İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF STAR COPOLYMERS BASED ON MULTIFUNCTIONAL INITIATORS

M. Sc. Thesis by

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Department : **Polymer Science and Technology**

Programme: **Polymer Science and Technology**

JUNE 2008

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LIST OF ABBREVIATIONS

ATRP	: atom transfer radical polymerization
Boltorn H20-MI	: Boltorn H20-Multifunctional initiator
PIBA-12-arm-MI	: poly(isobornyl acrylate)-12-arm-macroinitiator
IBA	: isobornyl acrylate
MMA	: methyl methacrylate
AzMA	: 3-azidopropyl methacrylate
AzHA	: 6-azidohexyl acrylate
PEO	: poly(ethylene oxide) linear homopolymer
PAA	: poly(acrylic acid) linear homopolymer
CRP	: controlled radical polymerization
RAFT	: reversible addition-fragmentation chain transfer
NMP	: nitroxide-mediated radical polymerization
CCT	: catalytic chain transfer polymerization
PDI	: polydispersity index
ATRA	: atom transfer radical addition
Cu	: copper
Ru	: ruthenium
Ni	: nickel
Fe	: iron
Pd	: palladium
Mo	: molibden
bpy	: 2,2'-bipyridine
PMDETA	: N,N,N',N'',N''-pentamethyl diethylenetriamine
DMSO	: dimethyl sulfoxide
DMF	: dimethyl formamide
MWD	: molecular weight distribution
DVB	: divinyl benzene
BiBEMI	: *N*-[2-(2-bromoisobutyryloxy)ethyl]maleimide
THF	: tetrahydrofurane
NEt_3	: triethylamine
TBAF	: tetrabutylammonium hydrogen sulfate
DMAP	: 4-dimethylaminopyridine
NMR	: nuclear magnetic resonance spectroscopy
GPC	: gel permeation chromatography
GC	: gas chromatography
MMA-*b*-AzMA	: star-shaped block copolymer of MMA and AzMA
IBA-*b*-AzMA	: star-shaped block copolymer of IBA and AzMA
IBA-*r*-AzMA	: star-shaped random copolymer of IBA and AzMA
PAzHA	: linear homopolymer of AzHA
H20-IBA	: star-shaped homopolymers of IBA
H20-MMA	: star-shaped homopolymers of MMA
EtOAc	: ethyl acetate

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LIST OF SYMBOLS

R_{act} : rate of activation
R_{deact} : rate of deactivation
$[P_n\text{-}X]$: concentration of initiator
$[P_n^{\cdot}]$: concentration of radicals
$[X\text{-}M_t^{n}/L]$: concentration of catalyst in lowest oxidation state
$[X\text{-}M_t^{n+1}/L]$: concentration of catalyst in highest oxidation state
$[R\text{-}X]$: initiator
$[R^{\cdot}]$: radical
k_{act} : activation rate constant
k_{deact} : deactivation rate constant
$P_n\text{-}P_m$: coupled polymer chains
$k_{t,c}$: termination by combination rate constant
$k_{t,d}$: termination by disproportionation rate constant
$P_n^{=}, P_m\text{-}H$: disproportionated chains
$P_n\text{-}P_m$: combinated chains
$P_1^{\cdot}$: active polymer chain in initiation step
$P_n^{\cdot}$: active polymer chain
k_i : initiation rate constant
k_p : propagation rate constant
k_{act}^{o} : activation rate constant during the initiation step
k_{deact}^{o} : deactivation rate constant during the initiation step
$[M]$: monomer concentration
$[M]_0$: monomer concentration at 0 minute time
k_p : propagation rate constant
k_t : termination rate constant
t : time
R_p : polymerization rate
$[R\text{-}X]_0$: concentration of the initiator at 0 min
M_w : mass average molecular weight
M_n : number average molecular weight
$[I_o]$: the initial concentration of the initiator
$NiBr_2(PPh_3)_2$: Ni(tripheylphosphine)bromide
$NaOH$: sodium hydroxide
HCl : hydrochloric acid
Bu_4NHSO_4 : tetrabutylammonium hydrogen sulfate
NaN_3 : sodium azide

SYNTHESIS OF STAR COPOLYMERS BASED ON MULTIFUNCTIONAL INITIATORS

SUMMARY

In this study, star-shaped copolymers based on multifunctional initiator and macroinitiator were synthesized *via* core-first approach, using atom transfer radical polymerization (ATRP) technique.

For synthesis of star-shaped copolymers, two different ATRP initiators were made: poly(isobornyl acrylate)-12-arm-macroinitiator (PIBA-12-arm-MI) based on dodecafunctional monodisperse initiator and Boltorn H20-multifunctional initiator (Boltorn H20-MI) based on Boltorn H20® polyester.

The azide-containing monomers: 3-azidopropyl methacrylate and 6-azidohexyl acrylate were also made for synthesis of azide-containing star copolymers. Using Boltorn H20-MI, star-shaped homopolymers were synthesized from isobornyl acrylate (IBA) and methyl methacrylate (MMA) monomers.

These star-shaped homopolymers could be used as macroinitiators for synthesis of star-shaped block polymers where second block contains reactive groups such as 3-azidopropyl methacrylate (AzMA), 6-azidohexyl acrylate (AzHA) or propargyl acrylate. The star-shaped block copolymers can further be reacted with functional groups *via* Cu (I)-catalyzed azide-alkyne cycloaddition reactions (click chemistry). Star-shaped random copolymers of isobornyl acrylate and 3-azidopropyl methacrylate (isobornyl acrylate-*r*-3-azidopropyl methacrylate) were also synthesized from the multifunctional initiator (Boltorn H20-MI). Star-shaped block copolymers of isobornyl acrylate and 3-azidopropyl methacrylate were synthesized using the other macroinitiator, PIBA-12-arm-MI. The characterization of the products were determined by ^{1}H NMR and GPC measurements.

When azide-containing monomer was used, the results were not satisfactory owing to some side-reactions which depends on the formation of a “triazoline ring”, cross-linked polymer chains and star-star coupling reactions. These results could be ascribed to the instability of the azide-containing monomer under conditions that are used for star copolymerization reactions.

Since satisfactory results were not obtained from azide-containing star copolymerization reactions, alkyne-containing star-shaped copolymers could be synthesized and azide-containing groups could be reacted with them *via* click chemistry.

MULTİFONKSİYONEL BAŞLATICILARA DAYANAN YILDIZ KOPOLİMERLERİNİN SENTEZİ

ÖZET

Bu çalışmada, azit içeren yıldız kopolimerlerinin multifonksiyonel başlatıcı ve makrobaşlatıcıya dayanan sentezi, çekirdek yöntemi kullanılarak, atom transfer radikal polimerizasyonu (ATRP) ile gerçekleştirilmiştir.

Yıldız kopolimerlerinin sentezi için iki farklı ATRP başlatıcısı sentezlenmiştir: monodispers dodekafonksiyonel başlatıcıya dayanan poli(izobornil akrilat)-12-kollu makrobaşlatıcı (PIBA-12-kol-MB) ve Boltorn H20® polyesterine dayanan Boltorn H20-multifonksiyonel başlatıcı (Boltorn H20-MB). Azit içeren yıldız kopolimerlerinin sentezi için gerekli olan azit monomerleri; 3-azidopropil metakrilat ve 6-azidohegzil akrilat'ın sentezi de yapılmıştır. Boltorn H20-MB kullanılarak izobornil akrilat (IBA) ve metil metakrilat (MMA) monomerlerinden yıldız homopolimerler sentezlenmiştir. Bu yıldız homopolimerler, yıldız blok kopolimerlerinin sentezi için makrobaşlatıcı olarak kullanılabilir, bunun için ikinci blok olarak 3-azidopropil metakrilat (AzMA), 6-azidohegzil akrilat (AzHA), propargil akrilat gibi reaktif gruplar içeren monomerlerle ATRP reaksiyona tabi tutulabilirler. Elde edilen bu fonksiyonalize edilmiş yıldız blok kopolimerler de, Cu(I) katalizli azit-alkin siklo katılma reaksiyonlarına dayanan klik kimyası tepkimelerinde kullanılabilirler. Multifonksiyonel başlatıcı (Boltorn H20-MB) kullanılarak aynı zamanda izobornil akrilat ve metil metakrilat ile yıldız rastgele kopolimerleri (izobornil akrilat-*r*-3-azidopropil metakrilat) de sentezlenmiştir. Diğer makrobaşlatıcı olan PIBA-12-kol-MB kullanılarak ise izobornil akrilat-b-3-azidopropil metakrilat yıldız blok kopolimerleri sentezlenmiştir. Ürünlerin karakterizasyonu ^{1}H NMR spektroskopisi ve GPC ile yapılmıştır. Azit monomeri ile yapılan polimerizasyon reaksiyonlarından, "triazolin halkası" oluşumuna dayanan yan reaksiyonlar, çapraz bağlanmış zincirlerin oluşumu ve yıldız-yıldız kapling reaksiyonları nedeniyle beklenilen sonuçlar alınamamıştır. Azit monomeri, yıldız kopolimerizasyonu koşulları ile polimerize edildiği zaman kararsız hale geçmektedir.

Klik kimyası, azit-alkin siklo katılma reaksiyonlarına dayandığından ve bu reaksiyonlarda kullanılmak üzere sentezlenmiş azit içeren yıldız kopolimerlerden beklenilen sonuçlar alınamadığından, azit içeren yıldız kopolimerler sentezlemek yerine, alternatif olarak alkin içeren yıldız kopolimerler sentezlenebilir ve bu yapılar, azit içeren gruplarla klik kimyası reaksiyonlarına tabi tutulabilirler.

1. INTRODUCTION

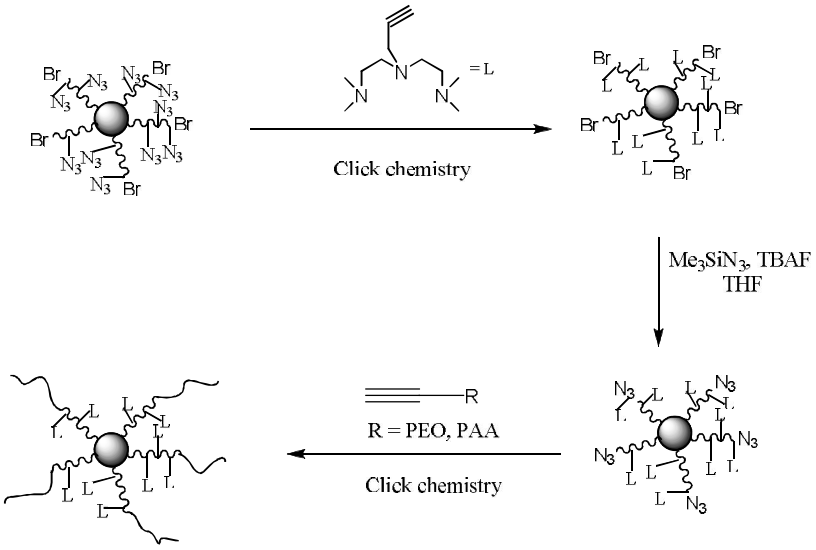
Recent developments in controlled/living radical polymerization have provided a large range of polymers with well-defined, complex structures and different functionalities [1]. One of these polymers are functionalized star-shaped polymers that may be synthesized using the controlled polymerization technique: atom transfer radical polymerization (ATRP) [2]. The formed star-shaped polymers have a known number of arms, controlled molecular weights and narrow polydispersities. Functionalities implanted onto their arms, cores and surfaces, provide unique properties and can be used in many fields including catalysis [3], drug delivery [4], pressure sensitive adhesives [5], etc. For synthesis of star-shaped polymers via ATRP, a metal/ligand complex is required as catalyst that has to be removed after the reactions. In ATRP process, the removal of copper catalyst using a neutral alumina or silica column cause some problems such as large-scale preparation difficulties, high cost (solvents, silica gel, alumina, loss of polymers) and difficulties in separating the catalyst from functional polymers that interact with copper complexes. In addition to these, the metal catalyst can not be recycled for cost-saving. Due to these reasons, researchers have developed some techniques to improve catalyst separation such as: self-separating homogeneous copper (I) catalysts [6], functional star-like polystyrenes as organic supports [7], amphiphilic thermosensitive Ruthenium (II)-bearing star-polymer catalysts [8], catalyst immobilization on solid surface, immobilized/soluble hybrid ATRP catalyst systems, reversible supported catalyst approaches [9].

The aim of this project is to synthesize star-shaped polymers which contain ligand-Cu complexes.

These “functionalized” star-shaped polymers can be used as a catalytic system for ATRP reactions and also for Cu(I)-catalyzed azide-alkyne cycloaddition reactions [10]. This cycloaddition type proceeds quantitatively without any by-product under mild conditions and is tolerant to a broad variety of functional groups. This coupling reaction between an azide and a terminal alkyne by a 1,3-dipolar cycloaddition

reaction leads to the formation of 1,2,3-triazole ring, a chemically very stable compound [11].

This master thesis is a part of a project where new kind of catalysts are synthesized based on a star-shaped structure (Scheme 1.1).

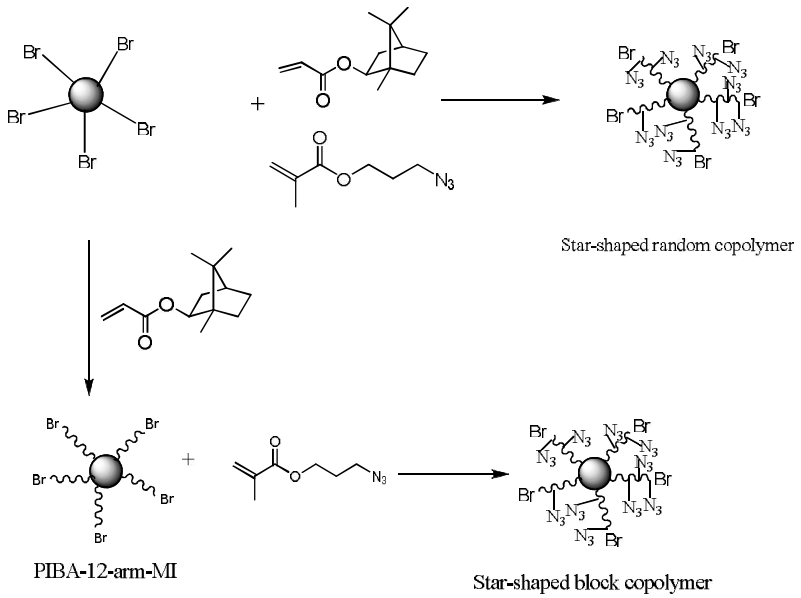


Scheme 1.1: Synthesis of amphiphilic star-shaped polymer catalyst

To synthesize such catalyst multifunctional initiator and macroinitiator are first synthesized from a commercially available polyester Boltorn H20 and dodecafunctional monodisperse initiator respectively. Then, using these structures, random and block copolymers based on azide-containing monomers are synthesized *via* ATRP. In a second step, these azide-functionalized star-shaped copolymers are reacted with alkyne-functionalized ATRP ligand *via* click chemistry in order to obtain functionalized star-shaped polymers. Then, the bromide end-groups of the arms are converted into azide end-groups by nucleophilic substitution reaction. Finally, alkyne-containing poly(ethylene oxide) or poly(acrylic acid) linear homopolymers can be reacted with the azide-containing star-shaped copolymers *via* click reactions in order to form a catalytic system for the reaction of hydrophobic monomers in aqueous environment. This catalytic system can be separated from the reaction media easily and it can be reused for further reactions.

In this master thesis, the first step of this project was generated (Scheme 1.2). The multifunctional initiator Boltorn H20-MI and macroinitiator PIBA-12-arm-MI were synthesized following the route described by Klok et al. [12]. Star-shaped homopolymers of IBA (isobornyl acrylate) and MMA (methyl methacrylate) were

synthesized to use these star-shaped homopolymers as macroinitiators for the synthesis of star-shaped block copolymers. In this thesis, not only star-shaped block copolymers but also star-shaped random copolymers based on IBA and AzMA were synthesized from the synthesized initiators in order to obtain azide-containing star-shaped copolymers. These star-shaped block and random copolymers that have azide moities can further be used for click reactions with alkyne-containing ligand.



Scheme 1.2: Synthesis of azide-containing star-shaped copolymers from multifunctional initiator and macroinitiator

This master thesis is divided into six main parts apart from this chapter including, theoretical part (Section 2), experimental work (Section 3), results and discussion (Section 4) and conclusion (Section 5).

2. THEORETICAL PART

2.1 Atom transfer radical polymerization (ATRP)

2.1.1 Generalities of controlled radical polymerization

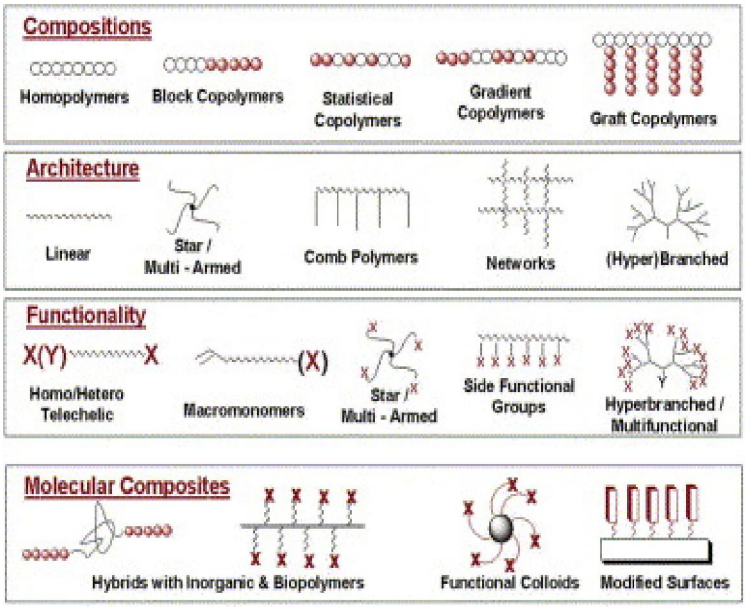
Free radical polymerization is industrially the most widely used method to produce polymeric materials such as plastics, rubbers and fibers [13]. The main advantages of this polymerization technique over ionic or coordination polymerizations are the easy preparation and purification, the use of a large number of different vinyl monomers and tolerance towards temperature, solvent and impurities [14]. However, the major limitation of conventional radical polymerization is the lack of control over the polymerization structure. Due to the slow initiation, fast propagation and subsequent transfer or termination reactions, polymers with high molecular weights and high polydispersities are generally produced. These features are reflected in the physical and mechanical properties of the produced polymers [15].

Controlled radical polymerization (CRP) allows the preparation of well-defined polymers with controlled molecular weight, composition, chain architecture,

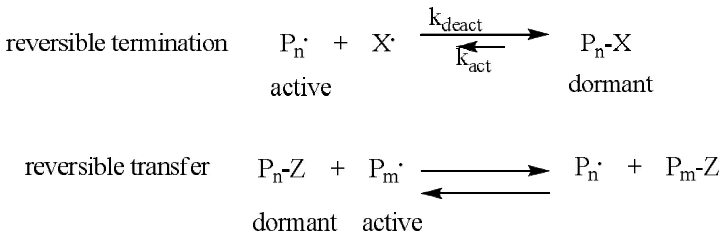
end-group functionality and low polydispersity index [16]. Various well-defined polymer structures can be produced *via* CRP with different functionalities and molecular compositions (Scheme 2.1.1).

In this field, several systems have been applied and the most promising CRP methods are [17]: RAFT (reversible addition-fragmentation chain transfer) [18], ATRP [19] (atom transfer radical polymerization), NMP (nitroxide-mediated radical polymerization) [20], CCT [21] (catalytic chain transfer polymerization)".

The success of controlled radical polymerization is based on a fast and dynamic equilibrium between dormant and active species [22] (Scheme 2.1.2).



Scheme 2.1.1: Topologies, compositions and functionalities of polymers [23]



Scheme 2.1.2: Main equilibriums involved during controlled radical polymerization

In case of ATRP and NMP, the equilibrium is shifted toward the dormant species (reversible termination, Scheme 2.1.1.2), concentration of radicals is maintained low allowing a good control of the polymerization during complete reaction time.

The polymers obtained by controlled/living systems have the following characteristics [24]:

- Controlled molecular weights, with the degree of polymerization (DP_n) is predetermined by the ratio of the concentrations of consumed monomer to the introduced initiator. DP_n = [Monomer]/[Initiator]$_0$
- All chains are end-functionalized
- Concentration of radicals are constant in time
- PDI is close to Poisson distribution PDI $\approx 1 + 1/DP_n$

Experimentally, well-controlled systems need the following requirements:

- If the reaction is first-order with respect to monomer conversion, linear kinetic plots in semilogarithmic coordinates ($\ln([M]_0/[M])$ vs. time) are obtained. In some of these plots, acceleration may indicate slow initiation, however, deceleration may indicate termination or deactivation of the catalyst (Figure 2.1.1-a).
- There is a linear evolution of molecular weights with conversion. If the molecular weights are lower than predicted, this situation indicates transfer reactions. If the molecular weights are higher, this indicates inefficient initiation or chain coupling (Figure 2.1.1-b).

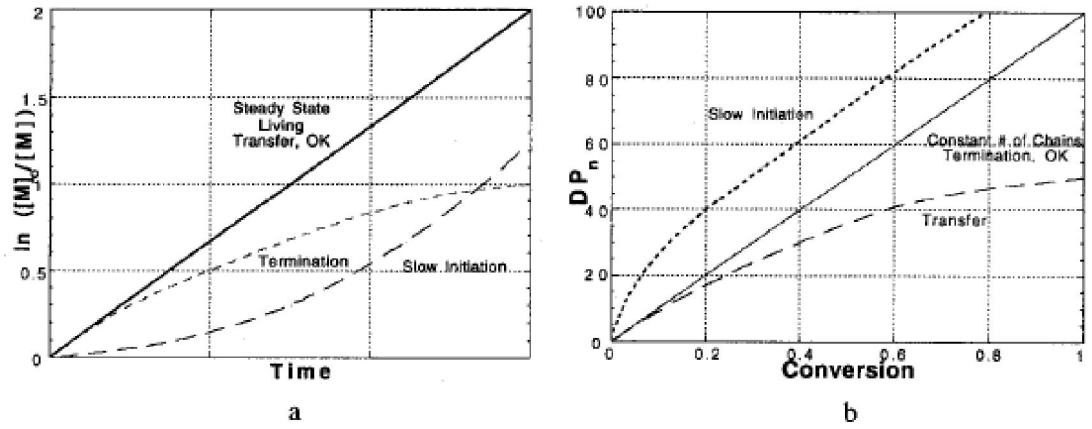


Figure 2.1.1: Effects of slow initiation, transfer, termination and exchange on (a) first order kinetic plot: $\ln([M]_0/[M])$ as a function of time and (b) degree of polymerization as a function of conversion [17]

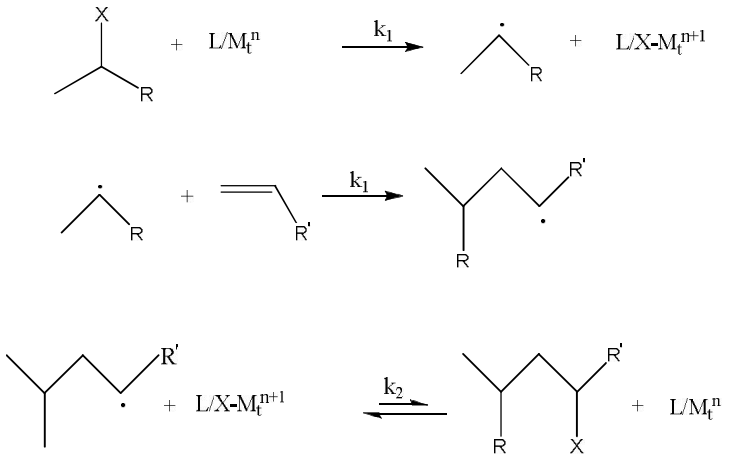
In this thesis, the ATRP technique will be applied.

2.1.2 Meachanism of ATRP

Atom transfer radical polymerization (ATRP) [25,26] is one of the most powerful and versatile methods in CRP and was developed in 1995, further refined by several research groups including the ones of Sawamoto [27], Matyjaszewski [28], Haddleton [29], Armes [30], and others [31].

ATRP is a modified type of atom transfer radical addition (ATRA) [32], where a halogen reversibly transfers from an organic halide to a transition-metal complex to generate the radicals. A metal catalyst, usually a complex based on a copper(I)halide (although Ni, Pd, Ru, Fe and other metals have been used as well) and a ligand undergoes the one electron oxidation with concomitant abstraction of a halogen atom

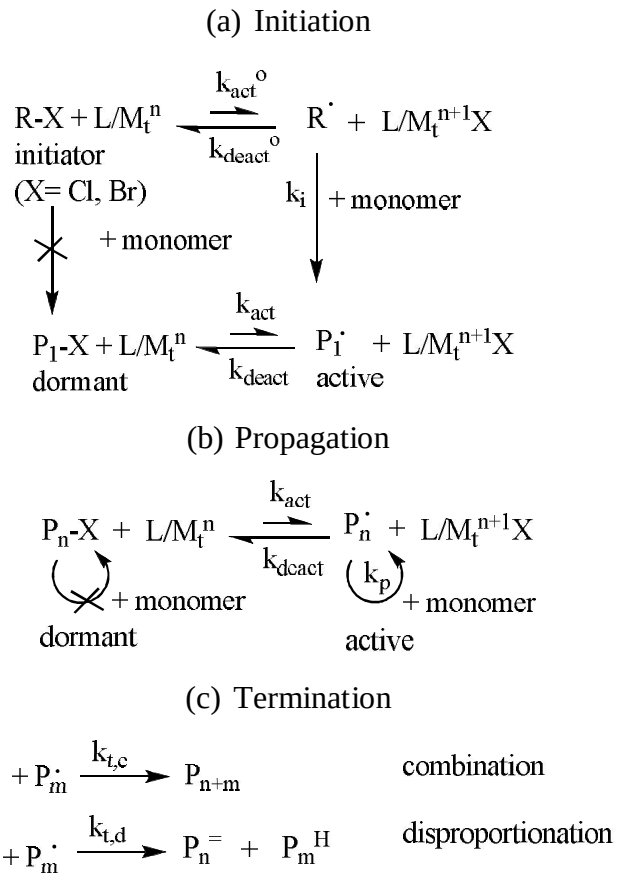
from a species. Because the intermediate radical is much less stabilized than the initial radical, only one addition step is possible in ATRA (Scheme 2.1.3). The intermediate radical essentially reacts irreversibly with the transition metal complex to form an inactive alkyl halide product. In ATRA, only one addition step occurs, but in ATRP, the initial and the intermediate radical have equal reactivity, and then more than one alkene unit can be added. The activation-addition-deactivation cycle will continue until all unsaturated species are consumed.



Scheme 2.1.3: Mechanism of ATRA

The polymerization of ATRP (Scheme 2.1.4) is based on the cleavage of a halogen atom of the initiator R-X or a dormant polymer chain P_n-X (k_{act}) by a transition metal in its lower oxidation state (M_t^n) complexed with a ligand (L) [33]. A radical R$^{\cdot}$ or an active polymer chain $P_n^{\cdot}$ is generated and the transition metal complex is converted to higher oxidation state (X-M_t^{n+1}/L). During the propagation step, monomer is added to grow a polymer chain until the dormant species (P_n-X) are formed again by abstraction of a halogen atom of X-M_t^{n+1}/L with formation of M_t/L (k_{deact}). Control over molecular weight, polydispersity index and functionality are thus obtained by a dynamic equilibrium (k_{act}/k_{deact}) between a dormant chain P_n-X and an active chain ($P_n^{\cdot}$) by an exchange of electrons (redox potential) between the transition metal complex and the radical of the active species. Due to this dynamic equilibrium, the radical concentration is maintained low during the polymerization reaction. However, irreversible termination can result in a small amount of coupled polymer chains P_n-P_m in case of combination ($k_{t,c}$), or can result in disproportionated chains

$P_n^=$ or P_m-H in case of disproportionation ($k_{t,d}$). For a successful ATRP, the initiation step and reversible deactivation must be generated rapidly, therefore uniform growth of all chains is accomplished. If the equilibrium constant is too low, a good control can not be obtained while a too high equilibirum constant leads to a too high radical concentration. To overcome this situation, one possible solution may be the addition of a higher oxidation state metal complex in a small amount, which will shift the equilibrium toward dormant species (deactivator) and may result in a slower and a better controlled polymerization.



Scheme 2.1.4 : Detailed mechanism of ATRP

2.1.3 Kinetics of ATRP

Knowledge of the dimension and impact of the kinetic parameters in a controlled/"living" radical polymerization (CRP) is of critical importance for the design of well-defined macromolecules. The polymerization rate and molecular weight distribution are a direct consequence of the kinetics.

The kinetic equation for ATRP [34] can be derived from the reaction shown in Scheme 2.1.4. If the initiation is considered as quantitative and fast in comparison to

propagation, and if termination is ignored, the rate for activation (R_{act}) and deactivation (R_{deact}) is:

$$R_{act} = k_{act}[P_n\text{-}X][M_t^n] \quad \textbf{(2.1.3.1)}$$

$$R_{deact} = k_{deact}[P_n^{\cdot}][M_t^{n+1}] \quad \textbf{(2.1.3.2)}$$

R_{act} : rate of activation
R_{deact} : rate of deactivation
$[P_n\text{-}X]$: concentration of initiator
$[P_n^{\cdot}]$: concentration of radicals
$[M_t^n]$: concentration of catalyst in lowest oxidation state
$[M_t^{n+1}]$: concentration of catalyst in highest oxidation state

The rate of polymerization (Rp) is given by:

$$R_p = -d[M]/dt = k_p[P_n^{\cdot}][M] \quad \textbf{(2.1.3.3)}$$

$[P_n]$: concentration of radicals
$[M]$: concentration of monomer

If the steady-state concentration of the propagating radicals are supposed, R_{act} is equal to R_{deact}. It means that an equation for the concentration of growing polymer chains can be derived:

$$[P_n^{\cdot}] = k_{act}/k_{deact}\,[P_n\text{-}X][M_t^n]/[M_t^{n+1}] \quad \textbf{(2.1.3.4)}$$

If equations 2.1.3.3 and 2.1.3.4 are filled with $[R\text{-}X]_0 = [P_n\text{-}X]$, the below equation is obtained.

$$R_p = k_p\,k_{act}/k_{deact}\,[P_n\text{-}X] = [M_t^n]\,[M]/[M_t^{n+1}] = k_p\,k_{act}/k_{deact}\,[R\text{-}X]_0\,[M_t^n]\,[M]/[M_t^{n+1}] \quad \textbf{(2.1.3.5)}$$

So, this equation means that the polymerization rate (R_p) is first order with respect to the monomer concentration [M], the initiator [R-X] and the transition metal complex

$[M_t^n]$. Integration according to the condition that $[M] = [M]_0$ at $t = 0$, leads to the following formula:

$$\ln ([M]_0/[M]) = k_p k_{act}/k_{deact} [P_n\text{-}X] [M_t^n] t / [M_t^{n+1}] = k_p^{app} t \quad \textbf{(2.1.3.6)}$$

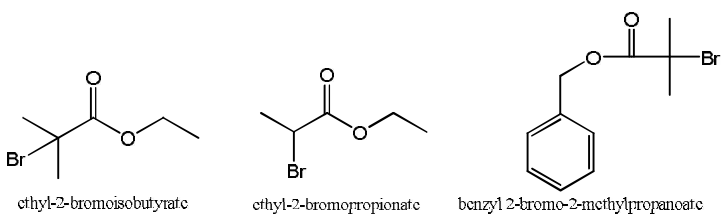
Plotting of $\ln\left(\frac{[M]_0}{[M]_t}\right)$ as a function of time leads to a straight line with k_p^{app} as the slope for controlled polymerization. This linear behaviour is ascribed to the constancy of radical concentration throughout the polymerization. However, it should be considered that a slight deviation from linearity is often observed as a result of termination reactions in the early stages of the polymerization reaction, since the equilibrium between the active and dormant polymer chains is not yet fully established.

2.1.4 Components of the ATRP mechanism

2.1.4.1 Initiator

The initiator in ATRP [35] plays an important role. The initiation must be fast (transfer and termination are negligible) to get a constant number of growing chains. In ATRP, the structure of the used initiator is usually similar to that of monomer.

To obtain well-defined polymers, the organic halides with carbon-halide bonds are mostly used [36,37], that can easily generate a radical species through electronic and steric effects of their substituents. Preferably, alkyl bromides and alkyl chlorides are used. An alkyl fluoride bond is too strong to cleave homolytically and use of an alkyl iodide can generate some undesired side-reactions. In general, alkyl halide with activating substituents on the alpha carbon (aryl, carbonyl, or allyl groups) can be used as ATRP initiators. In addition, tertiary alkyl halides are favoured because they have the fastest homolytic cleavage. Some examples of initiators are shown in Scheme 2.1.5.



Scheme 2.1.5 : Examples of initiators used for ATRP

2.1.4.2 Catalyst

The catalyst, consisting in a metal catalyst and a ligand [38], determines the dynamic equilibrium between the dormant and active species. The metal center must have at least two readily accessible oxidation states separated by one electron, it should also have reasonable affinity toward a halogen, the coordination sphere around the metal should be expandable upon oxidation to selectively accommodate a (pseudo)-halogen, and the ligand should complex the metal relatively strong. Various transition metals (Cu, Ru, Ni, Fe, Pd, Mo) are used for ATRP reaction [39]. However copper-based catalyst complexes are the most studied in ATRP due to their relatively low price and reactivity. Different post-polymerization methods have been developed for removal of the catalyst because of the toxicity of the catalyst and the intense colour of the resulting polymers [40-42]. Since the removal of the catalyst is rather expensive and time-consuming process, solid-phase catalyst systems have been developed to overcome this handicap.

Cu-based ATRP is one of the most versatile and powerful techniques as mentioned before. In Cu-catalyzed ATRP, most commonly used ligands are tertiary amines [43]. Some examples of the ligands are given in Scheme 2.1.6.

The ligand also affects the ATRP equilibrium by the electronic and steric effects [44]:

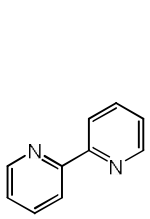
- Bulky ligands reduce the rate of activation, as the copper center is harder to access for the halogen.
- Electronic interactions of the ligand and Cu is the predominant factor; good π-acceptor ligands stabilize the lower oxidation state of the metal center and shifts the atom transfer equilibrium toward the dormant species.

Another important role of the ligand in ATRP is to solubilize the transition-metal catalyst in the organic media and to adjust the redox potential of the metal center for appropriate reactivity and dynamics for the atom transfer. Activity of nitrogen-based ligands in ATRP decreases with the number of coordinating sites $N_4 > N_3 > N_2 >> N_1$ and with the number of linking Carbon atoms $C_2 > C_3 >> C_4$ [45]. In general, the activity of the ligands decreases in the following order:

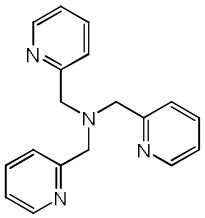
Alkyl amine ≈ pyridine > alkyl imine >> aryl imine > aryl amine.

The amines are of interest in ATRP for 2 reasons [46]:

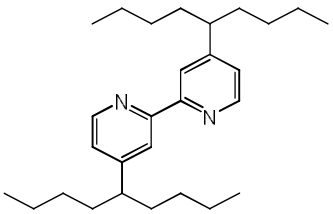
- Most of the amines are relatively cheap.
- Since the coordination complexes between copper and amines tend to have lower redox potentials, the employment of amines as the ligand in ATRP may lead to faster polymerization rates.



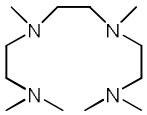
2,2'-bipyridine
(bpy)



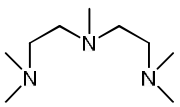
tris[(2-pyridyl)methyl]amine
(TPMA)



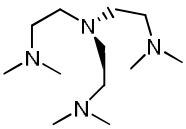
4,4'-di(5-nonyl)-2,2'-bipyridine
(dNbpy)



1,1,4,7,10,10-hexamethyltriethylenetetramine
(HMTETA)



N,N,N',N'',N''-pentamethyl-diethylenetriamine
(PMDETA)



tris[2-(methylamino)ethyl)]-amine
(Me_6TREN)

Scheme 2.1.6: Some examples of ligands used for ATRP

2.1.4.3 Solvent

ATRP can be proceeded in bulk and in solution. Various solvents such as benzene, toluene, anisole, diphenylether, ethylacetate, acetone, alcohol, water can be used. If diluted conditions are used, heat transfer and viscosity are better controlled [47]. Solvent is very significant for the rate of polymerization. Both polar and non-polar solvents can be used.

However, polar solvents (DMSO, methanol, DMF) can interact with copper and influence the rate of reaction. In addition, side-reactions due to the solvent such as elimination of HX from polyhalides and catalyst poisoning by solvent should be considered.

2.1.4.4 Temperature

The choice of the optimal temperature for ATRP is of great importance and depends on the whole used system. The rate of polymerization in ATRP increases with the temperature due to the increase of both radical propagation rate constant and atom transfer equilibrium constant. As a result of the higher activation energy for the radical propagation than for the radical termination, higher k_p/k_t ratios and better control (livingness) may be observed at higher temperatures. However, chain transfer and other side reactions become more pronounced at elevated temperatures [48]. In addition, the solubility of the catalyst increases with temperature while a catalyst decomposition may also occur at high temperature.

2.1.4.5 Monomer

Various vinyl monomers, mostly conjugated monomers, such as styrene and its derivatives [49], methacrylates [50], acrylates [51], acrylonitrile [52], meth(acrylamides) [53] and meth(acrylic) acids [54] can be polymerized *via* ATRP and they have also been used to prepare well-defined polymers with wide range of functionalities, compositions and architectures including liquid crystalline [55] polymers, block [56], star [57], graft [58], comb [59], dendrimer-like and hyperbranched [60] (co)-polymers as well as other complex structures.

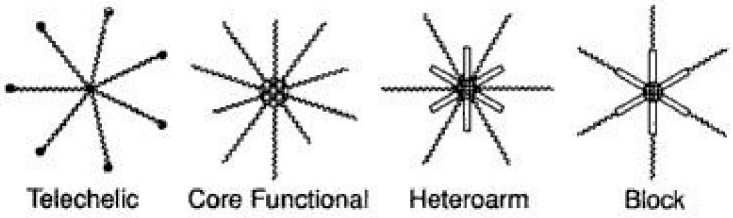
2.2 Star-shaped polymers

During the last decade, a large amount of branched structures [61-63], including dendrimers [64-67], hyperbranched polymers [68] and star-shaped polymers [69,70] were designed. These structures are defined as molecules with more than one backbone where not only the elementary composition, but also molecular architecture of a molecule have a significant influence on the properties of a material. Since the branched structures have different molecular characteristics than their linear analogues, they generally exhibit lower solution and melt viscosities compared to linear polymers of the same molar mass [71]. These characteristics of branched structures help facilitating some polymerization processes such as coating and extrusion. The main interest is shifting to an exploration for the investigation of potential uses and applications. These involve nanoscale-ordered materials,
low-viscosity paints, thickeners, drug carriers, rheology modifiers, pressure sensitive adhesives, micelles and encapsulation, electroactive dendrimers, sensors, conductive and ionic conductive polymers [72].

The star-shaped polymers are the simplest case of branched species where all chains of a given macromolecule are connected to a single nodulus referred as the core [73]. These polymers are particularly interesting owing to the simplicity of their preparation processes. One of the biggest advantages of these structures is the ability to design star-shaped polymers with a varying number of physical properties by varying the composition, size, number of arms, etc. Because of their compactness, star-shaped molecules show a typical solution behaviour [74]. Provided the number of branches is sufficiently high, the solution properties of star-shaped polymers are determined chiefly by the average length of their arms. Their intrinsic globular structure and large number of functional groups also influence on thermal and dissolving properties [75].

Beyond regular star-shaped polymers, various other kinds of star-shaped macromolecules have attracted interest and have lead to specific applications, including telechelic, core-functional, heteroarm and block star-shaped polymers
[76-78] (Scheme 2.2.1).

In this thesis, the synthesis of star-shaped polymers will be described.



Scheme 2.2.1: Different types of branched structures [79]

2.2.1 Synthesis of star-shaped polymers via controlled living polymerization techniques

Star-shaped polymers are mostly synthesized by living anionic [80], cationic [81] and controlled radical polymerization [82] techniques. The basic routes for synthesizing star-shaped polymers were explained in the following paragraphs.

The methodology of living polymerization is used for the synthesis of well-defined, star-shaped polymers and copolymers with low degrees of compositional heterogeneity [83]. Because termination and chain transfer reactions are absent and the chain ends may be stable for a sufficient time period, these polymerization techniques have the following useful synthetic attributes for star-shaped polymer synthesis:

- The degree of polymerization ($DP_n = [M]/[I_o]$) can be predetermined before the reaction, by dividing the concentration of monomer with the concentration of initiator. One polymer is formed from each initiator molecule I, 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 *n* arms. If the rate of initiation is rapid or competitive with the rate of propagation, polymers (precursor arms) with narrow molecular weight distributions ($M_w/M_n \leq 1.1$) are formed.
- When all of the monomer has been consumed, the so-obtained polymer with reactive chain ends can participate in a variety of postpolymerization reactions such as: block copolymerization by addition of a second monomer, and/or end-linking with multifunctional linking agents to form the corresponding star-branched polymers with uniform arm lengths.

Controlled-living cationic and anionic polymerization processes have been an important tool for the precision synthesis of macromolecules with predetermined number average molar mass (M_n), terminal functionality, and narrow molar mass disribution (MWD) for star-shaped polymers until the discovery of living polymerization of isobutylene and vinyl ethers in early 1980's [84,85]. In addition to these, recent reports have also detailed the application of Nitroxide mediated polymerization or ATRP as controlled/living radical polymerizations to the synthesis of star-shaped polymers [86].

Using living polymerization techniques, star-shaped polymers can be synthesized with the following methods.

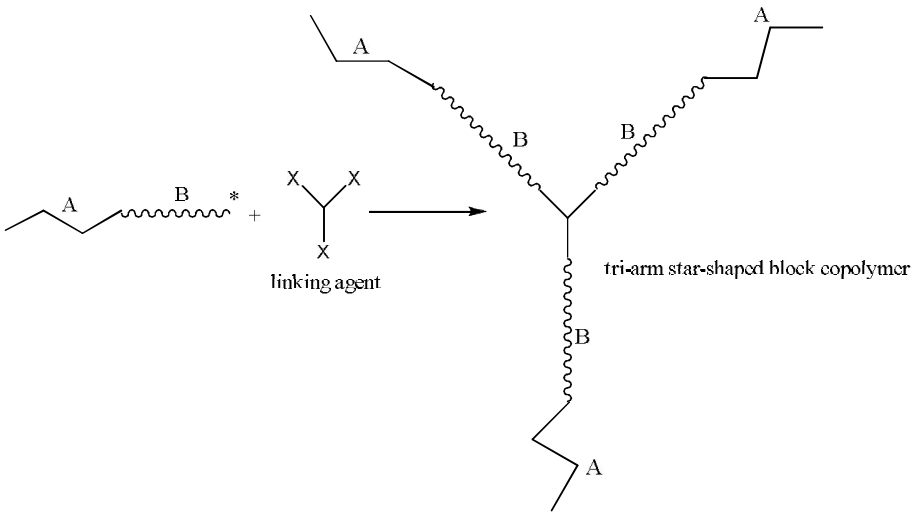
Recently, Penfold et al. [87] synthesized star-shaped polymers of styrene and alkyl (meth)acrylates from a porphyrin initiator core via ATRP. For synthesis of branched poly(styrene-*b*-tert-butyl acrylate) and poly(styrene-*b*-acrylic acid) polymers by ATRP using a dendritic poly(propylene imine)$(NH_2)_{64}$ core Mourey et al. [88] has also published an interesting paper.

2.2.1.1 Arm-first method

The arm-first approach [89] involves the synthesis of preformed arms, usually through living polymerization, followed by reaction with a multifunctional linking agent (coupling-onto method) or by using a difunctional comonomer which is linked to the living linear polymer chain (nodule method).

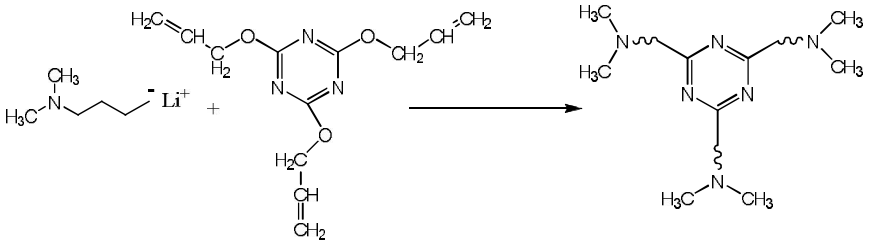
Coupling-onto method

In this method, polymer arms with living chain ends are reacted with a multifunctional compound having an appropriate number of functional groups equal to the number of arms of the desired final star-shaped polymer [90] (Scheme 2.2.2). The functional groups must be able to react with the living centers in a quantitative, fast and controlled way, giving no byproduct. In order to improve the coupling efficiency, excess amount of arms are used and these excess arms can be eliminated, from the mixture reaction by fractionation for instance. The major advantage of this synthetic methodology is that the number of arms present on each star macromolecule is well-defined and predetermined, leading to well-defined star-shaped polymers.



Scheme 2.2.2: Schematic representation of "coupling on-to" method

Burchard [91] developed an approach to synthesize star-shaped polymers with tertiary amine groups at the outerend of the branches. For instance, the polymerization of styrene was initiated with ((3-dimethylamino)propyl)lithium and the living carbanions were reacted stoichiometrically with tris(allyloxy)-1,3,5-triazine (Scheme 2.2.3) [91].

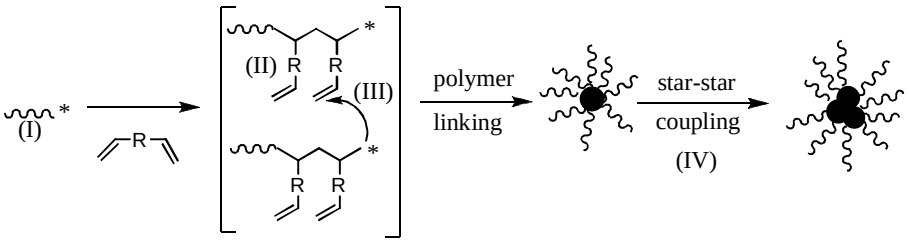


Scheme 2.2.3: Synthesis of functional star-shaped polymers via 'arm-first' approach ("coupling on-to method")

Nodule method

In nodule method, the reactive macroinitiators (arms) produced by a living polymerization technique are cross-linked by a divinyl agent to form star-shaped polymers [92]. The mechanism of the "nodule" method is shown in Scheme 2.2.4. First, linear polymers as reactive macroinitiators are synthesized (I), then a few units of divinyl agents are added to the reactive macroinitiators to form short block copolymers with vinyl end-groups (II). Then, the reactive macroinitiator chain ends react with the vinyl end-groups to form a microgel core (III). Finally, core-core coupling reaction can occur to form a higher order star-shaped polymer (IV). Due to the existence of two reactive sites, the polymerization results in the formation of a

network of small dimensions, which serves as a connecting point for the arms. By this procedure, star-shaped polymers with a relatively broad distribution in the number of arms are prepared. Therefore, the number of arms in the final star-shaped polymer is not well-defined. Although some control can be exercised through the ratio of the concentration of the difunctional monomer to the concentration of the active centers. The main disadvantages are the amount of unlinked arms present in the final crude reaction product and occasional presence of gel formation.



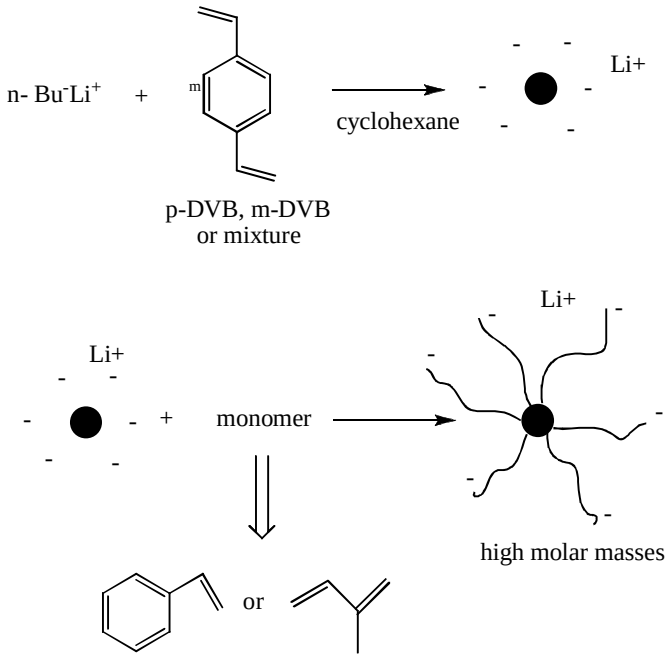
Scheme 2.2.4 : The reaction mechanism of "nodule" method

Matyjaszewski et al. [93] reported an interesting study in 1999, about synthesis of (poly)styrene star-shaped polymers by the nodule method, using copper-mediated ATRP.

2.2.1.2 Core-first method

The "core-first approach" involves the use of a multifunctional initiator or "core" for initiation of the polymerization of the arms. When a core is generated, there is a diversity in number of arms and in the last step, the chains are terminated with new end-groups [94]. The most commonly used core-first method is actually derived from Burchard's method and requires an efficient soluble polyfunctional initiator that can be used in polar solvents [95] (Scheme 2.2.5). Here, the initiator system developed by Burchard is based on lithium as a counter-ion. The soluble precursor chains containing metal organic sites, serve as efficient initiator for the polymerization of a small amount of bis-unsaturated monomer divinyl benzene (DVB). Upon polymerization of DVB, tightly cross-linked cores are formed, each of them being connected with the precursor chains that have contributed to its initiation. The monomers are added and polymerization is generated. After the polymerization of the first generation of branches is complete, a second monomer can be initiated and polymerized or the extremities can be functionalized. Recently, preparation of several well-defined star-shaped polymers from hyperbranched macroinitiators by

the use of well-defined multifunctional initiators were described by Johnson et al. [96] and Yu et al. [97]. The polymer chains are grown from this multifunctional initiators and control over the number of arms and molecular weights can be obtained. However, synthesis of these well-defined macroinitiators are complicated because of the low yields. In ionic polymerization, the number of arms that can be synthesized are limited and the multiply charged initiator molecules exhibit poor solubility. Therefore, core-first methods were developed extensively in polar solvents to access star-shaped macromolecules exhibiting functional groups at the outer chain ends [98]. Once such species are obtained, they can serve as valuable intermediates in the elaboration of a large scope of macromolecular architectures. However, in living radical polymerization, star-shaped polymers with large number of arms can be prepared with easy introduction of functional groups because there exist no linear polymer chains [99].

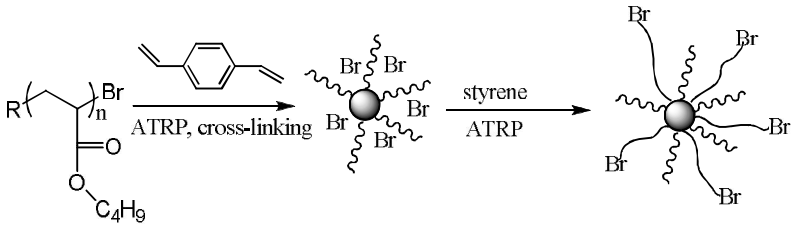


Scheme 2.2.5: "Core-first" method based on *n*-butyl lithium and divinylbenzene

2.2.1.3 In-out method

Star-shaped polymers obtained from the arm-first method preserve multiple initiating sites within the cores that can be further used as macroinitiators (MI) for the synthesis of miktoarm star-shaped polymers by initiating the polymerization of another monomer. This technique, termed as '*in-out*' method, is an important method that allows the synthesis of star-shaped polymers containing two types of arms with different chemical composition and/or molecular weight [100]. The word "*in*" refers

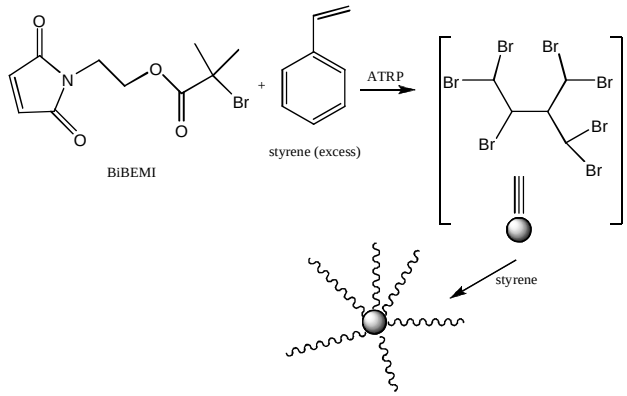
to the arm-first method for formation of the star-shaped polymer macroinitiator (MI) and the word "*out*" represents the subsequent growth of the second generation of arms from the multifunctional core (Scheme 2.2.6). The resulting star-shaped polymers generally have a statistical distribution of the number of arms.



Scheme 2.2.6: Synthesis of miktoarm star-shaped polymers via "in-out" approach [101]

2.2.1.4 One-pot method

In literature, to synthesize star-shaped polymers, at least two separated steps are applied that can be a limitation for industrial preparation procedures. Therefore, a simple way of synthesis is highly appreciated. One-pot strategy is based on ATRP of *N*-[2-(2-bromoisobutyryloxy)ethyl]maleimide (BiBEMI) and styrene. When excess of styrene is used, preferentially copolymerization of BiBEMI, as an inimer, with styrene may be expected with formation of a branched structure [102] (Scheme 2.2.7).

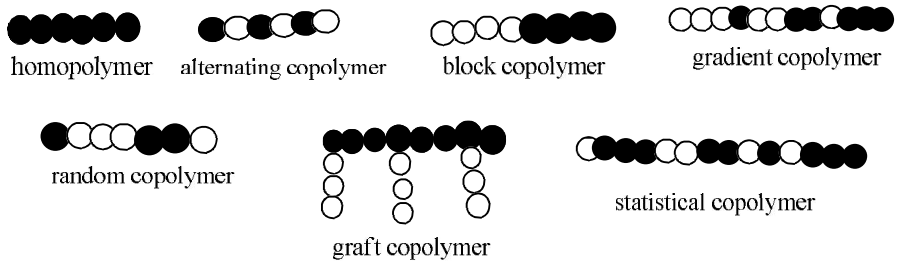


Scheme 2.2.7: Synthesis of star-shaped polymers via "one-pot" approach

In this project, we used the "core-first" method for ATRP reactions, using multifunctional initiators in order to synthesize star-shaped homo, random and block copolymers.

2.2.2 Star-shaped copolymers

A copolymer consists of two or more monomeric species, which are classified based on how these units are arranged along the chain, as opposed to a homopolymer where only one monomer is used. The structure of a homopolymer and some of the copolymers are shown in (Scheme 2.2.8) [103].



Scheme 2.2.8: Different types of copolymers

In this project, block copolymers and random copolymers will be synthesized.

Block copolymers are a fascinating class of polymeric materials belonging to a big family known as ‘‘soft materials.’’ This class of polymers is made by the covalent bonding of two or more polymeric chains that, in most cases, are thermodynamically incompatible giving rise to a rich variety of microstructures in bulk and in solution. The length scale of these microstructures is comparable to the size of the block copolymers molecules (typically 5–50 nm). Therefore, the microstructures are highly coupled to the physical and chemical characteristics of the molecules. The variety of microstructures gives rise to materials with applications ranging from thermoplastic elastomers and high-impact plastics to pressure-sensitive adhesives, additives, foams, etc [104]. In addition, block copolymers are very strong candidates for potential applications in advanced technologies such as information storage, drug delivery, and photonic crystals.

A series of well-defined star-shaped block copolymers have been synthesized by controlled radical polymerization techniques [105], i.e., Hong et al. [106] synthesized well-defined dendritic star-shaped block

poly(l-lactide)-*b*-poly(2-(*N*,*N*-dimethylamino)ethyl methacrylate) copolymers with hydroxyl-terminated dendrimer polyester initiator.

The copolymers, with a relatively random distribution of the different monomers in its structure is referred to as a random copolymer. Due to the lower crystallinity, random copolymers have lower melting points and specific gravities than

homopolymers. The glass-transition temperature of random copolymers are generally lower than homopolymers, depending on type, amount and distribution of copolymer. Random copolymers are primarly used in film, blow molding and injection molding applications that require high clarity, good impact strength at low temperatures, some stiffness and moisture barrier properties [107]. Blow molding applications include hot filled and multi-layer barrier bottles and refrigerated products for medical and food packaging. Rigid and semi-rigid packaging, video casette cases, toys, storage trays and reusable food containers are also usage areas of random copolymers where injection molding is applied [108,109]. Also polymer coating for rubber articals can be given as an example for the application area of star-shaped random copolymers [110].

Recently, Kim et al. [111] synthesized star-shaped random copolymers from resorcinarene octa-fuctional alkoxyamine initiator via controlled radical polymerization.

3. EXPERIMENTAL WORK

3.1 Materials

Boltorn H20® (Perstorp) was dried under vacuum. Tetrahydrofurane (Aldrich, HPLC grade) was distilled on sodium/benzophenone. Triethylamine (Alrich, HPLC grade) was refluxed on CaH_2 (bp: 89°C). Isobornyl acrylate (Aldrich, technical grade) was purified by vacuum distillation (121°C/18 mmHg).

N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, Acros, 99%) was distilled (85-86°C/12mmHg). Copper(I)bromide (Cu(I)Br, Aldrich, 98 %) was purified by stirring with acetic acid, then by filtering and washing with ethanol, diethylether, finally by drying in a vacuum oven at 70°C. Methyl methacrylate (MMA, Fluka, 99%) was purified by passing over a basic aluminum oxide filtration column. Methanol (Fiers, 99.85%), sodium azide (Aldrich, 99.5%), tetrabutylammonium hydrogen sulphate (Acros, 98%), 3-chloropropanol (Aldrich, 98%), diethyl ether (Sodes, 99.85%), sodium sulfate (Fisher scientific, laboratory reagent grade), hydroquinone (Fluka, 99%), methacryloyl chloride (Fluka, >97%), hydrochloric acid (Fiers, 37%), 6-chloro-1-hexanol (Fluka, >95%), acryloyl chloride (Aldrich, +96%), 2,2'-bipyridine (bpy, Acros, +99%),
ethyl-2-bromoisobutyrate (Acros, 98%), chloroform (Fisher scientific, HPLC grade), 2-bromo-2-methylpropionylbromide (Acros, 99%), acetone (Alrich, HPLC grade),
4-(dimethylamino)pyridine (Acros, 99%), Ni(tripheylphosphine)bromide (Acros, 99%), *n*-hexane (Fisher scientific, HPLC grade) were used as received.

3.2 Equipments

3.2.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H NMR spectra were recorded in $CDCl_3$ at room temperature, with a Bruker AM500 or a Bruker Avance 300 spectrometer.

3.2.2 Gel-permeation Chromatography (GPC)

GPC analysis was performed on a Waters instrument, using a refractive index detector (2410 Waters), equipped with Waters Styragel 10^3-10^4-10^5 Å serial columns (5 µm particle size) at 35°C. Polystyrene standards were used for calibration and $CHCl_3$ as eluent at a flow rate of 1.5 mL/min. GPC samples were injected using a Gilson autoinjector type 234.

3.3 Preparation methods

3.3.1 Synthesis of 3-azidopropyl methacrylate (AzMA)

1st Step: Synthesis of 3-azidopropanol

Sodium azide (47 g, 0.716 mol) was weighed in a flask using a plastic spatula. Then 40 mL of water, 1g of tetrabutylammonium hydrogen sulfate and 3-chloropropanol (30 mL, 33.9 g, 0.358 mol) were added. The flask, equipped with a reflux condensor, was stirred at 80°C for 24 hours. Then it was stirred at room temperature for 14 hours. The product was washed 3 times with 100 mL diethyl ether. The combined organic phases were dried using sodium sulfate. After purification of the obtained product by vacuum distillation, colourless liquid was acquired at 27°C (1 mbar).

2nd Step: Synthesis of 3-azidopropyl methacrylate

A mixture of 3-azidopropanol (23.5 mL, 0.253 mol), triethylamine (45 mL, 0.323 mol), hydroquinone (0.1 g) and diethyl ether (100 mL) under nitrogen atmosphere was cooled to 0°C in an ice-bath. Methacryloyl chloride (29.0 mL, 0.300 mol) was added dropwise during a period of 30 minutes. The reaction was then stirred at 0°C for one hour and at room temperature for 24 hours. After adding 100 mL of diethyl ether to the reaction mixture, it was washed two times with 100 mL HCl (10 vol%), 100 mL NaOH (10 wt%) and 100 mL water respectively. The diethyl ether phase was dried with sodium sulfate. After removal of sodium sulfate with a glass filter, the product was put in a rotavapor to evaporate diethyl ether. Finally, 3-azidopropyl methacrylate was obtained as yellow liquid. Yield: 68%. ^{1}H NMR (300 MHz, $CDCl_3$): 6.10 ppm (s, 1H, CH_2=CCH_3-), 5.58 ppm (s, 1H, CH_2=CCH_3-), 4.05-4.38 ppm (t, 2H, -O-CH_2-), 3.30-3.50 ppm (m, 2H, CH_2-N_3), 1.85-2.38 ppm (m, 5H, CH_2-CH_2-CH_2, =CH_3).

3.3.2 Synthesis of 6-azidohexyl acrylate (AzHA)

1st Step: Synthesis of 6-azidohexanol

Sodium azide (19.5 g, 0.3 mol) was weighed in a flask using a plastic spatula. Then 40 mL of water, tetrabutylammonium hydrogen sulfate (0.5 g, 1 mmol) and 6-chloro-1-hexanol (20 mL, 20.48 g, 0.15 mol) were added. The flask, equipped with a reflux condensor under nitrogen atmosphere, was stirred at 80°C for 24 hours. Then, it was stirred at room temperature for 14 hours. The product was washed 3 times with 100 mL of diethyl ether. The combined organic phases were dried using sodium sulfate. After purification of the obtained product by vacuum distillation, colourless liquid was acquired at 58-60°C (1mbar).

2nd Step: Synthesis of 6-azidohexyl acrylate

A mixture of 6-azidohexanol (8.234g, 57.5 mmol), triethylamine (15.3 mL, 0.11 mol), hydroquinone (0.1 g) and diethyl ether (34 mL) was cooled to 0°C in an ice bath. Acryloyl chloride (5.53 mL, 68.1 mmol) was added dropwise during a period of 30 minutes. The reaction was then stirred at 0°C for one hour and at room temperature for 24 hours. After adding 100 mL of diethyl ether to the reaction mixture, it was washed two times with 100 mL HCl (10 vol%), 100 mL NaOH (10 wt%) and 100 mL water respectively. The diethyl ether phase was dried with sodium sulfate. After removal of sodium sulfate with a glass filter, the product was put in a rotavapor to evaporate diethyl ether. Finaly, 6-azidohexyl acrylate was obtained as yellow liquid. Yield: 20%. ^{1}H NMR (300 MHz, $CDCl_3$): 6.30-6.40 ppm (d, 1H, CH_2=CH-), 6.00-6.10 ppm (m, 1H, CH_2=CH-), 5.70-5.80 ppm (d, 1H, CH_2=CH-), 4.05-4.20 ppm (m, 2H, -O-CH_2-), 3.15-3.33 ppm (m, 2H, -CH_2-N_3), 1.50-1.75 ppm (m, 8H, CH_2-(CH_2)$_4$-CH_2-).

3.3.3 Synthesis of Boltorn H20® modified multifunctional initiator

(Boltorn H20-MI)

Vacuum-dried Boltorn H20 (2.00 g, 0.016 mol of hydroxyl groups), 100 mL THF, 4-(dimethylamino)pyridine (DMAP, 2.93 g, 0.024 mol) and triethylamine (NEt_3, 4.86 g, 6.69 mL, 0.048 mol) were added under nitrogen flow.

2-bromo-2-methylpropionyl bromide (11.03 g, 5.93 mL, 0.048 mol) was added dropwise at room temperature. After 48 h, salts were filtered off and solvent was

evaporated. The viscous oil was purified in a membrane filter of 1000 MWCO. Finally, the obtained yellowish viscous oil was dried under vacuum. Yield: 38.5%. ^{1}H NMR (300 MHz, DMSO-d_6): 4.10-4.45 ppm (d, 48H, -O-CH_2-), 1.89 ppm (d, 96H, Br-C(CH_3)$_2$-C=O-), 1.20-1.45 ppm (d, 36H, -CH_3-C(O-CH_2)$_2$C=O).

3.3.4 Synthesis of PIBA-star-shaped homopolymer from Boltorn H20-MI

Boltorn H20-MI and acetone were added in a two-necked flask equipped with a stirrer. Then, IBA and PMDETA were added to the reaction mixture. The mixture was degassed by 3 freeze-pump-thaw cycles. Then, Cu(I)Br was added under nitrogen flow. Afterwards, the mixture was stirred at room temperature in order to obtain homogeneity. The reaction mixture was immersed in an oil bath at 50^{o}C. Samples were withdrawn periodically to monitor the monomer conversion (by ^{1}H NMR) and the number average molecular weight (by GPC). The reaction was ended by cooling the mixture to room temperature and by adding THF. The product was then passed through a neutral alumina column to remove copper. After most of the solvent evaporated in rotavapor, the polymer was precipitated into methanol (10-fold excess). The obtained white powder was dried in a vacuum oven.

3.3.5 Synthesis of PMMA-star-shaped homopolymer from Boltorn H20-MI

Boltorn H20-MI and MMA were added in a two-necked flask equipped with a stirrer. The mixture was degassed under nitrogen flow for 30 min. Then Ni(triphenylphosphine)bromide was added and the flask was again purged with nitrogen for 5 minutes. After a homogeneous mixture was obtained by stirring, the flask was immersed in an oil bath at 90^{0}C. Samples were withdrawn periodically to monitor the monomer conversion (by ^{1}H NMR) and the number average molecular weight (by GPC) before ending the reaction. The process was terminated by cooling the mixture to room temperature and by adding THF. The product was then passed through neutral alumina column to remove catalyst. After most of the solvent evaporated in rotavapor, the polymer was precipitated into *n*-hexane (10-fold excess). The obtained white powder was dried in vacuum oven.

3.3.6 Synthesis of PIBA-PAzMA star-shaped random copolymer from Boltorn H20-MI

A typical procedure is as follow: macroinitiator, solvent, ligand, IBA and AzMA were added to a reaction flask. The mixture was degassed by three freeze-pump-thaw cycles. After adding Cu(I)Br under nitrogen flow, the flask was immersed in an oil bath under nitrogen atmosphere. Samples were withdrawn periodically to monitor the monomer conversion (by ^{1}H NMR) and the number average molecular weight (by GPC). For termination of the reaction, the mixture was put in an ice bath and diluted in THF. Most of the solvent was evaporated in rotavapor and the obtained polymer was precipitated into cold methanol (10-fold excess). After filtration, the obtained white powder was dried under vacuum oven.

3.3.7 Synthesis of PIBA star-shaped polymer macroinitiator from monodisperse dodecafunctional initiator (PIBA-12-MI)

The dodecafunctional monodisperse initiator was dissolved in acetone in a two-necked flask equipped with a stirrer and a septum. Then, IBA and PMDETA were added. The mixture was degassed by three freeze-pump-thaw cycles and then Cu(I)Br was added under nitrogen flow. The mixture was stirred at room temperature for 15 min to homogenize. After that, the flask was immersed in an oil bath at 55^{o}C. Samples were withdrawn periodically to monitor the monomer conversion (by ^{1}H NMR) and the number average molecular weight (by GPC). The reaction was ended by cooling the reaction mixture in liquid nitrogen. It was diluted in THF and copper was removed by passing the reaction mixture over a neutral alumina column. Most of the solvent was evaporated in rotavapor and the obtained polymer was precipitated into cold methanol (10-fold excess). After filtration, the obtained white product was dried under vacuum oven.

3.3.8 General polymerization procedure for synthesis of star-shaped block copolymers from PIBA-12-MI

A typical procedure is as follow: PIBA-12-arm-MI, solvent, ligand and AzMA were added to a reaction flask. The mixture was degassed by three freeze-pump-thaw cycles. After adding Cu(I)Br under nitrogen flow, the flask was stirred at room temperature to obtain homogeneity. Then, the flask was immersed in a preheated oil

bath under nitrogen atmosphere. Samples were withdrawn periodically to monitor the monomer conversion (by ^{1}H NMR) and the number average molecular weight (by GPC). For termination of the reaction, the mixture was put in an ice bath and diluted in THF. The mixture was passed through a neutral alumina column to remove copper. Most of the solvent was evaporated in rotavapor and the obtained polymer was precipitated into cold methanol (10-fold excess). After filtration, the product was dried under vacuum oven.

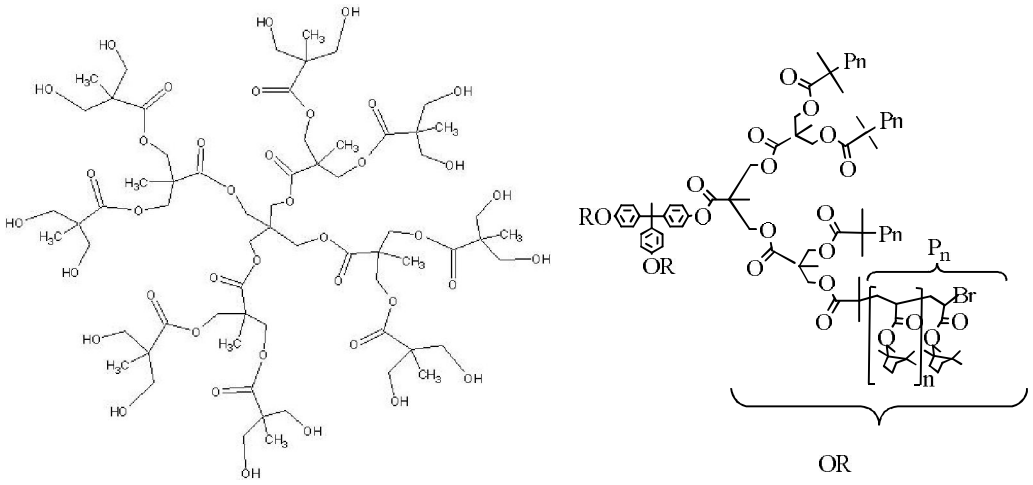
3.3.9 Synthesis of PAzHA homopolymer

6-azidohexyl acrylate and acetone were added to a two-necked flask. The mixture was degassed by 3 freeze-pump-thaw cycles. After adding Cu(I)Br and 2,2'-bipyridine under nitrogen flow, the mixture was immersed in an oil bath at 35^{o}C. Finally, ethyl-2-bromo-isobutyrate was added. Samples were withdrawn periodically to monitor the monomer conversion (by ^{1}H NMR) and the number average molecular weight (by GPC). To end the reaction, the flask was removed out of the oil bath and the mixture was diluted with chloroform. The mixture was passed through a neutral alumina column to remove copper. After most of the solvent was evaporated in rotavapor, the obtained polymer was precipitated into methanol (10 fold excess). After filtration, the obtained white powder was dried under vacuum oven.

4. RESULTS AND DISCUSSION

For synthesis of star-shaped polymer structures via “core-first” method, ATRP (Chapter 2.1) was used which provides predetermined molecular weights and low polydispersities. In these reactions, the halogen end-groups are preserved and stay present on the polymer. They can further be transformed into other functionalities using nucleophilic substitution reactions and the star-shaped polymers can further be used in click reactions. The introduction of functional groups at the outer end of the arms and control over star-shaped architectures can be achieved with a well-defined core.

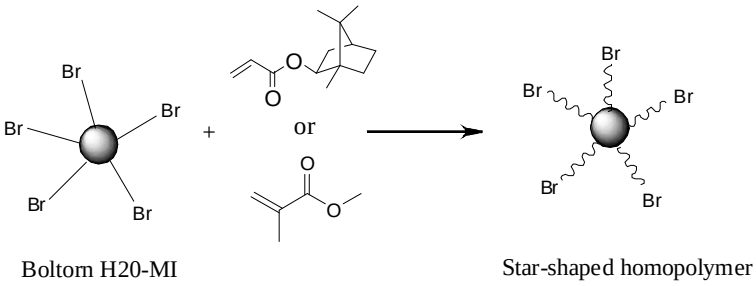
To synthesize star-shaped polymers, two different ATRP macroinitiators were used: PIBA-12-arm-MI, based on a monodisperse multifunctional initiator and Boltorn H20-MI, based on a commercially available polyester Boltorn H20® (Scheme 4.1).



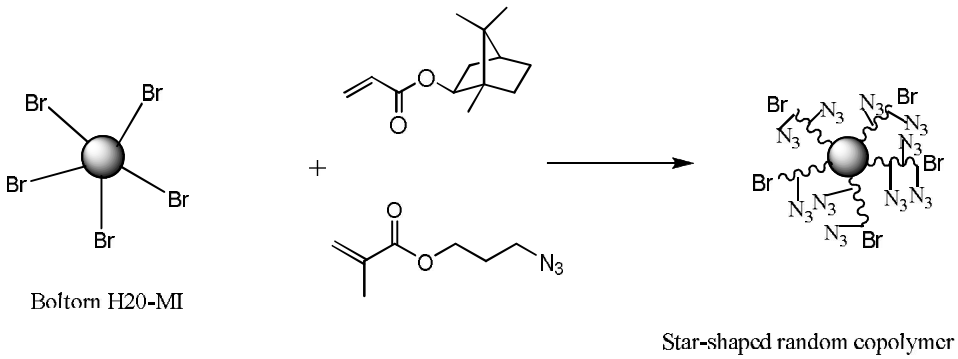
Scheme 4.1: The structure of hyperbranched commercially available polyester Boltorn H20® (left side) and dodecafunctional monodisperse initiator (right side)

The synthesized macroinitiator based on Boltorn H20® was used for synthesis of star-shaped homopolymers based on MMA (methyl methacrylate) and IBA (isobornyl acrylate) (Scheme 4.2). In a second step, these star-shaped homopolymers can then be used as macroinitiators for the synthesis of star-shaped block copolymers

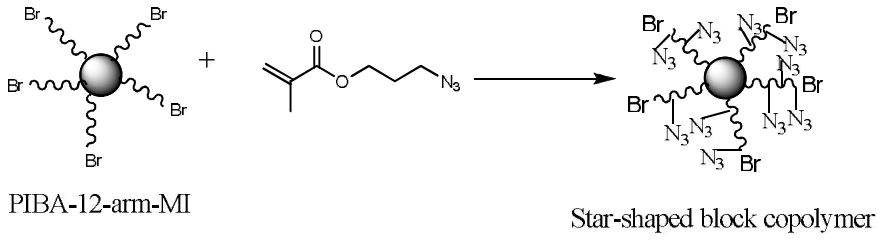
based on MMA-*b*-AzMA and IBA-*b*-AzMA. The star-shaped random copolymers based on IBA-*r*-AzMA were also synthesized from this multifunctional initiator (Scheme 4.3). The other macroinitiator (PIBA-12-arm-MI) was used for synthesis of star-shaped block copolymers based on IBA-*b*-AzMA (Scheme 4.4).



Scheme 4.2: Synthesis of star-shaped homopolymers based on Boltorn H20-MI



Scheme 4.3: Synthesis of star-shaped random copolymers based on Boltorn H20-MI



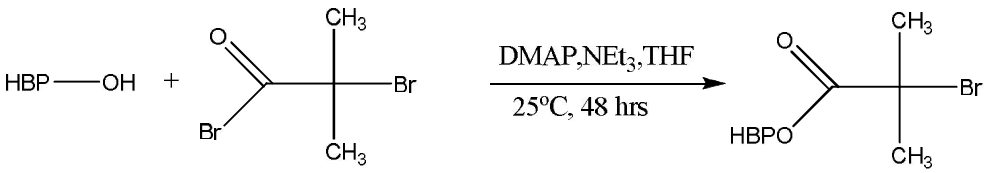
Scheme 4.4: Synthesis of star-shaped block copolymers based on PIBA-12-arm-MI

4. 1 Synthesis of ATRP macroinitiators

For synthesis of star-shaped polymers *via* "core-first" method, first the ATRP macroinitiators were synthesized.

4.1.1 Synthesis of multifunctional initiator based on Boltorn H20®

Boltorn H20® is a commercially available pseudogeneration polyester elaborated by Perstorp. The hyperbranched structure offers unique possibilities by combining excellent reactivity with low viscosity and enhanced mechanical properties. Its ability to promote dense branching of a polymer backbone and a large number of hydroxyl groups without crosslinking is highly appreciated in many applications. Important application areas of Boltorn H20® include coating, plastics and encapsulation of the substances. This hygroscopic polyester, using ethoxylated pentaerythritol as central core and 2,2-bis(methylol)propionic acid (bis-MPA) as dendritic units, can be transformed into ATRP initiators *via* esterification reaction. The main advantage of this multifunctional initiator consists on the possibility to synthesize a high number of arms when compared to other multifunctional initiators. The esterification reaction of Boltorn H20® was carried out with 2-bromo-2-methylpropionylbromide in dry THF with 4-(dimethylamino)pyridine (DMAP) as catalyst and triethylamine (NEt_3) as proton scavanger (Scheme 4.5). The hydroxyl groups of Boltorn H20® was converted into bromide end-groups.



Scheme 4.5: Synthesis of Boltorn H20®-Macroinitiator (Boltorn H20-MI)

GPC analysis of modified Boltorn H20® exhibited an increase in M_n from 1940 to 3100 g/mol which proves the substitution of hydroxyl functions of Boltorn H20®. In the ^1H NMR spectra (Figure 4.1), the existence of $-CH_3$ groups of isobutyryl moiety at 1.89 ppm and the disappearance of $-CH_2OH$ peak of starting Boltorn H20®,

between 3.35-3.60 ppm is suggesting that the desired multifunctional initiator was formed.

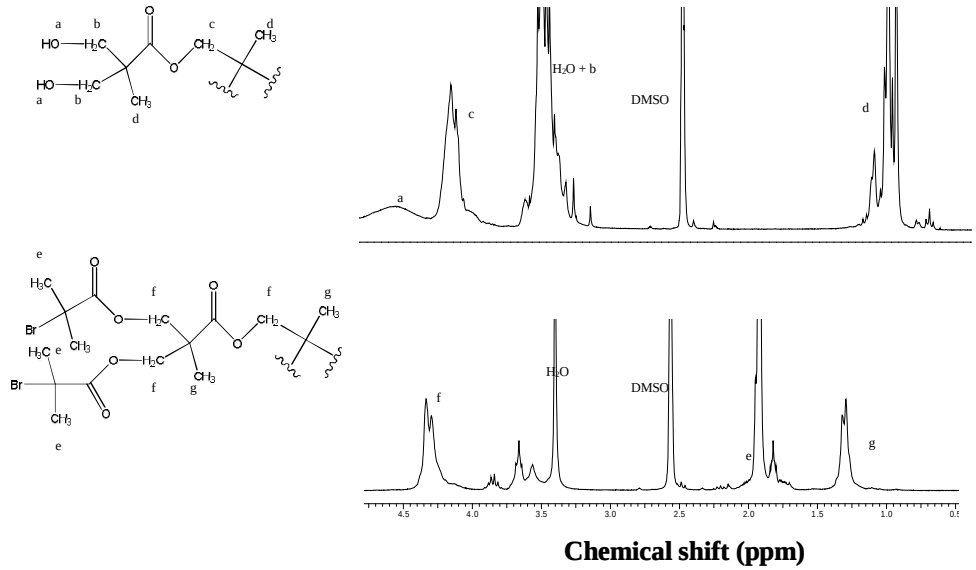


Figure 4.1 : ^{1}H NMR spectra of Boltorn H20® (DMSO-d_6, 300 MHz, top), ^{1}H NMR spectra of Boltorn H20-MI (DMSO-d_6, 300 MHz, bottom)

4.1.2 Synthesis of Poly(isobornyl acrylate) star-shaped homopolymer (PIBA-12 arm-MI) from dodecafunctional monodisperse initiator

IBA was used as monomer because the high Tg of PIBA results in an easier purification when compared to other acrylates. Secondary carbon at the end of the chain can be used for SN_2 reactions (while this situation is not possible for methacrylates that have tertiary carbons), i.e. conversion of bromide end-groups into azide end-groups then allowing further click reactions.

ATRP reaction of IBA was carried out from a monodisperse dodecafunctional initiator in acetone by Cu(I)Br/PMDETA as catalytic system at 55^{o}C (Table 4.1). From GPC analysis and ^{1}H NMR data, could be concluded that well-defined polymers were obtained.

Table 4.1: Reaction conditions and results of PIBA-12-arm-MI based on dodecafunctional monodisperse initiator

Code	[IBA]/[Ini]/[Cu(I)Br]/ [PMDETA] [a]	T (min)	Conversion [b] (%)	M_n [c] (g/mol)	M_w/M_n [c]
PIBA-12-arm-1	900/1/1/4	250	38	91 500	1.07
PIBA-12-arm-2	900/1/1/4	100	13	9 200	1.08

[a] Molar ratios of monomer, initiator and catalyst system. [b]Determined by ^{1}H NMR spectroscopy ($CDCl_3$). [c] Number average molecular weight (M_n), polydispersity index (M_w/M_n) determined by GPC, using polystyrene standards. Reaction temperature: 50°C.

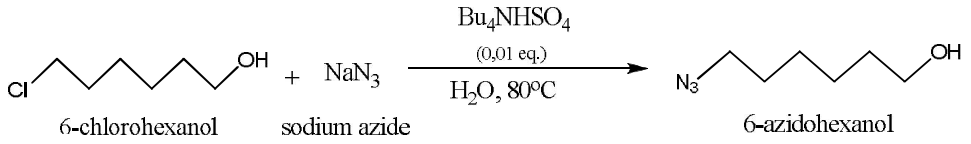
4.2 Synthesis of azide-functionalized monomers

To synthesize azide-containing star-shaped polymers, two monomers were synthesized, 3-azidopropyl methacrylate (AzMA) and 6-azidohexyl acrylate (AzHA). The polymerization of AzMA with ATRP did not exhibit very controlled polymerizations [112] in literature until now and that's why AzHA monomer was also tried next to AzMA. AzHA was chosen as an alternative monomer because of two reasons. It is safer than the other azide-containing monomer AzMA because of the higher C/N ratio (C+O /N ≥ 3) as defined by Sharpless [113]. AzHA is also hydrophobic like IBA that will be used for futher reactions.

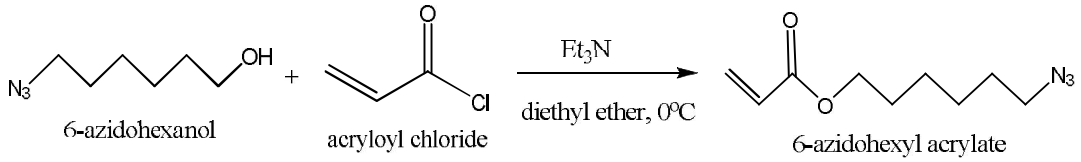
4.2.1 Synthesis of 6-azidohexyl acrylate monomer

The synthesis of 6-azidohexyl acrylate involved a two step reaction (Scheme 4.6). In the first step, 6-azidohexanol was synthesized by nucleophilic substitution reaction of the chlorine atom of 6-chloro-1-hexanol using sodium azide as nucleophile and TBAF as phase transfer agent. In the second step, 6-azidohexyl acrylate was formed from 6-azidohexanol and acryloyl chloride using triethylamine (NEt_3) as proton scavanger. ^{1}H NMR spectra shows all expected peaks proving that the desired compound was formed (Figure 4.2). However, the resultant product had some impurities. Since the product is an azide-containing compound, no further purifications were done because of the safety reasons.

1st Step



2nd Step



Scheme 4.6: Synthesis of 6-azidohexyl acrylate in a 2-step reaction

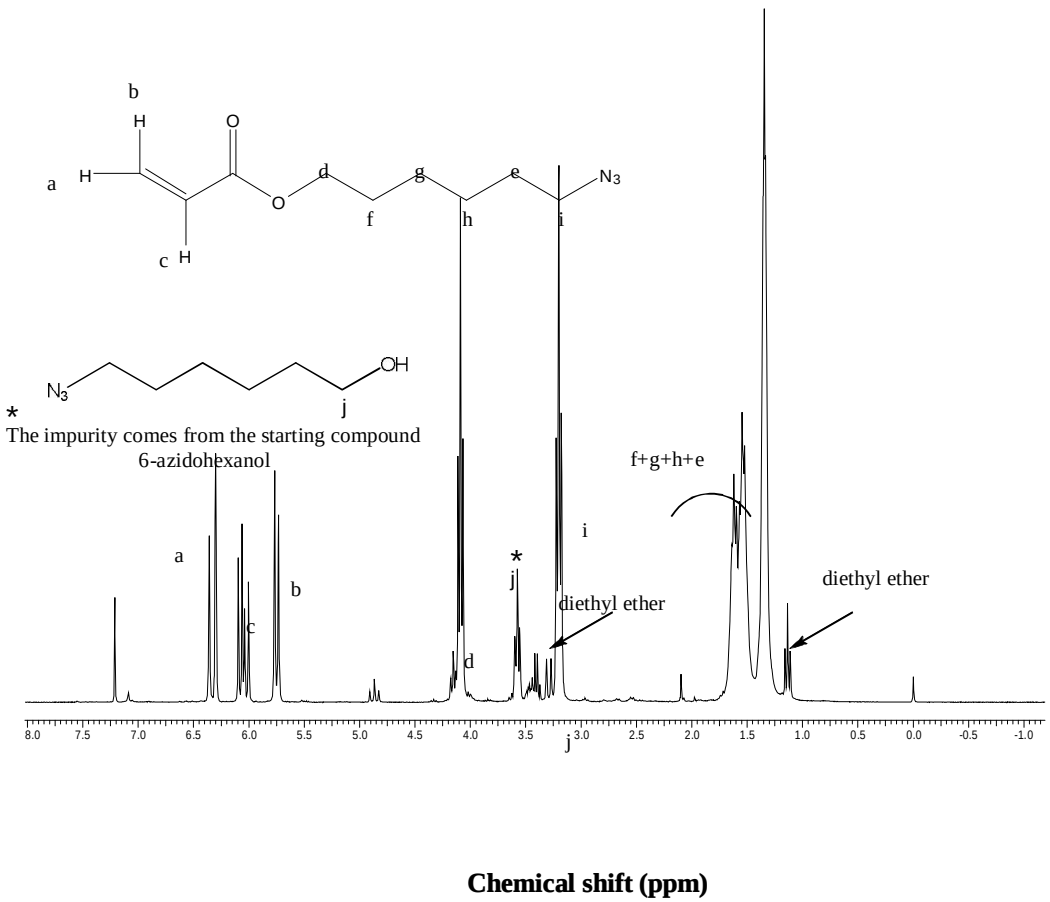
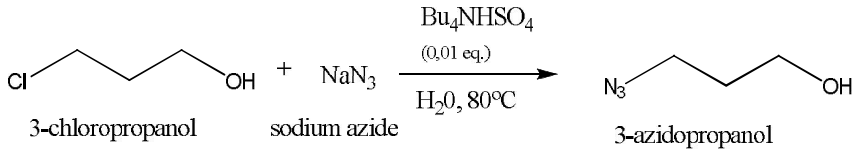


Figure 4.2: ^{1}H NMR spectra of 6-azidohexyl acrylate monomer ($CDCl_3$, 300 MHz)

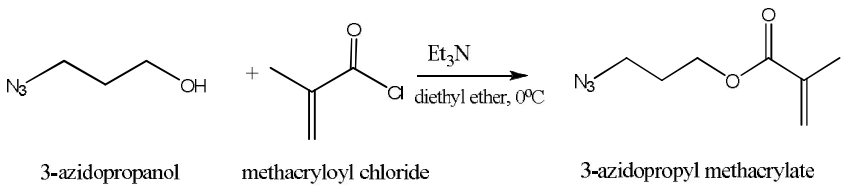
4.2.2 Synthesis of 3-azidopropyl methacrylate monomer

The synthesis of 3-azidopropyl methacrylate involved a two step reaction (Scheme 4.7). In the first step, 3-azidopropanol was made by nucleophilic substitution reaction of the chlorine atom of 3-chloropropanol using sodium azide as nucleophile and TBAF as phase transfer agent. In the second step 3-azidopropyl methacrylate was formed from 3-azidopropanol and methacryloyl chloride using triethylamine (NEt_3) as a proton scavanger. ^1H NMR spectra shows that the desired compound was formed (Figure 4.3).

<u>1st Step</u>



<u>2nd Step</u>



Scheme 4.7: Synthesis of 3-azidopropyl methacrylate monomer in a 2-step reaction

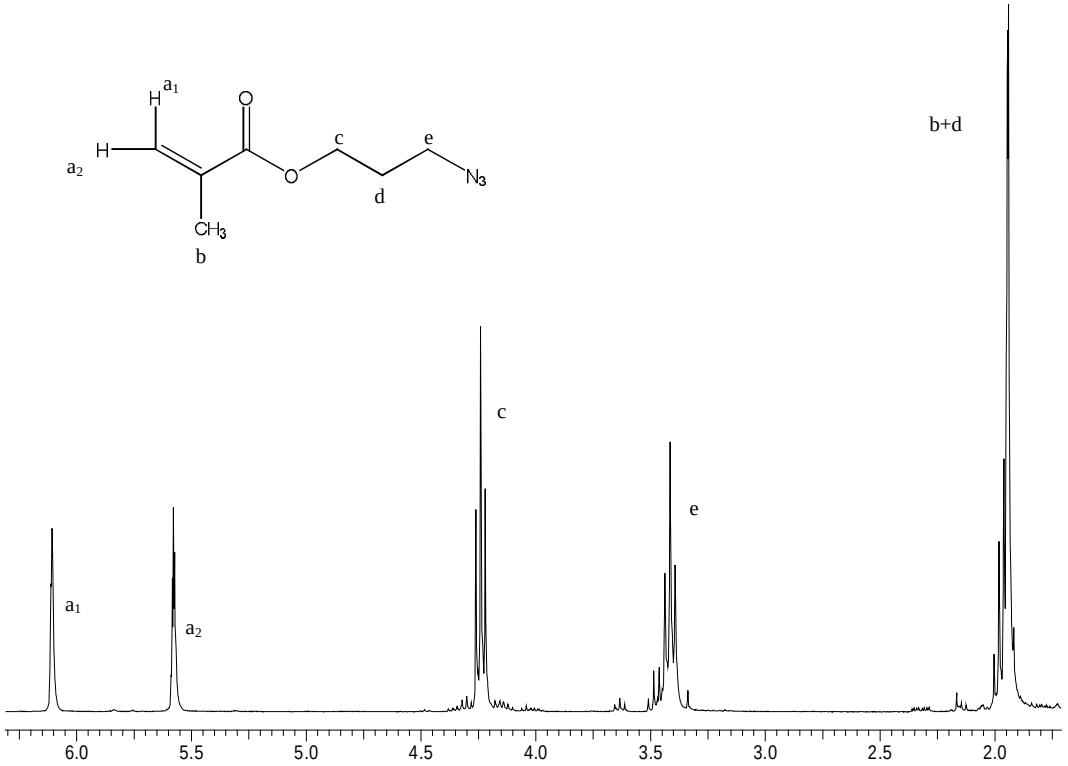


Figure 4.3: ^{1}H NMR spectra of 3-azidopropyl methacrylate monomer ($CDCl_3$, 300 MHz)

4.2.3 Synthesis of PAzHA linear homopolymer

First, linear homopolymers of AzHA were synthesized as a model reaction.

For this purpose, ATRP of AzHA was performed in 66 vol% acetone at 35^{o}C using ethyl-2-bromoisobutyrate as initiator and 2,2'-bipyridine/Cu(I)Br as the catalyst [114] (Table 4.2).

Table 4.2 : Reaction conditions and results of PAzHA-linear homopolymer

Code	**[AzHA]/[Ini]/[Cu(I)Br]/[2,2'-bipy]**[a]	**T (°C)**	**T (min)**	**Conversion**[b] **%**	**M_n**[c] **(g/mol)**	**M_w/M_n**[c]
PAzHA	100/1/1/2	35	180	100	71 000	1.22

[a] Molar ratios of monomer, initiator, catalyst system. [b]Determined by ^{1}H NMR spectroscopy. [c] Number average molecular weight (M_n), polydispersity index (M_w/M_n) determined by GPC, using polystyrene standards.

According to the GPC data, well-defined polymers were formed with low polydispersity index.

^{1}H NMR analysis showed the complete conversion of monomer after 3 hours reaction time. ^{1}H NMR spectra of the synthesized polymer is given in Figure 4.4 suggesting that the desired product was obtained.

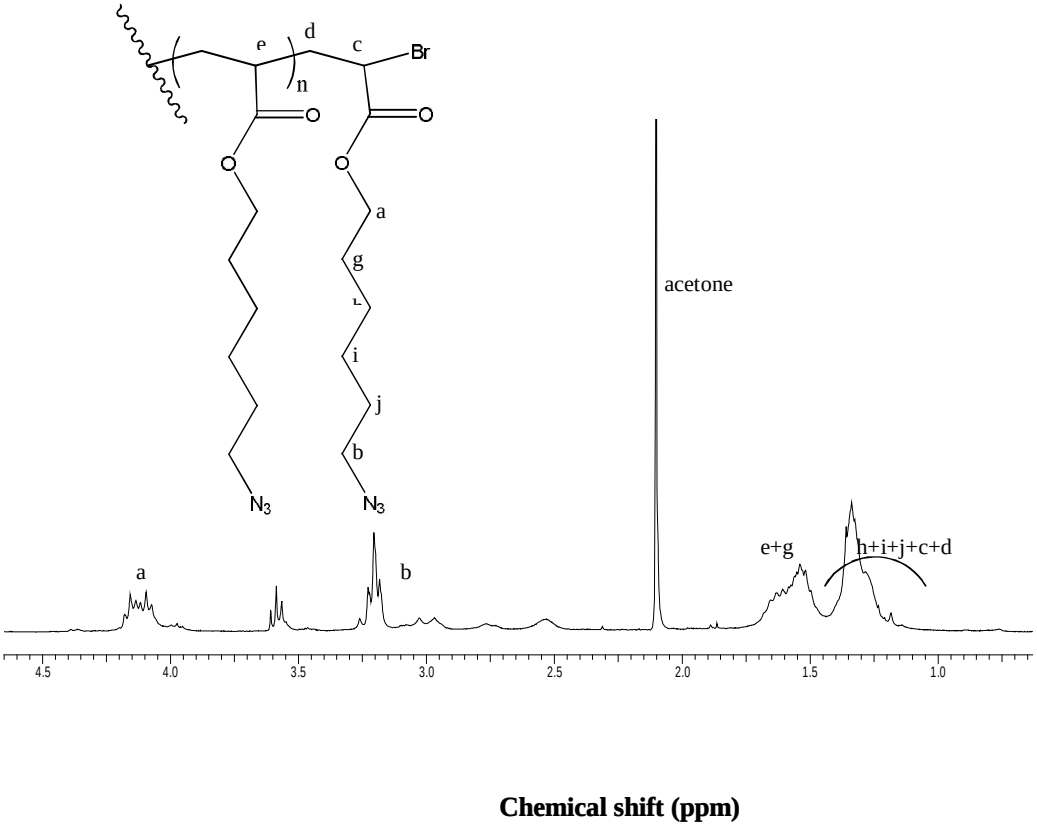


Figure 4.4: ^{1}H NMR spectra of PAzHA

4.3 Synthesis of star-shaped homopolymers

The synthesis of Boltorn H20-MI is easier, star-shaped polymers with more arms can easily be synthesized *via* ATRP using this macroinitiator.

4.3.1 Synthesis of star-shaped poly(isobornyl acrylate) homopolymer (H20-IBA) from Boltorn H20-MI

Well-defined PIBA star-shaped homopolymer was synthesized in 50 vol% ethyl acetate using Cu(I)Br/PMDETA as the catalyst system at 50^0C. The reaction conditions are mentioned in Table 4.3. Before ending the reaction, a sample was withdrawn from the reaction media for GPC and ^{1}H NMR measurements. In Figure

4.5, GPC traces of the synthesized star-shaped hopolymer and Boltorn H20-MI are shown. A slight shift of M_n is observed toward higher M_n, proving the polymerization from Boltorn H20-MI. However, the existence of a shoulder at higher M_n may be explained by the star-star coupling reactions [115].

Table 4.3 : Reaction conditions and results of PIBA star-shaped homopolymer

Code	**[M]/[Ini]/ Cu(I)Br/PMDETA** [a]	**T (°C)**	**T (min)**	**Conversion** [b] **(%)**	**M_n** [c] **(g/mol)**	**M_w/M_n** [c]
H20-IBA	900/1/12/12	50	180	66	11 000	1.32

[a] Molar ratios of monomer (IBA, MMA), initiator and catalyst system. [b]Determined by ^{1}H NMR spectroscopy. [c] Number average molecular weight (M_n), polydispersity index (M_w/M_n) determined by GPC, using polystyrene standards.

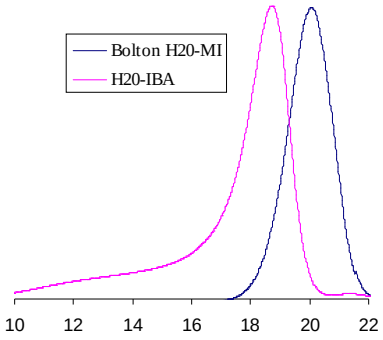


Figure 4.5: GPC traces of Boltorn H20-MI and synthesized H20-IBA star-shaped homopolymer from Boltorn H20-MI

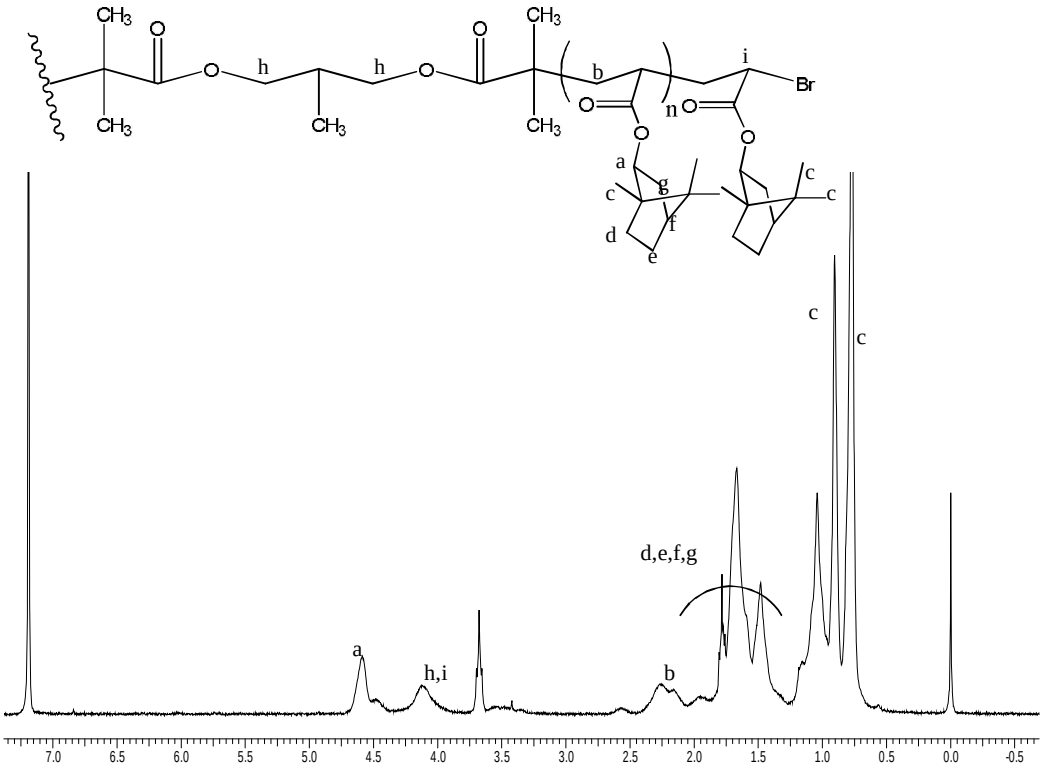


Figure 4.6: ^{1}H NMR spectra of H20-IBA star-shaped homopolymer ($CDCl_3$, 300 MHz)

Monomer conversion (66%) was calculated from ^{1}H NMR by integrating the acrylate signals at 5.8 ppm with the signal of PIBA at 4.7 ppm (Figure 4.6). From ^{1}H NMR and GPC data could be concluded that, the desired polymer was obtained. However the reaction was not very good controlled because of some transfer reactions.

4.3.2 Synthesis of star-shaped poly(methyl methacrylate) homopolymer (H20-MMA) from Boltorn H20-MI

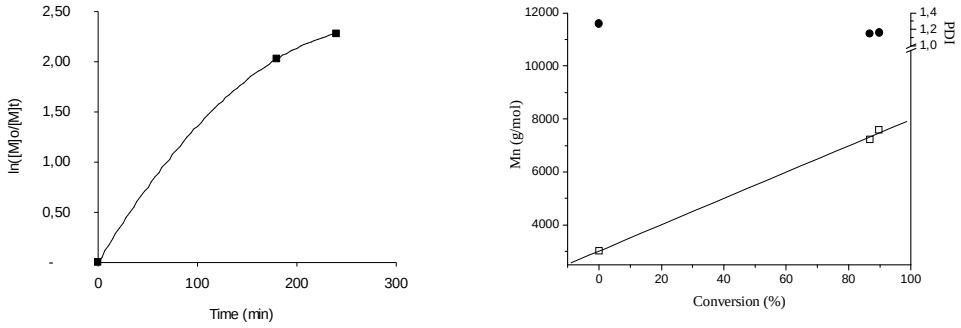
In this project, not only PIBA, but also a PMMA star-shaped homopolymer was synthesized to use as macroinitiator for synthesis of star-shaped block copolymers. Star-shaped PMMA was synthesized *via* ATRP on Boltorn H20-MI and the reaction occured in bulk at 90^{o}C using $NiBr_2(PPh_3)_2$ as catalytic system (Table 4.4) [116, 117].

Table 4.4: Reaction conditions and results of PMMA star-shaped homopolymer

Code	[MMA]/[Ini]/[a] $NiBr_2(PPh_3)_2$	T (°C)	T (min)	Conversion[b] (%)	M_n[c] (g/mol)	M_w/M_n[c]
H20-MMA	900/1/3.6	90	240	89	6 300	1.36

[a] Molar ratios of monomer, initiator, catalyst system. [b]Determined by ^1H NMR spectroscopy. [c] Number average molecular weight (M_n), polydispersity index (M_w/M_n) determined by GPC using polystyrene standards.

According to the kinetic study, the polymerization was not controlled because first order kinetics did not perform a straight line (Figure 4.7-a). This situation may be ascribed to the existence of termination reactions or deactivation of the catalyst. On the other hand, it can be noticed that the molecular weight is increasing in time while PDI is remaining low (1.17) (Figure 4.7-b).



(a) **(b)**

Figure 4.7: (a) Kinetic plot for ATRP of MMA using Boltorn H20-MI as the macroinitiator, (b) Evolution of number-average molecular weight (M_n) as a function of conversion for the ATRP of MMA

GPC curves of the polymers are shown in Figure 4.8. The shoulders on the right side may indicate that the reaction was not controlled. One explanation can be the presence of side reactions.

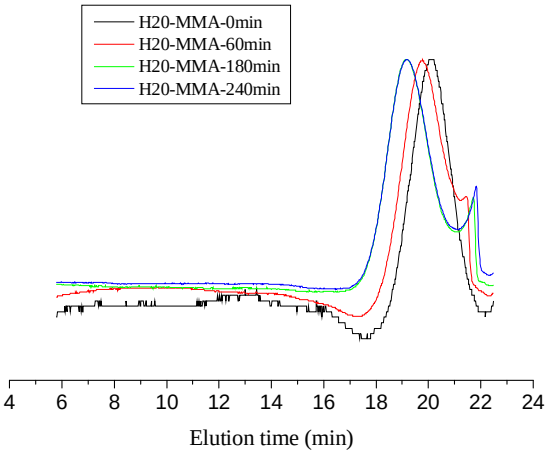


Figure 4.8: GPC traces of H20-MMA from Boltorn H20-MI

From the ^{1}H NMR result, could be concluded that, the desired polymer was obtained. However there existed some side reactions during the polymerization (Figure 4.9).

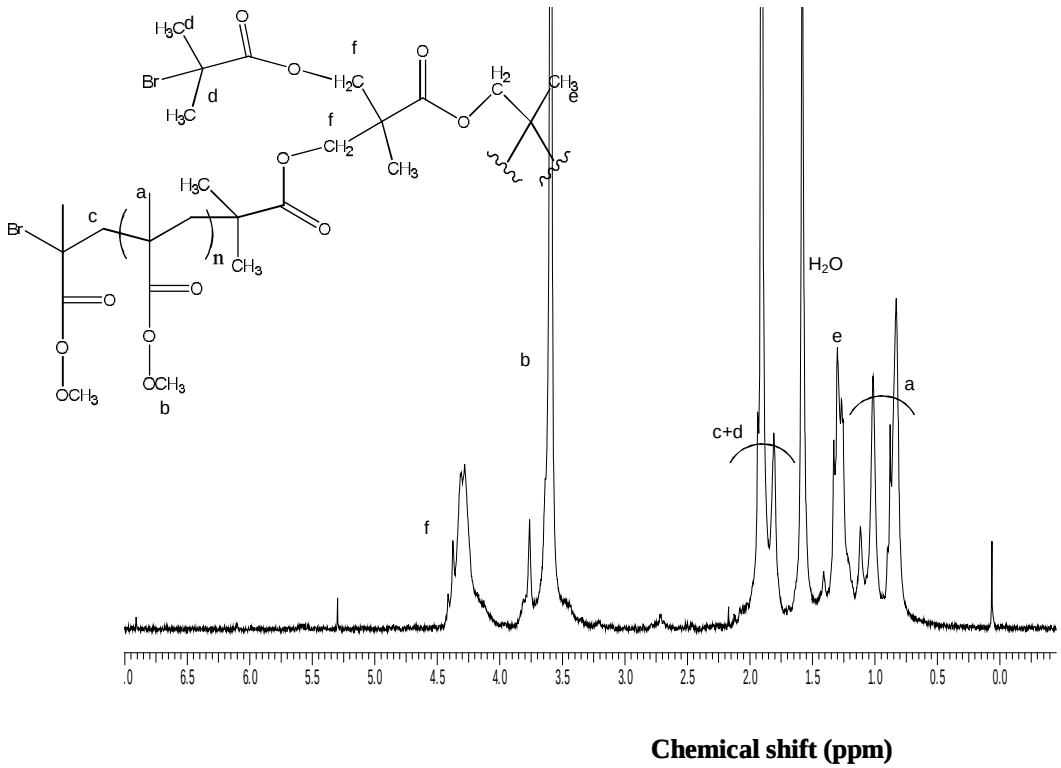


Figure 4.9: ^{1}H NMR spectra of H20-MMA star-shaped homopolymer ($CDCl_3$, 300 MHz)

4.4 Synthesis of star-shaped copolymers containing azide groups

The azide-containing star-shaped copolymers can further be used for Cu(I)-catalyzed azide-alkyne click reactions. Large number of products with terminal alkyne functions are commercially available or can be synthesized relatively easily with many interesting functional groups including propargyl alcohol, propargyl acrylate, etc.

4.4.1 Synthesis of IBA-AzMA star-shaped block copolymer

The copolymerization reactions of AzMA were done in two different solvents (acetone, ethyl acetate) with Cu(I)Br/PMDETA as catalytic system (Table 4.5).

Table 4.5: Reaction conditions and results of IBA-AzMA star-shaped block copolymers

Code	[M]/[Ini]/[Cu(I)Br]/[PMDETA][a]	T(°C)	T(min.)	Solvent (vol%)	M_w/M_n[b]
IBA-AzMA-1p	900/1/4/4	55	180	Acetone (25)	--[c]
IBA-AzMA-2p	900/1/2/2	55	1320	EtOAc (75)	11
IBA-AzMA-3p	900/1/2/2	50	180	Acetone (75)	15
IBA-AzMA-4p	900/1/2/2	50	180	Acetone (86)	16
IBA-AzMA-5p	900/1/1/1	50	180	Acetone (75)	18
IBA-AzMA-6p	900/1/1/1	50	180	EtOAc (90)	16

[a] Molar ratios of monomer, initiator, and catalyst system. [b]Polydispersity (M_w/M_n) determined by GPC using polystyrene standards. [c]Due to the insolubility of this crosslinked product, polydispersity index of this product could not be measured.

Test reactions were performed in order to find optimal conditions. Considering the instability of the azide monomer at elevated temperatures, the polymerization was carried out at relatively low temperature. The desired polymers were obtained, however, side-reactions occurred during the polymerizations. Since the first trial did not work, resulting in a cross-linked structure, PMDETA, Cu(I)Br ratios and also reaction temperature were decreased for the next trials while increasing the solvent ratio to obtain well-defined polymers. From Table 4.5, could be concluded that, polymerization of the azide monomer is difficult [112] because the azide group is often unstable under conditions normally used for star polymerization reactions.

Figure 4.10 exhibits GPC traces from the kinetic study of IBA-*b*-AzMA star-shaped copolymers. The broad GPC curves are suggesting that star-star coupling [118-120] has occurred due to the side reactions mentioned above.

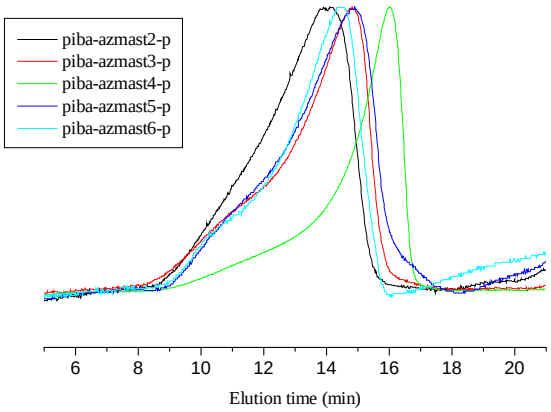


Figure 4.10: GPC traces of IBA-*b*-AzMA star-shaped copolymers

^{1}H NMR spectra of IBA-*b*-AzMA star-shaped copolymers is shown in Figure 4.11. Beside all the peaks attributed to the formation of IBA-*b*-AzMA star-shaped copolymer, a signal at 2.95 ppm can also be seen which suggests that a "*triazoline*" has been formed between the side-chain azide groups of IBA-AzMA and AzMA monomer [112]. In these ATRP reactions, the decomposition of either azide groups or newly formed *triazolines* accompanied by nitrogen elimination may caused the coupling of star-shaped block copolymer chains.

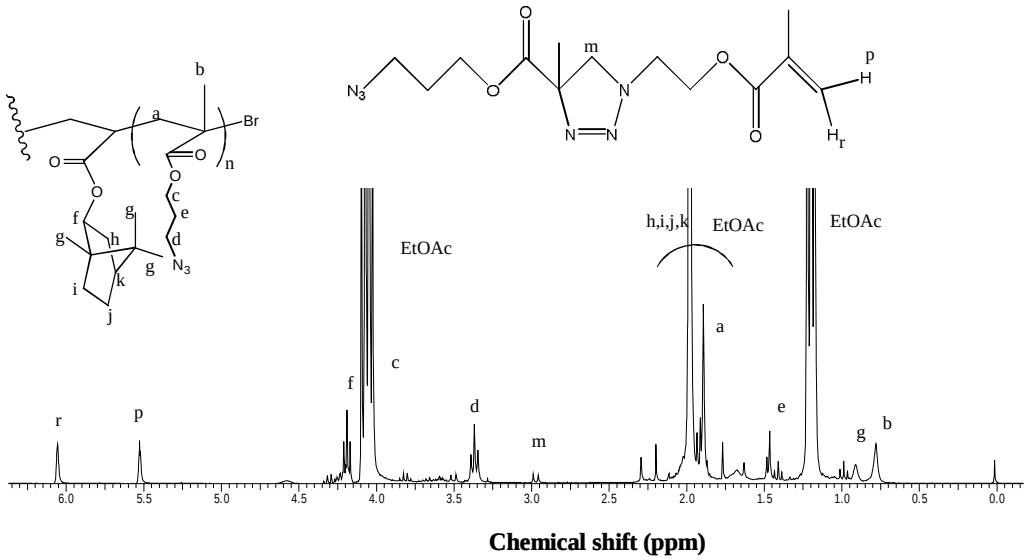


Figure 4.11 : ^{1}H NMR spectra of IBA-*b*-AzMA star-shaped copolymer ($CDCl_3$, 300 MHz)

Because the obtained star-shaped block copolymers did not exhibit good results, star-shaped random copolymers were synthesized.

4.4.2 Synthesis of IBA-AzMA star-shaped random copolymer

Random copolymers were synthesized in order to perform star-shaped copolymers with more azide groups that are also present along the arms. Star-shaped random copolymers of IBA and AzMA were synthesized in 75 vol% ethyl acetate as solvent with different molar ratios of [AzMA]/[BoltornH20-MI]/[Cu(I)Br]/[PMDETA], 100/1/4/4 and 100/1/1/1 respectively at 50^{o}C. The duration of the reaction was 3 hours. In these experiments, insoluble materials were obtained due to the secondary reactions, leading to cross-linked polymers.

In all these star-shaped copolymer trials, if the azide groups on the side chains of PAzMA are unstable at 50^{o}C, they may either decompose to nitrenes or react with AzMA monomer via cycloaddition. This can cause coupling or branching of polymer chains.

Organic azides have been widely used for cross-linking reactions since azide groups can easily decompose under thermal or photochemical conditions to nitrogen gas and reactive nitrenes that undergo insertion reactions [121]. In addition to these, azides can also react with methacrylate derivatives in order to produce triazolines which are usually thermally unstable and decompose to aziridines [122].

5. CONCLUSION

The main objective of this master thesis was to synthesize a functional star-shaped polymer catalyst for ATRP and click reactions that can be reused and easily removed from the reaction media. In this master thesis, star-shaped homopolymers and star-shaped random and block copolymers were synthesized for this purpose. The polymerization technique used was ATRP due to the ability to tune and control the architecture and the composition of the materials.

Star-shaped polymers were then synthesized *via* ATRP using multifunctional initiator and macroinitiator based on Boltorn H20® and dodecafunctional monodisperse initiator with core-first method.

First, macroinitiators were synthesized and successfully characterized. These macroinitiators were used in order to synthesize PMMA and PIBA star-shaped homopolymers. These polymers could be used as macroinitiators for synthesis of star-shaped block polymers where second block contains reactive groups like AzMA, AzHA, propargyl acrylate which can be reacted with functional groups *via* click chemistry to further allow the anchor of the catalyst.

The synthesized PIBA star-shaped homopolymers were used as ATRP macroinitiators for synthesis of star-shaped block copolymers P(IBA-*b*-AzMA). Results were not satisfactory, owing to the formation of a triazoline structure between the side chain azide groups of formed star-shaped block copolymers and AzMA monomer.

Since these reactions were not successful, star-shaped random copolymers were also synthesized from Boltorn H20® multifunctional initiator inorder to perform star-shaped copolymers with more azide groups that are also present along the arms. In these trials, insoluble materials were also obtained due to the formation of cross-linked structures between the star-shaped polymer chains that can be attributed to the cycloaddition reaction or decomposition of PAzMA. This situation can cause coupling or branching of polymer chains.

The final conclusion from these results is that, PIBA and PMMA star-shaped homopolymers were synthesized based on Boltorn H20® and dodecafunctional monodisperse initiator resulting in low PDI values and controlled molecular weights. However, during the polymerizations some side reactions were generated.

Star-shaped random and block copolymers based on AzMA could not generate well-defined structures using Boltorn H20-MI and PIBA-12-arm-MI as multifunctional initiator and macroinitiator due to the existence of star-star coupling reactions.

The intramolecular cyclization may occurred due to the steric hindrance of the initiator or backfolding of the growing polymer chains, which may be prevented by increasing the rigidity of the initiator for example by introducing aromatic groups to the structure [123].

The undesired side reactions could be suppressed using dilute conditions and reducing the temperature to even room temperature in order to decrease the contribution of the active radicals during the polymerization.

Instead of azide-containing monomers, alkyne-containing monomers i.e. propargyl acrylate can be used for ATRP reactions [124, 125]. Therefore, these alkyne-containing star-shaped polymers, can be reacted with azide-containing ligands *via* click reactions.

REFERENCES

[1] **Q. Zheng, C.-Y. Pan**, 2006, *European Polymer Journal*, **42**, 807.

[2] **B. Rieger**, 2006, *Late transition metal polymerization catalysis,*259, Ed: Wiley- VCH.

[3] **T. Terashima, M. Ouchi, T. Ando, M. Kamigaito, M. Sawamoto**, 2006 *Journal of Polymer Science Part A: Polymer Chemistry*, 44, 4966.

[4] **T. Nie, A. Baldwin, N. Yamaguchi, K. L. Kiick**, 2007, *Journal of Controlled Release*, **122**, 287.

[5] **L. Xie, P. Krish, T. L. McCartney**, 1997, Composite pressure sensitive adhesive, *US Patent*, No:815383, 1997. 03. 11.

[6] **D. E. Bergbreiter, P. N. Hamilton, N. M. Koshti**, 2007, *Journal of American Chemical Society*, **129**, 10666.

[7] **C. Bouilhac, E. Cloutet, A. Deffieux, D. Taton, H. Cramail**, 2007 *Macromolecular Chemistry and Physics*, **208**, 1349.

[8] **T. Terashime, M. Ouchi, T. Ando, M. Kamigaito, M. Sawamoto**, 2007, *Macromolecules*, **40**, 3581.

[9] **Y. Shen**, 2004, *Progress in polymer science*, **29**, 1053.

[10] **W. H. Binder, R. Sachsenhofer**, 2007, *Macromolecular Rapid Communications*, **28**, 15.

[11] **D. Fournier, R. Hoogenboom, U. S. Schubert**, 2007, *Chemical Society Reviews*, **36**, 1.

[12] **G. Kreutzer, C. T. Ternat, T. Q. Nguyen, C. J. G. Plummer, J.-A. E. Manson, V. Castelletto, I. W. Hamley, F. Sun, S. S. Sheiko, A. Herrmann, L. Ouali, H. Sommer, W. Fieber, M. I. Velazco, H.-A. Klok**, 2006, *Macromolecules*, **39**, 4507.

[13] **S. Lee**, 2006, *Encyclopedia of chemical processing*, 1057, Ed: CRC Press.

[14] **G. B. Kharas, S. M. Russell, V. Tran, Q. L. Tolefree, D. M. Tulewicz, A. Gora, J. Bajgoric, M. T. Balco, G. A. Dickey, G. Kladis**, 2008, *Journal of macromolecular science Part A*, **45**, 5.

[15] **R. H. Huyck, S. R. Trenor, B. J. Love, T. E. Long**, 2008, *Journal of macromolecular science Part A*, **45**, 9.

[16] **T. N. T. Phan, S. Maiez-Tribut, J.-P. Pascault, A. Bonnet, P. Gerard, O. Guerret, D. Bertin**, 2007, *Macromolecules*, **40**, 4516.

[17] **K. Matyjaszewski**, 1997, *Controlled Radical Polymerization, ACS Symposium Series* 685, Ed: ACS Washington DC.

[18] **V. Abetz**, 2005, *Block copolymers I*, 35, Ed: Birkhäuser**.**

[19] **M. Lazzari, G. Liu, S. Lecommandoux**, 2007, *Block copolymers in nanoscience*, 25, Ed: Wiley VCH.

[20] **K. A. Davis, K. Matyjaszewski**, 2006, *Advances in polymer science, statistical, gradient block and graft copolymers by controlled living radical polymerizations*, **159**, 8, Ed: Springer.

[21] **H. R. Kricheldorf, O. Nuyken, G. Swift**, 2005, *Handbook of polymer synthesis*, 265, Ed: CRC Press.
[22] **M. R. Buchmeiser**, 2006, *Polymeric materials on organic synthesis*, 292, Ed: Wiley VCH.
[23] **K. Matyjaszewski, J. Spanswick**, 2005, *Materials Today*, **8**, 26.
[24] **I. W. Hamley**, 2004, *Developments in block copolymers science and technology*, 3, Ed: Wiley VCH.
[25] **S. J. Wang, K. Matyjaszewski**, 1995, *Macromolecules*, **28**, 7901.
[26] **D. Braun, H. Cherdron, M. Rehahn, H. Ritter, B. Voit**, 2005, *Polymer Synthesis: Theory and practice, fundamentals, methods, experiments*, 184, Ed: Springer.
[27] **Y. Kotani, M. Kato, M. Kamigaito, M. Sawamoto**, 1996, *Macromolecules*, **29**, 6979.
[28] **T. E. Patten, J. H. Xia, T. Abernathy, K. Matyjaszewski**, 1996, *Science*, **272**, 866.
[29] **S. Perrier, S. P. Armes, X. S. Wang, F. Malet, D. M. Haddleton**, 2001, *Journal of Polymer Science Part A: Polymer Chemistry*, **39**, 1696.
[30] **K. L. Robinson, M. V. D. Khan, M. A. Banez, X. S. Wang, S. P. Armes**, 2001, *Macromolecules*, **34**, 3155.
[31] **V. Percec, H. J. Kim, B. Barboiu**, 1997, *Macromolecules*, **30**, 6702.
[32] **W. T. Eckenhoff, T. Pintauer**, 2007, *Inorganic Chem*istry, **46**, 5844.
[33] **L. Zhang , Q. Xu, J. Lu, X. Xia L. Wang**, 2007, *European Polymer Journal*, 43, 2718.
[34] **M. Buback, A. M. V. Herk**, 2007, *Radical polymerization: kinetics and mechanism*, 1, Ed: Wiley VCH.
[35] **K. Matyjaszewski**, 2003, *Advances in controlled/living radical polymerization*, ACS Sympossium series 854, Ed: ASC Washington DC.
[36] **B. Nottelet, P. Lacroix- Desmazes, B. Boutevin**, 2007, *Polymer*, **48**, 50.
[37] **I. D. Grishin, E. V. Kolyakina, D. N. Cheredilin, I. T. Chizhevskii**, 2007, *Polymer Science Series A*, 49.
[38] **S. Minko**, 2006, *Responsive polymer materials, design and applications*, 72, Ed: Blackwell Publishing.
[39] **W. A. Braunecker, K. Matyjaszewski**, 2006, *Journal of molecular catalysis A*, **254**, 155.
[40] **Y. Shen, S. P. Zhu, F. Q. Zeng, R. H. Pelton**, 2000, *Macromolecules*, **33**, 5427.
[41] **S. C. Hong, D. Neugebauer, Y. Inoue, J-F. Lutz, K. Matyzaszewski**, 2003, *Macromolecules*, **36**, 27.
[42] **J. Gromada, J. Spanwick, K. Matyzaszewski**, 2004, *Journal of Chemical Physics*, **205**, 551.
[43] **C. Fang, X.-Y. Qi1, Q.-L. Fan, L.-H. Wang, W. Huang**, 2007, *Nanotechnology*, **18**, 5.
[44] **J. Xia, K. Matyjaszewski**, 1997, *Macromolecules*, **30**, 7697.
[45] **M. H. Acar, C. R. Becer, H. A. Ondur, S. Inceoglu**, 2005, *Polymer Preprints*, **46**, 433.
[46] **K. Matyjaszewski, B. Gobelt, H.-J. Paik, C. P. Horwitz**, 2001, *Macromolecules*, **34**, 430.
[47] **R. París, J. Luis de la Fuente**, 2005, *Journal of Polymer Science Part A: Polymer Chemistry*, **43**, 6247.
[48] **K. Matyjaszewski, J. Xia**, 2001, *Chemical Reviews*, **101**, 2921.

[49] **K. Zhang, Z. Ye, R. Subramanian**, 2008, *Macromolecules*, **41**, 640.
[50] **I. D. Grishin, E. V. Kolyakina, D. N. Cheredilin, I. T. Chizhevskii, D. F. Grishin**, 2007, *Polymer Science Series* A, **49**, 1079.
[51] **S. Maria , T. Biedron , R. Poli , P. Kubisa**, 2007, *Journal of Applied Polymer Science,* **105**, 278.
[52] **C. Hou , Z. Guo , J. Liu , L. Ying , D. Geng**, 2007, *Journal of Applied Polymer Science,* **104**, 1382.
[53] **L. He, E. S. Read, S. P. Armes, D. J. Adams**, 2007, *Macromolecules*, **40**, 4429.
[54] **S. Tugulu, R. Barbey, M. Harms, M. Fricke, D. Volkmer, A. Rossi, H.-A. Klok**, 2007, *Macromolecules*, **40**, 168.
[55] **X. He, D. Yan**, 2007, *Macromolecular rapid communication*, **25**, 949.
[56] **O. Colombani, M. Ruppel, F. Schubert, H. Zettl, D. V. Pergushov, A. H. E. Mu1ller**, 2007, *Macromolecules*, **40**, 4338.
[57] **Y. Miura , H. Dote, H. Kubonishi, K. Fukuda, T. Saka**, 2007, *Journal of Polymer Science Part A: Polymer Chemistry,* **45**, 1159.
[58] **M. Abbasian, S. Rahmani, R. Mohammedi, A. A. Entezami**, 2007, *Journal of Applied Polymer Science,* **104**, 611.
[59] **E. Östmark, S. Harrisson, K. L. Wooley, E. E. Malmström**, 2007, *Biomacromolecules,* **8**, 1138.
[60] **S. G. An, G. H. Li, C. G. Cho**, 2006, *Polymer*, **47**, 4154.
[61] **Jacques, A. Hult, M. Johansson, E. Malmström, J. J. Freire, W. Burchard, T. C. B. Mc Leish, S. T. Milner**, 1999, *Advances in Polymer Science,* **143**, 1, Ed: Springer.
[62] **H. Galina**, 2001, *Macromolecular Symposia*, *Polymer Networks*, 57, Ed: Wiley VCH.
[63] **J. J. Vosloo, A. J. P. V. Zyl, T. M. Nicholson, R. D. Sanderson, R. G. Gilbert**, 2007, *Polymer*, **48**, 205.
[64] **K. Kono, C. Kojima, N. Hayashi, E. Nishisaka, K. Kiura, S. Watarai, A. Harada**, 2008, *Biomaterials*, **29**, 1664.
[65] **S. Liu, C.-H. Changa, B. K. Paul, V. T. Remchoc**, 2008, *Chemical Engineering Journal*, **135**, 333.
[66] **R. Matmour, Y. Gnanou**, 2008, *Journal of American Chemical Society*, **130**, 1350.
[67] **J. Lim, E. E. Simanek**, 2008, *Organic Letters,* **10**, 201.
[68] **C. W. Tse, K. W. Cheng, W. K. Chan**, 2008, *Journal of inorganic and organometallic polymers and materials*, **18**, 59.
[69] **L. K. Brel, R. F. Storey**, 2008, *Polymer*, **49**, 1154.
[70] **A. Blencowe, G. T. Kit, S. P. Best, G. G. Qiao**, 2008, *Polymer*, **49**, 825.
[71] **D. R. Robello, A. André, T. A. Mc Covick, A. Kraus, T. H. Mourey**, 2002, *Macromolecules*, **35**, 9334.
[72] **N. Hadjichristidis, M. Pitsikalis, S. Pispas, H. Iatrou**, 2001, *Chemical Reviews*, **101**, 3747.
[73] **P. Romiszowski, A. Sikorski**, 2006, *Journal of Mathematical Chemistry*, **40**, 295.
[74] **R. Diab, G. Degobert, M. Hamoudeh, C. Dumontet, H. Fessi**, 2007, *Expert Opinion on Drug Delivery*, **4**, 513.
[75] **S. Muthukrishnan, F. Plamper, H. Mori, A. H. E. Müler**, 2005, *Macromolecules,* **38**, 10631.

[76] **F. L. Verso, C. N. Likos, C. Mayer, H. Löwen**, 2006, *Physical review letters*, **96**, 187802.
[77] **J. Zhu, X. Zhu, E. T. Kang , K. G. Neoh**, 2007, *Polymer*, **48**, 6992.
[78] **B. Dufour, C. Tang, K. Koynov, Y. Zhang, T. Pakula, K. Matyjaszewski**, 2008, *Macromolecules*, **41**, 2451.
[79] **K. Hatada, T. Kitayama, O. Vogl**, 1997, *Macromolecular design of polymeric materials*, 380, Ed: CRC Press.
[80] **H. L. Hsieh, R. P. Quirk**, 1996, *Anionic polymerization, principles and practical applications*, 69, Ed: CRC Press.
[81] **S. Kobayashi**, 2000, *Advanced Organic Chemistry Ionic polymerization*, 88, Ed: Wiley VCH.
[82] **Y. Yağcı, J. Kahovec**, 2000, *Macromoleculer sympossia*, **161**, 19, Ed: Wiley VCH.
[83] **Y.-H. Zhao, B.-K. Zhu, L. Kong, Y.-Y. Xu**, 2007, *Langmuir*, **23**, 5779.
[84] **S. Penczek, P. Kubisa, K. Matyjaszewski**, 1985, *Advances in Polymer Science*, **37**, 61, Ed: Springer Verlag, Berlin, Heidelberg, New York.
[85] **S. Plentz, M.-P. J. Lutz, D. Rein**, 1999, *Star shaped polymers via anionic polymerization*, 77, Ed: Marcel Dekker.
[86] **L. Angiolini, T. Benelli, L. Giorgini, F. Paris, E. Salatelli, T. Zuccheri**, 2007, *Journal of Polymeric Materials*, **56**, 789.
[87] **L. R. Hermann High, Simon J. Holder, H. V. Penfold**, 2007, *Macromolecules*, **40**, 7157.
[88] **Y. H. Kim, W. T. Ford, T. H. Mourey**, 2007, *Journal of Polymer Science Part A: Polymer Chemistry*, **45**, 4623.
[89] **E. Themistou, C. S. Patrickios**, 2007, *Macromolecules*, **40**, 5231.
[90] **K. Müllen, M. Klapper, B. Iván**, 2007, *Macromolecular Chemistry and Physics*, **208**, 1315.
[91] **R. Jordan**, 2007, *Advance in Polymer Science*, **198**, 9, Ed: Springer.
[92] **X. Zhang, J. Xia, K. Matyjaszewski**, 2000, *Macromolecules*, **33**, 2340.
[93] **J. Xia, X. Zhang, K. Matyjaszewski**, 1999, *Macromolecules*, **32**, 4482.
[94] **C. Liu, Y. Zhang, J. Huang**, 2008, *Macromolecules*, **41**, 325.
[95] **W. Burchard, H. Eschway**, *U.S. Patent*, No: 4847308, Hybrid acrylic star polymers, **16**, 180.
[96] **J. A. Johnson, M. G. Finn, J. T. Koberstein, N. J. Turro**, 2007, *Macromolecules*, **40**, 3589.
[97] **X. Yu, T. Shi, L. An, G. Zhang, P. K. Dutta**, 2007, *Journal of Polymer Science Part A: Polymer Chemistry*, **45**, 147.
[98] **H. Eschwey, M. L. Hallensleben, W. Burchard**, 1973, *Macromolular Chemistry*, **173**, 235.
[99] **N. A. Peppas, J. Z. Hilt, J. B. Thomas**, 2007, *Nanotechnology in therapeutics*, 321, Ed: Horizon Scientific Press.
[100] **G. Deng, D. Ma, Z. Xu**, 2007, *European Polymer Journal*, **43**, 1179.
[101] **G. Lapienis, S. Penczek**, 2004, *Journal of Polymer Science Part A: Polymer Chemistry*, **42**, 1576.
[102] **G. Deng, Y. Chen**, 2004, *Macromolecules*, **37**, 18.
[103] *Introduction to polymer chemistry*, **2006**, C. E. Carraher, 2, Ed: CRC Press.
[104] **V. Abetz**, 2005, *Block copolymers II*, **190**, 53, Ed: Springer.
[105] **C. Ternat, G. Kreutzer, C. J. Plummer, T. Q. Nguyen, A. Herrmann, L. Ouali, H. Sommer, W. Fieber, M. I. Velazco, H.-A. Klok, J.-A. E. Manson**, 2007, *Macromolecular Chemistry and Physics*, **208**, 131.

[106] **W. Yuan, J. Yuan, S. Zheng, X. Hong**, 2007, *Polymer*, **48**, 2585.
[107] **Y. Wang, Y. Gao, J. Shi**, 2007, *Journal of applied polymer science*, **107**, 309.
[108] **W. Andrew**, 1997, *Handbook of plastics*, 25, Ed: Plastic design library.
[109] **A. Rudin**, 1999, *The elements of polymer science and engineering*, 342 Ed: Academic Press.
[110] **A. Mukherjee, J. S. Thomaides, Z. Li, C. Xiao, S. Petrash**, 2000, Polymer coating for rubber articles, *US Patent*, No: 663468, 2000. 09. 15.
[111] **S. Abraham, J. Choi, J. Lee, C. Ha, I. Kim**, 2007, *Macromolecular Research*, **15**, 324.
[112] **Y. Li, J. Yang, B. C. Benicewicz**, 2007, *Journal of Polymer Science Part A: Polymer Chemistry*, **45**, 4300.
[113] **K. B. Sharpless, M. G. Finn, H. C. Kolb**, 2001, *Angewandte Chemie International Edition*, **40**, 2004.
[114] **B. S. Sumerlin, N. V. Tsarevsky, G. Louche, R. Y. Lee, K. Matyjaszewski**, *Macromolecules*, **38**, 7540.
[115] **S. Strandman, H. Tenhu**, 2007, Polymer, **48**, 3938.
[116] **H. Uegaki, Y. Kotani, M. Kamigaito, M. Sawamoto**, 1997, *Macromolecules*, **30**, 2249.
[117] **G. Moineau, M. Minet, P. Dubois, P. Teyssie´, T. Senninger, R. Je´rome**, 1999, *Macromolecules*, **32**, 27.
[118] **A. Heise, J. L. Hedrick, M. Trollsas, R. D. Miller, C. W. Frank**, 1999, *Macromolecules*, **32**, 231.
[119] **B. S. Sumerlin, D. Neugebauer, K. Matyjaszewski**, 2005, *Macromolecules*, **38**, 702.
[120] **A. W. Bosman, M. J. Bruining, H. Kooijman, A. L. Spek, R. A. J. Janssen, E. W. Maijer**, 1998, *Journal of the American Chemical Society*, **120**, 8547.
[121] **C. J Ruud, J. P. Jia, G. L. Baker**, 2000, *Macromolecules*, **33**, 8184.
[122] **G. T. Anderson, J. R. Henry, S. M. J. Weinreb**, 1991, *Organic Chemistry*, **56**, 6946.
[123] **Y. Zhao, X. Shuai, C. Chen, F. Xi**, 2004, *Chemical Communications*, 1608.
[124] **M. Malkoch, J. R. Thibault, E. Drockenmuller, M. Messerschmidt, B. Voit, T. P. Russel, C. J. Hawker**, 2005, *Journal of American Chemical Society*, **127**, 14942.
[125] **V. Ladmiral, G. Mantovani, G. J. Clarkson, S. Cauet, J. L. Irwin, D. M. Haddleton**, 2006, *Journal of American Chemical Society*, **128**, 4823.

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