The dissertation/thesis of Maryam Altaher is approved by the examination committee.

Committee Chairperson: Professor Nikos Hadjichristidis
Committee Member: Professor Mohamed Eddaoudi
Committee Member: Professor Niveen Khashab
**ABSTRACT**

Synthesis and Characterization of Novel Polymethylene-Based 3-Miktoarm Star Copolymers by Combining Polyhomologation with Other Living Polymerizations  
Maryam Altaher

Polyethylene (PE) is produced on a huge scale globally and has plenty of desirable properties. It is used in coating, packaging, and artificial joint replacements. The growing need for high performance polyethylene led to the development of new catalysts, monomers and polymerizations. The synthesis of polymethylene (equivalent to polyethylene) by living polyhomologation opened the way to well-defined polymethylene-based polymeric materials with controlled structure, molecular weight and narrow polydispersity. Such model polymers are substantial to study the structure-properties relationships. This research presents a new strategy based on the *in situ* formation of B-thexyl-silaboracyclic serving as initiating sites for the polyhomologation of dimethylsulfoxonium methylide. Combination with metal-free ring-opening polymerization (ROP) of ε-caprolactone (CL) and atom transfer radical polymerization (ATRP) of styrene led to three polymethylene-based 3-miktoarm stars copolymers PCL(PM-OH)$_2$, Br-PCL(PM-OH)$_2$ and PS(PM-OH)$_2$.

Scheme A. Novel polymethylene-based 3-miktoarm stars copolymers, PCL(PM-OH)$_2$, Br-PCL(PM-OH)$_2$ and PS(PM-OH)$_2$ synthesized in this work.
ACKNOWLEDGMENTS

At the first place, I would like to express my deepest appreciation to my advisor Prof. Nikos Hadjichristidis for his persistent support of my master study and research, motivation, enthusiasm and vast knowledge, as well as for introducing me to the beautiful field of Polymer Chemistry. In addition to my advisor, very special thanks go to Dr. Zhen Zhang for his excellent guidance, tolerance, and dedicated time and effort in laboratory training. My sincere thanks also go to Dr. Kedar Ratkanthwar for teaching me anionic polymerization High Vacuum Techniques. Furthermore, I thank my colleague Haleema Alamri for the useful discussions in ring opening polymerization. Besides, I would like to thank the rest of my thesis committee: Prof. Mohamed Eddaoudi and Prof. Niveen Khashab for their encouragement and insightful comments. My heartfelt thanks convey to my caring, cheering, supportive husband who stood by me during my master journey and life. Finally, I like to thank my sympathetic parents, lovely children, and my children’s nanny for their endless support, encouragements and patience throughout my master study and life.
# TABLE OF CONTENTS

ABSTRACT ........................................................................................................................ 3

ACKNOWLEDGMENTS .................................................................................................. 4

TABLE OF CONTENTS .................................................................................................... 5

CHAPTER 1. SYNTHESIS OF LINEAR PM-OH BY POLYHOMOLOGATION ........ 8

1.1. General Introduction to Polyhomologation ................................................................. 8

1.2. General Remarks ........................................................................................................ 15

1.2.1. Materials ................................................................................................................. 15

1.2.2. Characterizations and Measurements ..................................................................... 16

1.2.2.1. Nuclear Magnetic Resonance (NMR) ................................................................. 16

1.2.2.2. High Temperature Size Exclusion Chromatography (HT-SEC) ...................... 17

1.2.2.3. Size-exclusion chromatography (SEC) ............................................................... 17

1.2.2.4. Differential Scanning Calorimetry (DSC) ......................................................... 17

1.3. Synthesis of Linear PM-OH....................................................................................... 18

1.3.1. Experimental Section .............................................................................................. 18

1.3.1.1. Synthesis of Dimethyl Sulfoxonium Methylide ................................................. 18

1.3.1.2. Synthesis of Thexylborane ............................................................................... 19

1.3.1.3. Synthesis of Linear PM-OH by Using Different Borane Compound Initiators... 20

1.3.2. Results and Discussion of the Synthesized Linear PM-OH................................. 21

1.3.3. Conclusions ............................................................................................................. 23

CHAPTER 2. SYNTHESIS OF 3-MIKTOARM STARS PCL(PM-OH)₂ and Br-PCL(PM-OH)₂ BY RING OPENING POLYMERIZATION AND POLYHOMOLOGATION .......................................................... 25
2.1. General Introduction of Ring Opening Polymerization of Cyclic Esters .......... 25

2.2. Synthesis of 3-Miktoarm Stars PCL(PM-OH)_2 and Br-PCL(PM-OH)_2 .......... 27

2.2.1. Experimental Section ............................................................................. 28

2.2.1.1. Synthesis of the Initiator CH_3(Vinyl)_2Si-PrOH ............................................. 28

2.2.1.2. Ring Opening Polymerization of \(\varepsilon\)-Caprolactone ................................................. 29

2.2.1.3. Hydroboration of PCL-Si(Vinyl)_2CH_3 ................................................................. 30

2.2.1.4. Polyhomologation Using PCL-Si(CH_3)(B-Thexyl) as Initiator ....................... 31

2.2.2. Results and Discussion of the Synthesized PCL(PM-OH)_2 and Br-PCL(PM-OH)_2 .................................................................................................................. 31

2.2.3. Conclusions ................................................................................................. 39

CHAPTER 3. SYNTHESIS OF 3-MIKTOARM STAR PS(PM-OH)_2 BY ATOM TRANSFER RADICAL POLYMERIZATION AND POLYHOMOLOGATION .... 40

3.1. General Introduction to Living/Controlled Polymerization ......................... 40

3.2. Attempt to Synthesize PS-Si(Vinyl)_2CH_3 from Cl_3SiCH_3 by Anionic Polymerization
High Vacuum Techniques ...................................................................................... 44

3.2.1. Experimental Section ................................................................................. 44

3.2.2. Results and Discussion .............................................................................. 48

3.2.3. Conclusions ................................................................................................. 50

3.3. Attempt to Synthesize PS-Si(Vinyl)_2CH_3 from Dichloromethylvinyl silane by
Anionic Polymerization High Vacuum Techniques ........................................... 51

3.3.1. Experimental Section ................................................................................. 51

3.3.2. Results and Discussion .............................................................................. 51

3.3.3 Conclusions ................................................................................................. 54
3.4. Synthesis of 3-Miktoarm Star PS(PM-OH)$_2$ by Combining ATRP and Polyhomologation

3.4.1. Experimental Section

3.4.1.1. Synthesis of the Initiator CH$_3$(Vinyl)$_2$Si-Isobutylbromide

3.4.1.2. Synthesis of PS-Si(Vinyl)$_2$CH$_3$ by ATRP

3.4.1.3. Hydroboration of PS-Si(Vinyl)$_2$CH$_3$

3.4.1.4. Polyhomologation Using PS-Si(CH$_3$)(B-Thexyl) as Initiator

3.4.2. Results and Discussion of the Synthesized PS(PM-OH)$_2$

3.4.3. Conclusions

GENERAL CONCLUSIONS

REFERENCES

LIST OF ABBREVIATIONS

LIST OF SCHEMES

LIST OF FIGURES AND TABLES
CHAPTER 1. SYNTHESIS OF LINEAR PM-OH BY POLYHOMOLOGATION

1.1. General Introduction to Polyhomologation

Over 79 million tons of polyethylene (PE) is produced every year globally. The commercial PE is synthesized either by high pressure high temperature (HPHT) free radical polymerization or metallocene and Ziegler-Natta catalytic polymerization. The commercial PE is recyclable, processable and low priced. Besides, its diverse physical properties resulted in providing an extensive variety of applications such as packaging, and artificial joint replacements, etc. However, synthetic challenges are accompanied along with the traditional approaches. For instance, it’s not possible to polymerize the highly substituted olefins derivatives. In addition, the catalysts used for the conventional polymerization are not compatible with several functional groups. Moreover, the limited petroleum supply is the sole source for the most monomers polymerized by conventional methods. Finally, industrial methods are not suitable to control the polymer macromolecular architecture, molecular weight and polydispersity.

Anionic polymerization is the only method to produce well-defined PE with different macromolecular architectures by hydrogenation of the corresponding polybutadiene-1,4 (PBd-1,4). Since always PBd-1,4 contains 1,2 (vinyl) units, the resulting PE is a copolymer of ethylene and butene.

Lately, Shea has found a novel alternative polymerization system to synthesize PEs. Polyhomologation, a nonolefin polymerization, provides various advantages. Indeed, it leads to well-defined polyethylene based polymeric materials, controlled
molecular weight, low molecular weight distribution, and distinct topology and composition. All these properties guide to synthesize new polymer architectures that are not provided by olefin polymerization and hence study their structure-property relationship.10

In fact, PE synthesized by polyhomologation is beneficial in applications such as optic devices, since it has uniformed molecular weight.9 Polyhomologation is a C1 polymerization in which one carbon is built at a time unlike the olefin polymerization in which two carbons are constructed at a time (Scheme I-1).11

In homologation, on which Shea based, equimolar amounts of the dimethylsulfoxonium methylide I-1 and organoborane I-2 are reacted then oxidized to the terminal alcohol. To illustrate the mechanism, the ylide I-1, which possesses a nucleophilic site and a good living group, attacks the trialkylborane I-2 to form a zwitterion complex which goes through 1,2 migration of the alkyl group to produce a homologated alkyl borane and DMSO as a leaving group. This step is followed by oxidative cleavage of the bond between carbon and borane to yield three products I-3, I-4, and I-5 (Scheme I-2).12
Scheme I-2. The homologation mechanism.

In polyhomologation, dimethylsulfoxonium methyliide (monomer) works as a source of methylene, while trialkylborane (Lewis acid) serves as an initiator. Since the ylide is added in large excess, the methylene group is added one after another one into the three branches of trialkylborane equally resulting in the formation of 3-arm PM (equivalent to polyethylene) star. This step is followed by oxidation/hydrolysis of the star polymethylene to produce a hydroxyl terminated polymethylene (Scheme I-3).  

Scheme I-3. The polyhomologation mechanism.
Novel PM complex macromolecular architectures, which can’t be achieved by traditional PE polymerization, can be constructed using polyhomologation in six different methodologies. In the first methodology, reported by Shea, stitching reactions (transformation of boron to carbon) are used to produce a variety of different architectures. Depending on the condition the B-star I-6 can give either a mixture of a symmetrical PM ketone and OH-terminated PM I-8 or a C-star I-7 (Scheme I-4).\textsuperscript{13}

![Scheme I-4. Three arm and two arm stitching reactions.](image)

An example of this transformation is given in Scheme I-5. After polyhomologation of ylide with I-9, the 3-arm borane star (PM) can undergo stitching reaction with α,α-dichloromethyl methyl ether and a base, followed by oxidation to afford the three arm star-PM-OH I-10, in which all arms on borane are connected to a carbon in I-10.\textsuperscript{14} A distribution of PM architectures was prepared by using this method such as star, and linear PM (Scheme I-5).\textsuperscript{15}

![Scheme I-5. An example of three-arm stitching reaction.](image)
In the second methodology, PM-OH is served as a macroinitiator. This methodology described by Ma\textsuperscript{36} is combining polyhomologation with ATRP to afford PM-based diblock copolymers. For example, first PM-OH is synthesized by polyhomologation of the ylide with borane dimethylsulfide initiator followed by oxidation (Scheme I-6). Then, the terminal hydroxyl group of PM-OH is transformed to PM macroinitiator PM-MIs which is served as initiator for the ATRP of a monomer, e.g. tert-butyl acrylate (tBA), to result in well-defined diblock copolymers of PM-\textit{b}-P\textsuperscript{3}BA. PM-MIs can be also used as an initiator for the ring opening polymerization (ROP) or reversible addition-fragmentation chain transfer (RAFT) as well.\textsuperscript{16}

\begin{center}
\includegraphics[width=\textwidth]{Scheme_I-6.png}
\end{center}

Scheme I-6. Combination of polyhomologation and ATRP.

The third method is using PM-OH to afford a macromonomer. This approach was developed by our group in which polyhomologation and ring opening metathesis polymerization (ROMP) are combined to synthesize well-defined PE molecular brushes. PE-OH, synthesized by polyhomologation, is reacted with 5-norbornene-2-carboxylic acid to give norbornyl PE macromonomer (PE-MM) which is polymerized by ROP using Grubbs catalyst (1\textsuperscript{st} generation) to afford well-defined PE molecular brushes (Scheme I-7).\textsuperscript{17}
Scheme I-7. Combination of polyhomologation and ROMP.

The forth strategy, the so called initiator-based topological control, was developed by Shea and uses cyclic borane initiators to provide well defined PM architectures. In particular, three tube-like macrocyclic organoboranes $I-12$ are produced by polyhomologation of ylide $I-1$ with 1-boraadamantane $THF I-11$ followed by oxidation to yield three arm star PM $I-13$ (Scheme I-8).\textsuperscript{18}

Scheme I-8. Initiator-based topological control.

The fifth method, proposed by our group, is incorporating anionic polymerization and polyhomologation through a bridge molecule ($BF_3\cdot OEt$). A macroanion reacts with $BF_3\cdot OEt$ to produce a star-like polymer which serves as macroinitiator for the polyhomologation of ylide resulting in the formation of 3-arm star block copolymer, followed by oxidation to afford a OH-terminated block copolymer (Scheme I-9).\textsuperscript{19}
Scheme I-9. Combination of anionic polymerization and polyhomologation.

The sixth method is the topological control from a combination of initiator and post-polymerization modification. According to this strategy, a cyclic borane initiator like thexyl borane I-14 is used to polymerize the ylide I-1 and produce boracyclic I-15. Then stitching reaction is followed by using sodium cyanide and benzyl chloride. Finally, after oxidation the cyclic ketones I-16 is obtained (Scheme I-10). ²⁰

Scheme I-10. Oligomeric cyclic ketone I-16 resulting from polyhomologation of ylide I-1 with thexyl borane I-14.

In fact, none of the illustrated methods above are able to produce 3-miktoarm star copolymers with two PE arms. As a result, our group has designed and synthesized a novel strategy based on the in situ construction of B-thexyl-silaboracyclic I-17 in which it possesses three sites, two sites serve as initiator precursor for polyhomologation and the third site acts as an initiator for ROP of ε-caprolactone or ATRP of styrene (Scheme I-11). ²¹

The objective of this work is to synthesize 3-miktoarm star PE-based copolymers by combining polyhomologation with other controlled/living polymerizations such as ROP and ATRP. In the first chapter, the synthesis and characterization of linear PM-OH produced using various borane initiators are discussed. In the second and third chapters we propose for the first time a new strategy to synthesize the 3-miktoarm star copolymers PCL(PM-OH)$_2$, Br-PCL(PM-OH)$_2$ and PS(PM-OH)$_2$ by combining polyhomologation of the ylide with ROP of $\varepsilon$-caprolactone and ATRP of styrene, respectively.

1.2. General Remarks

1.2.1. Materials

Borane tetrahydrofurane complex solution 1.0 M in THF, trimethylsulfoxonium iodide, dichloromethane, benzytributylammonium chloride, celite-545, methanol, trimethylamine $N$-oxide dehydrate, deuterochloroform (CDCl$_3$), toluene-$d_8$, phenolphthalein, borane dimethyl sulfide complex, triethyl borane, trichlorobenzene, trichloro(methyl)silane, dichloromethylvinylsilane, vinyl magnesium chloride solution 1.6 M in THF, *sec*-butyllithium solution 1.4 M in cyclohexane, trichloro(methyl)silane, 2-Chloro-1-propanol, methylmagnesium chloride solution 3 M in THF, magnesium, 1,2-Dibromoethane, $\varepsilon$-caprolactone, triethylamine, diphenyl phosphate, copper(I) bromide,
pyridine, and pentamethyldiethylenetriamine (PMDETA) were used as received without further purification.

Tetrahydrofuran (THF) and toluene were refluxed over sodium-benzophenone and distilled under N2 before use. 2,3-Dimethyl-2-butene was refluxed over CaH2 and distilled under argon before use. Sodium hydride (NaH) 60% dispersion in mineral oil was washed with hexane and dried before use. Styrene was stirred over CaH2 for 24 hours and distilled under argon. Then, it was treated with di-n-butylmagnesium 1 M in heptane and degassed. Later, styrene was distilled under reduced pressure and stored under argon before use. Benzene was purified on a high vacuum line. First, it was stirred under argon with concentrated sulphuric acid (H2SO4) for a week. Then, stirred with CaH2, degassed and distilled into a calibrated cylinder containing polystyryllithium (PSLi) made from n-BuLi and styrene. All chemicals were purchased from Sigma Aldrich.

1.2.2. Characterizations and Measurements

1.2.2.1. Nuclear Magnetic Resonance (NMR)

The 1H NMR (600 MHz) measurements were carried out on a Bruker AVANCED III 600 spectrometer. The 1H NMR was used to determine the molecular weight (Mn,
NMR) of the following polymers: linear PM-OH, 3-miktoarm stars copolymers PCL(PM-OH)2, Br-PCL(PM-OH)2, and PS(PM-OH)2 from the integrals of the characteristic chemical shifts of the initiating end group and the main body of the listed polymers.
$^1$H NMR spectra of monomers and initiators were recorded on a Bruker AVANCED 400 spectrometer with CDCl$_3$ as solvent and tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard.

1.2.2.2. High Temperature Size Exclusion Chromatography (HT-SEC)

High-temperature size-exclusion chromatography (HT-SEC) measurements were carried out on a Viscoteck HT-GPC model 350 instrument using 1,2,4-trichlorobenzene (TCB) as a eluent at a flow rate of 0.8 ml min$^{-1}$ at 150 °C. The system was calibrated with PS standards. HT-SEC was used to determine the molecular weights ($M_n$, SEC) and molecular weight distributions ($M_w/M_n$) of linear PM-OH, 3-miktoarm stars copolymers PCL(PM-OH)$_2$, Br-PCL(PM-OH)$_2$, and PS(PM-OH)$_2$.

1.2.2.3. Size-exclusion chromatography (SEC)

Size-exclusion chromatography (SEC) linked with RI and UV detectors was performed in THF at 35 °C using two 7.8 mm x 300 mm (5 µm) Styragel columns (Styragel HR 2 and Styragel HR 4) at a flow rate of 1.0 ml min$^{-1}$. Apparent number-average molecular weight ($M_n$, SEC) and disparities ($M_w/M_n$) of the rest of polymers were obtained based on a series of polystyrene (PS) standards.

1.2.2.4. Differential Scanning Calorimetry (DSC)

DSC measurements were obtained by using a Mettler Toledo DSC1/TC100 system in an inert atmosphere (nitrogen). First, the samples were heated to 160 °C, then cooled to -80 °C and finally heated back to 160 °C with heating/cooling rate of 10 °C/min. To
determine the melting temperature ($T_m$) and degree of crystallinity, the second heating curve was used.

1.3. Synthesis of Linear PM-OH

1.3.1. Experimental Section

1.3.1.1. Synthesis of Dimethyl Sulfoxonium Methylide

There are two steps to synthesize the monomer, dimethyl sulfoxonium methylyde

\[
\begin{align*}
\text{SO} & \quad \text{I} \quad \text{CH}_2\text{Cl}_2 \quad \text{H}_2\text{O} \\
\text{S} & \quad \text{O} \quad \text{Cl} \\
\text{rt, 24 hours} \\
\end{align*}
\]


First step: 42.8 g of trimethylsulfoxonium iodide (0.2 mmol), 330 ml of dichloromethane, 440 ml of deionized water and 65.8 g of tributylbenzylamino chloride (0.2 mmol) were added into a 2L round bottom flask (Scheme I-12). The mixture was stirred vigorously at room temperature for 24 hours. The aqueous phase then was collected and washed with 60 ml of CH$_2$Cl$_2$ and evaporated under reduced pressure. White yellowish crystals were obtained after the removal of water. Then, 50 ml of methanol was poured and placed in an oil bath at 50 °C until crystals were dissolved completely. Then the flask was cooled to room temperature naturally followed by cooling to 5 °C in refrigerator overnight. A needle like crystal product of trimethylsulfoxonium chloride was obtained. The salt can be stored at room temperature and used for several monomer preparations.$^{22}$

Second step: to a flame dried three neck (250 ml) round bottom flask capped with rubber septum and a condenser in the middle neck, equipped with a stirring bar and deoxygenated by degasing and backfilling argon three times, 5 g of NaH was added (Scheme I-13). Then, 150 ml of THF was injected and stirred followed by addition of 17 g of trimethylsulfoxonium chloride. The flask was heated and refluxed at 70 °C for 4-5 hours until the gas stopped. Later, THF was evaporated under low pressure followed by the injection of 100 ml of toluene. Then, celite-545 (3 cm height) was used to filtrate the solution. A clear light yellowish solution was achieved. The product (monomer) flask was purged with argon, sealed and kept in the fridge. It can be stored and used up to one month. To determine the ylide concentration, a 1 ml of the product solution was added to 5 ml of distilled water and titrated with 0.89 M HCl by using phenolphthalein indicator. The ylide concentration was 0.736 M and the yield of the ylide was 80%.22

1.3.1.2. Synthesis of Thexylborane

\[
\text{BH}_3 \text{THF} + \text{I-18} \xrightarrow{0-5^\circC, 3 \text{ h}} \text{BH}_2 \text{I-19}
\]


In a 50 ml flame dried Schlenk flask capped with a rubber septum and equipped with a stirring bar and deoxygenated by degasing and backfilling argon three times, 5 ml of I-18
(5 mmol) was injected and cooled down to 0 °C followed by slow addition of 0.6 ml of 1-19 (5 mmol). The solution was stirred at 0-5 °C for 3 hours (Scheme I-14). The concentration of the produced thexylborane was 0.89 M (5.0 mmol/5.6 ml).23

1.3.1.3. Synthesis of Linear PM-OH by Using Different Borane Compound Initiators

To a flame dried 50 ml Schlenk flask equipped with a stir bar, capped with a rubber septum and deoxygenated by degasing and backfilling argon three times, 10 ml of distilled toluene and 0.1 ml of thexylborane (0.89 M, 0.089 mmol) were charged, stirred and preheated at 70 °C (Scheme I-15).

![Scheme I-15. Synthesis of PM-OH using thexylborane, borane dimethyl sulfide complex and triethylborane as initiators.](image)

Then, 24 ml of the ylide (0.736 M, 17.7 mmol) was added to the heated mixture, which was stirred for 20 minutes). Meanwhile, a 0.1 ml aliquot was withdrawn and injected into 2 ml of distilled water containing a drop of phenolphthalein indicator. The resultant color of the solution was transparent indicating the consumption of the ylide. Oxidation process was followed by adding 0.1 g of TAO·2H₂O to the flask and stirred at 80 °C overnight. Later, the polymer solution was concentrated, precipitated in methanol, filtrated, and dried for ¹H NMR and HT-SEC measurements. The same
experimental procedures were applied for the polyhomologation by using borane
dimethyl sulfide complex and triethyl borane (Scheme I-14).24

1.3.2. Results and Discussion of the Synthesized Linear PM-OH

Table I-1. Results of PM-OH synthesized by polyhomologation with three different
borate initiators

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Ylide/Borane</th>
<th>( M_n, \text{theo} )^a</th>
<th>( M_n, \text{SEC} )^b</th>
<th>( M_n, \text{NMR} )^c</th>
<th>( M_w/M_n )^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Thexylborane</td>
<td>200</td>
<td>1337</td>
<td>3700</td>
<td>1960</td>
<td>2.01</td>
</tr>
<tr>
<td>2. BH3:S(CH3)2</td>
<td>120</td>
<td>560</td>
<td>1500</td>
<td>2100</td>
<td>1.30</td>
</tr>
<tr>
<td>3. Et3B</td>
<td>180</td>
<td>840</td>
<td>1000</td>
<td>1260</td>
<td>1.18</td>
</tr>
</tbody>
</table>

^a The theoretical molecular weight is calculated based on the theoretical degree of polymerization from the initial ylide to borane ratio. ^b Determined by HT-SEC in TCB using PST standards. ^c Determined by \(^1\)H NMR in \(d\)-toluene at 80 °C

The synthesis of linear PM-OH by using three borane initiators, thexyl borane, borane
dimethyl sulfide complex and triethylborane, are illustrated in Scheme I-4. The results of
the synthesized PM-OH are summarized in Table I-1. Since the polyhomologation of the
ylide with different borane initiators leads to the formation of the same polymer PM-OH,
one \(^1\)H NMR spectrum is displayed. \(^1\)H NMR spectrum of the PM-OH obtained from
thexyl borane initiator reveals the presence of PM segments (Figures I-1). The peak c is
assigned to methylene protons next to an oxygen atom (\(-\text{CH}_2\text{O}^-\), \(\delta = 3.4\) ppm). The peak
b is assigned to the protons of the methylene groups (\(-\text{CH}_2^-\), \(\delta = 1.2-1.3\) ppm). While the
peak d is assigned to the protons of the internal methyl group (\(-\text{CH}_3\), \(\delta = 0.9\) ppm).
Figure I-1. $^1$H NMR spectrum of the linear PM-OH synthesized by reacting the ylide with thexyl borane in C$_6$D$_6$ at 600 MHz.

HT-SEC traces of the linear PM-OH produced by polyhomologation using three borane initiators are illustrated in Figure I-2. Peak (a) is a bimodal peak indicating to another initiation process due to the presence of oxidized borane species. In contrast, peak (b) and (c) look much narrower and symmetrical indicating that PM-OH was initiated by the desired initiators; (CH$_3$)$_2$S$^+$BH$_3$ and Et$_3$B, respectively.

Figure I-2. SEC traces of the obtained PM-OH by using various borane initiators, thexyl borane (a), borane dimethyl sulfide complex (b), and triethylborane (c).
Finally, DSC measurements were performed to analyze the thermal properties of the linear PM-OH initiated from Et₃B (Figure I-3). The melting temperature of the linear PM-OH clearly appears in the DSC (second heating curve) at 101 °C. and the degree of crystallinity is 66.95%.

![DSC Analysis](image)

Figure I-3. DSC analysis (second heating curve) of linear PM-OH produced using Et₃B initiator.

1.3.3. Conclusions

In summary, linear PM-OH has been synthesized by several borane initiators. The results showed that Et₃B has proven to be the most effective hydroboration agent to initiate the polyhomologation comparing with thexylborane and borane dimethylsulfide. Its HT-SEC analysis revealed a unimodal polymer distribution. In addition, the $M_{n,SEC}$
agrees with the $M_{n,\text{theo}}$. On the other hand, thexylborane and borane dimethylsulfide initiators showed remarkable increase in $M_{n,\text{SEC}}$ comparing to $M_{n,\text{theo}}$. In fact, borane the unstable Lewis base complexes like BH$_3$S(CH$_3$)$_2$ and organoborane such as thexylborane are oxygen-sensitive. Indeed, traces of oxygen during the preparation and purification of the initiator can produce a small amount of borinic ester R$_2$BOR, which is not easy to be removed. The structures of the produced polymers were confirmed by $^1$H NMR and HT-SEC. In addition, the thermal properties were examined by DSC.

In the next chapter, ROP of $\varepsilon$-caprolactone is combined with polyhomologation to synthesize for the first time the 3-miktoarm star copolymers PCL(PM-OH)$_2$. 
CHAPTER 2. SYNTHESIS OF 3-MIKTOARM STARS PCL(PM-OH)$_2$ AND Br-PCL(PM-OH)$_2$ BY RING OPENING POLYMERIZATION AND POLYHOMOLOGATION

2.1. General Introduction of Ring Opening Polymerization of Cyclic Esters

ROP of cyclic ester monomers are usually achieved using two methods: metal-based catalyst/initiator and metal-free catalyst/initiator. Although the organometallic catalytic route is a powerful method to produce well-defined polyesters, the removal of unfavorable heavy metal from catalysts is required in many advanced applications. As a result, organocatalyzed polymerization has acquired a great attention to provide significant synthetic approaches for the production of polyesters in the absence of metals. Polyesters produced by metal-free polymerization are important as they play a remarkable role in tissue engineering, drug gene and delivery, besides environmentally friendly packaging materials. In addition, they are used as electric and biocompatible materials.

Living polymerization techniques utilizing organocatalysts are used to produce complex macromolecular architectures of polymers with well-controlled molecular weight and narrow polydispersity index (PDI). More interestingly, the macromolecules maintain the hydroxyl end groups that can be used for chain extension.

Cyclic ester monomers can be polymerized through ROP by using a wide range of organocatalysts. Basic-catalyzed ROP is obtained through either basic activation of the initiation/propagation agent, or nucleophiles activation of the monomer. In contrast, acid-catalyzed ROP is utilized as an efficient catalyst for ROP of cyclic monomers. Both mechanisms are resulting in the formation of controlled living polymerization.
As a consequence, ROP mechanism can be described depending on the organocatalysts type. Based on the acid-catalyzed ROP, the mechanism is called activated monomer and resulted in well-defined polyesters. An example of this mechanism is ROP of CL II-1 initiated by 3-Phenyl-1-propanol (PPA) II-3 and catalyzed by diphenyl phosphate (DPP) II-2 (Scheme II-1).33

Scheme II-1. Activated monomer mechanism for DPP catalyzed ROP of CL using PPA.

Indeed, organocatalyzed ROP has facilitated the synthesis of a wide variety of polyesters with complex macromolecular architectures including diblock copolymers34, and triblock terpolymers35. The versatility of polymerization methods and their resultant macromolecular architectures are needed to expand the functionality in such systems and therefore broaden their applications. Toward this goal, recently ROP has been combined with other living polymerizations to synthesize polyester copolymers with well-defined architectures and different chemical composition. For instance, PM-\(b\)-PCL-\(b\)-PAA triblock terpolyemrs have been synthesized by combining polyhomologation, ROP and ATRP.36
PCL attracted the attention of researchers because it is degradable, biocompatible, and drug permeable. In addition, the incorporation of PCL in nonpolar polyolefin has improved polyolefin properties such as adhesion, wettability, printability, reactivity, and compatibility.\(^{37}\)

Until now, 3-miktoarm star-shaped polymers containing one arm of PCL and two arms of PM-OH has not been reported. In this chapter, we present a facile route to synthesize 3-miktoarm stars PCL(PM-OH)\(_2\) and Br-PCL(PM-OH)\(_2\) by combining ROP and polyhomologation. This approach is based on the acid-catalyzed ROP of caprolactone initiated by 3-(methyldivinylsilane)propan-1-ol and catalyzed by DPP.

We have used \(\varepsilon\)-caprolactone (CL) as a monomer since its polymers (PCL) have huge applications in biomaterials and tissue engineering.\(^{38}\)

The initiator, methyldivinylsilane propanol, was designed and synthesized by our group to facilitate the synthesis of the miktoarm star. On the other hand, we used diphenyl phosphate (DPP) as a weak acid to catalyze ROP of \(\varepsilon\)-caprolactone.

Noteworthy, DPP organocatalyst has many advantages in which it is obtainable commercially, stable chemically and has less poisoning effect.\(^{39}\)

This study describes a novel strategy toward the synthesis and characterization of 3-miktoarm star copolymers PCL(PM-OH)\(_2\) and Br-PCL(PM-OH)\(_2\) by incorporating ROP with polyhomologation.

\textbf{2.2. Synthesis of 3-Miktoarm Stars PCL(PM-OH)\(_2\) and Br-PCL(PM-OH)\(_2\)}

The 3-miktoarm stars PCL (PM-OH)\(_2\) and Br-PCL(PM-OH)\(_2\) were achieved by using the heterofunctional initiator 3-(methyldivinylsilane)propan-1-ol which possesses two
sites linked to silicon and one OH group. The hydroxyl group initiates ROP of \( \varepsilon \)-caprolactone, and the divinyl groups lead to the synthesis of the two PM-OH arms by hydroboration followed by polyhomologation (Scheme II-2). \(^{21}\)

![Scheme II-2. Heterofunctional initiator 3-(methyldivinylsilane)propan-1-ol.](image)

### 2.2.1. Experimental Section

#### 2.2.1.1. Synthesis of the Initiator CH\(_3\)(Vinyl)\(_2\)Si-PrOH

![Scheme II-3. Synthesis of the initiator 3-(methyldivinylsilane)propan-1-ol.](image)

To a flame dried 150 ml Schlenk flask (A), equipped with a stir bar, capped with a rubber septum, deoxygenated by degasing and backfilling argon three times, 3.34 ml of II-4 (40 mmol) and 50 ml of THF were injected against argon flow. Then, the reaction mixture was cooled down to 0 °C followed by slow addition of 13.3 ml of CH\(_3\)MgCl (40 mmol) to the reaction flask, which then was stirred for 20 minutes (Scheme II-3). Next, 1.05 g of Mg (44 mmol) and dibromoethane were added to the reaction solution which was heated and refluxed at 80 °C for 6 hours. Meanwhile, to a flame dried 250 ml round bottom flask (B), 75 ml of THF and 4.7 ml of Cl\(_3\)SiCH\(_3\) (40
mmol) were injected by syringe and stirred at ice bath. After consuming all the Mg in flask (A), the reaction mixture was transferred by a syringe against argon flow to flask (B) which was stirred at room temperature for 12 hours. After that, the reaction mixture was cooled at 0 °C followed by the addition of 50 ml of Grignard reagent (80 mmol) by a syringe pump. Then, it was stirred at room temperature for 12 hours. Afterwards, the reaction mixture was added to 500 ml of distilled water then transferred to a funnel separation where EA and NH₄Cl were added. The yellowish oily product phase was washed again but with a brine of NaCl. Then it was separated from the aqueous phase, collected and stirred with MgSO₄ for 20 minutes. After that, the product was filtrated from the salt followed by the removal of the solvent. The crude product was purified by flash chromatography on silica gel (eluent: PE/EA = 4/1) and the product 3-(methyldivinylsilane)propan-1-ol was isolated as colorless oil (60% yield). Later, it was dried and analyzed by ¹H NMR.²¹

2.2.1.2. Ring Opening Polymerization of ε-Caprolactone

![Scheme II-4. ROP of CL initiated by CH₃(Vinyl)₂Si-PrOH and catalyzed by DPP.](image)

First, the initiator was stirred with Na₂SO₄ and DCM then filtrated followed by the removal of solvent under vacuum for ROP. Second, ε-caprolactone, the monomer, was stirred over CaH₂ overnight then distilled under vacuum and collected against argon flow, sealed with teflon stopcock and stored at 4 °C for ROP. Third, to a flame dried 150 ml
Schlenk flask, equipped with a stir bar, capped with teflon stopcock, deoxygenated by degasing and backfilling argon three times, 0.1 g of the initiator 3-(methyldivinylsilane)propan-1-ol (1 mmol) and 50 ml of toluene were charged against argon flow and stirred followed by injecting 5.2 ml of CL (50 mmol) (Scheme II-4). Then, 0.25 g of DPP was added to the reaction flask which was then heated at 30 °C for 12 hours. After that, 0.4 ml of Et₃N (2 mmol) was injected into the reaction mixture and stirred followed by the removal of the solvent. Then, it was precipitated in cold MeOH and filtrated. Later, 5 mg of the precipitated polymer was dissolved in THF for SEC analysis and the rest was dried in vacuum for ¹H NMR measurements.⁴⁰

2.2.1.3. Hydroboration of PCL-Si(Vinyl)₂CH₃

![Scheme II-5. Hydroboration of PCL-Si(Vinyl)₂CH₃.](image)

To a 50 ml flame dried Schlenk flask, 0.4 g of PCL-Si(Vinyl)₂CH₃ (0.025 mmol) II-5 was added, followed by the addition of THF (Scheme II-5). The solution was stirred until the polymer dissolved completely and cooled down to 0 °C. Then, 0.4 ml of thexylborane (0. 35 mmol, 0.89 M) was added slowly under argon atmosphere to the reaction mixture which was stirred at increasing temperature 0-25 °C overnight. Later, NMR tube was sealed with a rubber septa cap and deoxygenated by degasing and backfilling argon three times. Then, a 0.2 ml aliquot was withdrawn and injected into the tube followed by the removal of solvent under vacuum and the addition of 0.5 ml of CDCl₃ for ¹H NMR analysis to determine the disappearance of vinyl groups.
Then, 1 ml of degased MeOH (0.45 mmol) was added and stirred for 10 minutes. The solvents then were evaporated under vacuum.

2.2.1.4. Polyhomologation Using PCL-Si(CH₃)(B-Thexyl) as Initiator

Scheme II-6. Synthesis of 3-miktoarm star copolymers PCL(PM-OH)₂.

To the dry hydroboration flask PCL-Si(CH₃)(B-Thexyl) II-6, 5 ml of toluene and 5 ml of the ylide (5.8 mmol) were charged under argon flow (Scheme II-6). The solution was stirred and heated at 80 °C for an hour. Then, a 0.1 ml aliquot was withdrawn and injected into a 1 ml of water containing a drop of phenolphthalein indicator. Then, the solution was treated with 0.15 g of TAO and stirred at 80 °C for 12 hours.

2.2.2. Results and Discussion of the Synthesized PCL(PM-OH)₂ and Br-PCL(PM-OH)₂

The synthesis of the initiator CH₃(Vinyl)₂Si-PrOH for ROP of CL is illustrated in Scheme II-3. The ¹H NMR spectrum of the initiator (Figure II-1) reveals the presence of characteristic chemical shifts of vinyl groups segments. Chemical shifts at δ = 6.18-5.95 and 5.76-5.69 ppm (peaks g and f, respectively) are assigned to protons of vinyl groups. Chemical shift at δ = 3.3 ppm is assigned to the protons of the methylene group connected to the hydroxyl group, while chemical shifts at δ = 1.4 and 0.5 ppm are
corresponded to the protons of methylene groups (–CH2–CH2–Si, peak c and b, respectively). Chemical shift at δ = 0.1 ppm is attributed to methyl group, peak a.

Figure II-1. ¹H NMR spectrum of CH₃(Vinyl)₂Si-PrOH at 400 MHz in CDCl₃.

The first ¹H NMR spectrum in Figure II-2 reveals the presence of the linear PCL-Si(Vinyl)₂CH₃ II-5 segments. The characteristic peaks due to PCL are shown at the ranges 4.03-3.9, 2.3-2.2, 1.7-1.6, 1.4-1.3 ppm, respectively. In addition, the presence of the initiator peaks is appeared. The peaks of divinyl groups are observed at chemical shifts δ = 6.1, 5.7 ppm (peak i and j, respectively). Moreover, chemical shift at δ = 3.6 ppm is assigned to the methylene protons next to the oxygen atom (O–CH₂–, peak f). Furthermore, chemical shifts at δ = 1.2, 0.6, and 0.1 ppm are assigned to the two methylene protons, and methyl protons, respectively (–CH₂–CH₂–Si–CH₃ peaks, k, l, and a, respectively). The second spectrum appears the presence of characteristic chemical shifts of the miktoarm PCL(PM-OH)₂ II-8 segments. Chemical shifts at δ = 1.7-0.7 ppm are assigned to the protons of polymethylene segments. The protons of the methylene
adjacent to the oxygen atom (–CH₂–O–) are shown at chemical shift δ = 3.35 ppm. Besides, the presence of PCL segments is confirmed in the ranges of 4.01-3.9 and 2.15-2.07 ppm (peaks f+g, and e, respectively). The rest of PCL signals are integrated with PM segments. ¹H NMR results imply that the polymerization was initiated from the silane divinyl initiator.

Figure II-2. ¹H NMR spectra of the linear PCL-Si(Vinyl)₂CH₃ (II-5) in CDCl₃ at 400 MHz, and PCL(PM-OH)₂ (II-8) in d-toluene at 600 MHz.

Further evidence for the formation of the miktoarm star PCL(PM-OH)₂ is obtained from the SEC analysis. The linear PCL appears at retention volume 15.5 mL while the miktoarm star appears at 14.5 mL (Figure II-3 a and b, respectively). The decrease in the retention volume indicates an increase in the molecular weight and hence the formation of the 3-miktoarm star PCL(PM-OH)₂. In addition, SEC traces reveals monomodal peaks of the linear PCL and 3-miktoarm star copolymers PCL(PM-OH)₂ which indicates that the main polymers were initiated from CH₃(Vinyl)₂Si-PrOH. However, the small
shoulder in the peak of linear PCL (Figure II-3, a) is assigned to the formation of high molecular weight side product in a small scale. The side product is formed due to the presence of impurities coming from the catalyst DPP or/and the base Et3N. As a consequence, the number-average molecular weight obtained from SEC ($M_{n, \text{SEC}} = 16 \text{ kg mol}^{-1}$) doesn’t agree with the theoretical molecular weight ($M_{n, \text{theo}} = 6 \text{ kg mol}^{-1}$). Besides, PS standard is used for SEC calibration.

![SEC traces of PCL-Si(Vinyl)$_2$CH$_3$ in THF at room temperature (a), and miktoarm star copolymers PCL(PM-OH)$_2$ in C$_6$H$_6$ at 150 °C (b).](image1)

Another proof for the formation of the 3-miktoarm star PCL(PM-OH)$_2$ is obtained by the DSC measurement. It performed to characterize the thermal properties of the linear
PCL and 3-miktoarm star PCL(PM-OH)$_2$ (Figure II-4). The melt temperatures of the linear PCL and the miktoarm clearly appear in the DSC traces (second heating curve) at 54 and 115 °C, respectively. After the formation of the miktoarm star, the melting temperature of PCL is covered by the melting process of the PM-OH arms. The degree of crystallinity for PCL and the star are 24.47 % and 44.60%, respectively.

![DSC traces (second heating curves) of the linear PCL and miktoarm star PCL(PM-OH)$_2$.](image)

Figure II-4. DSC traces (second heating curves) of the linear PCL and miktoarm star PCL(PM-OH)$_2$.

Noteworthy, there are three possible sites in functionalized PCL to react with thexyllborane, two sites providing by vinyl groups to produce the cyclic borasilane and initiate polyhomologation later. In addition, the third site is provided by the terminal hydroxyl group in which the thexyllborane reacts with the oxygen. Undoubtedly, the oxygen-borane bond is not capable to initiate polyhomologation$^{41}$ (Scheme II-7).
Scheme II-7. Three possible sites in PCL-Si(Vinyl)$_2$CH$_3$ to react with the xylborane.

In contrast, precaution has been taken to avoid the reaction between the xylborane and hydroxyl group in PCL-Si(Vinyl)$_2$CH$_3$. The hydroxyl group was protected by α-bromoisoobutyl bromide in the presence of base at THF. Then, hydroboration and polyhomologation were followed to result in the formation of functionalized miktoarm star Br-PCL(PM-OH)$_2$. The resultant polymer is functionalized with bromine which can initiate styrene or MMA by ATRP in the future (Scheme II-8).

Scheme II-8. Synthesis of Br-PCL(PM-OH)$_2$.

The $^1$H NMR spectra reveal the presence of the miktoarm star Br-PCL(PM-OH)$_2$ (Figure II-6). The first spectrum of II-5 is illustrated already in Figure II-2. The second spectrum reveals the presence of the dimethyl groups in which their protons are shown at
chemical shifts $\delta = 1.9$ ppm. This confirms the protection of hydroxyl group with $\alpha$-bromoisobutyl bromide. The third spectrum shows the absence of vinyl group protons indicating to successful hydroboration. The forth spectrum reveals the presence of characteristic chemical shifts of PM segments. Chemical shifts at $\delta = 1.8$-0.8 ppm are assigned to the protons of PM monomeric units ($-\text{CH}_2-$, peak r). In addition, chemical shift at $\delta = 3.0$ ppm is attributed to methylene group linked to the hydroxyl group ($\text{HO}-\text{CH}_2-$, peak s). The characteristic peak due to PCL is observed at the ranges 4.06-3.90 ppm. The other signals related to PCL are integrated with PM segments.

Figure II-5. $^1$H NMR spectra of PCL-Si(Vinyl)$_2$CH$_3$ (II-5), Br-PCL-Si(Vinyl)$_2$CH$_3$ in $d$-benzene at 500 MHz (II-9), Br-PCL-Si(CH$_3$)(B-Thexyl) in CDCl$_3$ at 400 MHz (II-10), and Br-PCL(PM-OH)$_2$ in $d$-toluene at 600 MHz (II-11).
SEC analysis is used to determine the molecular weight and PDI of the resulted polymers. In addition, it shows unimodal peaks of the obtained PCL-Si(Vinyl)₂CH₃ and Br-PCL(PM-OH)₂ (Figure II-6, a and b, respectively), indicating both polymers were initiated from the desired initiator CH₃(Vinyl)₂Si-PrOH.

Figure II-6. SEC traces of the synthesized PCL-Si(Vinyl)₂CH₃ in THF at room temperature (a), and Br-PCL(PM-OH)₂ in TCB at 150 °C.

DSC measurement was performed to analyze the thermal properties of the linear functionalized Br-PCL and the miktoarm star Br-PCL(PM-OH)₂ (Figure II-7). The melt temperatures of the linear Br-PCL and the miktoarm clearly appear in the DSC (second heating curve) at 54 and 109 °C, respectively. After the formation of the miktoarm star,
the melting temperature of Br-PCL is barely visible because it was covered by the melting process of (PM-OH)$_2$. The degree of crystallinity for Br-PCL is 24.47 % and for the star is 24.44 %.

![DSC traces (second heating curves) of the linear Br-PCL and 3-miktoarm star Br-PCL(PM-OH)$_2$.](image)

**2.2.3. Conclusions**

In this chapter, we achieved the synthesis of miktoarm star PCL(PM-OH)$_2$ and Br-PCL(PM-OH)$_2$ by combining ROP and polyhomologation using the new designed and synthesized heterofunctional initiator CH$_3$(Vinyl)$_2$Si-PrOH. The structure of the obtained polymers was confirmed by $^1$H NMR and SEC. In addition, their thermal properties were tested by DSC. In the next chapter, 3-arm star PS and miktoarm star PS(PM-OH)$_2$ are synthesized.
CHAPTER 3. SYNTHESIS OF 3-MIKTOARM STAR PS(PM-OH)₂ BY ATM TRANSFER RADICAL POLYMERIZATION AND POLYHOMOLOGATION

3.1. General Introduction to Living/Controlled Polymerization

Recently, living/controlled polymerization has attracted much interest because it tolerates many functional groups, operates in simple experimental setup, and suits many kinds of monomers. In addition, they lead to a narrow molecular weight distribution which is a significant implementation to control polymers morphology. Furthermore, the resulted polymers possess predetermined molecular weight and controlled polymer architectures. Anionic polymerization and Atom Transfer Radical Polymerization (ATRP) are two examples of living and controlled/living polymerizations, respectively.

Anionic polymerization is a living polymerization that produces living polymers in which their chain-ends maintain the reactivity forever, allowing continuous propagation in the absence of both chain termination and transfer. The chains in such polymers propagate simultaneously and share identical length subsequently after a period of time. In addition, the chain-end anions of the living anionic polymers are greatly reactive yet stable at suitable conditions. As a result, this type of polymerization is a great tool to produce a wide range of complex polymer architectures with high homogenized molecular composition.

Many monomers have been polymerized by anionic polymerization, such as styrene, 1,3-butadiene and isoprene. In general, anionic polymerization of the vinyl and diene monomers can be initiated by electron-deficient initiators such as
organolithium derivatives. The initiation starts with the addition to the double bond of the monomer. Then, the propagation is followed in which all the chains are growing at nearly the same time with the no termination reaction (Scheme III-1).47

\[
\text{Initiation} \quad \text{RLi} + \text{H}_2\text{C} = \text{CHR}_1 \quad \text{RH}_2\text{C} = \text{CHR}_1^{-} \quad \text{Li}^+ \\
\text{Propagation} \quad \text{RH}_2\text{C} = \text{CHR}_1^{-} \quad \text{Li}^+ + n\text{H}_2\text{C} = \text{CHR}_1 \quad \text{RH}_2\text{C} = \text{CHR}_1^{-} \quad \text{Li}^+ \\
\text{No termination}
\]

Scheme III-1. Anionic polymerization mechanism of vinyl monomers using metal alkyl initiators.

Precisely, the anionic polymerization high vacuum technique (HVT) is the best method to produce model complex structures.48 Although HVT technique is challenging, involving a lot of time and effort, and resulting finite amount of products, it has enormous advantages to enable the synthesis of specific well-defined macromolecule structures that are important and demanded for particular applications. Anionic polymerization HVT is considered to be the most effective system for the synthesis of well-defined polymers with complex macromolecular architectures because it can be conducted in the absence of impurities and on the scale of 10 g or less.49

On the other hand, ATRP is a controlled/living radical polymerization, which is a catalytic technique, using a metal complex.50 In ATRP, a dynamic equilibrium is establishing in between the dormant species and propagating radicals.51 A transition metal halide catalyst (MtzY/L) activates reversibly a dormant species like alkyl halide
(R-X). The halogen atom (X) in the dormant species is abstracted by the metal halide catalyst to create a radical R’ and oxidized metal complex (XMt^{z+1} Y/L). X and Y are halogens such as Cl or Br, Mt is a transitional metal (Cu, Ni, Pd, Rh, Ru, Mo), and L is a suitable ligand. So far, most ATRP employs copper (I) complexes based on a range of N-donor ligands.\textsuperscript{52}

Scheme III-2 illustrates an example of typical ATRP mechanism in which a complex of Cu(I)Cl and the ligand 2,2 bipyridal is the catalyst. The chlorine is abstracted from an alkyl halide (e.g. 1-phenyl ethyl chloride) by the catalyst and a reversible redox process is occurred. While, the Cu(II)Cl\textsubscript{2}/(2bipy) species acts as the mediating radical.\textsuperscript{47}

ATRP methods are suitable for extensive range of vinyl monomers such as styrene, (meth)acrylates, (meth)acrylamides and acrylonitrile.\textsuperscript{53} Moreover, it has features for appropriate commercial applications. The resultant polymers from the ATRP have been used as sealants\textsuperscript{54}, lubricants\textsuperscript{55} and viscosity modifiers\textsuperscript{56}.
On the other hand, various well-defined complex architectures of PS-based copolymers have been synthesized by living-controlled polymerizations. Up to now, 3-miktoarm star PS(PM-OH)$_2$ copolymers are not obtained yet. The purpose of such a combination is to study the structure-properties relationships. In addition, blinding polyolefin with PS can result in formation of effective compatibilizers.

The aim of this chapter is to synthesize miktoarm star PS(PM-OH)$_2$ by two methods. The first method was an attempt to synthesize a functionalized PS which planned to be used later as a macroinitiator for polyhomologation. Since anionic polymerization HVT of styrene is the best process leading to well-defined PS macromolecular architectures, we used this method. Although such a strategy consumed great deal of time and effort, no miktoarm was obtained (Scheme III-3). Instead, unexpectedly 3-arm star PS has formed in a new way. Because, the main objective of this research is to produce PM-based copolymers, further work and examinations on these extraordinary results have been deferred to the future work.

A second method was proposed based on a designed and synthesized initiator by our group. This initiator is capable to initiate ATRP of styrene and can serves as a precursor for polyhomologation of the ylide to achieve successfully monomodal 3-miktoarm star copolymers PS(PM-OH)$_2$ (Scheme III-3).
Scheme III-3. Two methods used to synthesize 3-miktoarm star copolymers PS(PM-OH)₂, anionic polymerization HVT (not successful), and incorporation of ATRP and polyhomologation via heterofunctional initiator (successful).

3.2. Attempt to Synthesize PS-Si(Vinyl)₂CH₃ from Cl₃SiCH₃ by Anionic Polymerization High Vacuum Techniques

Anionic polymerization high vacuum techniques were used to attempt obtaining functionalized PS-Si(Vinyl)₂CH₃. HVT requires designing of polymerization reactors from glass apparatus provided with breakseals and constructions.⁵⁹

3.2.1. Experimental Section

First, living PS was prepared as following: styrene, monomer, was stirred with CaH₂ then dibutylmagnesium (DBMg). Then, styrene was distilled into a calibrated ampule (3 ml, 0.03mol). While sec-BuLi, initiator (3ml, 1.04x 10⁻⁴ mol), was degased and distilled into a calibrated ampule. Both ampules were stored at -20°C.

Second, living PS apparatus was prepared as shown in Figure III-1. Anionic polymerization of styrene (Scheme III-4) was obtained as follows; 2 ml of n-BuLi, a solution in hexane, was injected in flask A. Then, hexane was evaporated followed by benzene distillation form calibrated flask B to the main apparatus C.

Benzene was degased, and then the whole reactor was removed from the vacuum line by heat sealing at constriction 1 (Figure III-1). The apparatus was purged by the solution of \( n \)-BuLi then transferred to flask C which was placed in a water bath and heated at 50 °C. Benzene was refluxed and condensed over the whole reactor. After that, the break-seal of the monomer was ruptured and poured into flask C. The addition of \( \text{sec-BuLi} \), the initiator, was followed in which the color of the solution became yellowish indicating the formation of the living PS chain ends (SchemeIII-4). A 3 ml aliquot was taken and injected into 6 ml of MeOH and analyzed it by SEC analysis. Later, empty ampules were removed by heat sealing at constrictions 4 and 5.

Figure III-1. Apparatus for the preparation of living PS.

Second, \( \text{Cl}_3\text{SiCH}_3 \) ampules were prepared as follows. In a round flask D, 3 ml of distilled \( \text{Cl}_3\text{SiCH}_3 \) (0.0117 mol) was added and connected to the vacuum (Figure III-2, left). Apparatus F, which connected to two calibrated ampules 3 and 4 (1.5 ml each ampule), was connected to the vacuum as well. Flask D was degased then cooled down to
room temperature followed by distilling $\text{Cl}_3\text{SiCH}_3$ from flask D to ampules 3 and 4 which then were sealed at the constriction regions. The ampules were sealed under vacuum and stored at room temperature. Third, 0.8 ml of vinylmagnesium chloride $(3.5 \times 10^{-4} \text{ mol})$ was injected to ampule 5 by syringe followed by degasing and storing at room temperature (Figure III-2, right).

**Figure III-2.** Apparatus for distilling $\text{Cl}_3\text{SiCH}_3$ (left), and introducing vinylmagnesium chloride (right).

Forth, the prepared ampules of silane, linking agent, Grignard reagent, and living PS were attached into the terminating apparatus and then connected to the vacuum line.
as shown in Figure III-3. After that, the apparatus was purged and washed with \( n \)-BuLi followed by benzene distillation. The procedures were explained previously in the second point. Fifth, terminating the living PS chain ends with the linking agent \( \text{Cl}_3\text{SiCH}_3 \) (Scheme III-5), which was introduced by placing flask \( H \) in an ice bath followed by break-seal silane ampule in which it was ruptured, poured into flask \( H \) and stirred vigorously.

![Scheme III-5. Terminating living chain ends PS with Cl\(_3\)SiCH\(_3\).](image)

Then, a hot towel was applied on living PS ampule, ruptured and poured immediately and quickly to flask \( H \) in which the yellowish color of the living PS chain ends disappeared indicating the termination of living PS chain ends. Reactor was stirred for a few minutes (Figure III-3).\(^6\)

Then, the polymer was washed with benzene several times and then removed. After that, 50 ml of benzene was distilled to flask \( H \) followed by keeping the apparatus under vacuum for 48 hours. Later, 50 ml of THF was distilled to apparatus \( H \), followed by degassing. The apparatus was removed from the vacuum line. Then, a 3 ml aliquot was taken and injected into 6 ml of MeOH and analyzed by SEC analysis. Later, Grignard reagent ampule was ruptured and poured into flask \( H \) which then was heated at 45 °C overnight (Scheme III-5). The reaction was monitored by taking an aliquot and analyzed by SEC analysis.
3.2.2. Results and Discussion

$^1$H NMR spectrum reveals the presence of PS segments III-1 (Figure III-4). Chemical shifts at $\delta = 6.3$-7.2 and 0.5-2.5 ppm are assigned to protons of phenyl ring and aliphatic chain protons connected to the phenyl (peak d and b, respectively). The second spectrum confirms the presence of divinyl groups segments in which their protons show at the ranges 5.5-5.7 (peak e) and 5.8-6.09 (peak f) ppm. However, the number average molecular weight ($M_{n,NMR}$) of the resulted polymer III-2 determined from the $^1$H NMR doesn’t agree with the theoretical molecular weight ($M_{n,\text{theo}}$) calculated from the ratio [Styrene]$_o$/[s-BuLi]$_o$. The higher molecular weight of the obtained polymer III-2 indicates that the divinyl groups were not connected to the PS.

Figure III-4. $^1$H NMR spectra for PS (III-1), functionalized PS (III-2), in CDCl$_3$ at 400 MHz.
To investigate, several experiments are conducted considering large excess of Cl$_3$SiCH$_3$ and Grignard reagent. In addition, stirring time is considered from one day to 90 days after the addition of Grignard reagent (Table III-1). Meanwhile, an aliquot is taken to examine the reaction by $^1$H NMR measurements and SEC analysis. Yet, functionalized PS with divinyl silane is not formed.

<table>
<thead>
<tr>
<th>Table III-1. Attempt to synthesize divinyl silane PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entry</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
</tbody>
</table>

Although SEC traces show symmetrical peaks of PS, PS with Cl$_3$SiCH$_3$, and PS with Grignard reagent (Figure III-5, a, b, and c, respectively), the $^1$H NMR results don’t fairly fit with SEC results. This means that the PS wasn’t terminated with divinyl silane. As results, we couldn’t proceed with hydroboration and polyhomologation.

![SEC analysis of PS (a).](image-url)
Figure III-5. SEC traces of PS after adding Cl$_3$SiCH$_3$ (b) and Grignard reagents (c), respectively.

3.2.3. Conclusions

In summary, synthesis of the functionalized PS with divinyl silane by anionic polymerization HVT is not obtained and hence hydroboration and polyhomologation are not preceded. Thus, 3-miktoarm star PS(PM-OH)$_2$ has not achieved by this method. Since linking agent Cl$_3$SiCH$_3$ has not led to divinyl PS, dichloromethylvinyl silane was considered as alternative linking agent.
3.3. Attempt to Synthesize PS-Si(Vinyl)$_2$CH$_3$ from Dichloromethylvinyl silane by Anionic Polymerization High Vacuum Techniques

3.3.1. Experimental Section

The same experimental procedures of section 3.2.1 were applied here. Instead, dichloromethylvinyl silane was used as a linking agent to terminate the living chain ends PS (Scheme III-6).

![Scheme III-6. Attempt to synthesize PS-Si(Vinyl)$_2$CH$_3$ from Cl$_2$Si(Vinyl)CH$_3$](image)

3.3.2. Results and Discussion

The $^1$H NMR spectrum of PS after the addition of Grignard reveals the chemical shifts of the presence of PS segments (Figure III-6). The protons of the aromatic ring are assigned to peak d, and the protons of the aliphatic chain are assigned to peak b. The protons of divinyl groups signals appear at chemical shifts $\delta = 6.1$-$5.7$ ppm. However, the molecular weight of the obtained PS estimated from the $^1$H NMR is ($M_{n,\text{NMR}} = 87$ kg mol$^{-1}$) which is three times more than the theoretical values ($M_{n,\text{theo}} = 23$ kg mol$^{-1}$).
Further evidence for the formation of triple $M_w$ of PS was obtained from the SEC analysis. It shows one peak of PS (Figure III-7, a). After terminating the living PS with the linking agent $\text{Cl}_2\text{Si(Vinyl)CH}_3$, the SEC measurements show two peaks indicating to the presence of two polymers (Figure III-7, b). The peak at retention volume 14-15 mL, is assigned to one arm of PS and $M_{n,SEC} = 27$ kg mol$^{-1}$ is fairly fits the $M_{n,\text{theo}} = 23$ kg mol$^{-1}$ (Scheme III-6). While the peak at retention volume 12-14 mL is assigned to three arms of PS. It’s $M_{n,SEC} = 84$ kg mol$^{-1}$ found to be three times more than the targeted value (Figure III-7, b). The probable explanation of this result is that the living PS chain ends replaced two chlorines and attacked the vinyl as well forming 3-arm star PS. After addition of Grignard, SEC shows two peaks as well at the same retention volume (Figure III-7, c) indicating to unsuccessful Grignard reaction and formation of the star.
Figure III-7. SEC analysis of PS (a), PS after adding Cl₂Si(Vinyl)CH₃, and Grignard reagents (b) and (c), respectively.
3.3.3 Conclusions

$^1$H NMR and SEC analysis reveals interesting results for the first time in the field of polymer science. 3-arm star PS homopolymers have been formed using anionic polymerization HVT in few minutes using Cl$_2$Si(Vinyl)CH$_3$ as a terminating (linking) agent. Since the objective of this research is to synthesize PM-based copolymers; extra work and investigations on these remarkable results have been postponed to the future work. ATRP is used as a second method to produce the PS arm in the 3-miktoarm star copolymers PS(PM-OH)$_2$ successfully.

3.4. Synthesis of 3-Miktoarm Star PS(PM-OH)$_2$ by Combining ATRP and Polyhomologation

The miktoarm star PS(PM-OH)$_2$ is achieved by using the heterofunctional initiator methyldivinylsilane isobutyl bromide which contains two vinyl sites linked to silane and one isobutyl bromide moiety. The bromide initiates the ATRP of styrene and the divinyl groups are precursors leading to the two PM-OH arms by hydroboration followed by polyhomologation (Scheme III-7).

![Scheme III-7. The heterofunctional initiator methyldivinylsilane isobutyl bromide.](image)

3.4.1. Experimental Section

3.4.1.1. Synthesis of the Initiator CH$_3$(Vinyl)$_2$Si-Isobutylbromide

CH$_3$(Vinyl)$_2$Si-PrOH **III-3** was synthesized as explained previously in section 2.2.1.1. Then, 1.4 g of **III-3** (9.2 mmol) was dissolved in 15 ml of THF followed by the addition of pyridine (0.88 g, 11.1 mmol) (Scheme III-8). The mixture was then cooled down to 0 °C followed by slow addition of 2-bromoisobutyl bromide (2.56 g, 11.1 mmol). The reaction was stirred overnight at room temperature. Then, it was diluted with hexane and washed with brine. The organic phase was collected and dried over MgSO$_4$ followed by filtration and concentration. Flash chromatography on silica gel (eluent: hexane) was used to purify the crude product which was isolated as a yellowish oily product **III-4** (70% yield).$^{21}$

### 3.4.1.2. Synthesis of PS-Si(Vinyl)$_2$CH$_3$ by ATRP

In a 50 ml flame dried Schlenk flask capped with a rubber septum and equipped with a stirring bar and deoxygenated by degasing and backfilling argon three times, CuBr (0.070 g, 0.55 mmol) was added followed by the addition of 5.73 ml of styrene (5.2 g, 50 mmol) (Scheme III-9). Then, 8 ml of toluene as a solvent was charged into the reaction flask.
which then was subjected to two freeze-pump thaw cycles. Then, 0.27 ml of PMDETA (0.23g, 1.35 mmol) was injected in to the reaction flask followed by the addition of the initiator III-4 (0.15 g, 0.5 mmol). The flask then was subjected again to two cycles of freeze-pump thaw. Then, it was immersed in preheated oil bath at 90 °C and stirred overnight. Then, the flask was cooled down with liquid nitrogen bath to stop the polymerization. The mixture was diluted with THF and passed through short silica gel column to remove the residues of copper. The collected solution was concentrated and precipitated into 250 ml of MeOH two times. Then the product III-5 was dried under vacuum and analyzed by ¹H NMR and SEC analysis.61

3.4.1.3. Hydroboration of PS-Si(Vinyl)₂CH₃

In to 50 ml Schlenk flask, PS-Si(Vinyl)₂CH₃ III-5 (0.2 g, 0.025 mmol) was added followed by adding 4 ml of THF. Then, 0.5 ml of freshly prepared thexylborane (0.89 M in THF) was charged slowly into the solution at 0 °C (Scheme III-10). The reaction was stirred at room temperature overnight. Later, a 0.2 ml aliquot was withdrawn and injected into NMR tube followed by the removal of solvent under vacuum and the addition of 0.5 ml of CDCl₃ for ¹H NMR analysis which confirms the absence of vinyl groups indicating successful hydroboration and formation of III-6. Then, excess of
degased MeOH was added and stirred for 10 minutes followed by the removal of the solvents under vacuum.

3.4.1.4. Polyhomologation Using PS-Si(CH₃)(B-Thexyl) as Initiator

![Scheme III-11. Synthesis of 3-miktoarm star copolymers PS(PM-OH)₂.](image)

To the hydroboration flask, 8 ml of the ylide (1.05 M in toluene) was injected and stirred at preheated oil bath at 90 °C (Scheme III-11). After 2 hours, a 1 ml aliquot of the reaction mixture was withdrawn and added to water containing phenolphthalein indicator which resulted in colorless solution indicating the consumption of the ylide. Then, the solution was treated with 0.3 g of TAO·2H₂O and stirred overnight at 80 °C. Later, the mixture was cooled down, concentrated, precipitated in cold MeOH and filtrated. Then, the polymer III-8 was dried under vacuum and analyzed by ¹H NMR and SEC analysis.

3.4.2. Results and Discussion of the Synthesized PS(PM-OH)₂

The synthesis of the initiator CH₃(Vinyl)₂Si-isobutyl bromide III-4, PS-Si(Vinyl)₂CH₃ III-5, PS-Si-B III-6 and the miktoarm star copolymers PS(PM-OH)₂ III-8 are illustrated in Schemes III-8, 9, 10, 11, respectively. First the ¹H NMR of the initiator CH₃(Vinyl)₂Si-isobutyl bromide III-4 reveals the presence of vinyl groups protons of which are shown at chemical shifts δ = 6.18-6.13 and 5.7-5.8 ppm peak g and f,
respectively (Figure III-8). In addition, chemical shift at δ = 4.1 ppm is assigned to the protons of the methylene group linked to hydroxyl group. The methyl groups protons shown at chemical shift at δ = 1.9 ppm. Moreover, chemical shift at δ = 1.7-1.6 and 0.7-0.6 ppm are assigned to the protons of methylene groups (–CH2–CH2–Si, peak c and b, respectively). Finally, chemical shift at δ = 0.19 ppm is attributed to methyl group protons.

Figure III-8. 1H NMR spectrum of methyldivinylsilane isobutyl bromide III-6 in CDCl3 at 400 MHz.

The first 1H NMR spectrum of PS-Si(Vinyl)2CH3 III-5 (Figure III-9) revealed the presence of characteristic chemical shifts of PS and vinyl groups segments. The presence of PS segments is confirmed by chemical shifts at δ =7.28-6.32 and 2.28-1.18 ppm which are assigned to the phenyl ring protons and aliphatic chain protons linked to the phenyl
(peak of i and h, respectively). In addition, chemical shifts at $\delta = 6.18\text{-}5.71$ ppm are assigned to the protons of vinyl groups, (peak g and f respectively). The second spectrum is assigned to PS-Si(CH$_3$)(B-Thexyl) III-6. The absence of vinyl group’s protons indicates complete hydroboration between the vinyl groups and thexylborane and the B-thexyl-silaboracyclic has been formed. The third spectrum reveals the presence of characteristic chemical shifts for the PM and PS. Chemical shifts at $\delta = 1.8\text{-}1.1$ ppm are assigned to PM protons. Furthermore, chemical shift at $\delta = 3.3$ ppm are assigned to the methylene group adjacent to the hydroxyl group. These results confirm that both polymerizations, ATRP and polyhomologation, were initiated from CH$_3$(Vinyl)$_2$Si-isobutyl bromide III-4

Figure III-9.$^1$H NMR spectra of PS-Si(Vinyl)$_2$CH$_3$ (III-5), PS-Si(CH$_3$)(B-Thexyl) (III-6) in CDCl$_3$ at 400 MHz ,and PS(PM-OH)$_2$ (III-8) in $d$-toluene at 600 MHz.
Further evidence, SEC traces (Figure III-10) show unimodal distributions of PS-Si(Vinyl)$_2$CH$_3$ **III-5** and the miktoarm star PS(PM-OH)$_2$ **III-8** which means the initiator CH$_3$(Vinyl)$_2$Si-isobutyl bromide **III-4** was definitely connected to the PS and (PM-OH)$_2$ arms. The peak of **III-5** appears at retention volume 14.5-16.5 mL. While the miktoarm star PS(PM-OH)$_2$ **III-9** shows at 11.5-15.5 mL which indicates the increase in the molecular weight of the resultant copolymer. $M_{n,SEC} = 6.2$ kg mol$^{-1}$ for **III-5** is close to $M_{n, theo} = 10$ kg mol$^{-1}$.

![SEC traces of PS-Si(Vinyl)$_2$CH$_3$ and the miktoarm star PS(PM-OH)$_2$ in TCB at 150 °C.](image)

**Figure III-10.** SEC traces of PS-Si(Vinyl)$_2$CH$_3$ and the miktoarm star PS(PM-OH)$_2$ in TCB at 150 °C.

DSC measurement was performed to analyze the thermal properties of the functionalized linear PS **III-5** and the 3-miktoarm star PS(PM-OH)$_2$ **III-8** (Figure III-11). The melt temperatures of the linear PS and the miktoarm clearly appear in the DSC (second heating curve) at 108 and 115 °C, respectively. The crystallinity of PS arm after
the formation of the 3-miktoarm star has been prevented due to the melting process of PM arms. The crystallinity of the star is 31.55%.

![Figure III-11. DSC traces (second heating curves) of the linear PS-Si(Vinyl)$_2$CH$_3$ and miktoarm star PS(PM-OH)$_2$.](image)

3.4.3. Conclusions

To summarize, this chapter includes two methods to synthesize the miktoarm star PS(PM-OH)$_2$. The first method was based on synthesizing macroinitiator PS by anionic polymerization high vacuum technique. However, it was not achieved successfully. Instead, 3-arm PS was formed accidentally. The second method is by combining ATRP and polyhomologation using a designed and synthesized heterofunctional silane initiator to facilitate the formation of the miktoarm star. New 3-miktoarm star PS(PM-OH)$_2$ copolymers was successfully synthesized for the first time. The structure of the produced
polymer was confirmed by $^1$H NMR and SEC. In addition, its thermal properties were examined by DSC.
GENERAL CONCLUSIONS

In conclusion, three novel 3-miktoarm star copolymers \{PCL(PM-OH)\_2, Br-PCL-(PM-OH)\_2, and PS(PM-OH)\_2\} were successfully synthesized by using a new and general strategy which opens new horizons in the synthesis of well-defined PE-based polymeric materials with different macromolecular architectures. This strategy is based on the \textit{in situ} formation of B-thexyl-silaboracyclic groups which serve as initiators for the polyhomologation of dimethyl sulfoxonium methyldide to afford well-defined PE. Combination with ring opening polymerization of \(\varepsilon\)-caprolactone or atom transfer radical polymerization of styrene leads to the synthesized miktoarm star copolymers.

Molecular characterization of all precursors and final products by NMR and SEC confirmed the successful synthesis of the star copolymers. Further confirmation was obtained by differential scanning calorimetry.

Finally and unexpectedly, we found a new way to prepare a 3-arm star polystyrene but we have not continued to fractionating the crude product and characterizing the purified star since it was not the topic of this research.
REFERENCES

(5) Boffa, L. S.; Novak, B. M. Chem. Rev. 2000, 100, 1479
(23) Negishi, E.; Brown, H. C. Synthesis. 1974, 77
(27) Zhang, L; Pratt, R; Nederberg, F; Horn, W; Rice, J; Waymouth, Wade, C; Hedrick, J. Macromolecules, 2010, 43, 1660–1664
(46) Schulz GV.Z. Elektrochem. 1956, 60, 199
(47) J.M.G. Cowie, Valeria Arrighi, Polymers: Chemistry and Physics of Modern Materials. Third addition

(60) Roovers, J.; Toporowski, P. M. *Macromolecules*, **1983**, *16*, 843-849

**LIST OF ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BH$_3$THF</td>
<td>Borane tetrahydrofurane complex</td>
</tr>
<tr>
<td>TAO2H$_2$O</td>
<td>Trimethylamine N-oxide dehydrate</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>Deuterochloroform</td>
</tr>
<tr>
<td>BH$_3$S(CH$_3$)$_2$</td>
<td>Borane dimethyl sulfide complex</td>
</tr>
<tr>
<td>Et$_3$B</td>
<td>Triethyl borane</td>
</tr>
<tr>
<td>TCB</td>
<td>Trichlorobenzene</td>
</tr>
<tr>
<td>Cl$_3$SiCH$_3$</td>
<td>Trichloromethylsilane</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofurane</td>
</tr>
<tr>
<td>s-BuLi</td>
<td>sec-Butyllithium</td>
</tr>
<tr>
<td>CaH$_2$</td>
<td>Calcium hydride</td>
</tr>
<tr>
<td>NaH</td>
<td>Sodium hydride</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>Sulphuric acid</td>
</tr>
<tr>
<td>PSLi</td>
<td>Polystyryllithium</td>
</tr>
<tr>
<td>n-BuLi</td>
<td>n-Butyllithium</td>
</tr>
<tr>
<td>PM-OH</td>
<td>Polymethylene hydroxyl</td>
</tr>
<tr>
<td>PCL-(PM-OH)$_2$</td>
<td>Polycaprolactone dipolymethylene hydroxyl</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PS(PM-OH)$_2$</td>
<td>Polystyrene dipolymethylene hydroxyl</td>
</tr>
<tr>
<td>$M_n$ NMR</td>
<td>Number average molecular weight estimated from $^1$H NMR</td>
</tr>
<tr>
<td>$M_n$ theo</td>
<td>Theoretical number average molecular weight</td>
</tr>
<tr>
<td>PDI</td>
<td>Polydispersity index</td>
</tr>
<tr>
<td>PBd-1,4</td>
<td>1,4-Polybutadiene</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>CuBr (I)</td>
<td>copper(I) bromide</td>
</tr>
<tr>
<td>PMDETA</td>
<td>Pentamethyldiethylenetriamine</td>
</tr>
<tr>
<td>PM</td>
<td>Polymethylene</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>------------------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>ATRP</td>
<td>Atom transfer radical polymerization</td>
</tr>
<tr>
<td>'BA</td>
<td>tert-Butyl acrylate</td>
</tr>
<tr>
<td>MIs</td>
<td>Macroinitiators</td>
</tr>
<tr>
<td>PM-MIs</td>
<td>Polymethylene macroinitiators</td>
</tr>
<tr>
<td>RAFT</td>
<td>Radical atom-fragmentation polymerization</td>
</tr>
<tr>
<td>ROMP</td>
<td>Ring opening metathesis polymerization</td>
</tr>
<tr>
<td>PE-MM</td>
<td>Polyethylene macromonomer</td>
</tr>
<tr>
<td>BF$_3$OEt</td>
<td>Boron trifluoride diethyl etherate</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>ROP</td>
<td>Ring opening polymerization</td>
</tr>
<tr>
<td>CL</td>
<td>$\varepsilon$-Caprolactone</td>
</tr>
<tr>
<td>PPA</td>
<td>3-Phenyl-1-propanol</td>
</tr>
<tr>
<td>DDP</td>
<td>Diphenyl phosphate</td>
</tr>
<tr>
<td>PM-$_b$-PCL-$_b$-PAA</td>
<td>Polymethylene block polycaprolactone block polyacrylic acid</td>
</tr>
<tr>
<td>PCL</td>
<td>Polycaprolactone</td>
</tr>
<tr>
<td>CH$_3$MgCl</td>
<td>Methylmagnesiumchloride</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>Ammonium chloride</td>
</tr>
<tr>
<td>MgSO$_4$</td>
<td>Magnesium sulfate</td>
</tr>
<tr>
<td>PE</td>
<td>Petroleum ether</td>
</tr>
<tr>
<td>EA</td>
<td>Ethyl acetate</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>Sodium sulfate</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>Et$_3$N</td>
<td>Trimethylamine</td>
</tr>
<tr>
<td>CH$_3$(Vinyl)$_2$Si-PrOH</td>
<td>3-(methyldivinylsilane)propan-1-ol</td>
</tr>
<tr>
<td>PCL-Si(Vinyl)$_2$CH$_3$</td>
<td>Polycaprolactone methyldivinyl silane</td>
</tr>
<tr>
<td>PCL-Si(CH$_3$)(B-Thexyl)</td>
<td>B-thexyl-silaboracyclic polycaprolactone</td>
</tr>
<tr>
<td>Br-PCL-(PM-OH)$_2$</td>
<td>2-Bromoisobutyl polycaprolactone dipolymethylene hydroxyl</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Compound Name</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------------------------------------</td>
</tr>
<tr>
<td>HVT</td>
<td>High vacuum technique</td>
</tr>
<tr>
<td>Cl₂Si (Vinyl) CH₃</td>
<td>Dichloromethylvinyl silane</td>
</tr>
<tr>
<td>PS-Si(Vinyl)₂CH₃</td>
<td>Polystyrene methyldivinyl silane</td>
</tr>
<tr>
<td>Mg</td>
<td>Magnesium</td>
</tr>
<tr>
<td>DBMg</td>
<td>Di-n-butylmagnesium</td>
</tr>
<tr>
<td>MMA</td>
<td>Methyl methacrylate</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl methacrylate</td>
</tr>
<tr>
<td>CH₃(Vinyl)₂Si-isobutyl bromide</td>
<td>3-(methyldivinylsilane)propyl 2-bromo-2-methylpropanoate</td>
</tr>
<tr>
<td>PS-Si(CH₃)(B-Thexyl)</td>
<td>B-thexyl-silaboracyclic polystyrene</td>
</tr>
</tbody>
</table>
LIST OF SCHEMES

Scheme I-1. Polyhomologation and olefin polymerization ........................................9
Scheme I-2. The homologation mechanism.................................................................10
Scheme I-3. Polyhomologation mechanism...............................................................10
Scheme I-4. Three arm and two arm stitching reactions ...........................................11
Scheme I-5. An example of three-arm stitching reaction..........................................11
Scheme I-6. Combination of polyhomologation and ATRP .......................................12
Scheme I-7. Combination of polyhomologation and ROMP .....................................13
Scheme I-8. Initiator-based topological control.........................................................13
Scheme I-9. Combination of anionic polymerization and polyhomologation ............14
Scheme I-10. Oligomeric cyclic ketone I-16 resulting from polyhomologation of ylide I-1
with thexyl borane I-14 ...............................................................................................14
Scheme I-11. A novel strategy based on the in situ formation of B-thexyl-silaboracyclic I-17
.........................................................................................................................................15
Scheme I-12. Synthesis of trimethylsulfoxonium chloride........................................18
Scheme I-13. Synthesis of dimethylsulfoxonium methylide......................................19
Scheme I-14. Synthesis of thexylborane .....................................................................19
Scheme I-15. Synthesis of PM-OH by using thexylborane, borane dimethyl sulfide
complex and, triethylborane as initiators .................................................................20
Scheme II-1. An activated monomer mechanism for DPP catalyzed ROP of CL using
PPA...............................................................................................................................26
Scheme II-2. Heterofunctional initiator 3-(methyldivinylsilane)propan-1-ol...............28
Scheme II-3. Synthesis of the initiator 3-(methyldivinylsilane)propan-1-ol...............28
Scheme II-4. ROP of CL initiated by CH₃(Vinyl)₂Si-PrOH and catalyzed by
DPP.............................................................................................................................29
Scheme II-5. Hydroboration of PCL-Si(Vinyl)₂CH₃.................................................30
Scheme II-6. Synthesis of 3-miktoarm star copolymers PCL(PM-OH)₂........................31
Scheme II-7. Three possible sites in PCL-Si(Vinyl)₂CH₃ to react with
thexylborane...............................................................................................................36
Scheme II-8. Synthesis of Br-PCL(PM-OH)₂………………………………………………………36
Scheme III-1. Anionic polymerization mechanism of vinyl monomers using metal alkyl initiators……………………………………………………………………………………………….41
Scheme III-2. ATRP mechanism ……………………………………………………………………42
Scheme III-3. Two methods used to synthesize 3-miktoarm star copolymers PS(PM-OH)₂; anionic polymerization HVT (not successful ), and incorporation of ATRP and polyhomologation (successful) via heterofunctional initiator ………………………….43-44
Scheme III-4. Synthesis of living PS chain ends……………………………………………………44
Scheme III-5. Terminating living chain ends PS with Cl₃SiCH₃……………………………………47
Scheme III-6. Attempt to synthesize PS-Si(Vinyl)₂CH₃ from Cl₂Si(Vinyl)CH₃………………………………………………………………………………………………………………51
Scheme III-7. Heterofunctional initiator methyldivinylsilane isobutyl bromide……………54
Scheme III-8. Synthesis of methyldivinylsilane isobutyl bromide…………………………55
Scheme III-9. The synthesis of PS-Si(Vinyl)₂CH₃…………………………………………………55
Scheme III-10. Synthesis of PS-Si(CH₃)(B-Thexyl) III-6……………………………………56
Scheme III-11. Synthesis of 3-miktoarm star copolymers PS(PM-OH)₂………………….57
LIST OF FIGURES AND TABLES

Table 1. Results of PM-OH synthesized by polyhomologation with three different borane initiators

Figure I-1. $^1$H NMR spectrum of the linear PM-OH synthesized by reacting the ylide with thexyl borane in C$_6$D$_6$ at 600 MHz

Figure I-2. SEC traces of the obtained PM-OH obtained by using various borane initiators, thexyl borane (a), borane dimethyl sulfide complex (b), and triethylborane (c)

Figure I-3. DSC trace (second heating curve) of linear PM-OH produced using Et$_3$B initiator

Figure II-1. $^1$H NMR spectrum of the CH$_3$(Vinyl)$_2$Si-PrOH at 400 MHz in CDCl$_3$

Figure II-2. $^1$H NMR spectra of the linear PCL-Si(Vinyl)$_2$CH$_3$ (II-5) in CDCl$_3$ at 400 MHz, and PCL(PM-OH)$_2$ (II-8) in d-toluene at 600 MHz

Figure II-3. SEC traces of PCL-Si(Vinyl)$_2$CH$_3$ in THF at room temperature (a), and miktoarm star copolymers PCL(PM-OH)$_2$ (b) in C$_6$H$_6$ at 150°C

Figure II-4. DSC traces (second heating curves) of the linear PCL and miktoarm star PCL(PM-OH)$_2$

Figure II-5. $^1$H NMR spectra of PCL-Si(Vinyl)$_2$CH$_3$ (II-5), Br-PCL-Si(Vinyl)$_2$CH$_3$ in d-benzene at 500 MHz (II-9), Br-PCL-Si(CH$_3$)(B-Thexyl) in CDCl$_3$ at 400 MHz (II-10), and Br-PCL(PM-OH)$_2$ in d-toluene at 600 MHz (II-11)

Figure II-6. SEC traces of the synthesized PCL-Si(Vinyl)$_2$CH$_3$ in THF at room temperature (a), and Br-PCL(PM-OH)$_2$ in TCB at 150°C

Figure II-7. DSC traces (second heating curves) of the linear Br-PCL and the 3-miktoarm star Br-PCL-(PM-OH)$_2$

Figure III-1. Apparatus for the preparation of living PS

Figure III-2. Apparatus for distilling Cl$_3$SiCH$_3$ (left), and introducing vinylmagnesium chloride (right)

Figure III-3. Apparatus for terminating living PS
Figure III-4. $^1$H NMR spectra for PS (III-1), and functionalized PS (III-2) in CDCl$_3$ at 400 MHz………………………………………………………………………………….48

Table III-1. Attempt to synthesize divinyl silane PS…………………………………….49

Figure III-5. SEC traces of PS (a), PS after adding Cl$_3$SiCH$_3$ and Grignard reagents, (b) and (c) respectively………………………………………………………………………………….49-50

Figure III-6. $^1$H NMR of PS after the addition of Grignard reagent…………………………...52

Figure III-7. SEC analysis of PS (a), PS after adding Cl$_3$SiCH$_3$ (b) and Grignard reagents (c), respectively………………………………………………………………………………53

Figure III-8. $^1$H NMR spectrum of methyldivinylsilane isobutyl bromide III-6 in CDCl$_3$ at 400MHz……………………………………………………………………………………58

Figure III-9. $^1$H NMR spectra of PS-Si(Vinyl)$_2$CH$_3$ (III-5), PS-Si(CH$_3$)(B-Thexyl) (III-6) in CDCl$_3$ at 400 MHz, and PS(PM-OH)$_2$ (III-8) in d-toluene at 600 MHz………………….59

Figure III-10. SEC traces of PS-Si(Vinyl)$_2$CH$_3$ (III-5), and the 3-miktoarm star PS(PM-OH)$_2$ (III-8)…………………………………………………………………………………………60

Figure III-11. DSC traces (second heating curves) of the linear PS-Si(Vinyl)$_2$CH$_3$ and 3-miktoarm star PS(PM-OH)$_2$……………………………………………………………………….61