LIVING CARBOCATIONIC POLYMERIZATION OF ISOBUTYLENE BY EPOXIDE/LEWIS ACID SYSTEMS: THE MECHANISM OF INITIATION

A Dissertation

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirement for the Degree

Doctor of Philosophy

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May, 2009
ABSTRACT

The objective of the work presented in this dissertation was to generate a fundamental understanding of the synthesis of star-branched polyisobutylanes (PIBs) arising from hexaepoxysqualene (HES)/Lewis acid (LA) initiating systems, using BCl₃ and TiCl₄ as LAs.

The understanding of initiation and propagation mechanisms by HES is crucial to control the number of arms and arm lengths of star PIBs expected from this initiator. The initiation by monofunctional epoxides, such as α-methylstyrene epoxide (MSE), 1,2-epoxy-2,4,4-trimethylpentane (TMPO-1), and 2,3-epoxy-2,4,4-trimethylpentane (TMPO-2), was investigated. In situ FTIR spectroscopy, which was highly utilized in this research, provided valuable information. Most importantly, the ability to identify the head group by in situ FTIR of growing PIB chains initiated by an epoxide, i.e. the –C–O–LA complex, contributed significantly to the understanding of initiation of IB polymerization. This technique allowed the monitoring of the rate of initiation with the multifunctional epoxy initiator.

Previous research showed that TiCl₄ gave 40% initiating efficiency in conjunction with the aromatic epoxy initiator MSE, whereas the aliphatic initiators TMPO-1 and TMPO-2 gave only 3 and 10% efficiency, respectively. In this research it was found that BCl₃ is more efficient with the aliphatic initiator, TMPO-1, yielding an
asymmetric telechelic PIB carrying an $\alpha$-primary OH and an $\omega$-tertiary Cl functional group with 70% initiator efficiency, while MSE gave only 1-4% efficiency. The TMPO-2/BCl$_3$ system gave 20% initiator efficiency. The various initiation mechanisms were discussed.

IB polymerization was successfully initiated by HES in the presence of excess BCl$_3$ and monitored by $\textit{in situ}$ FTIR spectroscopy. The gradual increase of the IR band assigned to the –C–O–BCl$_2$ group demonstrated that slow initiation was occurring. Chain extension with the HES/BCl$_3$ initiated PIB was achieved leading to high molecular weight PIBs in the presence of TiCl$_4$.

It was also demonstrated for the first time that BCl$_3$ invariably leads to $\beta$-proton expulsion, leading to chain transfer in IB polymerization.

In addition, 1,2-epoxycyclohexane and epoxycyclohexyl-functional siloxanes, i.e. epoxycyclohexylisobutyl polyhedral oligomeric silsesquioxane (POSS) and $\textit{bis}[3,4-(epoxycyclohexyl)ethyl]tetramethyldisiloxane$, were found to be initiators for the polymerization of IB. 1,2-epoxycyclohexane/TiCl$_4$ was an efficient initiating system for the IB polymerization yielding up to 45% initiator efficiency. It was proposed that initiation of IB polymerization involves an $S_N2$ reaction between IB and TiCl$_4$-coordinated epoxide.
DEDICATION

I dedicate this dissertation to the loving memory of my father, Ismail Hayat.
ACKNOWLEDGEMENTS

I would like to express my gratitude to my advisor Dr. Judit E. Puskas for her guidance, support and encouragement throughout the course of this research. I would like to thank all my group members for their help. I would like to thank my graduate committee members, Dr. Roderic P. Quirk, Dr. Joseph P. Kennedy, Dr. Li Jia and Dr. Chrys Wesdemiotis. I would also like to thank Dr. David A. Modarelli for helpful discussions in computational approach of epoxide reactions, Dr. Goy Teck Lim for his help in TEM analysis, and Dr. Val Krukonis and Dr. Paula Wetmore for supercritical fluid fractionation.

I would like to acknowledge financial support by LANXESS Inc., Canada, and by the National Science Foundation under DMR-0509687. I would like to thank The Ohio Board of Regents and The National Science Foundation (CHE-0341701 and DMR-0414599) for funds used to purchase the NMR instrument used in this work.

Finally, I would like to thank my family for their support throughout my education and my husband, Mehmet, whose unconditional love and support have helped to make this possible.
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CHAPTER I
INTRODUCTION

This research was part of a Research Agreement between The University of Akron and LANXESS Inc. to generate fundamental knowledge in polymer structure-property relationships using model structures based on polyisobutylene (PIB) synthesized by living carbocationic polymerization. The R&D Department of LANXESS Inc., in Sarnia, is focused on research related to the production of butyl rubber, i.e., a copolymer of isobutylene (IB) and a small amount (1-2%) of isoprene, which is the base polymer for halobutyl elastomers. PIB can be used as a rheology model of butyl and halobutyl rubbers. Because of its fully saturated backbone PIB has outstanding chemical, oxidative and thermal stability which makes it ideally suitable as a model to study mechanical and viscoelastic properties of elastomers, and to correlate properties with structure. In the framework of this collaborative research project, star-branched PIB model structures were to be synthesized by living carbocationic polymerization for systematic structure-property relationship studies. This will provide invaluable tools for new product development in an industrial setting.

A part of this collaborative project which is discussed in the dissertation was focused on the synthesis and characterization of star-branched PIB. Isobutylene (IB) can only be polymerized by a carbocationic mechanism. For anionic polymerizability, there
must be substituents on the double bond that can stabilize the negative charge that
develops in the transition state for monomer addition. IB cannot be polymerized by an
anionic mechanism because of the instability of the resulting carbanion r electron sulting
from the releasing inductive effect of the methyl substituents. Theoretically, isobutylene
can be polymerized by radical polymerization as any alkene; however, a high molecular
weight polymer cannot be obtained. IB has low radical reactivity because of the
stabilizing effect of the methyl substituents on the tertiary radical via hyperconjugation.
Most importantly, IB has easily abstractable H-atoms that participate in chain transfer. In
the case of carbocationic polymerization, the active center is a tri-coordinated
carbocation.1,2 The most important IB-based products range from viscous oils to high
molecular weight elastomers, such as butyl and halobutyl rubbers, i.e., chlorobutyl and
bromobutyl rubber.1 Butyl and halobutyl rubbers are used as inner tubes or inner liners in
vehicle tires because of their low permeability towards gases and moisture.3 They are also
used as machinery mounts to reduce vibration because of their very high damping (high
tan δ).3 They also have outstanding chemical, thermal and oxidative stability, which
make them suitable as seals, adhesives, condenser caps, and pharmaceutical stoppers.3
PIB-based thermoplastic elastomers found applications in the field of biomedicine as
implants because of their biocompatibility.4

Carbocationic polymerization can be initiated by a variety of chemical and
physical methods. Examples include initiation by Brönsted acids, Lewis acids, Lewis
acids in conjunction with a proton or carbenium ion source, UV or γ-irradiation,
photochemical reactions, and high electric field.5 Brönsted acids are potential sources of
protons and are, by definition, initiators of carbocationic polymerization. The acid strength of a Brönsted acid, characterized by the following equation,

$$\text{HA} \rightarrow \text{H}^+ + \text{A}^- \quad (1.1)$$

and the nucleophilicity of the counteranion derived from the Brönsted acid determine its ability to initiate carbocationic polymerization. If the nucleophilicity of the conjugate base (counteranion, $\text{A}^-$) is high, initiation may rapidly be followed by ion pair collapse, which is equivalent to termination of a propagating chain:

$$\text{H}^+ + \text{A}^- + \text{C} = \text{C} \rightarrow \text{H} + \text{C} - \text{C}^+ + \text{A}^- \rightarrow \text{H} - \text{C} - \text{C} - \text{A} \quad (1.2)$$

Generally, Brönsted acids produce high molecular weight products with highly reactive monomers, for example, $N$-vinylcarbazole. Solvation by polar solvents helps to stabilize the charged intermediates and to delay the collapse of the ion pair, leading to high MW polymers.

Certain Lewis acids are able to initiate the carbocationic polymerization in the absence of proton or cation source, which was called “direct initiation”. Hunter and Yohe proposed the formation of zwitterions by metalation for IB polymerization in the presence of AlCl$_3$:

$$\text{AlCl}_3 + \text{CH}_2=\text{C(CH}_3)_2 \rightarrow \text{Cl}_3\text{Al}-\text{CH}_2-\text{C(CH}_3)_2 + \text{M} \rightarrow \text{Cl}_3\text{Al}\text{CH}_2\text{C(CH}_3)_2 \quad (1.3)$$

Later Korshak and Lebedev suggested auto-ionization of a Lewis acid dimer, followed by its addition to monomer:

$$\text{Mt}_2\text{X}_n \rightleftharpoons \text{MtX}_n^+ + \text{MtX}_n^- \quad (1.4)$$
The combination of Lewis acids with a proton or cation sources results in a significantly more efficient initiating system. Proton or cation sources could be moisture, Brönsted acids, alkyl or aryl halides, esters, ethers, peroxides, or epoxides. Lewis acid cinitiators provide a dynamic equilibrium between the dormant polymer chain and active growing carbocations, which is the key to controlled carbocationic polymerization. The mechanism of the initiation with Lewis acid/carbocation source can be written as follows:

Ionization:

\[
R-Y + MtX_n \rightleftharpoons R^+ /\!\!/ MtX_nY^- \rightleftharpoons R^+ + MtX_nY^- \tag{1.5}
\]

\[
R-X + MtX_{n-1}Y
\]

Initiation:

\[
R^+ /\!\!/ MtX_nY^- \rightleftharpoons R^+ + MtX_nY^- \tag{1.6}
\]

\[
+ M \downarrow \rightleftharpoons + M \downarrow
\]

\[
RM^+ /\!\!/ MtX_nY^- \rightleftharpoons RM^+ + MtX_nY^- 
\]

where \(R^+ /\!\!/ MtX_nY^-\) and \(R^+\) represent paired and free ions, respectively. The above equilibria are strongly dependent on the nucleophilicity of the \(Y\) group, the strength of the Lewis acid, the stability of the carbenium ion, the stability/nucleophilicity of the counteranion, and the type of the polymerization medium. The strength of a Lewis acid generally increases with increasing atomic number within the same group (\(BCl_3 < AlCl_3 < GaCl_3\)), with the oxidation state (\(SnCl_2 << SnCl_4\)), and with ligands in the following order: aryl, alkyl << carboxyl, alkoxy  << I < Br < Cl < F. Kennedy introduced the
terms “initiator” and “coinitiator” instead of “catalyst” and “co-catalyst”. He argued that since the entities that induce the carbocationic polymerizations are usually consumed during polymerization and become part of the polymer, the terms “catalysis” or “catalyst” are incorrect in the view of the classical concept of catalysis.

Controlled/living carbocationic polymerization of IB was achieved only about 30 years ago. Carbocationic polymerization was considered uncontrolled because of the high reactivity of the carbocations, which tend to have irreversible termination and chain-transfer reactions via β-proton expulsion.\(^{12}\) Although living conditions in carbocationic polymerization had been observed experimentally as early as 1974,\(^{13,14}\) the breakthrough was the successful synthesis of high molecular weight and nearly uniform PIB by Kaszas and Puskas in Kennedy’s group\(^{15}\) The control of the number and type of initiating species and the dynamics of the equilibria involved in propagation are two important concepts to be understood to achieve living polymerization. The importance of reversible termination was first outlined by Kennedy et al.\(^{16}\) by using initiating systems with Lewis acids that supply an appropriate nucleophilic counterion:

\[
C^\ominus + MtX_{n+1}C^+ \rightleftharpoons C^\ominus MtX_n + C^\ominus X \tag{1.7}
\]

Controlled initiation is one of the important elements of controlled carbocationic polymerization. As mentioned earlier the initiating systems mostly used in controlled carbocationic polymerization are Lewis acids in conjunction with a carbocation source. The inverse relationship between the stability and reactivity of carbenium ions plays an important role in the initiation as well as in propagation step. As an optimum combination of carbocation stability and monomer nucleophilicity is necessary for effective polymerization, it is essential to match the stability of the propagating
carbenium ion with that of the initiating species to achieve high initiator efficiency.\textsuperscript{1}

Successful initiators in living carbocationic polymerization of IB include esters,\textsuperscript{17} ethers,\textsuperscript{18,19} alkyl and aryl halides,\textsuperscript{15} alcohols,\textsuperscript{20,21} and substituted epoxides.\textsuperscript{22-26}

One of the goals of this dissertation was to understand the mechanism of initiation by hexaepoxysqualene (HES), in conjunction with BCl\textsubscript{3} and TiCl\textsubscript{4} Lewis acid (LA) coinitiators. Since the understanding of initiation and propagation mechanisms from HES is crucial to control the number of arms and arm lengths of the star PIB expected from this initiator, first initiation from monofunctional epoxide/LA systems, such as $\alpha$-methylstyrene epoxide (MSE), 1,2-epoxy-2,4,4-trimethylpentane (TMPO-1), and 2,3-epoxy-2,4,4-trimethylpentane (TMPO-2), was investigated.

In this research it was found that BCl\textsubscript{3}, compared to TiCl\textsubscript{4}, is more efficient with the aliphatic initiator TMPO-1, yielding a telechelic PIB carrying an $\alpha$-primary OH and an $\omega$-tertiary Cl group at 70\% initiator efficiency, while MSE gave only 1-4\% efficiency. Another aliphatic initiator, the TMPO-2/BCl\textsubscript{3} system, was less reactive, yielding 20\% initiator efficiency. The ability to identify the head group of the growing PIB chains initiated by an epoxide, i.e., the polarized $-\text{CO}–\text{LA}$ complex, by \textit{in situ} FTIR is a significant contribution to the understanding of epoxy initiation of IB polymerization. This technique also allowed the monitoring of the rate of initiation with mono- or multifunctional epoxy initiators. Another important contribution is the demonstration that BCl\textsubscript{3} invariably leads to $\beta$-proton expulsion, leading to chain transfer in IB polymerizations. This has not been reported in the literature.
CHAPTER II
BACKGROUND

This research concerned the investigation of delineation of the mechanism of epoxy ring-opening in the presence of Lewis acids, and the use of epoxides as initiators in the living carbocationic polymerization of IB. The background necessary to understand this research is detailed in the sections below.

2.1. Controlled/Living Carbocationic Polymerization of IB

The key to controlled/living carbocationic polymerization of IB is the promotion of an equilibrium between active and dormant chain ends. The significance of reversible termination in order to achieve control over the polymerization was first expressed by the “quasiliving” concept. \(^\text{(2.1)}\)

\[
P_n \times + Y \rightleftharpoons P_n^* \times // X-Y^*
\]

\[
P_n^* \times // X-Y^* + M \rightarrow P_{n+1}^* \times // X-Y^*
\]

This concept was successfully applied to the quasiliving polymerization of IB initiated by the C$_6$H$_5$C(CH$_3$)$_2$Cl (cumylCl)/TiCl$_4$ system by the use of MeCl/Hx (60/40, v/v) solvent mixture at -50 °C. \(^\text{(2.2)}\) Thereafter the living nature of the polymerization has been extensively studied under a variety of conditions, such as different solvent systems, initiators, coinitiators, additives and temperature. The quasiliving polymerization of IB
was first demonstrated by the linear plot of $M_n$ vs. monomer consumption, as shown in Figure 2.1.\textsuperscript{27} Although two propagating species were present due to unavoidable traces of water, protic initiation was virtually eliminated by the use of a large excess of cumyl chloride initiator. It was foreseen that living polymerization of IB could be achieved with a single propagating active center in the total absence of moisture; that was later accomplished by the use of proton traps.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{M_n_vs_monomer_consumption.png}
\caption{\textit{M}_n vs. monomer consumption plot of IB polymerization initiated by cumyl-Cl/TiCl\textsubscript{4} using continuous gaseous monomer addition. \(A = 5.5 \times 10^{-3} \text{ mol/min IB}, [I]_0 = 1 \times 10^{-2} \text{ mol/dm}^3, [\text{TiCl}_4] = 3.6 \times 10^{-2} \text{ mol/dm}^3, T = -50 \degree C\).\textsuperscript{27} Reprinted with permission from \textit{J. Macromol. Sci. Chem.} \textbf{1982-83}, \textit{A18}, 1229-1244. Copyright © 1982 Taylor & Francis.}
\end{figure}

In controlled carbocationic polymerization of IB, the initiating systems are usually Lewis acids (mostly BCl\textsubscript{3} and TiCl\textsubscript{4}) in conjunction with a carbocation source such as alkyl or aralkyl esters, ethers, alcohols, halides and epoxides.\textsuperscript{28} The role of the Lewis acid cointitiators is to activate the carbocation source leading a carbocation that initiates the polymerization, and to reactivate the dormant polymer chain end to produce...
the growing carbocation. Polyisobutlenes (PIB) with tert-Cl chain end are obtained, regardless of the method of termination, by BCl₃ or TiCl₄ coinitiated IB polymerization.

After the first conceptualization of living IB polymerization by reversible termination, several carbocationic sources were examined in the presence of a Lewis acid, generally BCl₃ and TiCl₄, achieving living IB polymerization. Linear and star-branched tert-Cl-telechelic PIBs were synthesized from di-, tri- and tetra-functional acetate initiators.²⁹⁻³² Also, PIBs with Mₙ > 40,000 g/mol and Mₙ/Mₚ ~ 1.1 were readily obtained by ester/TiCl₄ initiated living IB polymerization in CH₃Cl/hexane mixture.³³ It was proposed that when BCl₃ (or TiCl₄) is complexed with the tert-acetate, the strong electron donation toward the Lewis acid facilitates the formation of the electrophilic center. This idea also led to the use of tert-ethers as cationogens for IB polymerization:

![Figure 2.2. Ionization of tert-acetate and tert-ether groups with BCl₃.](image)

(CH₃)₃CH₂C(CH₃)₂OCH₃ and C₆H₅C(CH₃)₂OCH₃ initiated living IB polymerization in the presence of BCl₃ yielding tert-chloride terminated PIB in CH₂Cl₂ at -10 and -30 °C.¹⁹ Similarly to tert-acetate initiators, di- and tri-functional tert-ethers were used with BCl₃ in CH₂Cl₂ or CH₃Cl for the synthesis of linear and three-arm star tert-Cl telechelic PIBs.³⁴,³⁵ The first high molecular weight PIBs with Mₙs up to 120,000-130,000 g/mol and Mₙ/Mₚ ~1.1 were obtained by using the 1,4-bis-(2-methoxy-2-propylbenzene/TiCl₄ system in CH₃Cl/Hx mixture at -80 °C.¹⁸ In view of the structural similarity between tert-ethers and tert-alcohols, the latter were also investigated as
initiators in conjunction with BCl3 for the living polymerization of IB. Mono-, di- tri-functional tert-alcohols such as cumyl alcohol, 2,4,4-trimethyl-2-pentanol, 2,6-dihydroxy-2,4,4,6-tetramethylheptane, and 1,3,5-tri(2-hydroxyisopropyl)benzene were demonstrated to be efficient initiators for the living polymerization of IB in CH3Cl and CH2Cl2 in the range of -10 to -80 °C.20,21 Although the controlled initiation of IB polymerization by the tert-alcohol/BCl3 was discovered in the early 1980s,36 the living nature of the polymerization was recognized only in 1989. Dicumyl chlorides were successfully used for the synthesis of tert-Cl terminated di-telechelic PIBs.37

The addition of electron pair donors and/or proton traps to BCl3 or TiCl4-coinitiated living polymerization of IB enhanced process control and product quality, particularly molecular weight distribution (MWD). It also helped to reduce side reactions, such as indanyl ring formation by intramolecular cycloalkylation when using a cumyl-type initiator that leads to chain transfer (Scheme 2.1). Elimination of indanyl ring formation by a suitable electron pair donor was rationalized by carbocation stabilization or steric hindrance caused by the presence of an electron pair donor in close proximity of the carbocation.38

\[
\text{Indanyl ring formation and proton generation}
\]

\[
\text{Reinitiation by proton}
\]

Scheme 2.1. Indanyl ring formation in cumyl-type initiator/BCl3 system.
The use of a proton trap is very important because of the extreme sensitivity of IB polymerization to cationogenic impurities (mostly H$_2$O) that induce undesirable protic initiation. The role of additives in living IB polymerization will be discussed in detail in the next section.

2.1.1. The Role of Additives in Living IB Polymerization

Two main categories of additives have been introduced and extensively utilized in living cationic polymerization of IB: (1) Lewis bases$^{39}$ (also called as “electron pair donors”$^{15,40}$ or “nucleophiles”;$^{39}$ and (2) proton traps.$^{41}$

The role of these basic additives and the mechanisms of enhanced livingness have been longstanding controversies. The theory of carbocation stabilization by nucleophilic additives through weak nucleophilic interaction was proposed by Higashimura et al.$^{42}$ A similar opinion was also expressed by Kennedy et al.$^{43}$ In contrast to this view, Matyjaszewski proposed that these bases decrease the concentration of active species by reversible formation of non-propagating onium ions, or by complexing with Lewis acids.$^{39}$

It was also argued that the main function of electron donors is proton trapping, not carbocation stabilization.$^{41}$ If protic initiation is prevented by trapping protic impurities by a hindered base, e.g. 2,6-di-$\text{tert}$-butylpyridine (D$t$BP), which is unable to stabilize the carbocationic center, aliphatic $\text{tert}$-chlorides, e.g. TMPCl, less efficient initiators relative to protic impurities, are able to initiate polymerization of IB.$^{44}$ In this study, the authors verified by $^1$H NMR spectroscopy that the products are $\omega$-chloro PIBs and that terminal unsaturation is absent which contradicts a previous report which showed the presence of
exo-olefinic chain ends with the CumCl/BCl₃/DrBP/CH₂Cl₂/-50 °C system.⁴⁵ It was argued that DrBP is able to abstract protons from –CH₃ groups flanking the propagating PIB carbocations resulting in exo-olefinic chain ends. Although the possibility of β-proton elimination by DrBP from living PIB chain ends was proposed in other reports,⁴³,⁴⁶-⁴⁷ it is commonly held view that DrBP is too sterically hindered to react with carbenium ions. A report examined the scope and limitations of pyridine bases, including 2- and 2,6-alky-substituted pyridines, as proton traps in the living carbocationic polymerization of IB.⁴⁸ Faust and Bae⁴⁹ offered a different interpretation of this phenomenon, attributing β-proton abstraction to the presence of impurities in DrBP, in their case a cyclic imine, which they postulated is sterically too hindered to quantitatively complex with Lewis acid but is sufficiently unhindered to allow approach to the carbocation. Wu and coworkers⁵⁰ showed that controlled high conversion polymerization of IB yielding PIB with narrow molecular weight distribution is possible with the H₂O/TiCl₄ initiating system in the presence of various electron pair donors (EDs), namely dimethylacetamide, dimethyl sulfoxide, pyridine, triethylamine, methyl acetate, methyl acrylate, methyl benzoate, and sulfolane. Their results indicated that these electron pair donors with different chemical structure and basicity play very important roles in controlled polymerization. The effectiveness of these electron pair donors on the polymerization processes and MWD cannot be explained by proton scavenging because the polymerization proceeded to high conversion and the polymer produced had narrow MWD even when the concentration of electron pair donors was higher than that of H₂O. They also demonstrated that the EDs reduce the rate of polymerization and, depending on their strength, change the reaction order in TiCl₄ from 2 to 1.
Although there have been controversies about the true role of these additives, they, in fact, mediate living carbocationic polymerizations and help to open avenues for macromolecular engineering by carbocationic polymerization. It is of considerable interest in both academia and industry to synthesize various well-defined polymer architectures including stars, brush-like chains, hyperbranched and arborescent structures and to establish systematic structure-property relationships. Synthetic and characterization methods of polymers initiated by a multifunctional epoxide initiator will be discussed later; but, first, background information on epoxides and the mechanism of ring-opening is given.

2.2. Ring-opening Polymerization (ROP) of Epoxides

An epoxide is a highly strained three-membered cyclic ether. It is also a Lewis base due to the electron donating ability of oxygen. Due to the ring strain epoxides are less stable than conventional ethers and hence more reactive, especially towards nucleophiles. Therefore, they can be polymerized by both anionic and cationic initiators. The mechanism of cationic polymerization of epoxides will now be briefly discussed.

2.2.1. Cationic Polymerization of Epoxides

The mechanism of cationic ring-opening polymerization (ROP) of epoxides is still controversial. Some researchers suggest carbocation involvement by an S_N1 mechanism, while others claim an S_N2 mechanism via oxonium ions. For processes which proceed by the S_N2 pathway, there are two accepted mechanisms: (1) the “active chain end (ACE) mechanism” in which the ionic active centers are located on the growing chains and
propagation involves a non-charged monomer; (2) the “activated monomer (AM) mechanism” in which propagation involves positively charged monomer, adding to the electrically neutral polymer terminus (Scheme 2.2).

![Scheme 2.2. Active chain end mechanism vs. activated monomer mechanism.](image)

AM and ACE mechanisms generally compete with each other. Initiation in the ACE involves the reaction of protonated monomer with a non-charged monomer, whereas initiation by the AM involves the reaction of a protonated monomer with an alcohol. The ratio of the rates of AM-to-ACE mechanism depends on [ROH]/[M] and the ratio of the rate constants of the two reactions. Assuming the two rate constants are comparable, the AM process is dominant at high [ROH] to low [M]. This means that the AM process will occur under monomer-starved conditions. Although the ACE processes are more frequent in cationic ROP, the AM mechanism is important for the synthesis of low to medium molecular weight reactive oligomers, mostly \(\alpha,\omega\)-dihydroxytelechelics. Higher molecular weights are difficult to obtain with the AM mechanism because a large amount of alcohol is needed to suppress the ACE mechanism. Scheme 2.3 shows the mechanisms of ring-opening by \(S_N1\) and \(S_N2\) mechanisms.\(^{51}\)
Scheme 2.3. Suggested ring-opening mechanisms of epoxides in the presence of acid.

$S_N1$ ring-opening has been observed mostly for epoxides with two alkyl substituents at the $\alpha$-position, for example, 2,2-dimethyloxetane.$^{52,53}$ In case of ring-opening polymerization by the $S_N1$ mechanism the rate determining step is carbocation formation which is then followed by the attack of the epoxy ring.

Eisch et al.$^{54}$ investigated the regioselectivity in cleaving the epoxide of a typical terminal olefin by various metal halides, including TiCl$_4$ in donor and non-donor media under various conditions. They used 1,2-epoxydecane (1 in Scheme 2.4) and determined the yield and the ratio of the 1-halo-2-decanol (2 in Scheme 2.4) and 2-halo-1-decanol (3 in Scheme 2.4) obtained upon hydrolysis.

\[
\begin{align*}
\ce{R-H-C-(O)-CH_2} &\xrightarrow{1. \text{MtX}_n} \ce{R-OH} + \ce{X-OH} \\
\ce{R-H-C-(O)-CH_2} &\xrightarrow{2. \text{H}_2\text{O}} \ce{R-H-C-(CH_2}_2 + \ce{R-OH}} \\
\end{align*}
\]

R = 1-octyl

Scheme 2.4. Cleavage and hydrolysis of an epoxide by a metal halide.
The results were explained in terms of two limiting models for the transition state: a) the complex of 1 and MtXₙ undergoes opening to form the more stable secondary carbenium ion-like transition state to form 3, or b) the complex of 1 and MtXₙ undergoes nucleophilic attack by X⁻, from MtXₙ, at the more accessible primary carbon to form 2, as shown in Scheme 2.5. In the first mechanism, since the more highly substituted carbon atom bears a considerable positive charge, it is likely that the epoxide ring will open giving a stable carbocation and then the nucleophile will attack this carbon even though it is more highly substituted. The –OMtXₙ₋₁ is the leaving group which departs with the electron pair that bonded it to the carbon. This step is rate determining in the reaction followed by the attack of the nucleophile (S_N1). In the second mechanism, the nucleophile attacks the more accessible carbon causing the breakage of the C–O bond. This means that the rate determining step involves two species: a nucleophile, X⁻, and the leaving group, –OMtXₙ₋₁ (S_N2). They concluded that strongly acidic conditions, e.g., in the presence of TiX₄, where X = Cl or Br, favor the formation of 3, which requires a more stable carbenium ion-like transition state.

![Scheme 2.5. Mechanistic pathways of epoxide cleavage.](image)

Epoxides are prone to rearrange in the presence of Lewis acids, yielding the corresponding aldehydes, ketones or dioxanes. The ring-opening products of styrene
epoxide (SE), which was based on an study of Friedel-Crafts alkylation in the presence of SnCl₄ in toluene at 0 °C, is shown in Scheme 2.6.⁵⁷ The products 2 and 3 were produced via the formation of benzylic carbocations (SN1 mechanism) which in turn alkylated toluene. The product 4 is a cyclic dimer of 1 formed by an SN2 mechanism and 5 is an isomerization product. The product distribution of 2/3/4/5 was 31:12:13:33 by GC analysis. The product ratios indicated that the rates of dimerization/isomerization, i.e., the formation of the dioxane and benzaldehyde, were comparable to the rate of carbocation formation. That means that both SN1 (43%) and SN2 pathways competitively take place in the reaction of an epoxide and Lewis acid with comparable reaction rates. In the case of α-methylstyrene epoxide (MSE), isomerization to aldehyde was reported to occur even during distillation.⁵⁸

Scheme 2.6. Ring-opening of SE by SnCl₄.
To be able to use epoxides as carbocationic initiators, the SN1 mechanism must be operational. Indeed, it was proposed that, depending on the structure of the epoxide, carbocations formed, which initiated IB polymerization. The current understanding of the mechanism of initiation and propagation in carbocationic IB polymerization using epoxy initiators will now be discussed.

2.3. Epoxy Initiators for IB Polymerizations

It has been reported that substituted epoxides such as α-methylstyrene epoxide (MSE), 1,2-epoxy-2,4,4-trimethylpentane (TMPO-1), 2,3-epoxy-2,4,4-trimethylpentane (TMPO-2) and hexaepoxysqualene (HES), in conjunction with titanium tetrachloride (TiCl₄), initiated the living carbocationic polymerization of IB. These epoxide initiators can be synthesized easily by the reaction of the corresponding olefins with m-chloroperoxybenzoic acid (m-CPBA) in dichloromethane at room temperature. Linear polyisobutylenes (PIBs) were obtained from MSE, TMPO-1 and TMPO-2, whereas HES yielded star-branched polymers.

Dreyfuss and Kennedy attempted to initiate the polymerization of tetrahydrofuran (THF) by 2,3-epoxy-2,4,4-trimethylpentane/BF₃, which did not initiate the THF polymerization. The grafting of THF from epoxidized butyl rubber was also unsuccessful. It was reasoned that steric hindrance of the substituted epoxide prevented initiation. Less substituted epoxides were reactive but produced ill-defined products because of side reactions.
Puskas\textsuperscript{10} theorized that if substituted epoxides are cleaved by an \( \text{S}_\text{N1} \) mechanism by Lewis acids in the presence of olefins such as IB, the formed tertiary carbocation may initiate carbocationic polymerization. In contrast, oxonium ion formation by \( \text{S}_\text{N2} \) mechanism would yield polyethers. The following competitive reaction scheme was proposed for initiation and polymerization of IB. (Scheme 2.7).\textsuperscript{22}

\[
\begin{align*}
\text{O} & \quad \text{OTiCl}_3 \\
\text{O} & \quad \text{TiCl}_4 \\
\text{Polyether} & \quad \text{2-phenylpropanal}
\end{align*}
\]

Scheme 2.7. Proposed initiation and propagation mechanism for the MSE/TiCl\textsubscript{4}/IB system.\textsuperscript{22}
MSE, TMPO-1 and TMPO-2 were shown to initiate the living polymerization of IB in conjunction with TiCl₄ yielding linear telechelic PIBs with an α-primary OH head group and an α-tertiary Cl end group, whereas HES formed star telechelic PIBs containing secondary OH core and tertiary Cl end groups.²² Initiation efficiency (I_eff) is defined as the percentage of initiator that yields tertiary carbocations to induce the polymerization and calculated by \( I_{\text{eff}} = \frac{M_{n,\text{theo}}}{M_n} \), where \( M_n \) and \( M_{n,\text{theo}} \) are the measured and theoretically expected (g PIB/mol initiator) number-average molecular weights, respectively. This formula defines “external” initiation efficiency (I_eff,ext) for HES. “Internal” initiator efficiency (I_eff,int) for HES is defined as the fraction of the six epoxide groups per molecule that initiate chain growth. I_eff is strongly affected by reaction conditions, such as initiator/monomer ratio, initiator/Lewis acid ratio, solvent polarity, and the structure of the epoxide. It was found that the MSE/TiCl₄ and HES/TiCl₄ systems gave I_eff of 35% and 40%, respectively, while the TMPO-1/TiCl₄ and TMPO-2/TiCl₄ systems resulted in 3% and 10% efficiencies, respectively. The higher I_eff of TMPO-2 was attributed to the steric strain of the methyl substituents, aiding carbocation formation, similarly to that in the TMPCl/TiCl₄ and tBuCl/TiCl₄ systems where the latter is a poor initiator of IB polymerization.⁶⁰,⁶¹ Brown and Fletcher⁶² systematically investigated the effect of structure upon the hydrolysis of tertiary aliphatic chlorides. When they compared the effects of replacing one of the hydrogen atoms in t-butyl chloride by a small alkyl group, they observed that replacing the hydrogen with methyl produced a relatively moderate increase in the rate constant as 0.033 hr⁻¹ and 0.055 hr⁻¹ for t-butyl and t-amyl chlorides, respectively. Introduction of longer groups, such as ethyl or n-propyl instead of the methyl group, didn’t show a large effect. In contrast, a similar
replacement of an hydrogen atom in \( t \)-butyl chloride by a \( t \)-butyl group greatly increased the rate constant, as \( 0.74 \text{ hr}^{-1} \) for 2-chloro-2,4,4-trimethylpentane. Since the structural changes were relatively remote from the reaction center, neither the inductive effect nor hyperconjugation could account for the large increase in the rate constant. Examination of \( t \)-butyl derivatives showed that the molecule has essentially the molecular configuration of di-\( t \)-butylmethane, which is under considerable strain. Ionization of the strained molecule would relieve the strain because of the planar conformation of the carbenium ion, as shown Scheme 2.8.

Scheme 2.8. Release of the strain by ionization of \(-\text{Cl}\) in 2-chloro-2,4,4-trimethylpentane.

Initiator incorporation into the polymer chain for the MSE/TiCl\(_4\) system was demonstrated by triple-detection SEC and pyrolysis GC-MS analyses. The SEC chromatogram of PIB is UV-transparent. The response by the UV detector indicated the presence of the aromatic head group in the PIB chain.\(^6\)}
The presence of an –OH group was also verified by $^1$H NMR spectroscopy (Figure 2.3) and FTIR calibrated for –OH absorption using 2-phenyl-1-propanol as a model. The functionality of the PIB-OH samples was found to be one within experimental error ($F_n = 0.96-1.10$).

In addition, a model experiment was carried out using MSE/TiCl$_4$ and 2,4,4-trimethyl-1-pentene (diisobutylene, DIB), a non-polymerizable monomer, to investigate the presence of –OH group.$^{64}$ Based on the results of elemental analysis, $^1$H and $^{13}$C NMR spectroscopy, and IR spectroscopy, the structure of the end product was identified as the product of the following reaction:
This model study proved the formation of the carbocation and the presence of the oxygen in the head group although the formation of a five-membered ring is also possible under the polymerization conditions for this aromatic initiator, as shown in Scheme 2.9, and would reduce initiator efficiency. However, ring formation is unlikely and the polymerization proceeds in the living manner once propagation passed the critical dimer stage.

Other styrene-based epoxides, namely, styrene epoxide (SE), \( p \)-methylstyrene epoxide (pM-SE) and \( \alpha \)-methyl-\( p \)-methylstyrene epoxide (pM-MSE), were also investigated as initiators in conjunction with TiCl\(_4\) for the polymerization of IB.\(^6\) The structures of these epoxides are shown in Figure 2.4.

![Scheme 2.9. Reaction of MSE/TiCl\(_4\) with DIB.](image)

Figure 2.4. Structures of styrene-based epoxy initiators.

It was found that all of these styrene-based epoxides initiated IB polymerization (albeit non-living in some cases) and yielded low initiator efficiency (\( I_{\text{eff}} \)). MSE initiated
the living polymerization of IB, as demonstrated by linear $M_n$ vs. conversion and pseudo-first-order kinetic plots; initiator efficiency was 35%. The $M_n$-conversion plots of SE and pM-MSE were linear although they were well above the theoretical line, indicating low $I_{eff}$ (i.e., 8% and 30% for SE and pM-MSE, respectively). The low $I_{eff}$ resulted from the loss of initiator due to side reactions, such as the formation of polyethers from the competition between the $S_N1$ and $S_N2$ pathways as shown in Scheme 2.7 and the isomerization/rearrangement to the corresponding aldehydes or dioxanes. The methyl substituent in pM-MSE increased the proportion of carbocations through steric strain and stabilization by electron-donation, showing $I_{eff}$ values comparable to MSE. The $p$-methyl substituent of pM-SE alone gave a non-linear $M_n$-conversion plot and lower $I_{eff}$ (20-30%). SE initiated IB polymerization also showed linear pseudo-first order kinetics of monomer consumption, similar to MSE, whereas both pM-SE and pM-MSE initiated IB polymerizations deviated from first-order kinetics, implying non-living conditions. When the epoxide ring opens by an $S_N1$ mechanism, MSE and pM-MSE will yield tertiary carbocations while SE and pM-SE will yield less stable secondary carbocations. Therefore, the formation of polyethers by the competitive $S_N2$ pathway is more likely for SE and pM-SE, which explains the lower initiator efficiencies. A $para$ methyl group in the aromatic ring (pM-SE and pM-MSE) would be expected to stabilize the corresponding carbocation by a positive inductive effect. However, hyperconjugation between the $\pi$-electrons of the aromatic ring and the $para$-methyl substituent would exert a destabilizing effect. Steric hindrance may also play a role. In summary, similarly to MSE, the SE/TiCl$_4$ system initiated the living polymerization of IB; however, it yielded lower initiator efficiency than MSE ($I_{eff} = 8$ vs 40%).
The mechanism of IB polymerization initiated by TMPO-1/TiCl₄ was investigated using real-time FTIR.²³ As discussed previously, competition between the S_N1 and S_N2 pathways (Scheme 2.7) was proposed. TMPO-1 was first reacted with an equimolar amount of TiCl₄ in the absence of IB to monitor ring-opening. Opening of the epoxide ring was demonstrated by the decrease in the intensity of the band at 1260 cm⁻¹, the characteristic of the C–O–C stretching bond in an epoxide ring, as shown in Figure 2.5.

![Real-time FTIR spectra of the reaction of TMPO-1 and TiCl₄.](image)

Figure 2.5. Real-time FTIR spectra of the reaction of TMPO-1 and TiCl₄. [TMPO-1] = [TiCl₄] = 0.1 M, [D₆BP] = 0.007 M, Hx/MeCl (60/40), T = -80 °C.²³ Reprinted with permission from *Macromolecules* 2000, 33, 3518-3524. Copyright © 2000 American Chemical Society.

The two strong signals at 1665 cm⁻¹ and 1635 cm⁻¹ that appeared after the addition of TiCl₄ were assigned to the isomerization product, 2,4,4-trimethylpentanal-1 (TMPA-1) and the complex of TMPA-1 with TiCl₄, respectively. The isomerization of epoxides by Lewis acids was discussed above. It has been shown that complexation of TMPA-1 with TiCl₄ would shift the carbonyl stretch of aldehydes (1765-1645 cm⁻¹) to lower
wavenumbers.\textsuperscript{66,67} The broad band that appeared at 1100 cm\textsuperscript{-1} is typical of polyethers formed by self polymerization of the epoxide, as proposed. After an initial delay of 780 seconds, IB was added to monitor initiation, but the intensity of the peak at 1655 cm\textsuperscript{-1}, the characteristic of C=C stretching band, did not change over 6 minutes, which indicated that no species were available to initiate the polymerization. It was explained that a neutral compound, such as [I] in Scheme 2.7, would have formed after the formation of the intermediate tertiary carbocation by the S\textsubscript{N}1 pathway. Therefore, excess TiCl\textsubscript{4} was necessary to produce a tertiary carbocation by the ionization of [I].

![Figure 2.6. Real-time FTIR monitoring of IB polymerization: 1550-1800 cm\textsuperscript{-1} region. [TMPO-1] = 0.1 M, [TiCl\textsubscript{4}] = 0.1 M + 0.2 M, [IB] = 0.3 M, [D\textsubscript{2}BP] = 0.007 M, Hx/MeCl (60/40), T = -80 °C.\textsuperscript{23} Reprinted with permission from Macromolecules 2000, 33, 3518-3524. Copyright © 2000 American Chemical Society.](image)

After the addition of excess TiCl\textsubscript{4}, polymerization was evidenced by the gradual decrease of the intensity of this C=C stretching at 1655 cm\textsuperscript{-1} and of the overtone band of the C–H wag in the =CH\textsubscript{2} of IB (Figure 2.6) as well as by the progressively growing
signal at 1230 cm\(^{-1}\), identified as the vibrations of the distorted carbon tetrahedrons (\(–C(CH_3)_2\) groups) of the PIB.\(^{68}\)

When TMPO-1 was reacted with excess TiCl\(_4\) in the presence of IB, polymerization was immediately observed by the gradual disappearance of IB signals (Figure 2.7). Both isomerization and polyether formation were observed in real time.

![Real-time FTIR monitoring of IB polymerization: 1600-1800 cm\(^{-1}\) region.](image)

Figure 2.7. \textit{Real-time} FTIR monitoring of IB polymerization: 1600-1800 cm\(^{-1}\) region. \([\text{TMPO-1}] = 0.1 \text{ M}, [\text{IB}] = 1 \text{ M}, [\text{TiCl}_4] = 0.3 \text{ M}, [\text{DzBP}] = 0.007 \text{ M}, \text{Hx/MeCl} (60/40), T = -80 \text{ °C}.\)\(^{23}\) Reprinted with permission from \textit{Macromolecules} \textbf{2000}, \textit{33}, 3518-3524. Copyright © 2000 American Chemical Society.

Investigation of IB polymerization via \textit{real-time} FTIR confirmed the proposed mechanism of initiation by TMPO-1. The competitive occurrence of both \(S_N1\) and \(S_N2\) pathways were observed. The latter pathway led to dimer or oligoether formation, while carbocations forming via the \(S_N1\) pathway initiated IB polymerization. Scheme 2.10
outlines the mechanism, including the observed isomerization of the TMPO-1 into 2,4,4-trimethylpentanal (TMPA). The 1-40% \( I_{\text{eff}} \) observed in TiCl\(_4\)-initiated systems indicated that the \( S_N2 \) pathway was dominant.

![Chemical reaction diagram](image)

**Scheme 2.10.** Proposed initiation mechanism for IB polymerization by the TMPO-1/TiCl\(_4\) system.

HES was used to synthesize star-branched PIBs. Polymers with molecular weights (MW) as high as \( M_n = 415,000 \) g/mol and molecular weight distributions (MWD) as low as \( M_w/M_n = 1.17 \) were obtained.\(^6\) The livingness of the polymerization was demonstrated by linear \( M_n \) vs. conversion plots as well as linear semilogarithmic first order rate plots. The initiator efficiency (\( I_{\text{eff}} \)) and MWD were influenced by several factors, including initiator/monomer ratio, initiator/Lewis acid ratio and solvent nature. Solvent composition had a profound effect on both \( I_{\text{eff}} \) and molecular weight distribution (MWD). Although PIBs with narrower MWD (\( M_w/M_n = 1.18 \)) were obtained via the
HES/TiCl₄ initiating system in hexane (Hx)/methyl chloride (MeCl) (60/40, v/v), the first sample showed a slightly bimodal distribution, which turned into monodisperse and narrow distribution with increasing conversion. Furthermore, when the polymerization was carried out in a methylcyclohexane (MeCHx)/MeCl mixture, even the slight change in solvent polarity by the change in the ratio of the solvent influenced $I_{\text{eff}}$ and MWD. While the highest $I_{\text{eff}}$ of 94% was achieved in MeCHx/MeCl (70/30, v/v), the MWD was narrowest ($M_w/M_n=1.17$) in MeCHx/MeCl (60/40, v/v) at $[I]/[M]=5.0 \times 10^{-4}$. A bimodal distribution was initially observed in MeCHx/MeCl (70/30, v/v), which narrowed as the reaction progressed, resulting in a monodisperse distribution by the end of the reaction ($M_w/M_n=1.28$). A similar phenomenon was found in IB polymerization initiated by the TMPO-1/TiCl₄ system, while a monodisperse distribution was observed throughout the polymerization initiated by TMPO-2/TiCl₄. Under the same reaction conditions, TMPO-2 was found to be a better initiator compared to TMPO-1, which was attributed to its more strained structure as explained earlier. In HES the end groups are less hindered, as shown in Figure 2.8.

![Hexaepoxysqualene (HES)](image)

It was also theorized that there is a difference between the reactivity of the terminal and the interior epoxide groups in HES. The difference in reactivity disappears when all growing chains possess tert-chloride end groups. 1,1-Diphenylethylene (DPE) end capping of a relatively low MW ($M_n = 21,000$ g/mol at $[I]/[M]=0.02$) living star in
MeCHx/MeCl (60/40, v/v) showed that the “internal” efficiency ($I_{\text{eff, int}}$, the fraction of the six epoxide groups per molecule that initiated chain growth) was 85%, yielding an average of 5.2 PIB arms per HES. However, the “external” $I_{\text{eff}}$, i.e., the fraction of the initiator that induced polymerization was found to be only 10%. When HES was reacted with TiCl₄ in 1:1 ratio in the absence of IB, followed by the addition of IB and excess TiCl₄, and finally DPE end capping, NMR showed an average of 10 PIB arms in the star. This can be explained by the coupling of two HES molecules prior to initiation. At lower $[I]/[M]_0$ ($5.0 \times 10^{-4}$) $I_{\text{eff}}$ was 55 and 40% at $[I]/[\text{TiCl}_4] = 0.003$ and 0.007 or higher, respectively, but due to the high MW only indirect evidence supported the claim of ~6 PIB arms/chain.⁷⁰

In this dissertation another Lewis acid coinitiator, BCl₃ was explored. Therefore the background on the use of BCl₃ in carbocationic polymerization will now be discussed.

2.4. Boron Trichloride as a Coinitiator in IB Polymerizations

Boron trichloride (BCl₃), a strong Lewis acid, is potentially capable of reacting with compounds containing functional groups such as oxygen, sulfur, nitrogen, phosphorous, or halogen. It is also capable of selectively cleaving C–O bonds in ethers and acetal protecting groups.⁷¹ It was investigated and extensively used by generations of chemists along with the other boron halides, BF₃, BBr₃ and BI₃. The polymerization activity of those boron halides was investigated systematically. The studies of Marek⁷², Seymour⁷³, Plesch⁷⁴, Williams⁷⁵ and others seemed to indicate that BCl₃ and BBr₃ were ineffective coinitiators for cationic olefin polymerization under various conditions while
BF₃, a weaker Lewis acid, was much more effective. In contrast to these authors, Kennedy et al.⁷⁶ discovered that under suitable conditions, i.e. low temperature, polar solvent and carefully controlled sequence of addition of reagents, BCl₃ was an excellent, efficient coininitiator for olefin polymerization. Later, it was found that BCl₃ could be used as a coininitiator for IB polymerization in the presence of cumyl-type initiator-transfer ("inifer") agents to synthesize telechelic polyisobutylenes (PIBs).⁷⁷-⁸⁰ Nuyken et al.⁸¹ further investigated the inifer technique to examine the degree to which the termination step can be considered a reversible process. They used a telechelic polymer, namely α,ω-dichloroPIB, and successfully extended the polymer chains in the presence of BCl₃. They also suggested the use of 2-chloro-2,4,4-trimethylpentane as a model compound for telechelic PIB. First it was shown that aliphatic tertiary chlorides were not polymerization initiators in conjunction with BCl₃ in MeCl diluent⁷⁹ while under the same conditions tertiary aralkyl chlorides ("inifers") were efficient, albeit nonliving, initiators.⁷⁷-⁸⁰ Later, it has been reported that in the presence of strong electron donors, e.g. dimethylsulfoxide (DMSO), dimethylacetamide (DMA) or dimethylformamide (DMF), inifer type cumyl-chloride/BCl₃ systems exhibited living character and the polymerization-inactive aliphatic tert-chloride/BCl₃ system became active and induced living IB polymerization.³⁸ Later BCl₃ was successfully used as a coininitiator for living IB polymerization in the presence of various initiators including tertiary aliphatic esters, ethers, chlorides and alcohols, cumyl acetates, cumyl methyl ether, cumyl chlorides and cumyl alcohols.¹⁷,¹⁹-²⁰

As shown previously in section 2.3, the in situ FTIR technique permits the real-time clarification of the polymerization mechanism for polymerization processes.
Because this technique was often utilized in this research it will be discussed in the next section.

2.5. *In situ* FTIR Monitoring

Polymerization reaction data are traditionally obtained by careful sampling followed by gravimetric and molecular weight analysis. Sample removal can be very difficult, especially for polymerizations that are extremely sensitive to atmospheric water and oxygen, such as in anionic and cationic polymerizations. *In situ* FTIR spectroscopy is a state-of-the-art monitoring technique well suited to obtain real time structural and kinetic data of polymerizations without the need of sampling. In addition, reactions are analyzed without complicated reactor modification or deuterated monomers. Advantages of *in situ* polymerization monitoring include evaluation of reaction variables for optimization of reaction conditions, analysis of polymerizations that use hazardous or air-sensitive reagents, and elimination of experimental uncertainties associated with sampling. In addition, instantaneous changes in reactants, intermediates, and products can be followed by *in situ* monitoring, which allows the tracking of concentration changes, reaction end points and percent conversion. The information from *in situ* monitoring can provide an in-depth understanding of reaction pathways.

In a typical set-up of an *in situ* FTIR monitoring system, an IR beam is transported into the reaction medium with fiber optic cables or a conduit system and a probe is immersed in the reaction medium. A focusing apparatus narrows the light source to a diameter of the transmitting fiber optic probe. After transmission or reflection of the light in the reaction medium depending on the type of sensor used (Transmittance, TR or
Attenuated Total Reflection, ATR), the light is transferred back to the spectrometer by collector fibers or conduit. TR probes are generally used for samples that are sufficiently clear or transparent for transmission measurements. Advantages of this probe include high signal to noise ratio, no distortion of the spectra and ease of quantification of collected data. ATR probes are based on the principle of total internal reflection and are generally used for high concentration or for samples that are not transparent and have poor transmission. A crystal with a high index of refraction, in which total internal reflection occurs, is used at the tip of the probe. A small amount of energy penetrates into the sample. The ATR probe is less sensitive than TR, but can be used for the monitoring of heterogeneous polymerizations such as emulsion and suspension. Since the absorption of a dissolved substance is proportional to its concentration for dilute solutions, i.e. Beer-Lambert Law (\(A = \varepsilon \cdot b \cdot c\), where \(A\) is absorbance, \(\varepsilon\) is the molar absorptivity \([\text{Lmol}^{-1}\text{cm}^{-1}]\), \(b\) is path length of the sample \([\text{cm}]\) and \(c\) is the concentration of the compound in solution \([\text{mol L}^{-1}]\)), in situ FTIR can be used to monitor the kinetics of monomer consumption. However, calibration is advised to confirm the proportionality.

The frequently analyzed regions by in situ monitoring are mid-IR \((\nu, 400-4000 \text{ cm}^{-1})\) and near-IR (NIR) \((\nu, 4000-12500 \text{ cm}^{-1})\). In the mid-IR region, primary resonances are detected and IR bands are clearly defined; while, in the NIR region, peaks are usually broad and overlapping. Although the cable length is limited to about 1 m for mid-IR monitoring, for NIR, the signal can be transmitted long distances by fiber optic cables.

In situ FTIR monitoring in the NIR region was used to study the living anionic polymerizations of styrene, isoprene, methyl methacrylate, ethylene oxide and butadiene by the groups of Long,\(^82\) Fieberg\(^83\) and Müller.\(^84\) The groups of Puskas\(^85\) and Storey\(^86\)
used in situ FTIR monitoring to follow the polymerizations of IB and styrene in the mid-IR region. Storey’s research group used the FTIR-ATR technique with a ReactIR 1000 reaction analysis system that uses a light conduit technology. When this system is coupled with a DiComp (diamond-composite) probe, it has a low-end spectral cutoff of 650 cm\(^{-1}\). They generally followed monomer consumption by the decay of the absorbance of \(=\text{CH}_2\) wag of IB, observed at 887 cm\(^{-1}\).\(^{86}\) Puskas’ research group uses a mid-IR fiber optic technology with both TR and ATR probes. The TR probe is able to monitor reactions in very dilute (mmol/L) solution; therefore, they can monitor not only monomer consumption but also the initiation at reasonably low initiator concentrations. They generally monitored either the C=C bond of IB, observed at 1655 cm\(^{-1}\), or the overtone of the \(=\text{CH}_2\) wag of IB, observed at 1780 cm\(^{-1}\).\(^{23}\) Details of FTIR monitoring for the monitoring of epoxide-initiated IB polymerization will be discussed in detail in the Experimental and Results and Discussion sections.

LANXESS’ main interest was the synthesis of star-branched PIBs for structure-property relationships. Therefore, a background of well-defined, star-branched polymers will now be discussed.

2.6. Star-branched Polymers

Star-shaped polymers consist of a central core from which a number of polymer chains radiates. Star-branched polymers are of substantial commercial interest due to their distinctly lower solution and bulk viscosities and less shear sensitivity than their linear counterparts.\(^{87}\) Commercially, they are produced by living anionic polymerizations and are used as viscosity improvers in lubricating oils.\(^{88}\) The first successful attempt of
model star-branched polymer synthesis was that of Schaefgen and Flory in 1948.\textsuperscript{89} They were able to synthesize four- and eight-armed polyamide stars by condensation polymerization using a tetrabasic (cyclohexanonetetrapropionic) and an octabasic (dicyclohexanoneoctapropionic) acid, respectively, as multifunctional reactants. The synthesis of star polymers is generally performed by living polymerization methods, such as cationic,\textsuperscript{70,90-105} anionic,\textsuperscript{106,107,108} radical,\textsuperscript{109-111} and group transfer (GTP).\textsuperscript{112-114} The two major synthetic routes used for the production of tailor-made star polymers are the arm-first and the core-first method, first developed in anionic systems.\textsuperscript{115}

2.6.1. Arm-first Method: Linking Agent

The first example of a star-branched polymer was prepared by the linking method, a sub-class of the arm-first method, using living anionic polymerization by Morton et al.\textsuperscript{116} in 1962. They prepared and studied the properties of three- and four-arm star polystyrenes by the reaction of methyltrichlorosilane and tetrachlorosilane, respectively, with polystyryllithium, as shown in Scheme 2.11. Following the work of Morton and coworkers, this method was subsequently extended to polybutadiene.\textsuperscript{108,117} Later, Roovers et al.\textsuperscript{118-123} have synthesized a series of four- and six-arm polystyrene and polyisoprene stars using 1,2-\textit{bis}(dichlorosilyl)- and 1,2-\textit{bis}(trichlorosilyl)ethane.
Scheme 2.11. Anionic synthesis of four-arm star polystyrene by a linking agent.

The advantage of this method is that the number of arms per molecule within a given sample is invariant and precisely controlled by the functionality of the linking agent. The extent and efficiencies of the linking reactions, however, are dependent on the steric requirements of the carbanionic chain ends.\textsuperscript{87} In general, the efficiency of the linking reaction decreases in the order poly(butadienyl)lithium > poly(isoprenyl)lithium > poly(styryl)lithium, for a given multifunctional silicon halide.\textsuperscript{108,124-125} Two general approaches have been used to increase the efficiency of the linking reactions of polymeric organolithium compounds with multifunctional silyl halides: the first one was to add a few units of butadiene to either the poly(isoprenyl)lithium or poly(styryl)lithium chain ends to convert them to the corresponding less sterically hindered poly(butadienyl)lithium chain ends.\textsuperscript{125} The second method was to utilize a polychlorosilane compound in which the silyl halide units are more separated to reduce the steric repulsion in the linked product.\textsuperscript{118} Star polymers of high uniformity with as many as 18 arms have been produced in this way\textsuperscript{126} and the same general method is used to produce linear and three-arm star block copolymer thermoplastic elastomers on a
commercial scale. This method has also been used for the synthesis of hetero, three-armed star polystyrenes and polybutadienes by Pennisi and Fetters,\textsuperscript{127,128} as shown in the following equations:

\[
\text{PLi} + \text{excess CH}_3\text{SiCl}_3 \rightarrow \text{PSi(Cl)}_2\text{CH}_3 + \text{LiCl} + \text{CH}_3\text{SiCl}_3 \tag{2.3}
\]

\[
\text{PSi(Cl)}_2\text{CH}_3 + \text{excess P'Li} \rightarrow \text{P(P')}_2\text{SiCH}_3 + 2 \text{LiCl} \tag{2.4}
\]

This procedure is based on the decreased reactivity of poly(styryl)lithium compared to poly(dienyl)lithiums with respect to linking reactions with polyhalosilanes, which has been attributed primarily to chain-end steric effects. Another linking agent, (CH\textsubscript{3})HSiCl\textsubscript{2}, was used by Khan et al.\textsuperscript{129} to prepare hetero three-armed poly(styrene-arm-styrene-arm-2-vinylpyridine) star copolymers. After linking living polystyrene pre-arms, the reactive Si-H group was linked to allyl functionalized poly(2-vinylpyridine) by hydrosilylation. A similar method has been used to prepare star polymers, especially PMMA-based stars, by GTP.\textsuperscript{130,131}

In cationic polymerization, nucleophilic linking agents have been used to link electrophilic chain ends. Sawamoto et al.\textsuperscript{132-135} have prepared tri- and tetra-arm star poly(vinylether) and poly(α-methylstyrene) using tri- and tetra-functional silyl enol ethers as a linking agent as shown in Figure 2.9. An example of the coupling reaction is also shown in Scheme 2.12.\textsuperscript{132}
Figure 2.9. Tri- and tetra-functional silyl enol ethers as linking agents.

Scheme 2.12. Model coupling reaction with silyl enol.132
Multifunctional isocyanates have been used as linking agents for hydroxy- or amine-functionalized polystyrene, polyisoprene, polybutadiene, polystyrene-diene block copolymers and poly(ethylene oxide) by condensation polymerizations.\textsuperscript{136-139}

Kennedy and Omura\textsuperscript{140} used the multifunctional linking method to synthesize multiarm PIB-based star in two steps: first, they prepared allyl-terminated PIB pre-arms by functionalizing living PIB\textsuperscript{+} chains with allyl trimethylsilane, and then linked the allyl-terminated arms to hydromethylsiloxane cores by hydrosilation, as shown in Scheme 2.13. The same method was used for the synthesis of a star block copolymer of polystyrene-\textit{b}-polyisobutylene.\textsuperscript{141}

![Scheme 2.13. Synthesis strategy for multi-arm star PIB by a linking agent.](image)

Although star polymers with uniform arm length, composition, and a known number of arms can be prepared by this method, long reaction times and/or forced reaction conditions are required for completion since the most of the linking reactions are diffusion controlled.\textsuperscript{118} In case of high molecular weight arms and/or bulky chain ends complete linking would be difficult, if not impossible. Moreover, since, in practice, an
excess of living chains is used relative to the functionality of the linking agents or in cases where mixed products are formed, fractionation is required to remove the precursor chains or separate the products.\textsuperscript{142}

2.6.2. Arm-first Method: Microgel Core

Star-branched polymers have also been synthesized by sequential addition of di- or multifunctional vinyl compounds, e.g. divinylbenzene (DVB), to living monofunctional polymeric anions. In this method, a microgel core is formed by the intermolecular addition reaction of pendent vinyl groups at the ends of the polymer chains created by the crossover of monofunctional polymeric anions to polyfunctional vinyl compounds, as shown in Scheme 2.14.

![Scheme 2.14. Multiarm star polymer by arm first method with divinylbenzene.](image)

This method was first explored by Milkovich\textsuperscript{143} in 1965 and successfully utilized for preparation of star-branched polystyrene by Rempp et al.\textsuperscript{144,145} Although star-branched polymers possessing many arms can be synthesized, the stoichiometry is not exact and predictable, and the molecular weights distribution of the branched polymers is ill-defined.
The success of this linking process and the uniformity of the length of the DVB blocks depend on the relative rate of the crossover reaction compared to the subsequent homopolymerization of DVB and the linking reactions. In principle, \( j \) molecules of DVB could link \((j + 1)\) polymer chains.\(^8\) However, the linking efficiency is lower than predicted. Although the number of arms in the star depends on the ratio of DVB to polymeric organolithium compound, the degree of linking obtained is a complex function of reaction variables.\(^1\) The crossover and subsequent homopolymerization of \( m \)- and \( p \)-DVB with butadienyl- and isoprenyllithium were studied by Young and Fetters.\(^2\) \( p \)-DVB was found to react slightly faster with dienyllithium chain ends than the \( meta \) isomer. Nevertheless, \( m \)-DVB was found to be more efficient than the \( para \) isomer for linking dienyllithium chains to a star-branched architecture. This behavior was explained by the fact that the overall homopolymerization of the \( meta \) isomer is faster than that of the \( para \).

Higashimura et al.\(^3\) have used the same idea to prepare star polymers by cationic polymerization. They prepared star poly(alkyl vinyl ethers),\(^4\) star polyalcohol/poly(alkyl vinyl ether) block copolymer,\(^5\) and hetero-arm star poly(vinyl ethers),\(^6\) using divinyl ethers as a linking agent, as shown in Figure 2.10. Star polymers containing \( p \)-alkoxystyrene arms have also been synthesized by a similar procedure.\(^7\)

![Figure 2.10. Divinyl ether linking agents for synthesis of star polymers from cationic monomers.](image-url)
Matyjaszewski and coworkers\textsuperscript{109} achieved the synthesis of star polystyrenes via atom transfer radical polymerization (ATRP) using the arm-first technique with DVB. Recently, they applied this method for the synthesis of miktoarm star copolymers containing two or more arm species, including polyacrylate, polystyrene, polymethacrylate and poly(ethylene oxide), by ATRP using DVB.\textsuperscript{151}

In carbocationic IB polymerization systems, the arm-first method with microgel core was also used for the synthesis of star-branched polyisobutylenes (PIBs) with 6-70 arms.\textsuperscript{101,152-155} In this process, the pre-grown monofunctional living PIB chains were reacted with bifunctional monomers such as divinyl- or diisopropyl-benzene to form the crosslinked core, Scheme 2.15. This method leads to ill-defined cores; thus, the number of arms cannot be controlled precisely, and the reaction times are very long (10-100 h.).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{scheme2.png}
\caption{Scheme 2.15. Carbocationic synthesis of multiarm star PIB by arm first method with divinylbenzene.}
\end{figure}

Short-arm star PIBs were prepared in a “one-pot” synthesis. After preparation of living PIB arms from the 2-chloro-2,4,4-trimethylpentane(TMPCl)/TiCl\textsubscript{4} initiating system, DVB was added. Almost complete conversion was obtained after \textasciitilde96 hours.\textsuperscript{156} The authors used an “two-pot” synthesis to prepare long-arm star where PIB arms having desired molecular weight containing \textit{tert}-chloride end groups were first synthesized from
the cumyl chloride/TiCl₄ initiating system. After the arms were purified and dried, the tert-chloride chain ends were reactivated by TiCl₄ in the presence of DVB to perform the linking reaction. The number of arms and the linking efficiency were found to be a complex function of reaction variables. The number of arms and dispersity of the stars were high for short arm star polymers (Nₒ > 100, where Nₒ is the number average number of arms), whereas, with long-arm precursors, uniform stars with relatively a low number of arms (Nₒ ~ 8) were obtained. Formation of star with high arm-numbers was attributed to star-star coupling, which is not possible for long-arms due to steric hindrance.

Later, Storey and Shoemake reported the synthesis of star PIB using reactive core-forming divinyl comonomer, namely, 1,3-diisopropenylbenzene (DIPB) or DVB. DVB was found to be significantly superior to DIPB by forming the star polymers more rapidly and leaving a much lower amount of residual PIB arms.

2.6.3. Core-first Method

The core-first method is based on the use of multifunctional initiators, which are either prepared externally to the polymerization reaction or in situ, from which the star arms are grown. Examples of externally prepared multifunctional initiators in anionic polymerization are few due to poor solubility of low molecular weight polyanions which requires the presence of a polar solvent. Fijumoto et al. prepared a number of tri- and tetrafunctional anionic initiators for the synthesis of star α-methyl-styrene. The trifunctional initiator was synthesized by the reaction of 1,3,5-tris(α-methoxybenzyl)benzene with an alkali metal by electron transfer, as shown in Scheme 2.16. It was used
to polymerize α-methylstyrene in THF in the presence of digylme at -80 °C; however, the products contained one- and two-arm polymers as well as three-arm stars in low yield (~35%). The formation of one- and two-branched polymers was attributed to the incomplete dissociation of the third initiating site.

Scheme 2.16. Synthesis of a trifunctional initiator for star polymer via anionic polymerization.

Burchard and coworkers\textsuperscript{159} used DVB to form a multifunctional initiator for anionic polymerization. DVB was first polymerized using butyllithium in benzene to form a soluble high molecular weight microgel with anionic groups. Later, Rempp and coworkers\textsuperscript{160,161} extended this method as a general core-first method to prepare star-branched polymers via anionic polymerization. A schematic representation of this star synthesis is shown in Scheme 2.17.
Scheme 2.17. Anionic synthesis of star polymers from a DVB-based multifunctional initiator.

Star homopolymers and block copolymers synthesized by using this type of macroinitiator had broad polydispersities (PDI = 6-10), which were attributed to a random distribution of core sizes and functionalities. The synthesis of star acrylates and methacrylates was reported by Teyssie.\textsuperscript{162,163} Star block copolymers with an arm functionality from 22 to 1300 and broad and multimodal size distribution were synthesized.

One of the few successful examples of a hydrocarbon-soluble anionic initiator for preparation of tri-arm homo-, block-, and functionalized stars was described by Quirk and Tsai.\textsuperscript{164} They prepared a hydrocarbon soluble, trifunctional initiator by the addition of three moles of sec-butyllithium to 1,3,5-\textit{tris}-(1-phenylethenyl)benzene (Scheme 2.18). Well-defined, three-arm polystyrene, polybutadiene, and poly(styrene-\textit{b}-methyl methacrylate) were prepared by the use of this initiator with stoichiometric amounts of THF and lithium sec-butoxide in benzene.
Scheme 2.18. Anionic synthesis of three-arm star polystyrene by a trifunctional initiator.\textsuperscript{164}

Burchard and Eschwey\textsuperscript{165} generated multifunctional initiators by the reaction of polymeric organolithium compounds with multifunctional monomers and prepared hetero-arm star polymers.

Quirk et al.\textsuperscript{166-168} used the similar chemistry, i.e. the addition of polymeric organometallic compound to a multifunctional initiator and then crossover to a second monomer to prepare heteroarm star polymer. As it is shown in Scheme 2.19, this process involved two reactions: in the first step, two living carbanionic polymer chains were coupled with a living coupling agent, 1,3-\textit{bis}(1-phenylethenyl)benzene (MDDPE), to generate the corresponding dianion. In the second step, this polymeric dianion reinitiated
the polymerization of a second monomer to form a hetero four-arm star-branched homopolymer or block copolymer.

\[
\begin{array}{c}
\text{CH}_2 \text{CH}_2 \\
\text{CH}_2 \text{Li Li CH}_2 \text{P}^1 \\
\end{array}
\]

\[
\xrightarrow{2 \ P^1 \text{Li}}
\]

\[
\begin{array}{c}
\text{CH}_2 \text{P}^1 \text{Li} \text{Li CH}_2 \text{P}^1 \\
1) \ n \ M^2 \\
2) \ ROH
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_2 \text{P}^2 \\
\text{P}^2 \text{CH}_2 \text{P}^1 \\
\end{array}
\]

\[
P^1 = \text{polystyrene, } M^2 = \text{styrene or butadiene} \\
P^2 = \text{polystyrene or polybutadiene}
\]

Scheme 2.19. Synthesis of four-arm star polymer by anionic polymerization.

Three- and four-arm star poly(isobutyl vinyl ether)s, poly(IBVE), were synthesized via cationic polymerization by Higashimura and coworkers\textsuperscript{169-173} using tri- and tetra-functional [tris-(trifluoroacetate)-type] initiators in conjunction with EtAlCl\textsubscript{2} and 1,4-dioxane. This procedure was further extended for the synthesis of amphiphilic star block copolymers of poly(IBVE) and poly(2-hydroxyethyl vinyl ether).

The core-first method has also been utilized successfully for the synthesis of star polymers via ATRP. Matyjaszewski and coworkers\textsuperscript{174,175} reported the synthesis of star polystyrene and poly(methyl acrylate) using either organic or siloxane and cyclotriphosphazene-derived inorganic multifunctional initiators. Sawamoto and coworkers\textsuperscript{176,177} reported the synthesis of star poly(methyl methacrylate) by ruthenium-mediated ATRP using tri-, tetra-, hexa- and octafunctional dichloroacetate initiators.
Similarly, Gnanou et al.\(^{178}\) reported the synthesis of star polystyrene using octafunctional calixarene derivatives.

The core first method was successfully employed for the synthesis of three- and four-arms star PIBs in non-living systems\(^{34,179}\) and later for the synthesis of three-arm star PIBs in living systems.\(^{15,180}\) Well-defined PIB-based stars were prepared using tricumyl-based initiators by Kennedy et al.,\(^{21,181,182}\) as shown in Scheme 2.20. The \(\text{tert}-\text{methoxy},^{181}\) \(\text{tert}-\text{hydroxy},^{21}\) and \(\text{tert}-\text{chloride}^{182}\) tricumyl derivatives were used in conjunction with either BCl\(_3\) or TiCl\(_4\) coinitiator to obtain a wide range of products, from telechelic stars\(^{182}\) to PIB-based thermoplastic elastomers.\(^{180,183}\) Storey and coworkers\(^{184}\) have also used the same class of initiators for the synthesis of PIB-base thermoplastic elastomers. Kennedy et al.\(^{32}\) have prepared tetra-functional initiator using the similar approach for the synthesis of four-arm star PIB.

\[\text{R} = -\text{OCH}_3, -\text{OH}, -\text{Cl}\]

Scheme 2.20. Synthesis of tri-arm PIB-based star polymers by carbocationic polymerization.

Puskas and Wilds\(^{90}\) reported a multifunctional carbocationic macroinitiator carrying \(\text{tert}-\text{hydroxy}\) functionalities prepared by the radical copolymerization of 4-(1-
hydroxy-1-methylethyl)-styrene with styrene. Macroinitiators with average functionalities of 8-73 were used to synthesize the star-branched PIBs. They also reported the synthesis of star PIB homopolymer and PIB-b-PS block copolymers from a six-functional epoxy initiator, hexaepoxysqualene (HES) in conjunction with TiCl$_4$.\textsuperscript{22,69,70}

Faust and Bae\textsuperscript{103} used a living coupling agent, 2,2-\textit{bis}-[4-(1-tolyethenyl)phenyl]-propane (BDTEP), to synthesize amphiphilic A$_2$B$_2$ type star block copolymers of PIB and poly(methyl vinyl ether) (PMeVE). They prepared the living coupled PIB via the living coupling reaction of BDTEP with linear living PIB, synthesized by TMPCl/TiCl$_4$/-80 $^\circ$C system using Hx/CH$_2$Cl$_2$ (50/50, v/v) as solvent in the presence of DrBP. Then, chain ramification reaction of methyl vinyl ether (MeVE) at the junction of the living coupled PIB was commenced by the addition of MeVE, as shown in Scheme 2.21.

![Scheme 2.21. Synthesis of A$_2$B$_2$ star-block copolymer via carbocationic polymerization.\textsuperscript{103}](image-url)
Kennedy et al.\textsuperscript{93} reported a well-defined octafunctional initiator derived from calix[8]arenes for the preparation of octa-arm PIBs, as shown in Scheme 2.22. The synthesis was accomplished with the use of octafunctional calixarene derivative initiators, specifically, \textit{tert}-methoxy or \textit{tert}-hydroxy derivatives of 5,11,17,23,29,35,41, 47-octaacetyl-49,50,51,52,53,54,55,56-octamethoxycalix[8]arene, in conjunction with BCl\textsubscript{3}/TiCl\textsubscript{4} coinitiators in Hx/CH\textsubscript{3}Cl solvent mixture at -80 °C. The eight-arm star PIBs were subjected to core destruction, a technique used to selectively destroy the aromatic moieties by exhaustive oxidation, as shown in Scheme 2.23.\textsuperscript{93,152}

Scheme 2.22. Carbocationic synthesis of eight-arm star PIB by octafunctional calix[8]arene-based initiator.
Scheme 2.23. Core destruction of PIB star with a calixarene core.

After core destruction, it was possible to identify the molecular weight of the arms, and also the number of arms by comparing the molecular weight of arms to that of star polymer. The number-average number of arms and the weight-average number of arms were found to be 7.6 and 7.7, respectively, i.e., slightly lower than theoretical value.

2.7. Characterization of Star Polymers

Several methodologies have been used to determine the molecular weight of star polymers, including vapor pressure osmometry (VPO), membrane osmometry, end group analysis, nuclear magnetic resonance (NMR) spectroscopy, size exclusion chromatography (SEC), and light scattering. SEC is a well-established technique for the characterization of molecular weights of linear polymers, in which particles are separated based on their hydrodynamic volume. Since stars are more compact and have higher segment density than linear
polymers of the same molecular weight, the hydrodynamic volume of a star is lower than that of corresponding linear polymer. Therefore, the apparent molecular weights of stars determined by SEC calibrated with linear homologues are much lower than the true molecular weights. This limitation was partially solved by the use of the “Universal Calibration Principle” proposed by Benoit and coworkers. This method is based on the fact that the hydrodynamic volume is proportional to the product of intrinsic viscosity, [η], and molecular weight, M. As a result, molecular weights were estimated from the universal calibration curve made by plotting M x [η] vs. elution volume, V_e. However, this method cannot give the true molecular weight distribution and has limitations for highly branched polymers.

Absolute molecular weights and sizes of macromolecules can be determined by using light scattering; Debye established the theoretical basis of this method in 1944. Later, Zimm developed a practical method to extract the molecular parameters from the measured data. The light scattering from a dilute polymer solution was expressed by the following general formula:

\[
\frac{R_\theta}{K^* c} = \frac{1}{P(\theta)} \left[ \frac{1}{M_w} + 2A_2c + 3A_3c^2 + \ldots \right]
\]

where \( R_\theta \) = measured excess scattering intensity of solution over that of pure solvent (excess Rayleigh ratio)

\( c \) = concentration of solute

\( M_w \) = weight average molecular weight
K* = an optical constant, 

\[ K* = \frac{4(\pi n_0 \frac{dn}{dc})^2}{(N \lambda_0^4)} \]

where \( n_0 \) is the refractive index of the solvent at the incident radiation wavelength, \( \lambda_0 \) is the incident radiation wavelength, \( N \) is the Avogadro’s number, and \( \frac{dn}{dc} \) is the differential refractive index increment of the solution with respect to a change in solute concentration.

\[ P(\theta) = \text{theoretically derived form factor, } \left( P(\theta) = 1 - \frac{2 \mu^2 \langle R_g^2 \rangle}{3!} + \ldots \right) \text{ where } \mu = \left( \frac{4\pi}{\lambda} \right) \sin \left( \frac{\theta}{2} \right) \text{ and } \langle R_g^2 \rangle \text{ is the mean square radius of gyration} \]

\( A_2 \) and \( A_3 = \) second and third virial coefficients, respectively.

When the value of \( P(\theta) \) is substituted in the above equation and it is expanded to first order, the following equation is obtained:

\[ \frac{K* \cdot c}{R_\theta} = \frac{1}{M_w} \left[ 1 + \frac{16 \pi^2}{3 \lambda^2} \langle R_g^2 \rangle \sin^2 \left( \frac{\theta}{2} \right) \right] + 2 A_2 c \]

(2.6)

The molecular parameters \( A_2, \langle R_g^2 \rangle, \) and \( M_w \) can be obtained from this equation by considering three limits in either Zimm plot, \( K* \cdot c / R_\theta \) vs. \( \sin^2 \left( \frac{\theta}{2} \right) + k \cdot c \) where \( k \) is a stretch factor, or Debye plot, \( R_\theta / K* \cdot c \) vs. \( \sin^2 \left( \frac{\theta}{2} \right) + k \cdot c \): \( \theta = 0 \) line gives the \( A_2; c = 0 \) line gives the \( \langle R_g^2 \rangle; \) and \( \theta = 0, c = 0 \) point gives the \( M_w \).

The combination of low-angle laser light scattering and SEC was reported to be a useful technique for direct determination of molecular weight and molecular weight distribution.\(^{201,202}\) Recently, characterization of all molecular parameters of various polymer architectures with a multidetection SEC system was reported by Puskas et al.\(^{203}\) They used a SEC system equipped with a Wyatt Technology Viscostar viscometer (VIS), a Wyatt Optilab DSP RI detector, a Wyatt DAWN EOS 18 angle multi-angle laser light
scattering (MALLS) detector and a Wyatt quasi-elastic light scattering QELS detector to identify the branching parameters based on radii of gyration, \( R_{g,z} \), and hydrodynamic radii, \( R_{h,z} \).

Several branching parameters based on the radius of gyration, \( R_g \), the hydrodynamic radius, \( R_h \), and the intrinsic viscosity, \( [\eta] \), have been described for the characterization of branched polymers.\(^{204,205}\) These branching parameters, \( g \), \( h \), \( \rho \) and \( g' \), give insight into polymer architectures.

\[
g = \left( \frac{\langle R_g^2 \rangle_{br}}{\langle R_g^2 \rangle_{lin}} \right)_{M_w} \quad (2.7)
\]

\[
h = \left( \frac{D_{lin}}{D_{br}} \right)_{M_w} = \left( \frac{R_{h,br}}{R_{h,lin}} \right)_{M_w} \quad (2.8)
\]

\[
\rho = \left( \frac{\langle R_g^2 \rangle^{1/2}}{R_{h,z}} \right) \quad (2.9)
\]

\[
g' = \left( \frac{[\eta]_{br}}{[\eta]_{lin}} \right) \quad (2.10)
\]

where \( \langle R_g^2 \rangle_{br} \) and \( \langle R_g^2 \rangle_{lin} \) are the mean-square radii of branched and linear polymers of the same weight-average molecular weight, respectively, \( R_{h,z} \) is the effective \( z \)-average Stokes-Einstein hydrodynamic radius and \( [\eta]_{br} \) and \( [\eta]_{lin} \) are the intrinsic viscosities of branched and linear polymers of the same molecular weight. The effect of functionality is different on monodisperse and polydisperse star polymers as shown in the plots of \( g \), \( \rho \).
and $h$ vs. functionality ($f$), as shown in Figure 2.11 and 2.12. However, this effect becomes almost constant for both monodisperse and polydisperse stars beyond a functionality of 12.

Figure 2.11. Dependence of $g$ (geometric branching factor) and $\rho$ factor on the functionality for monodisperse and polydisperse stars. Reprinted with permission from Macromolecules 1980, 13, 1265-1272. Copyright © 1980 American Chemical Society.

Figure 2.12. Dependence of $h$ (hydrodynamic branching factor) on the functionality for monodisperse and polydisperse stars. Reprinted with permission from Macromolecules 1980, 13, 1265-1272. Copyright © 1980 American Chemical Society.
2.7.1. Dilute Solution Properties

Dilute solution viscosities of star polymers have been investigated for decades by many scientists. The unique viscosity behavior of non-linear polymers was first mentioned by Flory.\textsuperscript{206} Later it was shown that star polymers exhibit much lower intrinsic viscosities than linear polymers with the same molecular weight and composition in $\theta$ and good solvents.\textsuperscript{87,202,207-209} This phenomenon was explained by comparing the structures of star and linear polymers.\textsuperscript{89,210,211} The stars have condensed structures because of the restriction imposed by the central core so that they have high chain segment density near the star center. Because of this restriction, the expansion factors of star-branched polymers are less than those of linear chains in good solvent. Investigation of several star-branched samples, especially polystyrene and polyisoprene, with varied number of arms clearly showed that dilute solution viscosities are lower for branched polymers than for a linear material of the same molecular weight.\textsuperscript{87,209} The following plot shows experimentally determined values of $g$ and $g'$ for star-branched polystyrenes.
2.7.2. Glass Transition

The glass transition temperature \((T_g)\) of a non-crystalline star polymer is expected to be slightly lower than that of a linear polymer with the same molecular weight. The phenomenon of \(T_g\) depression for linear polymers of low molecular weight is well-known and generally is attributed to the disruptive effects of chain ends on packing of the polymer chain above \(T_g\), leading to increased values of specific volume and hence free volume. Since branched polymers have a larger number of chain ends for a given molecular weight, the same phenomenon is expected. Meares suggested that the conventional relationship between \(T_g\) and \(M_n\) should be modified as

\[
g(\theta), \square^{212}, \Delta^{213, 214}, +^{215}, \text{dotted line (---) calculated from } g = (3f-2)/f^2, \text{ where } f \text{ is functionality; } g'(\theta), \blacktriangle^{216}, \bullet^{217, 218}, \ast^{213, 214}, \bigcirc^{215}, \text{dark solid line (─) is theoretical line}.^{209}
\]
\[ T_g = T_g^\infty - \frac{K \cdot f}{2M_n} \]

where \( f \) is the number of chain ends per molecule, \( K \) is a constant \((K=2\theta \rho N_A/\alpha_f, \theta \) is free volume, \( \rho \) is density, \( N_A \) is Avogadro’s constant, \( \alpha_f \) is thermal expansion coefficient of the free volume) and \( T_g^\infty \) is the value for infinitely high molecular weight polymer. The investigation of \( T_g \) for linear, four- and six-branched star polystyrenes with low arm molecular weights confirmed this relationship. In contrast to this findings, Sokolov recently showed that the value of \( T_g \) is dependent on the total molecular weight of the molecule but independent of its architecture for polybutadiene. Although this observation disagreed with the prediction \((T_g \propto f/M_n)\), there was no ready explanation for this phenomenon.

In this dissertation, all polymers obtained by either monofunctional or multifunctional initiators have been characterized by SEC and NMR spectroscopy.
CHAPTER III
EXPERIMENTAL

3.1. Materials

α-Methylstyrene (α-MS, Aldrich), 2,4,4-trimethyl-1-pentene (TMP-1, Aldrich) and 2,4,4-trimethyl-2-pentene (TMP-2, Aldrich) were vacuum-distilled prior to use. m-Chloroperoxybenzoic acid (m-CPBA, Aldrich, max. 77%) was purified as described in the literature. Specifically, 50 g of raw m-CPBA was washed 3 times with a total of 1000 mL of the mixture of the buffer solution of sodium phosphate dibasic heptahydrate, Na₂HPO₄·H₂O, (67.1 g in 500 mL of DI water) and potassium dihyrogen phosphate, KH₂PO₄, (34 g in 500 mL of DI water) and then with DI water to remove the excess salt. It was dried in a desiccator under vacuum until constant weight. Squalene (Aldrich), sodium phosphate dibasic heptahydrate (Na₂HPO₄·H₂O, Aldrich), potassium dihyrogen phosphate (KH₂PO₄, Aldrich), sodium sulfite (Na₂SO₃, Aldrich), sodium bicarbonate (NaHCO₃, Fisher Sci.), magnesium sulfate (MgSO₄, EMD), methanol (MeOH, EMD), TiCl₄, BCl₃ (1 M in dichloromethane and 1 M in hexane (Aldrich); neat (Linde Gas)), 2,6-di-t-butylpyridine (DtBP, Aldrich or Acros Organics) and d-chloroform (Aldrich or Cambridge Isotope Laboratories) were used as received. Dichloromethane (CH₂Cl₂, EMD) was dried by distillation from calcium hydride prior to use. Hexane (Hx, Aldrich or EMD) was dried by distillation from Na/Benzophenone prior to use. Methyl chloride
(MeCl, 99%) and IB (99%) were supplied by LANXESS Inc., Canada and were dried by passing the gases over drying columns packed with CaCl$_2$ and BaO before condensing them from the gas phase. 1,2-Epoxyclohexane (Fluka, ≥98%, GC) was vacuum distilled prior to used. Epoxyclohexylisobutyl POSS® (Hybrid Plastics) was dried in vacuum oven for 2 weeks prior to use. $\text{bis}[3,4-(\text{epoxycyclohexyl})\text{ethyl}]\text{tetramethyl-disiloxane}$ (SIB1092.0, Gelest Inc.; courtesy of Susan Rhodes) was used as received.

3.2. Instrumentation/Characterizations

Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, size exclusion chromatography (SEC), transmission electron microscopy (TEM) were utilized in this research.

3.2.1. Fourier Transform Infrared (FTIR) Spectroscopy

Real-time FTIR monitoring was performed using a liquid transmission (TR) or an attenuated total reflectance (ATR) probe (REMSPEC Inc.) interfaced with a Bio-Rad FTS 175C, later replaced by a Varian 3100-Excalibur Series FTIR unit (source cable), and a MID-IR fiber optic detector module (a liquid nitrogen cooled 0.5 x 0.5 mm MCT detector, receiver cable).
The fiber optic cables with a probe were fed into the glove box through a port and immersed into the reactor, which was a three-necked, round-bottom flask equipped with an overhead stirrer. The reactor was immersed in a hexane bath maintained at the specified reaction temperature using either a Flexi-Cool chiller (FTS Systems) or coils through which liquid nitrogen was fed. For best signal output the attached cable ends were aligned manually. Optimum signal/noise ratios (>10) were obtained when the center burst maximum (negative peak on the on-screen display) was about -5 to -7 V at a sensitivity (amplifier gain) between 1 and 3 within the ±10 V signal range. To cool the infrared probe to the reaction temperature, the sensor was kept above the surface of the solvent/solvent mixture for 15 min before immersing it into the cold liquid. Background scans of the solvents and DrBP, proton trap, were taken at a resolution of 8 cm⁻¹.
3.2.2. \(^1\)H and \(^{13}\)C Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR analyses were performed by the use of deuterated chloroform (CDCl\(_3\)); either tetramethylsilane (TMS, \(\delta = 0\) ppm) or the undeuterated chloroform peaks (\(\delta = 7.27\) ppm for \(^1\)H NMR and \(\delta = 77.23\) ppm for \(^{13}\)C NMR) were used as an internal reference. Sample concentrations were 10-50 weight %. Spectra were recorded on a Varian Gemini 300, a Varian Mercury 300 and a Varian NMRS 500 (UA) and a Bruker Avance 500 MHz (LANXESS Inc.) spectrometer.

ACD/1D & 2D NMR Processor (Advanced Chemistry Development, Inc.) was used for the analysis of NMR spectra. ACD/C + H NMR Predictor (Advanced Chemistry Development, Inc.) was used to simulate NMR spectra of some structures not well-characterized in the literature.

3.2.3. Size Exclusion Chromatography (SEC)

Molecular weights (MW), molecular weight distributions (MWD), viscosity, radii of gyration and hydrodynamic radii of the polymers were determined by Size Exclusion Chromatography (SEC). The University of Akron’s SEC instrument was a Waters system equipped with six Styragel-HR columns (HR0.5, HR1, HR3, HR4, HR5 and HR6) thermostated at 35 °C, a Dawn EOS 18 angle laser light scattering (MALLS) detector (Wyatt Technology), an Optilab DSP refractive index (RI) detector (Wyatt Technology) thermostated at 40 °C, a 2487 Dual Absorbance UV detector (Waters), a quasi-elastic light scattering (QELS) detector (Wyatt Technology), and a Viscostar viscosity detector (Wyatt Technology). THF, freshly distilled from CaH\(_2\), was employed as the mobile phase and was delivered at 1 mL/min. ASTRA (Wyatt Technology) was used to obtain
absolute MW data with dn/dc = 0.108 for PIB in THF or assuming 100% recovery on the columns. LANXESS Inc. system was a Viscotek Triple Detector Model 300, equipped with a 4-capillary differential viscometer (VIS), right-angle light scattering (RALS) and DRI detectors, and a single mixed bed column (Viscogel GMHHRH). THF was used as the mobile phase with a flow rate of 0.5 mL/min at 35°C. Samples of 100 µL (2-3 g/L in THF) were injected and the data was processed with the TriSEC (version 3.00) software.

3.2.4. Transmission Electron Microscopy (TEM)

TEM imaging was performed using a Philips Tecnai 12 (120 kV) electron microscope. For film casting, a carbon-coated copper TEM grid was floated over a bath of boiling water, and a droplet of the polymer solution was carefully dropped over the floating grid. The casted TEM grid was first kept in a vacuum oven overnight at room temperature. After that, staining was performed on the grid using the vapors of aqueous RuO₄ solution (0.67 wt%) for 30 min. Finally, the grid was again kept in vacuum overnight to remove toxic vapors before TEM imaging.

3.3. Procedures

Procedures for initiator synthesis and polymerizations are discussed in the following sections.

3.3.1. Initiator Syntheses

MSE, TMPO-1, TMPO-2 and HES were synthesized by the reaction of their corresponding olefins (α-methylstyrene, 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-
pentene and squalene, respectively) with pure CPBA in dichloromethane at 0 °C, as shown in Scheme 3.1.

Scheme 3.1. A representative synthesis of epoxy initiators.

The procedure for epoxidation was as follows: 2.5 equivalents/olefin double bond of \( m \)-CPBA was dissolved in 500 mL of \( CH_2Cl_2 \) and charged to a three-necked, round-bottom flask equipped with a magnetic stirrer and submerged in an ice-water bath. The corresponding olefin mixed with 30 mL of \( CH_2Cl_2 \) was placed into an addition funnel and added dropwise to the \( m \)-CPBA solution. After addition of the olefin solution, the reaction was allowed to proceed for 30 minutes. Termination was effected with the addition of 300 mL of 20 wt% solution of sodium sulfite in DI \( H_2O \) to remove the by-product, \( m \)-chlorobenzoic acid. The content of the reaction flask was transferred into a separatory funnel and shaken vigorously. Two distinct layers were formed upon settling: a lower organic layer containing the desired product and an upper aqueous phase. The aqueous phase was decanted and the organic phase was washed with a sodium sulfite solution twice more to clean-up any by-product left. The organic layer was then washed with 300 mL of a saturated \( NaHCO_3/DI \ H_2O \) solution three times, with the organic phase being collected each time. Finally, the organic layer was washed with DI \( H_2O \) until it was neutral and dried with MgSO\(_4\). MgSO\(_4\) was removed by filtration and, subsequently, \( CH_2Cl_2 \) was removed by rotary evaporation. MSE, TMPO-1 and TMPO-2 were further
purified by vacuum distillation and the purity checked by $^1$H NMR. MSE was found to isomerize upon distillation to the corresponding aldehyde and enol even in the absence of a Lewis acid. Indeed, it has been reported that MSE isomerizes very readily, even in the absence of acids. MSE, $^1$H: CH$_3$ (a): 1.72 ppm, CH$_2$ (d$_1$,d$_2$): 2.80-2.99 ppm, aromatic protons: 7.24-7.50 ppm (Figure 4.2) and $^{13}$C: CH$_3$ (a): 21.81 ppm, CH$_2$ (b): 57.03 ppm, C (c): 56.73 ppm, C (d): 141.17 ppm, CH (e): 123.27 ppm, CH (f): 128.32 ppm, CH (g): 127.44 (Figure 4.3). TMPO-1, $^1$H: CH$_3$ (a): 1.00 ppm, CH$_3$ (b): 1.39 ppm, CH$_2$ (c): 2.58-2.64 ppm, CH$_2$ (d): 1.26-1.31 and 1.71-1.76 ppm (Figure 4.18) and $^{13}$C: CH$_3$ (a): 30.61 ppm, CH$_3$ (d): 23.36 ppm, CH$_2$ (e): 51.04 ppm, CH$_2$ (f): 54.63 ppm, C (b): 30.85 ppm, C (e): 55.78 ppm (Figure 4.19). TMPO-2, $^1$H: CH$_3$ (a): 1.02 ppm, CH$_3$ (b): 1.29 ppm, CH$_3$ (c): 1.42 ppm, CH (d): 2.49 ppm (Figure 4.28) and $^{13}$C: CH$_3$ (a): 27.72 ppm, CH$_3$ (c): 19.54 ppm, CH$_3$ (d): 27.11 ppm, CH (f): 72.53 ppm, C (b): 31.56 ppm, C (e): 59.22 ppm (Figure 4.29). The HES was a very viscous, clear liquid that was used without further purification. The residual solvent was removed by placing the product in a vacuum oven until it reached a constant weight and purity was checked by $^1$H NMR.

3.3.2. Polymerizations

Polymerizations were carried out both in the laboratories of LANXESS Inc., Canada, and The University of Akron (UA). The LANXESS system was a Vacuum Atmospheres Co. glove box under dry nitrogen atmosphere; moisture <5 ppm and oxygen <10 ppm contents were continuously monitored and maintained. The UA system was an MBraun LabMaster 130 glove box under dry nitrogen atmosphere; moisture <1 ppm and
oxygen <5 ppm contents were continuously monitored and maintained. Details are discussed in the following sections.

3.3.2.1. General Procedure

A three-necked, round-bottom flask equipped with an overhead stirrer was immersed in a hexane bath maintained at the specified reaction temperature using either a Flexi-Cool chiller (FTS Systems) or coils through which liquid nitrogen passing for cooling. The flask was charged with the specified solvents followed by the proton trap, DtBP, and the initiator. Depending on the addition sequence, the reaction was started either by the addition of the Lewis acid (BCl₃ or TiCl₄) following the addition of IB, or by IB following the addition of the Lewis acid. Exact reaction conditions are specified in the text, table and figure captions. In some polymerizations, aliquots were subsequently taken at specified times and quenched in chilled culture tubes containing MeOH for gravimetric conversion analysis. The reactions were terminated by the addition of MeOH/NaOH. After the evaporation of all volatiles, the samples were dissolved in hexane and solutions were washed with distilled water until they were neutral, dried over MgSO₄ and filtered. PIBs were recovered by either precipitation into methanol or by evaporating the solvent with a rotary evaporator and drying in a vacuum oven, depending on their molecular weights. Final conversions were determined gravimetrically.

3.3.2.2. Real-time FTIR Monitoring

The fiber optic cables with a probe were fed into the glove box through a port and immersed into the reactor, a three-neck round bottom flask equipped with an overhead...
stirrer and immersed in a hexane bath maintained at the specified reaction temperature. After aligning the cable ends manually, the sensor was kept above the surface of the solvent/solvent mixture for 15 min before immersing it into the cold liquid to cool the infrared probe to the reaction temperature. For monitoring the ring-opening reaction, initiator was added into the reaction vessel and the IR spectrum was recorded after taking the background spectrum of solvent and the proton trap. Specific conditions are given in the text, tables and figure captions. IR spectra of the reactions were then taken every 8 to 24 s and collected into one multi-file by the Bio-Rad Win-IR or the Varian Resolution Pro 4.0 software. The data were evaluated with the GRAMS software package (Galactic Industries Corp.).

Calibration with known IB concentrations demonstrated direct proportionality between both the area and height of the 1655 cm\(^{-1}\) band (C=C stretch) in the 0.001-0.5 mol/L IB range and the 1780 cm\(^{-1}\) band (overtone of the C–H wag of \(=\text{CH}_2\)) in the 0.3-6 mol/L IB range.\(^{23}\) Because of the sensitivity of the TR probe, the 1655 cm\(^{-1}\) band saturates beyond 0.5 mol/L IB concentration so the proportionality would not apply. On the other hand, the 1780 cm\(^{-1}\) band can be monitored well only above about 0.3 mol/L IB concentrations.

3.3.2.3. Screening Reactions

Screening reactions were performed in 70 mL test tubes with Teflon-faced rubber lined screw caps immersed in a hexane bath at the specified reaction temperatures in MBraun glove box described above. The reaction tubes were charged with solvent/solvent mixture followed by D/tBP, initiator and IB. The reactions were started by the addition of the Lewis acid and stirred frequently with a Thermolyne #37600 Vortex
Mixer. The reactions were terminated by the addition of MeOH/NaOH. After evaporation of all volatiles, the polymers were purified by redissolving them in hexane, washing with distilled water, drying over MgSO₄ and filtering. PIBs were recovered by either precipitation from methanol or by evaporating the solvent with a rotary evaporator and drying in a vacuum oven, depending on their molecular weights. Final conversions were determined gravimetrically.

3.3.2.4. Two-stage Polymerizations

Two-stage polymerizations were performed for the synthesis of the high molecular weight PIB, which included the synthesis of low molecular weight PIB, “macroinitiator”, initiated by HES/BCl₃, followed by growing the PIB chains to high molecular weights in the presence of TiCl₄. Since ring-opening and initiation in the presence of BCl₃ requires a polar medium, the first stage of reactions was carried out in MeCl. A three-necked, round-bottom flask equipped with an overhead stirrer was immersed in a hexane bath maintained at the specified reaction temperature in the glove box. For the first part of the polymerization, the reaction vessel was charged with MeCl, the proton trap, DtBP, inititor and IB. The polymerization was started by the addition of BCl₃. After 4 to 8 hours, the reaction medium was diluted by the addition of hexane (for Hx/MeCl, 60/40, v/v) for the second stage of the polymerization. Additional IB was added, followed by TiCl₄. Aliquots were subsequently taken at specified times in the second part of the polymerizations and quenched in chilled culture tubes containing MeOH for gravimetric conversion analysis. The reactions were terminated by the addition of MeOH/NaOH. After the evaporation of all volatiles, the samples were
dissolved in hexane and solutions were washed with distilled water until they were neutral, dried over MgSO$_4$ and filtered. PIBs were recovered by either precipitation into methanol and drying in a vacuum oven. Final conversions were determined gravimetrically.
One of the objectives of this research was to synthesize star-branched polyisobutenes (PIB) by living carbocationic polymerization using a six-functional epoxy initiator, hexaepoxysqualene (HES), and to characterize the star-branched PIBs. The understanding of the initiation and propagation mechanisms by HES is crucial to control the number and lengths of the arms of the stars. Therefore, to get a better understanding of the mechanisms, the initiation of IB polymerization was investigated by the use of various substituted epoxides in conjunction with BCl₃ and TiCl₄ coinitiators.

4.1. Investigation of the Mechanism of Initiation and Propagation of Epoxy-initiated IB Polymerizations using Monofunctional Epoxides

Monofunctional epoxides used as initiators in this research are α-Methylstyrene epoxide (MSE), 1,2-epoxy-2,4,4-trimethylpentane (TMPO-1) and 2,3-epoxy-2,4,4-trimethylpentane (TMPO-2).

4.1.1. Aromatic Epoxy Initiator: α-Methylstyrene Epoxide (MSE)

MSE is a substituted epoxide which was found to be an effective initiator in conjunction with TiCl₄ for living IB polymerization yielding a unique asymmetric
telechelic PIB carrying an \( \alpha \)-primary OH and an \( \omega \)-tertiary Cl terminus. To get a better understanding of the mechanism of ring-opening and initiation of IB polymerization by MSE/TiCl\(_4\) and MSE/BCl\(_3\), IB polymerizations by the MSE/TiCl\(_4\) and MSE/BCl\(_3\) initiating systems were investigated using \textit{in situ} FTIR monitoring.

4.1.1.1. \textit{Real-time} FTIR Monitoring of the Reaction of MSE with TiCl\(_4\) in the Absence of IB

The initiation of IB polymerization by MSE/TiCl\(_4\) was monitored by \textit{in situ} FTIR and is discussed here. The FTIR spectrum of MSE is shown in Figure 4.1. In order to observe only the ring-opening reaction, MSE was first reacted with TiCl\(_4\) in the absence of IB. The band at 1260 cm\(^{-1}\) is characteristic of the C–O–C stretch in the oxirane ring. The two strong bands at 1685 and 1735 cm\(^{-1}\) were reminiscent of the two signals (at 1665 and 1635 cm\(^{-1}\)) seen in the reaction of TMPO-1 with TiCl\(_4\).\(^{23}\) Those bands appeared only after the addition of one molar equivalent of TiCl\(_4\) to TMPO-1; thus they were originally assigned to the carbonyl stretch in 2,4,4-trimethylpentanal-1 (TMPA-1) and TMPA-1 complexed with TiCl\(_4\) (TMPA-1→TiCl\(_4\)), respectively (Scheme 4.1). The IR bands observed at 1685 and 1735 cm\(^{-1}\) were assigned to the carbonyl stretch of 2-phenylpropanal (Ph=O) and the C=C double stretching of its enol, respectively.
Figure 4.1. FTIR spectrum of MSE and its isomerization products. \([\text{MSE}]_0 = 0.1 \text{ M}, \ [\text{DrBP}] = 0.007 \text{ M}, \text{Hx/MeCl (60/40, v/v), T = -80 }^\circ\text{C}.

Scheme 4.1. Proposed mechanism of IB polymerization initiated with the TMPO-1/TiCl4 system.
Analysis of MSE with $^1$H NMR spectroscopy (Figure 4.2) also demonstrated the presence of 2-phenylpropanal ($\text{CH}_3$: 1.6 ppm, $\text{CH}$: 4.3 ppm, $\text{HC}=\text{O}$: 9.7 ppm) and corresponding enol (=$\text{C–CH}_3$: 2.6 ppm, =$\text{CH}$: 6.0 ppm). Indeed, it has been reported that MSE isomerizes very readily, even in the absence of acids. The presence of 2-phenylpropanal was also demonstrated by the band at 1180 cm$^{-1}$ (IV in Figure 4.1) assigned to the C–H in-plane bending of the HC=O. The $^1$H NMR showed only ~6 mol% aldehyde and ~6 mol% enol, while the associated FTIR signals were very intense (Figure 4.2). Since $^{13}$C NMR is not as sensitive as $^1$H NMR, the signals from the isomers could not be well identified. (Figure 4.3)

Figure 4.2. $^1$H NMR spectrum of MSE and its isomerization products.
Upon addition of 1 molar equivalent of TiCl$_4$ to MSE in the absence of IB, the FTIR bands assigned to the aldehyde (II in Figure 4.4 and IV in Figure 4.5) and enol (III in Figure 4.4) disappeared in about 170 sec. The opening of the epoxide ring was demonstrated by the decreasing intensity of the band at 1260 cm$^{-1}$ (I in Figure 4.5), however, it did not disappear completely. The appearance of the broad band at 1100 cm$^{-1}$ (VI in Figure 4.5) signal the formation of ether bonds, i.e., oligoethers by oxonium-ion initiated polymerization of MSE (SN$_2$ pathway, see Scheme 4.1).

Figure 4.3. $^{13}$C NMR spectrum of MSE.
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Figure 4.4. *Real-time* FTIR monitoring of the reaction of MSE with TiCl₄ in 1:1 ratio: 1550-1800 cm⁻¹ region. [MSE]₀ = [TiCl₄] = 0.1 M, [D₄BP] = 0.007 M, Hx/MeCl (60/40, v/v) T = -80 °C.

The new band at 1615 cm⁻¹ (V in Figure 4.4) was assigned to the stretching vibration of the –COTiCl₃ group of the tertiary chloride (I in Scheme 4.2) formed by the reaction of MSE and TiCl₄ by the S₅₋₁ pathway, as shown in Scheme 4.2.

Figure 4.5. *Real-time* FTIR monitoring of the reaction of MSE with TiCl₄ in 1:1 ratio: 1050-1300 cm⁻¹ region. [MSE]₀ = [TiCl₄] = 0.1 M, [D₄BP] = 0.007 M, Hx/MeCl (60/40, v/v) T = -80 °C.
Scheme 4.2. Formation of a tertiary chloride in the reaction of MSE with TiCl₄.

The formation of the –OTiCl₃ group in the reaction of terminal epoxides (e.g. 1,2-epoxydecane) with TiCl₄ has been reported, and polarized/ionized organometallic compounds were shown to have a very intense IR absorption in the 1600-1800 cm⁻¹ range. We will also show later that this peak can be used to monitor the rate of initiation by epoxides. After 640 seconds of monitoring the reaction between MSE and TiCl₄, IB was added to the mixture and this stage was monitored for 240 additional seconds. Intensity of the 1655 cm⁻¹ peak, characteristic of the C=C stretching in IB, did not change, which indicated that the absence of any species to initiate polymerization. It is known that cationic polymerizations can be initiated by traces of water in the presence of Lewis acids. Such a reaction could also account for the ring-opening polymerization of epoxides. The fact that IB polymerization did not occur at this stage demonstrates that
protic impurities were eliminated by the proton trap. The addition of excess TiCl₄ ionized the tertiary chloride (I), and polymerization was evidenced by the progressive disappearance of the characteristic olefin peak of IB at 1655 cm⁻¹ (VII in Figure 4.6, C=C stretch), and the progressive growth of a signal at 1230 cm⁻¹ (VIII in Figure 4.7) assigned to distorted carbon tetrahedrons (–C(CH₃)₂ groups) in PIB. The intensity of the 1615 cm⁻¹ signal, representing the –COTiCl₃ group attached to [I] and/or the growing PIB chain, remained constant.

Figure 4.6. Real-time FTIR monitoring of IB polymerization initiated by MSE/TiCl₄: 1600-1800 cm⁻¹ region. [MSE]₀ = [TiCl₄] = 0.1 M, [IB]₀ = 0.3 M, time 0: addition of excess [TiCl₄] = 0.2 M, [DtBP] = 0.007 M, Hx/MeCl (60/40, v/v) T = -80 °C.
Figure 4.7. Real-time FTIR monitoring of IB polymerization initiated by MSE/TiCl₄: 1050-1250 cm⁻¹ region. [MSE]₀ = [TiCl₄] = 0.1 M, [IB]₀ = 0.3 M, time 0: addition of excess [TiCl₄] = 0.2 M, [D₆BP] = 0.007 M, Hx/MeCl (60/40, v/v) T = -80 °C.

The final product of the experiment shown in Figures 4.6 and 4.7 had $M_n = 8300$ and 10,000 g/mol by NMR and SEC, respectively, and $M_w/M_n = 1.25$. Due to the low $[IB]_0/[MSE]_0$ ratio, the initiator efficiency was low; $I_{eff} = 1.4\%$, calculated by using the $M_n$ by $^1$H NMR spectrum. This indicates that only a small fraction of the epoxide yielded the tertiary chloride initiator [I], and the rest formed oligoethers as shown in Scheme 4.4. It was shown earlier that higher ratios yield higher efficiencies ($[IB]_0/[MSE]_0 = 500$, $I_{eff} \sim 40\%$). NMR integrations demonstrated the presence of one primary hydroxyl head group and one tertiary chloride end group per polymer chain, similarly to that reported earlier.
4.1.1.2. \textit{Real-time} FTIR Monitoring of the Reaction of MSE with TiCl$_4$ in the Presence of IB

The FTIR spectrum of MSE + IB before addition of TiCl$_4$ is shown in Figure 4.8. The band at 1260 cm$^{-1}$ (I in Figure 4.8) is characteristic of the C–O–C stretch in the oxirane ring. The C=C stretching at 1655 cm$^{-1}$ (VII in Figure 4.8) as well as the two strong bands at 1685 and 1735 cm$^{-1}$ (II and III in Figure 4.8) due to the MSE isomers (aldehyde and enol), as explained in the previous section, were observed.

After the addition of an excess TiCl$_4$ to the mixture of MSE and IB, ring-opening was demonstrated by the disappearance of C–O–C stretching at 1260 cm$^{-1}$ (I in Figure 4.9). The disappearance of the band at 1180 cm$^{-1}$ (IV in Figure 4.9), assigned to the C–H in-plane bending of the 2-phenylpropanal, showed that the aldehyde isomer of MSE is somehow involved in initiation. In fact, Puskas et al.\textsuperscript{23} have shown that 2-butanone/TiCl$_4$
and acetophenone/TiCl₄ combinations initiated IB polymerization. The proposed mechanism of the formation of tertiary carbocation in the ketone/TiCl₄ system is shown in Scheme 4.3.

Scheme 4.3. Proposed formation of tertiary carbocation from the reaction of a ketone with TiCl₄.²³

The appearance of the broad band at 1100 cm⁻¹ (VI in Figure 4.9) signaled the formation of ether bonds, i.e., oligoethers by oxonium-ion initiated polymerization of MSE (S₉2 pathway, Scheme 4.4) (see also previous section). The polymerization ensued immediately, as evidenced by the progressive disappearance of the C=C stretching (1655 cm⁻¹) and C–H wag band (1780 cm⁻¹) in the =CH₂ group of IB (VII and IX in Figure 4.10, respectively) as well as the progressively growing PIB signal at 1230 cm⁻¹ (VIII in Figure 4.9).
Figure 4.9. *Real-time* FTIR monitoring of IB polymerization initiated by MSE/TiCl₄: 1050-1300 cm⁻¹ region. [MSE]₀ = 0.1 M, [IB]₀ = 0.3 M, [TiCl₄] = 0.3 M, [D₆BP] = 0.007 M, Hx/MeCl (60/40, v/v) T = -80 °C.

Figure 4.10. *Real-time* FTIR monitoring of IB polymerization initiated by MSE/TiCl₄: 1600-1800 cm⁻¹ region. [MSE]₀ = 0.1 M, [IB]₀ = 0.3 M, [TiCl₄] = 0.3 M, [D₆BP] = 0.007 M, Hx/MeCl (60/40, v/v) T = -80 °C.
The stretching vibration of the –COTiCl$_3$ group of the tertiary chloride (I in Scheme 4.2) by the reaction of MSE and TiCl$_4$ via the S$_N$1 pathway at 1615 cm$^{-1}$ was also observed (V in Figure 4.10).

In summary, *in situ* FTIR monitoring gave further insight into the mechanism proposed earlier for this system.$^{64}$ In contrast to the mechanism proposed earlier, the presence of aldehyde and enol isomers of MSE were found even in the absence of TiCl$_4$. It was proposed that both S$_N$1 and S$_N$2 pathways occur competitively. Oligoethers are obtained by cationic ring-opening polymerization of the epoxide by the S$_N$2 pathway. At the same time, the epoxide was cleaved by the proposed S$_N$1 pathway that formed the tert-Cl initiator, [I], which was activated later by excess TiCl$_4$ to initiate the polymerization of IB, as shown in Scheme 4.4.
Scheme 4.4. Proposed modified mechanism of IB polymerization initiated by MSE/TiCl₄.

As mentioned earlier in this chapter, the band at 1615 cm⁻¹, which appears just after the addition of TiCl₄ (or another Lewis acid) to the solution containing epoxide initiator, is assigned to the stretching vibration of the –COTiCl₃ group of the tertiary chloride (I in Scheme 4.4) forming in the reaction of epoxide and Lewis acid by the Sₙ₁ pathway. Since IR absorptivity is proportional to the concentration of a substance, the change in this absorption can be correlated to the amount of the tertiary chloride
initiator/polymer chain concentration. Therefore, it provides valuable information about
the rate of ring-opening/initiation.

MALDI-ToF mass spectroscopy (MS) verified the structure of a representative
PIB sample made by MSE/TiCl₄ having \( M_n = 5,100 \) g/mol and \( M_w/M_n = 1.08 \), as shown
in Figure 4.11. Each chain carried exactly one primary OH group as explained in detail
in Gautriaud’s M.S. Thesis. Under the conditions of the MALDI-ToF measurement,
quantitative dehydrohalogenation occurred.

![Figure 4.11. Structure of the PIB-OH molecule identified with MALDI-ToF MS.](image)

4.1.1.3. **Real-time** FTIR Monitoring of the Reaction of MSE with BCl₃ in the Absence of IB

It was of interest to explore another Lewis acid, BCl₃ cointitiator in conjunction
with epoxides. BCl₃ is effective with a variety of initiators such as tert-halides, tert-alkyl
esters, ethers and alcohols in polar solvents as discussed in the Chapter II, Background.

Before details of in situ FTIR studies are given, an NMR study of the ring-
opening with BCl₃ in the absence of IB will be briefly discussed. In order to observe the
possible products, MSE was qualitatively reacted with neat BCl₃ in methyl chloride
(MeCl) at -70 °C and the $^1$H NMR spectrum was recorded just after the sample was taken out of the cold bath to evaporate the volatiles without deliberate termination and/or further purification. The main signals observed in the $^1$H NMR spectrum (Figure 4.12) indicated ring-opening by the S$_{N}$1 mechanism forming a tert-Cl initiator: The $\text{-CH}_3$ protons (a) were shifted downfield and observed at 2.0 ppm because of the presence of $\text{-Cl}$ in close proximity; the $\text{-CH}_2$– protons (b) next to $\text{–OBCl}_2$ also shifted downfield and appeared at 4.40-4.54 ppm. The presence of a second set of doublets at ~4.7 ppm and singlets at ~ 2 ppm shows the formation of other structure(s), most likely oligoethers and/or a dimer of MSE formed by an S$_{N}$2 mechanism. The large signal at 3.0 ppm comes from MeCl, the reaction solvent.

Figure 4.12. $^1$H NMR spectrum of the products of the reaction of MSE with BCl$_3$. 
Next, the reaction between MSE and BCl₃ was also monitored by *in situ* FTIR to observe the ring-opening of the aromatic epoxide. Upon addition of an equimolar amount of BCl₃ (75 sec) to MSE, the band at 1260 cm⁻¹ (I in Figure 4.13), characteristic of the epoxide rings, completely disappeared (because BCl₃ in hexane was used, solvent peaks appeared in the 1000 – 1250 cm⁻¹ region).

![Figure 4.13. Real-time FTIR monitoring of the reaction of MSE with BCl₃ in 1:1 ratio: 1050-1300 cm⁻¹ region. [MSE]₀ = [BCl₃]₀ (in Hx) = 0.1 M; [D₄BP] = 0.007 M, MeCl, T = -80 °C.](image)

The two strong peaks (II and III in Figure 4.14), assigned to 2-phenylpropanal and its enol, also disappeared, and a new band at 1620 cm⁻¹ with a shoulder at around 1605 cm⁻¹ grew quickly (V, V' in Figure 4.14, respectively). These signals were assigned to the tertiary chloride initiator formed in the reaction of MSE with BCl₃, similar to [I] shown in Scheme 4.4 and π-complex between the aromatic ring and carbenium ion formed by the ring-opening of MSE with BCl₃ by the S_N1 mechanism. In fact, Nuyken et al.²²⁵ found a similar complex by UV/Vis and conductivity measurements when they investigated a dicumyl chloride/BCl₃ system for the polymerization of IB. Importantly,
polyether signal was absent at ~1100 cm\(^{-1}\), in contrast to that found in the MSE/TiCl\(_4\) system (Figure 4.5).

![Real-time FTIR monitoring of the reaction of MSE with BCl\(_3\) in 1:1 ratio: 1600-1800 cm\(^{-1}\) region. \([\text{MSE}]_0 = [\text{BCl}_3]_0\) (in Hx) = 0.1 M; \([\text{D}t\text{BP}]\) = 0.007 M, MeCl, T = -80 °C.]

Subsequently, IB was added to the reaction mixture at 815 seconds, and the reaction was monitored for another 417 seconds. Polymerization was not observed – the intensity of the IB signal (1655 cm\(^{-1}\)) remained unchanged as shown in Figure 4.15. The 1620 cm\(^{-1}\) peak and its shoulder, representing –COBCl\(_2\) attached to [I], and the π-complex of MSE – BCl\(_3\) also remained unchanged. At that point excess BCl\(_3\) (0.2M) was added, but decrease of the IB signal was not observed within the 2000 sec observation time. These results verify the absence of initiation by protic impurities as well as absence of any initiating species.
Upon addition of a half an equivalent of TiCl$_4$ at about 2000 seconds, the immediate disappearance of the IB signal demonstrated fast polymerization (Figure 4.15). The intensity of the 1620 cm$^{-1}$ peak decreased, while the shoulder at 1605 cm$^{-1}$ did not seem to change. It can be theorized that the 1620 cm$^{-1}$ signal represents the –COBCl$_2$ group attached to the tert-chloride initiator (I in Scheme 4.5), and the 1605 cm$^{-1}$ band represents a sandwich complex between the aromatic ring and BCl$_3$ – this will be discussed in more detail in conjunction the TMPO-1/BCl$_3$ system. The final conversion was determined as 60% gravimetrically and the final product of the polymerization was an αHO-PIB-ωCl with $M_n = 15,000$ g/mol and $M_w/M_n = 1.58$, and an $I_{	ext{eff}} = 0.7\%$.

Based on these studies, the mechanism of initiation can be proposed for the MSE/BCl$_3$/IB system (Scheme 4.5.) Addition of BCl$_3$ to MSE and its isomers (as discussed above, MSE isomerizes spontaneously to the corresponding aldehyde and enol)
yields oxonium ion intermediates, and/or the tert-Cl initiator I. Initiation by I with excess BCl$_3$ does not occur or it is slow. The amount of BCl$_3$ is insufficient for initiation because it is consumed by coordination with the aromatic ring. The addition of excess TiCl$_4$ starts the polymerization of IB. Polyether formation was not observed in this system by real-time FTIR.

Scheme 4.5. Proposed mechanism of initiation of IB polymerization by MSE/BCl$_3$. 
4.1.1.4. The Reaction of MSE with BCl₃ in the Presence of IB

MSE was reacted with BCl₃ in 1:3 ([MSE]/[BCl₃]) ratio in the presence of IB. After 4 hours, the viscosity of the charge did not change suggesting the absence of polymerization. Therefore, a small amount of TiCl₄ ([TiCl₄]/[MSE] = 0.5) was added after an aliquot was taken. Both the aliquot and the final sample were analyzed by NMR spectroscopy. Figure 4.16 shows the ¹H NMR spectrum of the sample taken before TiCl₄ addition. The products mostly arose by side reactions. The formation of a five-membered ring (A in Scheme 4.6) was observed in a model reaction between MSE/TiCl₄ and diisobutylene. Methylene protons (d and e in Figure 4.16) of the five-membered ring (A) were identified by ¹H NMR spectroscopy.

Scheme 4.6. Possible alternative reaction between MSE/BCl₃ and isobutylene.
The presence of an aldehyde (–CHO at 9.6 ppm), some unsaturation (–C=CH₂ at 4.6-4.8 ppm – doublet), which will be discussed later, and the other unidentified structure, possibly an indanyl ring by intramolecular cycloalkylation (Scheme 2.1), as well as IB incorporation forming α-hydroxy,ω-tert-chloride oligomers were also observed in minor amounts.

![Chemical Structure](image)

Figure 4.16. ¹H NMR spectrum of the products of the reaction of MSE with BCl₃ in the presence of IB. [MSE]₀ = 0.1 M, [IB]₀ = 0.3 M, [BCl₃]₀ = 0.3 M, [DτBP] = 0.007 M, MeCl, T = -75 °C, 4 hrs.

After addition of TiCl₄, a higher molecular weight PIB (Mₙ = 5,000 g/mol, Mₙ/Mₚ = 1.4 by SEC) was obtained; initiator efficiency was 3% at 97% conversion. The ¹H NMR spectrum (Figure 4.17) of the product showed the presence of the tert-chloride (–CH₂C(CH₃)₂Cl at 1.96 ppm and –CH₂C(CH₃)₂Cl at 1.65 ppm) and –OH chain ends.
(–CH₂ protons next to –OH at 3.2-3.3 ppm and aromatic protons at 7.2-7.4 ppm). The high integration value for the aromatic protons showed the presence of side products, most likely polyethers.

In summary, MSE was found to isomerize upon distillation to the corresponding aldehyde and enol even in the absence of a Lewis acid. In situ FTIR monitoring indicated that ring-opening of MSE in conjunction with TiCl₄ occurred competitively by the Sₕ₁ and Sₕ₂ pathways. However, oligoether formation was dominant as observed by in situ FTIR. Therefore, IB polymerizations with the MES/TiCl₄ system yields very low initiator efficiencies at low [IB]/[MSE] ratios. The formation of –CO(LA) by ring-opening of the epoxide was monitored via in situ FTIR for both the MES/TiCl₄ and MSE/BCl₃ systems.
When MSE was mixed with BCl₃ in the absence of IB, the formation of both the –COBCl₂ head group and the π-complex, similarly to that found by Nuyken et al., between a dicumyl chloride and BCl₃ system, was observed by in situ FTIR. In this case, 3 molar equivalent of BCl₃ to the initiator was insufficient to initiate the polymerization; however, the addition of a half an equivalent of TiCl₄ initiated polymerization of IB, although initiator efficiency was low. When MSE was mixed with BCl₃ in the presence of IB, it only yielded oligomers of IB. Side reactions, including the formation of a 5-membered ring by ring closure after addition of only one monomer unit, were dominant. Higher molecular weight polymer was synthesized by the addition of half an equivalent of TiCl₄ yielding low initiator efficiency. In conclusion, the MSE/BCl₃ system is inefficient for IB polymerization.

4.1.2. Aliphatic Epoxy Initiator I: 1,2-Epoxy-2,4,4-trimethylpentane (TMPO-1)

TMPO-1 is an aliphatic epoxide, as characterized by \(^1\)H and \(^{13}\)C NMR spectroscopy (Figure 4.18 and 4.19, respectively). TMPO-1 would yield a primary –OH by S\(_{N1}\) ring-opening in conjunction with a Lewis acid as shown in Scheme 4.7.
Figure 4.18. $^1$H NMR spectrum of TMPO-1.

Figure 4.19. $^{13}$C NMR spectrum of TMPO-1.
It has been shown that TMPO-1 is able to initiate IB polymerization in conjunction with TiCl₄ although with low initiator efficiency ($I_{eff} = 3\%$).²² The proposed initiation mechanism involves the formation of a tertiary carbocation by the S₈1 pathway (Scheme 4.7). It was proposed that both the S₈1 and S₈2 pathways competitively take place in the reaction of TMPO-1 and TiCl₄, the latter path leads to oligoether formation or dimerization. When the S₈2 pathway dominates, carbocationic initiator efficiency is low as in TMPO-1/TiCl₄ initiated IB polymerization.

Before a detailed investigation of IB polymerization initiated by TMPO-1/BCl₃ system by in situ FTIR monitoring, an NMR study of the ring-opening of TMPO-1 with BCl₃ will be discussed. To observe the possible products, TMPO-1 was qualitatively reacted with neat BCl₃ in methyl chloride (MeCl) at -70 °C and the $^1$H NMR spectrum was recorded just after the sample was taken out of the cold bath to evaporate the volatiles without deliberate termination and/or further purification. The $^1$H NMR spectrum (Figure 4.20) was interpreted in terms of the products expected from the S₈1 cleavage of epoxide ring by BCl₃. The expected positions of the $^1$H signals of tertiary chloride initiator, [(CH₃)₃CCH₂CCH₃ClCH₂OBCl₂], as well as dimer of TMPO-1 are similar and the integration ratios are the same. Besides, other signals showed the presence
of other structures. As discussed in Chapter II, isomerization of epoxides in the presence of a Lewis acid is possible as shown in Scheme 4.8:

Scheme 4.8. Isomerization of TMPO-1 in the presence of BCl₃.

The only distinction between the dimer and the S_N1 product would be the chemical shift of \(-\text{CH}_2\) protons (d or d') next to \(-\text{O}–\), which should be more upfielded at around 3-3.5 ppm in the dimer. The \(^1\text{H}\) signal at 4.22-4.33 ppm likely corresponds to the \(-\text{CH}_2\) protons (d) next to \(-\text{OBCl}\) of the tert-chloride. Therefore, methyl and methylene signals (a), (b) and (c) are assigned to the tert-chloride, whose integral values are in a good agreement. Based on these assignments, the main product was determined as the tert-chloride, as shown in Figure 4.20, and the yield is calculated as 60% using the ratio of the \(-\text{CH}_3\) protons (1.08 ppm, a) to the \(-\text{CH}_3\) protons at 0.92-0.94 ppm, assigned to the protons of the head group of the aldehyde and enol.
In fact, Edwards and coworkers\textsuperscript{226} found that when ethylene oxide was reacted with equimolar BCl\textsubscript{3} at -80 °C, ethylene oxide underwent ring-opening to produce 2-chloroethyl dichloroboronite (ClCH\textsubscript{2}CH\textsubscript{2}OBCl\textsubscript{2}). Methanolation of the propene oxide by reaction with BCl\textsubscript{3} yielded a mixture of 2-chloropropan-1-ol and 1-chloropropan-2-ol and a small residue, probably consisting of higher-boiling point alcohols (Equation 4.1).\textsuperscript{226}
The ring-opening mechanism was also investigated by a model reaction using TMPO-1/BCl₃ and 2,4,4-trimethyl-1-pentene (diisobutylene, DIB), a non-polymerizable monomer. The ¹H NMR spectrum (Figure 4.21) showed the proton signals of –CH₂ (3.56-3.67 ppm, h) next to –OH and –CH₃ (1.67 ppm, d) attached to –CCl of the expected product of the reaction of DIB with TMPO-1 following the expected S_N1 cleavage of the epoxide in conjunction with BCl₃. However, it was not the only product found in the previous study. The presence of aldehyde and enol isomers was verified by the characteristic aldehyde (–CHO, 9.5 ppm) and enol (–CHOH, ~6 ppm) peaks. Also, the presence of signals around 1.0 ppm and 3.0-3.5 ppm showed the presence of possible dimers or oligoethers. Ratio of integral value of protons of the –CH₂– (h in Figure 4.21) group next to –OH to that of the –CH₃ protons (d in Figure 4.21) attached to the –CCl is in a good agreement (2:3). Thus, the percentage of the expected structure, shown in Figure 4.21, was calculated from the ratio of the –CH₃ and –CH₂– protons of the product at 0.8-1.2 ppm to the all protons in the same region and found as 40%.
Figure 4.21. $^1$H NMR spectrum of the products of the reaction of DIB with TMPO-1/BCl$_3$.

The ring-opening study and model reaction indicated that a carbocation could be obtained in 40-60% yield, which was higher than that of TMPO-1/TiCl$_4$ system$^{22}$, by S$_{N}$1 cleavage of the epoxide ring by BCl$_3$ as proposed. The mechanisms of ring-opening and initiation of IB polymerization by TMPO-1/BCl$_3$ were investigated in this dissertation by using in situ FTIR monitoring.

4.1.2.1. Real-time FTIR Monitoring of the Reaction of TMPO-1 with BCl$_3$ in the Absence of IB

The reaction of TMPO-1 with BCl$_3$ in molar 1:1 ratio was monitored by in situ FTIR spectroscopy in the absence of IB. TMPO-1 did not have any isomers as shown in
Figures 4.18 and 4.19. Upon addition of 1 molar equivalent of BCl\textsubscript{3} to TMPO-1, the solution turned milky and a single strong band appeared at 1620 cm\textsuperscript{-1} (V in Figure 4.22) that was assigned to the –OBCl\textsubscript{2} attached to the \textit{tert}-Cl (I in Scheme 4.9). It was found earlier that Li-ethyl acetylene had a very strong IR absorption in this range.\textsuperscript{227} The TMPO-1/BCl\textsubscript{3} system did not produce a shoulder of the band at 1620 cm\textsuperscript{-1} in contrast to the reaction between MSE and BCl\textsubscript{3}.

In the reaction of TMPO-1 with TiCl\textsubscript{4} in 1:1 molar ratio, two strong signals were observed at 1665 and 1635 cm\textsuperscript{-1}, which were originally assigned to 2,4,4-trimethylpentanal-1 (TMPA-1) and TMPA-1 complexed with TiCl\textsubscript{4} (TMPA-1→TiCl\textsubscript{4}).\textsuperscript{23} The strong signal seen at 1100 cm\textsuperscript{-1} was originally assigned to oligoethers forming by the S\textsubscript{N}2 pathway. In contrast, oligoether formation was not observed in the reaction between TMPO-1 and BCl\textsubscript{3} (see Figure 4.22).

![Figure 4.22. Real-time FTIR monitoring of the reaction of TMPO-1 with BCl\textsubscript{3} in 1:1 ratio: 1050-1800 cm\textsuperscript{-1} region. [TMPO-1]\textsubscript{0} = [BCl\textsubscript{3}]\textsubscript{0} (in CH\textsubscript{2}Cl\textsubscript{2}) = 0.1 M; [D\textsubscript{t}BP] = 0.007 M, MeCl, T = -80 °C.](image)
Addition of IB to the TMPO-1 – BCl₃ (1:1) mixture did not result in reaction. This showed the absence of species capable of initiation, including protic impurities. However, upon addition of excess BCl₃ (the first step change in intensity represents dilution), a gradual decrease of the C=C stretching (VII, 1655 cm⁻¹) was observed, as shown in Figure 4.23, demonstrating monomer consumption.

Figure 4.23. Real-time FTIR monitoring of IB polymerization initiated by TMPO-1/BCl₃: 1600-1800 cm⁻¹ region. [TMPO-1]₀ = [BCl₃]₀ (in CH₂Cl₂) = 0.1 M; [IB]₀ = 0.3 M, [BCl₃] = 0.2 M; [DtrBP] = 0.007 M, MeCl, T = -80 °C.

In 30 minutes, ~ 24% monomer conversion was reached. The overall rate of propagation was much slower with BCl₃ than with TiCl₄. One explanation for this phenomenon is that BCl₃ is a stronger Lewis acid than TiCl₄;²²⁸ but the BCl₄⁻ counteranion is less stable than the counter ions forming of TiCl₄, that means termination by BCl₄⁻ is faster than that by TiCl₅⁻.²²⁹

Simultaneously with propagation, the intensity of the 1620 cm⁻¹ peak increased then decreased. This signal was assigned to the –OBCl₂ group attached to the tert-Cl
initiator [I] and/or to the polymer forming (Scheme 4.9). The increase in the 1620 cm$^{-1}$ peak suggested that ring-opening and/or initiation was slow since the peak intensity is proportional to concentration. The decrease might indicate the loss of some head groups. The significance of this finding is that this FTIR band can be used to monitor polymer concentration initiated by the epoxide. The importance of this will be discussed in the case of the multifunctional HES initiator.

The $^1$H NMR spectrum of the final product (Figure 4.24) demonstrated the formation of a fully aliphatic telechelic PIB oligomer with one primary hydroxyl and one tertiary chloride end group. The ratio of the two methylene protons adjacent to the hydroxyl group (8) to all aliphatic hydrogens indicates that, on the average, 2 monomer units were added to the initiator. Based on this information, the molecular weight and initiator efficiency were calculated as $M_n = 224$ g/mol and $I_{eff} = 75\%$, respectively.

Figure 4.24. $^1$H NMR spectrum of PIB-OH from the TMPO-1/BCl$_3$ initiating system. $[\text{TMPO-1}]_0 = [\text{BCl}_3]_0$ (in CH$_2$Cl$_2$) = 0.1 M; $[\text{IB}]_0 = 0.3$ M, $[\text{BCl}_3] = 0.2$ M; [DrBP] = 0.007 M, MeCl, $T = -80^\circ$C.
Based on the real-time FTIR study, the following mechanism of initiation is proposed for the TMPO-1/BCl₃/IB system (Scheme 4.9). When TMPO-1 is reacted with BCl₃, the majority (~70%) cleaves by the S_N1 pathway, forming a tertiary carbocation and a tert-Cl, [I]. The latter is activated by excess BCl₃ to initiate the polymerization of IB. Polyether formation was not observed by FTIR, but the loss of ~30% initiator indicates side reactions. The apparent dominance of S_N1 pathway leads to higher I_{eff} than with TiCl₄.

4.1.2.2. The Reaction of TMPO-1 with BCl₃ in the Presence of IB at Low [I]/[M] Ratio

Based on the previous findings, IB polymerization was initiated by TMPO-1/BCl₃ using a lower initiator-to-monomer ratio ([I]₀/[M]₀ = 0.003) and excess BCl₃ ([BCl₃]₀/[I]₀ = 25) in MeCl at -80 °C. The polymerization was performed for 4 hours, reaching 10% conversion, and yielding a PIB with $M_n = 2,050$ g/mol and $M_w/M_n = 1.68$. With the theoretical $M_n = 2,800$ g/mol, this yields $I_{eff} = 70\%$, similarly to the reaction discussed in 4.1.2.1. Thus BCl₃ was more effective with TMPO-1, an aliphatic initiator, while TiCl₄ was more effective with MSE, an aromatic initiator, under the conditions used. Data from samples that were taken throughout the reaction showed that the polymerization somehow stopped at around 10% conversion. $^1$H NMR analysis of the samples revealed presence of olefinic chain ends as shown in Figure 4.25. The formation of olefinic chain ends in BCl₃-cointiated polymerizations will be discussed in detail later.

Figure 4.25. $^1$H NMR spectrum of PIB-OH with partially olefinic chain ends from the TMPO-1/BCl₃ initiating system. [TMPO-1] = 0.005 M, [IB] = 1.95 M, [BCl₃] = 0.123 M, [D₃BP] = 0.007 M, MeCl, T = -80 °C.
Two samples of the same polymerization were further reacted with AlCl$_2$Et and TiCl$_4$. Addition of a small amount of AlCl$_2$Et resulted in a polymer with $M_n = 2,400$ g/mol and $M_w/M_n = 1.7$; however, the product didn’t have either the tert-Cl chain end or the –OH head group (Figure 4.26). This observation is not entirely unexpected since it has been shown that alkylaluminum-based Lewis acids lead to alkyl end groups. Kennedy et al.$^{230,231}$ showed that $t$-butylchloride undergoes ethylation and/or hydridation with EtAl$_2$Cl; however, reason behind the loss of the –OH head group is unknown.

![Figure 4.26. $^1$H NMR spectrum of ethylated/hydridated PIB.](Image)

After addition of a small amount (a drop into a 10 mL aliquot) of TiCl$_4$ to the sample taken from the reaction mixture, very fast polymerization was evidenced by the immediate precipitation of a high molecular weight polymer. This polymer was found to have primary hydroxyl head group and tert-Cl end group, with $M_n = 20,000$ g/mol and
M₉/M₈ = 1.3, which yields 55% initiator efficiency. This showed that higher molecular weight all aliphatic telechelic PIB carrying primary –OH and tertiary –Cl end groups, as shown in Figure 4.27, could be synthesized by a two step polymerization: the ring-opening of TMPO-1 with BCl₃ with higher efficiency, followed by growing the PIB chains to higher molecular weight by adding TiCl₄ after adjusting the solvent polarity to 60/40 (v/v, nonpolar/polar) to keep PIB in solution. This is the same composition that was used in the first living IB polymerization yielding high MW PIB²⁷ and is still the solvent mixture of choice.²⁵,²³²,²³³,²³⁴

Figure 4.27. ¹H NMR spectrum of PIB obtained by TMPO-1/BCl₃/TiCl₄.¹st: [TMPO-1]₀ = 0.01 M, [IB]₀ = 0.9 M, [BCl₃] = 0.09 M, MeCl; ²nd: [TiCl₄] = 0.02 M, Hx/MeCl (60/40, v/v), -80 °C.
4.1.3. Aliphatic Epoxy Initiator II: 2,3-Epoxy-2,4,4-trimethylpentane (TMPO-2)

TMPO-2 is an aliphatic epoxide, and was characterized by $^1$H and $^{13}$C NMR spectroscopy (Figures 4.28 and 4.29, respectively). TMPO-2 is expected to yield a secondary OH head group by $S_N1$ ring-opening in conjunction with a Lewis acid.

Figure 4.28. $^1$H NMR spectrum of TMPO-2.
Figure 4.29. $^{13}$C NMR spectrum of TMPO-2.

It has been shown that TMPO-2 is able to initiate the IB polymerization in conjunction with TiCl$_4$ although with low initiator efficiency ($I_{\text{eff}} = 10\%$).$^{22}$ Similarly to the mechanism of TMPO-1/TiCl$_4$ initiated IB polymerization, it was proposed that both $S_N1$ and $S_N2$ reaction pathways occur simultaneously, as shown in Scheme 4.10. While the formation of the tert-chloride initiator ([I] in Scheme 4.10) is achieved by an $S_N1$ mechanism, the $S_N2$ pathway may yield oligoethers, causing a reduction in carbocationic initiator efficiency.
Before going into the details regarding *in situ* FTIR studies of the IB polymerization initiated by the TMPO-2/BCl₃ system, the reaction of TMPO-2 with neat BCl₃ by using MeCl will be discussed. The ¹H NMR spectrum of the product (Figure 4.30) was recorded just after the sample was taken out of the cold bath and the volatiles were evaporated, without any deliberate termination and/or any further purification. Although all volatiles (MeCl and unreacted BCl₃) were evaporated as much as possible, residual MeCl is still present as shown in the Figure 4.30. The reaction of TMPO-2 with BCl₃ was expected to yield a *tert*-Cl initiator, similarly to [I] in Scheme 4.10, by the SN₁
cleavage of the epoxide ring. However, the ratio of d/a (0.6/9) or d/b+c (0.6/6) was smaller than expected (1/9 or 1/6, respectively).

Figure 4.30. $^1$H NMR spectrum of the product of the reaction of TMPO-2 with BCl$_3$.

The mechanism of ring-opening and initiation of IB polymerization by TMPO-2/BCl$_3$ were investigated by using in situ FTIR monitoring following the same methodology as discussed earlier. The results are discussed in the following section.

4.1.3.1. Real-time FTIR Monitoring of the Reaction of TMPO-2 with BCl$_3$ in the Absence of IB

The ring-opening of TMPO-2 in conjunction with BCl$_3$ in the absence of IB and then polymerization of IB after addition of excess BCl$_3$ were monitored with real-time FTIR utilizing a TR probe. When TMPO-2 was reacted with one molar equivalent of
BCl₃ (in CH₂Cl₂), the ring-opening (the disappearance of the 1260 cm⁻¹ peak) could not be observed because of an interference with the CH₂Cl₂ peak. However, a new band appeared quickly at 1618 cm⁻¹ (V in Figure 4.31) which was assigned to the stretching vibration of the polarized –COBCl₂ group of the tertiary chloride, [I] in Scheme 4.10, similar to the band at 1620 cm⁻¹ which was assigned to the stretching vibration of the polarized –COBCl₂ group of the tertiary chloride forming from the TMPO-1/BCl₃ system. This new band first gradually increased for ~4 minutes and then its intensity became constant.

Figure 4.31. *Real-time* FTIR monitoring of the reaction of TMPO-2 with BCl₃ in 1:1 molar ratio: 1050-1800 cm⁻¹ region. [TMPO-2]₀ = [BCl₃]₀ (in CH₂Cl₂) = 0.1 M; [D₅BP] = 0.007 M, MeCl, T = -75 °C.

Addition of IB, followed by excess BCl₃, to the TMPO-2 – BCl₃ (1:1) mixture did not result in any reaction in one hour. However, upon addition of half an equivalent of TiCl₄, a rapid decrease of the C=C stretching (VII, 1655 cm⁻¹) and the disappearance of the overtone of C–H wag of =CH₂ (IX, 1780 cm⁻¹) were observed as shown in Figure 4.32, demonstrating monomer consumption.
Figure 4.32. *Real-time* FTIR monitoring of IB polymerization initiated by TMPO-2/BCl₃: 1500-1850 cm⁻¹ region. [TMPO-2]₀ = [BCl₃]₀ (in CH₂Cl₂) = 0.1 M; [IB]₀ = 0.3 M, [BCl₃] = 0.2 M, [TiCl₄] = 0.05 M; [DrBP] = 0.007 M, MeCl, T = -75 °C.

In contrast to the TMPO-1/BCl₃ system, TiCl₄ was required to ionize the C–Cl bond which was formed by the reaction of TMPO-2 with BCl₃. It was proposed that excess BCl₃ was not able to activate the tert-Cl terminus of (I), due to the electron-withdrawing effect of the –COBCl₂ head group. Only half an equivalent of TiCl₄ was enough to polymerize IB. A fully aliphatic telechelic PIB with one secondary hydroxyl and one tertiary chloride end groups (Figure 4.33) was obtained with an initiator efficiency of 20%. The Lower $I_{\text{eff}}$ with TMPO-2, an “internal” epoxide, compared to TMPO-1, an “external” epoxide, shows that reactivity of those epoxides differs under the same reaction conditions.
Figure 4.33. $^1$H NMR spectrum of PIB obtained by TMPO-2/BCl$_3$.


HES, an aliphatic, hexa-functional epoxide, was characterized by $^1$H and $^{13}$C NMR spectroscopy (Figure 4.34 and 4.35, respectively). HES was proven to be able to initiate the living carbocationic polymerization of IB in conjunction with TiCl$_4$, yielding star-branched PIBs.$^{22,70}$
Figure 4.34. $^1$H NMR spectrum of HES.

Figure 4.35. $^{13}$C NMR spectrum of HES.
Star PIBs with MW as high as $M_n = 415,000$ g/mol and with MWD as low as $M_w/M_n = 1.17$ were obtained via the HES/TiCl$_4$ initiating system at $-80 \, ^\circ C$. Living conditions were obtained in Hx/MeCl 60/40 (v/v) mixed solvent, demonstrated by linear $M_n$ vs. conversion plots as well as linear semilogarithmic rate plots.\textsuperscript{22} The “external” $I_{eff}$, i.e. fraction of initiator that induced polymerization, was found to be 40%, while the “internal” efficiency ($I_{eff,int}$, fraction of six epoxide groups per molecule that initiated chain growth, determined by $^1$H NMR following 1,1-diphenylethylene end capping of living chain ends) was 85%, yielding an average of 5.2 PIB arms per HES molecule. HES was also used to synthesize star-branched poly(isobutylene-$b$-styrene (s-PIB-PS) block copolymer in methylcyclohexane (MeCHx)/ MeCl 70/30 and 60/40 (v/v) solvent mixtures.\textsuperscript{69,70} Interestingly, when MeCHx was used as a non-polar solvent, the $M_n$–conversion plot had a considerable intercept (at $M_n \sim 50,000$ g/mol). Addition of $N,N$-dimethylacetamide (DMA), and D$_{t}$BP led to living conditions with no intercept. In this dissertation, ring-opening with HCl, SiCl$_4$ and other Lewis acids was investigated.

4.2.1. Investigation of the Opening of the Epoxide Rings of HES

First, HES was reacted with hydrogen chloride (HCl), a Brønsted acid. The reaction was performed in a test tube in which HES was dissolved in deuterated chloroform (CDCl$_3$). HCl gas was obtained \textit{in situ} by a reaction of sodium chloride (NaCl) with concentrated sulfuric acid (H$_2$SO$_4$) and bubbled into the test tube which contained the HES solution for 15 minutes at 0 °C. Then the $^1$H NMR spectrum was recorded without any further treatment. The ring-opening of all six epoxy groups in HES was achieved as confirmed by the disappearance of the methine proton signals at 2.66-
2.83 ppm (i, j and k in Figure 4.34) of all epoxy groups (–CCHO–) of HES, forming the product that contains six tertiary –Cl and six secondary –OH groups as shown in Figure 4.36. The CH₃ protons were observed in the region of 0.95-1.60 ppm and the CH₂ protons were observed in the region of 1.60-2.50 ppm. The protons of the CH groups attached to –OH groups shifted downfield (3.10-4.10 ppm) because of the smaller shielding effect of oxygen compared to the less electronegative carbon. The ratios of the CH/CH₂/CH₃ proton signal integrals (6/20/24) are in a good agreement with the expected ratios.

![NMR Spectrum](image)

Figure 4.36. ¹H NMR spectrum of the product of the reaction of HES with HCl.

Similarly to the reaction of monofunctional epoxy initiators with BCl₃, as discussed in Section 4.1, HES was reacted with neat BCl₃ in methyl chloride (MeCl) at -70 °C and the ¹H NMR spectrum (Figure 4.37) was recorded just after the sample was taken out of
the cold bath to evaporate the volatiles without a deliberate termination and/or any further purification. Ring-opening of all six epoxy groups was demonstrated by disappearance of the –CHO protons of the epoxy rings in the region of 2.66-2.83 ppm. The CH protons next to the –OBCl₂ forming after the ring-opening were observed in the region of 3.50-4.75 ppm. The signals observed at 0.73-0.93 ppm and some signals observed in the region of 1.41-1.69 ppm exhibited larger integral values than expected and these peaks could not be assigned. These signals might represent side product such as dimers forming by the reaction between two HES molecules, or ring structures. The disappearance of the –CHO protons of epoxy rings showed that all six epoxy rings were opened by BCl₃.

Figure 4.37. ¹H NMR spectrum of the product(s) of the reaction of HES with BCl₃.

HES was reacted with SiCl₄ in the typical solvent mixture for IB polymerization, i.e. Hx/MeCl (60/40, v/v) at -70 °C. The ¹H NMR of product(s) was complex, indicating...
a mixture of products. BiCl$_3$ was not soluble under the same conditions, and a reaction was not observed in a suspension with HES. Therefore, SiCl$_4$ and BiCl$_3$ were not investigated further. The HES/BCl$_3$ system was investigated in this research using *in situ* FTIR.

### 4.2.2. Real-time FTIR Monitoring of the Reaction of HES with BCl$_3$ in the Absence of IB

When HES was reacted with six equimolars (one per epoxide) of BCl$_3$ in MeCl as a diluent in the absence of IB, a strong band appeared at 1618 cm$^{-1}$ (V in Figure 4.38), similarly to the band observed in the reaction of TMPO-1 and TMPO-2 with BCl$_3$. Intensity of this band, assigned to the –COBCl$_2$ groups forming at the initiating sites, remained constant throughout the monitoring. We cannot be sure from the FTIR monitoring which sites (external or internal) reacted first; the –COBCl$_2$ bands in TMPO-1 and TMPO-2 appeared at the same position within experimental error.

Intensity of the 1260 cm$^{-1}$ band (the C–O stretching, I in Figure 4.38) could not be monitored because of an interference of CH$_2$Cl$_2$ in which the BCl$_3$ was supplied. After addition of IB and a two molar excess BCl$_3$ relative to each epoxide, intensity of the C=C stretching of IB at 1655 cm$^{-1}$ did not change for one hour.
Figure 4.38. *Real-time* FTIR monitoring of the reaction of HES with BCl$_3$ in 1:1 ratio ([epoxide]/[BCl$_3$]): 1050-1700 cm$^{-1}$ region. [HES]$_0$ = 0.017 M, [BCl$_3$]$_0$ = 0.1 M (in CH$_2$Cl$_2$); [DrBP] = 0.008 M, MeCl, V$_T$ = 227 mL, T = -75 °C.

Based on the FTIR monitoring, BCl$_3$ was able to open the epoxy rings in HES, but once the carbocations were capped to form tert-Cl groups, addition of a two molar excess BCl$_3$ relative to the initiating sites was not able to reionize these end groups to initiate polymerization. This finding is consistent with that observed with TMPO-2 (Section 4.1.3.1)

4.2.3. *Real-time* FTIR Monitoring of the Reaction of HES with BCl$_3$ in the Presence of IB

The ring-opening reaction of HES by BCl$_3$ in the presence of IB was also monitored by *in situ* FTIR. In this case a larger excess of BCl$_3$ (7 to 18 molar excess per epoxide group) was used. When excess BCl$_3$ was added to HES in MeCl in the presence of IB, polymerization was evidenced by progressive disappearance of the C=C stretching of IB (VII) as shown in Figure 4.39. After addition of BCl$_3$ into the MeCl solution
containing the initiator and the monomer, the 1618 cm$^{-1}$ band, which was assigned to the –OBCl$_2$ group, (V in Figure 4.39) appeared and its intensity increased progressively, in contrast to the reaction of HES with BCl$_3$ in the absence of IB. This is a clear indication of slow initiation. When the initiation takes place either from the most accessible or the most strained epoxide sites of the initiator, the initiation from the other epoxy sites that become more sterically hindered may be delayed.

Figure 4.39. *Real-time* FTIR monitoring of IB polymerization initiated by HES/BCl$_3$: 1600-1675 cm$^{-1}$ region. [HES] = 0.01 M, [IB] = 1.0 M, [BCl$_3$] = 1.30 M, [D$_7$BP] = 0.009 M, MeCl, $V_T = 152$ mL, $T = -75$ °C; ATR probe.

The ability to monitor the formation of polymer chains initiated by epoxides via the strong FTIR band at 1618 cm$^{-1}$, assigned to the –COBCl$_2$ groups forming in the initiation step, is a significant contribution of this dissertation to the understanding of epoxy initiation of IB polymerization.
4.2.4. IB Polymerization by the HES/BCl₃ system

To get more insight into the ring-opening and polymerization steps, HES was reacted with BCl₃ in the presence of IB, using various ratios (Table 4.1). The SEC traces of all PIBs showed bimodal distributions as shown Figure 4.40.

Table 4.1. The reaction of HES with BCl₃ in the presence of IB.

<table>
<thead>
<tr>
<th></th>
<th>[HES] (mol/L)</th>
<th>[IB] (mol/L)</th>
<th>BCl₃/[Epoxide]</th>
<th>Conv. (%)</th>
<th>Mₙ* (g/mol)</th>
<th>Mₙ# [dn/dc] (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIB1</td>
<td>0.01</td>
<td>1.1</td>
<td>12</td>
<td>32</td>
<td>2,600</td>
<td>2,800 [0.101]</td>
</tr>
<tr>
<td>PIB2</td>
<td>0.01</td>
<td>1.0</td>
<td>18</td>
<td>37</td>
<td>2,600</td>
<td>3,600 [0.105]</td>
</tr>
<tr>
<td>PIB3</td>
<td>0.02</td>
<td>1.4</td>
<td>7.0</td>
<td>16</td>
<td>2,400</td>
<td>3,800 [0.103]</td>
</tr>
<tr>
<td>PIB4</td>
<td>0.02</td>
<td>1.1</td>
<td>13</td>
<td>28</td>
<td>2,500</td>
<td>5,000 [0.105]</td>
</tr>
</tbody>
</table>

* from ¹H NMR, # from SEC via 100% mass recovery, [D₅BP] = 0.007 M, MeCl, V_T = 20 mL, T = -75 °C, t = 8 hrs.

Figure 4.40. SEC-RI traces of the final samples from HES/BCl₃. Reaction conditions are given in Table 4.1. H : high MW trace; L : low MW trace.
The bimodal SEC-RI traces show the presence of two populations of polymer chains: high (H) and low (L) MW traces. PIB2 has the highest amount of L, and the highest MW of H. PIB1 under similar conditions but with less BCl$_3$ excess had lower conversion with lower MWs and less L fraction. Samples 3 and 4, with twice the amount of HES, do not have significantly lower MWs compared to samples 1 and 2. PIB3 have lower conversion, less L and somewhat lower MWs than PIB4. In both sets, increasing [BCl$_3$] increased the conversion and the amount of L. The two peaks clearly indicate two populations, with the higher MW peaks most likely having more arms, consequently growing faster.

The $^1$H NMR spectra of the products showed three different –C-H protons next to the –OH groups in the core, demonstrating that the three different epoxide rings were opened by BCl$_3$. A representative spectrum is shown in Figure 4.41, and peak assignments and integrals are summarized in Table 4.2. Residual unopened epoxy rings were not detected.

### Table 4.2. Integral values of the NMR spectrum shown in Figure 4.41.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a(a')</th>
<th>b</th>
<th>c</th>
<th>c'</th>
<th>i</th>
<th>j</th>
<th>k</th>
<th>h</th>
<th>g</th>
<th>f(f')</th>
<th>y</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIB-1</td>
<td>2.26</td>
<td>15.78</td>
<td>11.19</td>
<td>4.12</td>
<td>0.93</td>
<td>1.13</td>
<td>1.00</td>
<td>2.00</td>
<td>5.96</td>
<td>3.46</td>
<td>5.44</td>
</tr>
<tr>
<td>PIB-2</td>
<td>1.47</td>
<td>12.18</td>
<td>11.45</td>
<td>4.04</td>
<td>1.08</td>
<td>2.20</td>
<td>1.06</td>
<td>2.00</td>
<td>6.29</td>
<td>4.38</td>
<td>5.99</td>
</tr>
<tr>
<td>PIB-3</td>
<td>2.03</td>
<td>16.23</td>
<td>11.64</td>
<td>4.14</td>
<td>0.77</td>
<td>0.97</td>
<td>0.91</td>
<td>2.00</td>
<td>6.00</td>
<td>3.21</td>
<td>4.96</td>
</tr>
<tr>
<td>PIB-4</td>
<td>1.97</td>
<td>15.26</td>
<td>10.53</td>
<td>3.72</td>
<td>0.71</td>
<td>1.04</td>
<td>0.95</td>
<td>2.00</td>
<td>5.78</td>
<td>3.50</td>
<td>5.62</td>
</tr>
</tbody>
</table>

i, j and k, assigned to the methyne protons next to the OH groups, show that all six rings opened. The \(-\text{CH}_3\) protons in the HES core appear at 1.2 ppm (c), in a ratio of \(c/(i+j+k) \sim 24/6\). The signal at 1 ppm (a) can be assigned to \(-\text{CH}_3\) protons at the HES termini that are next to a tert-Cl that did not propagate after ring opening. \(c'\) at 1.5 ppm can be assigned to the \(-\text{CH}_3\) groups of the innermost tert-Cl, which formed upon the opening of the innermost ring but did not propagate. \(f\) was assigned to the protons of the \(-\text{CH}_2\) groups of the first IB unit attached to the outermost initiating sites.

![Figure 4.41. 1H NMR spectrum of PIB1 and the expanded spectrum for \(\delta\) 2.10-0.80 ppm. Conditions are given in Table 4.1.](image)

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Figure 4.41. $^1$H NMR spectrum of PIB1 and the expanded spectrum for δ 2.10-0.80 ppm. Conditions are given in Table 4.1. (continued)
Figure 4.42. Reverse two-dimensional $^1$H-$^{13}$C-correlated NMR spectrum with HSQC (heteronuclear single quantum coherence) method for PIB obtained by HES/BCl$_3$.

The characteristic proton signals of –CH$_3$ and –CH$_2$ for PIB repeat units are at 1.13 and 1.44 ppm, respectively. The –CH$_3$ and –CH$_2$ protons next to the tertiary –Cl groups in the PIB chain ends are at 1.70 and 1.98 ppm, respectively, in a ratio of 6/2 as expected. y at 0.9 may indicate the presence of PIB with $t$-butyl head groups, formed by protic initiation. HSQC NMR spectrum (Figure 4.42) helped to identify methyl and methylene groups since this technique provides information that is similar to a DEPT (Distortionless Enhancement by Polarization Transfer) method where CH and CH$_3$ signals are phased up and CH$_2$ signals are phased down. The HSQC NMR spectrum also showed the presence of methyl and methylene protons in very close proximity to the methyl and methylene protons of PIB repeating units hence they cannot be easily identified nor integrated in the $^1$H NMR spectrum.
Since all protons were not clearly identified by $^1$H and HSQC NMR, an NMR predictor program was utilized. The simulated $^1$H NMR of the expected structure is shown in Figure 4.43. The simulation suggests that the $-\text{CH}_3$ groups at each end of HES, assigned as $a$ and $a'$, are not equivalent, thus have different chemical shifts at 0.95 and 1.07 ppm, respectively. The $c$ and $c'$ have chemical shifts very close to each other, at 1.01 and 1.00 ppm, respectively, which are likely to overlap with the repeat unit protons of PIB.

![Figure 4.43. $^1$H NMR spectrum of PIB obtained by HES predicted by ACD11/CHNMRPRO (5 monomer units per chain were used).](image)

It is also possible that the epoxide ring opens but the tertiary carbocation will not add IB before being capped to form a tertiary chloride (Scheme 4.11).
Scheme 4.11. Possible reactions in the ring-opening of the terminal and internal epoxide rings in HES reacted with BCl₃.

Tutorskii et al.²³⁵ reported the epoxidation of squalene with perbenzoic acid (PBA) and showed that the terminal double bonds were more reactive, compared to the internal double bonds. They suggested the following reactivity order:

They found that the external double bonds reacted first, followed by the reaction of the innermost double bonds ($k_0'/k_0 = 2$). The ratio of the other rate constants were $k_1/k_0 = 0.67$ and $k_2/k_0 = 0.37$. In HES the internal rings appear to be more strained but also
more sterically hindered (Scheme 4.11). The more reactive epoxide rings are expected to open first to start the PIB chain growth. The less reactive rings will open later, which may have been the cause of the broad or bimodal MWDs.

The formation of some olefinic PIB chain ends (4.64 and 4.85 ppm, as reported in the literature),\textsuperscript{236} mostly \textit{exo}-olefins, was observed. The proton forming in these reactions most likely will be trapped by DrBP, but chain transfer leading to linear PIBs cannot be excluded.

MALDI-ToF MS analysis of PIBs synthesized with HES was attempted (courtesy of Prof. Wesdemiotis) but was unsuccessful since the polymer could not be ionized.

In summary, both HCl and BCl\textsubscript{3} opened all six epoxy rings of HES, demonstrated by the disappearance of \textit{CCHO} protons of the epoxy rings in the region of 2.66-2.83 ppm in the \textsuperscript{1}H NMR spectrum. Addition of IB and a two molar excess BCl\textsubscript{3} to each epoxide ring into the product of the reaction between BCl\textsubscript{3} and HES in 1:1 molar ratio did not result in polymerization. In contrast, when a large excess of BCl\textsubscript{3} was added into the mixture of HES and IB, polymerization proceeded. Initiation was monitored by the formation of the –COBCl\textsubscript{2} group upon ring opening via a gradual increase of the FTIR band at 1618 cm\textsuperscript{-1}. SEC analysis of the PIBs obtained by the HES/BCl\textsubscript{3} system showed the presence of two populations, with the low molecular weight fraction being the majority component.

The number of PIB arms could be calculated from the \textsuperscript{1}H NMR spectra from the ratio of the signal intensities (I) of the \textit{gem}-dimethyl protons of the \textit{tert}-chloride end groups (g) to either the protons of –CH groups next to the –OH (i, j, k) or the methyl protons (a) at each ends of the initiator, as shown in the following equation:
If the expected structure were formed, the ratio of the signal intensities (I) of the gem-dimethyl protons of the tert-chloride end groups (g) of the PIB to the protons of –CH groups next to the –OH (i, j, k) should be 6:1.

However, the number of arms of PIB could not be quantified because of the presence of any possible linear polymer, which also possesses the tert-Cl end groups, due to the chain transfer caused by β-proton elimination of the chain ends by BCl3, although opening of all six epoxides of HES was demonstrated by ¹H NMR spectrum. The presence of olefinic PIB chain ends were observed in the ¹H NMR spectrum (–(CH₃)C=CH₂, 4.64 and 4.85 ppm). The β-proton elimination will be discussed in details in Section 4.3.

4.2.5. Two-stage IB Polymerization by HES with BCl₃ and TiCl₄

A two-stage process was used to synthesize higher molecular weight PIBs by using HES: first, a low molecular weight PIB “macroinitiator” was synthesized with HES/BCl₃ as described in Section 4.2.4., followed by growing the PIB arms to high molecular weights in the presence of TiCl₄. For the second step it was necessary to adjust the solvent composition because PIB with molecular weight higher than about Mₙ = 3,000 g/mol is insoluble in MeCl.

The polymerization recipes are given in Table 4.3. The monomer conversion was monitored by real-time FTIR. Three sets of polymerization were conducted.
Table 4.3. Conditions and recipes for the two-stage polymerizations.

<table>
<thead>
<tr>
<th>ID</th>
<th>First Stage</th>
<th>Second Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I₀ (mol)</td>
<td>M₀,₁ (mol)</td>
</tr>
<tr>
<td>SH_052407</td>
<td>0.002</td>
<td>0.151</td>
</tr>
<tr>
<td>(PIB 8-1)³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SH_053107</td>
<td>0.002</td>
<td>0.151</td>
</tr>
<tr>
<td>(PIB 8-2)³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SH_061307</td>
<td>0.002</td>
<td>0.161</td>
</tr>
<tr>
<td>(PIB 4)⁴</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reactino time of the 1st stage is 8 hours.
Reactino time of the 1st stage is 4 hours.
1st Stage: Solvent = MeCl, [DtBP] = 0.001 M, T = -80 °C; 2nd Stage: Solvent = Hx/MeCl (60/40), [DtBP] = 0.007 M, T = -80 °C.

Polymerization where the first stage was performed for 4 hours resulted in 10% conversion, yielding a PIB with $M_n = 1,500$ g/mol and 45% initiator efficiency. The polymerizations with an 8-hour first stage resulted in 20 and 44% conversions yielding PIBs with $M_n = 3,300$ g/mol and $M_n = 2,900$ g/mol, respectively (Conversions were obtained from gravimetric analysis and $M_n$s were calculated from $^1$H NMR). The results are summarized in Table 4.4.

Table 4.4. Polymerization results for the 1st stage.

<table>
<thead>
<tr>
<th>Name</th>
<th>Conv. (%)</th>
<th>PIB (mol)</th>
<th>Macroinitiator, $M_n$ (g/mol) *</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gravimetry</td>
<td>FTIR</td>
<td>Gravimetry</td>
</tr>
<tr>
<td>PIB 8-1</td>
<td>20</td>
<td>35</td>
<td>0.0005</td>
</tr>
<tr>
<td>PIB 8-2</td>
<td>44</td>
<td>45</td>
<td>0.0013</td>
</tr>
<tr>
<td>PIB 4</td>
<td>10</td>
<td>20</td>
<td>0.0006</td>
</tr>
</tbody>
</table>

* by $^1$H NMR
Subsequently the reaction mixtures were diluted to Hx/MeCl (60/40, v/v) because this gives the optimum solvent polarity for the chain propagation in the presence of TiCl₄ and keeps the high molecular weight PIB soluble. Then, 3 mol/L IB, 0.07 mol/L TiCl₄, i.e. 8 molar excess per epoxide of HES, and additional DrBP, keeping the total concentration as 0.007 mol/L, were added to the mixture (all concentrations are relative to final volume of the reaction).

The monomer conversion was monitored via real-time FTIR. After the addition of BCl₃, the 1618 cm⁻¹ band (–COBCl₂ head group) appeared and grew gradually as it is shown in Figure 4.40. As it was explained in section 4.2.3, the progressive increase of this peak indicates sequential opening of the epoxide rings and/or slow initiation.

In the second stage, polymerization was evidenced by disappearance of the characteristic olefinic peak of IB at 1655 cm⁻¹ (VII in Figure 4.44, C=C stretch) as well as progressive growth of the signal at 1230 cm⁻¹ (VIII in Figure 4.45) assigned to the distorted carbon tetrahedrons (–C(CH₃)₂ groups) in the forming PIB. Intensity of the IR band at 1620 cm⁻¹ (V in Figure 4.44) increased, showing additional initiation.

Figure 4.44. Real-time FTIR monitoring of IB polymerization; 2nd stage: 1550-1850 cm⁻¹ region (PIB 8-1).
Figure 4.45. *Real-time* FTIR monitoring of IB polymerization; 2nd stage: 1050-1300 cm\(^{-1}\) region (PIB 8-1).

Now, each polymerization will be discussed individually.

**SH_052407 (PIB 8-1)**

The first aliquot taken after addition of TiCl\(_4\) showed a bimodal distribution, similarly to the PIBs synthesized by HES/BCl\(_3\) in one-step. The SEC traces of subsequent samples became monodisperse, with a small high MW tail. The SEC traces from refractive index (RI) and multi-angle laser light scattering (MALLS) are shown in Figure 4.46.
Figure 4.46. SEC traces of PIB 8-1: RI and MALLS. Conditions are given in Table 4.3.

First-order rate and M_n-conversion plots for the second stage of the polymerization are shown in the Figures 4.47 and 4.48. Upward curvature of the kinetic plot, especially in the beginning, might be an indication of slow initiation. Since the coinitiator was changed from BCl\textsubscript{3} to TiCl\textsubscript{4}, a higher polymerization rate is expected in the second stage. There might be an induction period during the transition from BCl\textsubscript{3} to TiCl\textsubscript{4}. 


Ti$_2$Cl$_9^-$ counterions until the polymerization proceeds with a rate expected from a TiCl$_4$-coinitiated polymerization. New chains might be initiated by the protons expelled from the chain ends, which caused the formation of the olefinic chain ends as discussed previously, if all protons were not trapped with DrBP. New chains might also be initiated from the initiating sites of HES that could not start the polymerization in the first stage. This finding agrees with the in situ FTIR monitoring that shows an increase of the intensity of the IR band at 1620 cm$^{-1}$ (–COBCl$_2$ or –COTiCl$_3$, V in Figure 4.44), indicating additional initiation from epoxides. The $M_n$ vs. conversion plot shows a sudden increase in the beginning, indicating a fast initial growth. After 20 minutes the plot becomes linear, indicating no chain transfer.

![Figure 4.47. First-order rate plot of the PIB 8-1 polymerization. Time 0: addition of TiCl$_4$.](image-url)

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Figure 4.48. $M_n$ vs. conversion plot of the PIB 8-1 polymerization. Conversion 0: “macroinitiator” with $M_n = 3,270$ g/mol.

Peak molecular weights of each aliquot (Table 4.5) were read from the RI traces to analyze the growth of each population of the growing polymer chains. The molecular weight of the high MW population was about twice as that of the low MW and the high MW population grew faster.

Table 4.5. Molecular weight data from SEC for PIB 8-1.

<table>
<thead>
<tr>
<th>Aliquot</th>
<th>Time (min)</th>
<th>Conv. (%)</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w/M_n$</th>
<th>PIB (mol)</th>
<th>Low MW peak</th>
<th>High MW peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0*</td>
<td>3.3**</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>21</td>
<td>17.6</td>
<td>1.26</td>
<td>0.0020</td>
<td>16.2</td>
<td>37.6</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>52</td>
<td>28.4</td>
<td>1.22</td>
<td>0.0032</td>
<td>30.6</td>
<td>73.0</td>
</tr>
<tr>
<td>3</td>
<td>55</td>
<td>70</td>
<td>34.2</td>
<td>1.20</td>
<td>0.0036</td>
<td>40.3</td>
<td>95.0</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>83</td>
<td>39.8</td>
<td>1.12</td>
<td>0.0043</td>
<td>44.4</td>
<td>104.0</td>
</tr>
</tbody>
</table>

*Conversion in the 1st stage was 20% gravimetrically, 35% from FTIR. For the second stage, the low MW PIB was treated as a macroinitiator and addition of TiCl$_4$ was considered as “zero” point.
** by $^1$H NMR (macroinitiator).
The first aliquot taken after addition of TiCl₄ showed a broad distribution having a high molecular weight shoulder, and then the SEC traces became monodisperse and narrower, with a smaller high MW tail. The SEC traces from refractive index (RI) and multi-angle laser light scattering (MALLS) are shown in Figure 4.49.

Figure 4.49. SEC traces of PIB 8-2: RI and MALLS. Conditions are given in Table 4.3.
First-order rate and $M_n$-conversion plots (Figure 4.50 and 4.51) for the second stage of the polymerization are similar to the previous experiment. The kinetic plot with an upward curvature indicates additional initiation and/or slow exchange of counterions in the beginning of the reaction. The $M_n$ vs. conversion plot shows an initial fast increase, followed by linear growth.

Figure 4.50. First-order rate plot of the PIB 8-2 polymerization. Time 0: addition of TiCl$_4$.

Figure 4.51. $M_n$ vs. conversion plot of the PIB 8-2 polymerization. Conversion 0: “macroinitiator” with $M_n = 2,900$ g/mol.
Peak molecular weights of each aliquot (Table 4.6) were read from the RI traces to analyze the growth of each population of growing polymer chains. The high molecular weight population grew faster compared to the low molecular weight population similarly to the previous experiment.

Table 4.6. Molecular weight data from SEC for PIB 8-2.

<table>
<thead>
<tr>
<th>Aliquot</th>
<th>Time (min)</th>
<th>Conv. (%)</th>
<th>( M_n ) (kg/mol)</th>
<th>( M_w/M_n )</th>
<th>PIB (mol)</th>
<th>Low MW peak (mol)</th>
<th>High MW peak (kg/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0*</td>
<td>2.9**</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>28</td>
<td>17.5</td>
<td>1.20</td>
<td>0.0028</td>
<td>17.6</td>
<td>41.8</td>
</tr>
<tr>
<td>2</td>
<td>31</td>
<td>56</td>
<td>24.8</td>
<td>1.16</td>
<td>0.0039</td>
<td>32.0</td>
<td>78.0</td>
</tr>
<tr>
<td>3</td>
<td>46</td>
<td>74</td>
<td>30.1</td>
<td>1.10</td>
<td>0.0042</td>
<td>41.8</td>
<td>104.8</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>99</td>
<td>37.0</td>
<td>1.05</td>
<td>0.0040</td>
<td>45.5</td>
<td>109.8</td>
</tr>
</tbody>
</table>

* The conversion in the 1st stage was 20% gravimetrically, 35% from FTIR. For the second stage, the low MW PIB was treated as a macroinitiator and the addition of TiCl₄ was considered as “zero” point. ** by \(^1\)H NMR (macroinitiator).

SH_061307 (PIB-4)

The first aliquot taken after addition of TiCl₄ showed a broad distribution having a high molecular weight shoulder, and then the SEC traces became monodisperse and narrower, with a smaller high MW tail. However, the last aliquot again became broader and showed a main chain population at higher molecular weight and a lower molecular weight shoulder. SEC traces from refractive index (RI) and multi-angle laser light scattering (MALLS) are shown in Figure 4.52.
First-order rate plot for the second stage of the polymerization is similar to the previous experiments, which showed an upward curvature, indicating additional initiation and/or a slow exchange of counterions. The $M_n$ vs. conversion plot shows an initial fast increase, similarly to the polymerizations discussed above. Interestingly, the $M_n$-conversion plot also showed an upward deviation from linearity. This may indicate
coupling of the polymer chains. This would also explain the bimodal distribution of the last aliquot; while some chain continued to grow regularly, some chains were coupled. The $M_n$ of the last aliquot is double of that of the previous aliquot as shown in Table 4.7. Reason for the coupling is not clear at this time but this phenomenon was also observed with HES/TiCl₄ initiated IB polymerization in MeCHₓ/MeCl (60/40, v/v) at -80 °C.⁷⁰

![Figure 4.53](image1.png)

**Figure 4.53.** First-order rate plot of the PIB 4 polymerization. Time 0: addition of TiCl₄.

![Figure 4.54](image2.png)

**Figure 4.54.** $M_n$ vs. conversion plot of the PIB 4 polymerization. Conversion 0: “macroinitiator” with $M_n = 1,500$ g/mol.
The peak molecular weights (Table 4.7) were read from the RI traces. The peak positions of the shoulders were not clear for all the aliquots except the last one, which showed twice as high MW of the high MW shoulder than that of the main peak.

Table 4.7. Molecular weight data from SEC for PIB 4.

<table>
<thead>
<tr>
<th>Aliquot</th>
<th>Time (min)</th>
<th>Conv. (%)</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w/M_n$</th>
<th>PIB (mol)</th>
<th>Low MW peak</th>
<th>High MW peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0*</td>
<td>1.5**</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>11</td>
<td>12.9</td>
<td>1.05</td>
<td>0.0015</td>
<td>16.0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>28</td>
<td>31</td>
<td>22.4</td>
<td>1.21</td>
<td>0.0024</td>
<td>27.8</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>45</td>
<td>29.6</td>
<td>1.20</td>
<td>0.0026</td>
<td>37.0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>99</td>
<td>63.2</td>
<td>1.27</td>
<td>0.0027</td>
<td>51.2</td>
<td>95.4</td>
</tr>
</tbody>
</table>

*The conversion in the 1st stage was 20% gravimetrically, 35% from FTIR. For the second stage, the low MW PIB was treated as a macroinitiator and the addition of TiCl$_4$ was considered as “zero” point.

**by $^1$H NMR (macroinitiator)

The SEC data for final samples of the three experiments discussed above are listed in Table 4.8, including the viscosity ratio of the PIBs synthesized by HES/BCl$_3$/TiCl$_4$ system relative to calculated viscosity of the linear PIB of the same $M_w$:

$$g' = \ln \left[ \frac{[\eta]_{w,br}}{[\eta]_{w,lin}} \right]$$  \hspace{1cm} (4.3)

where $\ln [\eta]_{w,lin} = 2.20 \cdot 10^{-2} (M_w)^{0.667}$, derived from the measurement of $[\eta]_w$ for a series of linear, narrow-MWD PIB standards.$^{237}$
Table 4.8. SEC analysis of the PIBs synthesized by using HES/BCl₃/TiCl₄.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ (kg/mol)</th>
<th>$M_w/M_n$</th>
<th>$R_g$ (nm)</th>
<th>$R_h$ (nm)</th>
<th>$[\eta_w]$ (mL/g)</th>
<th>$g'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIB 8-1*</td>
<td>39.8</td>
<td>1.12</td>
<td>12.8</td>
<td>5.7</td>
<td>25.4</td>
<td>0.92</td>
</tr>
<tr>
<td>PIB 8-2*</td>
<td>37.0</td>
<td>1.16</td>
<td>2.9</td>
<td>5.9</td>
<td>28.5</td>
<td>1.04</td>
</tr>
<tr>
<td>PIB 4#</td>
<td>63.2</td>
<td>1.27</td>
<td>9.2</td>
<td>8.9</td>
<td>38.2</td>
<td>0.93</td>
</tr>
</tbody>
</table>

*Reaction time of the 1st stage is 8 hours.
#Reaction time of the 1st stage is 4 hours.

The $g'$ of PIB 8-1 and PIB-4 is slightly below 1, mostly likely due to the presence of linear PIBs and/or the relatively short arms (the entanglement MW of PIB is $M_e \sim 10,000$ g/mol\(^{238}\)). The PIBs have molecular weights too low for the accurate measurement of the radius, especially the radius of gyration ($R_g$).

In summary, the two-stage polymerization of IB initiated by HES/BCl₃/TiCl₄ was successfully monitored by *in situ* FTIR using an ATR probe due to high concentration of monomer. The first-order rate plots showed an upward curvature that might indicate additional initiation and/or slow exchange of counteranions. The $M_n$ versus conversion plots had an intercept showing new initiation either because of the chain transfer caused by the protons that were removed from the chain ends in the first stage in the presence of BCl₃, or from non-active sites of HES/BCl₃ activated by TiCl₄. However, they were linear except for the last polymerization where the chain coupling was observed.

4.2.6. Two-stage IB Polymerization by HES with Incremental Monomer Addition

High molecular weight PIBs by using HES were also synthesized in two-stages with incremental monomer addition. A low molecular weight “macroinitiator” was
synthesized in the first stage by using the HES/BCl₃ system in MeCl. A sample was taken before proceeding to the second stage and analyzed by ¹H NMR (Mₙ = 1900 g/mol). Then the PIB chains were grown to higher molecular weight by adjusting the solvent composition to Hx/MeCl (60/40, v/v) mixture as explained in the previous section, and adding 8 molar equivalents of TiCl₄ relative to the active site concentration. Then, more IB was incrementally added to the polymerization to demonstrate further monomer consumption. The second stage of the reaction, including the incremental addition of IB, was monitored via in situ FTIR as shown in Figure 4.55.

![Figure 4.55. Real-time FTIR monitoring of IB polymerization with incremental monomer addition; 2nd stage: 1550-1850 cm⁻¹ region. “Macroinitiator” {[HES] = 0.01 M, [IB] = 1 M, [BCl₃] = 0.6 M, [D₄BP] = 0.007 M, MeCl}, 4 x [IB] = 1.7 M, [D₄BP] = 0.007 M, Hx/MeCl (60/40, v/v), Time 0: addition of [TiCl₄] = 0.12 M, T = -80 °C.](image)

Polymerization was evidenced by gradual decrease of the characteristic olefinic peak of IB at 1655 cm⁻¹ and disappearance of the C–H wag in –CH₂ of IB (VII and IX in Figure 4.55, respectively) as well as progressive growth of the signal at 1230 cm⁻¹ (VIII in Figure 4.56) assigned to the distorted carbon tetrahedrons (–C(CH₃)₂ groups) in the forming PIB. Intensity of the IR band at 1618 cm⁻¹ (V in Figure 4.55) increased in the
beginning of the second stage of the polymerization, and then stayed steady until the end of the polymerization. This likely indicates that there was new initiation from the initiating sites of HES that didn’t start the polymerization in the first stage as explained in the previous section.

![Graph showing FTIR monitoring of IB polymerization](image)

Figure 4.56. *Real-time* FTIR monitoring of IB polymerization with incremental monomer addition; 2nd stage: 1050-1300 cm⁻¹ region. “Macroinitiator” {[HES] = 0.01 M, [IB] = 1 M, [BCl₃] = 0.6 M, [D₃BP] = 0.007 M, MeCl}, 4 x [IB] = 1.7 M, [D₃BP] = 0.007 M, Hx/MeCl (60/40, v/v), Time 0: addition of [TiCl₄] = 0.12 M, T = -80 °C.

The sample of the first monomer increment showed a bimodal distribution (Figure 4.57) similarly to the low-conversion samples of the previous polymerizations. After the second and third monomer additions, molecular weight distribution became monodisperse and narrower as shown in Table 4.9.
The $M_n$ versus monomer consumption plot showed a fast initial increase, similarly to the two-stage polymerization that was discussed in the previous section; however, the $M_n$ increased linearly with monomer consumption after this rapid initial growth.
The rate plot (Figure 4.59) was linear after addition of the second monomer increment but it showed a rapid increase in the beginning of the polymerization of the first IB increments. This rate change might be due to an increase in the viscosity of the solution that became very high after addition of the second monomer increment. The in situ FTIR plots (Figure 4.55 and 4.56) also showed that monomer consumption was slower for the second through fourth monomer increments compared to the first monomer increment. Although the polymerization slowed down, monomer consumption was linear with time. Table 4.9 shows the molecular weight data of the samples. The viscosity ratio, $g'$, does not show the effect of branching.
Figure 4.59. The first-order rate plot of the IB polymerization with incremental monomer addition. Time 0: addition of TiCl$_4$.

Table 4.9. SEC analysis of the PIBs synthesized from HES by incremental monomer addition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (min)</th>
<th>$M_a$ (kg/mol)</th>
<th>$M_w/M_n$</th>
<th>$R_g$ (nm)</th>
<th>$R_h$ (nm)</th>
<th>$[\eta_w]$ (mL/g)</th>
<th>$g'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>20.9</td>
<td>1.35</td>
<td>-</td>
<td>5.6</td>
<td>20.6</td>
<td>1.09</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>27.5</td>
<td>1.24</td>
<td>-</td>
<td>5.8</td>
<td>25.1</td>
<td>1.17</td>
</tr>
<tr>
<td>3</td>
<td>47</td>
<td>39.3</td>
<td>1.20</td>
<td>5.9</td>
<td>7.3</td>
<td>28.8</td>
<td>1.07</td>
</tr>
<tr>
<td>PS_30K</td>
<td></td>
<td>29.2</td>
<td>1.00</td>
<td>-</td>
<td>4.7</td>
<td>22.1</td>
<td></td>
</tr>
</tbody>
</table>

4.2.7. Supercritical Fluid (SCF) Fractionation

The PIB8-2 synthesized using the HES/BCl$_3$/TiCl$_4$ initiating system in two-stages were subjected to supercritical fluid (SCF) fractionation and the fractions were analyzed by SEC. SCF fractionations were performed using an increasing pressure profiling
technique,\textsuperscript{240} with pressure gradually increasing from 1800 to 9000 psi. As the supercritical propane at 120 °C passes through the sample, it dissolves the soluble species, and when the solution of dissolved material in supercritical fluid is depressurized in the collection vessel, the dissolved material precipitates and is collected. The gas leaves the collection system at ambient conditions, flows through a rotameter and a dry test meter and is vented. After a selected amount of gas has passed through the chamber, the collection vessel is changed, the pressure and/or temperature are raised, and test is continued. The schematic of the apparatus is shown in Scheme 4.13. Table 4.10 shows the results of the SCF fractionation for the PIB 8-2 discussed in 4.2.5.

Table 4.10. SCF fractionation results of PIB 8-2.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Weight</th>
<th>Frac. (%)</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (kg/mol)</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;/M&lt;sub&gt;n&lt;/sub&gt;</th>
<th>R&lt;sub&gt;g&lt;/sub&gt; (nm)</th>
<th>R&lt;sub&gt;h&lt;/sub&gt; (nm)</th>
<th>[η&lt;sub&gt;w&lt;/sub&gt;] (mL/g)</th>
<th>g′</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.81</td>
<td>8.0</td>
<td>12.6</td>
<td>1.18</td>
<td>-</td>
<td>3.4</td>
<td>13.7</td>
<td>1.15</td>
</tr>
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<td>22.2</td>
<td>108</td>
<td>7.0</td>
<td>4.2</td>
<td>18.6</td>
<td>1.11</td>
</tr>
<tr>
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<td>20.4</td>
<td>30.7</td>
<td>1.03</td>
<td>-</td>
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<td>22.5</td>
<td>1.10</td>
</tr>
<tr>
<td>4</td>
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<td>30.5</td>
<td>37.0</td>
<td>1.01</td>
<td>4.0</td>
<td>5.3</td>
<td>24.6</td>
<td>1.07</td>
</tr>
<tr>
<td>5</td>
<td>1.23</td>
<td>12.2</td>
<td>42.1</td>
<td>1.02</td>
<td>1.9</td>
<td>5.7</td>
<td>27</td>
<td>1.06</td>
</tr>
<tr>
<td>6</td>
<td>0.24</td>
<td>2.4</td>
<td>49.8</td>
<td>1.22</td>
<td>2.5</td>
<td>8.5</td>
<td>33.4</td>
<td>1.03</td>
</tr>
<tr>
<td>Total</td>
<td>8.90</td>
<td></td>
<td>88.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The following figures show the SEC traces of the fractions and the parent polymer with RI and MALLS detectors.
In summary, PIB 8-2 synthesized using the HES/BCl₃/TiCl₄ system in two-stages were fractionated by SCF fractionation. Total 88% of the material was recovered in six fractions and the fractions were analyzed by multidetector SEC. All fractions except the
last one were monodisperse, with relatively narrow molecular weight distribution. The first fraction might be PIB grown from only one site of HES. The second fraction has double molecular weight, thus it might be bidirectionally growing PIB from two initiating sites. The fifth fraction has double of the molecular weight of the second fraction, indicating a four-arm star. The last fraction showed a bimodal distribution having the main population with molecular weight close to that of the fifth fraction. Unfortunately, the high molecular weight portion could not be fractionated effectively (Figure 4.60). Further work is necessary to better understand the properties of the fractions.

4.3. Olefinic Chain End Formation in BCl₃-coinitiated IB Polymerization

It was shown earlier in the Section 4.1.2.2 that olefinic chain ends formed in all BCl₃-coinitiated polymerization, especially in cases of large molar excess of BCl₃ and prolonged times. This phenomenon was further investigated by the 2-chloro-2,4,4-trimethylpentane (TMPCl)/BCl₃ initiating system. TMPCl was one of the first initiators used to initiate living polymerization of IB in conjunction with a Lewis acid yielding 100% initiator efficiency. ²⁴¹

A representative ¹H NMR spectrum of a PIB obtained by the TMPCl/BCl₃ system is shown in Figure 4.61. Although both exo- and endo-olefinic chain ends were observed, exo-olefins were always dominant. The fractional molar amounts of exo-olefinic and endo-olefinic chain ends were quantified by ¹H NMR integration using the following equations:
\[ F_{\text{exo}} = \frac{I_{\text{exo}}}{I_{\text{exo}} + I_{\text{endo}} + (I_{\text{tert-Cl}})/2} \]  

\[ F_{\text{endo}} = \frac{I_{\text{endo}}}{I_{\text{exo}} + I_{\text{endo}} + (I_{\text{tert-Cl}})/2} \]

where \( I_{\text{exo}} \) is the integration of one of the proton peaks of the \textit{exo}-olefinic chain end (=CH\textsubscript{2}), \( I_{\text{endo}} \) is the integration of the single proton of the –CH group of the \textit{endo}-olefinic chain end [CH=\text{C(CH\textsubscript{3})\textsubscript{2}}] and \( I_{\text{tert-Cl}} \) is the integration of the protons of the methylene group next to the \textit{tert}-Cl chain end (CH\textsubscript{2}-C(CH\textsubscript{3})\textsubscript{2}Cl), as shown in Figure 4.61.

Figure 4.61. \(^1\text{H} \) NMR spectrum of PIB obtained by TMPCL/BCl\textsubscript{3}. [TMPCL] = 0.01 M, [IB] = 0.72 M, [BCl\textsubscript{3}] = 0.27 M, [D\textsubscript{4}BP] = 0.01 M, MeCl, T = -40 °C. (PIB\textsubscript{D\textsubscript{4}BP} in Table 4.13).
Various reaction conditions, including polymerization temperature, polymerization time and effect of various electron pair donors (EDs) were examined. The first set of polymerizations was conducted at -40 °C in the presence of DtBP as proton trap that can be viewed as an ED as well. Both exo- and endo-olefinic chain ends were observed in all samples. The total amount of olefinic chain ends decreased in the first four hours and then started to increase. Table 4.11 summarizes the results and Figure 4.62 demonstrates the changes in the olefinic chain concentration.

Table 4.11. Results of the IB polymerization by TMPCl/BCl3 at -40 °C. [TMPCl]₀ = 0.04 M, [IB]₀ = 0.79 M, [BCl3] = 0.4 M, [DtBP] = 0.004 M, MeCl.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
</tr>
<tr>
<td>3</td>
<td>180</td>
</tr>
<tr>
<td>4</td>
<td>240</td>
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<tr>
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<td>360</td>
</tr>
<tr>
<td>7</td>
<td>420</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Mn* (g/mol)</th>
<th>exo-olefin (%)</th>
<th>endo-olefin (%)</th>
<th>Total olefins (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>490</td>
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<td>12</td>
</tr>
<tr>
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<td>720</td>
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<td>0.9</td>
<td>3.8</td>
</tr>
<tr>
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<td>1,020</td>
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<td>1.0</td>
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<td>1,320</td>
<td>2.8</td>
<td>1.9</td>
<td>4.7</td>
</tr>
</tbody>
</table>

*by ¹H NMR
Figure 4.62. $^1$H NMR spectra as a function of time for PIBs obtained by TMPCl/BCl$_3$ at -40 °C: olefinic region. [TMPCl]$_0$ = 0.04 M, [IB]$_0$ = 0.79 M, [BCl$_3$] = 0.4 M, [D$_r$BP] = 0.004 M, MeCl (Table 4.11).

When both the Mn vs. conversion and the rate plots (Figure 4.63) were examined, it was observed that they both deviate from linearity, especially towards the end of polymerization. However, the final Mn = 1320 g/mol is very close to the theoretical Mn = 1100 g/mol. It should be noted that the error in the conversion data is most likely large, because the low molecular weight PIBs are very difficult to handle.
Figure 4.63. IB polymerization initiated by TMPCl/BCl3 at -40 \(^\circ\)C: (a) pseudo first-order kinetic plot and (b) \(M_n\) vs. conversion plot. \([\text{TMPCl}]_0 = 0.04 \text{ M}, [\text{IB}]_0 = 0.79 \text{ M}, [\text{BCl}_3] = 0.4 \text{ M}, [\text{D}t\text{BP}] = 0.004 \text{ M}, \text{MeCl}].

The second set of polymerizations was performed at -60 \(^\circ\)C and the results are shown in Table 4.12. The amount of both \textit{exo}- and \textit{endo}-olefinic chain ends was relatively high at the beginning of the polymerization but decreased gradually in the first
three hours; then it started to increase again as shown in Figure 4.64. The \( \ln \left[ \frac{[M]_0}{[M]} \right] \) vs. time plot is linear, while the \( M_n \) vs. conversion plot shows an initial rapid increase followed by linear growth. The measured \( M_n \) has an excellent agreement with the theoretical \( M_n = 1340 \text{ g/mol} \).

Table 4.12. Results of the IB polymerization by TMPCl/BCl3 at -60 °C. \([\text{TMPCl}]_0 = 0.04 \text{ M, } [\text{IB}]_0 = 0.96 \text{ M, } [\text{BCl}_3] = 0.4 \text{ M, } [\text{DrBP}] = 0.004 \text{ M, MeCl.} \)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Time (min)</th>
<th>( M_n^* ) (g/mol)</th>
<th>exo-olefin (%)</th>
<th>endo-olefin (%)</th>
<th>Total olefins (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>700</td>
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<td>2.4</td>
<td>20</td>
</tr>
<tr>
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<td>120</td>
<td>860</td>
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<td>1.0</td>
<td>5.7</td>
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<td>1,090</td>
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<td>2.0</td>
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<tr>
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<td>1,150</td>
<td>8.1</td>
<td>1.8</td>
<td>9.9</td>
</tr>
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<td>300</td>
<td>1,270</td>
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<tr>
<td>6</td>
<td>360</td>
<td>1,340</td>
<td>13</td>
<td>1.7</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>420</td>
<td>1,360</td>
<td>27</td>
<td>4.1</td>
<td>31</td>
</tr>
</tbody>
</table>

* by \(^1\text{H} \text{ NMR}\)
Figure 4.64. $^1$H NMR spectra as a function of time for PIBs obtained by TMPCl/BCl$_3$ at -60 $^\circ$C: olefinic region. [TMPCl]$_0$ = 0.04 M, [IB]$_0$ = 0.96 M, [BCl$_3$] = 0.4 M, [DzBP] = 0.004 M, MeCl (Table 4.12).
Figure 4.65. IB polymerization initiated by TMPCl/BCl₃ at -60 °C: (a) pseudo first-order kinetic plot and (b) $M_n$ vs. conversion plot. $[\text{TMPCl}]_0 = 0.04 \text{ M}$, $[\text{IB}]_0 = 0.96 \text{ M}$, $[\text{BCl}_3] = 0.4 \text{ M}$, $[\text{DrBP}] = 0.004 \text{ M}$, MeCl.
In spite of the olefinic chain end formation, the polymerization at -60 °C showed living characteristics having the linear $M_n$ vs. conversion (except for the initial rapid growth) and $\ln([M]_0/[M])$ vs. time plots. If the olefinic chain end formation occurs because of $\beta$-proton abstraction by DtBP or by any impurities in DtBP, such as a sterically hindered cyclic imine base as found by Bae and Faust,$^{49}$ this would cause irreversible chain termination, hence a deviation should be seen in the $\ln([M]_0/[M])$ vs. time plot. Bae and Faust$^{49}$ examined the effect of DtBPs with two different grades; one with 99% purity and the other one with 94% purity, so called DtBP-94, at -80 °C. Although they found exo-olefinic chain end formation with DtBP-94 that increased with time, interestingly, the rate of polymerizations, $M_n$s and molecular weight distributions were nearly identical in parallel experiments with DtBP and DtBP-94.

Olefinic chain end formation was observed only with BCl$_3$ coinitiator in MeCl. Olefins were not observed in the TiCl$_4$-coinitiated systems using DtBP from the same manufacturer at -70 to -80 °C in our laboratory, although Faust et al.$^{242}$ reported $\beta$-proton elimination at -40 °C. They observed a linear $M_n$ vs. conversion plot but found deviation in the kinetic plot. They hypothesized that the $\beta$-proton elimination by the counteranion ($\text{Ti}_2\text{Cl}_9^-$) from living chain ends caused irreversible termination but didn’t provide a mechanism; and the eliminated protons were instantaneously trapped by DtBP. Therefore, there was irreversible termination but no chain transfer.

The $\beta$-proton abstraction by the counterion, BCl$_4^-$, could be visualized as shown in Scheme 4.14. The reversibility of this reaction was proposed first by Kennedy, Kelen, Tüdös$^{16}$ but has never been demonstrated experimentally.
Scheme 4.14. β-Proton elimination by BCl₄⁻.

The possibility of β-proton elimination during either termination or work-up was also considered, since the reactions were terminated by NaOH/MeOH solution. However, there is a clear relationship between polymerization time and the amount of the olefins formed, which cannot be explained by the loss of tert-Cl chain ends during work-up.

The polymerization of IB initiated by TMPCl/BCl₃ was also investigated in the presence of DMSO and DMF. Both have been used in IB polymerization; in the presence of those strong electron pair donors (ED), the non-living cumyl-chloride/BCl₃ system exhibited living character, indanyl ring formation was suppressed and the polymerization-inactive aliphatic tert-chloride/BCl₃ system became active and induced living IB polymerization.³⁸ Both DMSO and DMF are characterized by high Gutmann numbers, i.e. DN = 29.8 and 26.6, respectively.²⁴³ The Gutmann donor number is the negative enthalpy of 1:1 adduct formation between an ED and the standard Lewis acid, SbCl₅, in dilute solution of the non-coordinating solvent 1,2-dichloroethane whose donor number is zero.
The polymerization-regulating effect of strong EDs is still debated. In one proposal this was visualized as Scheme 4.15.\textsuperscript{38}

\[
\begin{align*}
\text{CH}_3 & \quad \text{Cl} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{Cl} \quad \text{BCl}_3 \\
\text{CH}_3 & \quad \text{Cl} \quad \text{BCl}_3 (m-1) \quad \text{BCl}_3 \\
\text{DMSO} & \\
\text{CH}_3 & \quad \text{C} \quad \text{DMSO} \quad \text{BCl}_4 (m-1-n) \quad \text{BCl}_3 \\
\text{CH}_3 & \quad \text{Cl} \quad \text{BCl}_3 \\
\text{CH}_3 & \quad \text{Cl} \quad \text{BCl}_3 \\
\text{CH}_3 & \quad \text{Cl} \quad \text{BCl}_3 \\
\end{align*}
\]

Scheme 4.15. Mechanism of carbocation stabilization by DMSO in IB polymerization.\textsuperscript{38}

Strong EDs were believed to help to stabilize incipient carbocations arising from aliphatic chlorides. In contrast to this explanation, it was argued that the main function of EDs is proton trapping, not carbocation stabilization.\textsuperscript{41,44}

In this dissertation, IB was polymerized in the presence of DIBP, DMSO and DMF using the TMPCl/BCl\(_3\) initiating system at -40 °C; at this temperature \(\beta\)-proton elimination is known to occur.\textsuperscript{236} Products of all three polymerizations have olefinic chain ends to some extent, listed in Table 4.13.

Table 4.13. Results of the IB polymerization by TMPCl/BCl\(_3\) in the presence of various Lewis bases. [TMPCl]\(_0\) = 0.01 M, [IB]\(_0\) = 0.75 M, [BCl\(_3\)] = 0.25 M, [Lewis base] = 0.01 M, MeCl, T = -40 °C, 100 min.

<table>
<thead>
<tr>
<th></th>
<th>(M_n) (g/mol)</th>
<th>exo-olefin (%)</th>
<th>endo-olefin (%)</th>
<th>Total olefin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIB(_{DIBP})</td>
<td>870</td>
<td>30</td>
<td>5.7</td>
<td>36</td>
</tr>
<tr>
<td>PIB(_{DMSO})</td>
<td>980</td>
<td>9.1</td>
<td>0</td>
<td>9.1</td>
</tr>
<tr>
<td>PIB(_{DMF})</td>
<td>910</td>
<td>16</td>
<td>1.6</td>
<td>18</td>
</tr>
</tbody>
</table>
The lowest amount of olefinic chain ends was observed in the presence of DMSO. As it was discussed in the Introduction, it is mostly agreed that DrBP acts only as a proton trap. On the other hand, strong EDs such as DMSO and DMF may stabilize the carbocation through weak nucleophilic interactions. In addition, they may also coordinate with Lewis acids. These interactions with both the Lewis acid and the carbocationic chain end would help in preventing $\beta$-proton elimination by $\text{BCl}_4^-$. Considering that DMSO is a somewhat stronger ED than DMF, less amount of olefin is expected. Based on these results, the formation of olefinic chain ends observed in the polymerization of IB in the presence of $\text{BCl}_3$ can be minimized by the adjusting the polymerization time and temperature and by the addition of external electron donors.
CHAPTER V
CHAIN EXTENSION

As explained at the beginning of this dissertation, this research was a part of a Research Agreement between The University of Akron and LANXESS Inc. to generate fundamental knowledge in polymer-structure property relationships. Model structures based on polyisobutylene (PIB) were to be synthesized by living carbocationic polymerization, and to enhance the understanding of the mechanism of initiation and propagation of epoxy/Lewis acid (LA) initiated isobutylene (IB) polymerizations. Since the next part of the dissertation contains research supported by the National Science Foundation under DMR-0509687, we were advised by the counsel of The University of Akron Research Foundation that it needs to be separated from the main body of the dissertation.

The first part of these additional chapters contains the synthesis and characterization of high molecular weight PIB from a macroinitiator. Although this research is closely related to the LANXESS-supported part of this dissertation, it will be discussed separately.
5.1. Chain Extension from a Macroinitiator

Low molecular weight PIB (SH_HES053006, \( M_n = 2,500 \) g/mol, \( M_n/M_w = 1.78 \)) synthesized by using the HES/BCl₃ initiator system was used as “macroinitiator”. The \(^1\text{H}\) NMR spectrum of this macroinitiator (Figure 5.1.) showed three different -C\(\text{H}\) protons (i, j, k) next to the OH groups in the core, demonstrating that the three different epoxide rings were opened by BCl₃. Residual unopened epoxy rings were not detected. Intensity of the i proton signal was somewhat lower than that of k and j, whose ratio was 1:1. The methyl and methylene protons of the tert-Cl terminated PIB chain ends (g and h) had the expected 2:6 ratio, but ratio of j+k+i to a+a’ was less than expected. Signal at 0.9 ppm indicated the presence of PIB with three methyl head groups\(^{244}\), indicating protic initiation in addition to initiation by HES. The NMR also reveals the presence of olefinic chain ends.
Figure 5.1. $^1$H NMR spectrum of a PIB synthesized with HES/BCl$_3$ (SH_HES053006). [HES]$_0 = 0.019$ M, [IB]$_0 = 1.91$ M, [BCl$_3$] = 2.89 M, [DyBP] = 0.008 M, MeCl, T = -75 °C, t = 8 hrs, conversion = 44%, $M_n = 2,500$ g/mol, $M_n/M_w = 1.78$.

The SEC analysis showed that the macroinitiator had a high molecular weight shoulder which showed a high intensity light scattering response as well as a small amount of low molecular weight fraction which was not detected by the light scattering (Figure 5.2). The high MW shoulder was approximately 20 wt% of the total sample. The peak MW of the high shoulder was approximately 5 times of that of the MW of the main peak.
Figure 5.2. SEC traces of PIB (macroinitiator) synthesized with the HES/BCl₃ (SH_HES053006): RI, viscosity and MALLS detectors. Conversion = 44%, $M_n = 2,500$ g/mol, $M_n/M_w = 1.78$, Peak Molecular Weights = 2,900 g/mol (main peak, elution time = 51 min), 13,500 g/mol (high MW shoulder, elution time = 48 min).

The chain extension reaction was conducted by using Hx/MeCl (60/40, v/v) solvent mixture in the presence of TiCl₄ – conditions are shown in the caption of Figure 5.3. Aliquots taken during the polymerization were analyzed by SEC and results are shown in Figure 5.3.
Figure 5.3. SEC traces of the PIB samples from the macroinitiator (SH_HES053006): RI and MALLS. [Macroinitiator] = 0.001 M, [IB] = 2.6 M, [TiCl$_4$] = 0.08 M, [D$_2$BP] = 0.007 M, Hx/MeCl (60/40, v/v), T = -80 °C.
The MW of both fractions increased, and the high MW peak is clearly separated in the last sample. The change of the peak molecular weights with conversion was analyzed and is shown in Figure 5.4. The high MW population grew faster compared to the lower MW population, but both showed linear growth with conversion.

![Figure 5.4. Peak molecular weight vs. conversion plots of IB polymerization initiated by the macroinitiator (SH_HES053006)/TiCl₄. [Macroinitiator] = 0.001 M, [IB] = 2.6 M, [TiCl₄] = 0.08 M, [DrBP] = 0.007 M, Hx/MeCl (60/40, v/v), T = -80 °C. ■, dark solid line: high MW peaks; □, light solid line: lower MW peaks.]

The ratio of the peak MWs in the chain extended samples was about 2:1 in all cases. The number average molecular weight (Mₙ) versus conversion plot (Figure 5.5) was also linear indicating the absence of chain transfer.
Interestingly, the monomer consumption rate was slow up to 20 min (38% conversion), then faster (Figure 5.6). This may indicate additional initiation from any epoxy initiating sites of the HES molecule which were opened but capped by a tert-chloride, as shown in Scheme 5.1.

Scheme 5.1. The ring-opening of HES with BCl₃.
Table 5.1 summarizes the results from SEC including peak molecular weights and

g' = [\eta]_{w,br} / [\eta]_{w,lin} \text{ values, where } [\eta]_{w,lin} = 2.20 \cdot 10^{-2} (M_w)^{0.667} \text{.}^{237}

![Figure 5.6. First-order rate plot of IB polymerization initiated by the macroinitiator (SH_HES053006)/TiCl_4. [Macroinitiator] = 0.001 M, [IB] = 2.6 M, [TiCl_4] = 0.08 M, [DrBP] = 0.007 M, Hx/MeCl (60/40, v/v), T = -80 °C.]

| Table 5.1. SEC analysis of PIBs synthesized by using the macroinitiator (SH_HES053006) with TiCl_4. |
|-------------------------------------------------|-------------------------------------------------|----------------|-------------------------------|----------------|----------------|----------------|----------------|
| | | | | | | | | |
| **Aliquot** | **Time (min)** | **Conv. (%)** | **M_n (kg/mol)** | **M_w/M_n** | **[\eta_w] (mL/g)** | **g’** | **Lower MW peak** | **High MW peak** |
| Macro. | 2.5 | 1.78 | 2.9 | 13.5 |
| 1 | 5 | 10 | 24.5 | 1.18 | 21 | 1.01 | 21.9 | 41.0 |
| 2 | 10 | 20 | 39.5 | 1.15 | 27.5 | 0.98 | 35.8 | 71.8 |
| 3 | 20 | 38 | 70.8 | 1.12 | 39.6 | 0.97 | 65.1 | 135 |
| 4 | 30 | 63 | 109.0 | 1.19 | 52.9 | 0.93 | 92.1 | 193 |
| 5 | 40 | 77 | 115.0 | 1.15 | 55.3 | 0.96 | 111 | 234 |
| 6 | 50 | 84 | 130.0 | 1.19 | 59.9 | 0.94 | 126 | 262 |
| 7 | 90 | 99 | 147.0 | 1.15 | 63.3 | 0.94 | 146 | 296 |
As discussed in Chapter IV.2.4, and shown in Figure 5.1., PIB obtained by HES/BCl₃ showed the presence of olefinic chain ends. In addition, β-proton expulsion from tert-Cl chain ends, causing olefin formation, might result in chain transfer if all expelled protons were not trapped by DtBP. Even though some olefinic chain ends were present in the macroinitiator used for the chain extension, polymerization could be reinitiated in conjunction with TiCl₄. The Mₙ increased linearly with conversion while the ln ([M]₀/[M]) vs. time plot showed a change in the polymerization rate. The viscosities measured on-line showed only a small reduction relative to that of a linear PIB of the same Mₚ calculated from \[ \eta_{w,\text{lin}} = 2.20 \cdot 10^{-2} (M_w)^{0.667} \]

In summary, chain extension from a low molecular weight PIB macroinitiator that was synthesized by the HES/BCl₃ initiating system was performed using Hx/MeCl (60/40, v/v) mixture in the presence of TiCl₄. While Mₙ increased linearly with conversion, the kinetic plot showed acceleration after about 20 min. Two populations of polymer chains were present, as demonstrated by SEC analysis. The lower molecular weight portion grew slower than the high molecular weight fraction; the latter had about twice the peak MW of the former. Full IB conversion was achieved in 90 minutes, reaching Mₙ \(\sim\) 150,000 g/mol. The peak MW of the higher MW fraction was about 300,000 g/mol.
CHAPTER VI

EPOXY-FUNCTIONAL SILOXANES

This part of the additional chapters describes the use of a new class of initiators for the synthesis of polyisobutylene (PIB): siloxane compounds that contain 1,2-epoxycyclohexane to initiate isobutylene (IB) polymerization. This research was supported by the National Science Foundation under DMR-0509687.

6.1. Background

Silsesquioxanes are compounds with the empirical formula RSiO\(_{3/2}\) where R is hydrogen or alkyl, alkyne, aryl, arylene, or their functional derivatives.\(^{245}\) \((RSiO\(_{3/2}\))_8\) is a well-defined polyhedral oligomeric silsesquioxane (POSS) which has received considerable amount of interest in polymer synthesis because of enhanced thermal and mechanical properties of organic-inorganic composite materials with POSS being either a pendant group or part of the polymer backbone.\(^{246-248}\) Synthesis of polymers containing POSS has been reported using conventional radical,\(^{246,248}\) controlled radical,\(^{249}\) condensation,\(^{250}\) and ring-opening metathesis polymerization.\(^{251}\) Recently, Faust and Kim\(^{252}\) reported the living carbocationic block copolymerization of isobutylene and styrene-based POSS macromers. They synthesized both poly(IB-\(b\)-styryl-POSS) diblock and poly(styrene-POSS-\(b\)-IB-\(b\)-styrene-POSS) triblock copolymers. The triblock co-
polymer was reported a strong, rubbery material. Thermal Gravimetric Analysis (TGA) showed that it was stable up to 400 °C at which temperature it showed rapid weight loss attributed to the cleavage of the polymer chains attached to the POSS core. Previously, octa(dimethylsiloxy) functionalized POSS was used as a linking agent for the synthesis of eight-arm star PIB by hydrosilation of ω-allyl terminated PIB with the linking agent.253

The use of an epoxy-functionalized POSS as initiator for the polymerization of IB will now be discussed.

6.2. IB Polymerization Initiated by 1,2-Epoxycyclohexane

Since the POSS that is used in this research contains an epoxycyclohexane group,

![Image of POSS](image)

Figure 6.1. Epoxycyclohexylisobutyl POSS®.

initiation of IB polymerization was first investigated with 1,2-epoxycyclohexane (Aldrich, Figure 6.2.) in conjunction with TiCl₄ as model reaction.
Figure 6.2. $^1$H NMR spectrum of 1,2-epoxycyclohexane.

The polymerization conditions are given in the caption of Figure 6.3. The $^1$H NMR spectrum of the product, as shown in Figure 6.3, demonstrated the presence of characteristic PIB methyl and methylene protons at 1.1 and 1.4 ppm. The signals of the $\text{–CH}_3\text{CCl}$ and $\text{–CH}_2\text{C(CH}_3\text{)_2Cl}$ protons at 1.70 and 1.98, respectively, were present in a ratio of 6/2 as expected. The $\text{–CHOH}$ proton of the sec-OH head group at 3.13-3.20 ppm split due to vicinal coupling of protons attached to the neighboring carbons.
Figure 6.3. $^1$H NMR spectrum of PIB synthesized by 1,2-epoxycyclohexane/TiCl$_4$. [1,2-epoxycyclohexane]$_0$ = 0.004 M, [IB] = 1.7 M, [TiCl$_4$] = 0.057 M, [D$_2$BP] = 0.007 M, Hx/MeCl (60/40, v/v), $T = -80^\circ$C, $t = 24$ min, conversion = 22%.

The ratio of the signal intensities of the proton of the hydroxyl head group (–CHOH, e) to the gem-dimethyl protons of the tert-chloride end groups (–CH$_3$CCl, c) confirmed one hydroxy functionality per polymer chain. Thus the polymerization yielded a PIB containing $\alpha$-secondary OH and $\omega$-tertiary Cl chain ends with $M_n = 11,000$ g/mol, $M_w/M_n = 1.05$ by SEC ($I_{eff} = 48\%$). $M_n = 12,000$ g/mol ($I_{eff} = 44\%$) was obtained by $^1$H NMR from the ratio of the intensities of the gem-dimethyl protons of the tert-chloride end groups (c) to the intensity of the main chain protons (8). Based on the ring-opening mechanism of epoxides presented in this dissertation, a secondary carbocation would form from 1,2-epoxycyclohexane as shown in Scheme 6.1.
Ring opening via $S_N^1$ mechanism

\[
\text{O} + \text{TiCl}_4 \xrightarrow{\text{Hx/MeCl (60/40, v/v)}} \text{CH}_2\text{O}^\ast\text{TiCl}_4 \xrightarrow{-80 ^\circ C} \text{CH}_2=\text{CH}_3
\]

Possible side reaction: oligoether formation via $S_N^2$ mechanism

\[
\text{O} + \text{TiCl}_4 \rightarrow \text{Cl} \rightarrow \text{Cl} \rightarrow \text{OH}
\]

Scheme 6.1. $S_N^1$ vs. $S_N^2$ mechanism of the ring-opening of 1,2-epoxycyclohexane with TiCl$_4$ in the presence of IB.

The initiation of IB polymerization from epoxycyclohexane that yields a secondary carbocation was thought to be less likely compared to an epoxide that yields a tertiary carbocation, for example 1,2-epoxy-2,4,4-trimethylpentane, 2,3-epoxy-2,4,4-trimethylpentane or $\alpha$-methylstyrene epoxide, i.e. the epoxides that were discussed previously in this dissertation. Therefore, a computational approach (courtesy of Dr. Modarelli, Department of Chemistry, The University of Akron) was utilized to calculate the enthalpy difference between the possible reactions of epoxycyclohexane/isobutylene mixture in the presence of TiCl$_4$, as shown in Scheme 6.2. The enthalpies of the following reactions (Scheme 6.2) were calculated using density functional theory (DFT) computational method with B3LYP/6-31G(d) theory level.
Scheme 6.2. Possible reactions of TiCl₄-coordinated epoxycyclohexane with isobutylene vs. epoxycyclohexane.

It is important to emphasize that both reactions in Scheme 6.2 proceed by Sₙ₂ mechanism. In Path A, the oxonium ion reacts with the nucleophilic IB, forming a tertiary carbocation. Path B represents polyether formation by the reaction of the oxonium ion with another epoxy ring. The enthalpy change (ΔH) of both reactions was found to be negative indicating that both reactions A and B are expected to be exothermic. The difference between the ΔH_{reaction, A} and ΔH_{reaction, B} was found to be only 1.32 kcal.mol⁻¹ slightly favoring reaction B. Such a small difference in the ΔH_{reaction} between reaction A and reaction B indicated that both reactions are possible. The $I_{\text{eff}} \sim 45\%$ found experimentally in the polymerization of IB initiated by 1,2-epoxycyclohexane in the presence of TiCl₄ is still slightly dominated by polyether formation through reaction B. The significance of this finding is that it supports a new mechanism for the initiation step in epoxy/TiCl₄-initiated IB polymerizations. Thus initiation most likely proceeds via an Sₙ₂ mechanism, and is influenced by the concentration of IB. Indeed, higher initiator efficiencies were found with high IB/epoxide ratios. More investigations are needed to verify the initiating mechanism. After this promising result epoxy-POSS
containing an epoxycyclohexane was investigated as an initiator for the polymerization of IB.

6.3. IB Polymerization Initiated by Epoxy-POSS/TiCl₄

The $^1$H and $^{13}$C NMR spectra of epoxy-POSS (supplied by Hybrid Plastics, further dried in a vacuum oven for 2 weeks prior to use) are shown in Figure 6.4 and 6.5, respectively. The ratios of the signals of the –CHO protons in the epoxide ring (j and k in Figure 6.4) to the proton signals of the methylene (–CH$_2$) and methyl (–CH$_3$) protons if the tert-butyl groups attached to the Si centers (b and c in Figure 6.4) are consistent with one epoxide per siloxane cage.

Figure 6.4. $^1$H NMR spectrum of epoxy-POSS.
IB polymerization was initiated by epoxy-POSS in conjunction with TiCl$_4$ using a hexane (Hx)/methyl chloride (MeCl) (60/40, v/v) mixture in the presence of D$_2$BP at -80 °C in a glovebox. Specific conditions are given in the figure captions. The polymerization was monitored by *in situ* FTIR by using an ATR probe. As soon as TiCl$_4$ was added to the reaction, a new, strong band was observed at 1614 cm$^{-1}$, which was assigned to –COTiCl$_4$ group at the initiating site as discussed in the previous chapters (Figure 6.6). A gradual decrease of the C=C stretching (1655 cm$^{-1}$) of IB demonstrated monomer conversion.

Figure 6.5. $^{13}$C NMR spectrum of epoxy-POSS.
Interestingly, the IR band at 1614 cm$^{-1}$, i.e. the stretching vibration of the –COTiCl$_3$ head group, was strong in the beginning of the reaction but gradually decreased in the first 6 minutes of the reaction and then stayed steady until the end of the reaction (Figure 6.6). As the coordination of TiCl$_4$ with –O– and ring-opening is characterized by this strong absorption, the decrease could indicate the loss of this coordination or this could be an artificial change in the IR absorption during the reaction; the exact reason for this phenomenon is unknown.

The SEC results are summarized in Table 6.1. Initiator efficiency was calculated as $I_{\text{eff}} = M_{\text{n, theo}} / M_n$ where $M_n$ and $M_{\text{n, theo}}$ are measured and theoretically expected (g PIB/mol initiator) number-average molecular weights, respectively.
Table 6.1. SEC analysis of PIB synthesized by epoxy-POSS/TiCl₄ (POSS_121207).

<table>
<thead>
<tr>
<th>Aliquots</th>
<th>Time (min)</th>
<th>Conv. (%)</th>
<th>Mₚ, theor. (g/mol)</th>
<th>Mₚ by SEC (g/mol)</th>
<th>Mₚ/Mₚ</th>
<th>Iₚeff (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>dn/dc = 0.108</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100% mass recovery</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>14</td>
<td>26</td>
<td>8,300</td>
<td>17,400*</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>29</td>
<td>61</td>
<td>19,200</td>
<td>50,800</td>
<td>53,800</td>
<td>1.16</td>
</tr>
<tr>
<td>3</td>
<td>43</td>
<td>85</td>
<td>26,500</td>
<td>69,400</td>
<td>74,200</td>
<td>1.13</td>
</tr>
</tbody>
</table>

*by ¹H NMR

The RI traces are monodisperse with narrow MWD. The SEC-MALLS traces showed a slight shoulder at the high MW end. A very small amount of high MW peak with peak MW of 2.6×10⁶ g/mol (Aliquot 1) and 5.1×10⁶ g/mol (Aliquot 2), only detectable by light scattering, was also observed.
Figure 6.7. SEC traces of the last two samples of PIB synthesized by epoxy-POSS/TiCl$_4$ (POSS_121207) by RI and MALLS.
The polymerization of IB initiated by the epoxy-POSS/TiCl$_4$ system with higher epoxy-POSS to IB ratio $[\text{epoxy-POSS}]/[\text{IB}] = 0.14$ vs. 0.002 (POSS_121207)] was also monitored by *in situ* FTIR. The exact conditions are given in the caption of Figure 6.8. The IR band at 1614 cm$^{-1}$, which was assigned to –COTiCl$_4$ group, appeared just after the addition of TiCl$_4$ and stayed steady throughout the reaction. Monomer consumption was demonstrated by the gradual decrease of the C=C double bond stretching of IB at 1655 cm$^{-1}$ as well as the overtone of C–H wag of =CH$_2$ at 1780 cm$^{-1}$.

![Figure 6.8](image_url)

**Figure 6.8.** *Real-time* FTIR monitoring of IB polymerization initiated by epoxy-POSS/TiCl$_4$ (POSS_040208) with a TR probe: 1500-1900 cm$^{-1}$ region. $[\text{epoxy-POSS}] = 0.07$ M, $[\text{IB}] = 0.5$ M, $[\text{DzBP}] = 0.007$ M, $[\text{TiCl}_4] = 0.3$ M, Hx/MeCl (60/40, v/v), $T = -80$ °C, $t = 15$ min, conversion = 100%.

The polymerization was terminated by the addition of MeOH/NaOH. After evaporation of all volatiles, the polymer was dissolved in hexane and the solution was washed with distilled water until it was neutral, dried over MgSO$_4$ and filtered. The PIB was recovered by precipitation into methanol. MeOH was expected to dissolve any polyether side products. Since the unreacted POSS also precipitated from MeOH, the
polymer was further cleaned. A very viscous solution was prepared by dissolving the PIB and unreacted POSS in a small amount of hexane and the solution was stirred vigorously with large amounts of acetone to remove the unreacted POSS. This process was repeated until a clear polymer was obtained.

The $^{1}$H NMR spectrum (Figure 6.9) of the product demonstrated the incorporation of the epoxy-POSS into the PIB chains. The ratio of the proton signals in the PIB synthesized by epoxy-POSS is consistent with the expected structure within experimental error: $(i+h)/(a+b) = 9/16$. The ratio of the signal integrals of $-CH_3$ (f) and $-CH_2$ (g) protons of the tert-Cl chain end of PIB is $f/g = 6/2$ as expected. The ratio of integration value of the $-CH_3$ protons of the tert-Cl chain ends (f) to that of the $-CH_2$ protons attached to the Si centers (a + b) is consistent with the incorporation of one epoxy-POSS into every polymer chain.

![NMR spectrum](image)

Figure 6.9. $^1$H NMR spectrum of the PIB synthesized by epoxy-POSS/TiCl$_4$ system (POSS_040208).
SEC analysis of the final product of POSS_040208 yielded $M_n = 7,000$ g/mol ($I_{\text{eff}} = 6\%$) with $dn/dc = 0.108$ for PIB, and $M_n = 10,600$ g/mol ($I_{\text{eff}} = 4\%$) using the 100% mass recovery method, and $M_w/M_n = 1.24$. $^1$H NMR gave $M_n = 10,900$ g/mol, using the ratio of methylene protons of the tert-Cl chain ends to the methyl and methylene protons of the PIB repeat unit. This agrees well with the SEC molecular weight from 100% mass recovery, and $dn/dc = 0.074$ was calculated by ASTRA.

6.4. IB Polymerization Initiated by $\text{Bis}[3,4-(\text{epoxycyclohexyl})\text{ethyl}]\text{tetramethyl-disiloxane/TiCl}_4$

Another siloxane epoxide that possesses two epoxycyclohexyl groups, namely $\text{bis}[3,4-(\text{epoxycyclohexyl})\text{ethyl}]\text{tetramethyl-disiloxane (SIB1092.0)}$ was also investigated as an initiator for IB polymerizations. Figures 6.10 and 6.11 show $^1$H and $^{13}$C NMR spectra of the SIB1092.0, respectively. The ratio of the proton signals of the epoxy ring (–CHO, i and j in Figure 6.10) to the proton signals of the –CH$_3$ or –CH$_2$ groups attached to the Si atoms (a and b, respectively, in Figure 6.10) demonstrated the presence of two epoxides per molecule.
Figure 6.10. $^1$H NMR spectrum of SIB1092.0.

Figure 6.11. $^{13}$C NMR spectrum of SIB1092.0.

The SIB1092.0/TiCl$_4$ system was used to initiate IB polymerization using Hx/MeCl (60/40, v/v) at -80 °C. The exact reaction conditions are given in the caption of
Figure 6.12. After mixing the solvents, DtBP, SIB1092.0 and IB, the polymerization was started by addition of pre-chilled TiCl₄. The reaction was monitored by in situ FTIR by using an ATR probe. Upon TiCl₄ addition, a new band was observed at 1614 cm⁻¹, which was assigned to –COTiCl₄ group (Figure 6.12). This band stayed steady until the end of the polymerization. A gradual decrease of the C=C stretching (1655 cm⁻¹) of IB demonstrated monomer conversion.

Figure 6.12. Real-time FTIR monitoring of IB polymerization initiated by SIB1092.0/TiCl₄ (SIB_121207) with an ATR probe: 1550-1700 cm⁻¹ region. [SIB1092.0] = 0.004 M, [IB] = 2.1 M, [DtBP] = 0.007 M, [TiCl₄] = 0.069 M, Hx/MeCl (60/40, v/v), T = -80 °C.
The $^1$H NMR spectrum (Figure 6.13) of the product demonstrated the incorporation of SIB1092.0 into the PIB chains by the presence of the proton signals of methyl groups attached to the Si at 0.05 ppm. The ring-opening of the epoxide was confirmed by the disappearance of –CHO protons at 3.12-1.16 ppm. In addition, a new chemical shift appeared at 3.42-3.43 ppm which is assigned to the –CH proton attached to the –OH.

![Figure 6.13. 1H NMR spectrum of PIB (SIB_121207) synthesized by the SIB1092.0/TiCl$_4$ system (first aliquot).](image)

The ratio of the integral of the –CH$_3$ protons of the tert-Cl chain ends (e) to the integral of the –CH$_3$ protons attached to Si (a), and that of the –CH proton attached to the –OH group (i) indicated that the average number of PIB chains per SIB1092.0 molecule was 1.4 and 1.3, respectively. This means that more than 50% of the polymer had only one “arm” (no bidirectional growth).
The SEC results are summarized in Table 6.2. Initiator efficiency was calculated as \( I_{\text{eff}} = \frac{M_{n,\text{theo}}}{M_n} \) where \( M_n \) and \( M_{n,\text{theo}} \) are measured and theoretically expected (g PIB/mol initiator) number-average molecular weights, respectively.

Table 6.2. SEC analysis of PIB synthesized by SIB1092.0/TiCl4 (SIB_121207).

<table>
<thead>
<tr>
<th>Aliquots</th>
<th>Time (min)</th>
<th>Conv. (%)</th>
<th>( M_{n,\text{theor.}} ) (g/mol)</th>
<th>( M_n ) by SEC (g/mol)</th>
<th>( \frac{dn}{dc} = 0.108 )</th>
<th>100% mass recovery</th>
<th>( \frac{M_w}{M_n} )</th>
<th>( I_{\text{eff}} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>5</td>
<td>1,700</td>
<td>22,300*</td>
<td></td>
<td></td>
<td></td>
<td>8*</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>39</td>
<td>12,300</td>
<td>50,400</td>
<td>56,200</td>
<td>1.16</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>61</td>
<td>19,200</td>
<td>77,200</td>
<td>82,600</td>
<td>1.16</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

*by \(^1\text{H} \) NMR

The SEC traces showed a high molecular weight shoulder for both samples (Figure 6.14). Also a very small amount of high MW polymer was observed with peak MW of \( 4.0 \times 10^6 \) g/mol (Aliquot 1) and \( 2.0 \times 10^6 \) g/mol (Aliquot 2), only detectable by light scattering. Bimodal distribution indicates the presence of two polymer chain populations, with the higher peak MW being twice as high as the lower peak MW. Most likely one population contains one PIB arm while the other one has two PIB arms per initiator molecule.
Figure 6.14. SEC traces of the last two samples of PIB synthesized by SIB1092.0/TiCl$_4$ by RI and MALLS (SIB_121207).

6.5. Transmission Electron Microscopic (TEM) Analysis of PIB Obtained by Epoxy-POSS and SIB1092.0

The final products synthesized with epoxy-POSS (POSS_121207) and SIB1092.0 (SIB_121207) were examined using Transmission Electron Microscopy (TEM). TEM
images of the PIB obtained by epoxy-POSS (POSS_121207) showed micron-sized clusters that were observed in various areas on the TEM grids. These clusters are most likely aggregates of POSS-PIB. For comparison, the radius of gyration of POSS-PIB with $M_n = 69,400$ g/mol was 13.3 nm while the size of a POSS molecule is 1.5 nm.$^{254}$ The formation of 50-150 nm aggregates in POSS-functionalized trifluorovinyl aryl ether-co-4,4$'$-Bis(4-trifluorovinyl-oxy)biphenyl copolymer was also found by Smith et al.$^{255}$

![TEM images of POSS_121207](image)

Figure 6.15. TEM images of POSS_121207.

The PIB obtained by SIB_1092 (SIB_121207) also showed a tendency to form aggregates as revealed by TEM (Figure 6.16). These aggregates were more dispersed than those of POSS-PIB. Most of the aggregates have a size of $\sim 100$ nm, which is about 8 times larger than the radius of gyration of the PIB (SIB_121207, $R_g \sim 12.2$ nm).
In summary, epoxycyclohexane containing a secondary epoxide carbon initiated IB polymerization in conjunction with TiCl$_4$ and yielded 45% initiator efficiency. The computed difference of reaction enthalpies was very small between initiation of IB polymerization by epoxycyclohexane and dimer/polyether formation in the presence of TiCl$_4$. Based on the results presented in this dissertation, it was proposed that initiation of IB polymerization involves an SN$_2$ reaction between IB and a TiCl$_4$-coordinated epoxide. Two types of epoxy siloxanes were used as initiators of IB polymerization. The epoxy-POSS yielded 38 and 6% initiator efficiencies with [I]/[M] = 1.8x10$^{-3}$ and 1.4x10$^{-1}$, which indicates that higher initiator efficiency is obtained at higher monomer concentration. These results also suggest that the initiation step involves IB as well as the epoxide, supporting the proposed SN$_2$ mechanism. The incorporation of one epoxy-POSS per polymer was demonstrated by $^1$H NMR spectroscopy. The SIB1092 epoxide that contains two epoxide rings yielded \(~1.4\) PIB arms per initiator. PIBs synthesized by both POSS and SIB showed aggregates by TEM analysis. While the SIB-PIB had well-defined aggregates, the POSS-PIB showed large clusters.
CHAPTER VII

CONCLUSION

The mechanism of initiation of carbocationic polymerization of isobutylene (IB) induced by epoxy/Lewis acid (LA) systems was investigated. The IB polymerizations initiated by single-site epoxy initiators, i.e., 1,2-epoxy-2,4,4-trimethylpentane (TMPO-1), 2,3-epoxy-2,4,4-trimethylpentane (TMPO-2) and \(\alpha\)-methylstyrene epoxide (MSE), in conjunction with various Lewis acids (LAs) (TiCl\(_4\), BCl\(_3\)) were monitored by real-time FTIR. Based on these results, it was proposed that when TMPO-1 is reacted with BCl\(_3\), the majority of the epoxy rings (~70%) cleaves by an \(S_N1\) pathway and forms a tertiary carbocation, which was then capped to form a tert-Cl initiator \([I]\). The latter can be activated by excess BCl\(_3\) to initiate the polymerization of IB. Polyether formation was not observed by FTIR, but side reactions did occur causing some loss of initiator. This system yielded a telechelic PIB carrying an \(\alpha\)-primary OH and an \(\omega\)-tertiary Cl group with 70% initiator efficiency. In contrast, the reaction of TMPO-2 with BCl\(_3\) did yield a tert-chloride initiator \([I]\) but it did not initiate the polymerization with excess BCl\(_3\). However, a small amount of TiCl\(_4\) was able to ionize the tert-Cl end groups and initiated the polymerization. An aliphatic telechelic PIB with one secondary hydroxyl and one tertiary chloride terminus was obtained with \(I_{eff} = 20\%\). The fact that excess BCl\(_3\) did not initiate IB polymerization with TMPO-2, an“internal” epoxide, compared with the
successful activation of TMPO-1, an “external” epoxide, demonstrated the difference in reactivities of these epoxides. The formation of the –CO-LA (LA = TiCl$_4$ or BCl$_3$) complex by the reaction of an epoxide with LA was observed via \textit{in situ} FTIR. The characteristic FTIR signal at ~ 1610-20 cm$^{-1}$ can be used to monitor the kinetics of initiation.

Hexaepoxysqualene (HES)-initiated IB polymerizations were successfully monitored by \textit{in situ} FTIR. The formation of the –CO-LA complex provided a method to monitor the rate of initiation by HES. It was found that IB polymerization by HES can be initiated by excess BCl$_3$, but the gradual increase of the IR band assigned to the –COBCl$_2$ group at the initiating site demonstrated that the initiation was slow. The bimodal distribution of SEC traces obtained at low conversions implied that there was a reactivity difference between terminal and interior epoxide groups of HES. It was proposed that the more reactive epoxide rings, which are likely the terminal epoxides that are sterically more accessible, will be opened first to start PIB chain growth. The less reactive rings might be opened later, resulting in broad or bimodal distributions at low conversion. The HES/BCl$_3$ initiating system yielded low molecular weight PIB. After the synthesis of the low molecular weight PIB macroinitiator with HES/BCl$_3$, chain extension was achieved in the presence of TiCl$_4$ which led to high molecular weight PIBs. Both populations of polymer chains present in the macroinitiator grew linearly with time. Further initiation after TiCl$_4$ addition was demonstrated by the increase of the IR band assigned to the –COTiCl$_3$ group at the initiating sites.

The formation of olefinic chain ends (mostly \textit{exo}-olefin) was observed in all BCl$_3$-coinitiated IB polymerizations. The accepted mechanism of olefin formation is $\beta$-
proton elimination from the active tert-carbocations. More olefinic chain ends formed at lower temperatures (-60 °C vs. -40 °C). Evidence for the reversibility of this reaction was found via NMR spectroscopy. This is the first demonstration of this phenomenon, predicted in 1983. Olefin formation was minimized by the use of a strong electron pair donor, DMSO.

In summary, BCl₃ coinitiator led to several complications, including slow initiation in conjunction with the hexa-functional epoxy initiator, β-proton elimination and chain transfer.

Finally, new initiators are introduced for the carbocationic polymerization of IB. 1,2-epoxycyclohexane and epoxycyclohexane containing siloxanes, namely epoxycyclohexylisobutyl polyhedral oligomeric silsesquioxane (POSS) and bis[3,4-(epoxycyclohexyl)ethyl]tetramethyldisiloxane, initiated IB polymerizations in conjunction with TiCl₄. The initiator efficiency was found to be dependent on the concentration of IB; higher initiator efficiency was achieved at higher IB concentration. Based on the results presented in this dissertation, a possible new initiation mechanism was proposed. It is theorized that formation of a carbocation from the ring-opening of an epoxide by S_N1 mechanism is not required to initiate the IB polymerization. Instead, initiation may proceed via an S_N2 reaction between IB and the TiCl₄-coordinated epoxide, which always yields a tertiary butyl carbocation.
REFERENCES


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