] reported independently, in 2004, that a novel trifunctional initiator bearing a hydroxy group (for ROP), tertiary bromide (for ATRP) and TEMPO (for NMP) could be used in the preparation of ABC miktoarm star polymer composed of PCL, P*t*BA [73] or PMMA [74] and PS arms.

The thermal properties of (PCL)(PS)(P*t*BA) miktoarm star polymers have been also investigated [73]. The synthetic strategy followed for the preparation of (PCL)(PS)(P*t*BA) and (PCL)(PS)(PMMA) miktoarm stars will be represented in the results and discussions part of this thesis.

2.1.6 Applications of star polymers

Polymers with star-shaped structures widely used as model branched polymers to evaluate the influence of branching on the properties of polymers [2, 107-109]. Since the properties of star polymers may be quite different in bulk, melt, and solution from those of linear polymers with the same molecular weight, they have been widely investigated from both synthetic and theoretical points of view [17, 30, 38, 110-113].

Star polymers are generally used instead of the same amount of linear polymers with same molecular weight to reduce the viscosity of polymer solutions. For example, star polymers are purposely added to paints and coatings to increase the solid content of the latter without affecting their viscosities or their spraying properties [114]. The presence of branching causes substantial changes in the solution and melt properties of polymers. Star-branched polybutadienes are produced for their reduced cold flow and improved storage [42]. Deformation of a polymer by continuous shearing produces non-equilibrium states that persist longer in branched polymers than in linear polymers [115-117]. In these non-equilibrium states, polymer have lower viscosities, lower elasticity as measured by die swell, and produce less surface roughness on processing. In solution, branched polymers are less sensitive to mechanical degradation than linear polymers [118]. This degradation occurs preferentially at the branching point and has little effect on the viscosity of the solution [119], it is a desirable property that is used in viscosity improvers for lubricating oil [120].

Recently, miktoarm star polymers have gained much attention due to its unique properties arising from their arm segments differ in molecular weight and chemical composition. Such star polymers are expected to exhibit interesting and unique properties originating from possible heterophase structures, in addition to branching architectures. For example, heterophase dissimilar structures are usually phase-separated at molecular level to promote self-assembly, thereby facilitating the fabrication of many new nanoscopic ordered suprastructures and characteristic nanomaterials, opening the possibility for the development of sophisticated nano-devices [8-13, 44, 45, 50, 121-141]. Therefore, the synthetic development of star polymers is now associated with the rapid growth of nanotechnology.

2.1.7 Characterization of star polymers

Star polymers are very compact in molecular dimensions and exhibit high segment densities in solution when compared to their linear homologs of the same molecular weight. This implies that the hydrodynamic volume of a star polymer is much smaller than that of a linear, randomly coiled macromolecule of the same molecular weight [38, 110, 142]. Therefore, the apparent molecular weight of star polymers, as obtained from standard size exclusion chromatography (SEC) analysis after calibration with linear homologous standards, are much lower than their true molecular weights [142, 143]. Also, the molecular weight distribution (MWD) of the sample with high arm functionality may be underestimated, because the hydrodynamic volume of a star polymer is found to become independent of the number of branches, f, especially when f exceeds five or six [144].

In order to determine the true molecular weights of star polymer sample, the universal calibration curve (UCC) introduced by Benoit, Grubisic and Rempp [145] has been commonly used. This method is based on the fact that the SEC elution volume is related to the hydrodynamic volume of the polymer molecules in solution, which is expressed by the product of their intrinsic viscosities, [η] and molecular weights, M, i.e., [η]M. The usefulness of this method has been experimentally confirmed for the analyses of graft and branched polymers [146] as well as di- and triblock copolymers [147, 148], and symmetric star polymers [142, 143, 149], however there are some limitations to the use of this method, such as in the case of comb-type polymers [150, 151].

Ambler et al. [152] found that low molecular weight poly(n-butyl isocyanate) fractions, as well as highly branched polystyrenes, deviate significantly from a common UCC. However, these polymers exhibited high molecular polydispersity, a key parameter for the determination of the molecular weight of the copolymers with the UCC.

Huang et al. [153] found that the UCC was valid for well-defined poly(styrene-*b*-isoprene) star-block copolymers having up to 32 arms. Timpa [154], by using a chromatographic system equipped with a differential refractive index and a viscometric detector, was able to calculate the [η] at each retention time of a

polydisperse sample and determine the molecular weight and the polydispersity index (PDI) of a natural cellulose sample.

More recently, Stogiou et al. [155] have tested the validitiy of the UCC by using a linear tetrablock copolymer and branched block copolymers having complex macromolecular architectures such as miktoarm star and H-shaped polymers. They concluded that the universal calibration curve of the SEC, which is expressed by the relation log(M [η]) vs. V_e (elution volume of polymer sample), is valid for molecules with complex macromolecular architectures that present high chemical and molecular weight asymmetry such as linear tetrablock copolymers, miktoarm stars, H-shaped polymers.

Nowadays, SEC apparatus fitted with three detectors in series (low-angle light scattering, photometer, continous viscometer) is efficient for rapid and proper characterization of star polymers [143]. It is now possible to simultaneously measure the diffusion at different angles, giving direct access to the molar mass and the radius of gyration (Wyatt technology) [156].

2.2 Azobenzene-Containing Polymers

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 crosslinked increasing the order of complexity. 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. In order to fully understand these effects, it is useful to select one or two simple photochemical reactions which are well-known and to study them in a macromolecular environment. Such a photochemical reaction is the *cis-trans* isomerism of an azobenzene. When the azobenzene group is incorporated into a polymer, its photoisomerization can have a wide range of unexpected possible consequences [157]. Azobenzene-containing polymers are potentially useful materials for optical and photonic applications [158-164]. In this respect, the preparation of systems containing azobenzene moieties appears to be very promising.

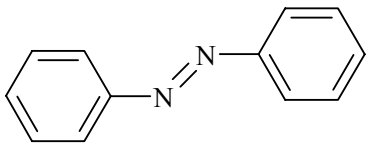
There exist two strategies to synthesize polymers containing azobenzenes [165]. The direct approach consists of a polymerization of monomers having azobenzenes. Linear polymers are obtained by condensation or by radical, cationic, or anionic addition [166]. The direct polymerization method is practically useful because it provides sensitive control over the sequence distribution in the polymer. The second way involves the chemical modification of preformed polymers. The advantage of this method stems from the fact that the starting material often is commercially available. The azobenzene groups can be introduced into either the main chain of polymers or on the side chains polymers; such as amides [167], esters [168], urethanes [169], and ethers [170]. However, methacrylates [171], acrylates [171], and isocyanates [173] are among the most synthesized backbones.

Athough there have been numerous reports on the synthesis and properties of azo polymers [174], there are few examples of living polymerization of azobenzene-containing momomers [175-178]. Especially, postpolymerization reactions were required in cationic polymerization to prepare azopolymers with narrow molecular weight distribution (MWD) [178].

There has been recently growing interest for azobenzene-containing polymers obtained from the CRP techniques [179-183]. Most recently, Erdogan et al. [93] have reported the synthesis of novel A_2B_2 miktoarm star polymer with an azobenzene moiety at core by combination of ATRP and NMP. The details of this work will be given results and discussion part of this book.

2.2.1 Azobenzene chromophores

Azobenzene compounds are organo-nitrogen derivatives with a characteristic –N=N- double bond functionality and the general formula *phenyl-N=N-phenyl* [165] as shown in 2.24. Due to the fact that these systems are highly conjugated, azobenzenes absorb light in the visible region and much interest is taken in their properties as chromophores.



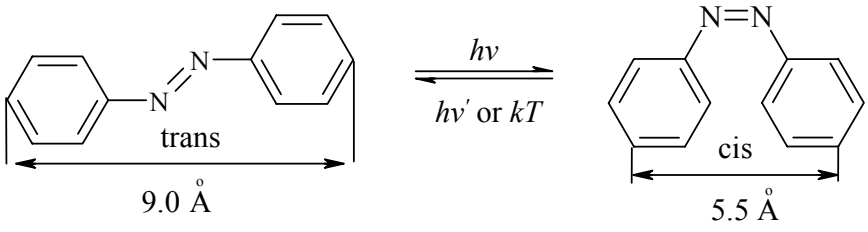
(2.24)

The absortion spectra of trans azobenzenes show similar features to those of carbonyl compounds (C=O) and stilbenes (phenyl-C=O-phenyl) [184]. In fact, a low-lying $n \rightarrow \pi^*$ transition band in the trans isomer, characteristic of a carbonyl absorption spectra, is symmetry forbidden but due to non-planar distortions and to vibrational couplings, this transition is intense. On the other hand, the cis form of the azobenzene compound has asymmetry allowed $n \rightarrow \pi^*$ transition; but demonstrates a low intensity because there is little spatial overlap between the n and π^* molecular orbitals. Hence, the $n \rightarrow \pi^*$ transition band is intense in the trans isomer and decreases in intensity in the cis form. The absorption band present at higher wavelengths in azobenzene systems is very similar to that in the stilbenes' one and has been attributed to the $\pi \rightarrow \pi^*$ transition. Moreover, the spectra of azoaromatic compounds are rather insensitive to solvent polarity; nevertheless, they heavily depend on the substituents on the phenyl rings.

2.2.2 Photoisomerization of azobenzene

2.2.2.1 Photochemistry of azobenzene: cis- trans isomerism

Azobenzene molecules are photochromic, showing significant changes in their optical absorbtion spectra when irradiated at certain wavelengths. This response arises because they have two geometric isomers which may be inter-converted through the absorbtion of light and which exhibit different absorbtion spectra. The process of photo-induced inter-conversion is known as photoisomerization. The isomerization of azobenzene and its derivatives has been extensively studied, characterized and used in various applications [157] because it is readily induced, reversible and produces no side reactions.



(2.25)

Trans-cis isomerization of azobenzene is shown in 2.25. The isomerization reaction is a light or a heat-induced interconversion of the two isomers. As the trans form is generally more stable by approximately 50 kJ mol^{-1} in the case of azobenzene [185], thermal isomerization is generally in the cis-trans direction. Light induces

transformations in both directions. The photoisomerization reaction begins by raising molecules to electronically excited states, and a nonradiative decay brings them back to the ground state, in either the trans or the cis form. This isomerization effectively reduces the distance between attachment points from 9.0 to 5.5 Å (2.25). When the azobenzene molecule is attached chemically to a polymer chain, photoinduced isomerization can result in conformational change being induced in the polymer chains. This can cause significant changes to physical properties such as the dipole moment, refractive index, and solution viscosity. Many of these changes can be reversed by heat or visible irradiation. These polymers 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.

There may be occured two mechanisms during the photoisomerization of azobenzene compounds: one from the high energy $\pi \rightarrow \pi^*$ transition, which leads to rotation around the –N=N- double bond, and the other from the low energy $n \rightarrow \pi^*$ transition, which induces isomerization by means of inversion through one of the nitrogen nuclei [185]. Both mechanisms lead to the same eventual conformational change of the molecule, but for each the process of photoisomerization is different [185]. For the photoisomerization of azobenzenes it has been shown that the free volume nedded for inversion is lower than for rotation.

The mechanism of isomerization is still under debate, and spectroscopists and photochemists have long been aware of the inversion-rotation dichotomy. Early suggestions [186] of a rotation about –N=N- double bond axis were followed by experiments showing a planar inversion via linear transition state [187]. Recently, femtosecond time-resolved fluorescence studies suggested inversion as being the dominant process [188, 189].

2.3 Controlled/ “Living” Radical Polymerization (CRP)

Conventional free radical polymerization (FRP) is a very important industrial process for the preparation of high molecular weight polymers and infinite number of copolymers since it can be employed for the polymerization of numerous vinyl monomers. Free radicals are active centers for chain propagation in a radical polymerization. They are highly active, but not as sensitive to impurities as ions due

to their neutral charge nature. Compared with ionic polymerizations, radical polymerization is much more tolerant to impurities (e.g. water), requiring an oxygen free medium, and can be conducted under mild reaction conditions and over a large temperature range (-80 to 250^{o}C) [190]. The polymers obtained via this method are used in the manufacture of numerous products such as fabrics, surface coatings, plastics, paints, packaging, and contact lenses [191].

One of the main disadvantages of FRP is the poor control over the microstructure of the synthesized macromolecules. This includes the relatively high polydispersity index (PDI), 1.5 or 2.0, and also the practical impossibility to synthesize block copolymers, and other advanced structures.

There is increasing interest in polymer chemistry to prepare well-defined polymers with control of the major variables affecting polymer properties. Living polymerizations [192-195] provide the maximum degree of control for synthesis of polymers with predictable, well-defined structures. Living polymerization was first defined by Szwarc [192] as a chain growth polymerization that proceed in the absence of irreversible chain transfer and chain termination. Until recently, ionic polymerizations (anionic or cationic) were the only living techniques that efficiently controlled the structure and architecture of vinyl polymers. Although these techniques ensure low polydispersity materials, controlled molecular weight and defined chain ends, they are not useful for the polymerization and copolymerization of a wide range of functionalized vinylic monomers. This limitation is due to the incompatibility of the growing polymer chain end (anion or cation) with numerous functional groups and certain monomer families [196]. Furthermore, these polymerization techniques require stringent reaction conditions including the use of very pure reagents and the total exclusion of water and oxygen. The necessity to overcome all these limitations emboldened synthetic polymer chemists to develop new concepts, which would permit the development of a free radical polymerization procedure possessing the characteristics of a living process. Since the term living is not appropriate for a radical process that inherently involves chain transfer and termination reactions, these new concepts are often called controlled radical polymerization, living radical polymerization, control/“living” radical polymerization and so on. Since the term “controlled/“living” radical polymerization

(CRP) describes the essence of these systems better, it will be used throughout this thesis. For terminology, the readers are referred to literature [197, 198].

A "controlled/"living" radical polymerization can be defined as a synthetic method for preparing polymers with predetermined molecular weights, low polydispersity and controlled functionality. Transfer and termination, which often occur in real systems, are allowed in a controlled polymerization if their contribution is sufficiently reduced by the proper choice of the reaction conditions such that polymer structure is not affected.

The last decade have witnessed the explosive growth in the development and understanding of new controlled/"living" radical polymerization (CRP) methods. A number of specialized books and reviews have been published in this general area [199-203].

2.3.1 Basic principles of CRP

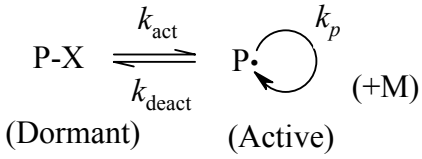
CRP requires all chains to begin growing (reversibly via exchange reactions) at the same time and retain functionalities until the very end of the reaction. This is in contrast to RP where all chains terminate and initiation is never completed, even when all monomer is consumed. Therefore, three basic prerequisites for CRP are

a. Initiation should be completed at low monomer conversions,
b. Relatively low molecular weight (degree of polymerization (DP) < 1000) should be targeted to avoid transfer effects. This requires high concentration of growing chains (for example $>10^{-2}$ M for bulk polymerization),
c. Concentration of propagating radicals ($[P\cdot]<10^{-7}$ M) should be sufficiently low to enable growth of chains to sufficiently high molecular weight, before they terminate.

The mismatch between concentration of growing chains and propagating chains (10^{-2} M$>>10^{-7}$ M) can be achieved by the *exchange reactions* between high concentration of growing chains in the dormant state and the minute amounts of propagating radicals. The other unique feature of CRP is the *persistent radical effect.*

2.3.1.1 Exchange between active and dormant species (reversible activation process)

Mechanistically, CRP is distinguished from conventional free radical polymerization (FRP) by the existence of a reversible activation process (with rate constants k_{act} and k_{deact}) (2.26). The dormant (end-capped) chain P-X is supposed to be activated to the polymer radical P· by thermal, photochemical, and/or chemical stimuli. In the presence of monomer M, P· will undergo propagation (with rate constant k_p) until it is deactivated back to P-X. In practically important systems, it usually holds that $[P\cdot]/[P\text{-}X] < 10^{-5}$, meaning that a living chain spends most of its polymerization time in the dormant state. Here, the term "living chain" is used as the sum of the active and dormant chains. CRP is accordingly defined as the radical polymerization that is structurally (and kinetically in many cases) controlled by the work of living chains. If a living chain experiences the activation-deactivation cycles frequently enough over a period of polymerization time, all living chains will have a nearly equal chance to grow, yielding polymers with low molecular weight distribution (MWD).



(2.26)

CRP is distinguished also from truly living systems like anionic living polymerization by the existence of bimolecular, chain transfer and all the other elementary reactions involved in RP. While it clearly limits the degree of structural control attainable, this feature of CRP provides a variety of unique polymerization systems that are particularly interesting from the viewpoint of polymerization kinetics. Given the rate constants of all the elementary reactions, including those of the activation and deactivation reactions, and details of experimental conditions such as the concentrations of reactants and temperature, one will be able to stimulate the whole process of a CRP run and predict the characteristics of the polymer produced, quite accurately in principle. This, in turn, indicates the feasibility of optimizating experimental conditions for the highest optional performance. The demerit of termination and other side reactions would be minimized in a well designed CRP run.

The reversible activation reactions in the most successful CRPs currently known may mechanistically be classified into three types, which are dissociation-combination (DC), the atom transfer (AT) and degenerative chain transfer (DT) mechanisms.

2.3.1.1a Dissociation- combination (DC)

In this mechanism P-X (2.27) is thermally or photochemically dissociated into P· and X·, where a stable (persistent) radical X· is assumed to be stable enough to undergo no reaction under than the combination with P· (and other alkyl radicals, if any present). Namely, an ideal stable free radical does not react between themselves, does not initiate polymerization, and does not undergo disproportionation with P·. The well- known examples of stable free radical are nitroxides such as 2,2,6,6-tetramethylpiperidinyl-1-oxy radical (TEMPO). Therefore, these type of CRPs are called stable free radical polymerization (SFRP) or nitroxide mediated radical polymerization (NMP) [5, 204, 205].

$$\text{P-X} \underset{k_c}{\overset{k_d}{\rightleftharpoons}} \text{P}\bullet + \text{X}\bullet \qquad (2.27)$$

The rate constants of dissociation k_d and combination k_c are related to k_{act} (pseudo-first-order activation rate constant) and k_{deact} (pseudo-first-order deactivation rate constant) by the rate equations (2.28, 2.29).

$$k_{act} = k_d \qquad \text{(DC)} \qquad (2.28)$$

$$k_{deact} = k_c[\text{X}\bullet] \quad \text{(DC)} \qquad (2.29)$$

2.3.1.1b Atom transfer mechanism (AT)

In this mechanism, P-X is activated by the catalysis of activator A, and the capping agent is transferred to form a stable species AX·. All currently known CRPs in this category use a halogen like Cl and Br as a capping agent X and a halide complex of transition metal like copper (Cu) and ruthenium (Ru) as an activator A. these CRPs are often termed atom transfer radical polymerization (ATRP) [3, 4]. The basic mechanism of AT was shown in 2.30 where k_a and k_{da} are rate constants of activation and deactivation, respectively.

$$\text{P-X} + \text{A} \underset{k_{da}}{\overset{k_a}{\rightleftharpoons}} \text{P}\bullet + \text{A X}\bullet \qquad (2.30)$$

The rate constants in 2.30 are related to k_{act} (pseudo-first-order activation rate constant) and k_{deact} (pseudo-first-order deactivation rate constant) by the rate equations (2.31, 2.32).

$$k_{act} = k_a[\text{A}] \qquad \text{(AT)} \qquad (2.31)$$

$$k_{deact} = k_{da}[\text{AX}\bullet] \qquad \text{(AT)} \qquad (2.32)$$

2.3.1.1c Degenerative chain transfer mechanism

In this mechanism (2.33), P-X is attacked by the propagating radical P′· to form the active species P· and the dormant species P′-X. This is an exchange reaction.

$$\text{P-X} + \text{P'}\bullet \underset{k'_{ex}}{\overset{k_{ex}}{\rightleftharpoons}} \text{P}\bullet + \text{X-P'} \qquad (2.33)$$

If the radicals P· and P′· are kinetically identical, then k_{ex} (degenerative chain transfer rate constant) is equal to k'_{ex}, and one can write the following rate equations (2.34) and 2.35).

$$k_{act} = k_{ex}[\text{P}\bullet] \qquad \text{(DT)} \qquad (2.34)$$

$$k_{deact} = k_{ex}[\text{P-X}] \qquad \text{(DT)} \qquad (2.35)$$

Two types of CRPs belong to this category: organotellurium-mediated living radical polymerization (TERP) [206] and reversible addition-fragmentation chain transfer [60]. These types of CRPs are out of scope of this book, therefore the readers are referred to literature [60, 206].

2.3.1.2 Persistent radical effect (PRE)

The stability of a system is both a kinetic and a thermodynamic notion. From a thermodynamic point of view, a system will be called *stable* if the variation in the standard free energy of the system (ΔG^o), dealing with any evolution in the system, is positive (2.36) :

$$\Delta G^o = \Delta H^o - T\Delta S^o >> 0 \tag{2.36}$$

The apparent stability of a system can also be due to a very slow reaction rate, and it is necessary to separate the stability of a system into two contributions: kinetic and thermodynamic. Thus, a radical is termed *persistent* if its lifetime is significantly higher than those for a transient radical such as methyl radical (typically $<10^{-3}$ s) under the same conditions. In other words, radicals are called persistent if their lifetimes exceed those of reactive radical species by many orders of magnitude. They may self-terminate slowly or disappear by other reactions, but these processes do not compete with the cross-coupling with usual transient radicals [207, 208]. A radical is called *stable* if it is particularly persistent, not reactive with air and not moisture sensitive, and is stockable without any specific conditions. The persistence of a radical depends more closely on kinetic factors (especially steric effects) than on electronic ones. It is a concept relevant to kinetics whereas stabilization is more of a thermodynamic notion. The latter term is an intrinsic property of the radical and depends on electronic factors.

Persistent radical effect (PRE) works in the following way: Assume that radicals X· and Y· are produced in a radical reaction sequence. The possible radical termination steps are self-termination of two X· or two Y· radicals or cross termination of an X· radical and a Y· radical (2.37).

$$\begin{aligned} X^{\bullet} + Y^{\bullet} &\longrightarrow X\text{-}Y \\ Y^{\bullet} + Y^{\bullet} &\longrightarrow Y\text{-}Y \end{aligned} \tag{2.37}$$

Further assume that self-termination of Y· and cross-termination are diffusion-controlled reactions, but self-termination of X· is much smaller than diffusion or thermodynamically unfavorable. In this situation, radical X· is a persistent radical, and the concentration of X· will build up early in the reaction. As the X· concentration becomes large, the velocity of the cross-termination between X· and Y· (occurring with a diffusion-controlled rate constant) increases because of the high X· concentration such that this process overwhelms the self-termination reaction of two Y· radicals. When this occurs, the products formed by radical-radical reactions will effectively be only those of the cross-coupling reaction X· and Y·.

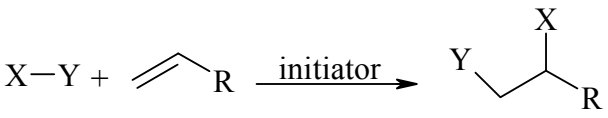
For successful control in polymerization, the trapping of transient carbon centered radicals with the persistent species must occur faster than the addition to the monomer. This ensures that all polymer chains grow at the same rate. However, if the concentration of persistent radicals becomes too high, virtually every transient radical that is formed is trapped before any addition to the monomer can take place. In this situation, polymerization is inhibited, and incomplete consumption of the monomer is observed. Thus, the concentration of the persistent species must be high enough to ensure selective cross-coupling but not so high that addition to the monomer (chain elongation) is prohibited. Thus, the chemical stability of the persistent species under polymerization conditions is critical. As a conclusion, PRE is the key underlying principle of controlled/"living" radical polymerization.

2.3.2 Examples of current CRP

In recent years, the use of CRP techniques in the synthesis of complex macromolecules has increased fast because of the variety of applicable monomers and more tolerant experimental conditions than that the living ionic polymerization routes require. Although several CRP methods were discovered in the past twenty years, the reversible addition fragmentation chain transfer (RAFT) [60, 61, 209] polymerization, the nitroxide-mediated free radical polymerization (NMP) [5, 204, 205] and the metal mediated controlled/ "living" radical polymerization often called as atom transfer radical polymerization (ATRP) [210-213] are the three most successful and promising CRP techniques. However, the latter two cases turned out to be more extensive and will receive detailed consideration in this work.

2.3.2.1 Atom transfer radical polymerization (ATRP)

Atom transfer radical addition (ATRA) is known as an efficient method for carbon-carbon bond formation in organic chemistry [214] and organometallic synthesis [215]. The basic transformation, sometimes called a Kharasch addition, is outlined in 2.38. A wide variety of heteroatom and carbon groups Y can be added. When Y is a heteroatom, a wide variety of atoms and groups X may be incorporated, due to the weak nature of most interheteroatom bonds [216]. When Y is a carbon, X is usually restricted to a univalent atom (H, Cl, Br, I). In a simple thermochemical analysis, the overall transformation exchanges one σ-bond and π-bond for two σ-bonds. This is often exothermic by > 20 kcal/mol, particularly when a weak X-Y bond is involved.

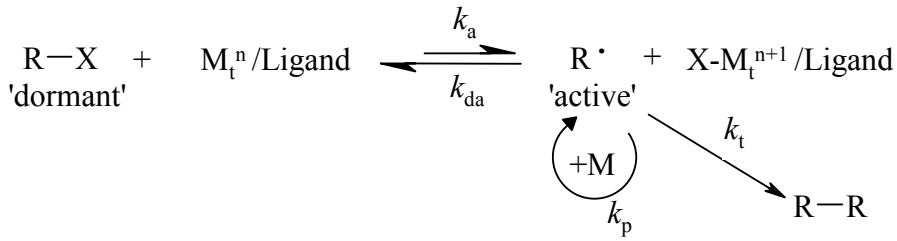


(2.38)

X= H, halogen
Y= carbon, heteroatom

In 1995, Matyjaszewski [212], Sawamoto [210] and Percec [213] reported independently that metal-catalyzed atom transfer radical addition can be successfully applied to radical polymerization processes to control the growth of chains. It was based on catalytic systems used by organic chemists by ATRA and therefore was termed atom transfer radical polymerization (ATRP).

An ATRP system consists of an initiator (alkyl halide), a low oxidation state metal halide complexed with a ligand, and a monomer. ATRP is based on the reversible homolytic cleavage of carbon-halogen bond by a redox reaction between the alkyl halide (R-X) and transition metal (metal compound complexed by amine ligand). A general mechanism for ATRP is represented by reaction 2.39. The halogen atom, X is abstracted by the transition metal complex, M_t^n/ Ligand from the dormant alkyl halide species, R-X by a one-electron oxidation step. This produces an alkyl radical and oxidized metal complex, X-M_t^{n+1}/ Ligand, the deactivator, to reform the dormant species and the activator. This process occurs with a rate constant of activation, k_a, and deactivation k_{da}, respectively. The formed alkyl radical, is able to propagate (add monomer with the rate constant k_p) and it is also able to abstract the halogen back from X-M_t^{n+1}/ Ligand, reforming alky halide (dormant species). This reversible activation/deactivation process is fast and the equilibrium is strongly on the side of dormant species, thus the propagating radical concentration is kept low, resulting in a reduced amount of irreversible radical-radical termination with the rate constant k_t.



(2.39)

According to this general ATRP scheme, the rate of polymerization is given by equation 2.40.

$$R_p = k_p[M][RX]_o\, k_a[M_t^n]/(k_{da}[M_t^{n+1}]) \quad (2.40)$$

The rate of polymerization is first-order with respect to monomer, alkyl halide and transition metal comlexed by ligand. The reaction is usually negative first order with respect to deactivator, X-M_t^{n+1}/ Ligand. However, the kinetics may be more complex due to the formation of X-M_t^{n+1} species via the persistent radical effect (PRE) [208]. The actual kinetics depend on many factors, including the solubility of activator and deactivator, their possible interactions, and variations of their structures and reactivities with concentrations and composition of the reaction medium. It should be also noted that the contribution of PRE at the initial stages might be affected by the mixing method, crystallinity of the metal compound and ligand, solubility of the reagents in the polymerization locus, etc [217].

Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. This process generates oxidized metal complexes, the deactivators, which behave as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination at later stages [208].

The rate coefficients of termination decrease significantly with the progress of the polymerization reaction due to the increase in the chain length and increased viscosity of the system. In fact, the progressive reduction of k_t is one of the most important features of many controlled radical polymerizations [218]. A successful ATRP run will have not only small contribution of terminated chains but also uniform growth of all the chains; this is accomplished through fast or competitive initiation relatively to propagation and rapid reversible deactivation.

Since ATRP is a multicomponent system, basic components of ATRP, namely, monomers, initiators, catalysts, ligands, and solvents should be discussed briefly.

(a) Monomers

The ATRP of each type of monomer requires a specific set of conditions due to a number of factors. Each monomer possesses an intrinsic radical propagation rate, so the concentration of propagating radicals and the rate of radical deactivation may

need to be adjusted to maintain polymerization control. For the polymerization of each monomer, the corresponding alkyl halide end group will possess its own unique redox potential. Therefore, in combination with the same metal catalyst, each end group will exhibit different atom transfer equilibrium constant, deactivation rate constant and corresponding concentration of propagating radicals.

A variety of monomers have been successfully polymerized using ATRP. Typical monomers include styrenes, (meth)acrylates, (meth)acrylamides, acrylonitrile, dienes and some others which contain substitutients that can be stabilize the propagating radical [3, 4, 219, 220]. Ethylene, α–olefins, vinyl chloride and vinyl acetate give non-stabilized, reactive radicals; therefore the currently used catalyst systems are not sufficient to polymerize these monomers although copolymerization is sometimes successful [198].

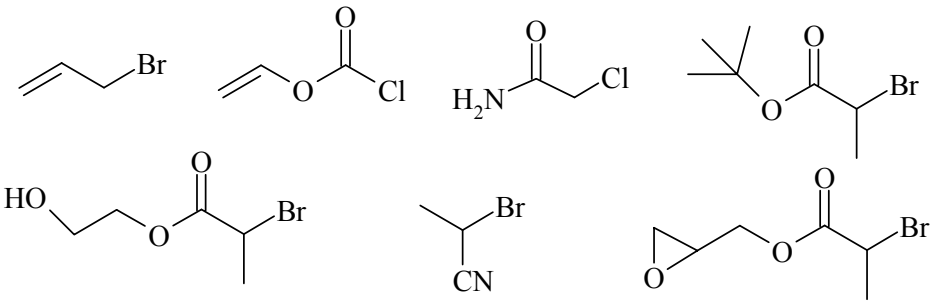
A big advantage of any radical process, ATRP included, is its tolerance to many functional groups such as amido, amino, ester, ether, hydroxy, siloxy and others. All of them have been incorporated as substituents into (meth)acrylate monomers and successfully polymerized. One current exception is a 'free' carboxylic acid group which potentially complexes with the catalyst and disables ATRP, and therefore, presently, it has to be protected. Recent work has shown that monomers bearing ionic substituents such as sodium 4-vinylbenzoate, sodium 4-vinylbenzylsulfonate and 2-trimethylammonioethyl methacrylate methanesulfonate and triflate, and dimethylaminoethyl methacryate can be polymerized directly [221].

(b) Initiators

Another important tool is the initiator, which, depending upon the propagation rate constant for a particular monomer and the equilibrium constant for the end group/catalyst pair, can be varied to assure that the apparent rate of initiation is faster than the apparent rate of propagation. The initiator is generally a simple, commercially available, alkyl halide. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, should rapidly and selectively migrates between the growing chain and the transition metal complex. Thus far, bromine and chlorine are the halogens that afford the best molecular weight control [210, 211, 222, 223]. Iodine works well for acrylate polymerizations; however, in styrene polymerizations the heterolytic elimination of hydrogen iodide is too fast at

high temperatures [224]. As for other X groups, some pseudohalogens, specifically thiocyanates, have been used successfully in polymerization of acrylates and styrenes [224].

Basically, the structure of the alkyl group of the alkyl halide should be similar to that of the monomer for quantitative generation of growing chains. Thus, 1-phenylethyl halides resemble dormant polystyrene chain ends, α-halopropionates approximate dormant acrylate end groups, and α-halopropionitriles are homologous to dormant acrylonitrile chain ends. Another advantage of ATRP is a multitude of commercially available initiators. Nearly all compounds with halogen atoms activated by the presence of β-carbonyl, phenyl, vinyl or cyano groups have been used as efficient initiators. Also compounds with a weak halogen–heteroatom bond can be used, such as sulfonyl halides [213]. Small molecule initiators can carry additional functionalities, a few examples are shown in 2.41, the functionality is incorporated at the residual chain end.



(2.41)

(c) Transition metals and ligands

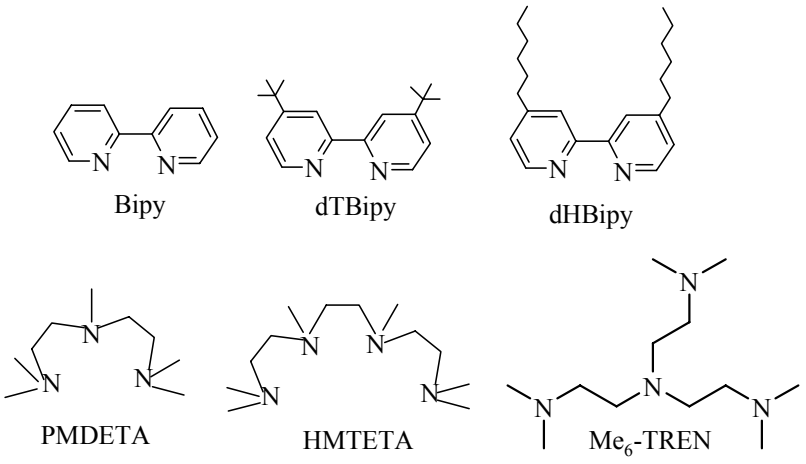
The most important system variables in selecting or designing good ATRP catalysts are the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several requirements for an effective ATRP catalyst. First, the metal complex must have an accessible one-electron redox couple to promote atom transfer, but this requirement alone is not sufficient, because as its name indicates ATRP is an atom transfer not an electron transfer process. Therefore, a second requirement is that upon one electron oxidation, the coordination number of the metal center must increase by one in order to accommodate a new ligand, X. A brief review of known copper-based ATRP catalysts shows that in most systems the lower oxidation state of the metal is presumed to be tetracoordinate and the higher oxidation state is presumed to be

pentacoordinate. A third requirement for a good ATRP catalyst is that the catalyst must show selectivity for atom transfer and therefore possess a low affinity for alkyl radicals and the hydrogen atoms on alkyl groups. If not, then transfer reactions, such as β-H elimination and the formation of organometallic derivatives, may be observed. Finally, the metal center must not be a strong Lewis acid, otherwise the ionization of certain initiators/end groups to carbocations may occur.

A variety of transition metal complexes with various ligands have been studied as ATRP catalysts. The majority of work on ATRP has been conducted using copper as the transition metal. Apart from copper-based complexes, Fe [225, 226], Ni [227], Ru [228], etc have been used to some extent.

The main roles of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex strongly with the transition metal. It should also allow expansion of the coordination sphere and should allow selective atom transfer without promoting other reactions.

Simple amine ligands have been used for ATRP because of their relatively inexpensive cost and commercially availability. Generally, more electron donating ligands stabilize better the higher oxidation state of the metal and accelerate the polymerization. The most widely used ligands for ATRP systems are substituted bipyridines, alkyl pyridylmethanimines and multidentate aliphatic tertiary amines such as *N,N,N′,N″,N″* -pentamethyldiethylenetriamine (PMDETA), and tris[2-(dimethylamino) ethyl]amine (Me_6-TREN). Examples of ligands used in copper-mediated ATRP are illustrated in 2.42 [211, 229].



(2.42)

(d) Solvents

ATRP has been successfully carried out in bulk, in solution [210-213], as well as in aqueous solution [230], emulsion [231], miniemulsion [232], and suspension [233, 234], and in other media (e.g., liquid or supercritical CO_2 [235] or ionic liquids) [236, 237].

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 in the polymerization of different monomers. A solvent is sometimes necessary, especially when the polymer is insoluble in its monomer (e.g., polyacrylonitrile). Several factors affect the solvent choice. Chain transfer to solvent should be minimal. In addition, potential interactions between solvent and the catalytic system should be considered. Catalyst poisoning by the solvent (e.g., carboxylic acids or phosphine in copper-based ATRP) [238] and solvent-assisted side reactions, such as elimination of HX from polystyryl halides, which is more pronounced in a polar solvent, [239] should be minimized.

e) Deactivators

The deactivator in ATRP is the higher oxidation state metal complex formed after atom transfer, and it plays a vital role in ATRP in reducing the rate of polymerization and the polydispersity of the resulting polymer. For copper–catalyzed ATRP, the deactivator is the corresponding copper (II) halide complex (e.g. CuX_2/PMDETA). In ATRP the concentration of deactivator continuously, but slowly, increases with conversion due to the persistent radical effect. While the final molecular weights do not depend upon the concentration of deactivator, the rate of polymerization will decrease with its increasing concentration.

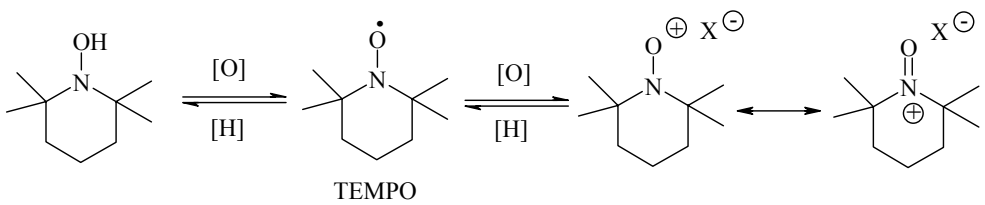
As a conclusion, ATRP is a powerful technique for the preparation of new functional polymers with novel and controlled compositions and topologies including block, graft copolymers, star and (hyper)branched polymers and a complete structure-property relationship has to be developed to allow a correlation of molecular structure with macroscopic properties. ATRP has been used successfully for the largest range of monomers, although the direct polymerization of vinyl acetate and acrylic acids has not yet been successful. The reaction conditions are not very stringent, because only the absence of efficient radical scavengers is required to

conduct the polymerization. Some tolerance to oxygen has been reported in the presence of zero-valent metals [240]. Moreover, ATRP has been carried out in bulk, solution, dispersion and emulsion at temperatures ranging from –20 °C to 130 °C. Finally, the composition, functionality, and architecture of the final polymer all can be controlled through variations in the side groups, end groups, and initiator structure.

2.3.2.2 Nitroxide-mediated radical polymerization (NMP)

Nitroxides are kinetically persistent free radicals that are easily oxidized or reduced and act as reversible traps for other free radical species. These unusual properties have led to a wide range of applications spanning their use in biology as spin labels [241-243] to the development of organomagnetic materials [244].

Nitroxides are N,N-disubstituted N–O compounds with an unpaired electron delocalized in the N–O π system. This three-electron π system effectively forms a bond order of one-and-a-half as indicated by the bond energy of 100 kcal/mol, midway between the energy of a N–O single bond (53 kcal/mol) and a N=O double bond (145 kcal/mol) [245]. The gain in energy from the delocalization of the unpaired electron has been calculated to be approximately 30 kcal/mol. Nitroxides are commonly formed by the treatment of corresponding hydroxylamines with mild oxidants such as oxygen, with or without a catalyst (2.43). Further oxidation of the nitroxide with a slightly stronger oxidant such as bleach or bromine produces oxammonium salt. The reduction of nitroxides with mild reducing agents such as phenyl hydrazine [246] and ascorbic acid [247] gives the corresponding hydroxylamine. The further reduction of the hydroxylamine with a stronger reducing agent can result in cleavage of the N–O bond, providing the corresponding secondary amine [248].



(2.43)

In polymer chemistry, nitroxide-mediated radical polymerization (NMP) [15] has become popular as a method for preparing living polymers under mild,

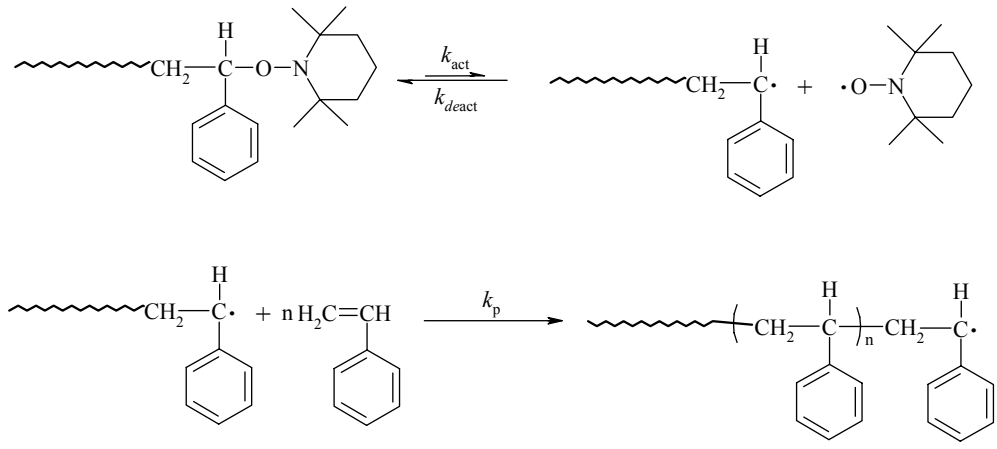
chemoselective conditions with good control over both the polydispersity and molecular weight. Rizzardo, Solomon and Moad [249-251] were the first to demontrate that the reversible end capping of the propagating chain ends by nitroxide free radicals, like 2,2,6,6-tetramethylpiperidinyl 1-oxy (TEMPO). At temperatures typically associated with the process (40-60 °C), the TEMPO capped molecules were stable and did not participate further in the reaction. Further work investigate the same concept at slightly elevated temperatures (80-100 °C), which yielded low molecular weight oligomers, but this seminal work generated a basis for future efforts in the field of CRP.

The use of TEMPO in CRP was finally realized by Georges et al. [204] who demonstrated that polystyrene with narrow MWD can be prepared using a mixture of benzoyl peroxide (BPO) and TEMPO as an initiating system. TEMPO was employed because in addition to not initiating polymerization, it was believed to contribute to the simultaneous initiation of all the polymer chains by promoting the dissociation of peroxide initiators. These two seminal reports resulted in developments of the modern of CRP era.

Subsequently a large number of publications [252-257] have appeared confirming the "living" nature of this novel procedure and demonstrating the usefulness of this approach to the preparation of a variety of well-defined and complex macromolecular architectures, a number of which cannot be prepared using traditional methods. NMP is the simplest of CRP techniques and the most environmentally friendly because it can be performed in an environment with little or no solvent. Reactions can be done in bulk, solution, dispersion, and emulsion [15]. In this process, polymerization proceeds in a controlled manner, with molecular weight increasing as a function of time while maintaining a narrow MWD. NMP has been successfully used to produce linear homopolymers as well as polymers with complex architecture. The success of this approach can be related to the ability of stable nitroxide free radicals, such as TEMPO, to react at near diffusion controlled rates with the carbon-centered free radical of the growing polymer chain end in a thermally (> 120 °C) reversible process (reversible combination/dissociation step). This dramatically lowers the concentration of free radicals in the polymerization system and, coupled with the inability of the nitroxide free radicals to initiate new chain growth, leads to controlled polymerization.

Mechanism of NMP

The polymerization mechanism is the key to the successful establishment of controlled/"living" type system. The basis for the control of the NMP process is the equilibrium that exists between the active and dormant species. At elevated temperatures, typically 100 °C or greater, the nitroxide radical either caps the carbon-centered radical or exists independently (2.44). The carbon-centered radical can then undergo chain extension with monomer (with rate contant k_p) to yield a similar radical in which the degree of polymerization has increased. The recombination of this finally formed radical with nitroxide then gives again dormant species and the cycle of homolysis /recombination/ monomer addition can repeated as seen in (2.44) resulting the polymerization controlled.



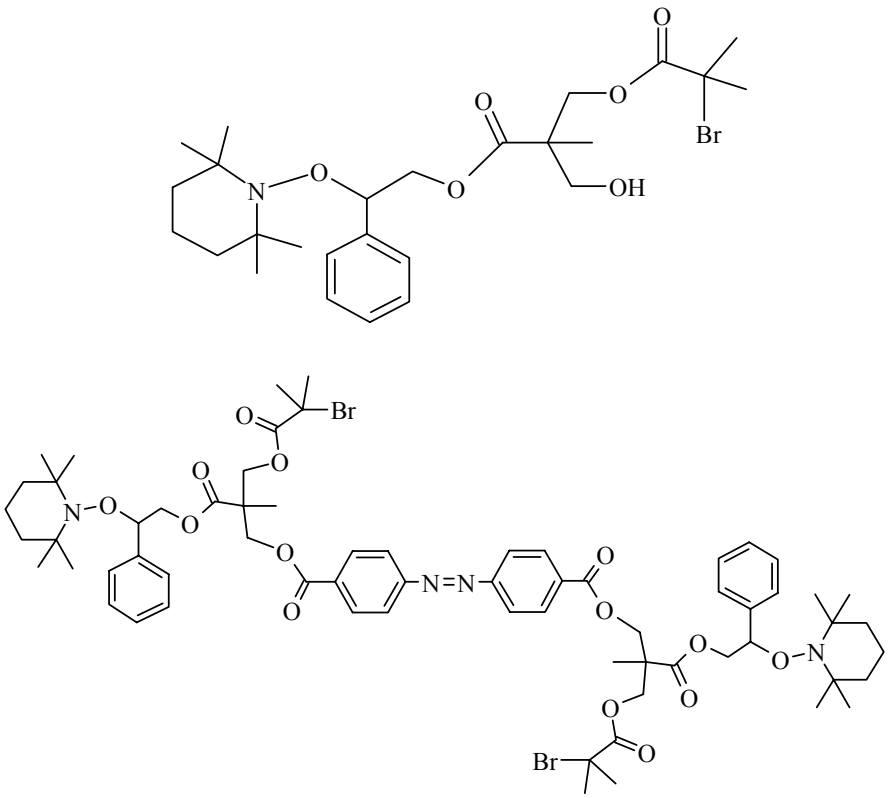
(2.44)

As a mechanical consideration, two general initiating systems have been used in NMP: The first NMP systems used a bimolecular system where BPO was employed as a radical source and TEMPO was included as the mediating agent. The original initiating approach possessed the possibility of decomposition products, which led to unfavorable effects on the molecular weight control, architecture, and any control of the polymer chain ends. Moreover, the actual initiator concentration was not consistent or completely controlled resulting in a less well-defined system [15].

Development a more well-defined initiation process prompted an investigation into unimolecular alkoxyamine initiators. Alkoxyamine initiators mimic the polymer chain end consisting of an alkyl group coupled to a stable nitroxide mediator. These small molecules will decompose at the homolytically unstable C—O bond generating an initiating radical and a nitroxide radical in the proper stoichiometric ratio.

Unimolecular initiators are nitroxide containing compounds that produce two radicals upon thermal decomposition being the carbon centered radical and a nitroxide. The structure of the typically used unimolecular initiator for nitroxide mediated CRP is found in 2.45. In this work, two general methods for the generation of an alkoxyamine initiator were reported.

Unimolecular initiators are easily synthesized and offer an alternative to using conventional free radical initiators. They are shelf-stable and the polymerization can be induced with simple monomer addition and heating. More importantly, the decomposition of these initiators yields a stoichiometric amount of nitroxide relative to the initiating radical. The importance of this is great as each polymer chain initiated will be capped by nitroxide leading to controlled living polymerization and



(2.45)

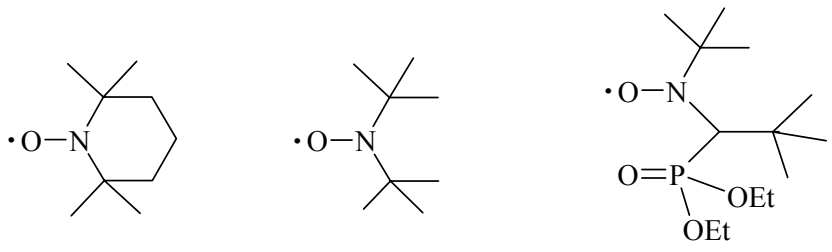
ultimately polymers with low MWD. The amount of initiator added to the polymerization can be accurately weighed, and subsequently, the resulting polymer chain length can be determined by the monomer to initiator ratio.

Although the polymerization remains controlled, there is a low occurrence of undesired side reactions (thermal initiation of monomer, chain transfer, and irreversible termination), allowing polymerization to proceed in a controlled manner.

The amount of irreversible termination is very small due to the low concentration of free radicals in comparison with dormant chains. Fukuda and coworkers have noted that another important side reaction to be considered is the abstraction of the β-proton of the polymer radical by the nitroxyl radical, producing a terminally unsaturated polymer and hydroxylamine; this side reaction can lead to loss of control and broadening of MWD [253].

Although TEMPO-mediated NMP proved effective in controlling the polymerization of styrene, extension of the polymerization process to other monomer families including dienes and acrylates was difficult and often resulted in polymer products with broad molecular weight distributions [15]. Polymerizations involving monomers, such as acrylates, were influenced significantly by the buildup of a large excess of the nitroxide species and lead to slowing of the reaction. This effect is due to the dormant and active chain equilibrium lying heavily in favor of dormant species and termination due to oxygen ingress. Eventually, the excess mediating agent reached levels where the propagation reaction essentially stopped due to those high levels of nitroxide species. The excess effectively halted all propagation because only the dormant state of the radical was present.

Several researchers have investigated alternative nitroxide mediators in order to extend the range of controllable monomers to include acrylates, dienes and acrylamides [256, 257]. The presence of an α-hydrogen seemed to be structurally significant in enhancing the capability to maintain low levels of excess mediator. Gnanou was the first to show this significance, demonstrating that the α-hydrogen enabled extensive control over the polymerization process of n-butyl acrylate [255, 257]. This *N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (DEPN) molecule included an open chain structure and a phosphonate ester functionality and exhibited results superior to those obtained with the simple TEMPO mediator.



(2.46)

TEMPO DBN DPEN

Fukuda and coworkers measured and studied the rate constants of activation in order to examine the effect of the nitroxide structure on resulting equilibrium [253]. In this report, TEMPO was investigated in addition to di-*tert*-butyl nitroxide (DBN) and the novel DEPN (2.46).

The discovery of facile alkoxyamine synthesis resulted in the generation of unimolecular initiators also capable of producing star polymers. Hawker and Gnanou have investigated the use of trifunctional alkoxyamines to yield well-defined three arm star polymers [258]. Gnanou's initiator possessed three alkoxyamine functionalities composed of a labile C—O bond and a DEPN mediating group. Star polymers of styrene and n-butyl acrylate were readily synthesized with relatively narrow molecular weight distributions ranging from 1.09 to 1.40. The addition of supplemental free nitroxide was critical to produce well-defined polymers.

As a conclusion, NMP is a versatile method to produce polymers with controlled molecular weights and narrow MWDs. The reversible homolysis of the carbon oxygen bond only requires heating to ~115 ^{o}C where the equilibrium becomes essentially a diffusion controlled process. NMP necessitates less rigorous laboratory procedures and purification of the reagents is minimal although the presence of oxygen in the reaction continues to be a concern for the radical process [259-262]. Although this polymerization has proven successful with styrene, extension of the technique to other monomer families requires further manipulation of the reaction conditions to provide greater control.

2.4 Ring-Opening Polymerization (ROP)

Ring-opening polymerization (ROP) is a unique polymerization process, in which a cyclic monomer is opened to generate a linear polymer. It is fundamentally different from a condensation polymerization in that there is no small molecule byproduct during the polymerization. Polymers with a wide variety of functional groups can be produced by ring-opening polymerizations. Examples of industrially important polymers made by ring-opening polymerizations are nylon 6, polysiloxane, polycaprolactone and epoxy resin. Ring-opening polymerization has a unique position in polymer chemistry. Preparation of cyclic monomers, studies of catalysis and mechanisms are active areas of research both in academia and industry [253-266].

The thermodynamic polymerizability of a cyclic monomer has been elegantly summarized by Ivin [267]. Negative free energy change from monomer to polymer is the thermodynamic driving force for the ring-opening.

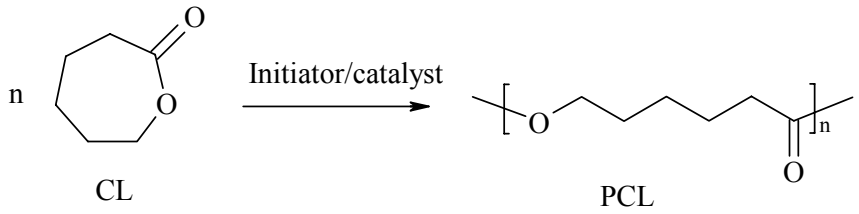
Nowadays, increasing attention is paid to degradable and biodegradable biocompatible polymers for applications in the biomedical and pharmaceutical fields, primarily because after use they can be eliminated from the body via natural pathways and also they can be a solution to problems concerning the global environment and the solid waste management. Aliphatic polyesters are among the most promising materials as biodegradable polymers. Many types of aliphatic polyesters have been prepared by both chemosynthetic and biosynthetic methods. The poly(ε-caprolactone) (PCL) family of polyesters is synthesized by ring-opening polymerization of ε-caprolactone (ε-CL), which is an industrially available petrochemical. PCL is known as a biodegradable and biocompatible thermoplastic.

2.4.1 Controlled ring-opening polymerization of cyclic esters

Polylactones and polylactides can be either synthesized by polycondensation of hydroxyl-carboxylic acids or by the ring-opening polymerization (ROP) of cyclic esters. The polycondensation technique yields low molecular weight polyesters (M_n<30.000) with poor control of specific end groups. In contrast, high molecular weight aliphatic polyesters can be prepared in short periods of time by ROP. Comparison of these two mechanisms is clearly in favor of polyaddition process.

The ring-opening reaction can be performed either as a bulk polymerization, or in solution, emulsion, or dispersion. In practice, the ROP of lactones and lactides requires an appropriate catalyst to proceed in reasonable conditions and to afford polymers with controlled properties (2.47). Since the pioneering work of Kleine et al. in the 1950s [268] metal-based catalytic systems have been the focus of considerable attention for the polymerization of cyclic esters, [269-271] and numerous studies have been carried out to elucidate the mechanism of such coordination polymerizations. Through variation in the nature of the metal center and of the surrounding ligands, a broad range of initiators have been prepared and evaluated [272]. These well-defined complexes have contributed significantly to a better understanding of the factors that govern the polymerization, and spectacular

improvements have thereby been achieved in terms of catalytic activity as well as polymerization control.



CL PCL (2.47)

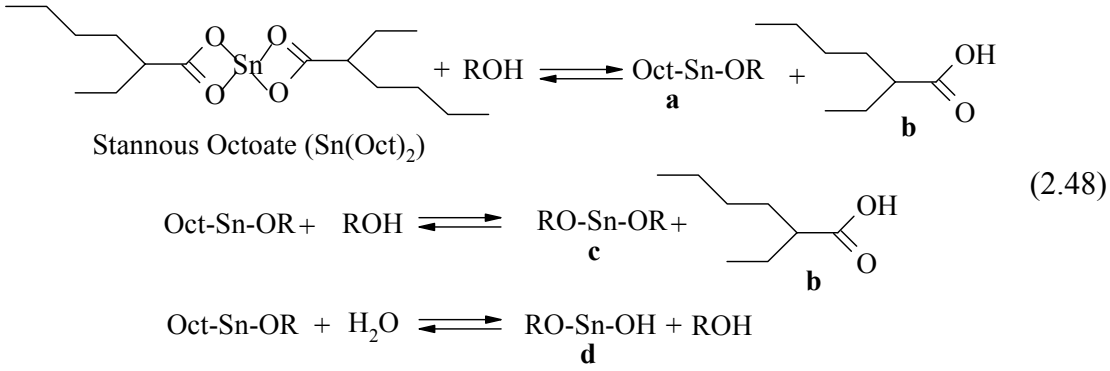
Besides the coordination-insertion mechanism, alternative strategies based on anionic [273], nucleophilic, or cationic promoters [274] have also been recently (re)evaluated, the preliminary results reported in these fields being rather promising.

2.4.1.1 Coordination-insertion ROP

Covalent metal carboxylates, particularly tin(II) bis(2-ethylhexanoate) usually referred to as tin(II) octanoate, $Sn(Oct)_2$ belong to the most frequently used initiators for polymerization of cyclic esters due to its low cost, low toxicity, and high efficiency. Although, there are controversial reports in the literature about the nature of $Sn(Oct)_2$ activity in the polymerization of lactones, two basic types of mechanism have been proposed.

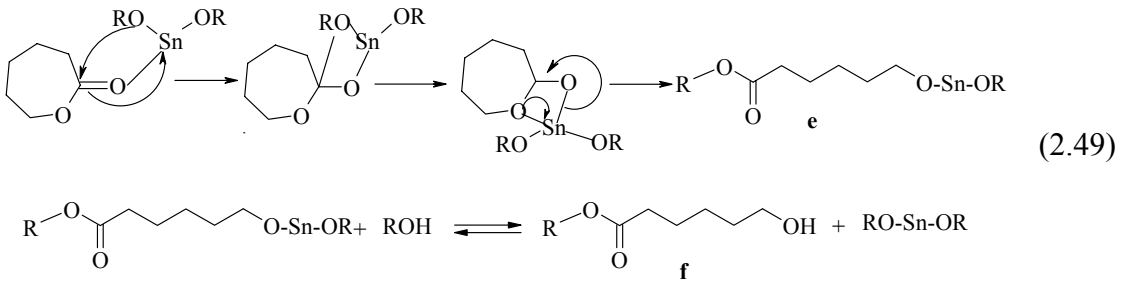
The first one is directly catalytic type where the catalyst serves to activate monomer through coordination with its carbonyl oxygen [275-278]. The second mechanism is the monomer insertion type mechanism where the catalyst acts as co-initiator along with either purposely added or adventitious hydroxyl impurities, and polymerization proceeds though an activated stannous alkoxide bond [279-285]. The $Sn(Oct)_2$ is not thought to be the actual initiator since the molecular weight does not depend on the monomer-to-$Sn(Oct)_2$ molar ratio.

Most recently, Sherman and coworkers [286] presented evidence that the bulk polymerization of ε-CL conducted at 130 °C displays the characteristic kinetic features of a polymerization that propagates through an active stannous alkoxide center co-initiated by stannous octoate and purposely added alcohol.



(2.48)

Kricheldorf and co-workers have recently illustrated how the structure of the alcohol initiator may influence the strength of the catalyst/alcohol interaction [277, 284]. According to these authors, this interaction, in the early stages of reaction, is responsible for formation of the "true" initiating species, subsequent ring opening, and formation of the active, propagating chain end. Prior to the beginning of polymerization, adventitious hydroxyfunctional impurities (e.g., water) or purposely added alcohol first complex and subsequently react with $Sn(Oct)_2$ producing a stannous alkoxide species (**a**) and free 2-ethylhexanoic acid (**b**) as shown in 2.48. Further reaction with **a** second equivalent of alcohol produces the stannous dialkoxide initiator (**c**) and releases a second equivalent of 2-ethylhexanoic acid (**b**) as depicted in 2.48 [280, 284]. Adventitious water, meanwhile, serves mainly as a catalyst deactivator via a reversible reaction with **a** or **c**, thereby decreasing the concentration of active initiator and producing a stannous alcohol derivative (**d**), such as shown in 2.48, which is more thermodynamically stable than the stannous dialkoxide and is less efficient as an initiator [284].



(2.49)

Reaction of **c** with monomer by means of coordination- insertion generates the first actively propagating chain end (**e**) consisting of not only the initiating alcohol fragment but also the active propagating center derived from the first monomer unit and stannous alkoxide. The **e** species may either propagate or undergo rapid intermolecular exchange of the stannous alkoxide moiety for a proton from either

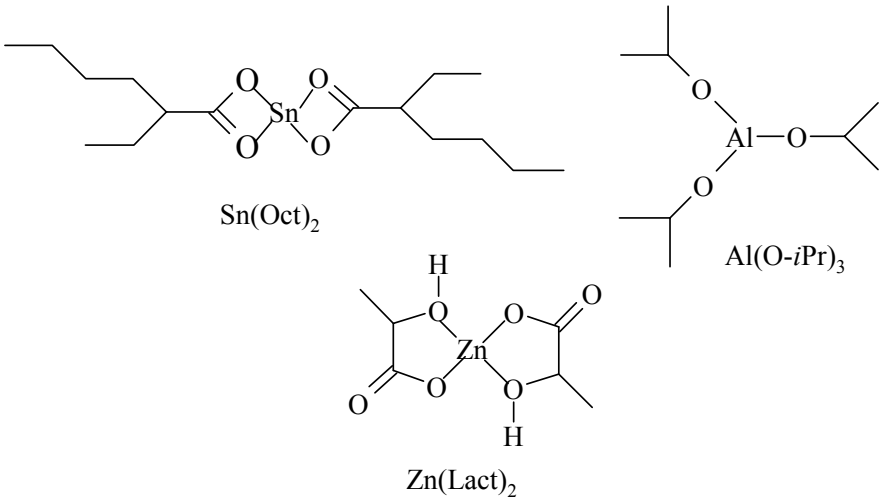
hydroxyl groups of initiator (if remaining) or another hydroxy chain end, either **e** or polymeric in nature. This rapid exchange of protons and stannous alkoxide moieties results in a dynamic equilibrium between activated and deactivated chain ends as depicted in 2.49, where R= unreacted alcohol initiator or hydroxy chain ends generated in situ. This process eventually consumes the remaining unreacted alcohol initiator not involved in the initial formation of **c**.

ROP based on coordination-insertion mechanism has been thoroughly investigated since it may yield well-defined polyesters through living polymerization [287, 288].

2.4.1.2 Organometallic compounds as initiators for the ROP of lactones and lactides

A large variety of organometallic compounds, such as metal alkoxides and metal carboxylates (2.50), has been studied as initiators or catalysts in order to achieve effective polymer synthesis [287]. The covalent metal alkoxides with free p or d orbitals react as coordination initiators and not as anionic or cationic inititors [288]. The most widely used complex for the industrial preparation of polylactones and polylactides is undoubtedly *Sn(Oct)$_2$*. It is commercially available, easy to handle, and soluble in common organic solvents and in melt monomers. It is highly active and allows for the preparation of high-molecular-weight polymers in the presence of an alcohol [289]. Although $Sn(Oct)_2$ has been accepted as a food additive by the U.S. FDA, the toxicity associated with most tin compounds is a considerable drawback in the case of biomedical applications.

Aluminum alkoxides have also proved to be efficient catalysts for the ROP of cyclic esters. The common example, namely*, aluminum (III) isopropoxide, Al(Oi-Pr)$_3$,* has been largely used for mechanistic studies. However, it has been revealed to be significantly less active than $Sn(Oct)_2$ [290]. Moreover, an induction period of a few minutes is systematically observed with $Al(O\textit{i}\text{-}Pr)_3$ attributed to aggregation phenomenon [291]. For all these reasons, $Al(O\textit{i}\text{-}Pr)_3$ is much less used for the preparation of biodegradable polyesters, and especially since aluminum ions do not belong to the human metabolism and are suspected of supporting Alzheimer's disease.



(2.50)

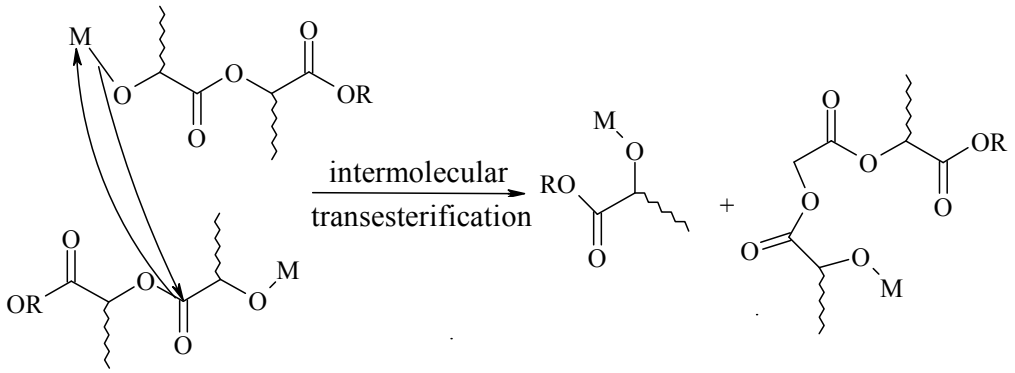
Much interest has thus been devoted to zinc derivatives as potential nontoxic catalysts. Zinc powder itself is a relatively good polymerization catalyst that is used industrially [292, 293]. With reaction times of several days at 140 °C in bulk, it is roughly as active as Al(O*i*-Pr)$_3$. Numerous zinc salts have also been investigated [294, 295]. So far, the best results regarding lactide conversion and degree of polymerization were observed with *zinc(II) lactate, Zn(Lact)$_2$,* which is commercially available and can be readily obtained from ZnO and ethyl lactate or lactide. Notably, Zn(Lact)$_2$ allows for a better control of the molecular weight of the resulting polymers compared with zinc powder.

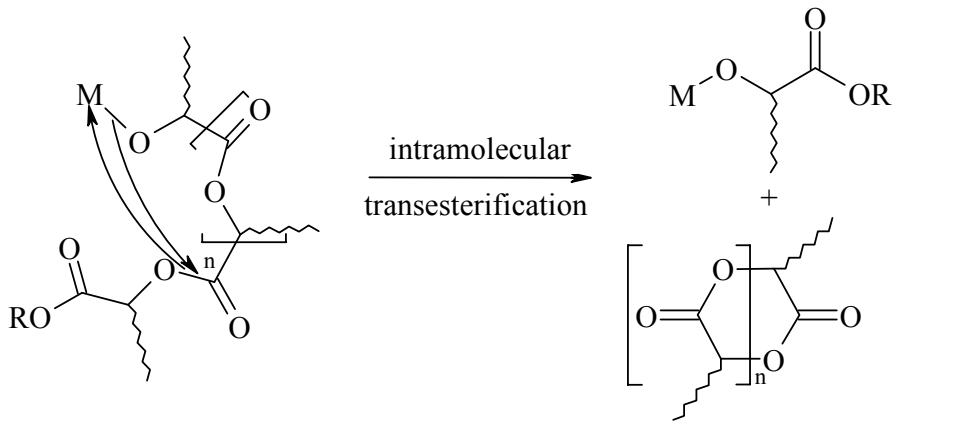
In such coordination-insertion polymerizations the efficiency of the molecular-weight control depends from the ratio $k_{propagation}/k_{initiation}$ but also from the extent of transesterification side reactions. These transesterification reactions can occur both intramolecularly (backbiting leading to macrocyclic structures and shorter chains) and intermolecularly (chain redistributions) (2.51-2.52) [296]. Intermolecular transesterification reactions modify the sequences of copolylactones and prevent the formation of block co-polymers. Intramolecular transesterification reactions cause degradation of the polymer chain and the formation of cyclic oligomers.

The polymerization/ depolymerization equilibrium should also be taken into account as a particular case of intramolecular transesterification reaction. All of these side reactions result in broader molecular-weight distributions, sometimes making the molecular weights of the resulting polymers irreproducible. The extent of these undesirable transesterification reactions was found to strongly depend on the metallic initiator [290]. Side reactions occur from the very beginning of the polymerization

with $Sn(Oct)_2$, leading to rather broad MWD (PDI indexes around 2) but only at high or even complete conversion with $Al(O\textit{i}\text{-}Pr)_3$, yielding lower PDI indexes (less than 1.5) [290, 297].

Parameters that influence the number of transesterifications are temperature, reaction time, and type and concentration of catalyst or initiator. Depending on the metal used, the initiator is more or less active towards transesterification reactions [297].





The promising results obtained with $Sn(Oct)_2$, $Al(O\textit{i}\text{-}Pr)_3$, and $Zn(Lact)_2$ have given rise to a growing interest in metal-based initiators that would display higher catalytic activity and better control the extent of the undesirable transesterification reactions.

2.4.2 Poly(ε-Caprolactone)

Poly(ε-caprolactone) (PCL) is a semicrystalline polymer which represents one of several aliphatic polyesters that undergo degradation and absorbtion *in vivo* [298, 299]. The repeating molecular structure of PCL homopolymer consists of five non-polar methylene groups and a single relatively polar ester group. Although not produced from renewable raw materials, PCL is a fully biodegradable thermoplastic

polymer due to the presence of the hydrolytically unstable aliphatic-ester linkage. PCL has good water, oil, solvent and chlorine resistance.

PCL has some unusual properties, including a low T_g (~ –60 °C) and T_m (~ 60 °C) and a high thermal stability. These properties are related to PCL's chain of carbons, as longer chains are give rise to less mobility and lower T_m's and T_g's. PCL is also highly permeable, which results from its low T_g and subsequent rubbery state at room temperature.

2.4.2.1 Degradation of PCL

Hydrolysis is the principal mode of degradation for polyglycolide (PGA), polylactide (PLA), PCL and copolymers. Degradation proceeds first by diffusion of water into the material (initially into the more amorphous zones), followed by random hydrolysis, fragmentation of the material; and finally a more extensive hydrolysis accompanied by phagocytosis, diffusion and metabolism. The hydrolysis is affected by the size and hydrophilicity of the particular polymer implant, the crystallinity of the polymer and the pH and temperature of the environment [299, 300].

2.4.2.2 Applications of PCL

PCL is compatiable with numerous other polymers, has the possibility of blending this aliphatic polyester with a number of commercial polymers such as poly(vinyl chloride) and bisphenol A polycarbonate. PCL is of interest as a packaging material and in biomedical applications since it is degradable and its degredation products are non-toxic. PCL and other copolymers have been evaluated for medical uses such as drug delivery systems, an external casting material for broken bones, as a material for use in making custom dental impression trays.

In addition to above, it is used mainly in thermoplastic polyurethanes, resins for surface coatings, adhesives and synthetic leather and fabrics. It also serves to make stiffeners for shoes and orthopedic splints, and fully biodegradable compostable bags, sutures, and fibres. Because the homopolymer has a degradation time on the order of 2 years, copolymers have been synthesized to accelerate the rate of bioabsorption. In Sweden there has been an attempt to produce PCL bags, but they degraded before reaching the customers.

3. EXPERIMENTAL WORK

3.1 Materials and Chemicals

3.1.1 Monomers

Styrene (St, 99 %; Merck), *tert*-butyl acrylate (*t*BA, 99 %; Aldrich) and methyl methacrylate (MMA, 99 %; Aldrich) were passed through a basic alumina column to remove inhibitor and distilled over CaH_2 *in vacuo* prior to use. ε-Caprolactone (ε-CL; Aldrich) was distilled over CaH_2 *in vacuo* before use.

3.1.2 Solvents

Dichloromethane (CH_2Cl_2, Aldrich)

It was dried with $CaCl_2$ and distilled over P_2O_5. It was stored over molecular sieve (4 ^oA).

Tetrahydrofuran (THF, J.T. Baker)

It was dried over potassium hydroxide and distilled over $LiAlH_4$.

Methanol (Technical)

It was used for the precipitation of polymers without further purification.

Chloroform ($CHCl_3$, J.T. Baker)

It was used as received.

Ethanol (99.5% J.T.Baker)

It was used as received.

Hexane (J.T. Baker)

It was dried prior to use.

Ethyl acetate (EtOAc)

It was dried prior to use.

3.1.3 Other chemicals

Copper (I) bromide (CuBr, Aldrich)

It was used as received.

Copper (I) chloride (CuCl, Aldrich)

It was used as received.

***N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, Aldrich)**

It was used as a ligand for ATRP after distilled over NaOH.

Thionyl chloride ($SOCl_2$, Fluka)

It was used as received.

Triethylamine (Et_3N, Merck)

It was used as received.

Stannous octanoate ($Sn(Oct)_2$, Sigma)

It was used as a catalyst for ROP without further purification.

2-Bromoisobutryl bromide (99%, Aldrich)

It was used as received.

2,2-bis(hydroxymethyl)propanoic acid (bis-MPA, 99% Acros)

It was used as received.

4-Dimethylaminopyridine (DMAP, 99% Aldrich)

It was used as received.

***p*-toluenesulfonic acid monohydrate (*p*-TSA, Merck)**

Water was removed by azeotropic distillation with benzene using Dean-Stark apparatus and followed by recrystallization from chloroform.

4-Dimethylamino pyridinium-4-toluene sulfonate (DPTS)

The synthesis of DPTS was carried out through the reaction of anhydrous *p*-toluenesulfonic acid (*p*-TSA) and 4-dimethylamino pyridine [301].

***N,N*-Dicyclohexylcarbodiimide (DCC, 99% Acros)**

It was used as received.

2,2,6,6-Tetramethylpiperidinyl-1-oxy (TEMPO, 98% Acros)

It was used as received.

2,2-Dimethoxypropane (98%, Acros)

It was used as received.

Benzoyl peroxide (BPO, 77% Fluka)

It was used as received.

Phosphorus penta chloride (PCl_5, Aldrich)

It was used as received.

α-D glucose (Aldrich)

It was used as received.

4-Nitrobenzoic acid (Aldrich)

It was used as received.

3.2 Equipment

3.2.1 Nuclear magnetic resonance spectroscopy (NMR)

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker NMR spectrometer (250 MHz for ^{1}H NMR) and a Varian Inova 500 spectrometer (125.66 MHz for ^{13}C) using $CDCl_3$ as solvent and tetramethylsilane as an internal standart.

3.2.2 Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) measurements were obtained with an Agilent model 1100 instrument 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 an eluent at a flow rate of 0.3 mL/min at 30 °C. BHT was used as an internal standard. The molecular weights of the polymers were calculated on the basis of linear PS standards (Polymer Laboratories).

3.2.3 Differential scanning calorimeter (DSC)

DSC analyses of ABC miktoarm star polymers were performed on a Netzsch DSC 204 at a heating rate of 20 °C/min and on a Perkin Elmer DSC 7 at various heating rates under a nitrogen atmosphere. DSC analyses of AB_2 miktoarm star polymers were conducted on a Perkin Elmer DSC 6 at a heating rate of 10 °C/min under nitrogen. The glass-transition temperatures (T_g's) and melting temperatures (T_m's) were determined from a second heating cycle.

3.2.4 Infrared spectrophotometer (IR)

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer.

3.2.5 UV-visible spectrophotometer

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.

3.2.6 Mass spectrometer (MS)

Mass spectroscopy measurements were carried out on a LCQ MS Thermo Finnigan equipped with an electrospray ionazation (ESI) source and on a Micromass Autospec instrument operating in ESI positive mode at 70 eV.

3.2.7 Thermogravimetric analyzer (TGA)

Thermogravimetric data were obtained using a Thermogravimetric Analyzer PL-1000 (PL-TGA), between 30-600 ^oC, under nitrogen, with a scan rate of 10 ^oC/min.

3.3 Preparation Methods

3.3.1 Synthesis of miktofunctional initiator for the preparation of AB_2 type miktoarm star polymers

3.3.1.1 Synthesis of 2,2-bis[methyl(2-bromopropianato) propionyl chloride

2,2-Bis[methyl(2-bromopropianato) propionyl chloride was synthesized in two steps following a literature [21] procedure:

A. In a 250 mL one-neck flask equipped with a magnetic stirrer, 2,2-bis(hydroxyl methyl) propionic acid (bis-MPA) (5 g, 37 mmol) was dissolved in dried THF (180 mL). Triethylamine (12.5 mL, 89 mmol) was added and the solution became homogeneous. The flask was cooled at 0 ^{o}C. A solution of 2-bromo propionyl bromide (9.5 mL, 89 mmol) in 15 mL THF was added dropwise through a cannula. The mixture was kept under stirring at room temperature overnight. The salt was filtered off and the solvent was removed completely under vacuum. A pale yellow viscous liquid was obtained in 78 % yield (10.8965 g) and used further without purification.

^{1}H-NMR ($CDCl_3$) (δ, ppm): 9.09 ppm (s, COO*H*), 4.43–4.13 ppm (m, 6H, C*H*$_2$OCO, C*H*(CH_3)Br, 1.81 ppm (d, 6H, CH(C*H*$_3$)Br), 1.29 ppm (s, 3H, CC*H*$_3$).

B. The latter compound (5 g, 12 mmol) was dissolved in benzene (50 mL). phosphoruspentachloride, PCL_5 (6 g, 28.8 mmol) was then added. The mixture turned immediately to green colour; the solution was kept under stirring at room temperature overnight. The salts were filtered off and benzene was removed by evaporation under vacuum. Hexane was added in order to remove the excess of PCl_5. The organic phase was recovered and the solvent evaporated under vacuum. A clearly green-brown liquid (oil like) was obtained in 43% yield.

^{1}H-NMR ($CDCl_3$) (δ, ppm): 4.40–4.20 ppm (m, 6H, C*H*$_2$OCO, C*H*(CH_3)Br, 1.79 ppm (d, 6H, CH(C*H*$_3$)Br), 1.33 ppm (s, 3H, CC*H*$_3$).

3.3.1.2 2-hydroxyethyl 3-[(2-bromopropanoyl)oxy]-2-{[(2-bromopropanoyl) oxy]methyl}-2-methyl-propanoate

The obtained 2,2-bis[methyl(2-bromopropianato) propionyl chloride (5.53 g, 13.08 mmol) was added into a molar excess (25 times) of ethylene glycol (18.26 mL), and

the mixture was reacted for 21 h in a jacketed Schlenk tube, which was cooled to 0 °C. The reaction mixture was dissolved in water and extracted with dichloromethane. The organic phase was washed with a saturated aqueous solution of $NaHCO_3$ (sodium bicarbonate), which was followed by water, and was dried over Na_2SO_4 (sodium sulphate). The solvent was distilled off under reduced pressure, and an orangelike oil was collected in a 40 % yield (2.3 g) without further purification.

^{1}H-NMR ($CDCl_3$) (δ, ppm): 4.50–4.18 ppm (m, 8H, C*H*$_2$OCO, C*H*(CH_3)Br, HOCH$_2$C*H*$_2$OCO), 3.81 ppm (t, 2H, HOC*H*$_2$CH$_2$OCO), 2.2 ppm (bs, 1H, *H*OCH$_2$), 1.79 ppm (d, 6H, CH(C*H*$_3$)Br), 1.31 ppm (s, 3H, CC*H*$_3$).

3.3.2 Synthesis of miktofunctional initiator for the preparation of ABC type miktoarm star polymers

3.3.2.1 Synthesis of benzoic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperin-1-yloxy)-ethyl ester

In a 1000 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 ^{o}C in an oil bath. After that period the excess of 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 4.44 g (11.64 mmol, 60 %) as white needles.

^{1}H NMR ($CDCl_3$) (δ, ppm): 0.75, 1.07, 1.21, 1.37 (each br s, 12H, C*H*$_3$), 1.38-1.52 (m, 6H, C*H*$_2$), 4.53 (ABq, *J* =6 Hz, 1H, C*H*H), 4.83 (ABq, *J* = 6 Hz, 1H, CH*H*), 5.06 (ABq, *J*=3 Hz, 1H, C*H*), 7.25-7.56 (m, 8H, Ar*H*), 7.91 (B of ABq, *J* =6 Hz, 2H, Ar*H*)

3.3.2.2 Synthesis of 2-phenyl-2-(2,2,6,6-tetramethyl-piperin-1-yloxy)-ethanol

Benzoic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperin-1-yloxy)-ethyl ester (4.44 g, 11.64 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 2.8 g (10.11 mmol, 87 %) as yellow viscous liquid without further purification.

^{1}H-NMR ($CDCl_3$) (δ, ppm): 1.15-1.58 (m, 18H), 3.72 (dd, *J* = 2.5 and 9.5 Hz, 1H, CH), 4.22 (dd, *J* = 9.5 and 12 Hz, 1H, CH_2), 5.31 (dd, *J* = 2.5 and 9.5 Hz, 1H, CH), 5.89 (brs, OH), 7.29-7.36 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$) (δ, ppm): 17.25, 20.66, 25.64, 32.30, 34.21, 39.99, 40.52, 61.03, 67.93, 69.18, 84.23, 126.96, 127.83, 128.31, 139.10.

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

The 2,2-bis(hydroxymethyl)propanoic acid, bis-MPA (4 g, 29.84 mmol) along with *p*-TSA (0.112 g, 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 (80 mL) , and once extracted with distilled water (20 mL). The organic phase dried with Na_2SO_4, concentrated to yield 4.01 g (77.3 %) as white solid after evaporation of solvent.

^{1}H-NMR ($CDCl_3$) (δ, ppm): 1.17 (s, 3H, -C*H*$_3$), 1.39-1.43 (d, 6H, -C(C*H*$_3$)$_2$), 3.62 and 4.20 (dd, 4 H, C(C*H*$_2$O-)$_2$).

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

2-phenyl-2-(2,2,6,6-tetramethyl-piperin-1-yloxy)-ethanol (2.80 g, 10.10 mmol), was dissolved in 20 mL of dry CH_2Cl_2 along with *2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid* (1.86 g, 10.68 mmol), and DPTS (0.45 g, 1.45 mmol) were added in that order. Dicyclohexylcarbodiimide (DCC) (2.58 g, 12.50 mmol) dissolved in CH_2Cl_2 (5 mL) was then immediately added and the mixture was stirred at room

temperature for 24 h. The precipitated dicyclohexylurea was filtered off, the solvent evaporated, and the remaining product was purified by column chromatography (silica gel) eluting with hexane then gradually increasing to 1:4 (hexane/ EtOAc) to give the final product as pale yellow oil. Yield 3.68 g (84 %).

^{1}H NMR ($CDCl_3$) (δ, ppm): 7.30-7.23 (m, 5H, Ar*H*), 4.93 and 4.91 (dd, 1H, ArC*H*), 4.57 and 4.52 (dd, 1H, ArCHC*H*H), 4.41 and 4.37 (dd, 1H, ArCHCH*H*), 3.98 and 3.93 (dd, 2H, C*H*$_2$O), 3.47 (d, 2H, C*H*$_2$O), 1.73-0.72 (m, 21H).

3.3.2.5 Synthesis of 3-hydroxy-2-hydroxymethyl-2-methyl-propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester

2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid 2-phenyl-2-(2,2,6-trimethyl-piperidin-1-yloxy)-ethyl ester (3.68 g, 8.5 mmol) was dissolved in a mixture of 22.2 mL of THF and 11.1 mL of 1 M HCl (aq). The reaction mixture was stirred for 4 h. The precipitated product was filtered off and washed with THF and evaporated at 45 °C to dryness. The crude product was dissolved in CH_2Cl_2 and washed with water. The combined organic phases were dried over Na_2SO_4, filtered and evaporated. The product was isolated as white solid. Yield: 3.14 g (94 %).

^{1}H NMR ($CDCl_3$) (δ, ppm): 7.35-7.27 (m, 5H, Ar*H*), 4.99 (t, 1H, ArC*H*), 4.51 (d, 2H, ArCHC*H*$_2$), 3.69-3.60 (m, 4H, C*H*$_2$OH), 2.74 (bs, 1H, CH$_2$O*H*), 2.61 (bs, 1H, CH$_2$O*H*), 1.65-0.81 (m, 21H).

3.3.2.6 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

3-hydroxy-2-hydroxymethyl-2-methyl-propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester (4.19 g, 10.67 mmol) was dissolved in dry Et_3N (3.28 mL, 23 mmol) and CH_2Cl_2 (20 mL) and cooled to 0 ^oC. 2-Bromoisobutyrylbromide (1.32 mL, 10.67 mmol) was added dropwise to the reaction mixture within 30 minutes. It was then stirred for 4 h at room temperature. After dilution with 200 mL of CH_2Cl_2, the mixture was extracted three times with 50 mL of saturated aqueous solution of $NaHCO_3$. The organic phase was dried over Na_2SO_4. The solution was purified by column chromatography on silica gel with 1:10 (ethylacetate/ hexane) to give 4.37 g (75 % yield) of product as pale yellow.

^{1}H NMR ($CDCl_3$) (δ, ppm): 7.33-7.28 (m, 5H, Ar*H*), 4.97 (t, 1H, ArC*H*), 4.53-4.45 (m, 2H, ArCHCH_2), 4.22 and 4.18 (dd, 2H, CH_2OCO), 3.55 (dd, 2H, CH_2OH), 2.78 (bs, 1H, CH_2O*H*), 1.85 (d, 6H, CBr(CH_3)$_2$), 1.60-0.78 (m, 21H).

^{13}C NMR ($CDCl_3$) (δ, ppm): 17.0, 17.2, 20.3, 28.3, 29.6, 30.5, 33.8, 40.1, 48.4, 55.3, 60.1, 64.9, 66.9, 83.5, 127.15, 127.18, 127.7, 128.14, 128.15, 140.0, 171.3, 173.6.

Anal. Calc. for $C_{26}H_{40}BrNO_6$: C, 57.56%; H, 7.43; N, 2.58%. Found: C, 57.52%; H, 7.40%, N, 2.60%.

MS (ESI): 542 (M^+), 544 (M+2), 386.8 (M-TEMPO)

3.3.3 Synthesis of miktofunctional initiator for the preparation of photoresponsive A_2B_2 type miktoarm star polymers containing an azobenzene moiety at the core

3.3.3.1 Synthesis of 4,4'-bis(chlorocarbonyl) azobenzene

4,4'-bis(chlorocarbonyl) azobenzene was synthesized in two steps following a literature [302-304] procedure: A. 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 2 h at 50 °C and overnight at room temperature, then air was bubbled within the resulting solution for 12 h. After addition of acetic 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.

B. Charge 5 g (18.5 mmol) of azodibenzoic acid, 25 mL (40.75 g, 340 mmol) of thionyl chloride, and 0.076 mL of Et_3N 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. (1 g, 16 %).

3.3.3.2 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

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 (1.15 g, 2.12 mmol) is dissolved in 20 mL of CH_2Cl_2. To this solution, added was DMAP (0.117 g, 0.96 mmol), Et_3N (0.3 mL, 2.16 mmol) in that order and the reaction mixture was stirred and cooled to 0 ^oC. 4,4'-bis(chlorocarbonyl) azobenzene (0.295 g, 0.96 mmol) dissolved in 5 mL of CH_2Cl_2 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 the desired product as viscous red liquid (Yield: 0.67 g, 53 %). It was solidified upon storage.

^1H NMR ($CDCl_3$, δ) 8.06 (d, J = 8.4 Hz, 4H, ArH of azobenzene), 7.95 (d, J = 8.4 Hz, 4H, ArH of azobenzene), 7.28-7.17 (m, 10H, ArH), 4.94 (t, 2H, ArCH), 4.59 and 4.46 (m, 4H, ArCHCHH), 4.45-4.24 (m, 8H, $CH_2OC{=}O$), 1.84 (12H, $CBr(CH_3)_2$), 1.69-0.73 (m, 42H), m.p. (DSC): 46-47 ^oC.

^{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 $(M+Na)^+$.

3.3.4 Synthesis of AB_2 type miktoarm star polymers via ROP-ATRP route

3.3.4.1 Synthesis of poly (ε-caprolactone) (PCL) macroinitiator by ROP

PCL macroinitiator was prepared by the ROP of ε-caprolactone in bulk using Stannous octanoate, $Sn(Oct)_2$ as a catalyst and *2-hydroxyethyl 3-[(2-bromopropanoyl)oxy]-2-{[(2-bromopropanoyl) oxy]methyl}-2-methyl-propanoate* as an initiator at 110 ^oC for a given time. To a previously flamed Schlenk tube equipped with a magnetic stirring bar, ε-CL (3 mL, 28.3 mmol), catalytic amount of $Sn(Oct)_2$

([Initiator]/[$Sn(Oct)_2$]=400) and miktofunctional initiator (0.422 g, 0.94 mmol) were added in the order mentioned. The tube was degassed by three freeze-pump-thaw (FPT) cycles left under vacuum and placed in a thermostated oil bath. After the polymerization, the resulting polymer was dissolved in THF, precipitated into excess amount of methanol and then isolated by vacuum filtration and dried at room temperature *in vacuo* for 1 day.

3.3.4.2 Synthesis of the PCL–(P*t*BA)$_2$ miktoarm star polymers by ATRP

The synthesis of the PCL–(P*t*BA)$_2$ miktoarm star polymers was accomplished by the ATRP of *t*BA (*tert*-butyl acrylate) in bulk with CuBr/PMDETA (Copper bromide/*N,N,N',N'',N''*-pentamethyldiethylenetriamine) as a catalyst and PCL as macroinitiator. To a Schlenk tube equipped with a magnetic stirring bar, the degassed *t*BA (2 mL, 13.65 mmol), PMDETA (28.2 μL, 0.14 mmol), CuBr (19.4 mg, 0.14 mmol) and PCL macroinitiator (0.25 g, 0.07 mmol) were added in the order mentioned. The polymerization was carried out at 100 ^{o}C under degassed conditions for the given time. After the polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove metal salt. The excess of THF and the unreacted monomer were evaporated under reduced pressure. The resulting polymer was dissolved in THF and precipitated into cold methanol/water (80/20; v/v). After decantation, the polymer was dissolved in CH_2Cl_2, extracted with water and dried over Na_2SO_4. Finally, the organic phase was removed by evaporation.

3.3.4.3 Synthesis of the PCL–(PMMA)$_2$ miktoarm star polymers by ATRP

The preparation of PCL–(PMMA)$_2$ was accomplished with MMA (7.5 mL, 70.1 mmol), diphenyl ether, DPE (3.75 mL) as a solvent, PMDETA (28.2 μL, 0.14 mmol) CuCl (13.4 mg, 0.14 mmol), and PCL macroinitiator (0.25 g, 0.07 mmol) at 90 °C. After the prescribed reaction time, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove metal salt. The excess of THF and the unreacted monomer were evaporated under reduced pressure. The resulting polymer was dissolved in THF, precipitated into methanol and then isolated by vacuum filtration and dried at room temperature *in vacuo* for 1 day.

3.3.4.4 Preparation of the amphiphilic PCL-$(PAA)_2$ miktoarm star polymer

PCL-(PtBA)$_2$ (0.4 g, 0.015 mmol) was dissolved in 5 mL of dichloromethane and 1 mL of trifluoroacetic acid (TFA). The reaction mixture was stirred for 24 h at room temperature and then precipitated into hexane, washed with dichloromethane. 0.235 g of amphiphilic polymer (PCL-PAA)$_2$ was recovered after vacuum drying (Yield: 60 %).

3.3.5. Synthesis of ABC miktoarm star polymers by ROP-NMP-ATRP route

3.3.5.1 Synthesis of PCL macroinitiators by ROP

PCL macroinitiator was prepared by the ROP of ε-CL in bulk using $Sn(Oct)_2$ as a catalyst and 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 as an initiator at 110 ^{o}C for a given time. To a previously flamed Schlenk tube equipped with a magnetic stirring bar, ε-CL (3 mL, 28.3 mmol), catalytic amount of $Sn(Oct)_2$ ([Initiator]/[$Sn(Oct)_2$] = 300) and initiator (0.384 g, 0.71 mmol) were added in the order mentioned. The tube was degassed by FPT cycles left under vacuum and placed in a thermostated oil bath. After the polymerization, the mixture was diluted with THF, precipitated into an excess amount of methanol and then isolated by filtration and dried at room temperature *in vacuo* oven for 1 day.

3.3.5.2 Synthesis of AB type PCL-*b*-PS precursors by NMP

The synthesis of PCL-*b*-PS precursors having bromine functionality in the core was accomplished by the NMP of St (3 mL, 26.2 mmol) in bulk using previously obtained PCL macroinitiator (0.25 g, 0.062 mmol). The reaction mixture was degassed by three FPT cycles, left *in vacuo*, placed in an oil bath at 125 °C, and stirred for a given polymerization time. After the polymerization, the polymerization mixture was diluted with THF, precipitated into methanol, isolated by filtration, and dried *in vacuo* at room temperature.

3.3.5.3 Synthesis of ABC type PCL-PS-P*t*BA miktoarm star polymers by ATRP

The synthesis of PCL-PS-PtBA miktoarm star polymers was carried out by the ATRP of tBA (1.4 mL, 9.83 mmol) in bulk using CuBr (2.4 mg, 0.0166 mmol)/PMDETA (3.5 μL, 0.0166 mmol) as a catalyst and previously obtained

PCL-*b*-PS macroinitiator (0.3 g, 0.0166 mmol). The polymerizations were carried out at 100 ^{o}C under degassed conditions for the given times. After the polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove metal salt. The excess of THF and the unreacted monomer were evaporated under reduced pressure. The resulting polymer was dissolved in THF and precipitated into excess amount of cold methanol/water (80/20; v/v). After decantation, the polymer was dissolved in CH_2Cl_2, extracted with water and dried over Na_2SO_4. Finally, the organic phase was evaporated to give PCL-PS-P*t*BA miktoarm star polymer.

3.3.5.4 Synthesis of PCL-*b*-PS via one-pot process by combination of NMP and ROP

To a previously flamed Schlenk tube equipped with a magnetic stirring bar, ε-CL (3 mL, 28.3 mmol), St (8.1 mL, 70.7 mmol), catalytic amount of $Sn(Oct)_2$ ([Initiator]/[$Sn(Oct)_2$] = 300) and miktofunctional initiator (0.384 g, 0.71 mmol) were added in the order mentioned. The tube was degassed by FPT cycles left under vacuum and placed in a oil bath at 125 °C for 20 h. The polymerization mixture was diluted with THF, precipitated in methanol and dried *in vacuo*.

3.3.5.5 Synthesis of PCL-PS-PMMA miktoarm star polymer by ATRP

The synthesis of PCL-PS-PMMA miktoarm star polymers was carried out by the ATRP of MMA (1.5 mL, 14 mmol) in DPE (1.5 mL) using CuCl (3 mg, 0.028 mmol)/PMDETA (6 μL, 0.028 mmol) as a catalyst system and previously obtained PCL-*b*-PS macroinitiator (0.275 g, 0.028 mmol). The polymerization was carried out at 90 ^{o}C under degassed conditions for the given time. Then, the polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and precipitated in methanol.

3.3.6 Synthesis of photoresponsive miktoarm star copolymer containing an azobenzene moiety at the core by ATRP-NMP route

3.3.6.1 Preparation of $(PMMA)_2$ macroinitiator by ATRP of MMA

$(PMMA)_2$ macroinitiator was prepared by ATRP of MMA using *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 as an initiator and CuCl complexed by PMDETA as the catalyst at 60 ^{o}C. To a Schlenk tube equipped with a magnetic stirring bar, the degassed MMA, (1 mL, 9.35 mmol), ligand, (PMDETA, 19.5 μL, 0.0934 mmol), CuCl (9.2 mg, 0.0934 mmol) and initiator (0.061 g, 0.0467 mmol) 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 ^{o}C for 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 ^{o}C.

3.3.6.2 Preparation of $(PMMA)_2$-$(PS)_2$ miktoarm star copolymer by NMP of St

$(PMMA)_2$-$(PS)_2$ miktoarm star copolymer was prepared using NMP of St (0.687 mL, 6.0 mmol) in the presence of TEMPO functionalized $(PMMA)_2$ as a macroinitiator, (0.09 g, 0.02 mmol). The reaction mixture was degassed by FPT cycles and left in *vacuo*. The tube was then placed in an oil bath thermostated at 125 ^{o}C for 19.5 h. 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 ^{o}C.

4. RESULTS and DISCUSSION

4.1 Synthesis of AB_2 type Miktoarm Star Polymers via ROP-ATRP Route

The preparation of AB_2 type miktoarm star polymers is based on a two-step reaction consisting of the synthesis of well-defined bromine terminated poly(ε-caprolactone), (PCL), using a miktofunctional initiator **(2)** in the ROP of ε-caprolactone, followed by the ATRP of *t*BA or MMA initiated with PCL macroinitiator thus obtained (4.2).

4.1.1 Synthesis of AB_2 type miktofunctional initiator (2)

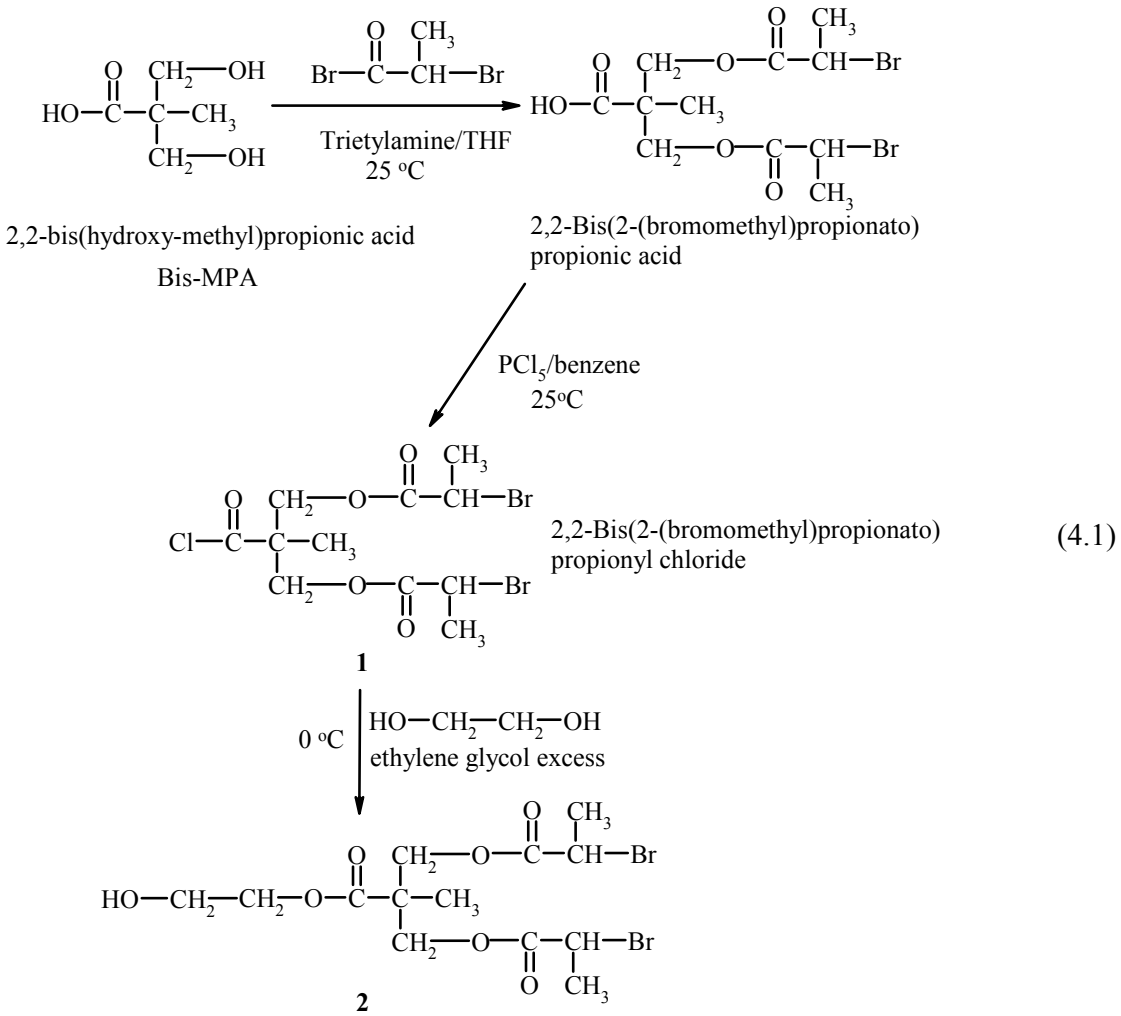
A novel miktofunctional initiator (**2**), 2-hydroxyethyl 3-[(2-bromopropanoyl)oxy]-2-{[(2-bromopropanoyl)oxy]methyl}-2-methyl-propanoate, possessing one initiating site for ROP and two initiating sites for ATRP is synthesized in a three-step reaction sequence shown in 4.1. Miktofunctional initiator (**2**) was prepared from 2,2-bis[methyl(2-bromopropianato)propionyl chloride (**1**) and ethylene glycol in 40% yield. The ^{1}H NMR spectrum of compound **2** shows the signals of the ethylene glycol segment (*H*O-C*H*$_2$: 2.2 and 3.81 ppm) together with the signals of the 2-bromopropanoate groups (C*H*(C*H*$_3$)Br: 4.50-4.18 and 1.79 ppm) (Figure 4.1).

4.1.2 Synthesis of PCL macroinitiator by ROP

PCL macroinitiator containing dual bromine end groups was prepared using a miktofunctional initiator **(2)** and $Sn(Oct)_2$ as a catalyst in bulk at 110 ^oC (4.2). The experimental conditions and the properties of PCL macroinitiator are given in Table 4.1. The ^{1}H NMR spectrum of PCL macroinitiator is shown in Figure 4.2 where the respective resonances including secondary bromine end groups were assigned**.** The theoretical M_n values of PCL were calculated by using the following equation:

$$M_{n,theo} = ([M]_o/[I]_o) \text{ X Conv. X } 114.15 + 448.104\ (MW_{initiator}) \quad (1)$$

where $MW_{initiator}$ is the molecular weight of the initiator (**2**) and $[M]_o$ and $[I]_o$ are the initial concentrations of the monomer and initiator, respectively.



(4.1)

The $M_{n,NMR}$ value, which was determined from the ratio of integrated peak areas of -CH_2OCO (4.0 ppm) and the initiator peaks around 4.3 ppm, were consistent with those derived from GPC and the theoretical one.

$$M_{n,\,NMR} = MW_{monomer} \times \frac{2_{CH(CH_3)Br} + 4_{COCH_2CH_2}}{2I_{CH_2OCO}} + MW_{initiator} \qquad (2)$$

where $MW_{monomer}$ and $MW_{initiator}$ are the molecular weight of the monomer (ε-CL) and initiator (**2**), respectively. Usually determining more precise the molecular weight for PCL a correction formula is used in the literature [305] :

$$M_{n,PCL} = 0.259 \text{ X } M_{n,GPC}^{1.073} \qquad (3)$$

where $M_{n,GPC}$ is the molecular weight determined from GPC using PS standards.

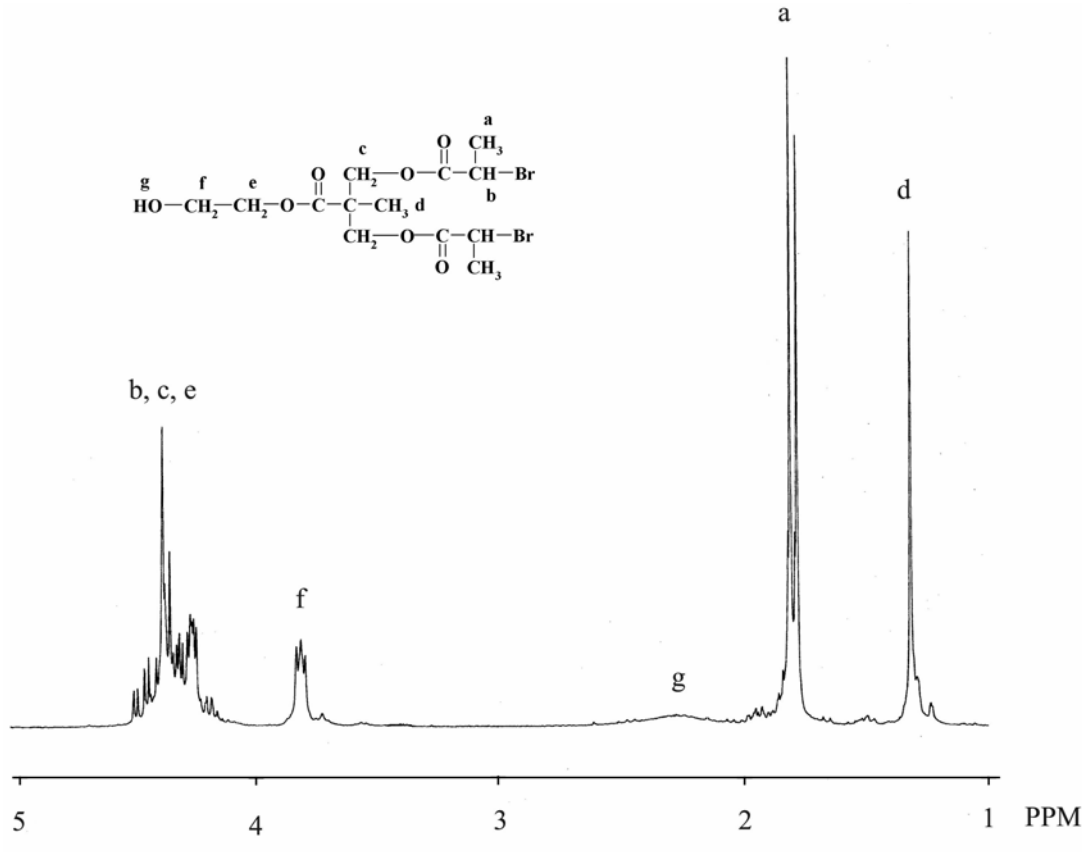


Figure 4.1: ^{1}H-NMR spectrum of AB_2 type miktofunctional initiator (**2**).

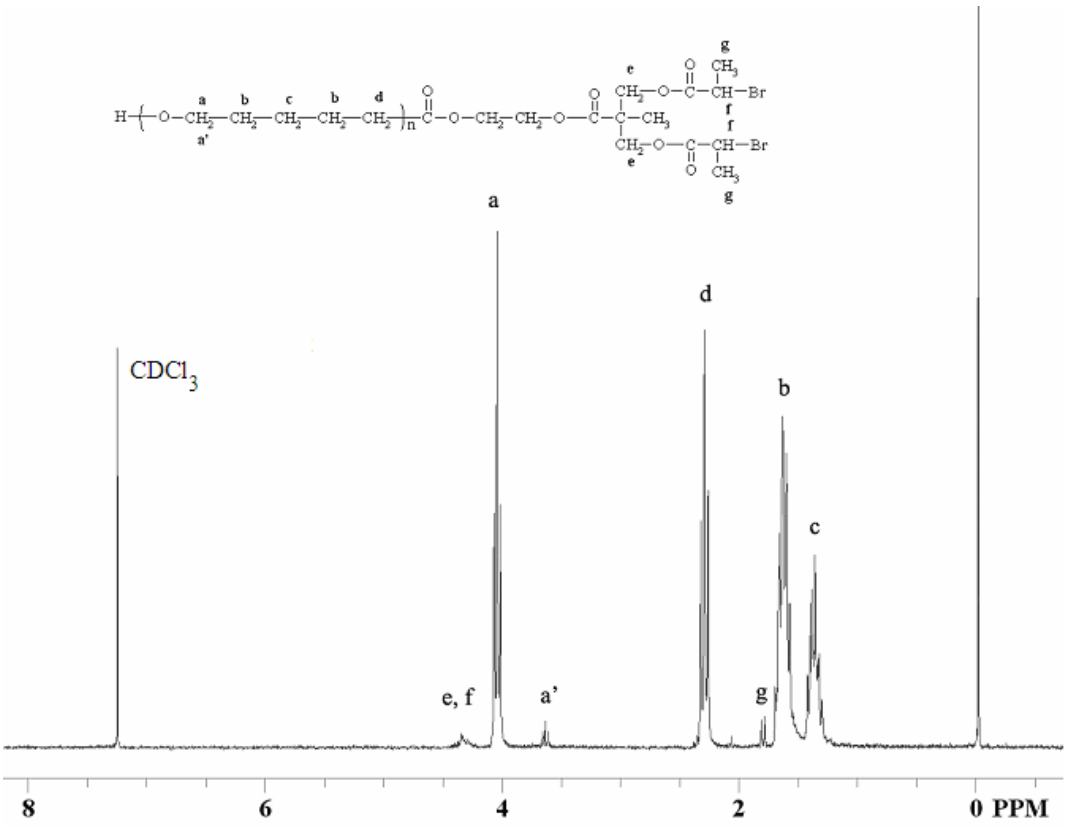


Figure 4.2: ^{1}H NMR spectrum of poly(ε-caprolactone) homopolymer (**T1**) in $CDCl_3$.

4.1.3 Synthesis of PCL–(P*t*BA)$_2$ miktoarm star polymers by ATRP

The functionalized PCL was employed as a macroinitiator for the ATRP of *t*BA in the presence of CuBr/PMDETA complex system as the catalyst in bulk at 100 ^{o}C (Table 4.1). The GPC traces of macroinitiator and AB_2 miktoarm star polymer are shown in Figure 4.3. These chromatograms show the formation of the P*t*BA blocks. After polymerization of *t*BA, the GPC trace shifts to the higher molecular weights region along with complete disappearance of the peak of the precursor indicating that efficient initiation has occurred. The polydispersity index of the miktoarm star polymer, PCL-(P*t*BA)$_2$, is relatively low (1.18).

Table 4.1: Synthesis of PCL-(P*t*BA)$_2$ and PCL-(PMMA)$_2$ miktoarm star polymers derived from PCL macroinitiator.

Run	Monomer	$[M]_o/[I]_o$	Initiator	Time (h)	Conv (%)	$M_{n,theo}$	$M_{n,NMR}$	$M_{n,GPC}$	M_w/M_n
T1[a]	ε-CL	30	**2**	64	75	3000	3700	2800[d]	1.12
T2[a]	ε-CL	50	**2**	46	55	3590	4180	3370[d]	1.23
T3[b]	*t*BA	80	**T1**	0.67	63	10160	11900	16550	1.27
T4[b]	*t*BA	200	**T1**	3	90	26770	27000	38300	1.18
T5[c]	MMA	1000	**T1**	2.75	66	69780	61400	89600	1.23
T6[c]	MMA	1000	**T2**	2.16	36	40220	43780	62850	1.17

[a]The polymerization was carried out at 110 ^{o}C; $[Initiator]_o/[Sn(Oct)_2]_o$ = 400.
[b]$[I]_o$:$[PMDETA]_o$:$[CuBr]_o$ = 1:2:2; the polymerization was carried out at 100 °C.
[c]$[I]_o$:$[PMDETA]_o$:$[CuCl]_o$ = 1:2:2;,the polymerization was carried out at 90 °C in DPE; MMA/DPE = 2 (v/v)
[d]Molecular weights were calculated with the aid of polystyrene standards by using an equation [305] (M_{PCL}= 0.259 X $M_{PSt}^{1.073}$).

The signals of the *tert*-butyl ester group were also assigned by means of ^{1}H NMR measurements confirming the incorporation of the P*t*BA blocks in the miktoarm star polymer (Figure 4.4).

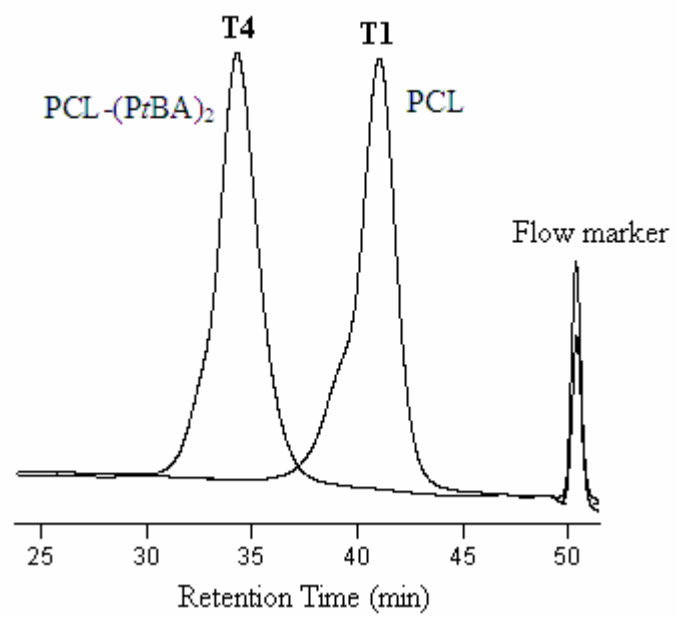


Figure 4.3: GPC traces of poly(ε-caprolactone) (**T1**), PCL-(P*t*BA)$_2$ (**T4**).

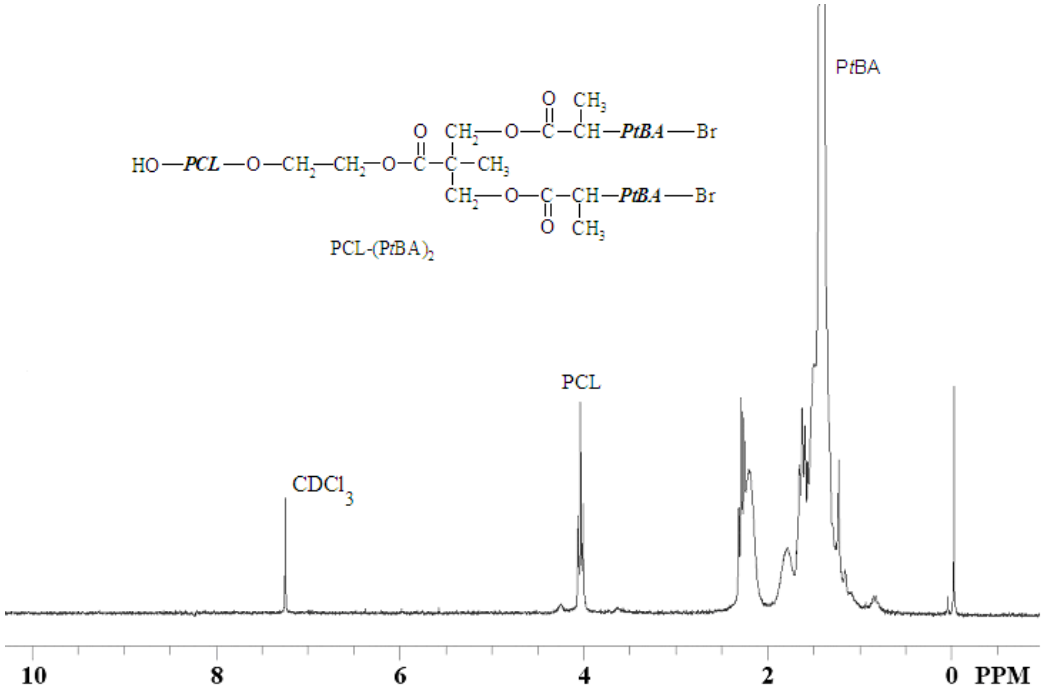


Figure 4.4: ^{1}H NMR spectrum of PCL-(P*t*BA)$_2$ miktoarm star polymer (**T4**) in $CDCl_3$.

The theoretical M_n value of PCL-(P*t*BA)$_2$ was calculated according to the following formula:

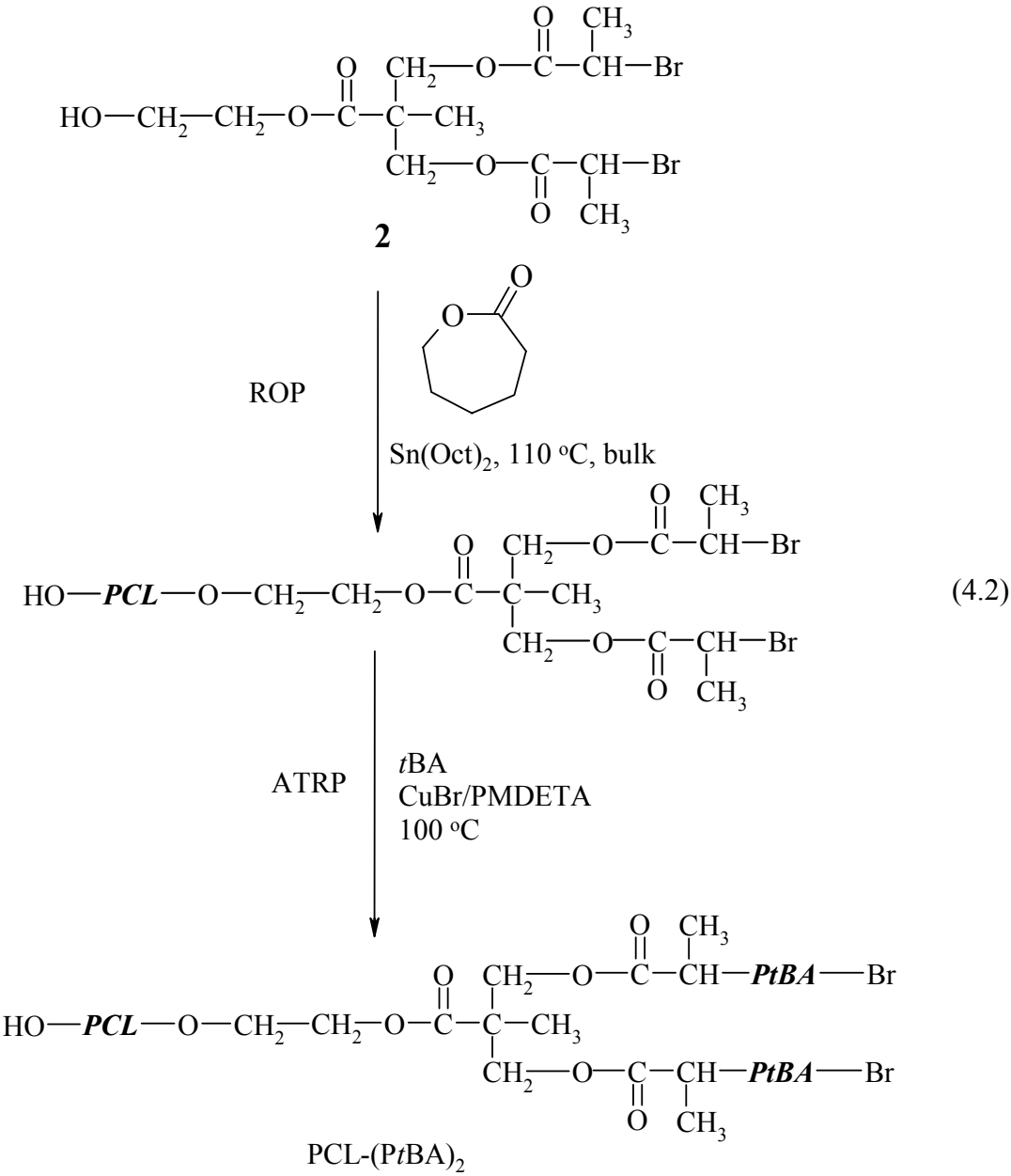
$$M_{n,theo} = ([M]_o/[I]_o) \text{ X Conv. X } 128.17 + M_{n,NMR} \text{ of PCL precursor} \quad (4)$$

where $[M]_o$ and $[I]_o$ are the initial concentrations of the monomer and macroinitiator, respectively.

The molecular weight ($M_{n,NMR}$) was determined from the integration of signals appeared at 1.41 ppm (-C(C*H*)$_3$) of *t*BA to 4.01- 4.06 ppm (C*H*$_2$OCO) of CL.

$$M_{\text{n, NMR}} = \text{MW}_{\text{monomer}} \times \frac{9\text{I}_{\text{C(CH}_3)_3}}{2\text{I}_{CH_2\text{OCO}}} + M_{\text{n,NMR}} \text{ of PCL precursor} \qquad (5)$$

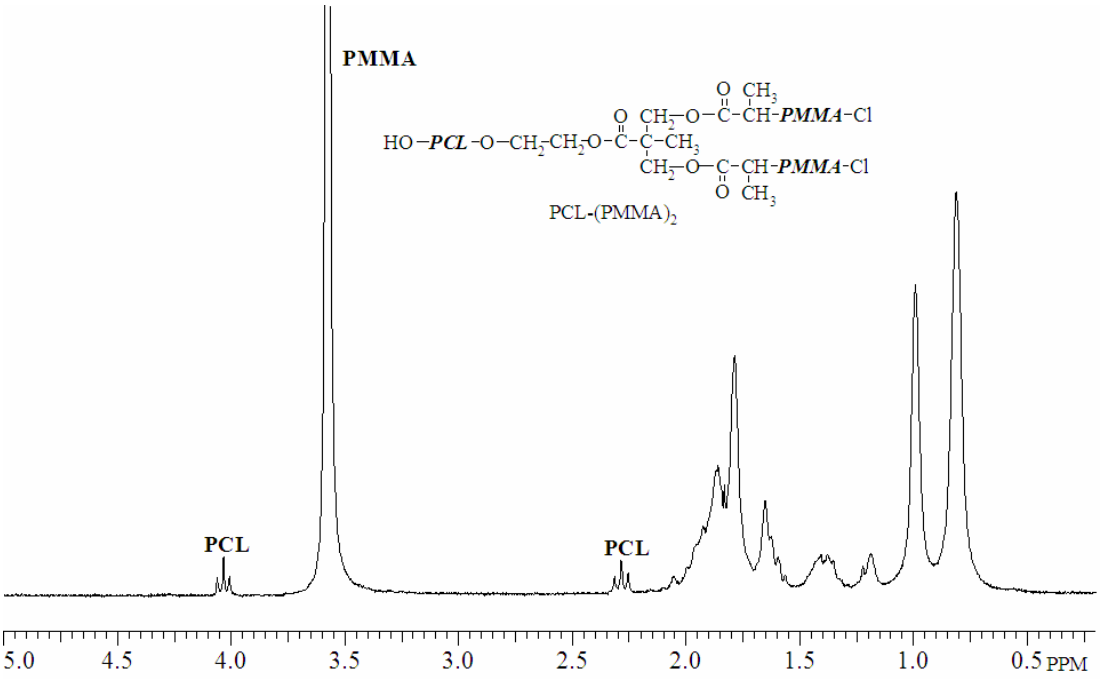
where $\text{MW}_{\text{monomer}}$ is the molecular weight of *t*BA.



(4.2)

4.1.4 Synthesis of PCL–$(PMMA)_2$ miktoarm star polymers by ATRP

The ATRP of MMA can also be carried out using PCL macroinitiator, CuCl/PMDETA as a catalyst, DPE (MMA/DPE = 2; v/v) at 90 ^{o}C (Table 4.1). The bromine terminal group of PCL macroinitiator was converted to chlorine soon after the polymerization of MMA started where CuCl was used as Cu(I) species, in which the halogen exchange enhanced the rate of the initiation over the rate of the propagation [306]. According to the ^{1}H NMR spectrum (Figure 4.5), the methyl ester peak around 3.5 ppm together with the characteristic peaks of PCL revealed the structure of PCL-$(PMMA)_2$ miktoarm star copolymer.



PCL-$(PMMA)_2$

Figure 4.5: ^{1}H NMR spectrum of PCL-$(PMMA)_2$ miktoarm star polymer (**T5**) in $CDCl_3$.

The theoretical M_n value of the star copolymer was also calculated using:

$$M_{n,theo} = ([M]_o/[I]_o) \text{ X Conv. X } 100.12 + M_{n,NMR} \text{ of PCL precursor} \quad (6)$$

and the molecular weight of the resulting miktoarm star ($M_{n,NMR}$) was determined from the ratio of the ^{1}H NMR integrated peak areas of the -OCH_3 groups of the PMMA relative to the -CH_2OCO groups of the PCL signals.

$$M_{n,\,NMR} = MW_{monomer} \times \frac{3I_{OCH_3}}{2I_{CH_2OCO}} + M_{n,\,NMR} \text{ of PCL precursor} \quad (7)$$

where $MW_{monomer}$ is the molecular weight of MMA. The characterization by GPC confirmed the clear shift between PCL-$(PMMA)_2$ miktoarm star polymers and its precursor (Figure 4.6). Moreover, the low polydispersity index (1.23) indicated a controlled growth of the PMMA blocks.

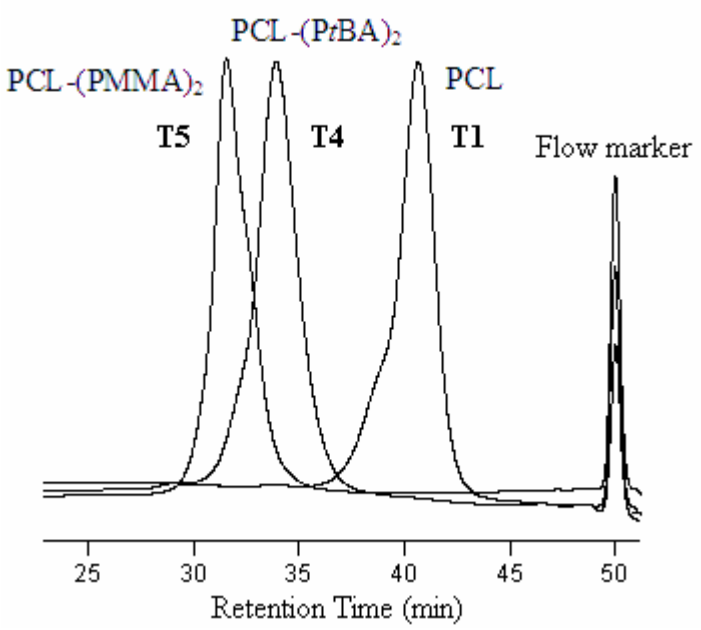


Figure 4.6: GPC traces of poly(ε-caprolactone) (**T1**), PCL-$(PtBA)_2$ (**T4**) and PCL-$(PMMA)_2$ (**T5**).

4.1.5 Preparation of amphiphilic PCL-$(PAA)_2$ miktoarm star polymer

The *tert*-butyl ester groups of the P*t*BA blocks were then cleaved by treatment with trifluoroacetic acid in dichloromethane yielding amphiphilic PCL-$(PAA)_2$ miktoarm star polymer with 60 % yield. The ^1H NMR spectrum showed no signal at 1.4 ppm due to the removal of the *tert*-butyl protons of the P*t*BA blocks (Figure 4.7). In addition, the evolution of a signal at 12.2 ppm is indicative of -COOH protons of PAA blocks. The resulting amphiphilic polymer is not soluble in THF and dichloromethane, and soluble in DMSO.

4.1.6 Investigation of thermal properties of synthesized polymers

Thermal behavior of polymers was investigated by DSC. PCL macroinitiator (**T1**) showed two transitions around –55 and 52 °C as T_g and T_m, respectively (Figure 4.8). However, PCL-$(PMMA)_2$ miktoarm star polymer (**T5**) showed only one T_g at 100 °C similar to that of poly(methyl methacrylate) homopolymer (Figure 4.9).

In the case of PCL-(P*t*BA)$_2$ (**T4**), corresponding single glass transition at 51.5 °C, which was consistent with that of P*t*BA homopolymer, was observed (Figure 4.9).

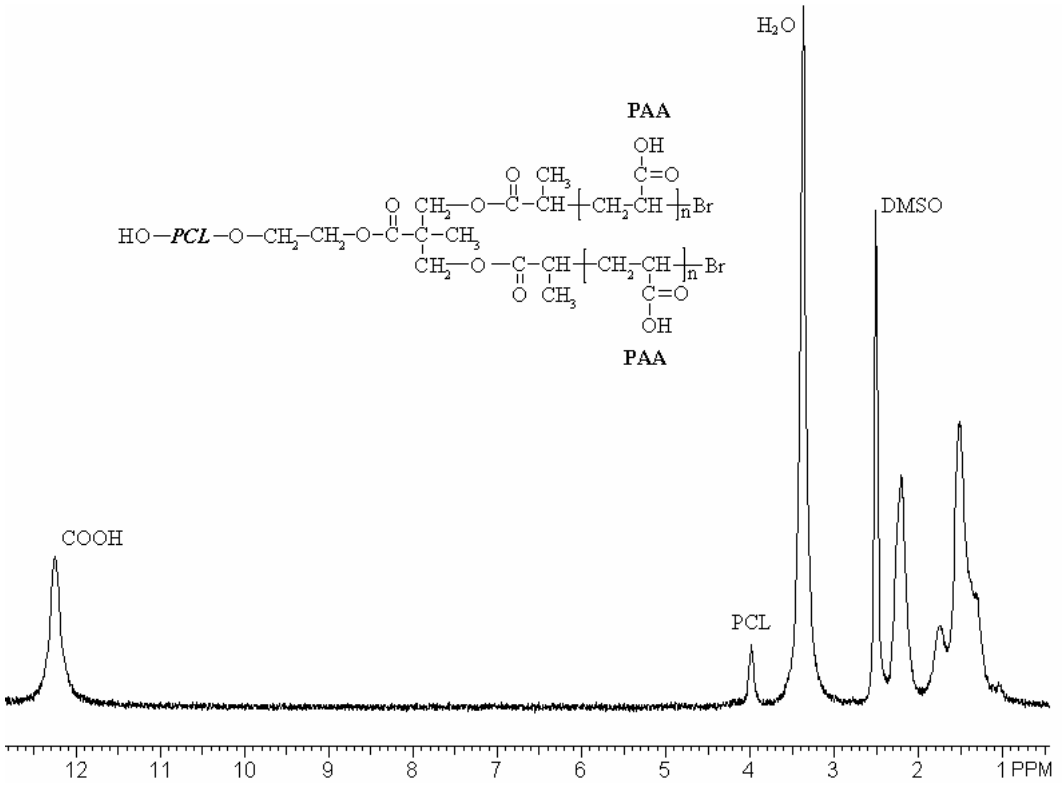


Figure 4.7: PCL-(PAA)$_2$ miktoarm star polymer in DMSO-d$_6$ (obtained from **T4**).

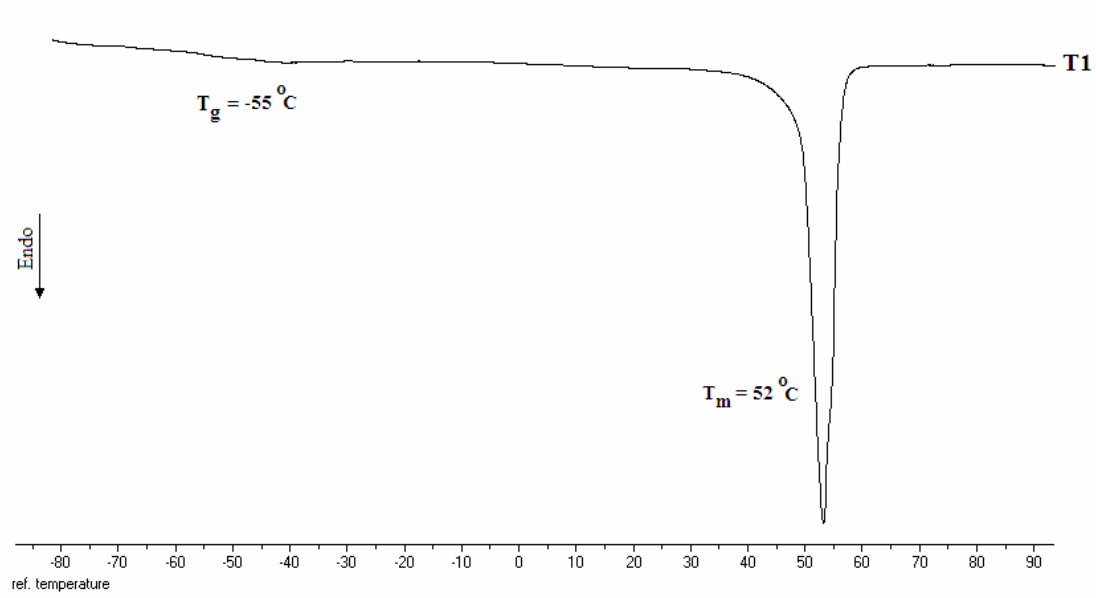


Figure 4.8: DSC trace of PCL **T1**

This behavior might be due to relatively very short PCL arm comparing with both PMMA and P*t*BA arms. Thus, the thermal transitions of the miktoarm star copolymers were dominated with the long PMMA or P*t*BA blocks.

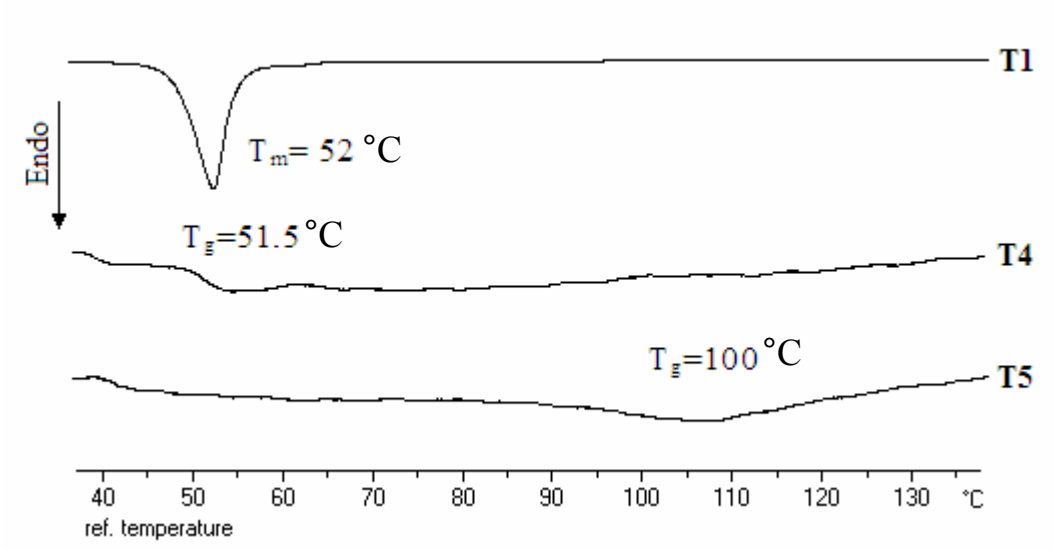
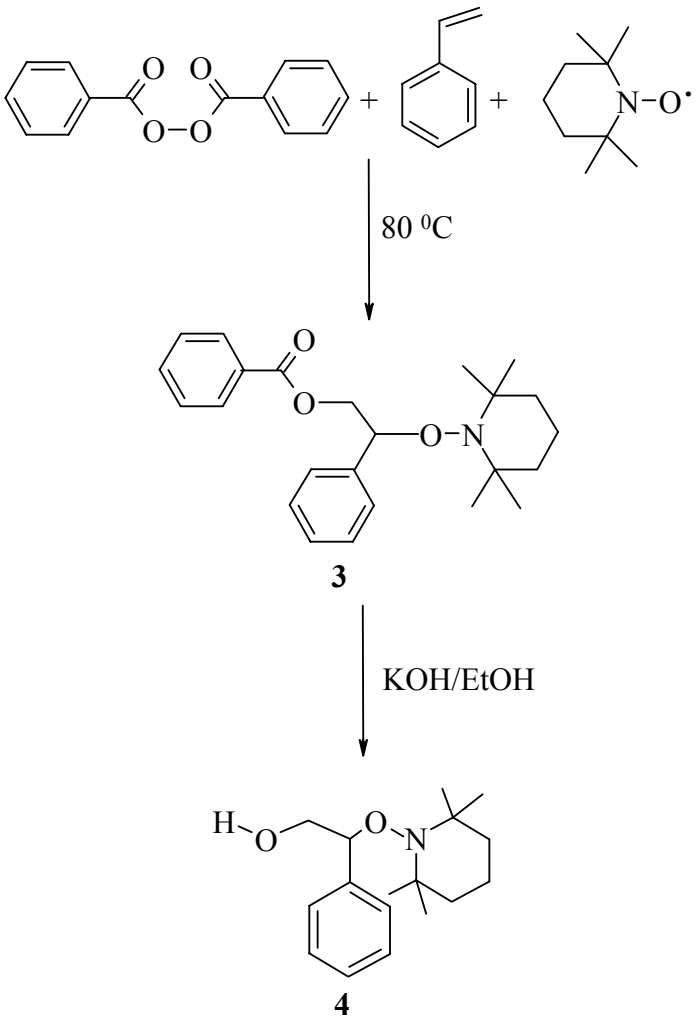


Figure 4.9: DSC traces of PCL **T1,** PCL-(P*t*BA)$_2$ **T4** and PCL-(PMMA)$_2$ **T5.**

4.2 Synthesis of ABC Miktoarm Star Polymers by ROP-NMP-ATRP Route

4.2.1 Synthesis of ABC type miktofunctional initiator

For the synthesis of ABC type miktofunctional initiator, first we obtained 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester (**3**) according to the procedure reported by Hawker et al. [307]. **3** was then hydrolyzed with aqueous potassium hydroxide (KOH) to give 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]-1-ethanol, **4** (4.3). 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 ^{1}H NMR spectra of the corresponding ester and alcohol precursors are presented in Figures 4.10 and Figure 4.11, respectively.



(4.3)

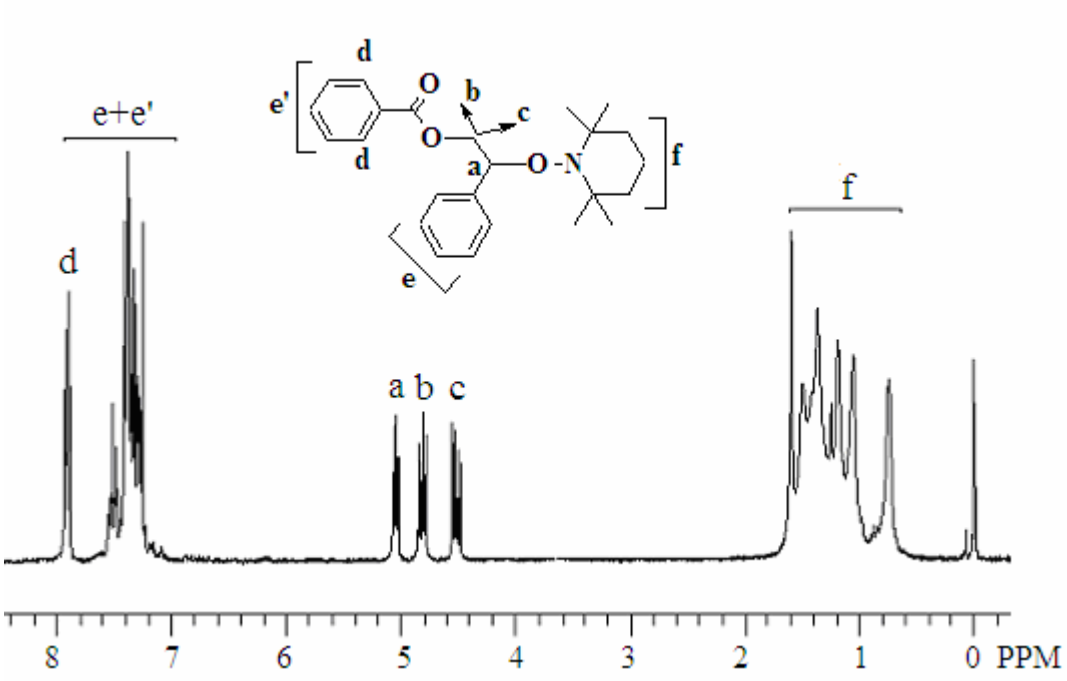


Figure 4.10: ^{1}H NMR spectrum of benzoic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperin-1-yloxy)-ethyl ester (**3**).

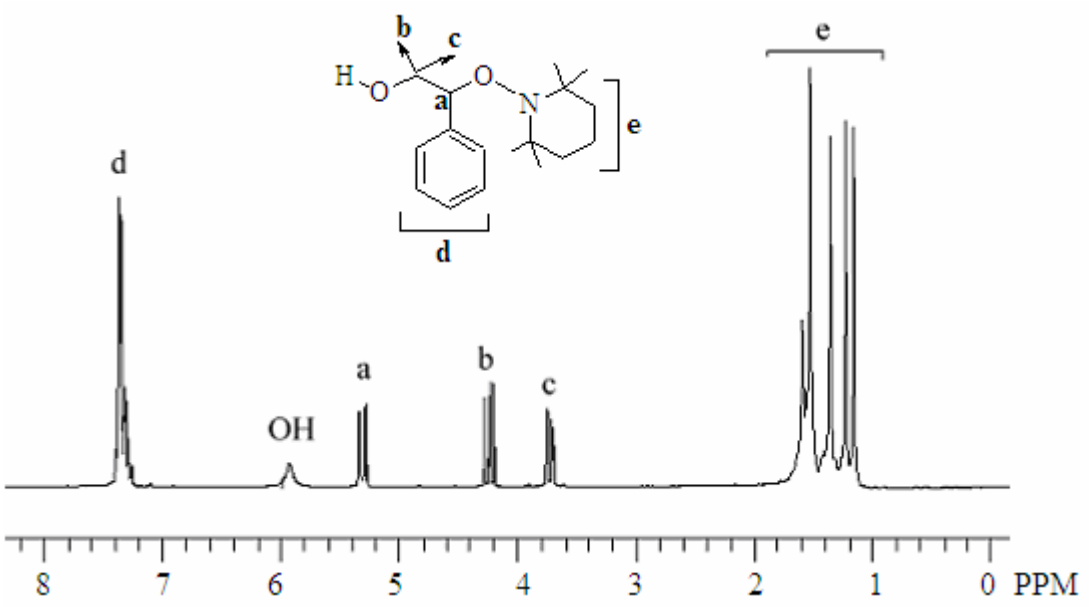
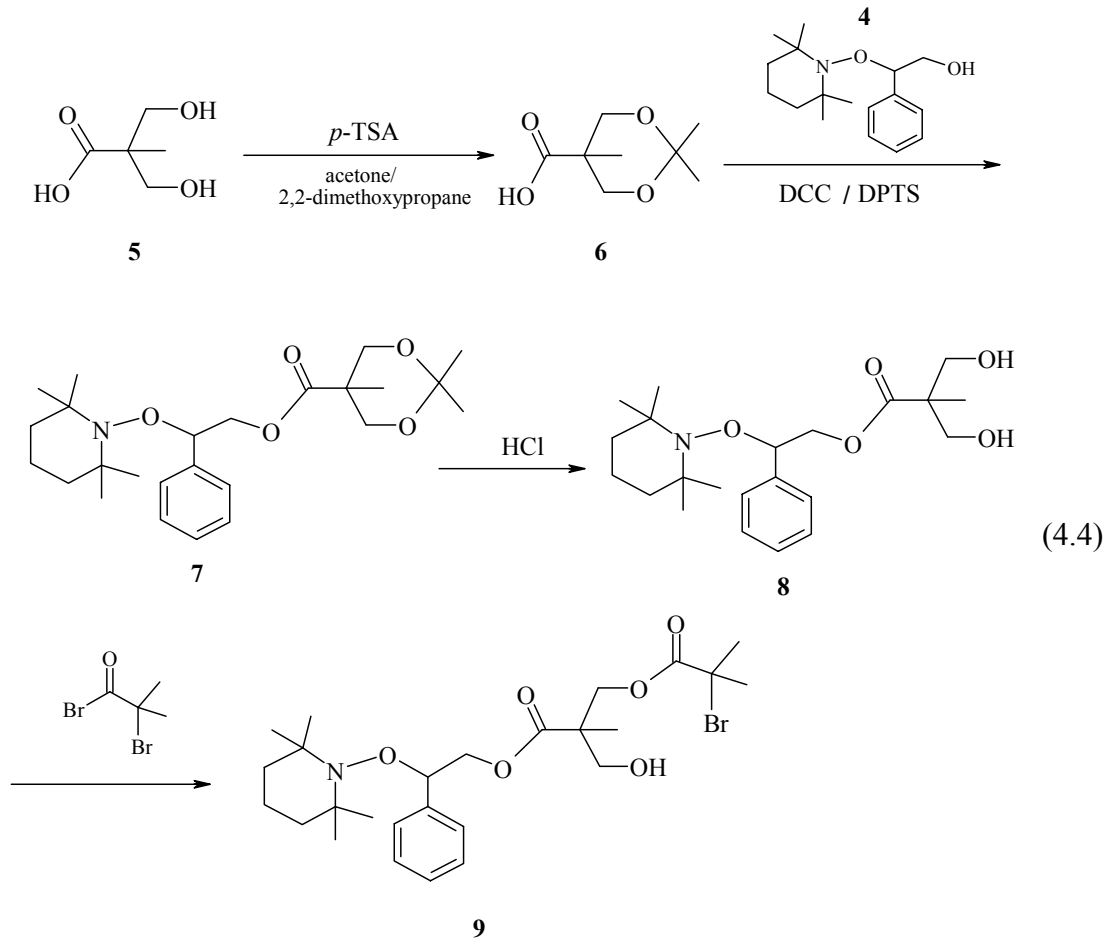


Figure 4.11: ^{1}H NMR spectrum of 2-phenyl-2-(2,2,6,6-tetramethyl-piperin-1-yloxy)-ethanol (**4**).



(4.4)

In order to convert the hydroxyl functionality of compound **4** into two hydroxyl functionalities, successive protection, esterification and deprotection reactions were realized. For this purpose, we synthesized diacetal of bis(hydroxymethyl)propionic

acid, **6**, as a core compound starting from 2,2-bis (hydroxymethyl)-propanoic acid**, 5** (4.4). In this reaction, **5** was reacted with excess amount of dry acetone using *p*-toluene sulfonic acid (*p*-TSA) as catalyst. Additionally, 2,2-dimethoxypropane was deliberately used to provide acetone during the reaction. The ^{1}H NMR spectrum of compound **6** is shown in Figure 4.12.

Then reaction of **6** with 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]-1-ethanol (**4**) produced the TEMPO functional compound **7** using DCC and DPTS in high yields after column chromatography purification. Although this procedure was reported to be a suitable method for the esterification reaction [308], 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. ^{1}H NMR spectrum of compound **7** clearly shows the signals of aromatic hydrogens appeared at 7.2-7.3 ppm (Figure 4.13).

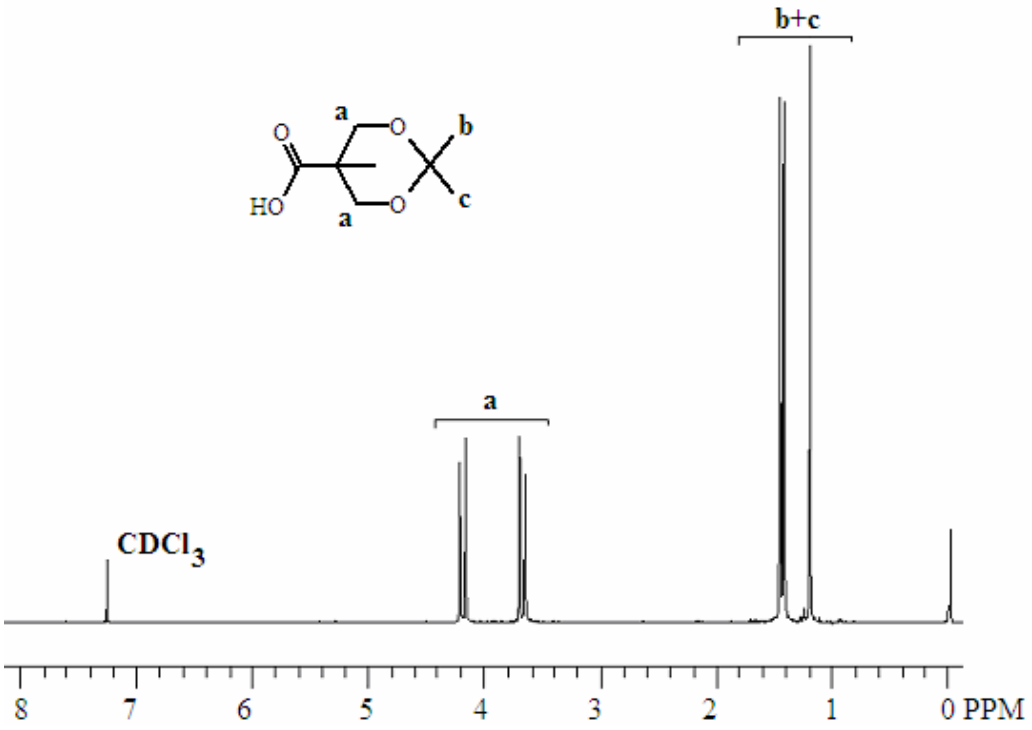


Figure 4.12: ^{1}H-NMR spectrum of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid (**6**).

Deprotection of the acetonide groups of compound **7** can easily be accomplished quantitatively in the presence of 1 M HCL to yield **8**. The hydroxyl groups of **8** can clearly be seen from δ = 2.61 and 2.74 ppm together with the signals associated with

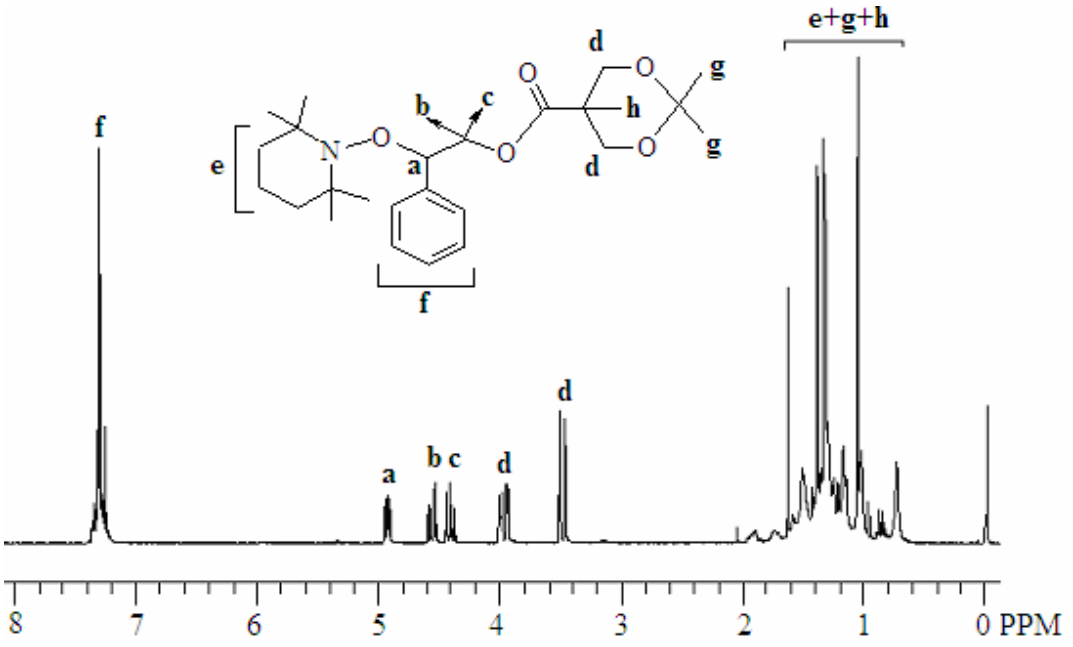


Figure 4.13: [1]H-NMR spectrum of 2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester (**7**).

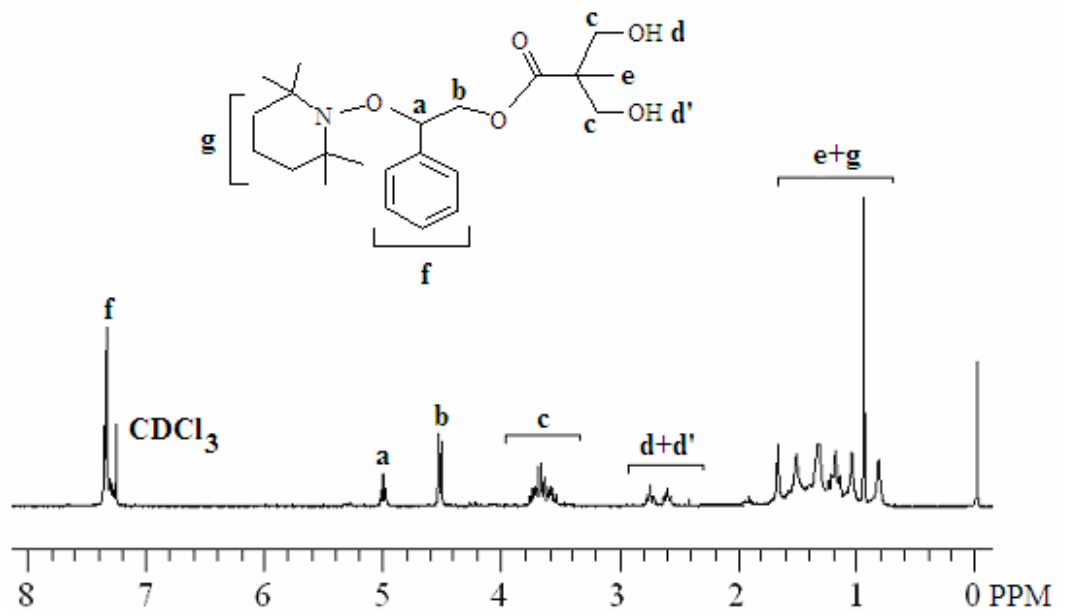


Figure 4.14: [1]H NMR spectrum of 3-hydroxy-2-hydroxymethyl-2-methyl-propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester (**8**).

The functionality serves as ATRP initiator was introduced into the core by esterification reaction of one hydroxyl group of **8** with 1 equivalent of 2-bromoisobutyrylbromide. It should be pointed out that at this step severe reaction conditions may cause the hydrolysis of the ester groups present in the structure.

Therefore, the esterification process was performed at room temperature and 2-bromoisobutryl bromide was added in a dropwise manner. The disubstituted product did not occur due to the probably steric hindrance, so that tri miktofunctional initiator **9** is obtained in high yields.

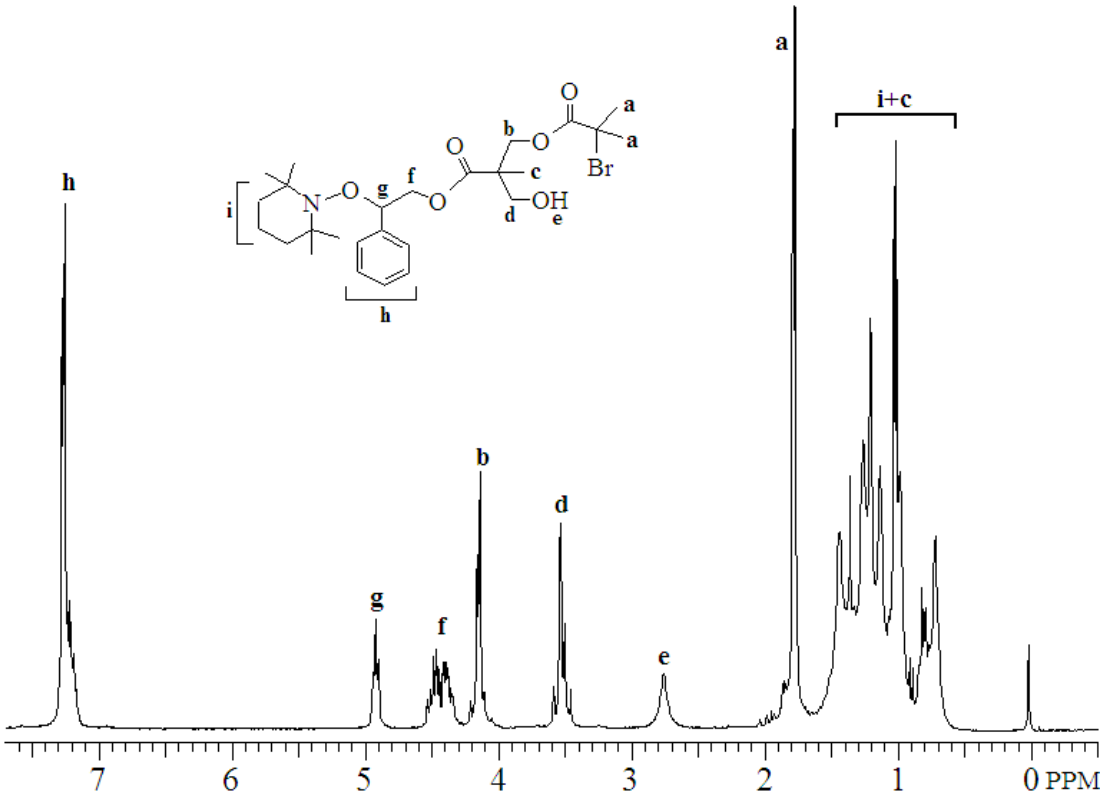


Figure 4.15: ^{1}H NMR spectrum of 2-(2-bromo-2-methyl-propionyloxymethyl)-3-hydroxy-2-methyl propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester (**9**).

The ^{1}H NMR spectrum of the compound **9** clearly shows that the –OH protons of compound **8** at δ 2.7 ppm completely removed and the signals arisen from ATRP initiator (δ = 1.85). Moreover, monofunctional hydroxyl groups (δ= 2.28) together with the shift of the -CH_2 protons adjacent to ATRP functionality to δ 4.1 ppm indicate that esterification reaction was carried out successfully. The ^{1}H NMR spectrum of the resulting compound **9** is shown in Figure 4.15.

Mass spectroscopy measurement was also carried out to elucidate the structure and to determine the exact molar mass of miktofunctional initiator, **9**. The mass spectrum of **9** was depicted in Figure 4.15.

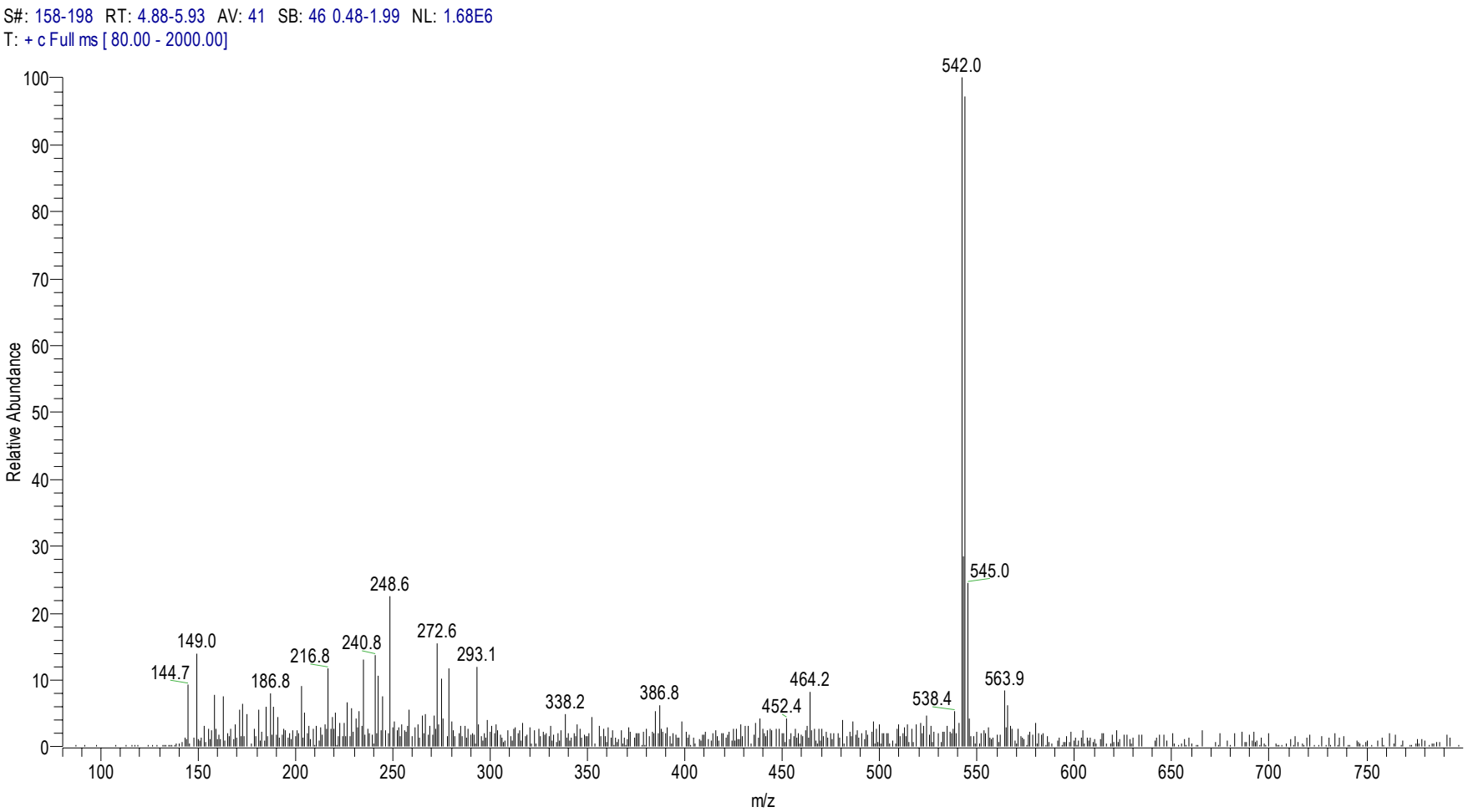


Figure 4.16: Mass spectrum of 2-(2-bromo-2-methyl-propionyloxymethyl)-3-hydroxy-2-methyl propionic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester (**9**).

4.2.2 Synthesis of PCL macroinitiators by ROP

ROP of ε-CL from the hydroxyl group of **9** was accomplished with $Sn(Oct)_2$ as a catalyst at 110 °C in bulk (4.5). The characteristics of the PCL macroinitiator (**T7**) are given in Table 4.2. The theoretical number-average molecular weight ($M_{n,theo}$) of the PCL macroinitiator was calculated according to the following formula:

$$M_{n,theo} = ([M]_o/[I]_o) \text{ X Conv. X } 114.15 + MW_{initiator}\,(542.511 \text{ g/mol}) \quad (8)$$

where $MW_{initiator}$ is the molecular weight of the initiator (**9**) and $[M]_o$ and $[I]_o$ are the initial concentrations of the monomer and initiator, respectively. In addition, $M_{n,NMR}$ which was determined from the ratio of the peak areas of the initiator peaks around 1.83 ppm and the CH_2OCO group of PCL around 4 ppm, was consistent with the theoretical M_n value.

$$M_{n,\,NMR} = MW_{monomer} \times \frac{6_{CBr(CH_3)_2}}{2I_{CH_2OCO}} + MW_{initiator} \quad (9)$$

where $MW_{monomer}$ and $M_{initiator}$ are the molecular weight of ε-CL and initiator (**9**), respectively. The ^{1}H NMR spectrum of the PCL homopolymer (**T7**) is shown in Figure 4.17.

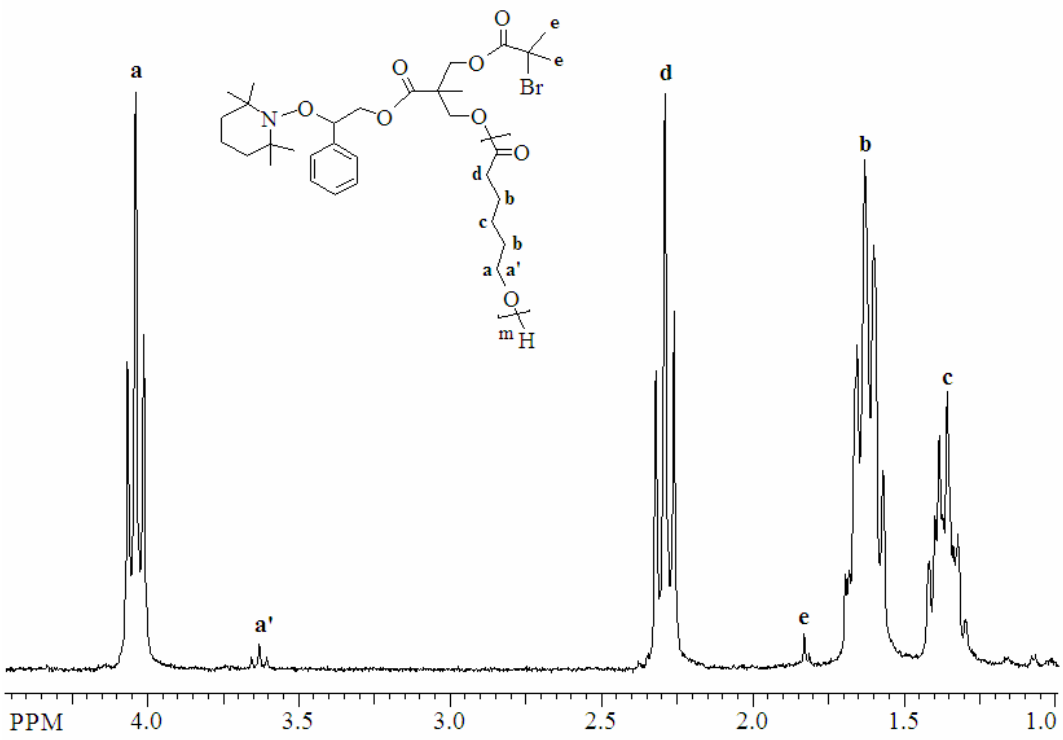
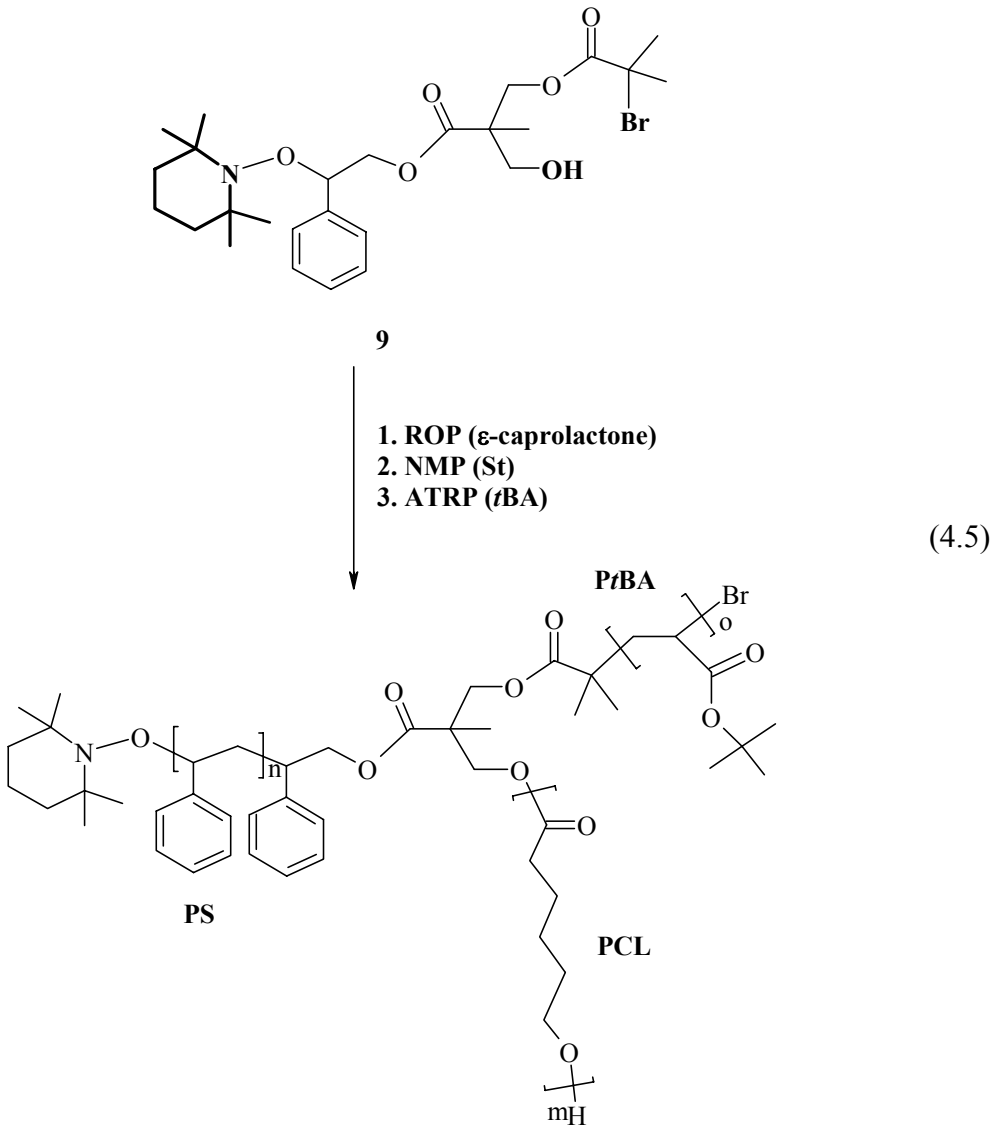


Figure 4.17: ^{1}H NMR spectrum of PCL homopolymer (**T7**) in $CDCl_3$.



(4.5)

4.2.3 Synthesis of PCL-*b*-PS by NMP

In the preparation of PCL-*b*-PS as precursor for further use in the synthesis of miktoarm star polymers, we applied different $[M]_o/[I]_o$ ratios to obtain block copolymers having different chain lengths and compositions. The other results and conditions are given in Table 4.2. For all block copolymers, the molar compositions were calculated using ^{1}H NMR measurements according to the integration of characteristic peaks of corresponding segments. PCL macroinitiator, containing both TEMPO and activated bromide groups, was used as a macroinitiator for NMP of St at 125 °C (Table 4.2). The signals of the aromatic group were assigned by means of ^{1}H NMR (Figure 4.18) and confirmed the incorporation of the St block into the block copolymer (**T8** and **T9**). The $M_{n,theo}$ value of PCL-*b*-PS was calculated with the following equation:

$$M_{n,theo} = ([M]_o/[I]_o) \text{ X Conv. X } 104.15 + M_{n,NMR} \text{ of PCL precursor (4000 g/mol)} \quad (10)$$

where $[M]_o$ and $[I]_o$ are the initial concentrations of the monomer and PCL macroinitiator, respectively.

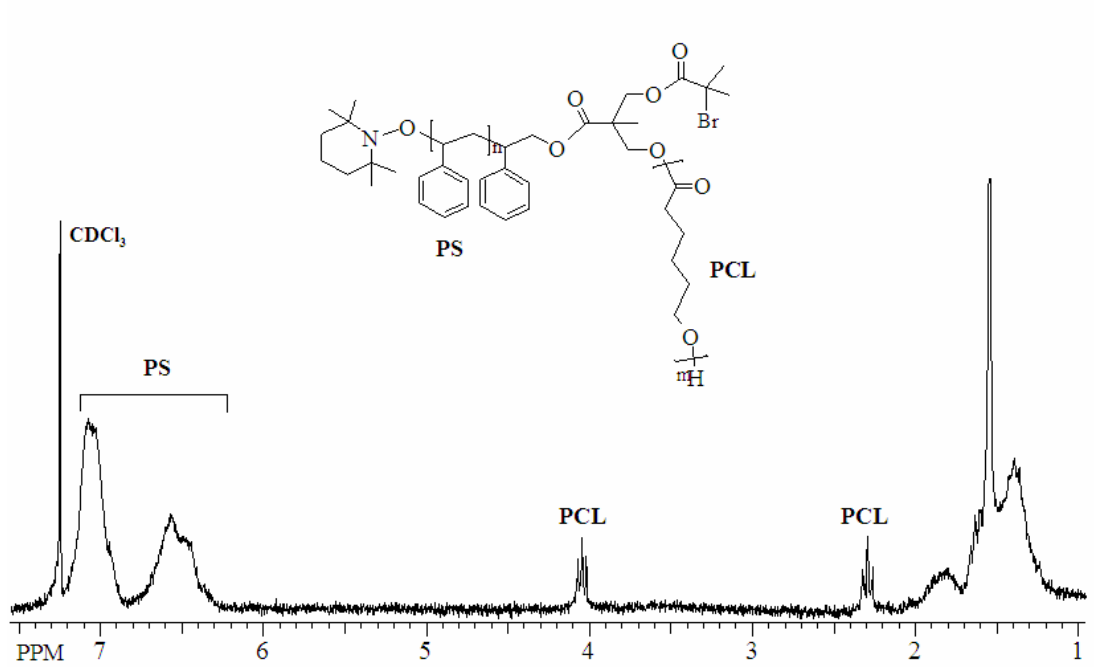


Figure 4.18: ^{1}H NMR spectrum of PCL-*b*-PS (**T8**) in $CDCl_3$.

$M_{n,NMR}$ of the PCL-*b*-PS block copolymer, determined from a ratio of integrated signals at 6.5–7.0 to 4 ppm, was consistent with $M_{n,theo}$ (Table 4.2).

$$M_{n,\,NMR} = MW_{monomer} \times \frac{5I_{Ar-H}}{2I_{CH_2OCO}} + M_{n,NMR} \text{ of PCL precursor} \quad (11)$$

where $MW_{monomer}$ is the molecular weight of St. On the other hand, the $M_{n,GPC}$ values of PCL-PS block copolymer are not in good agreement with the theoretical and NMR molecular weights due to the different hydrodynamic volume of PCL segment when compared to linear PS standards used in calibration.

The GPC traces of PCL precursor, PCL-*b*-PS are shown in Figure 4.19. The average molecular weight increased with styrene conversion in NMP, confirming the introduction of the PS block to the PCL precursor (Figure 4.19). Moreover, the disappearance of the PCL precursor peak revealed that the majority of the precursor chains having TEMPO moiety efficiently initiated the NMP of St.

However, a small shoulder detected in the low molecular weight region can be attributed to the unreacted PCL precursor, and disappeared upon increasing the styrene conversion.

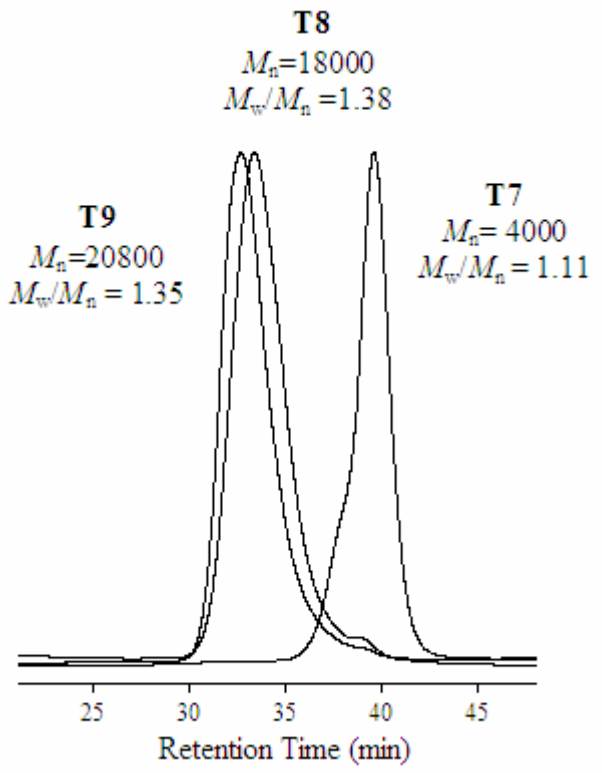


Figure 4.19. GPC traces of PCL (**T7**), PCL-PS (**T8, T9**).

4.2.4 Synthesis of PCL-PS-P*t*BA miktoarm star polymer by ATRP

As a third step, PCL-*b*-PS consisting of activated tertiary bromide functionality was utilized as a macroinitiator for ATRP of *t*BA in the presence of CuBr/PMDETA complex system as a catalyst in bulk at 100 ^{o}C (Table 4.2). The signals centered at 1.4 ppm revealed the incorporation of the *tert*-butyl ester arm affording ABC type miktoarm star polymer (**T11**-**T13**) (Figure 4.20). $M_{n,theo}$ of PCL-PS-P*t*BA was calculated according to the following formula:

$$M_{n,theo} = ([M]_o/[I]_o) \text{ X conversion X } 128.17 + M_{n,NMR} \text{ of PCL-PS precursor} \quad (12)$$

, where $[M]_o$ and $[I]_o$ are the initial concentrations of the monomer and PCL-*b*-PS macroinitiator, respectively.

Table 4.2: Characteristics of the PCL–PS–P*t*BA Miktoarm Star Polymers.

Run	Monomer	$[M]_0$ mol.L^{-1}	$[M]_0/[I]_0$	Initiator	Time (h)	Conv[e] (%)	$M_{n,theo}$	$M_{n,HNMR}$	$M_{n,GPC}$[d]	M_w/M_n[d]	Composition (%)[f]
T7[a]	ε-CL	9.43	40	**9**	41	65	3500	4000	3900	1.11	100 % PCL
T8[b]	St	8.72	420	**T7**	18	30	17120	18000	37800	1.38	82 % PS, 18 % PCL
T9[b]	St	8.72	420	**T7**	28.5	45	23700	20800	45450	1.35	84 % PS, 16 % PCL
T10[b]	St	8.72	200	**T7**	18.5	75	19620	17000	41600	1.36	81 % PS, 20 % PCL
T11[c]	*t*BA	6.82	590	**T8**	2	20	33120	36870	61350	1.25	45 % PS, 48 % P*t*BA, 7 % PCL
T12[c]	*t*BA	6.82	590	**T8**	3	35	44460	44200	70880	1.37	41 % PS, 53 % P*t*BA, 6 % PCL
T13[c]	*t*BA	6.82	400	**T9**	2.5	37	39770	37650	64900	1.4	59 % PS, 35.5 % P*t*BA, 5.5 % PCL

[a]Polymerization was carried out at 110 °C in bulk; $[Initiator]_o/[Sn(Oct)_2]_o = 300$.
[b]Polymerization was carried out at 125 °C in bulk.
[c]$[I]_o$: $[PMDETA]_o$: $[CuBr]_o$ = 1:1:1; Polymerization was carried out at 100 °C.
[d]Calculated from GPC calibrated with linear polystyrene standards.
[e]Conversions were calculated gravimetrically.
[f]Compositions were calculated by ^{1}H NMR analysis.

The molecular weight of the resulting ABC type miktoarm star polymer ($M_{n,NMR}$) was determined accordingly from the integration of the signals at 4.0 ppm (PCL protons) and 6.5-7.0 ppm (PS protons) to 1.41 ppm (P*t*BA protons),

$$M_{n,\,NMR} = MW_{monomer} \times \frac{5I_{Ar-H} + 2I_{CH_2OCO}}{9I_{C(CH_3)_3}} + M_{n,NMR}\ \text{of PCL-PS precusor} \quad (13)$$

The theoretical and NMR molecular weights are in good agreement. However, $M_{n,GPC}$ values of miktoarm star polymers calculated by using linear PS standards are not consistent with those $M_{n,theo}$ and $M_{n,NMR}$. It was attributed to the differences in hydrodynamic volume between linear and star polymers in solution.

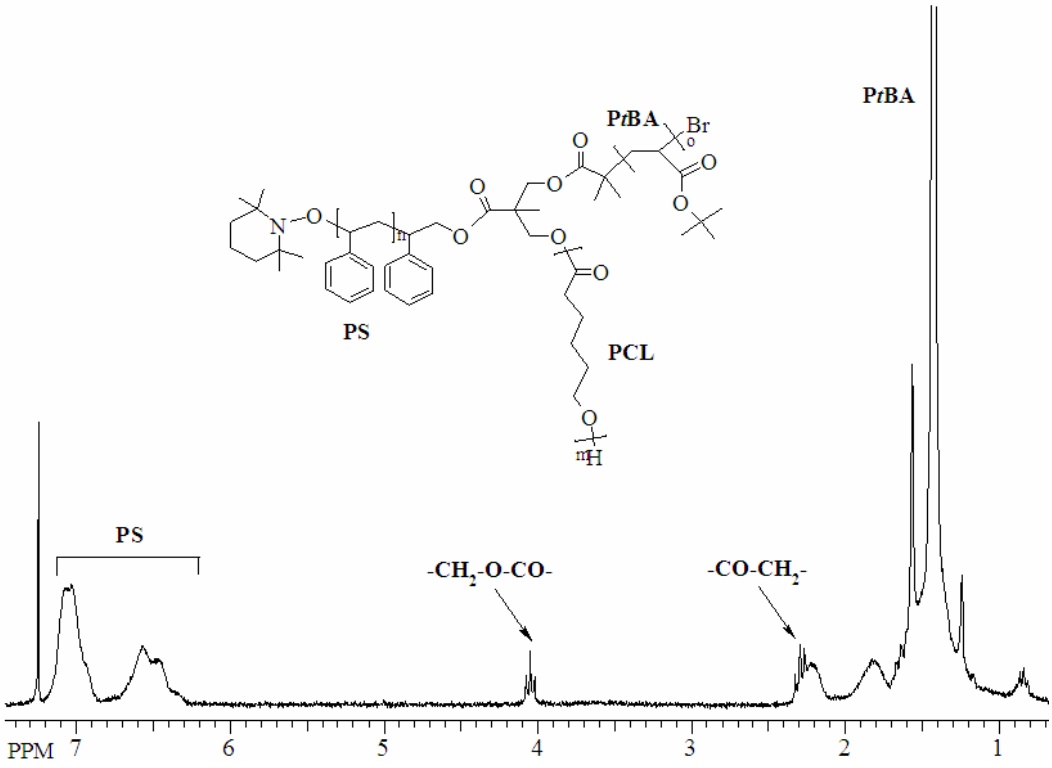


Figure 4.20: ^{1}H NMR spectrum of PCL-PS-P*t*BA miktoarm star polymer (**T11**) in $CDCl_3$.

Figure 4.21 shows the GPC traces of the polymers obtained from subsequent ROP-NMP-ATRP routes. A peak of the PCL-*b*-PS shifted to the higher molecular weight region with increasing monomer conversion in the ATRP of *t*BA. Moreover, any peak in higher molecular weight region of the GPC traces was not observed indicating the absence of the star-star coupling reaction.

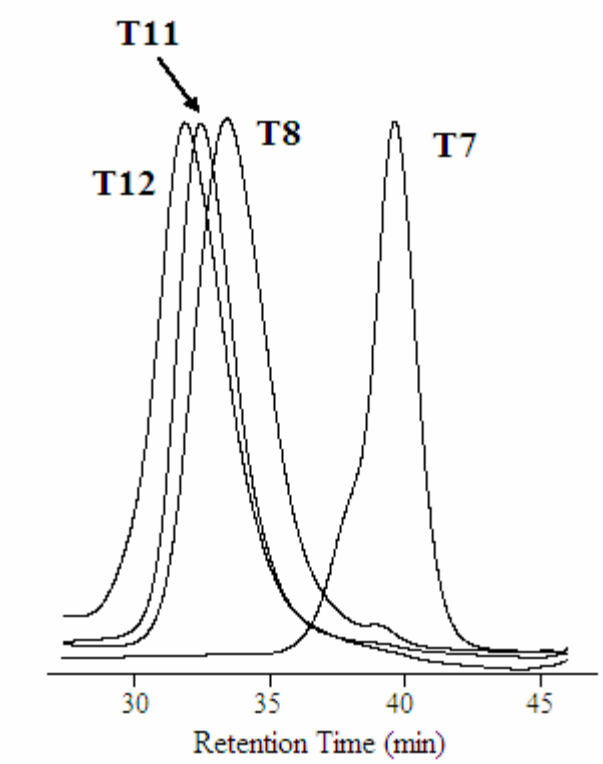
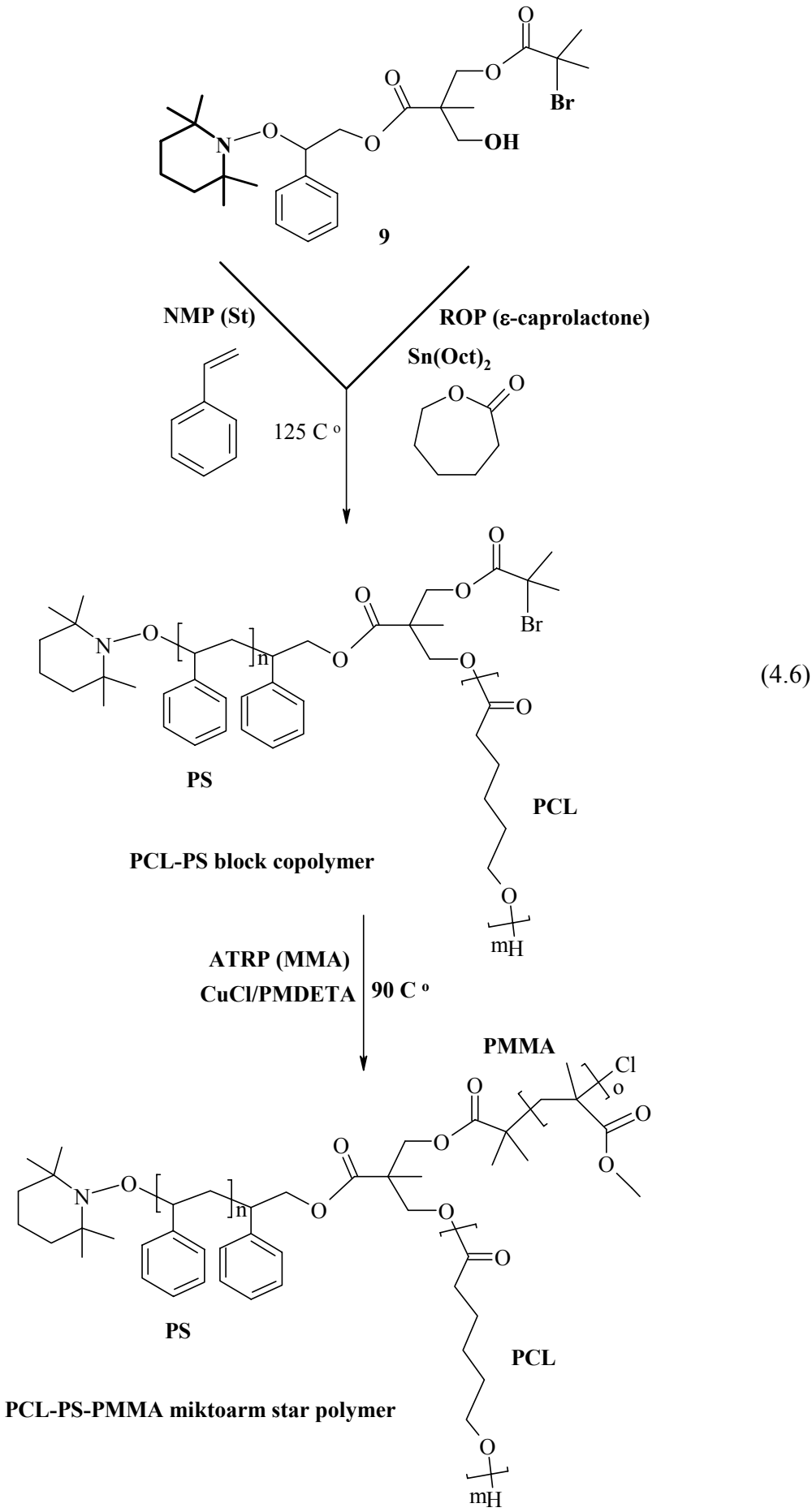


Figure 4.21: GPC traces of PCL (**T7**), PCL-PS (**T8**) and PCL-PS-P*t*BA (**T11, T12**).

4.2.5 Synthesis of PCL-*b*-PS via one-pot process by combination of NMP and ROP

Miktofunctional initiator **9** contains a single primary alcohol functionality, which is the initiation center for the living ROP of cyclic lactones (e.g. ε-caprolactone), as well as a secondary benzyl group linked to an alkoxyamine; the benzyl group is an efficient initiator for NMP of styrene. Polymerization of a mixture of St and ε-caprolactone (CL) initiated by **9** in the presence of $Sn(Oct)_2$ as ROP catalyst produces the block copolymer, PCL-*b*-PS (4.6). The characteristics of block copolymer are shown in Table 4.3. The confirmation of the block copolymer structure was accomplished by ^1H NMR that showed resonances correlating to both the polycaprolactone and polystyrene segments (Figure 4.22). The schematic representation of the synthetic strategy followed for the preparation of PCL-*b*-PS by one-pot process via combination of ROP-NMP routes was depicted in 4.6.


Br
OH
9
NMP (St)
ROP (ε-caprolactone)
Sn(Oct)2
125 C o
PS
PCL
PCL-PS block copolymer
ATRP (MMA)
CuCl/PMDETA
90 C o
PMMA
PS
PCL
PCL-PS-PMMA miktoarm star polymer

(4.6)

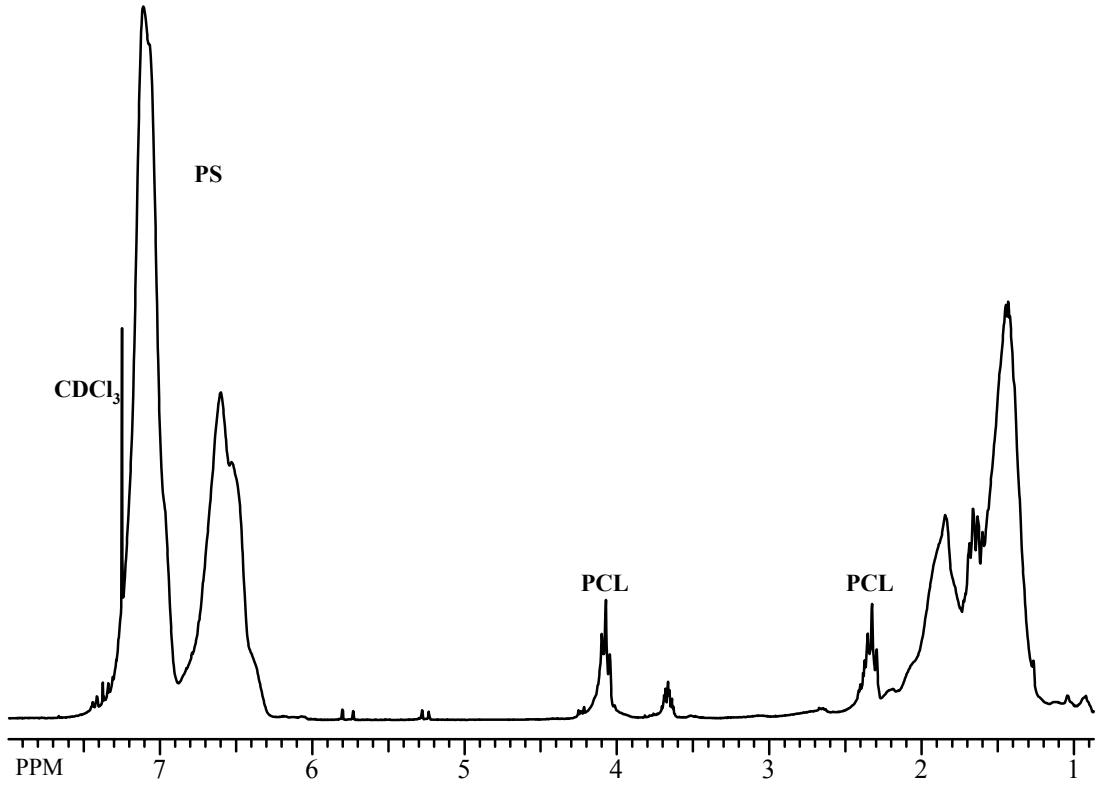


Figure 4.22: ^{1}H NMR spectrum of PCL-PS block copolymer (**T14**) in $CDCl_3$.

4.2.6 Synthesis of PCL-PS-PMMA miktoarm star polymer by ATRP

Previously obtained PCL-*b*-PS (**T14**) having tertiary bromide functionality was used as macroinitiator for ATRP of MMA in the presence of CuCl/PMDETA complex system as a catalyst in DPE as solvent at 90 °C to prepare PCL-PS-PMMA miktoarm star polymer (**T15**, **T16**).

Table 4.3: Characteristics of the PCL-*b*-PS and PCL–PS–PMMA Miktoarm Star Polymers

Run	Monomer	Type of Polym.	Initiator	Time (h)	Conv.[c] (%)	$M_{n,theo}$	$M_{n,GPC}$[e]	M_w/M_n
T14[a]	St + CL	NMP+ROP	**9**	20	68[d]	-	9800	1.15
T15[b]	MMA	ATRP	**T14**	1	7	13250	13620	1.10
T16[b]	MMA	ATRP	**T14**	2	17.5	18540	17470	1.20

[a]Polymerization was carried out at 125 ^{o}C in bulk; [Initiator]/ $[Sn(Oct)_2]$ = 300.
[b][MMA]: $[I]_o$: $[PMDETA]_o$: $[CuCl]_o$ = 500:1:1:1; Polymerization was carried out at 90 ^{o}C in DPE; (DPE/MMA=1 (v/v))
[c]Conversions were calculated gravimetrically.
[d]The value represents overall conversion.
[e]Calculated from GPC calibrated with linear polystyrene standards.

The structure of corresponding miktoarm star polymers was confirmed by ^{1}H NMR that showed resonances correlating to PCL, PS and PMMA segments (Figure 4.23). The polymerization conditions and the results of GPC analysis are summarized in Table 4.3.

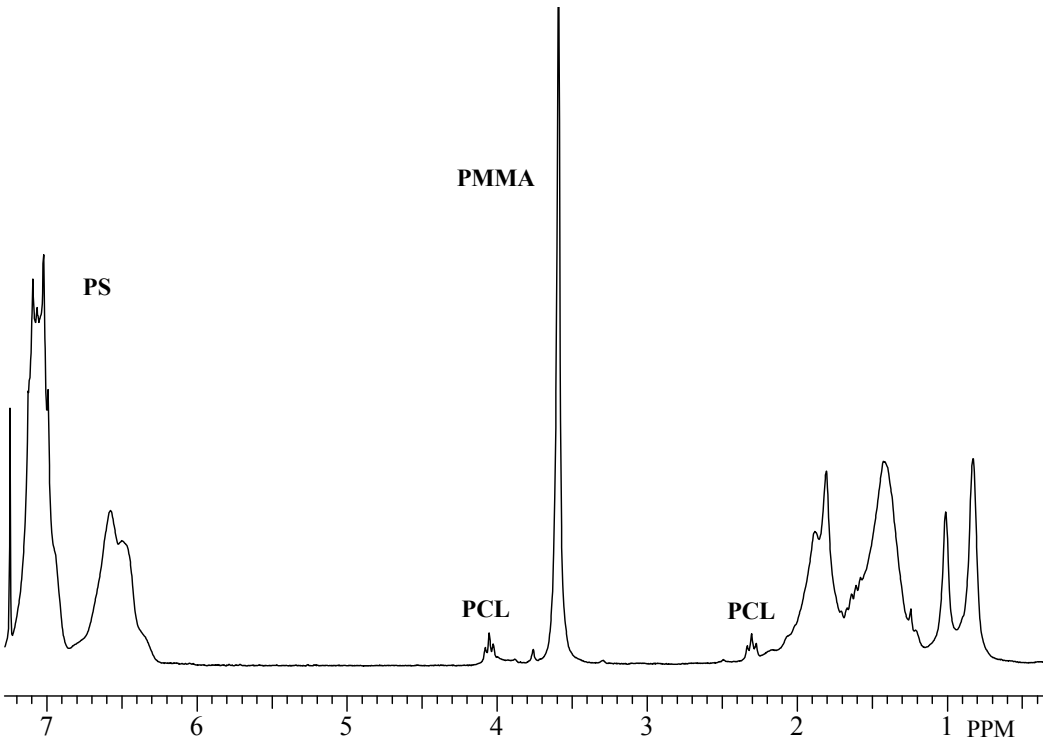


Figure 4.23: ^{1}H NMR spectrum of PCL-PS-PMMA miktoarm star polymer (**T15**) in $CDCl_3$.

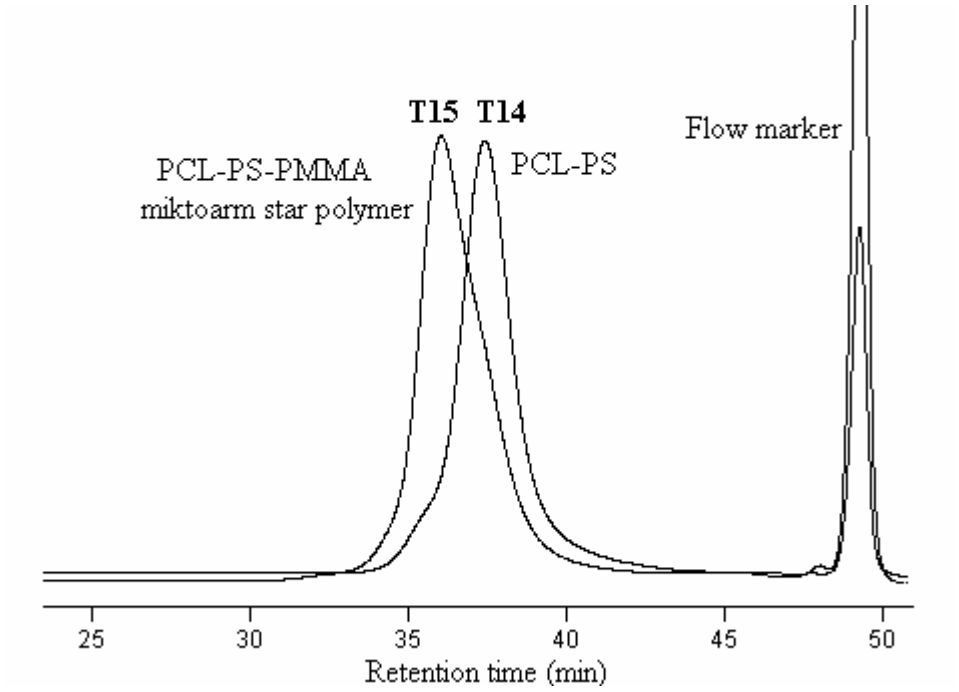


Figure 4.24: GPC traces of PCL-*b*-PS (**T14**) and PCL-PS-PMMA (**T15**).

GPC analysis (Figure 4.24) showed a single peak shifting to a higher molecular weight compared to that of the diblock copolymer macroinitiator (PCL-*b*-PS, **T14**), and the polydispersity remained rather low. However, a small shoulder was detected in the high molecular weight region of chromatogram that belongs to PCL-*b*-PS. This was attributed to inadequate kinetic control and occurrence of side reactions, particularly polyester transesterifications during ROP process [297].

Thermal behaviour of polymers

The thermal behaviour of starting macroinititors and derived miktoarm star polymers was followed by DSC and TGA under nitrogen.

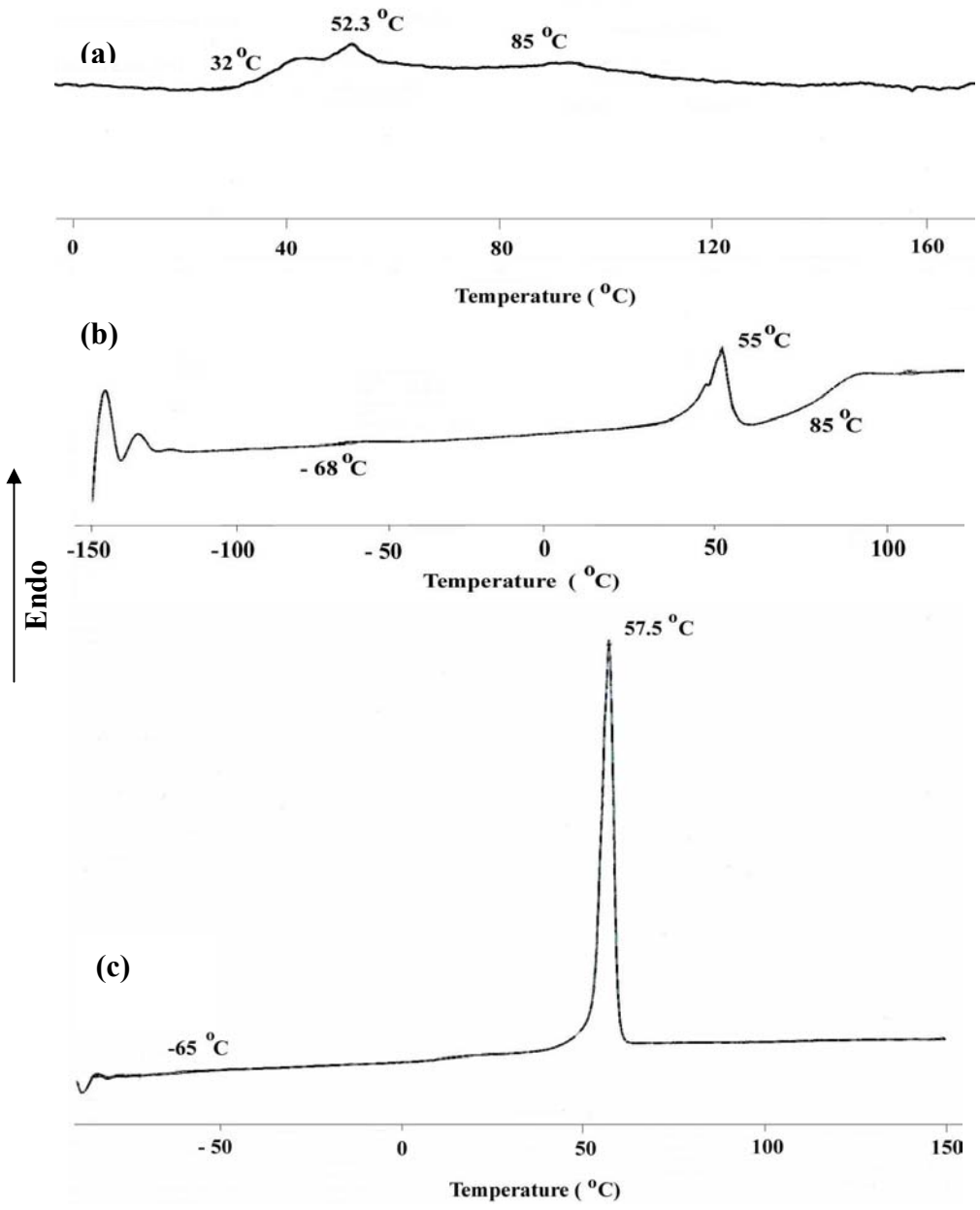


Figure 4.25: DSC thermograms of (a) PCL-PS-P*t*BA miktoarm star polymer (**T11**), (b) PCL-*b*-PS precursor (**T9**), and (c) PCL macroinitiator (**T7**).

The thermogravimetric behavior of a polymer depends on its structure and the type of subtituents in the main chain. As it was well established, the thermogravimetric analysis of TEMPO capped styrene shows three steps of decomposition [309]. The first at 100 °C corresponds to the glass transition where residual monomer and solvents can leave the polymer. This degradation step can also be seen for free radical formed PS. The second step at 225 °C, which can only be observed for nitroxide capped PS with a molecular weight lower than M_n = 30000 g/mol, is attributed to the presence of weak link at the end of the polymer due to the reversible capping with TEMPO. Since the capping of PS with nitroxide is reversible, the formation of this product can be explained by a homolytic scission resulting in a radical chain end. The third step at 400°C is the total decomposition found equal for all polystyrenes. The TGA curves of PCL-*b*-PS precursor (**T8**) as well as PCL-PS-P*t*BA miktoarm star (**T11**,**T12**) polymers under nitrogen at 10 °C/min are shown in Figure 4.26 and 4.27, respectively.

In the case of PCL-*b*-PS, the composition of polystyrene is produced a single sharp stage with a T_{max} at 416 °C. The absence of an additional step of mass loss at temperatures below 300 °C can be attributed to the different ratio of TEMPO terminated to dead end groups, which are formed by undesired side reactions during the polymerization. That means, that the abundance of nitroxide terminated end groups is reduced at lower concentrations of TEMPO.

The presence of PCL segment (<20 %) in the corresponding block copolymer has a slight influence on thermal stability of PS when compared to the thermal stability of pure PS [309]. This was easily detected as about 10 % residue in the TGA curve of PCL-*b*-PS (Fig. 4.26). This result indicated that the thermal stability of block copolymer is higher than pure PS. However, the presence of PCL segment in ABC miktoarm star polymer seemed to be no influence on thermal stability of star polymer (Fig. 4.27). This was attributed to the low composition of PCL in PCL-PS-P*t*BA miktoarm star polymer (<10 %).

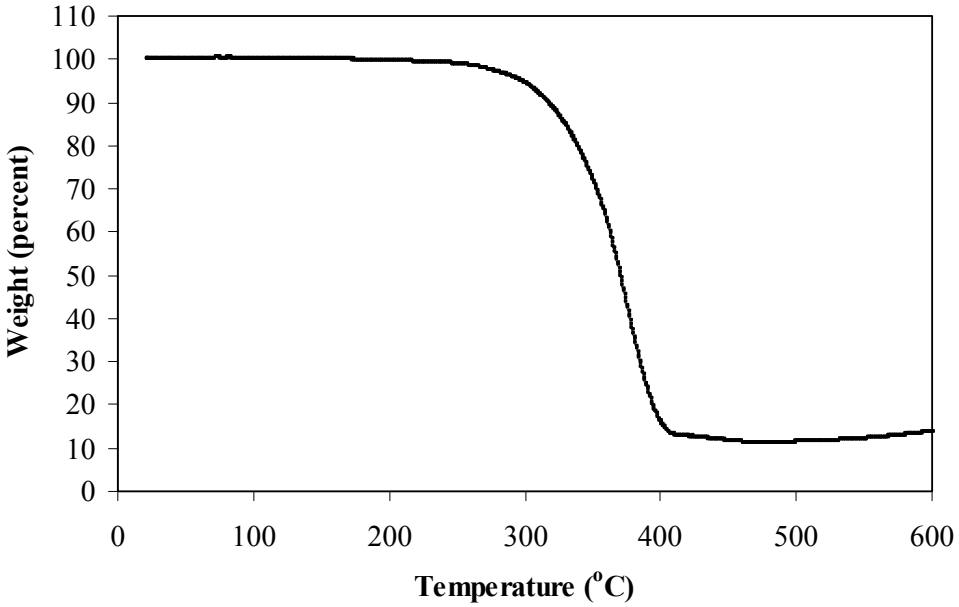
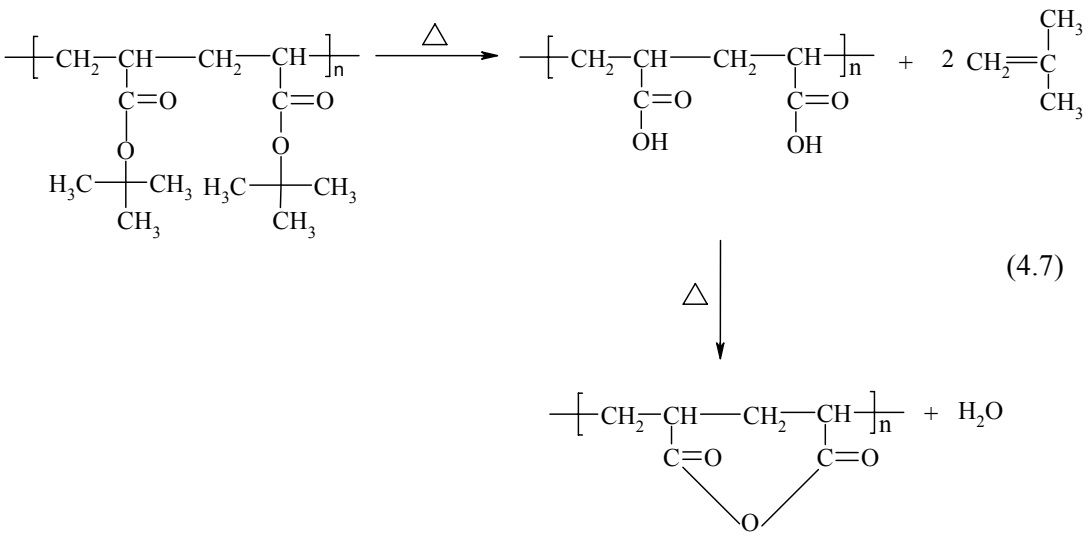


Figure 4.26: TGA curve of PCL-*b*-PS **T8**.

As it is well established, the decomposition of P*t*BA is produced in two stages [310]; the first one consists of the initial elimination of *tert*-butyl group given nearly quantitative yields of alkene per acrylate unit. The produced carboxylic acid groups dehydrate to give six-member cyclic anhydride structure and some water, as shown in the 4.7.



(4.7)

In the TGA curve of PCL-PS-P*t*BA miktoarm star (**T11**) polymer, two clear stages of thermal degradation appear, the first one is associated with the first stage of the degradation reaction in the backbone of the miktoarm star polymer by stimilitude with P*t*BA degradation. And second stage can be attributed to the thermal degradation of PS and PCL.

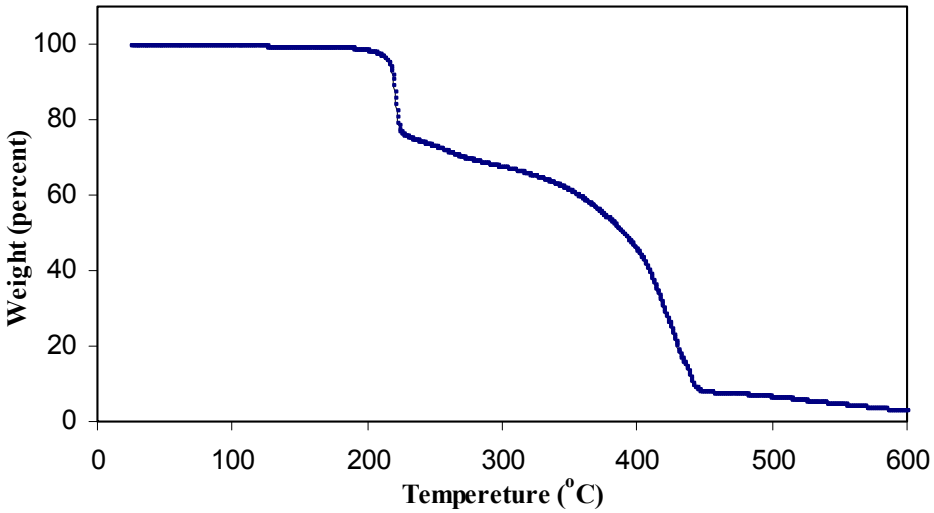


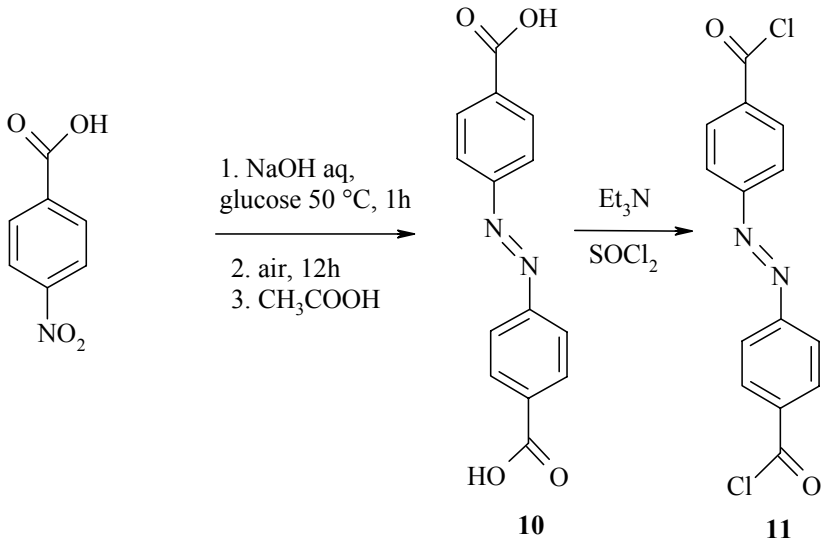
Figure 4.27: TGA curve of PCL-PS-P*t*BA miktoarm star polymer **T11.**

When TGA curve of P*t*BA block synthesized by ATRP was compared with that obtained by conventional free radical polymerization [311], similar thermal stability was observed. It can be concluded that the terminal halogen group has no remarkable effect on the thermal stability of P*t*BA in our analysis conditions. Thus, the remarkable thermal stability of P*t*BA is an indirect confirmation of the controlled/ 'living' character of the ATRP of P*t*BA catalyzed by CuBr/PMDETA.

4.3 Photoresponsive A_2B_2 Type Miktoarm Star Copolymer Containing an Azobenzene Moiety at the Core

4.3.1 Synthesis of azobenzene containing miktofunctional initiator

To introduce azobenzene functionality to previously obtained miktofunctional initiator (**9**), first trans-4,4'-dicarboxyazobenzene dichloride, **11** was obtained according to a literature procedure [312]. Trans-4,4'-dicarboxyazobenzene (**10**) was prepared in 99% yield by glucose reduction of 4-nitrobenzoic acid followed by air oxidation (4.8). Then the obtained **10**, reacted with thionyl chloride to obtain trans-4,4'-bis(chlorocarbonyl)azobenzene (**11)**.



(4.8)

The miktofunctional initiator (**12**) containing azobenzene at core and both two tertiary bromide and TEMPO end functional groups was successfully synthesized by reacting **9** with 4,4'-bis(chlorocarbonyl)azobenzene, **11** (4.9). Esterification reaction was monitored by ^{1}H NMR (Figure 4.28). 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.

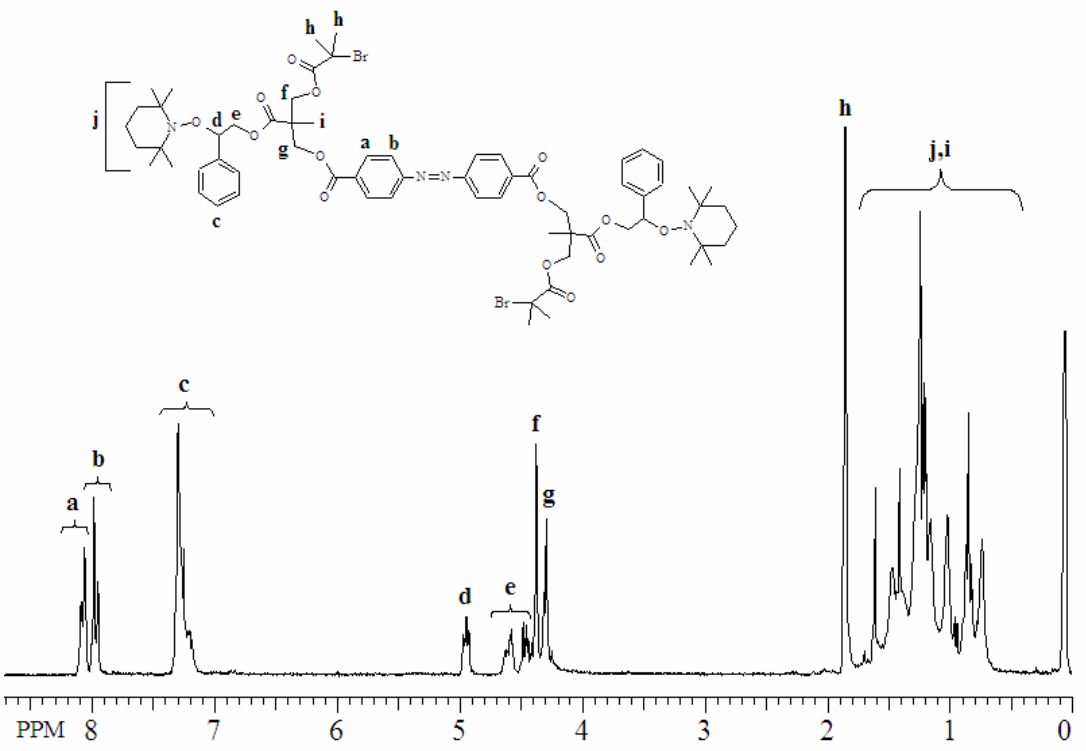
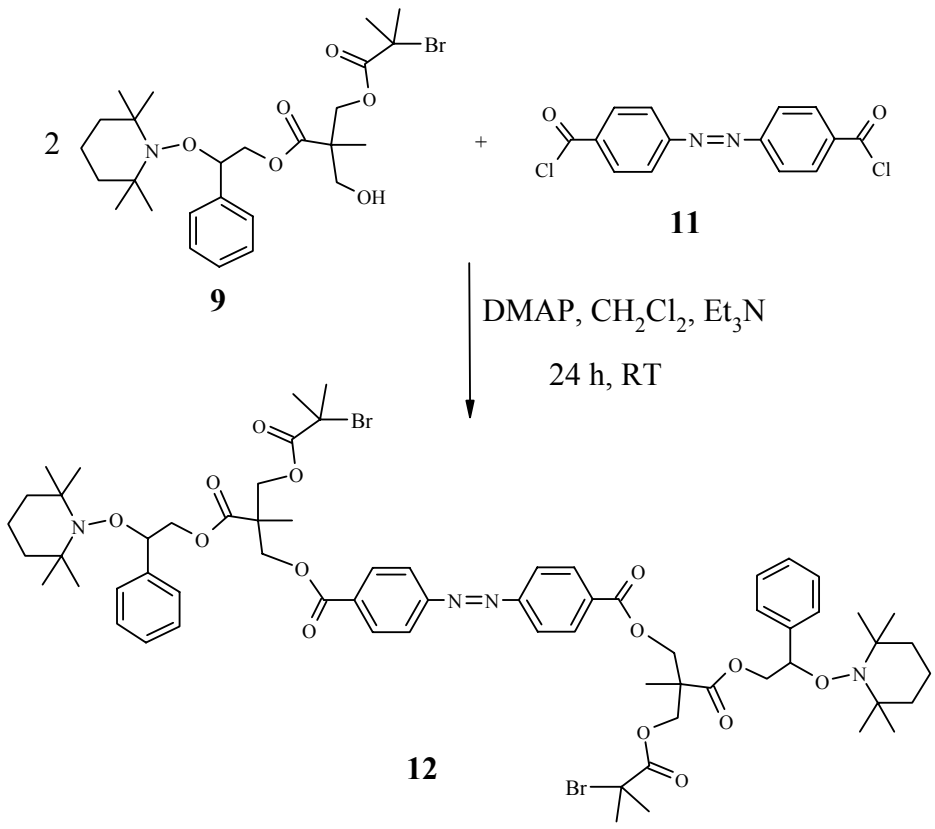


Figure 4.28: ^{1}H NMR spectrum of **12** in $CDCl_3$.

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. Mass spectroscopy measurement was also carried out to elucidate the structure and to determine the exact molar mass of miktofunctional initiator, **12**. The mass spectrum of **12** was depicted in Figure 4.29.



(4.9)

4.3.2 Preparation of $(PMMA)_2$ precursor and $(PMMA)_2$-$(PS)_2$ miktoarm star copolymer

The synthetic strategy to prepare azobenzene core containing A_2B_2 type miktoarm star copolymer using the miktofunctional initiator **12** by combining ATRP–NMP routes was depicted in 4.10. For this purpose, first ATRP of MMA was accomplished using **12** as an initiator in the presence of CuCl/PMDETA complex system as a catalyst in anisole at 60 °C (Table 4.4). The characteristics of $(PMMA)_2$ macroinitiators (**T17**-**T19**) were given in Table 4.4

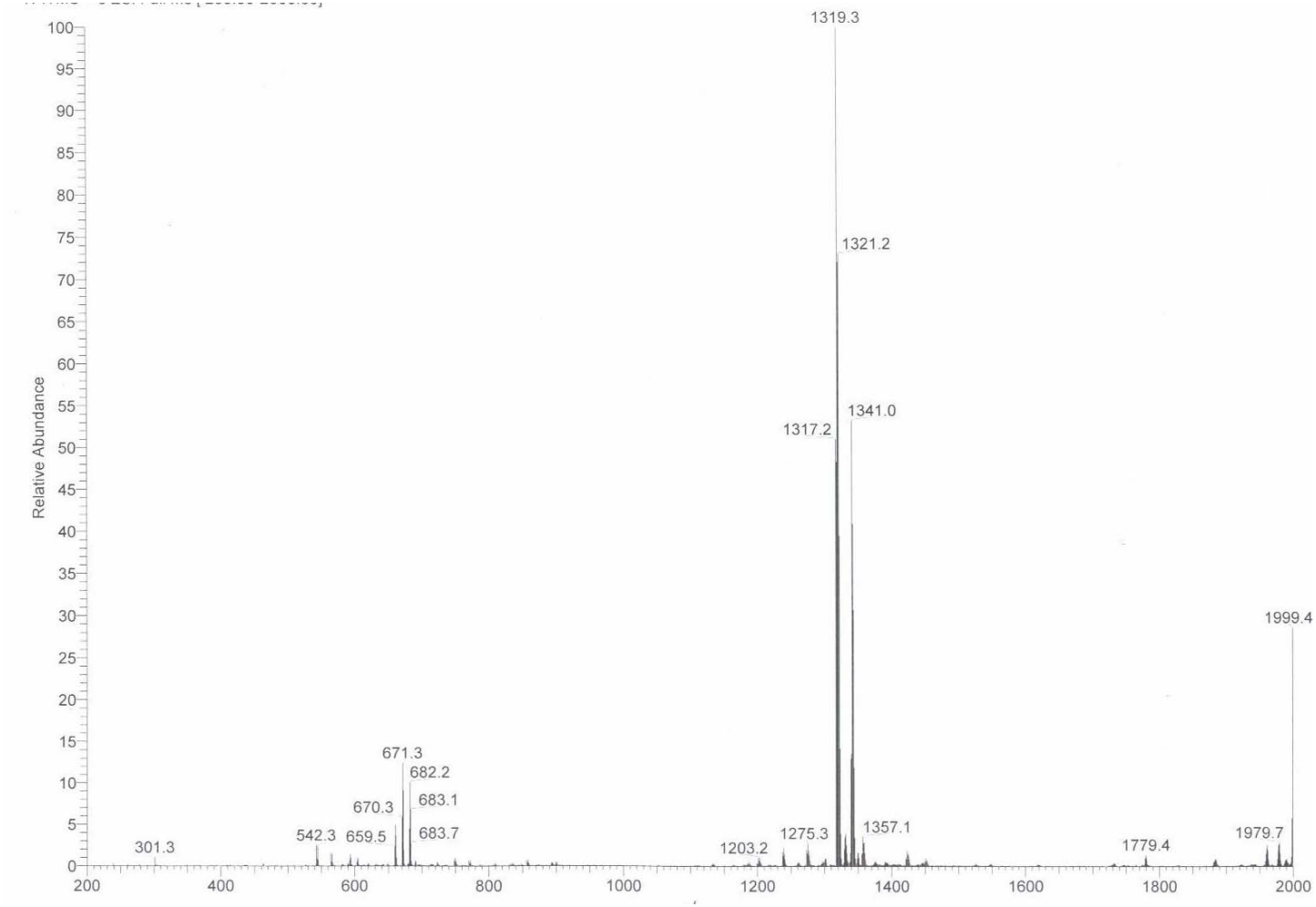


Figure 4.29: Mass spectrum of azobenzene containing miktofunctional initator (**12**).

$M_{n,theo}$ for **T17-T19** macroinitiators is calculated according to the following formula

$$M_{n,theo} = ([M]_o/[I]_o) \text{ X conversion X } 100.12 + MW_{initiator} \text{ (1319.25 g/mol)} \quad (14)$$

where $MW_{initiator}$ is the molecular weight of the initiator and $[M]_o$ and $[I]_o$ are the initial concentrations of the monomer and initiator, respectively. $M_{n,theo}$ values were almost consistent with those of the experimental number-average molecular weights $M_{n,GPC}$ and $M_{n,NMR}$.

$(PMMA)_2$ macroinitiator containing two TEMPO moieties was then used for NMP of St at 125 °C to give $(PMMA)_2$-$(PS)_2$ miktoarm star copolymer (**T20**, **T21**). The signals of the aromatic group were assigned by means of ^1H NMR confirming the incorporation of the St block into the miktoarm star copolymer (Figure 4.31). The $M_{n,theo}$ of $(PMMA)_2$-$(PS)_2$ miktoarm star copolymer was calculated by using following equation:

$$M_{n,theo} = ([M]_o/[I]_o) \text{ X conversion X } 104.15 + M_{n,NMR} \text{ of } (PMMA)_2 \text{ precursor} \quad (15)$$

It was found that $M_{n,theo}$ values were close to those of $M_{n,GPC}$ and $M_{n,NMR}$. The GPC traces of $(PMMA)_2$ precursor and $(PMMA)_2$-$(PS)_2$ miktoarm star copolymer are shown in Figure 4.30.

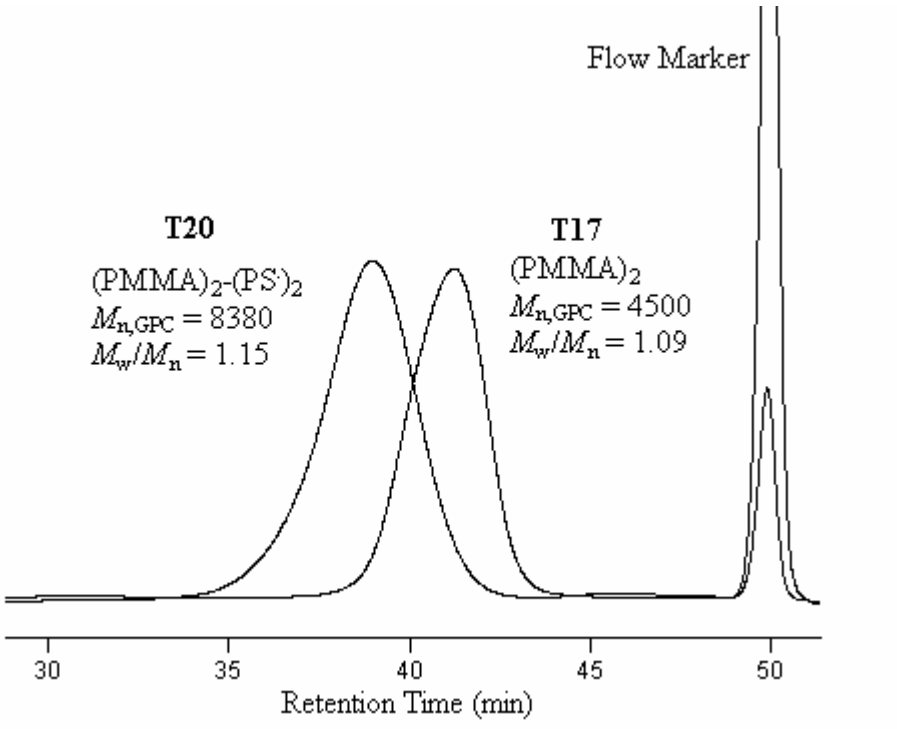
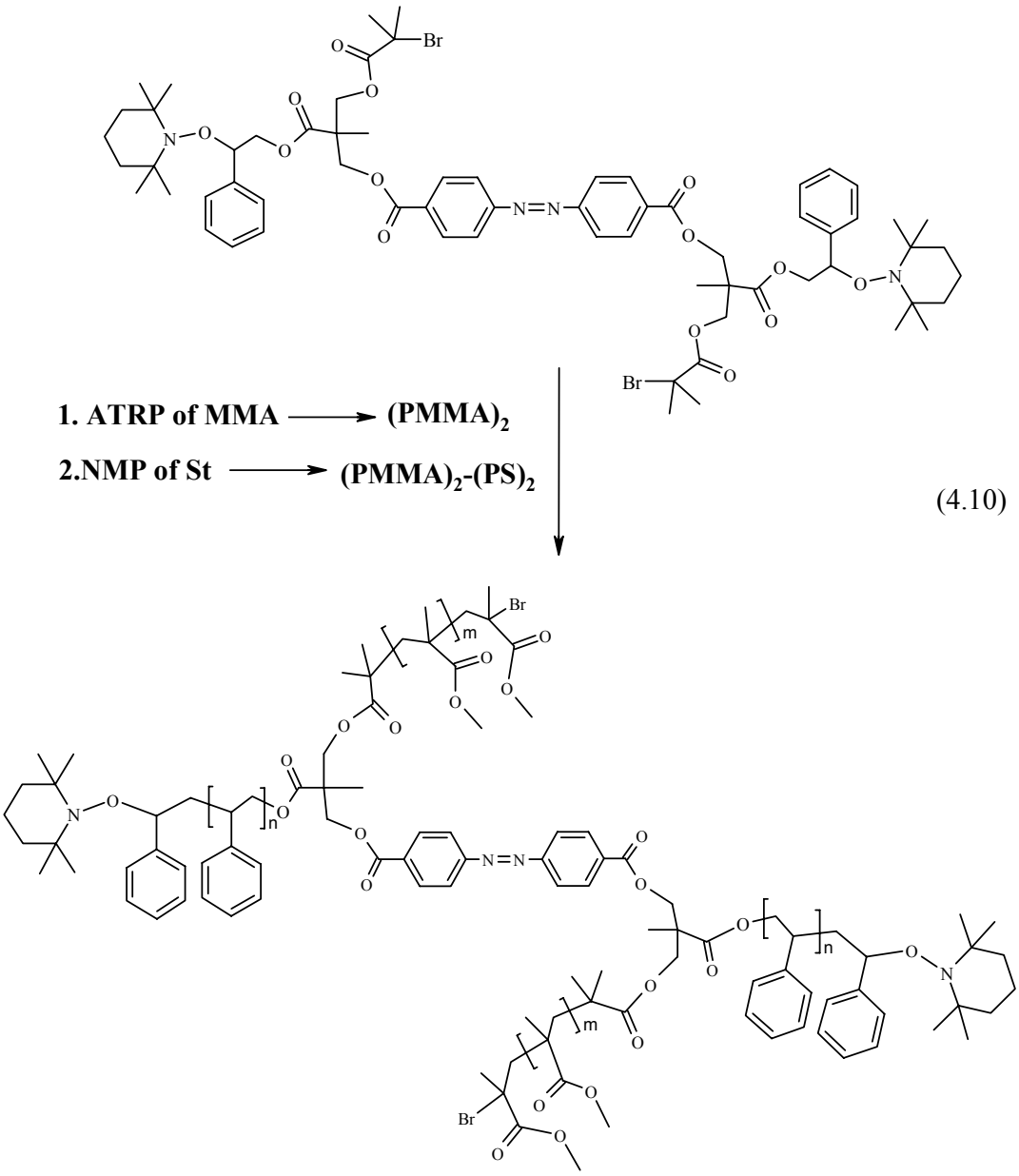


Figure 4.30: GPC traces of $(PMMA)_2$ precursor, **T17** and $(PMMA)_2$-$(PS)_2$ miktoarm star copolymer, **T20**.



(4.10)

The average molecular weight increased with MMA conversion in ATRP, confirming the introduction of the PMMA blocks to the initiator **12**. 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. Moreover, any peak in higher molecular weight region of the GPC traces was not observed, indicating the absence of the star–star coupling reaction.

Table 4.4: The characteristics of photoresponsive $(PMMA)_2$-$(PS)_2$ 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]	$M_{n,NMR}$	M_w/M_n
T17[a]	MMA	**12**	4.68	200	0.25	13	3920	4500	3550[d]	1.09
T18[a]	MMA	**12**	4.68	200	0.5	30	7330	8230	7150[d]	1.13
T19[a]	MMA	**12**	4.68	200	1	38	8950	10700	10490[d]	1.12
T20[b]	St	**T17**	8.73	300	19.5	11	7000	8380	7150[e]	1.15
T21[b]	St	**T19**	8.73	300	16	8	13000	14300	15000[e]	1.14

[a]$[I]_o/[CuCl]_o/[PMDETA]_o$ = 1/ 2/ 2. The polymerization was carried out at 60 °C. MMA / Anisole = 1 (v/v)
[b]The polymerization was carried out at 125 °C in bulk.
[c]Calculated from GPC calibrated with linear polystyrene standards.
[d]$M_{n,NMR}$=MW (MMA) X (8_{Ar-H} / $3I_{OCH3}$) + MW (miktofunctional initiator, **12**)
[e]$M_{n,NMR}$= MW (St) X ($5I_{Ar-H}$ / $3I_{OCH3}$) + $M_{n,NMR}$ of $(PMMA)_2$ precursor.

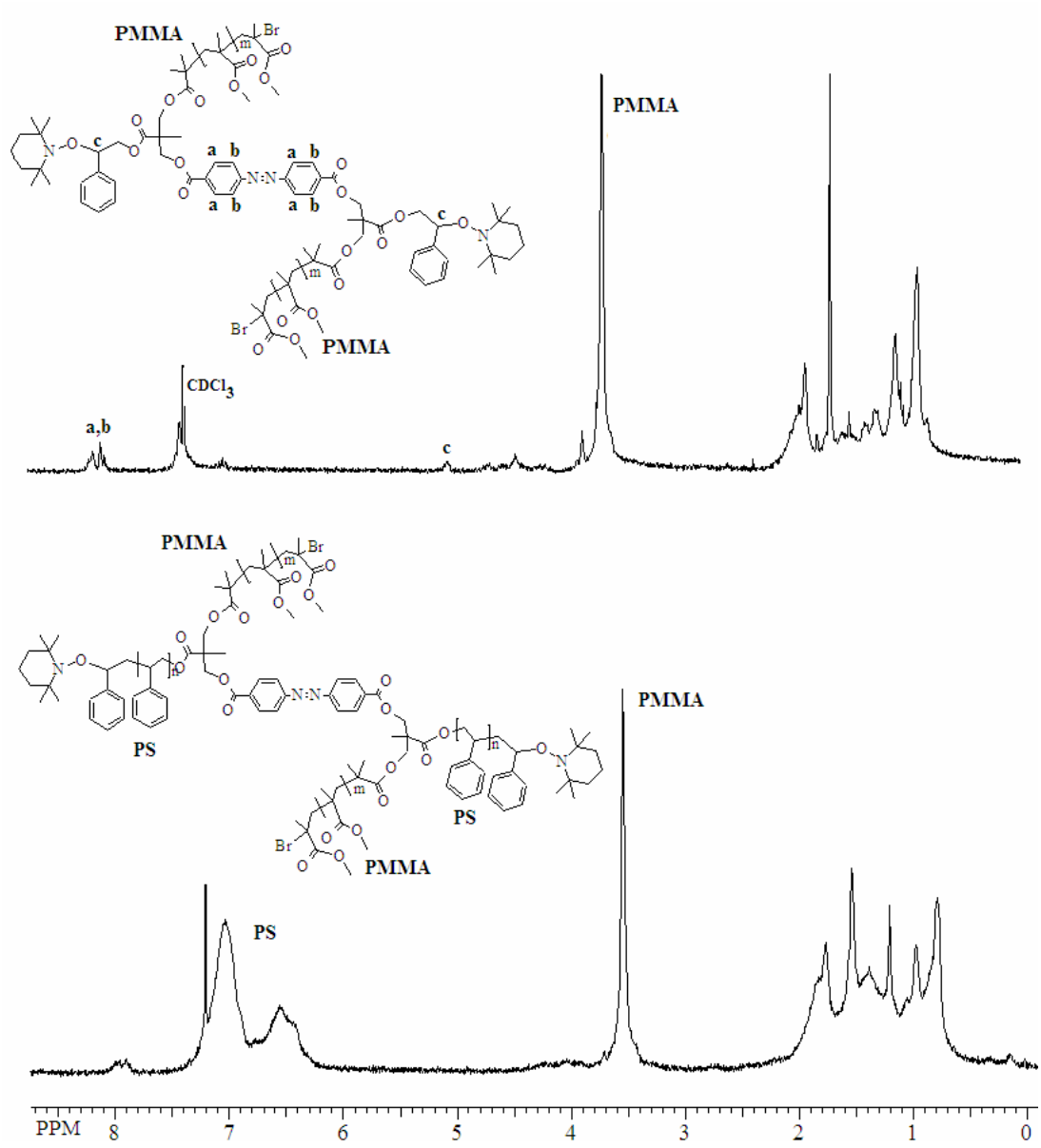
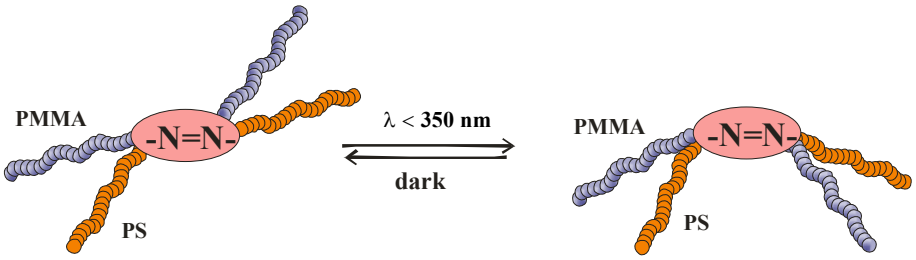


Figure 4.31: ^{1}H NMR spectra of $(PMMA)_2$ precursor (**T17**) and $(PMMA)_2$-$(PS)_2$ miktoarm star copolymer (**T20**) in $CDCl_3$.

Photoresponsive study

Trans to cis photoisomerization of **12** was determined by using UV spectrophotometer (4.11). The miktofunctional initiator **12** dissolved in $CHCl_3$ and was irradiated with UV light ($\lambda < 350$ nm) by 10 s intervals (0-120 s) (Figure 4.32). During the irradiation, the absorption maximum at 330 nm corresponding to the π-π* transition of *trans*-azobenzene was decreased and concurrently a weak band at 450 nm corresponding to n-π* transition of azo moiety increased with time. Thus upon irradiation of these solutions with $\lambda < 350$ nm UV light, energetically preferred trans-form turned to the cis- (photochemical isomerization process).



(4.11)

trans cis

When this solution was kept in the dark, the back isomerization (cis-to-trans) was 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 4.33).

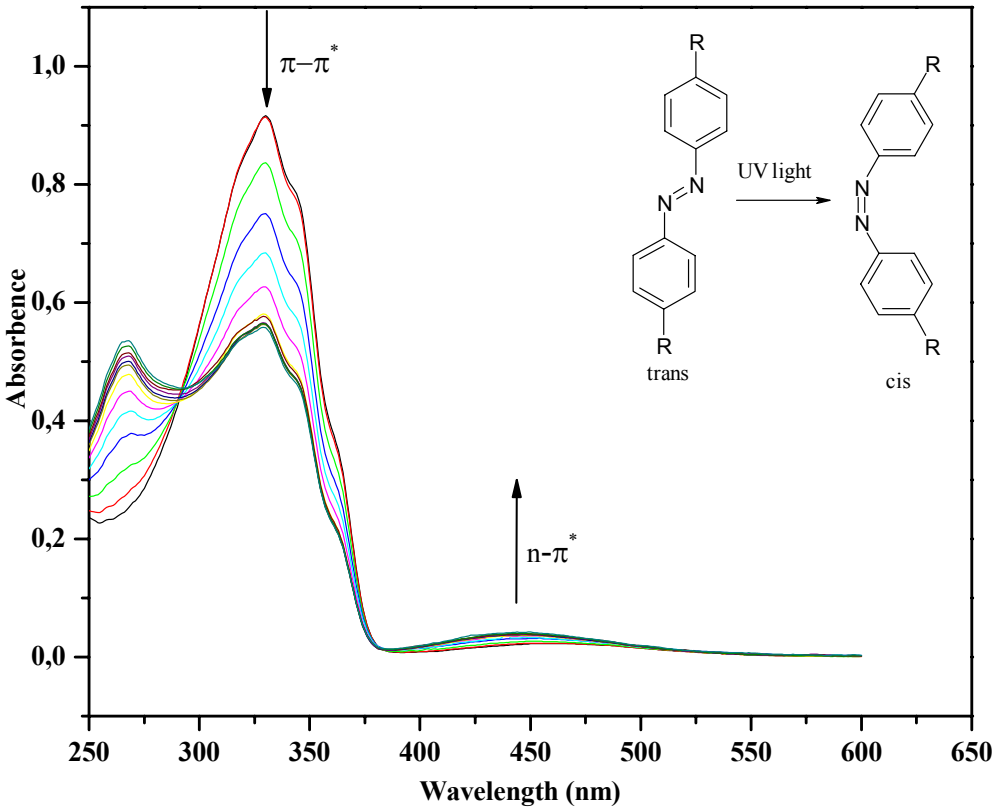


Figure 4.32: UV visible absorption changes of **12** in $CHCl_3$ (2.5 X 10^{-5} M) (trans-cis isomerization) under irradiation conditions (λ < 350 nm; 10 s interval; 0 to 120 s).

A similar behavior was observed upon UV irradiation (λ < 350 nm) of $(PMMA)_2$-$(PS)_2$ miktoarm star copolymer (**T20**) for 7 h. Trans to cis isomerization was recorded using UV spectrophotometer (Figure 4.34).

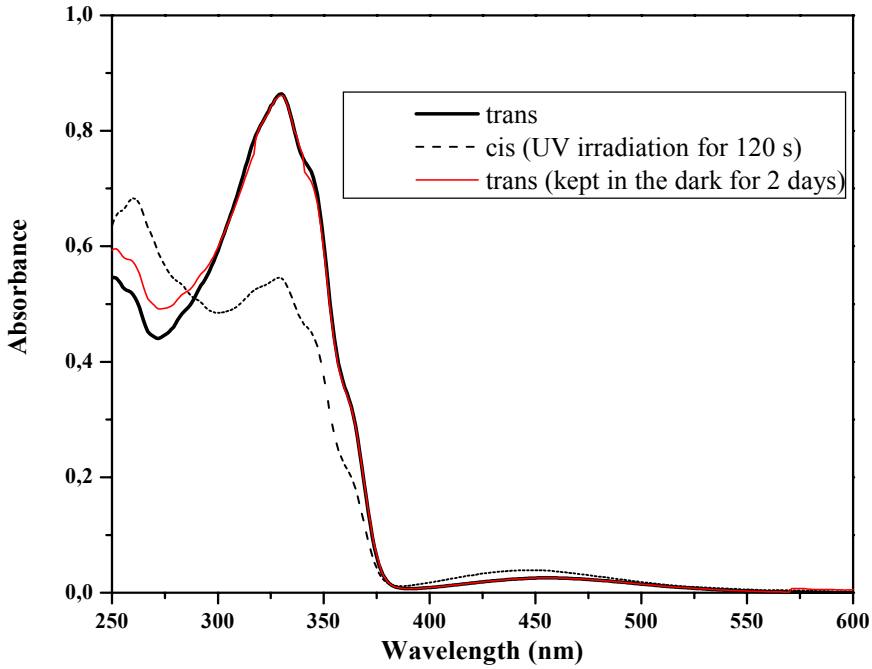


Figure 4.33: UV visible absorption changes of miktofunctional initiator, **12** in $CHCl_3$ (2.5 X 10^{-5} M); trans-cis isomerization occurred after 120 s irradiation at $\lambda <$ 350 nm, followed by cis-trans back isomerization after 2 days in the dark**.**

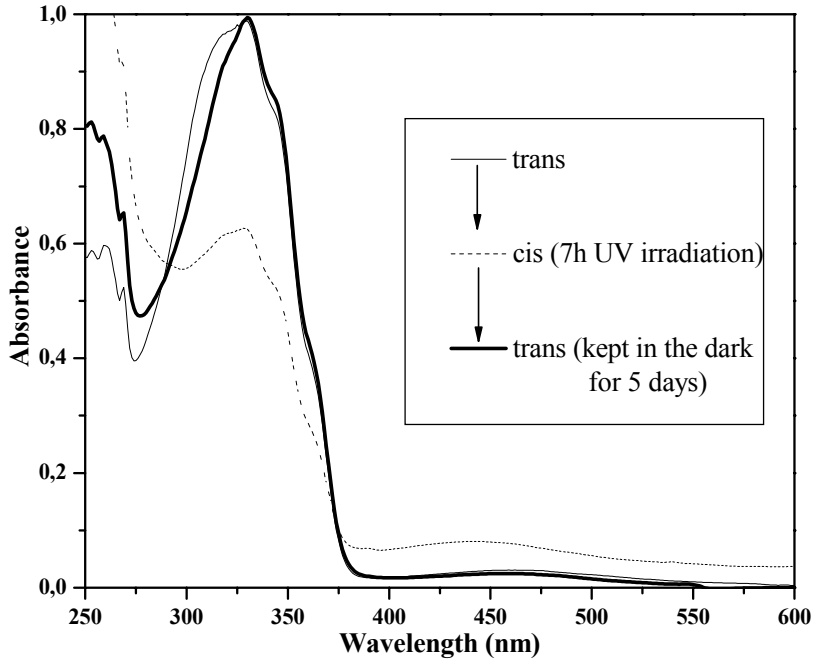


Figure 4.34: UV visible absorption changes of $(PMMA)_2$-$(PS)_2$ miktoarm star copolymer, **T20** in $CHCl_3$ (2.5 X 10^{-5} M); trans-cis isomerization occurred after 7 h irradiation at $\lambda <$ 350 nm, followed by cis-trans back isomerization after 5 days in the dark.

However, it was obvious that trans–cis isomerization of **T20** was quite slow when compared with that of initiator **12**. The back isomerization of **T20** (cis to trans) occurred when keeping it in the dark for 5 days (Figure 4.34). Overall, these results

were consistent with the data obtained in the literature [313] and clearly demonstrated that $(PMMA)_2$-$(PS)_2$ miktoarm star copolymer containing an azobenzene unit at the core displayed reversible isomerization by photochemical procedures.

Trans to cis isomerization of miktoarm star copolymer (**T20**) was also observed in GPC traces. As can be seen from Figure 4.35, a peak of $(PMMA)_2$-$(PS)_2$ miktoarm star (**T20**) in trans-form shifted slightly to lower molecular weight region (cis-form) when exposed to UV light ($\lambda < 350$ nm) for 7 h. However, it was noticed that all molecular weights obtained by GPC were calculated by using linear PS standards, which were obviously different in chemistry and structure than the prepared miktoarm star polymers.

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 [157]. 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 [157].

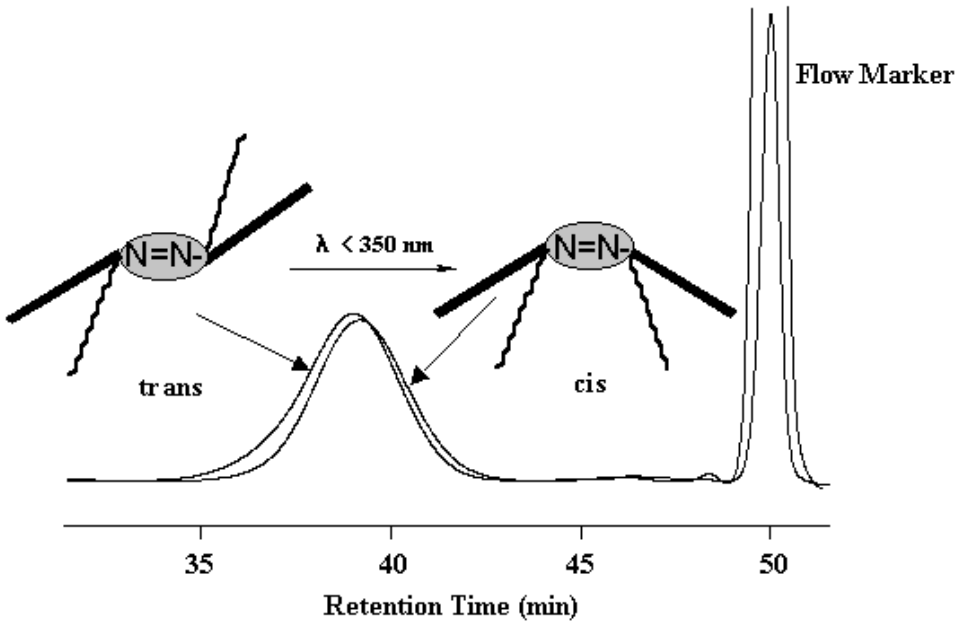


Figure 4.35: GPC traces of **T20** (trans) and **T20** (cis) after 7 h irradiation at $\lambda < 350$ nm.

5. CONCLUSIONS

In this PhD thesis, novel miktofuntional initiators having proper functionalities for controlled polymerization processes such as ATRP, NMP or ROP were successfully synthesized and used for the preparation of ABC-, AB_2- and A_2B_2-type miktoarm star polymers. For the synthesis of corresponding star polymers sequential polymerization steps were performed. As a result, well-controlled macromolecular architectures with controlled molecular weights and rather narrow molecular weight distributions were achieved.

For the synthesis of AB_2 type miktoarm star polymers, effective trifunctional initiator having one ROP functionality and two ATRP functionalities was designed and synthesized. This initiator was used in the polymerization of ε-CL in the presence of $Sn(Oct)_2$ catalyst while the compound with bromine moities initiated ATRP of *t*BA or MMA by using CuBr/PMDETA or CuCl/PMDETA. By these polymerization methods, AB_2 type miktoarm star polymers that posses designed molecular weights with narrow molecular weight distributions were prepared. Furthermore, an amphiphilic miktoarm star polymer containing PCL and poly(acrylic acid) (PAA) arms [PCL–$(PAA)_2$] was prepared by the hydrolysis of *tert*-butyl groups of PCL–$(Pt\text{BA})_2$.

Moreover, the synthesis of novel miktofunctional intiator having three different functionalities was described as a route to ABC-type miktoarm star polymers consisting of PCL, PS, and P*t*BA or PMMA arms via the combination of ROP, NMP, and ATRP techniques.

On the other hand, in order to get another novel architecture, a novel miktofunctional initiator with tertiary bromide (for ATRP) and TEMPO (for NMP) functionalities and an azobenzene moiety at core was obtained and then employed in consecutive CRP routes such as ATRP of MMA and NMP of St, respectively, to give A_2B_2 type miktoarm star copolymer, $(PMMA)_2$-$(PS)_2$ with an azobenzene unit at core. Furthermore, the photoresponsive properties of correponding initiator and

$(PMMA)_2$-$(PS)_2$ miktoarm star copolymer were investigated. Trans to cis and the back isomerization (cis to trans) of the initiator and $(PMMA)_2$-$(PS)_2$ miktoarm star copolymer were monitored by UV measurements. Trans to cis isomerization process of $(PMMA)_2$-$(PS)_2$ was also observed in GPC traces due to a change in hydrodynamic volume of polymers through isomerization process.

The structures of the synthesized initiators and star polymers were proved by spectral methods (^{1}H (^{13}C)-NMR, MS) and by GPC measurements. The thermal behavior of star polymers was studied by DSC and TGA measurements.

The study described herein clearly demonstrates that well-defined miktoarm star polymers whose arm segments differ in molecular weight and chemical composition can readily be synthesized by using the synthetic strategy followed above. Such star branched polymers are expected to exhibit interesting and unique properties originating from possible heterophase structures, in addition to branching architectures. For example, heterophase dissimilar structures are usually phase-separated at molecular level to promote self-assembly, thereby facilitating the fabrication of many new nanoscopic ordered suprastructures and characteristic nanomaterials, opening the possibility for the development of sophisticated nano-devices. Therefore, the synthetic development of star polymers is now associated with the rapid growth of nanotechnology. *As a conclusion,* the present research presents a versatile synthetic approach for obtaining well-defined miktoarm star polymers.

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AUTOBIOGRAPHY

Tuba Erdoğan Bedri was born in İstanbul in 1978. She graduated from Bahçelievler High School in 1994. In 1995, she was admitted to İstanbul University, Department of Chemistry of Engineering Faculty.

After her graduation in 1999, she was accepted as a M.Sc. Student to İstanbul Technical University, Institute of Science, Polymer Science and Technology Programme where she obtained M.Sc. degree in 2002.

She was registered as a Ph.D. student to Istanbul Technical University, Polymer Science and Technology Programme in 2002. During her Ph.D. study she was supported by TUBITAK-BDP Programme through a doctoral fellowship. As part of this doctoral fellowship programme, she worked as a visiting Ph.D. student at the Polymer Chemistry Research Group, Department of Organic Chemistry in Ghent University (Belgium) for 5 months.

She is co-author of the following 8 scientific papers published in international journals.

1. **T. Erdogan**, E. Gungor, H. Durmaz, G Hızal, U. Tunca, Photoresponsive Poly(methyl methacrylate)$_2$–(Polystyrene)$_2$ Miktoarm Star Copolymer Containing an Azobenzene Moiety at the Core, *Journal of Polymer Science: Part A: Polymer Chemistry*, 44, 1396–1403 **(2006).**
2. **T. Erdogan,** G. Hızal, U. Tunca, A New Strategy For The Preparation of Multiarm Star-Shaped Polystyrene via a Combination of Atom Transfer Radical Polymerization and Cationic Ring-Opening Polymerization, *Designed Monomers and Polymers*, 9, 393-401 **(2006).**
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6. U. Tunca, Z. Ozyurek, **T. Erdogan**, G. Hızal, Novel Miktofunctional Initiator for the Preparation of an ABC-Type Miktoarm Star Polymer via a Combination of Controlled Polymerization Techniques, *Journal of Polymer Science Part A: Polym Chem*, 42, 4228–4236 **(2004).**
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She has attended National and International Conferences with the following Proceedings.

- T. Erdogan, G. Hızal, U. Tunca "Synthesis of Miktoarm Star Polymers via Atom Transfer Radical Polymerization and Ring Opening Polymerization" (Poster)
The 5th International APME'5-2003 Conference,
Montreal, Canada, June 21-26, 2003

- T. Erdogan, G. Hızal, U. Tunca "Atom Transfer Radikal ve Yaşayan Halka Açılma Polimerizasyonu ile Yıldız Polimerlerin Sentezi" (Oral)
XVII. National Congress of Chemistry
Istanbul, Türkiye, Sept. 8-11th, 2003

- T. Erdogan, G. Hızal, U. Tunca "A Novel Miktofunctional Initiator for the Preparation of ABC type Miktoarm Star Polymer via Controlled Polymerization Techniques" (Poster)
The 40th International Symposium on Macromolecules, *Macro 2004, World Polymer Congress*
Paris, France, July 4-9, 2004

- T. Erdogan, G. Hızal, U. Tunca "A New Strategy for the Preparation of Multiarm Star-Shaped Polystyrene through Polystyrene-*block*-poly(glycidyl methacrylate) via Combination of ATRP and CROP" (Poster)
The 6th International APME'6-2005 Conference,
İstanbul, Türkiye, August 14-19, 2005

- T. Erdogan, K. V. Bernaerts, L. M. Van Renterghem, F. E. Du Prez
"Use of Dual Initiator for the Preparation of Star Block Copolymers by Combination of CROP and ATRP " (Poster)
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XIX. National Congress of Chemistry
Kuşadası, Türkiye, 30 Sept.- 4 Oct., 2005