Decomposition of Carbocations Paired with Weakly Nucleophilic Anions by Sterically Hindered Pyridines and Revision of the Complex Counteranion Theory

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Originally Composed in 2005

Preface

Originally I tried to disseminate some of this in my doctoral dissertation but was not permitted as I was told refuting a certain faculty member's theory was verboten. The following is a draft of a paper that I wrote several years ago (following graduation) in an attempt to bring to light my findings that sterically hindered pyridines were capable of decomposing carbocations *as well as necessary revisions to the complex counteranion theory*. Since it contained data from work that I conducted while serving in the capacity of a graduate student at the University of Akron I submitted this to my former doctoral advisor. What resulted was instead my former advisor had his postdoctoral student repeat experiments that I had initially conducted where I discovered that sterically hindered pyridines were capable of abstracting a proton from cumyl carbocation when paired with a weakly coordinating anion. In the end my revisions to the complex counteranion theory were again suppressed for an additional number of years.

This paper (hints of this are in my Ph.D. dissertation) is the first time anyone has successfully explained this behavior and unfortunately due to academic politics the release of this information was delayed by almost 5 years!!! **Moreover, I have a very good idea of how to make a soluble initiator system that is capable of producing isobutylene polymers with MWs mirroring those yielded by γ-radiation in a cost effective manner. Those companies that derive a significant portion of their business from such products might want to take notice of this and contact me (especially since I will eventually disclose the solution to this problem publically in a peer reviewed journal).**

In any event, I have decided to post the draft of this paper for those who are interested. Please note that some of my proposed mechanisms (proposed back in 2005) for decomposition of cumyl carbocation may be off slightly from what was discovered in subsequent NMR studies where my initial work was repeated and then expanded upon. Even so, my initial findings and suggestions as to why this occurs still hold true.

The Effect of Sterically Hindered Pyridines and Counteranion Nucleophilicity on the Polymerization of Isobutylene

Sterically hindered pyridines (SHPs) containing 2,6-di-*t*-butyl substituents have long been recognized as 'non-nucleophilic' bases that only react with protons. SHPs were shown to be unreactive towards Lewis acids[1] and carbocations[2]. Due to their unique properties SHPs have served as valuable additives in carbocationic polymerization. Early on SHPs were shown to thwart chain transfer[3] and prevent protic initiation[4] from occurring in such polymerizations. SHPs have also been shown to impart living characteristics to otherwise nonliving carbocationic polymerizations.[5]

In the carbocationic polymerization field much debate has centered on how SHPs accomplish the transformation of a nonliving system to a living system. During the evolution of the living polymerization of isobutylene (IB) two schools of thought have emerged on how SHPs operate. Early investigators[3] speculated that SHPs act as electron donors that stabilize the growing carbocationic chain-ends. This line of thinking was initially borne from the observation that the presence of SHPs could change the molecular weight (MW) controlling mechanism in the high temperature regime from chain transfer to termination. This was further supported by the fact that other sterically unencumbered electron donors (EDs) {*i.e.* dimethyl sulfoxide (DMSO), dimethyl acetamide (DMA)} could be used in place of SHPs to impart living character to nonliving systems.[6]

As living polymerization systems for IB matured a new theory on the role that SHPs play was developed. Evidence collected from a number of studies indicated that the primary function of SHPs[5] (and other EDs[5a,7]) was the removal of protic impurities. These studies showed that polymerization was living only when the [SHP] or [ED] > [protic impurities]. SHPs were shown to stop both chain transfer and protic initiation from occurring.[5a,b] The [SHP] did not affect the rate of polymerization implying no interaction with the growing carbocationic chain-ends. [5a,b] When substituted for SHPs under otherwise identical conditions, sterically unencumbered EDs (*i.e.* DMSO) gave rise to living polymerizations exhibiting similar polymerization rates and molecular weight dependencies on conversion. [5a,7] It was also found that onium salts of SHPs and other EDs (*i.e.* pyridine) that form by reaction with protic impurities precipitate resulting in efficient removal of such contaminates.[5b,7a,b] SHPs[5a,b] and EDs[7b] were found to be benign towards the growing carbocationic chain-ends with no loss of ω-chloro chain-end functionality.

The inertness of carbocations towards SHPs has been questioned at times. Prior to the advent of living IB polymerization two groups of investigators[8] found that SHPs had a negative impact on polymerizations conducted in polar media (*i.e.* CH_2Cl_2). In both studies the inclusion of a SHP led to reduction of ω-chloro chain-end functionality with concomitant production of polyisobutylene (PIB) bearing *exo*-olefinic end-groups. In one study[8a] Mayo plots indicated that inclusion of a SHP had no effect on chain transfer (absent in either case) but even minute amounts of SHP (*c.a.*, $2.5x10^{-6}$ M) did led to a significant increase in termination (*c.a.*, 25 times higher) while decreasing both molecular weight and conversion. From these findings the general consensus was that SHPs were able to abstract β-protons from the growing carbocationic chain-ends leading to termination and generation of dead PIBs bearing olefinic termini. Interestingly SHPs were believed to be benign towards the initiating cumyl carbocations used in these studies.[8a]

Spectroscopic studies[9] showed that SHPs increase the decomposition rate of carbocations; albeit, to a lesser degree than unencumbered EDs. The actual mechanism for decomposition and the role that SHPs play was not determined. SHPs were also shown to participate in terminative chain transfer when in the presence of small quantities of 2-*t*-butylpyridine.[10] The latter compound forms weak complexes with Lewis acids and is able to abstract β-protons from growing PIB carbocations. The abstracted protons are transferred irreversibly to the SHP resulting in termination and the production of dead PIBs with both *endo*- and *exo*-olefinic chain-ends. Other researchers[11] have demonstrated that SHPs facilitate β-proton elimination from living PIB that has been allowed to age for hundreds of half-lives beyond 98% conversion resulting in the exclusive formation of *exo*-olefinic chain-ends. In this paper we present conclusive evidence that shows under certain circumstances SHPs directly decompose initiating carbocations and can have a deleterious effect on the polymerization of IB.

Another subject that has been the focus of intense study is the effect that counteranion nucleophilicity has on the polymerization of IB. Early investigators[12] turned to Arrhenius style graphical analysis of ($\overline{M}$) data in an attempt to elucidate the mechanism of the process that controls molecular weight. The activation energy of the degree of polymerization ($\Delta E_{\overline{DP}}$) obtained as the slope of a line from a plot of ln($\overline{M}$) versus 1/T was used as a diagnostic for the molecular weight controlling event. Through the combined use of Arrhenius style plots with Mayo plots[13] it was discovered that three main groups of $\Delta E_{\overline{DP}}$ values exist that correspond to different molecular weight controlling mechanisms. $\Delta E_{\overline{DP}}$ values of -6.6 ± 1.0, -4.6 ± 1.0, and -1.8 ± 1.0 kcal mol^{-1} correspond to molecular weight control by chain transfer, chain transfer + termination, and termination respectively.

Support for this classification system comes from several observations. For IB polymerization the activation energies[12c,13] of the key reaction steps decrease as follows: chain transfer (E_{tr} = 6-8 kcal mol^{-1}), termination (E_t = 2-4 kcal mol^{-1}), and propagation (E_p = 0-2 kcal mol^{-1}). The extremities of the $\Delta E_{\overline{DP}}$ range thus correspond to molecular weight control by chain transfer ($E_p - E_{tr}$) and termination ($E_p - E_t$) whereas intermediate values of $\Delta E_{\overline{DP}}$ correspond to a combination of these processes. In addition, $\Delta E_{\overline{DP}} = -6.3 \pm 0.5$ kcal mol^{-1} is obtained for γ–ray initiated polymerization;[14a] because this system purportedly operates in the absence of a counteranion and MW is determined solely by chain transfer.

Since γ–ray initiated polymerization yields ultimate MW PIBs early investigators[14] speculated that counteranions of low nucleophilicity that cannot facilitate chain transfer or lead to irreversible termination are paramount for chemical initiator systems to produce PIBs of similar $\overline{M}$ at a given temperature. $\Delta E_{\overline{DP}}$ for γ–ray initiation should be limiting since chain transfer is least favorable in this case.[14] As a result, $\Delta E_{\overline{DP}}$ has long been used to gauge the ability of a counteranion to participate in chain transfer.

Whether $\Delta E_{\overline{DP}}$ is a sufficient measure of a system's ability to produce high MW polymers at elevated temperatures has been questioned on several occasions. Early on $\Delta E_{\overline{DP}}$ values for a number of chemical initiator systems[12c,14,15] were found to be almost identical to the value for γ–ray initiation although the latter system still yielded ultimate MW PIBs. Recent studies[16] on chemical initiating systems containing weakly coordinating anions (WCAs) have shown that although they give rise to PIBs with MWs approaching those produced by γ–rays the $\Delta E_{\overline{DP}}$ values for most WCA[16a-g] systems correspond to molecular weight control by termination or chain transfer + termination. The present paper will show that $\Delta E_{\overline{DP}}$ alone is not a sufficient diagnostic of a system's propensity to produce high MW polymers at a given temperature and a number of factors in addition to $\Delta E_{\overline{DP}}$ must also be taken into account.

Experimental Section

Unless otherwise noted, all reagents were obtained from commercial sources and purified as required. All synthetic procedures were carried out in glassware previously passivated with dichlorodimethylsilane and were conducted under N_2 using Schlenk techniques or in a glovebox. Hexanes, tetrahydrofuran, and toluene were purified by distillation from potassium and benzophenone under N_2 and stored over activated 4 Å mole sieves. Dichloromethane was purified by passage through activated alumina and Q-5 columns,[17] followed by vacuum transfer from tri(*n*-octyl)aluminum and stored over activated 4 Å mole sieves. α-Methylstyrene was purified by stirring over and distillation from CaH_2 under N_2. Cumyl chloride was prepared using an existing literature method,[18] degassed and stored under nitrogen at –30°C. Cumyl methyl ether was synthesized from cumyl alcohol and methyl iodide using a modified literature method[19] in which potassium hydride was substituted for sodium metal. 2,4,4-trimethyl-1-pentene (TMP) was purified by distillation from CaH_2 and stored over activated 4 Å mole sieves. 2,6-di-t-Butyl-4-methyl-pyridine (DTBMP) was purified by sublimation and a stock solution in dried hexane was stored over activated 4 Å mole sieves prior to use. Tris(pentafluorophenyl)borane was donated by Nova Chemicals and a hexane solution was dried over activated 4 Å mole sieves and filtered prior to recrystallization. 1,2-$C_6F_4[B(C_6F_5)_2]_2$ (**1**) was synthesized using a modified version[20] of the original[21] literature method.

Routine $^1H/^{19}F$ NMR spectra were obtained on either Varian Mercury or Gemini 300 MHz instruments. All ^1H and ^{13}C NMR spectra were referenced with respect to residual protonated solvent and deuterated solvent respectively. ^{19}F NMR spectra were referenced with respect to tetrafluoro-*p*-xylene (TFX: -146.21 CD_2Cl_2). Variable temperature $^1H/^{19}F$ NMR spectra were recorded on a Varian Inova 400 MHz instrument, the thermocouple of which had been calibrated to within 5% of the actual temperature using a methanol standard. The solvent used for variable temperature studies (CD_2Cl_2) was dried by vacuum transfer from P_2O_5 and stored over activated 4 Å mole sieves prior to use. C_6D_6 and toluene-d_8 were dried by distillation from potassium metal and stored over activated 4 Å mole sieves. $CDCl_3$ was dried by vacuum transfer from P_2O_5 and stored over activated 4 Å mole sieves.

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 mole sieves and Q-5 catalyst followed by a second column packed with alternating layers of activated 3 Å mole 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 mole 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. 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 $5x10^{-5}$ M. 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 11.60 g (17.50 mL) pre-dried hexanes, 0.820 g (1.00 mL) tri-octylaluminum, and a magnetic stir bar inside a glove box. This was then fitted with an 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 3.87g (5.50 mL at –78 ˚C) 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 DTBMP stock solution (5.00×10^{-1} M in hexane)
2) 7.66×10^{-1} mL of a stock solution of diborane **1** (6.50×10^{-2} M in toluene)
3) 1.72×10^{-1} mL of a CumCl stock solution (2.90×10^{-2} M in dichloromethane).

Polymerization was allowed to proceed for 1 h at –78°C under N_2 before quenching with 1.00 mL 2.00×10^{-1} 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 a clear solid.

Results and Discussion

Prior to use in polymerization the cumyl chloride (CumCl)/1,2-$C_6F_4[B(C_6F_5)_2]_2$ (**1**) initiator system was studied via ^{1}H and ^{19}F NMR spectroscopy in the presence and absence of the model monomer 2,4,4-trimethyl-1-pentene (TMP).[20a] ^{1}H NMR spectroscopic analysis of stock solutions containing TMP and **1** showed that the Lewis acidity of **1** is sufficient to bring about isomerization of TMP (Figure 1, A) although the system itself was dry enough to prevent oligomerization by protic initiation from occurring. Addition of

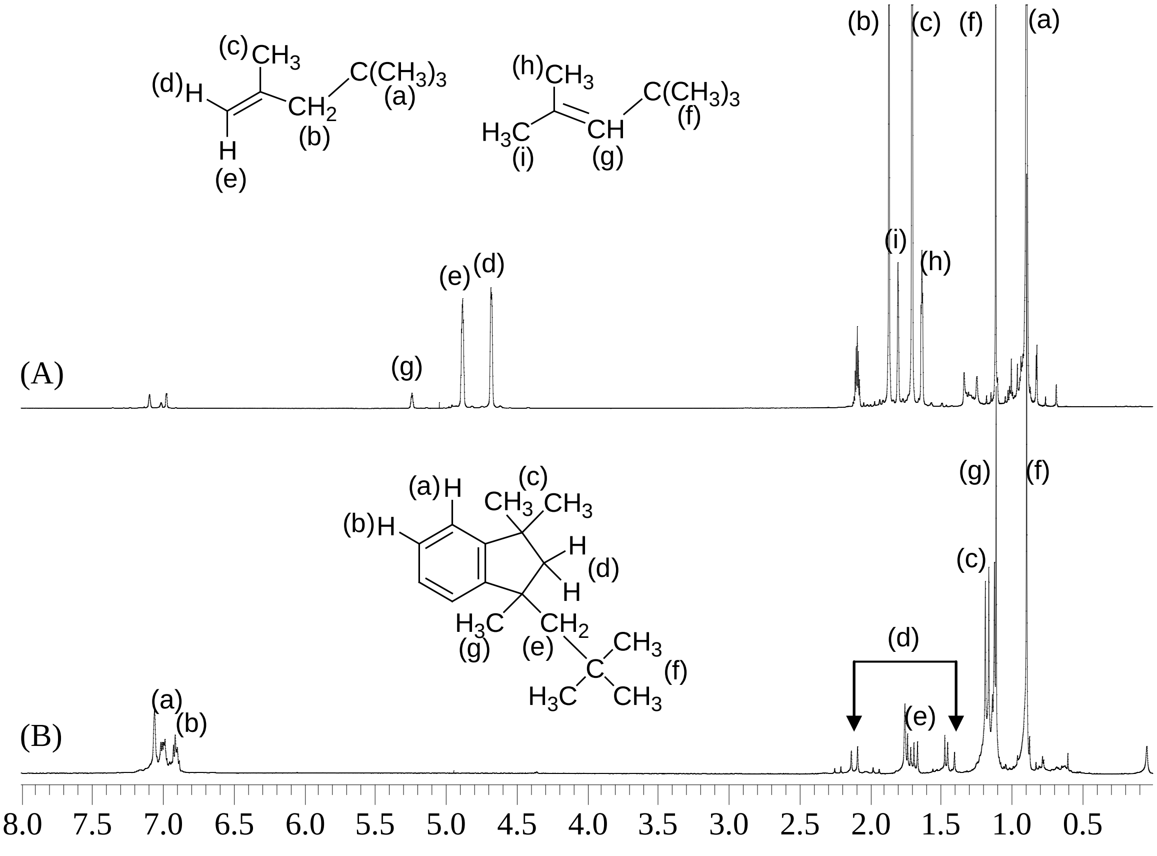
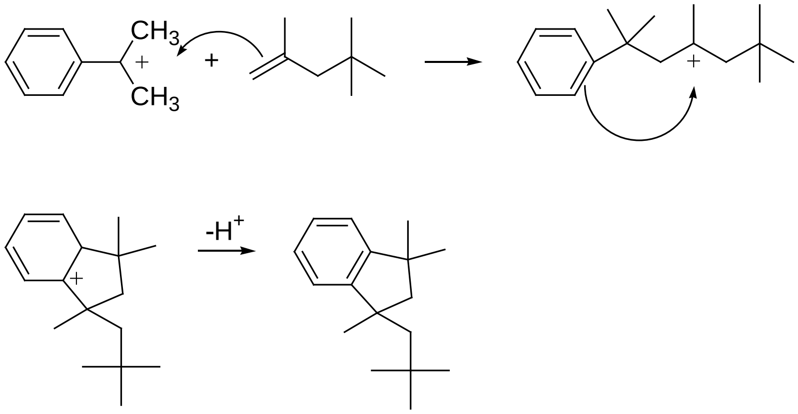


Figure 1. (A) ^{1}H NMR (toluene-d_8) TMP/1,2-$C_6F_4[B(C_6F_5)_2]_2$. (B) ^{1}H NMR (benzene-d_6) TMP/CumCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$.

CumCl to a quiescent stock solution at room temperature resulted in brief reflux with concomitant production of a bright red solution that gradually turned yellow. ^{1}H NMR analysis of the resultant reaction mixture showed that the primary constituent was 1-neopentyl-1,3,3-trimethylindane, the expected product from the reaction of TMP with cumyl carbocation[22] (Scheme 1; Figure 1, B). ^{19}F NMR analysis of the reaction mixture showed the presence of a new species in addition to unreacted **1** (Figure 2, A). This new species possessed 5 sharp, symmetrical ^{19}F signals in a pattern



Scheme 1

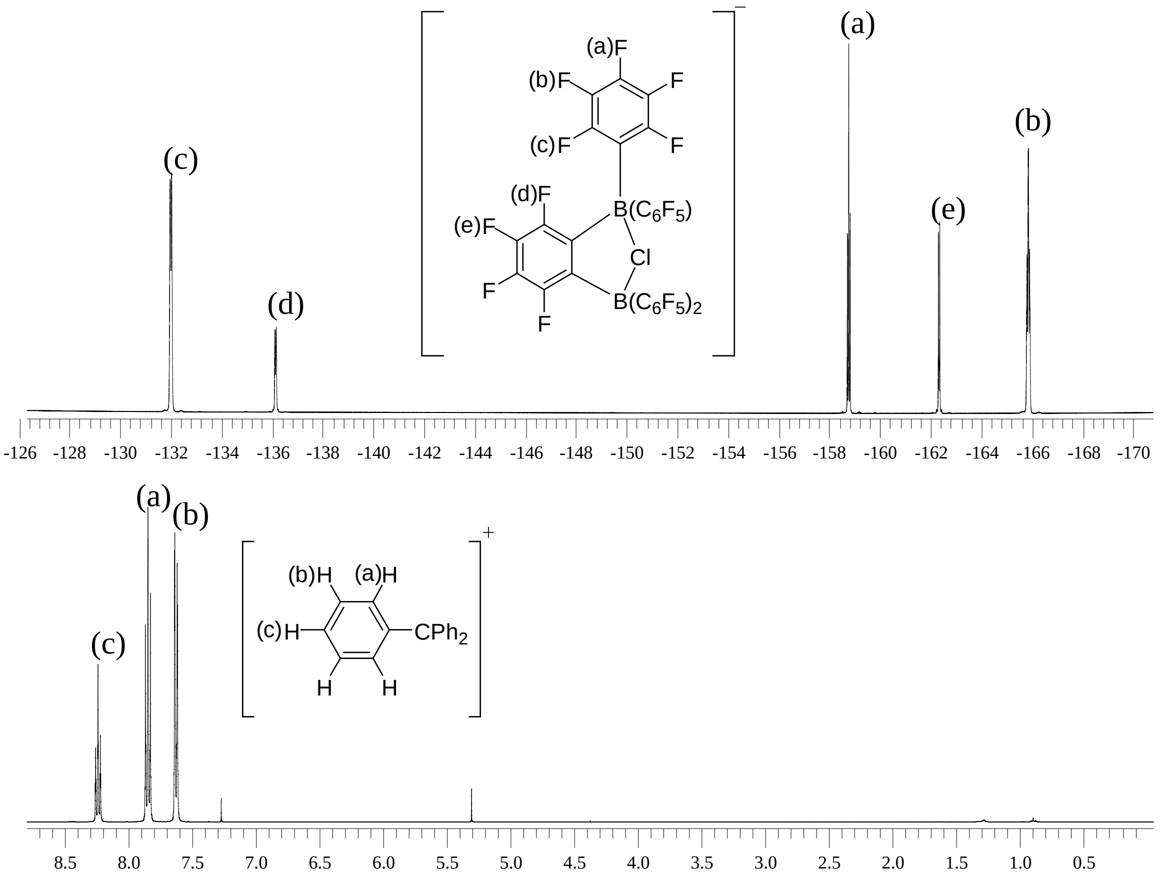
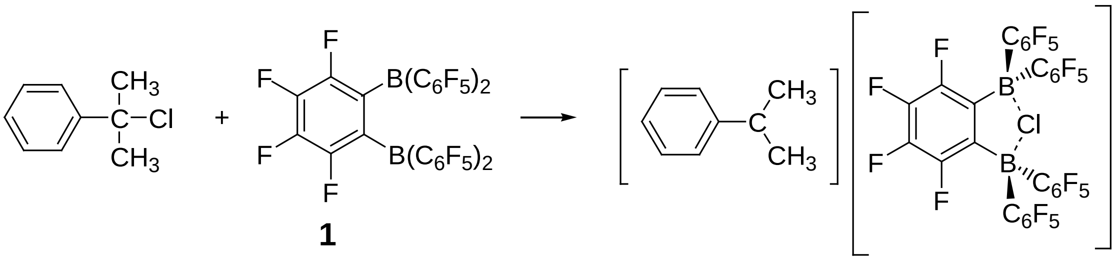


Figure 2. (A) ^{1}H and (B) ^{19}F NMR ($CDCl_3$) spectra overlay for $[Ph_3C][1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2(\mu\text{-}Cl)]$.

reminiscent to spectra for the previously described[21,23] C_{2v} symmetric anions $[1,2\text{-}C_6F_4[B(C_6F_5)_2]_2(\mu\text{-}F)]^-$ and $[1,2\text{-}C_6F_4[B(C_6F_5)_2]_2(\mu\text{-}OCH_3)]^-$. These findings suggested that reaction of CumCl with **1** results in the formation of the $[\text{cumyl}]^+[1,2\text{-}C_6F_4[B(C_6F_5)_2]_2(\mu\text{-}Cl)]^-$ (**2**) ion pair that acts as an efficient initiator for cationic polymerization (Scheme 2).

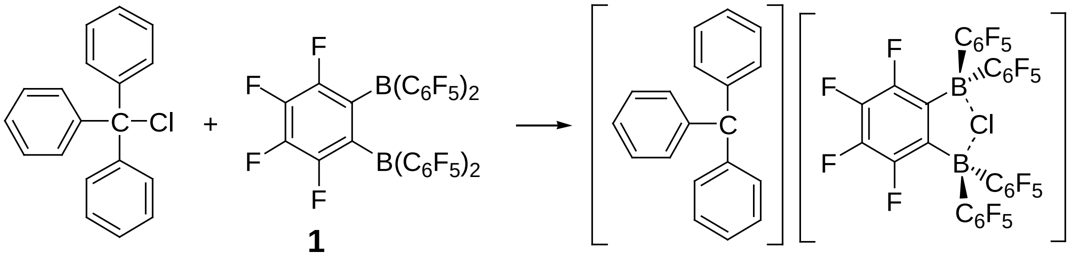


1

2

Scheme 2

The synthesis of a thermally stable model ion pair $[Ph_3C]^+[1,2\text{-}C_6F_4[B(C_6F_5)_2]_2(\mu\text{-}Cl)]^-$ (**3**) was conducted to verify the structure of the anion in **2**.[20] This was accomplished by reacting equimolar amounts of **1** and trityl chloride together in dichloromethane resulting in the production of quantitative yields of **3** (Scheme 3). The structure of **3** was confirmed by ^{1}H NMR (consistent with triphenylmethyl carbocation) and ^{19}F NMR (five sharp, symmetrical signals indicative of C_{2v} symmetry with the *p*-fluorine resonance shifted upfield relative to the *m*-fluorine signal for the C_6F_5 rings signifying conversion of the neutral borane centers to partially anionic centers[24] {Figure 2, B}). ^{11}B NMR spectroscopy showed the presence of a single broad peak at 7.15 ppm, well within the 0-9 ppm region typical for four-coordinate boron centers with a –0.5 formal charge. Through the use of $^{13}C\{^{1}H\}$ and $^{19}F\text{-}^{13}C\{^{19}F\}$ HETCOR (Figure 3) it was possible to make assignments for every ^{13}C resonance of **3**. The solid state structure of **3** as determined by x-ray diffraction[20] confirmed the structural assignments made in solution where Cl^- is bound to both borane centers of **1** to form a puckered 5-membered ring. Comparison of the ^{19}F NMR spectrum for **3** (Figure 2, B) with the ^{19}F NMR spectrum for the model polymerization (Figure 2, A) verified that reaction of CumCl with **1** does indeed generate the $[1,2\text{-}C_6F_4[B(C_6F_5)_2]_2(\mu\text{-}Cl)]^-$ counteranion. Subsequent VT ^{1}H and ^{19}F NMR experiments[20] gave direct evidence that reaction of equimolar amounts of CumCl with **1** in CD_2Cl_2 gives rise to **2** as a stable species in quantitative yields at –80 °C.



1

3

Scheme 3

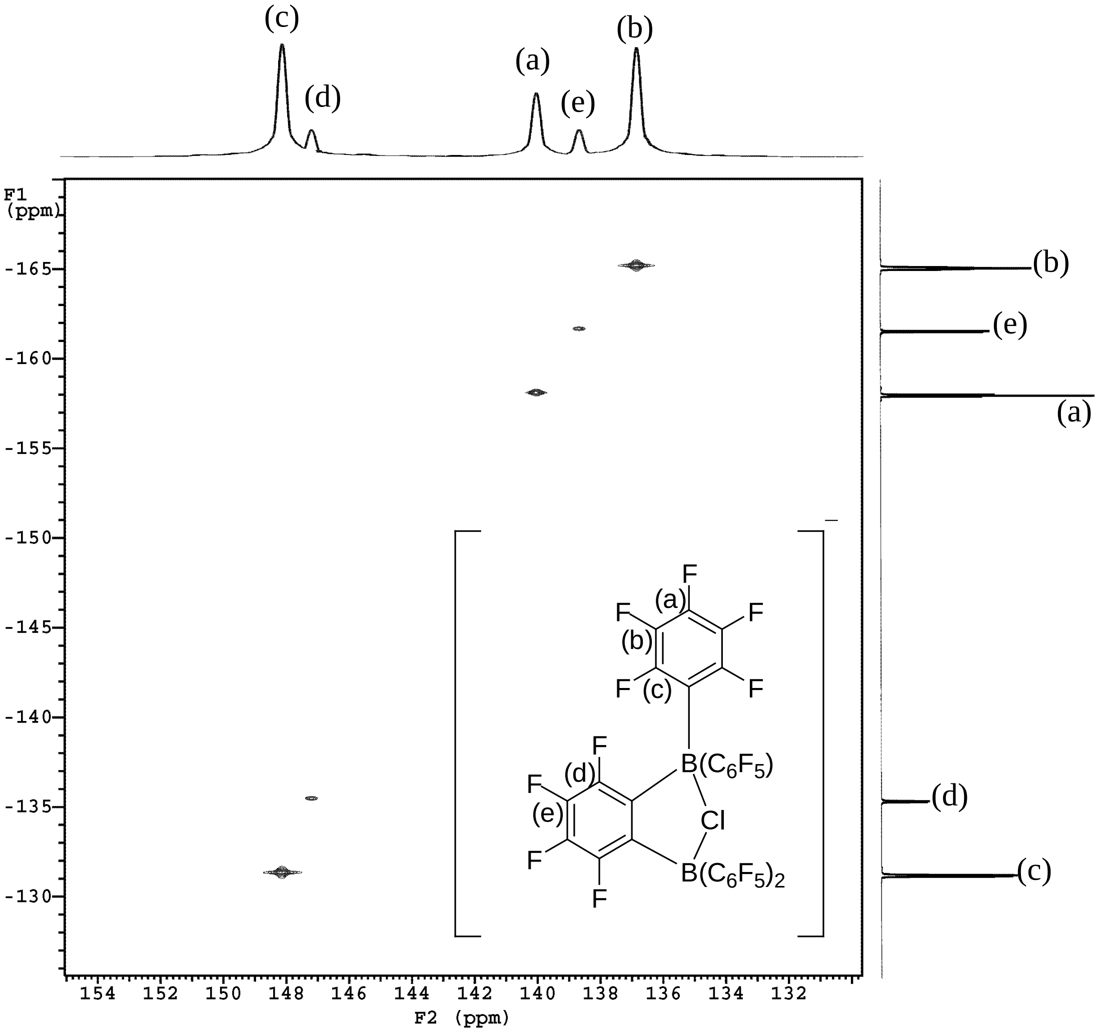


Figure 3. ${}^{19}F$-${}^{13}C\{{}^{19}F\}$ HETCOR NMR ($CDCl_3$) spectrum for $[Ph_3C][1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2(\mu\text{-}Cl)]$.

Despite the rigorous purification procedure employed, **1** was found to be a highly effective Lewis acid for the polymerization of IB in conjunction with the low levels (c.a., 5×10^{-5} M) of adventitious moisture present (Table 1). All polymerizations were exothermic and gave rise to quantitative yields of PIB with the exception of those involving very low [**1**]. The efficacy of **1** for the polymerization of IB is demonstrated by the fact that quantitative yields are obtained even in the presence of excess water (entries 7 and 8). Polymerization was believed to be initiated by direct protonation of monomer by the aqua adduct of **1**, $H_2O\cdot1,2\text{-}C_6F_4[B(C_6F_5)_2]_2$ (**4**), which functions as a strong Brönsted acid (Scheme 4). The use of **4** as an initiator for IB was later adapted for polymerization under aqueous reaction conditions[25] and its existence was subsequently demonstrated by other researchers.[26] From experiments involving the use of the monodentate perfluoroaryl borane $B(C_6F_5)_3$ conducted under otherwise identical conditions (entries 10 and 11) it is apparent that the activity of **1** is due to its ability to chelate substrates.

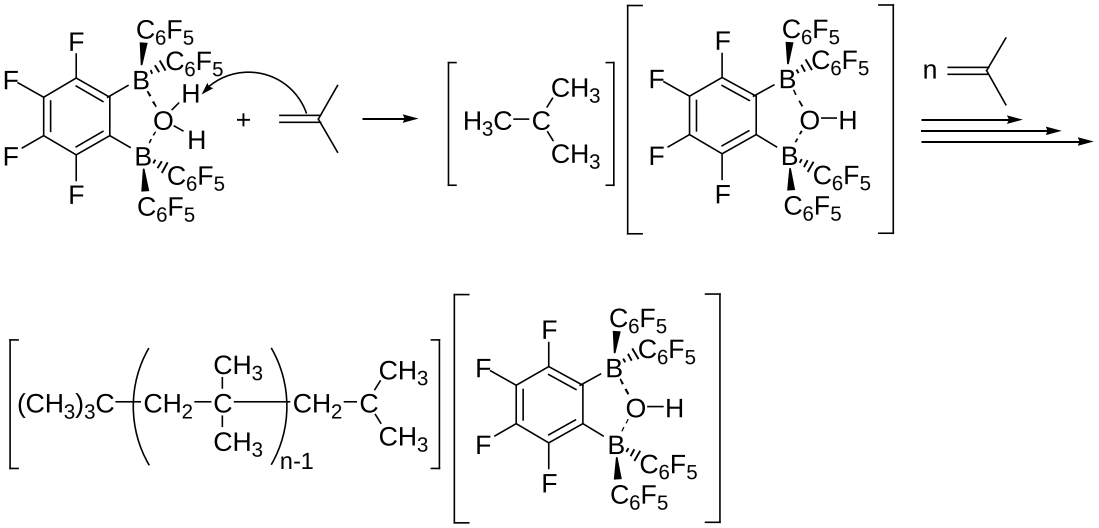
Table 1. Polymerization of IB using the $H_2O/1,2\text{-}C_6F_4[B(C_6F_5)_2]_2$ system.[a]

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 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

High I_{eff} values were obtained for every experiment and polymer molecular weights were lower than the theoretical value ($\overline{M}_n$ = $3.10\text{x}10^6$ g mol^{-1}) based on the $[H_2O]$ (*i.e.* each molecule of water gives rise to one polymer chain). This behavior is probably the result of chain transfer.

The polymerization of IB in hexane as initiated by adventitious moisture in conjunction with **1** was studied over a wide range of temperatures to determine the identity of the molecular weight controlling process (Table 2). An Arrhenius style plot of



Scheme 4

Table 2. Polymerization of IB in hexane using the H_2O/1,2-$C_6F_4[B(C_6F_5)_2]_2$ system as a function of temperature.[a]

Entry	Temp. (°C)	$\overline{M}_w$ ($x10^3$)	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.

this data yielded $\Delta E_{\overline{DP}}$ = –2.12 kcal mol^{-1} indicative of molecular weight control by termination. This is in agreement with values of $\Delta E_{\overline{DP}}$ obtained for a number of IB polymerizations conducted in the presence of WCAs[16a-g] where molecular weight control was either by termination or by chain transfer + termination. As was witnessed in the previous experiments conducted at –80 °C (Table 1), the values for I_{eff} were high in every run and increased with a concomitant decrease in polymer MW as the polymerization temperature was raised (Table 2). This may be due to chain transfer, which is intensified by the nonisothermal nature of these polymerizations.

As protic initiation proved difficult to control the use of carbocation precursors in combination with **1** was explored for the well-behaved polymerization of IB. Given the propensity of **1** for inducing protic initiation it was recognized that either all traces of moisture had to be removed or polymerization must be conducted in the presence of an additive that prevents protic initiation. Attempts at using alkylaluminums (*i.e.* trimethylaluminum) as *in situ* scrubbing agents for the removal of adventitious moisture were abandoned due to their incompatibility with **1**.[20a] It was therefore decided that polymerizations would be conducted in the presence of the SHP, DTBMP. A number of stopping experiments were conducted where the [DTBMP] was incrementally increased each run until polymerization did not occur (Table 3). From this it was determined that a 10-fold excess of DTBMP to **1** was required to thwart protic initiation.

Table 3. Stopping experiments in hexane.[a]

Entry	DTBMP (M)	$\overline{M}_w$ ($x10^3$)	PD	Yield (%)
1	$2x10^{-3}$	302	2.48	5.76
2	$5x10^{-3}$	552	3.61	1.44
3	$1x10^{-2}$	163	3.97	0.499
4	$1.5x10^{-2}$	753	4.89	0.473
5	$2x10^{-2}$	—	—	0

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

Cumyl chloride (CumCl) was selected as the first carbocation precursor to be used in conjunction with **1** in the presence of DTBMP (Table 4). This system had several characteristics similar to polymerizations initiated by adventitious moisture. First, all polymerizations were exothermic and Arrhenius style graphical analysis of the data yielded $\Delta E_{\overline{DP}}$ = –1.97 kcal mol^{-1} suggesting molecular weight control by termination. Second, all polymer MWs were lower than the theoretical value based on the [CumCl] ($\overline{M}_n$ = 7.74x10^6 g mol^{-1}) resulting in values of I_{eff} > 100%. Third, use of the monodentate perfluoroaryl borane $B(C_6F_5)_3$ in place of **1** under similar conditions did not lead to polymerization. In contrast, yields obtained from the CumCl/**1**/DTBMP system were drastically reduced in comparison to those obtained in polymerization initiated by adventitious moisture. ^{1}H NMR analysis of PIBs afforded by the CumCl/**1**/DTBMP system showed the presence of signals attributable to *exo*-olefinic end groups and no signals characteristic of *endo*-olefinic end groups (Figure 4). The substitution of 2,4,4-trimethyl-2chloropentane (TMPCl) in place of CumCl under otherwise identical conditions (Table 5) resulted in polymerization behavior similar to that witnessed for the

Table 4. Polymerization of IB in hexane using the CumCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$ system as a function of temperature.[a]

Entry	Temp. (°C)	$\overline{M}_w$ (x10^3)	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

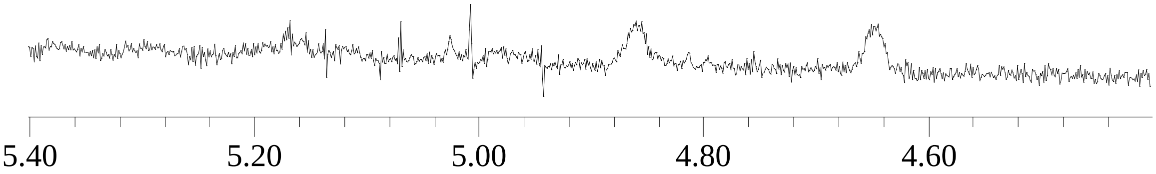


Figure 4. 1H NMR spectrum of PIB afforded by the CumCl/**1**/DTBMP system.

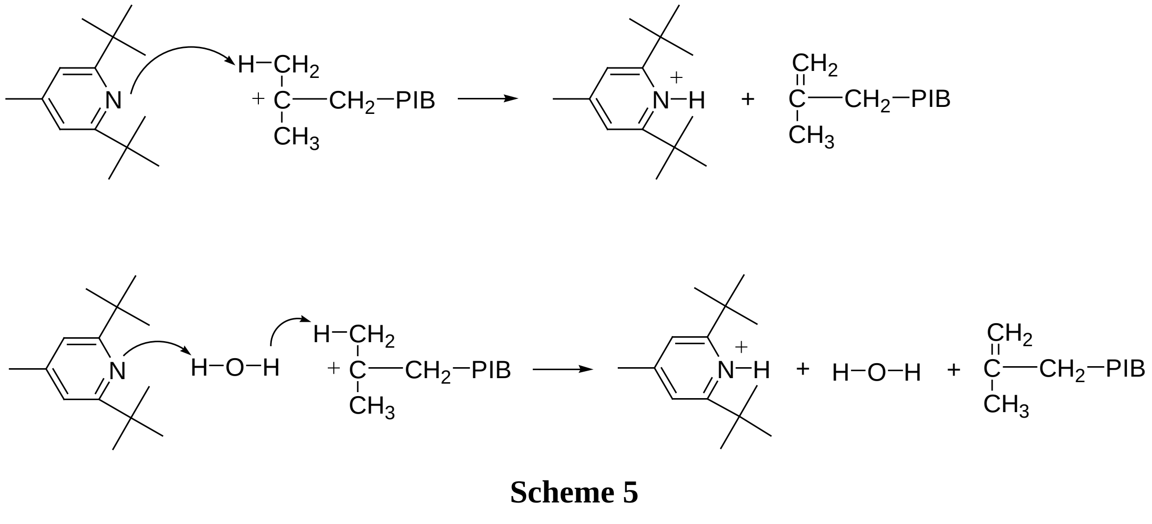
Table 5. Polymerization of IB in hexane using the TMPCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$ system as a function of temperature.[a]

Entry	Temp. (°C)	$\overline{M}_w$ (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.

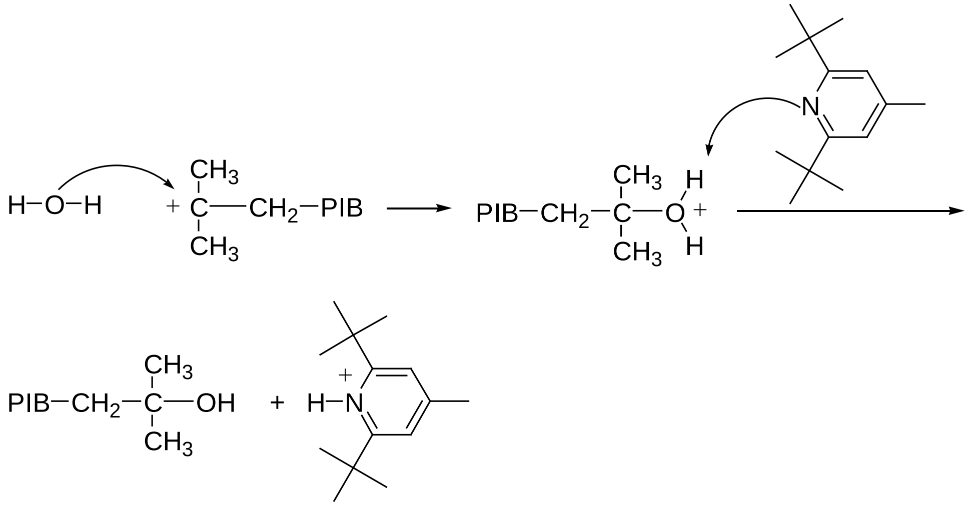
CumCl/**1**/DTBMP system (i.e. $\Delta E_{\overline{DP}}$ = –1.23 kcal mol^{-1}, reduced yields, Ieff > 100%). These findings were difficult to explain initially and it was believed that DTBMP might cause this behavior.

First, DTBMP could bring about a process known as terminative chain transfer. This process leads to the production of dead polymer and a species incapable of reinitiating polymerization and is equivalent to termination. Such a process would lower both yield and molecular weight resulting in values of $I_{eff} > 100\%$. This could occur by abstraction of a β-H^+ from the carbocationic chain-end of growing polymer by DTBMP to generate dead PIB bearing an *exo*-olefinic end group and a pyridinium ion incapable of initiating further polymerization (Scheme 5). DTBMP might directly abstract the β-H^+ or adventitious moisture might aid the process. Most chemical initiator systems give rise to PIBs with a mixture of *exo*- and *endo*-olefinic groups[27] and the exclusive formation of PIBs bearing *exo*-olefinic termini is unique to



Scheme 5

only a few systems.[28] It would appear that the presence of a sterically hindered base (which may also be the counteranion[28]) is necessary to limit β-H^+ abstraction to the methyl protons of the propagating carbocation. Terminative chain transfer could also involve initial reaction of adventitious moisture with the growing carbocation to yield an oxonium ion that is deprotonated by DTBMP to yield dead PIB bearing a hydroxylic end group and a pyridinium ion incapable of initiating further polymerization (Scheme 6). This mechanism is possible as the [H_2O] present in the system is ~ ¼ the [CumCl]; however, it cannot by itself account for the drastic reductions in yield (*c.a.*, 60%) witnessed in these polymerizations.



Scheme 6

Second, DTBMP might decompose initiating cumyl carbocations. A VT ^1H and ^{19}F NMR experiment was conducted in an attempt to determine whether DTBMP could react with cumyl carbocation of **2** as generated from **1** and CumCl. This involved the addition of 1 equivalent CumCl to an NMR tube containing a mixture of 1 equivalent **1** and 2 equivalents DTBMP cooled to –80 °C. The reaction mixture was then gradually warmed to room temperature and spectra were collected at increments of 10 °C. In contrast to previous experiments involving reaction of equimolar amounts of **1** and CumCl that produced **2** as a stable species at –80 °C in quantitative yields[20] the inclusion of DTBMP resulted in immediate and complete decomposition of cumyl carbocation as **2** was generated (Figure 5).

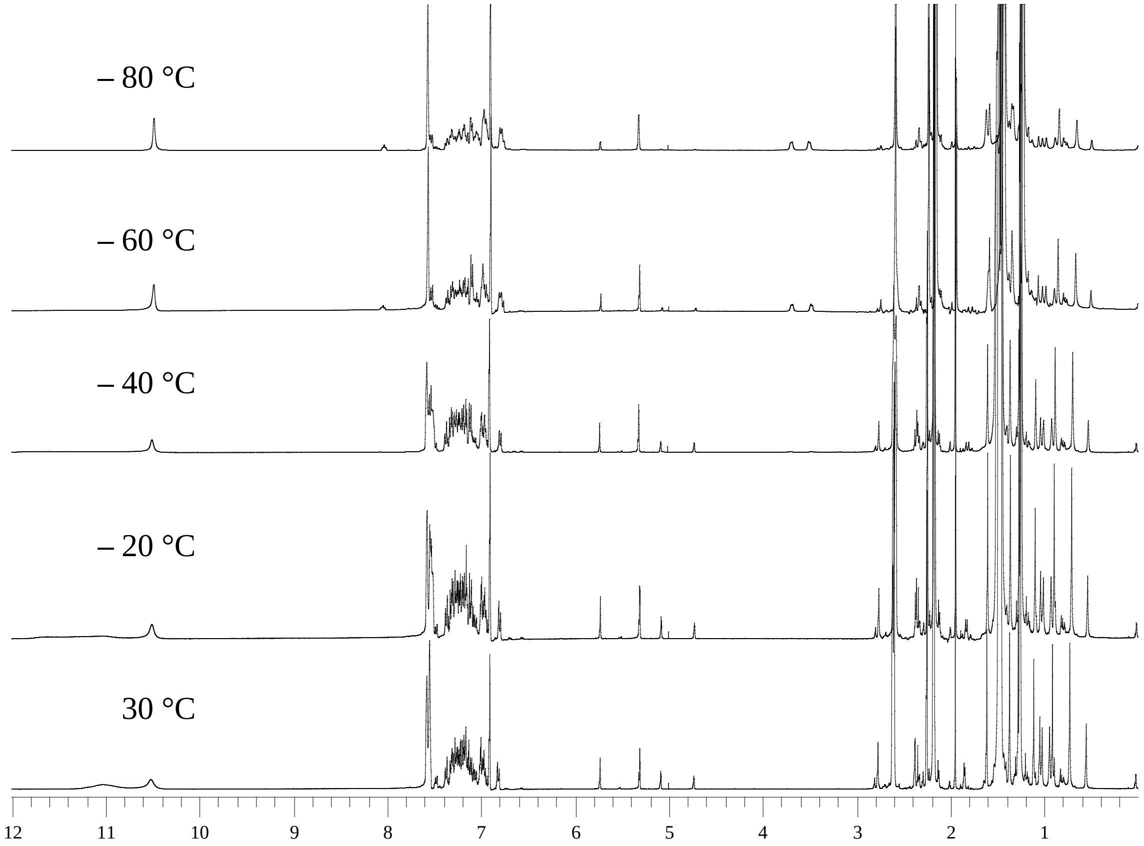
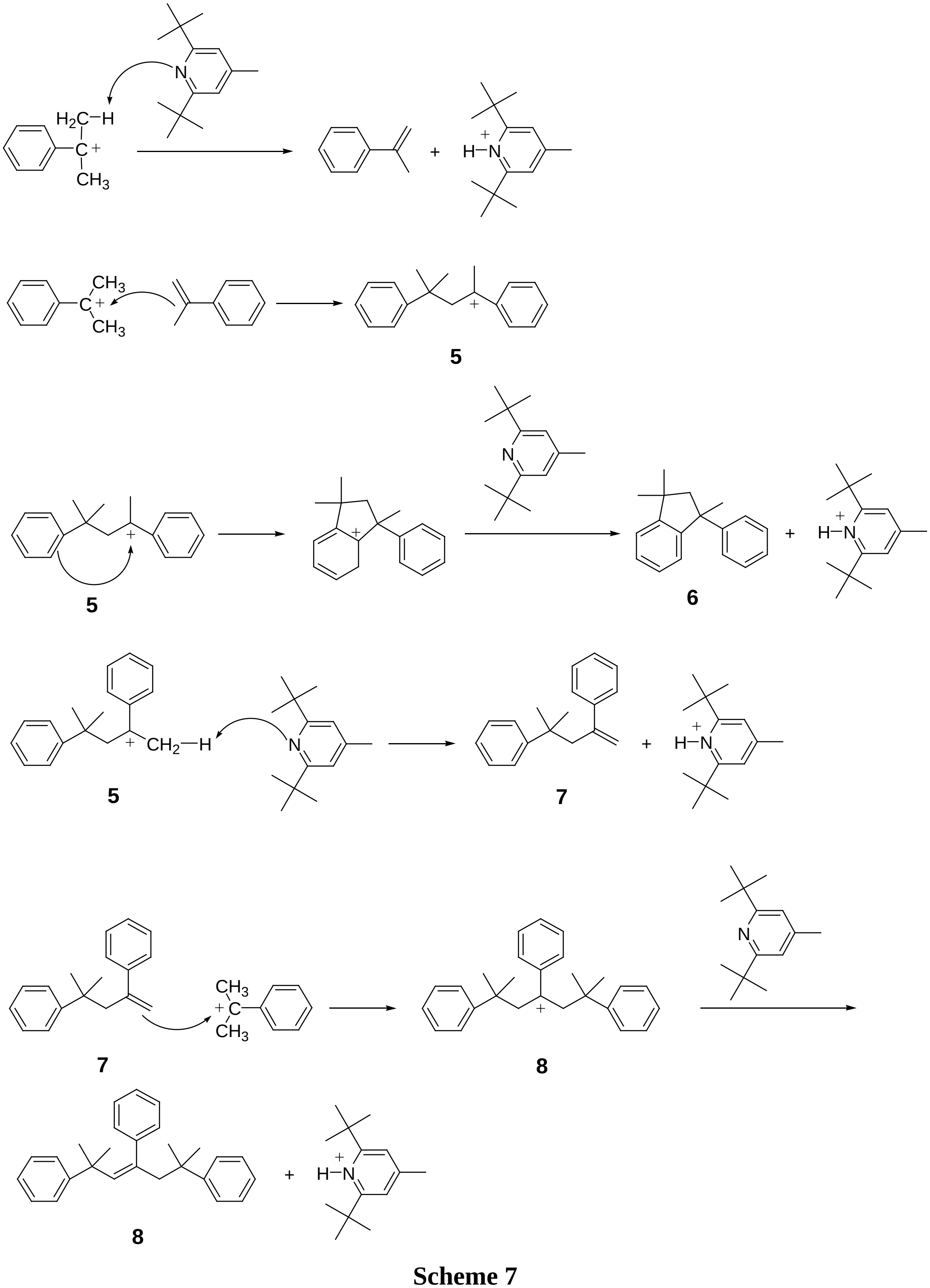
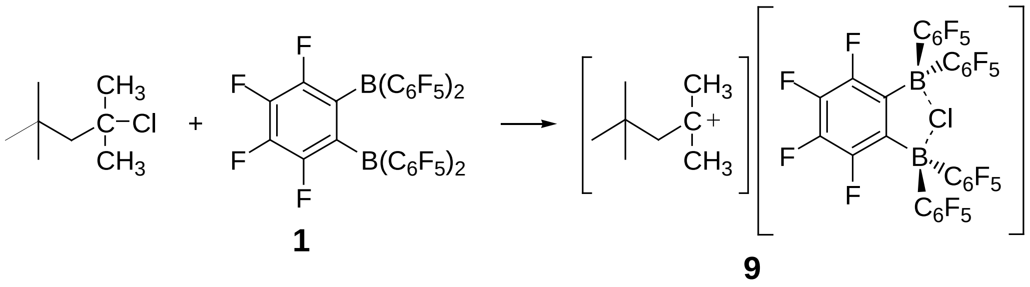


Figure 5. ^{1}H NMR (toluene-d_8) DTBMP/CumCl/1,2-$C_6F_4[B(C_6F_5)_2]_2$.

The key steps in this process are outlined in Scheme 7. DTBMP initially abstracts a β-H^+ from cumyl$^+$ of **2** to generate [DTBMPH]$^+$ [1,2-$C_6F_4\{B(C_6F_5)_2\}_2$ (μ-Cl)]$^-$ and α-methylstyrene. As α-methylstyrene is generated it immediately reacts with additional cumyl$^+$ to form the dimeric cation **5**. Some of the dimeric cation **5** undergoes internal alkylation to form indan **6** with loss of H^+ that is trapped by DTBMP. DTBMP abstracts a β-H^+ from the remaining **5** as it is generated to form alkene **7**. Alkene **7** then undergoes immediate reaction with cumyl$^+$ to form the trimeric cation **8**. Generation of trimeric cation **8** is steady until all the cumyl$^+$ of **2** has been consumed by DTBMP. Trimeric cation **8** then undergoes decomposition to form alkene **9** by loss of a β-H^+, which may be spontaneous or involve abstraction by DTBMP. This process is essentially complete once the reaction temperature has reached – 40 °C leading to disappearance of signals associated with the diastereotropic methylenes of trimeric cation **8** (ppm) and a steady concentration of alkene **7** is obtained. As evidenced by the ^{1}H NMR spectra the first five reactions in Scheme 7 are fast on the NMR time scale in comparison to decomposition of trimeric cation **8**. This is the first report for observation of decomposition of cumyl$^+$ by a SHP through use of NMR spectroscopy. Additional kinetic studies on the decomposition of trimeric cation (**8**) by DTBMP are underway in an attempt to more fully elucidate the steps involved in decomposition. DTMBP should have a slightly greater effect on the TMPCl/**1**/DTBMP initiator system as the 2,2,4-trimethyl-4-pentylium carbocation of the expect ion pair ({**9**}, Scheme 8) would be stabilized by hyperconjugation as opposed to resonance for cumyl$^+$ increasing the acidity of the β-CH_3s of the former resulting in more facile β-H^+ abstraction. This might explain



Scheme 7



Scheme 8

why both MWs and yields are lower and I_{eff} values are higher on average for the TMPCl/**1**/DTBMP system (Table 5) compared to the CumCl/**1**/DTBMP system (Table 4).

Given these findings the question arises as to why this behavior was not witnessed by previous investigators? The answer appears to be directly related the degree of association between the growing carbocationic PIB chain-end and the counteranion. The bulk majority of systems studied to date contain counteranions derived from traditional Lewis acids and these species have a higher degree of nucleophilicity compared to anions derived from perfluoroarylated Lewis acids (*e.g.* **1**). Such traditional counteranions are more closely associated to the growing carbocationic PIB chain-end (especially in apolar media) and this prevents decomposition by SHPs from occurring. In two previous studies[8] the inclusion of a SHP in polymerizations using the traditional Lewis acid BCl_3 conducted in CH_2Cl_2 led to reductions in yield, molecular weight, and ω-chloro chain-end functionality with concomitant production of PIBs bearing exo-olefinic end groups. Although chain transfer was absent for polymerization conducted in both the presence and absence of a SHP the rate of termination was found to be 25 times higher for systems containing a SHP.[8a] These results are characteristic of β-H^+ abstraction by the SHP and could arise from of the use of polar media since this would decrease the degree of association between the propagating carbocation and the counteranion. It is unlikely that water facilitates this process under these conditions as BCl_3 readily scavenges water. As anions (*e.g.* **2**) derived from perfluoroarylated Lewis acids are weakly coordinating and highly soluble in organic solvents (including apolar solvents) they would be associated to the propagating carbocationic chain-end to a lesser degree than traditional counteranions. Under these conditions both the initiating carbocation and the growing carbocationic chain-end are more accessible to SHPs providing an opportunity for β-H^+ abstraction.

From the foregoing it is worthwhile to compare Arrhenius style plots of $\overline{M}_w$ versus 1/T obtained for polymerization systems containing counteranions derived from other perfluoroarylated Lewis acids and traditional Lewis acids to the γ–ray initiated polymerization (Figure 6). A number of conclusions can be drawn from this data. First, many of the systems that contain either WCAs or counteranions derived from traditional Lewis acids possess $\Delta E_{\overline{DP}}$ values (slopes) that are essentially the same as that for γ–ray initiated polymerization. This suggests that each of these systems has a similar degree of chain transfer despite the apparent differences in counteranion nucleophilicity in each system. This would require a threshold value of nucleophilicity below which the extent of chain transfer is constant regardless of the degree of counteranion nucleophilicity. From this data it would appear that ($Me_2AlCl_2^-$) closely approximates this threshold value for counteranion nucleophilicity. Even though $MeAlCl_4^-$ is a

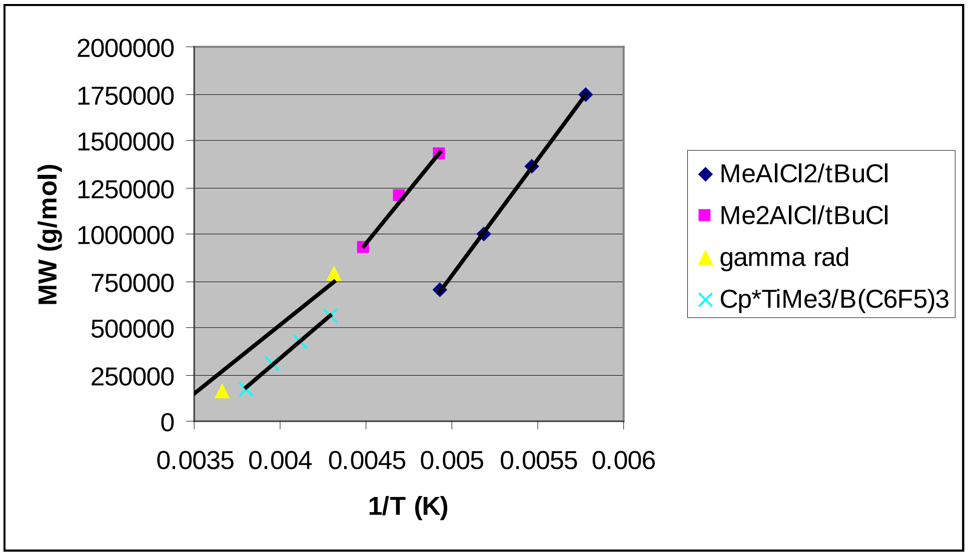


Figure 6. MW versus 1/T for select initiator systems for isobutylene polymerization. MW = $\overline{M}_v$ for Me_2AlCl[14b] and $MeAlCl_2$[14b]; MW = $\overline{M}_w$ for γ–ray[14a] and $Cp^*TiMe_3/B(C_6F_5)_3$[16g].

weaker nucleophile its solubility is not as great as $Me_2AlCl_2^-$ and thus why that latter system gives rise to higher MW polymer at higher temperature. One should note that this comparison is not without limitations given the sparse data available and its scatter. The main difference between these systems is not $\Delta E_{\overline{DP}}$ but the vertical displacement (*i.e.* y-intercept) of the Arrhenius line for each system. This is equivalent to the ratio of the frequency factor for propagation to that for chain transfer to monomer ($A_p/A_{tr,m}$). Because propagation has a more compact transition state compared to chain transfer[14a,29] it is affected to a greater extent by the degree of association present in the propagating ion pair as monomer must displace the counteranion to obtain π–orbital overlap necessary for polymerization to occur and this involves a negative entropy. For initiator systems where the degree of chain transfer is identical the ease to which propagation can occur becomes paramount in determining ultimate MW. Systems where the degree of association of the counteranion to the growing carbocationic chain end are lower due to increased solubility in addition to reduced nucleophilicity of the anion will in turn give rise to polymers of higher MW due to more facile propagation.

Conclusions

SHPs will abstract β-H^+ from growing carbocations when paired with a counteranion of sufficiently low nucleophilicity and high enough solubility to allow the SHP access to them. Counteranion nucleophilicity is only one variable that determines ultimate molecular weights. Once nucleophilicity has dropped below a certain threshold other factors such as solubility become important.

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