# An Excerpt from Chapter IV of Dr. Lewis' Ph.D. Dissertation

result of the reduced nucleophilicity of the $[B(C_6F_5)_4]$ counteranion compared to those of the other systems.

## 4.2 Results and Discussion on Solution Polymerization of IB Coinitiated by $1,2\text{-}C_6F_4[B(C_6F_5)_2]_2$

### 4.2.1 Introductory Polymerization Work

Following the encouraging results obtained in the oligomerization of TMP with protic and cationogenic initiators in conjunction with $1,2\text{-}C_6F_4[B(C_6F_5)_2]_2$ (Section 3.3.2.1), the homopolymerization of isobutylene as coinitiated by this chelating Lewis acid was investigated. Initial attempts at the polymerization of isobutylene as coinitiated by diborane **1** in conjunction with CumCl and DTBMP led to highly variable results for polymerization. This variability was believed to stem from additional initiation arising from reaction of diborane **1** with adventitious moisture in the system, despite the presence of the added proton trap. During this introductory series of experiments it was discovered that diborane **1** was an extremely effective Lewis acid coinitiator for polymerization in conjunction with adventitious moisture. Polymerizations induced in this manner were so favorable that addition of stock solutions of diborane **1** to hexane solutions of isobutylene at – 80 °C led to immediate reflux of monomer with instantaneous solidification of the charge, resulting in production of polymer in quantitative yields. Apparently the Brönsted acid formed from reaction of diborane **1** with adventitious moisture, $[H][1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2(\mu\text{-}OH)]$, is extremely proficient at initiating polymerization by direct protonation of monomer. As will be seen in subsequent sections of this chapter and also in Chapter V, the competency of diborane **1** as a coinitiator for protic initiation is such that it leads to efficient polymerization of isobutylene even under the most demanding of conditions.

Following these introductory polymerizations, it was soon realized that in order for controllable polymerization to be achieved, steps had to be taken to minimize the effects of adventitious moisture and restrict polymerization to that as initiated by added cationogens. Therefore, all polymerizations were conducted with highly purified monomer and solvents that were further purified by drying over trioctylaluminum followed by immediate vacuum transfer to the reactor prior to polymerization. Titrations of these purified isobutylene solutions using a standardized ketyl solution showed them to contain a consistent level of adventitious moisture on the order of $5\text{x}10^{-5}$ M. Despite this low level of water, DTBMP had to be added to polymerizations prior to the addition of diborane **1** in order to prevent protic initiation from occurring. In order to determine the optimal concentration of DTBMP, a series of stopping experiments were conducted in which the concentration of proton trap was steadily increased to the point that polymerization did not occur. As can be seen from the data in Table 24, a 10-fold excess

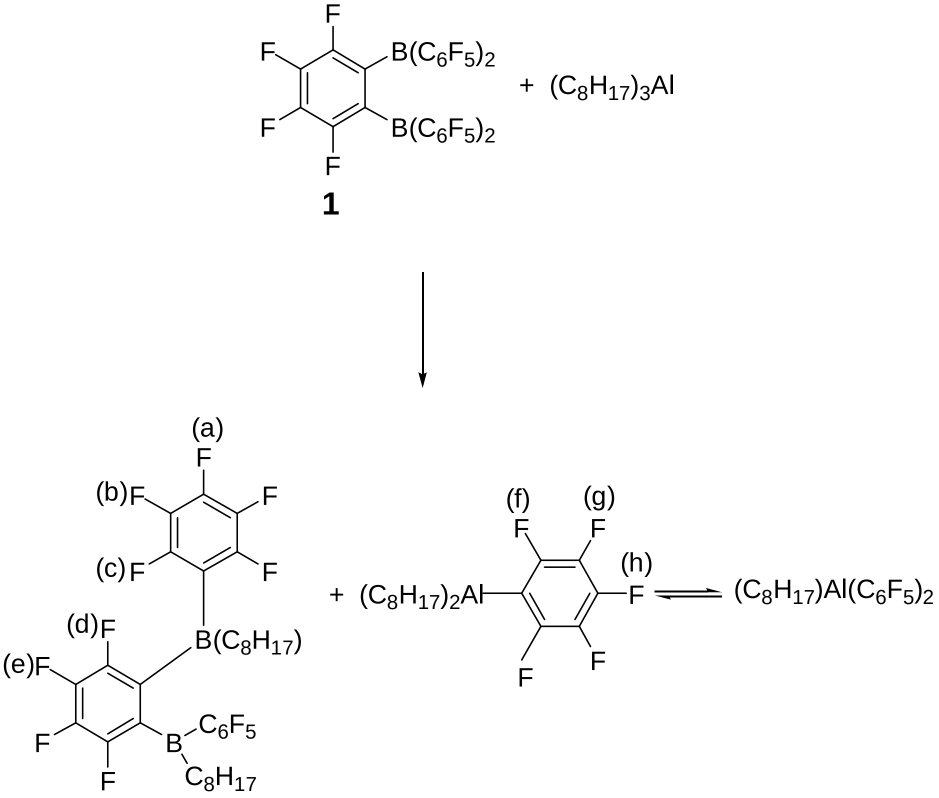
Table 24. Stopping experiments in hexane.[a]

| Entry | DTBMP (M) | $\overline{M}_w$ ($\text{x}10^3$) | PD | Yield (%) |
|---|---|---|---|---|
| 1 | $2\text{x}10^{-3}$ | 302 | 2.48 | 5.76 |
| 2 | $5\text{x}10^{-3}$ | 552 | 3.61 | 1.44 |
| 3 | $1\text{x}10^{-2}$ | 163 | 3.97 | 0.499 |
| 4 | $1.5\text{x}10^{-2}$ | 753 | 4.89 | 0.473 |
| 5 | $2\text{x}10^{-2}$ | — | — | 0 |

a. [diborane 1] = 2 mM, [IB] = 2.76 M, [DTBMP] = 20 mM, –78 °C for one hour.

of DTBMP to diborane **1** was required to prevent protic initiation under the standard conditions chosen for polymerization.

In an attempt to reduce the moisture level even further, several aluminum compounds bearing hydrolysable alkyl groups were investigated for use as potential *in situ* scrubbing agents. Initial attention was focused on the use of simple alkylaluminum compounds, trimethylaluminum (TMA) and trioctylaluminum; however, from preliminary studies on the compatibility of these compounds with 1,2-$C_6F_4[B(C_6F_5)_2]_2$, it was found that both led to undesirable ligand exchange reactions with diborane **1** (Scheme 39 and Figure 36). TMA is a potential active coinitiator for isobutylene



Scheme 39. Reaction of TOA with diborane **1**.

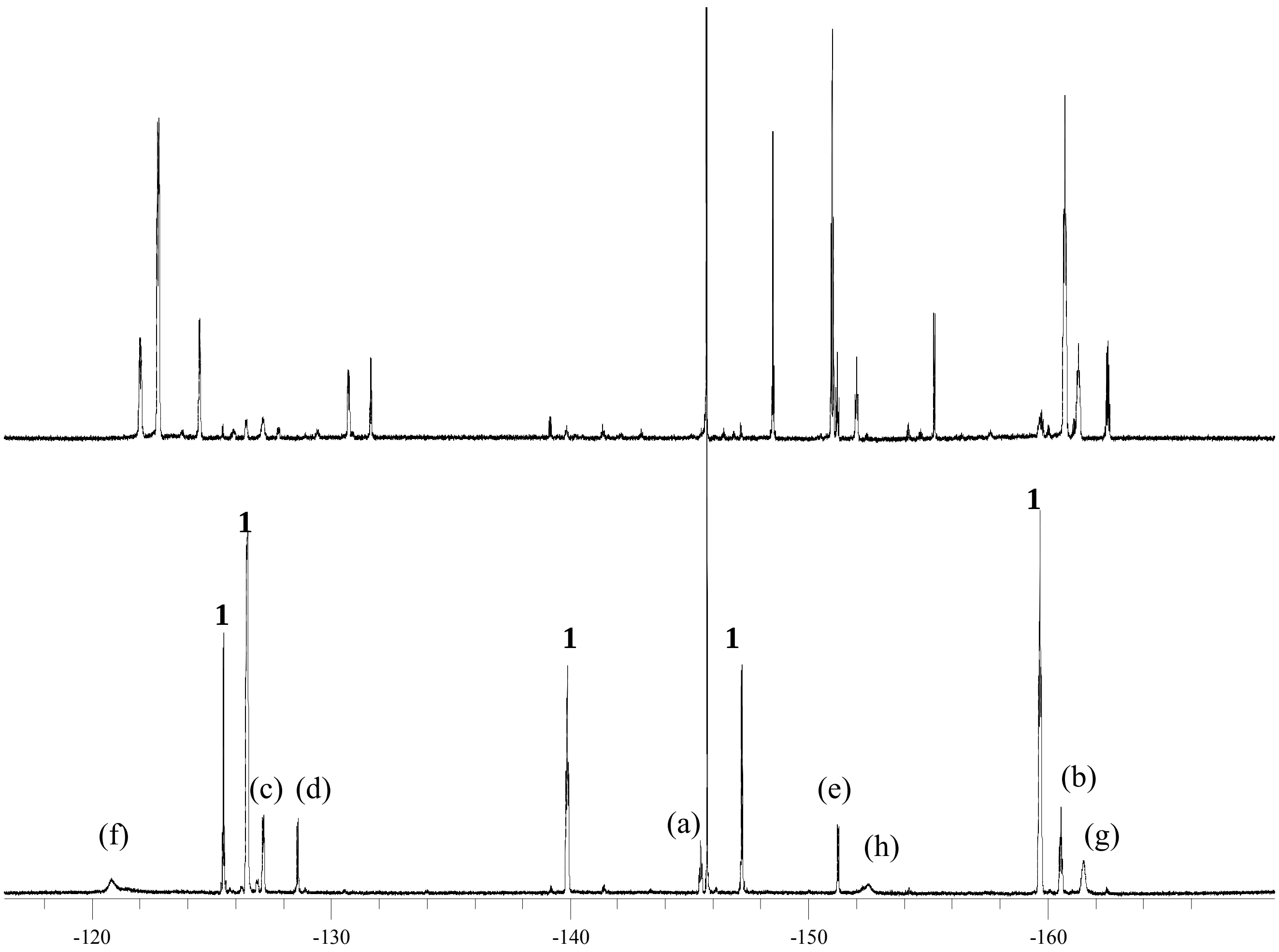


Figure 36. $^{19}$F NMR (toluene-$d_8$) spectra overlay for TMA/1,2-$C_6F_4[B(C_6F_5)_2]_2$ and TOA/1,2-$C_6F_4[B(C_6F_5)_2]_2$. (see Scheme 39 for assignments)

polymerization in conjunction with cationogens such as CumCl. As a result, this material cannot be used as an *in situ* scrubbing agent for isobutylene polymerization with CumCl as such a combination may lead to the initiation of polymerization. Similar behavior was witnessed for TOA as this material immediately initiated oligomerization of TMP in conjunction with CumCl. Due to the shortcomings associated with these reactive alkylaluminums, focus was shifted towards the use of the less reactive, sterically encumbered aluminoxane, bis(2,6-di-*t*-butyl-4-methylphenoxy)methylaluminoxane (MAD), as a scrubbing agent. Initial studies on the compatibility of this compound with 1,2-$C_6F_4[B(C_6F_5)_2]_2$ showed that it did not cause decomposition of diborane **1**. 2,6-Di-*t*-butyl-4-methylphenol (BHT), a possible hydrolysis product of MAD was shown to bring about oligomerization of TMP (Figure 37) in conjunction with diborane **1** thereby precluding its use as a scrubbing agent for isobutylene polymerization. These results are not surprising as other neutral boranes such as trispentafluorophenyboron are known to be incompatible with simple scrubbing agents such as TMA and tri-isobutylalmuminum.[188]

### 4.2.2 Polymerization of Isobutylene Initiated by Cationogen/1,2-$C_6F_4[B(C_6F_5)_2]_2$ Systems

Studies were conducted on the solution polymerization of isobutylene in hexane using various cationogens [CumCl, 1-chloro-2,4,4-trimethylpentane (TMPCl), and CumOMe] in conjunction with diborane **1** and DTBMP. The general polymerization procedure used for these studies is as follows. First, monomer and solvent were dried over TOA for ½ hour at – 80 °C followed by vacuum transfer to the reactor, which was

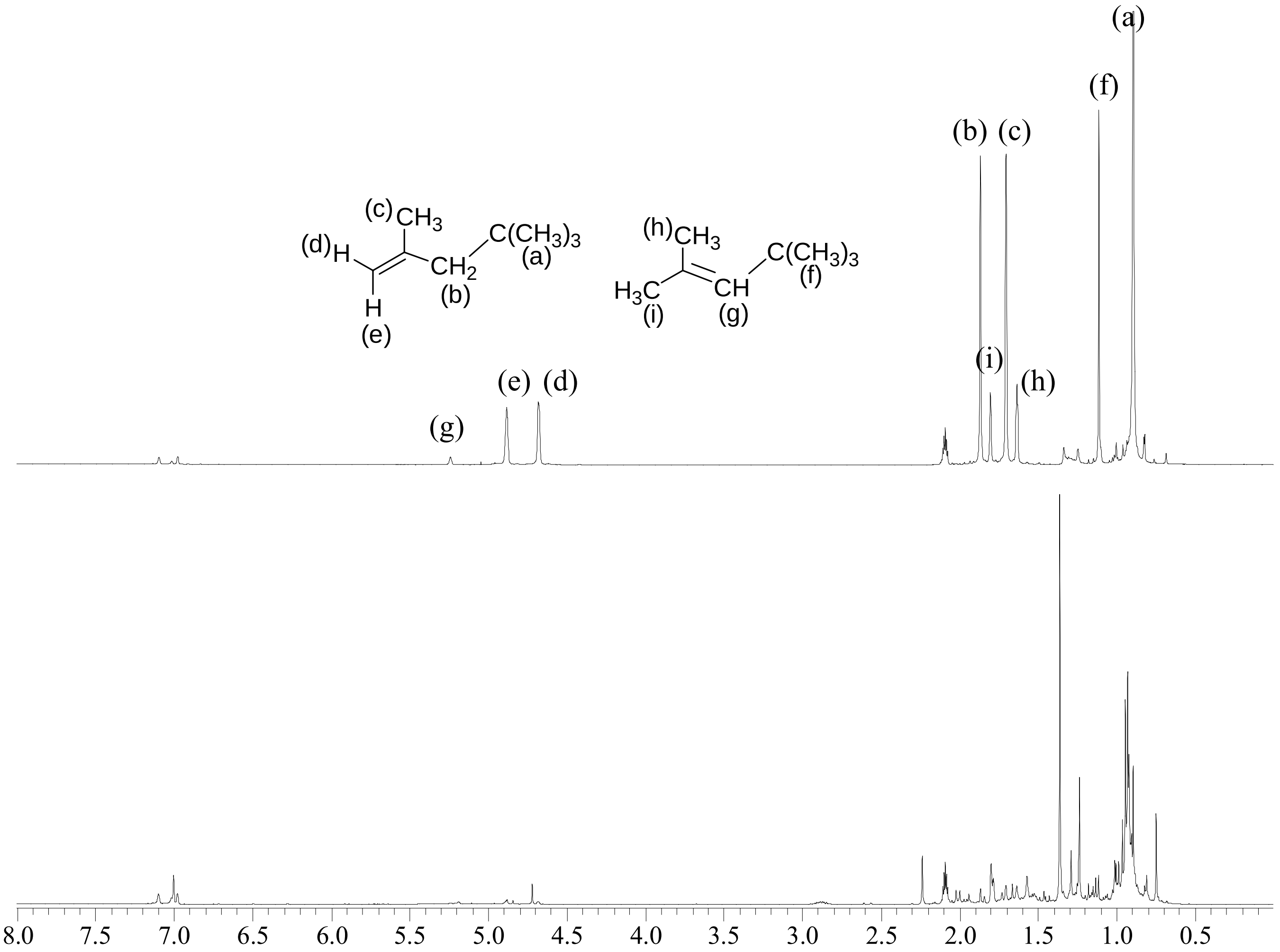


Figure 37. $^1$H NMR (toluene-d$_8$) spectra overlay for TMP/1,2-$C_6F_4[B(C_6F_5)_2]_2$ vs. TMP/1,2-$C_6F_4[B(C_6F_5)_2]_2$/BHT.

then subsequently warmed to the appropriate polymerization temperature and stirred magnetically under $N_2$ (g). Next, the following were injected in the order listed; DTBMP, followed by diborane **1**, and finally cationogen. For all cationogens, with the exception of CumOMe, polymerization ensued immediately and exothermically. With the exception of CumOMe, solidification of the charge occurred within 1 min following the addition of the cationogen at temperatures below – 40 °C. For polymerizations conducted at or above – 40 °C, addition of the cationogen led to large increases in charge viscosity for all systems, excluding those based on CumOMe. All polymerizations were stopped after one hour by quenching with methanol solutions of NaOMe. In order to determine $\Delta E_{\overline{DP}}$ for each initiating system, polymerizations were conducted over a large temperature range (– 80 to – 20 °C) for each of the investigated cationogens.

### 4.2.3 Polymerization of Isobutylene Initiated by the CumCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$ System

The study of the polymerization of isobutylene in hexane as initiated by the CumCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$ system in presence of proton trap was undertaken (Table 25). This resulted in the polymerization of isobutylene to relatively high molecular weights. Attempts at initiating polymerization under similar conditions using the monofunctional borane $B(C_6F_5)_3$ in place of diborane **1** ended in failure (entry 5, Table 25). It should be noted that in all runs the obtained polymer molecular weights were lower than the theoretical value based on the assumption that each molecule of CumCl gives rise to a single polymer chain. Such behavior may be the result of chain transfer due to the non-isothermal nature of these polymerizations as initiator efficiencies are all above 100%.

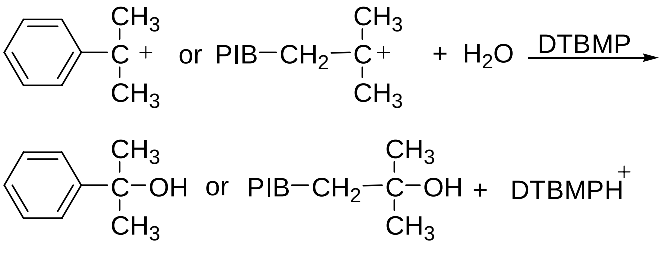
Table 25. IB polymerization in hexane using the $CumCl/1,2\text{-}C_6F_4[B(C_6F_5)_2]_2$ system.[a]

| Entry | Temp. (°C) | $\overline{M}_w$ ($\times 10^3$) | PD | Yield (%) | $I_{eff}$ (%) |
|---|---|---|---|---|---|
| 1 | -90 | 512 | 1.68 | 50.8 | 129 |
| 2 | -90 | 427 | 1.59 | 48.4 | 140 |
| 3 | -80 | 361 | 1.72 | 42.2 | 156 |
| 4 | -80 | 327 | 1.81 | 38.1 | 164 |
| 5[b] | -80 | — | — | — | — |
| 6 | -64 | 267 | 1.61 | 36.3 | 169 |
| 7 | -64 | 212 | 1.68 | 35.5 | 216 |
| 8 | -40 | 155 | 1.61 | 27.2 | 219 |
| 9 | -40 | 132 | 1.59 | 23.1 | 215 |
| 10 | -20 | 99.0 | 1.59 | 15.6 | 194 |
| 11 | -20 | 90.2 | 1.58 | 13.4 | 182 |

a. [diborane **1**] = 2.00 mM, [CumCl] = 0.200 mM, [IB] = 2.76 M, [DTBMP] = 20.0 mM, time = one hour.
b. $[B(C_6F_5)_3]$ = 4.00 mM

Through use of an Arrhenius style plot it was found that for this system $\Delta E_{\overline{DP}} = -1.97$ kcal mol$^{-1}$, implying that molecular weights are controlled by termination.

This finding may indicate that active chains and initiating carbocations are decomposed by DTBMP. These species may also readily undergo irreversible termination with adventitious moisture, as DTBMP readily traps active protons generated by such a process preventing additional polymerization via chain transfer (Equation 38).



Equation 38.

Such a process would led to an overall reduction in the number of active carbocations and in turn may yield a $\Delta E_{\overline{DP}}$ consistent with molecular weight control by termination although initiator efficiencies suggest significant amounts of chain transfer.

As previously mentioned, it was speculated that DTBMP might not be benign towards the cumyl carbocations generated *in situ* and may actively abstract a β proton from this species leading to the formation of α-methylstyrene in addition to generating a polymerization inactive pyridinium ion. Such a process could reduce the number of active chains leading to a $\Delta E_{\overline{DP}}$ consistent with molecular weight control by termination. Polymer yields for these polymerizations were relatively low especially given the long time of reaction. This may be in part due to the fact that chain transfer as mediated by adventitious moisture that could increase yield is prevented by DTBMP and instead leads to termination (Equation 38). Due to the high viscosities of the charges during polymerization, propagation probably becomes mass transfer limited.

In order to determine the validity of these assumptions, several additional experiments were conducted using the CumCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$ system. The first study involved the use of variable-temperature NMR spectroscopy to monitor the effect that DTBMP had on the ion pair formed from the CumCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$ system. This involved the initial reaction of equimolar amounts of CumCl with diborane **1** at – 80 °C in $CD_2Cl_2$ in the presence of a 10 fold excess of DTBMP. $^{19}F$ and $^{1}H$ NMR spectra corresponding to this reaction in the temperature range of – 80 to 30 °C are provided as stack plots in Figures 38 and 39, respectively. From the data provided in Figure 38, it is evident that diborane **1** abstracts $Cl^-$ from CumCl resulting in the formation of the [1,2-$C_6F_4\{B(C_6F_5)_2\}_2$ (μ-Cl)] counteranion as witnessed in previous experiments conducted

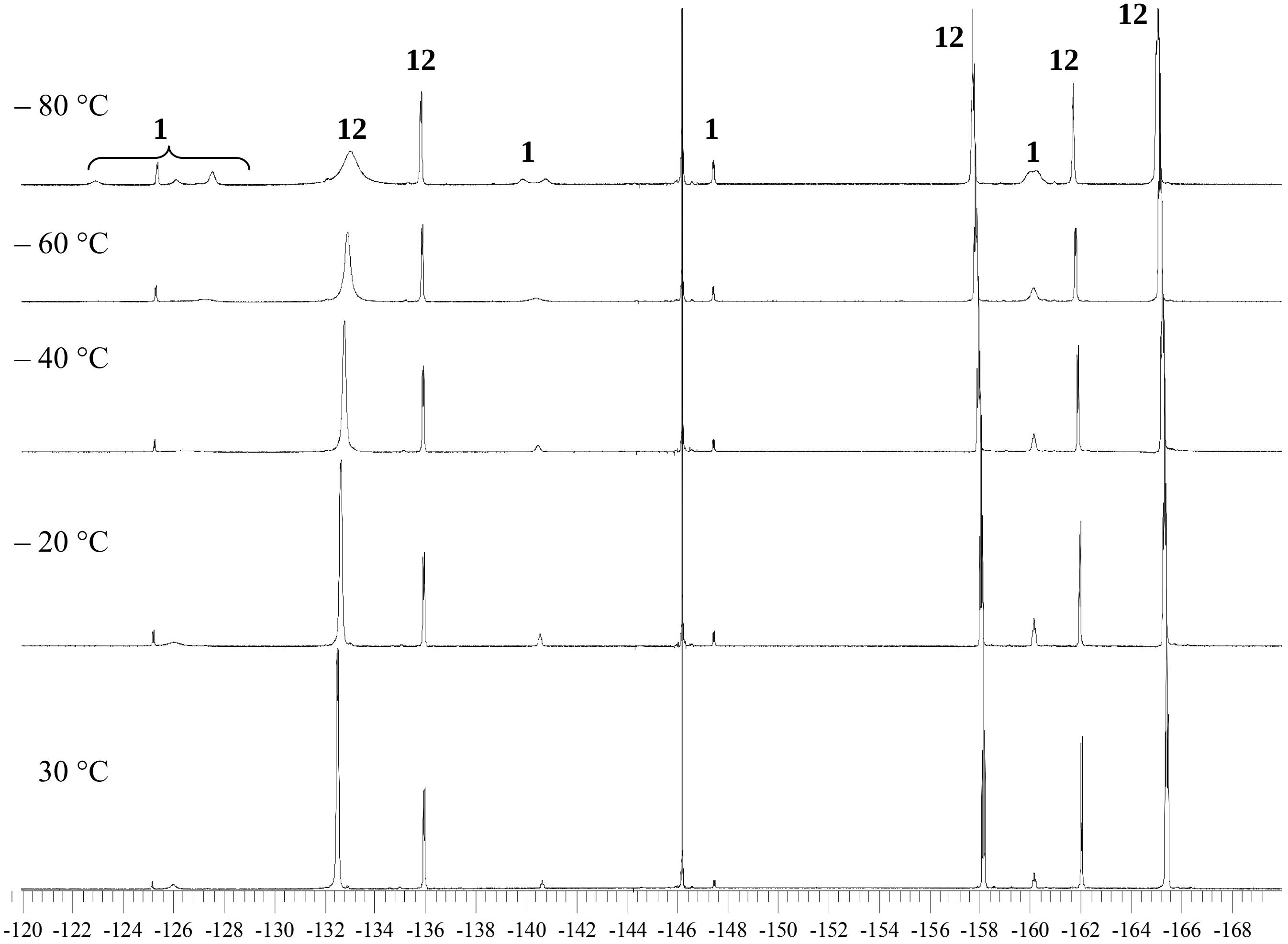


Figure 38. $^{19}$F NMR ($CD_2Cl_2$) spectra overlay for reaction of CumCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$ in the presence of DTBMP.

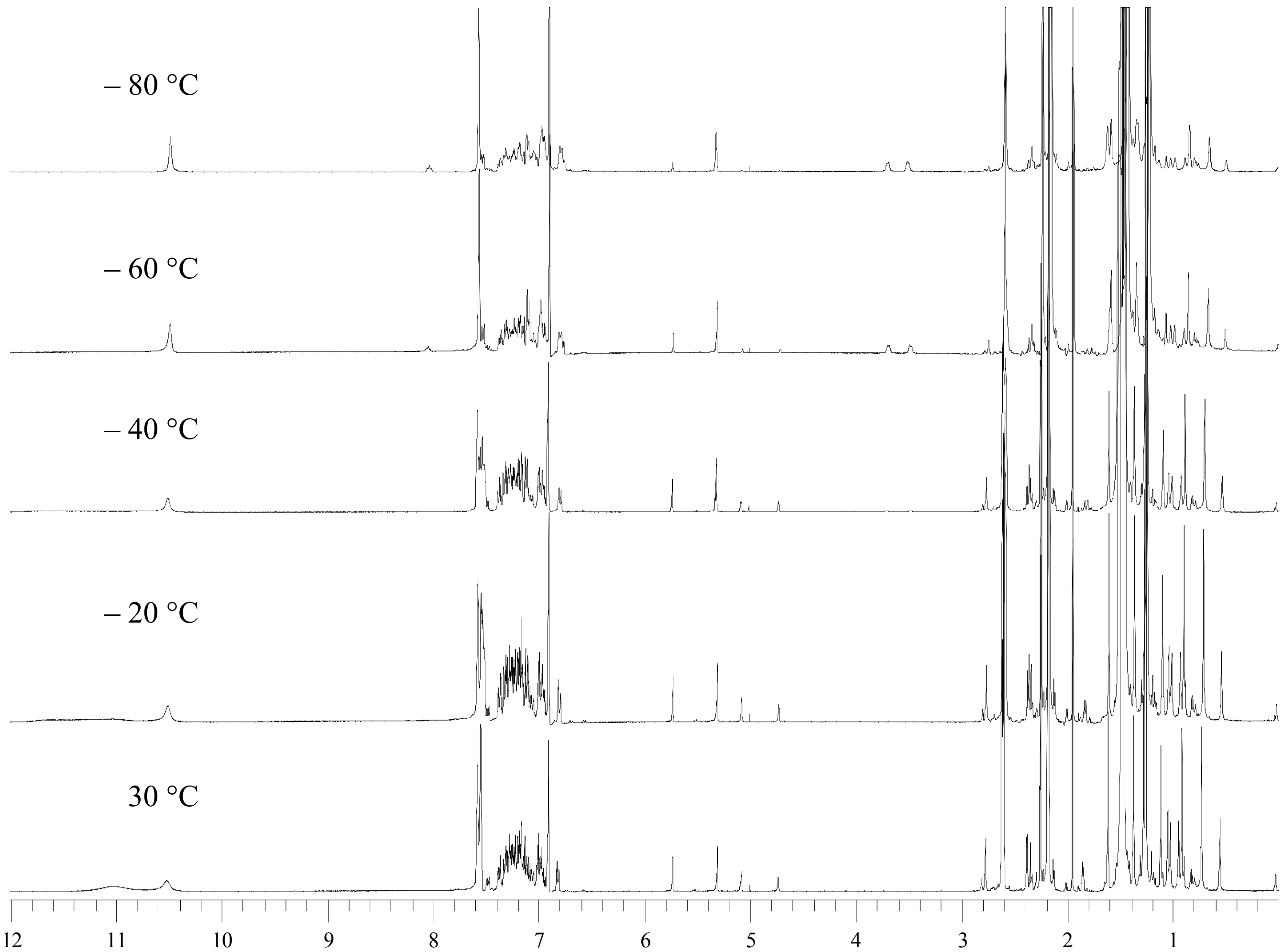
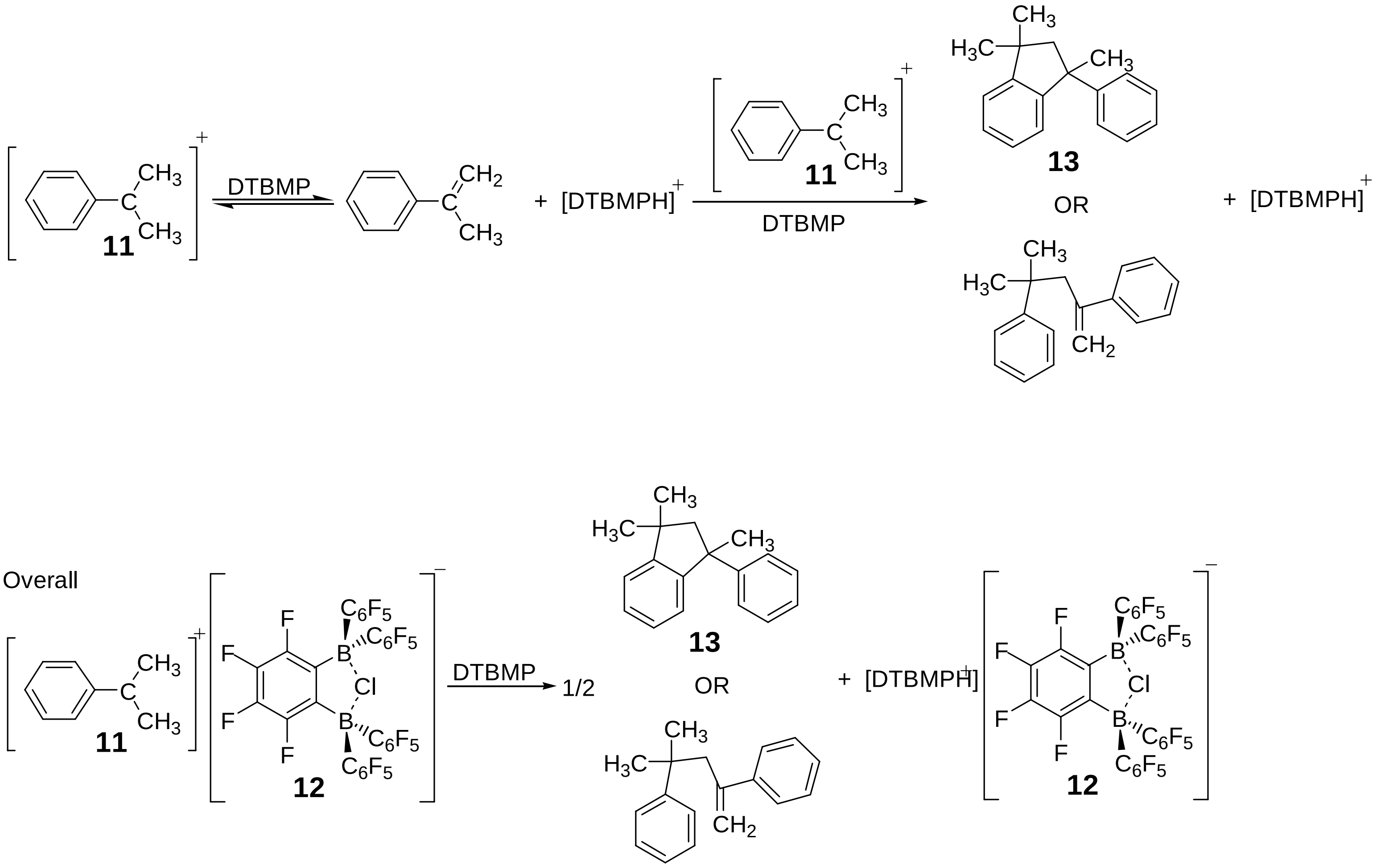


Figure 39. $^{1}$H NMR ($CD_2Cl_2$) spectra overlay for reaction of CumCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$ in the presence of DTBMP.

on the ionization of CumCl by diborane **1** in the absence of DTBMP. Unlike previous experiments conducted in the absence of DTBMP no evidence for the existence of cumyl carbocation was found in the $^{1}$H NMR spectra corresponding to ionization conducted in the presence of proton trap. Instead, the data provided in Figure 39 indicate that the main products from this reaction are the pyridinium ion of DTBMP, α-methylstyrene, 2,4-diphenyl-4-methyl-1-pentene, and 1-phenyl-1,3,3-trimethylindane. It is believed that DTBMP catalyzes the decomposition of cumyl carbocation in a manner summarized in Scheme 40. According to this reaction scheme, DTBMP immediately abstracts a β proton from cumyl carbocation as it is evolved, producing the pyridinium ion of DTBMP and α-methylstyrene. The α-methylstyrene formed by this process can further react with cumyl carbocation to yield an indanyl carbocation or an oligomeric cumyl carbocation both of which subsequently lose a proton to DTBMP to form 1-phenyl-1,3,3-trimethylindane and 2,4-diphenyl-4-methyl-1-pentene, respectively, in addition to protonated DTBMP. Since DTBMP traps the active protons involved in this decomposition process, the $[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2\,(\mu\text{-Cl})]$ counteranion remains intact throughout the course of reaction.

A second set of experiments on isobutylene polymerization as initiated by the $CumCl/1,2\text{-}C_6F_4[B(C_6F_5)_2]_2$ system in the presence of lower levels of DTBMP were conducted to further verify the deleterious effect that this additive has on the outcome of polymerization (Table 26). From these experiments it was found that lowering of the DTBMP concentration led to corresponding increases in yields for polymerization conducted at all temperatures. The use of lower levels of DTBMP resulted in the



Scheme 40. Decomposition of by [Cumyl][1,2-$C_6F_4\{B(C_6F_5)_2\}_2$ (μ-Cl)] DTBMP.

Table 26. Polymerization of IB in hexane using the CumCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$ system with reduced DTBMP.[a]

| Entry | Temp. (°C) | $\overline{M}_w$ (x$10^3$) | PD | Yield (%) | $I_{eff}$ (%) |
|---|---|---|---|---|---|
| 1 | -90 | 243 | 1.77 | 73.0 | 412 |
| 2 | -80 | 236 | 1.74 | 67.4 | 384 |
| 3 | -80 | 222 | 1.70 | 65.2 | 385 |
| 4 | -64 | 206 | 1.76 | 55.6 | 368 |
| 5 | -64 | 151 | 1.75 | 47.6 | 427 |
| 6 | -40 | 136 | 2.09 | 32.6 | 386 |
| 7 | -20 | 103 | 1.83 | 28.9 | 397 |

a. [diborane **1**] = 2.00 mM, [CumCl] = 0.200 mM, [IB] = 2.76 M, [DTBMP] = 2.00 mM, time = one hour.

production of polymers of reduced molecular weight for all temperatures compared to those formed under similar conditions but in the presence of higher levels of DTBMP. The molecular weights of the polymers as produced in this series of experiments were again lower than the theoretical value assuming one polymer chain per molecule of CumCl indicating that high amounts of chain transfer. This is a result of the higher initiator efficiencies obtained in the presence of lower amounts of DTBMP. These results further support the assumption that DTBMP reduces the overall number of active chains by decomposing active carbocations. Use of an Arrhenius style plot for the data corresponding to this set of experiments gave $\Delta E_{\overline{DP}} = -1.32$ kcal mol$^{-1}$, which implies molecular weight control by termination. This finding is similar to that obtained for polymerization by the same system in the presence of high levels of DTBMP and may result from reaction of the growing chain end with adventitious moisture which ultimately results in termination in the presence of proton trap with the formation of an unreactive pyridinium ion.

### 4.2.4 Polymerization of Isobutylene Initiated by the TMPCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$ System

The polymerization of isobutylene in hexane was further explored using the TMPCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$ initiating system in the presence of DTBMP (Table 27).

Table 27. Polymerization of IB in hexane using the TMPCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$ system.[a]

| Entry | Temp. (ºC) | $\overline{M}_w$ ($x10^3$) | PD | Yield (%) | $I_{eff}$ (%) |
|---|---|---|---|---|---|
| 1 | -90 | 325 | 1.58 | 22.9 | 86.0 |
| 2 | -80 | 214 | 1.67 | 35.4 | 214 |
| 3 | -80 | 219 | 1.67 | 34.4 | 203 |
| 4 | -64 | 184 | 1.62 | 26.0 | 177 |
| 5 | -64 | 164 | 1.64 | 24.9 | 194 |
| 6 | -40 | 158 | 1.72 | 23.2 | 194 |
| 7 | -40 | 147 | 1.59 | 20.5 | 171 |
| 8 | -20 | 94.7 | 1.59 | 18.8 | 244 |
| 9 | -20 | 112 | 1.62 | 19.3 | 215 |

a. [diborane **1**] = 2.00 mM, [TMPCl] = 0.200 mM, [IB] = 2.76 M, [DTBMP] = 20.0 mM, time = one hour.

Molecular weights for the polymers produced by this system were found to be lower than those obtained for analogous polymerizations using CumCl. This difference in polymerization behavior may reflect a difference in reactivity of DTBMP with the *t*-butyl carbocation formed from TMPCl in comparison to that for the cumyl carbocation derived from CumCl. Whereas DTBMP was found to catalyze decomposition of initiating carbocations derived from the latter, similar reaction with carbocations derived from the former may not be as favorable. Although ionization of CumCl by diborane **1** should be more facile than ionization of TMPCl due to resonance stabilization present in cumyl carbocation, the initiating efficiency of the latter may be slightly higher because carbocations derived from this cationogen are more stable with respect to reaction with

DTBMP than cumyl carbocation. Molecular weights for polymers as produced by this system were lower than the theoretical value for polymerization conducted at all temperatures; and this may be the result of chain transfer caused by the nonisothermal behavior of these polymerizations. Analysis of the data afforded by this system using an Arrhenius style plot gave $\Delta E_{\overline{DP}} = -1.23$ kcal mol$^{-1}$, which again corresponds to molecular weight control by termination. This fact, coupled with the low yields obtained for these polymerizations, may indicate that termination of the growing chain involves reaction with water in which DTBMP prevents further polymerization by chain transfer from occurring.

### 4.2.5 Polymerization of Isobutylene Initiated by the CumOMe/1,2-$C_6F_4[B(C_6F_5)_2]_2$ System

The polymerization of isobutylene in hexane initiated by the CumOMe/1,2-$C_6F_4[B(C_6F_5)_2]_2$ in conjunction with DTBMP was also investigated (Table 28). A

Table 28. Polymerization of IB using the CumOMe/1,2-$C_6F_4[B(C_6F_5)_2]_2$ system.[a]

| Entry | Solvent | Temp. (°C) | $\overline{M}_w$ (x$10^3$) | PD | Yield (%) | $I_{eff}$ (%) |
|---|---|---|---|---|---|---|
| 1 | hexane | -80 | — | — | — | — |
| 2 | hexane | -20 | — | — | — | — |
| 3 | $CH_2Cl_2$ | -80 | 214 | 1.91 | 1.82 | 12.6 |
| 4 | $CH_2Cl_2$ | -80 | 148 | 1.52 | 2.24 | 17.8 |
| 5[b] | hexane | -80 | — | — | — | — |

a. [diborane **1**] = 2.00 mM, [CumOMe] = 0.200 mM, [IB] = 2.76 M, [DTBMP] = 20.0 mM, time = one hour.
b. Preformed initiator

cursory investigation on the use of this initiating system showed it to be ineffective for the polymerization of isobutylene in hexane. This was believed to be due to the nonpolar nature of the polymerization system preventing ionization of CumOMe by diborane **1** from readily occurring. Therefore, polymerization in dichloromethane under similar conditions was studied. Even in polar media this system was not very effective in initiating polymerization. A final attempt at initiating polymerization with this system was undertaken in which the initiating system was preformed under more concentrated conditions in dichloromethane at – 60 °C before being introduced into the polymerization reactor. Under these conditions this system still failed to initiate polymerization in hydrocarbon. Although it is apparent that it is necessary to use polar solvent in order to induce polymerization by this system the reason for its inefficiency is still unknown. Perhaps active chains are quickly terminated by higher levels of adventitious moisture present in this solvent, as further polymerization by chain transfer is prevented by DTBMP, or possibly $[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2\,(\mu\text{-OMe})]$ anion readily transfers $OMe^-$ to growing polymer chain-ends leading to termination.

### 4.2.6 Polymerization of Isobutylene Initiated by the $H_2O/1,2\text{-}C_6F_4[B(C_6F_5)_2]_2$ System

Protic initiation of isobutylene polymerization arising from adventitious moisture in conjunction with diborane **1** was studied in-depth. Polymerizations as induced by this form of initiation were extremely exothermic and resulted in solidification of the polymerization charge except in cases when very low levels of diborane **1** were used. Protic initiation was found to be highly effective for polymerization of isobutylene in a host of solvents giving rise to quantitative yields of polymer for a wide range of diborane

Table 29. Polymerization of IB using the 1,2-$C_6F_4[B(C_6F_5)_2]_2$ system.[a]

| Entry | Solvent | $\overline{M}_w$ ($x10^3$) | PD | Yield (%) | $I_{eff}$ (%) |
|---|---|---|---|---|---|
| 1 | hexane | 195 | 3.18 | 100 | 5060 |
| 2[b] | hexane | 151 | 2.90 | 100 | 5910 |
| 3[b] | hexane | 172 | 2.60 | 100 | 4790 |
| 4 | $CH_2Cl_2$ | 170 | 3.48 | 100 | 6360 |
| 5[c] | hexane | 132 | 5.68 | 100 | 13300 |
| 6[c] | hexane | 140 | 3.82 | 100 | 8440 |
| 7[d] | hexane | 305 | 1.99 | 97.7 | 2020 |
| 8[d] | hexane | 257 | 2.03 | 100 | 2460 |
| 9[e] | hexane | 483 | 1.90 | 3.02 | 36.8 |
| 10[f] | hexane | 132 | 1.90 | 0.0260 | 1.14 |
| 11[f] | 60 v% hex<br>40 v% $CH_2Cl_2$ | 350 | 1.80 | 0.480 | 7.74 |

a. [diborane **1**] = 2.00 mM, [IB] = 2.76 M, at –78 °C for one hour.
b. [diborane **1**] = 0.480 mM dissolved in 4.50 mL hexane
c. [diborane **1**] = 0.200 mM
d. [diborane **1**] = 0.0200 mM
e. [diborane **1**] = 0.00200 mM
f. $[B(C_6F_5)_3]$ = 4.00 mM

concentrations (Table 29). For example, use of hexane solutions of diborane **1** (entries 2 and 3, Table 29) were just as effective as toluene solutions of diborane **1** (entries 1 and 5-9, Table 29) for polymerization of isobutylene in hexane. Polymerization also occurred readily in the more polar solvent dichloromethane. Polymerization in more polar media did not lead to the production of higher molecular weight polymer. Attempts at initiating polymerization under similar conditions using the monodentate Lewis acid $B(C_6F_5)_3$ in place of diborane **1** led to inefficient polymerization at best (entries 10 and 11, Table 29), thus, diborane **1** derives its high activity as a coinitiator for protically induced polymerization of isobutylene from its chelating ability.

All polymerizations gave rise to polymers with greatly reduced molecular weights compared to the theoretical value ($3.10x10^6$ g mol$^{-1}$) based on the assumption that every molecule of water gives rise to one polymer chain. Due to the high exothermicity of polymerization as conducted in this manner it is believed that chain transfer severely limits molecular weights as this process is favored at higher temperatures. This assumption is supported by the fact that as the magnitude of exothermicity was decreased by using lower levels of diborane **1** (polymerization was noticeably less exothermic at lower [diborane **1**]) molecular weights increased (entries 7-9, Table 29). The proficiency of diborane **1** for coinitiating polymerization is so great that it leads to quantitative polymerization even in the presence of excess water (entries 7 and 8, Table 29).

In an attempt to obtain a better knowledge of the capabilities of this initiating system a series of experiments were conducted to study the effect that [$H_2O$] had on the outcome of polymerization. The results previously obtained for polymerizations conducted at low levels of diborane **1** raised two questions. The first being, if the [$H_2O$] can be decreased will this led to a corresponding increase in polymer molecular weight? Secondly, can diborane **1** readily induce polymerization under less stringent conditions (i.e. unpurified hexanes)?

A series of experiments were conducted using different drying methods to reduce the [$H_2O$]. The first experiment of this type simply involved drying the monomer and solvent over TOA for an extended period of 1 hour (entry 2, Table 30). As can be seen from the data for this experiment, molecular weights are almost double that obtained under similar conditions in which monomer and solvent were dried over TOA from ½ hour (entry 2 vs. entry 1, Table 30). In order to reach very low levels of moisture using this method would require even longer drying periods and therefore the use of small

Table 30. Polymerization of IB using the $1,2\text{-}C_6F_4[B(C_6F_5)_2]_2$ system as a function of $[H_2O]$.[a]

| Entry | TMA (M) | $\overline{M}_w$ ($x10^3$) | PD | Yield (%) |
|---|---|---|---|---|
| 1 | — | 195 | 3.18 | 100 |
| 2[b] | — | 285 | 2.38 | 100 |
| 3[c] | $2.00x10^{-3}$ | 56.0 | 3.47 | 70.2 |
| 4[c] | $2.00x10^{-3}$ | 50.7 | 1.94 | 82.4 |
| 5[c] | $2.00x10^{-5}$ | 217 | 2.72 | 100 |
| 6[c] | $2.00x10^{-5}$ | 179 | 1.91 | 100 |
| 7[d] | — | 255 | 10.4 | 100 |
| 8[d] | — | 160 | 6.00 | 100 |

a. [diborane **1**] = 2.00 mM, [IB] = 2.76 M, at – 78 °C for one hour.
b. Dried over TOA for 1 hour.
c. TMA added to reaction ½ before diborane **1**.
d. Solvent not purified.

amounts of TMA as a scrubbing agent was investigated as an alternative means of reducing the moisture level. In these experiments, polymerization was conducted in the usual manner except that TMA was added to the polymerization reactor 30 min prior to the addition of diborane **1**. Initial experiments using [TMA] = [diborane **1**] led to the production of polymer with lower molecular weights and in lower yields compared to that obtained by similar polymerizations conducted in the absence of TMA (entries 3-4 vs. entry 1, Table 30). Since the [TMA] for these experiments greatly exceeds the known concentration of water ($5x10^{-5}$ M) unreacted TMA most likely decomposes diborane **1** via ligand exchange reactions and these materials give rise to lower molecular weight polymers. Follow-up experiments involving lower levels of TMA were conducted (entries 5 and 6, Table 30). This led to the production of quantitative yields polymers with molecular weights similar to those obtained for polymerization conducted under essentially identical conditions in the absence of TMA.

Several experiments were conducted to determine if polymerization would readily proceed under less stringent conditions (entries 7 and 8, Table 30). This involved polymerization of isobutylene in undried solvent in which the $[H_2O] = 2.5x10^{-3}$ M for the charge. Polymerizations behaved similarly to those conducted under drier conditions giving rise to relatively high molecular weight polymer in quantitative yields. MWDs for the resultant polymers were much broader than those obtained under drier conditions (entries 7 and 8 vs. entry 1, Table 30) and this is possibly the result of high levels of chain transfer occurring in the former due to the higher moisture content.

In order to determine the main molecular weight controlling events for the protically induced polymerization of isobutylene as coinitiated by diborane **1** this system was further studied over a wide range of temperatures (Table 31). An Arrhenius style plot of this data showed $\Delta E_{\overline{DP}} = -2.12$ kcal mol$^{-1}$, which indicates molecular weight control by termination. The molecular weights of the polymers as yielded by this series of experiments are all below the theoretical value ($3.10x10^6$ g mol$^{-1}$) while initiator

Table 31. Polymerization of IB in hexane using the 1,2-$C_6F_4[B(C_6F_5)_2]_2$ system as a function of T.[a]

| Entry | Temp. (ºC) | $\overline{M}_w$ ($x10^3$) | PD | Yield (%) | $I_{eff}$ (%) |
|---|---|---|---|---|---|
| 1 | -90 | 232 | 3.24 | 100 | 4290 |
| 2 | -80 | 195 | 3.18 | 100 | 5010 |
| 3 | -64 | 166 | 2.87 | 100 | 5300 |
| 4 | -40 | 84.5 | 2.25 | 99.4 | 8280 |
| 5 | -40 | 83.7 | 3.75 | 100 | 13700 |
| 6 | -20 | 35.2 | 2.27 | 100 | 19800 |
| 7 | -20 | 32.9 | 2.39 | 100 | 22400 |

a. [diborane **1**] = 2.00 mM, [IB] = 2.76 M, time = one hour.

efficiencies are very high indicating that chain transfer is most likely operating. This is most likely a consequence of the non-isothermal behavior of these polymerizations.

### 4.3 Conclusions on Solution Polymerization of IB Coinitiated by 1,2-$C_6F_4[B(C_6F_5)_2]_2$

Initial attempts at the polymerization of isobutylene using the CumCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$ initiating system in the presence of DTBMP gave highly variable results. From these introductory studies it was soon discovered that protic initiation of isobutylene as coinitiated by diborane **1** was highly effective for the polymerization of isobutylene. Given the high efficacy of diborane **1** as a coinitiator for protically induced polymerization of isobutylene a procedure involving the use of highly purified monomer and solvent was adopted to reduce the background moisture level down to the ppm range. This procedure was shown to consistently yield polymerization charges where $[H_2O] = 5x10^{-5}$ M (2 ppm). Stopping experiments in which [DTBMP] was steadily increased until polymerization ceased to occur showed that a 10-fold excess of proton trap to diborane **1** was still necessary to prevent protic initiation from occurring despite the low levels of moisture.

In an attempt to reduce the background moisture level even further the use of several alkylaluminum compounds (TMA, TOA, MAD) as *in-situ* scrubbing agents was studied. Two of these compounds were found to bring about the decomposition of diborane **1**. TMA and TOA are also incompatible with CumCl leading to the ionization of this material thereby further precluding their use as *in-situ* scrubbing agents. BHT that is a potential hydrolysis product of MAD was also found to act as a protogen for oligomerization of TMP in conjunction with diborane **1**; thus, use of MAD to eliminate moisture actually leads to the production of a new protic source for initiation.

Through use of high purity monomer and solvent in conjunction with DTBMP it was found that the CumCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$ initiating system led to the thermally controlled polymerization of isobutylene in hexane. Attempts at similar polymerization using $B(C_6F_5)_3$ in place of diborane **1** resulted in failure and the higher activity of the latter most likely arises from the chelating ability of this compound. Polymerizations as initiated by this system were exothermic and accompanied by large increases in viscosity often resulting in solidification of the charge. The molecular weights of the polymers produced from this system were lower than the theoretical value for all temperatures investigated. Initiator efficiencies were generally above 100 % implying that chain transfer is occurring; however, analysis of the data for this system using an Arrhenius style plot gave $\Delta E_{\overline{DP}} = -1.97$ kcal mol$^{-1}$, signifying that molecular weights are controlled by termination.

These findings are believed to result from at least two causes. First, DTBMP was believed to bring about decomposition of cumyl carbocation and possibly the propagating polymer chain-end. Second, reaction of reactive carbocations with water was believed to result in termination, as DTBMP would prevent further growth from occurring by chain transfer. Several experiments were conducted which confirm these assumptions. Variable-temperature NMR spectroscopic analysis of the ionization of CumCl by diborane **1** in the presence of DTBMP showed that proton trap readily decomposed cumyl carbocation as it formed. Isobutylene polymerizations as initiated by the

CumCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$ system in the presence of lower levels of DTBMP gave rise to higher yields of polymers with even lower molecular weights due to higher initiator efficiencies. Even at lower levels of DTBMP, Arrhenius plot analysis of the data for this system indicated that termination still controlled molecular weights ($\Delta E_{\overline{DP}} = -1.32$ kcal mol$^{-1}$); thus, DTBMP is not a benign additive in these polymerizations.

The use of additional cationogens (TMPCl, CumOMe) in conjunction with diborane **1** for the polymerization of isobutylene in the presence of DTBMP was also studied. In the case of the former cationogen, polymerization behavior was found to mirror that for similar systems based on CumCl. Initiator efficiencies were high and polymer molecular weights were lower than the theoretical value. A $\Delta E_{\overline{DP}} = -1.23$ kcal mol$^{-1}$ was found for this system indicating molecular weight control by termination. Systems using TMPCl did lead to the production of polymers with lower molecular weights than those produced from systems using CumCl and this may be due to higher stability of initiating cations derived from TMPCl as opposed to those formed from CumCl towards DTBMP. The CumOMe/1,2-$C_6F_4[B(C_6F_5)_2]_2$ system was not very effective as an initiator for the polymerization of isobutylene in the presence of DTBMP. This may be a result of the fact that this system requires polar solvents for ionization and such solvents generally have higher levels of moisture, which in the presence of DTBMP would lead to higher rates of termination. The [1,2-$C_6F_4\{B(C_6F_5)_2\}_2$ (μ-OMe)] anion may also terminate chains by transferring $OMe^-$ to the growing chain-end.

Diborane **1** was shown to be highly effective as a coinitiator for protically induced polymerization of isobutylene under a variety of conditions. $B(C_6F_5)_3$ was very inefficient as a coinitiator for isobutylene polymerization under similar conditions, thus, the unique activity of diborane **1** is most likely due to its chelating ability. Such polymerizations as coinitiated by diborane **1** led to the production of quantitative yields of polymer under a variety of solvent conditions, even in the presence of excess water. Although a $\Delta E_{\overline{DP}} = -2.12$ kcal mol$^{-1}$ was found for this system, molecular weights of these polymers were much less than the theoretical value indicating that chain transfer instead of termination most likely controls the molecular weight. Chain transfer may be caused by the nonisothermal behavior of these polymerizations. Attempts to limit chain transfer by reducing the background moisture level using TMA as a scrubbing agent ended in failure. From these results in addition to those obtained for solution polymerizations using cationogens, it can be concluded that diborane **1** is a highly effective coinitiator for isobutylene polymerization.

## 4.4 Experimental for Conventional Polymerization of IB Coinitiated by $1,2\text{-}C_6F_4[B(C_6F_5)_2]_2$

### 4.4.1 NMR Reaction of TMA,TOA, and MAD with Diborane **1**

To a screw-top, septum-sealed, 5mm NMR tube was added 10.0 mg (0.0120 mmole) of **1** followed 0.400 mL of a solution of 2,3,5,6-tetrafluoro-*p*-xylene in toluene-$d_8$ (35.0 mM). The spectrum of the resulting solution was then recorded to verify the concentration of **1** with respect to TFX standard. Next, 0.100 mL of a solution of TMA in toluene-$d_8$ (60.0 mM) was injected. An identical procedure was used for reaction with TOA and MAD.

### 4.4.2 Reaction of Diborane **1**/TMP with BHT

Inside a glove box 2.00 mL of TMP in toluene-$d_8$ (4.50 M) was added to a vial and premixed with 1.00 mL of diborane **1** in benzene-$d_6$ (12.0 mM). Next, 1.00 mL of BHT in toluene-$d_8$ (12.0 mM) was injected into the quiescent TMP/diborane **1** charge. The charge immediately turned yellow and became exothermic.

### 4.4.3 NMR Reaction of Diborane **1**/CumCl/DTBMP

To a screw-top, septum-sealed, 5mm NMR tube was added 13.0 mg (0.0160 mmole) of **1** followed 0.100 mL of a $CD_2Cl_2$ solution of DTBMP (0.160 M) and 0.500 mL of a solution of 2,3,5,6-tetrafluoro-*p*-xylene in $CD_2Cl_2$ (50.0 mM). The spectrum of the resulting solution was then recorded to verify the concentration of **1** with respect to TFX standard. The sample was subsequently cooled to –80˚C in the spectrometer and initial $^1$H and $^{19}$F NMR spectra were recorded at this temperature. The sample was ejected and immediately immersed in a dry ice acetone bath after which 0.100 mL of a CumCl solution in $CD_2Cl_2$ (0.150 mM) was injected via syringe. The sample tube was then shaken and immersed in the probe at –80˚C where both $^1$H and $^{19}$F NMR spectra were recorded. The probe was warmed in 10˚C increments during which both $^1$H and $^{19}$F NMR spectra were collected.

### 4.4.4 General Polymerization Procedure

Nitrogen gas was purified by passing it first through a column packed with a 50:50 v:v mixture of activated 3 Å molecular sieves and Q-5 catalyst followed by a second column packed with alternating layers of activated 3 Å molecular sieves and Sicapent®. Isobutylene was purified by passing it through a column packed with a mixture composed of 50:50 v:v activated 3 Å molecular sieves and Q5 catalyst. The pre-purified monomer was next condensed into a graduated collection vessel held at –78˚C under a blanket of nitrogen. The collected monomer was then degassed via three sequential freeze-pump-thaw cycles prior to use. A representative procedure for polymerization is given below with initiation using diborane **1** and CumCl:

A 250-mL, round-bottom, 24/40, single-neck flask was charged with 11.4 g (18.0 mL) of pre-dried hexanes, 0.82 g (1.00 mL) of trioctylaluminum, and a magnetic stir bar inside a glove box. This was then fitted with a 24/40 vacuum adapter equipped with a Teflon vacuum stopcock and the apparatus connected to a vacuum line. The mixture of solvent and drying agent was degassed using three freeze-pump-thaw cycles and then charged with 5.50 mL monomer via vacuum transfer.

This solution was then stirred at –78˚C for 30 min before vacuum transferring both monomer and solvent to a second, two-neck, round-bottom flask attached to the vacuum line through another 24/40 vacuum adapter and equipped with a septum inlet. The contents of this flask were then warmed to –78 ˚C and stirred for 15 min under $N_2$ prior to injection of the following solutions listed in order of addition:

1. 1.00 mL of DTBMP stock solution (0.500 M in hexane)
2. 0.970 mL of a stock solution of diborane **1** (52.0 mM in toluene)
3. 0.190 mL of a CumCl stock solution (26.0 mM in hexane).

The charge solidified in 30 s after injection of CumCl and polymerization was allowed to proceed for 1 h at –78˚C under $N_2$ (g) before quenching with 1.00 mL 0.200 M $NaOCH_3$ in methanol. All volatiles were removed and solids were washed with methanol prior to being taken up in hexanes. The resultant polymer solution was filtered, stripped of solvent, and dried in a vacuum oven at 30 in. Hg at 90˚C for 24 hours to yield 1.47g (38.1 %) polyisobutylene with $\overline{M}_w = 3.27\text{x}10^5$ gmol$^{-1}$, $\overline{M}_w / \overline{M}_n = 1.81$.

An identical procedure was followed for polymerizations using other cationogens (TMPCl and CumOMe). Protically-induced polymerizations were also conducted in an analogous manner with the exception that only diborane **1** was injected into the polymerization reactor.