An Abbreviated Summary of Findings for Solution and Aqueous Suspension/Emulsion Polymerization of Isobutylene Coinitiated by 1,2-$C_6F_4[B(C_6F_5)_2]_2$

Act I: Quest for the Holy Grail

In the summer of 2001 I began work on the solution polymerization of isobutylene as coinitiated by 1,2-$C_6F_4[B(C_6F_5)_2]_2$ (**1**)[1] in the presence of added cationogens (cation synthetic equivalents) or adventitious moisture.[2] Diborane **1** was referred to as "Holy Grail" by its original investigators because not only was it the first fully perfluoroarylated chelating diborane but as I soon learned it was also very difficult to synthesize on a reasonable scale. My initial quest to synthesize the Holy Grail was quite arduous and labor intensive; however, after a period of about 4 months I had developed a set of improved reaction conditions that allowed for its production on a gram scale.[3]

Act II: Polymerization of Isobutylene in Hydrocarbon Media.

Introductory studies for the reaction of diborane **1** with trityl chloride showed it to be an extremely effective Lewis acid for the abstraction of chloride anion giving rise to quantitative yields of the previously unknown $[Ph_3C]^+[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2(\mu\text{-Cl})]^-$ salt, which served as a thermally stable model for the initiator system based on diborane **1** and cumyl chloride (CumCl).[3a,c] Subsequent variable temperature (VT) ^1H and ^{19}F nuclear magnetic resonance (NMR) spectroscopy experiments on the reaction of diborane **1** with CumCl showed that chloride abstraction was facile and quantitative even at -80 °C giving rise to the desired ion pair, $[\text{Cumyl}]^+[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2(\mu\text{-Cl})]^-$.[3] This ion pair decomposed to form 1/2 equivalent 1-phenyl-1,3,3-trimethylindane and 1 equivalent HCl while regenerating free diborane **1** as the temperature of the reaction mixture was allowed to warm to room temperature.

The reaction of the model monomer 2,4,4-trimethyl-1-pentene (TMP) in conjunction with the diborane **1**/CumCl initiating system was then used as a means of gauging the propensity of this system for the polymerization of isobutylene.[3c] ^1H NMR spectroscopy of the starting stock solution of TMP/diborane **1** showed that although diborane **1** is Lewis acidic enough to bring about isomerization of TMP, the system was dry enough to avert protic initiation from occurring. Once CumCl was added to the quiescent TMP/diborane **1** stock solution instantaneous and exothermic oligomerization occurred forming 1-neopentyl-1,2,3-trimethylindane; thus, indicating that this initiating system would be highly effective for polymerization of isobutylene.

The diborane **1**/CumCl initiating system proved to be effective for the polymerization of isobutylene in hydrocarbon media to high molecular weights and relatively high conversions at elevated polymerization temperatures in the presence of the proton trap, 2,6-di-*t*-butyl-4-methylpyridine (DTBMP).[3] On the other hand, the monodentate Lewis acid, $B(C_6F_5)_3$, proved to be inactive as a coinitiator in conjunction with CumCl under identical conditions and equivalent molar concentrations of boron $\{[B(C_6F_5)_3] = 2\ [\text{diborane } \mathbf{1}]\}$ suggesting that diborane **1** is an effective coinitiator due to its chelating ability.[3a,c] An interesting side note is that later VT ^1H and ^{19}F NMR spectroscopic studies on the reaction of diborane **1** with CumCl in the presence of DTBMP showed that there was no interaction between diborane **1** and DTBMP; however, the latter actively decomposed cumyl carbocation as it was formed to ultimately generate $[\text{DTBMPH}]^+[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2(\mu\text{-Cl})]^-$ and various decomposition products of cumyl carbocation.[3c] These results refute the long standing notion that proton trap is somehow benign towards carbocations and such erroneous conclusions may have been the result of ion pairing preventing such decomposition reactions from occurring in studies conducted by previous investigators!

The deleterious effect that proton trap has on carbocations is further supported by the fact that the activation energy of the degree of polymerization ($\triangle E_{DP}$)[4] for the diborane **1**/CumCl/DTBMP system was found to vary from -1.97 kcal mol^{-1} to -1.32 kcal mol^{-1} (depending on [DTBMP]) and these values are indicative of molecular weight control by termination.[4] The reader is strongly cautioned on the use of $\triangle E_{DP}$ as a diagnostic for determining the identity of molecular weight controlling events! I say this because during my work on polymerization systems containing weakly coordinating anions (WCAs) I noticed that the values for the polymerization of isobutylene as induced by many chemical initiator systems were essentially identical to that for polymerization initiated by γ-ray radiation and only differed from γ-ray radiation by the magnitude of their intercepts. Since a large negative value for $\triangle E_{DP}$ is supposed to be indicative of molecular weight control by counteranion unassisted chain transfer[4] (as this mode of chain transfer should have the highest activation energy) the value of $\triangle E_{DP}$ for γ-ray radiation induced polymerization would in theory exceed that for all chemically initiated systems as chain transfer is limited exclusively to the counteranion unassisted route. Many chemically initiated systems, including some that do not possess WCAs, have $\triangle E_{DP}$ values similar to that for γ-ray radiation induced polymerization; thus, the value of $\triangle E_{DP}$ alone is inadequate for determining the exact nature of the molecular weight determining process. Instead, a combination of $\triangle E_{DP}$ and the magnitude of the intercept maybe more instrumental in determining the exact nature of the molecular weight controlling process as all chemically initiated systems to-date posses intercepts with lower magnitudes compared to that for γ-ray radiation induced polymerization. The intercept value is most likely a composite function of counteranion nucleophilicity and solubility; these factors will have a strong bearing on the internal degree of freedom present in the system and thus in determining the nature of the molecular weight controlling event. These seemingly obvious facts raise serious doubts about the validity of the so-called "complex counteranion" theory.[5]

The main reason for using DTBMP in conjunction with the CumCl/diborane **1** initiator system was that diborane **1** proved to be a highly effective coinitiator for polymerization of isobutylene in hydrocarbon solution as initiated by adventitious moisture present even at low [H_2O] (c.a. 5 ppm).[3] These polymerizations were extremely rapid and exothermic giving rise to quantitative yields of polyisobutylene (PIB) in hydrocarbon media within seconds after the addition of diborane **1**. The efficacy of diborane **1** as a coinitiator also proved to be unparalleled as μM levels gave rise to quantitative yields of polymer in hydrocarbon solution even when [H_2O] = [diborane **1**]. The monodentate Lewis acid, $B(C_6F_5)_3$, proved to be inactive as a coinitiator in conjunction with adventitious moisture under identical conditions at equivalent molar concentrations of boron {[$B(C_6F_5)_3$] = 2 [diborane **1**]} suggesting that diborane **1** is an effective coinitiator due to its chelating ability. Regardless of whether the initiator is a cationogen or a protogen, diborane **1** is unique as a coinitiator for isobutylene polymerization in that high yields of high molecular weight PIB can be obtained in the absence of chlorinated solvents and at elevated polymerization temperatures!

Act III: The Mythical Methanol Adduct.

Of the many reactions between various cationogens and protogens with diborane **1** that were explored spectroscopically[3c] one in particular, the system based on cumyl methyl ether

(CumOMe) and diborane **1**, displayed unusual behavior as the reaction temperature was allowed to reach 25 °C.[3c,6a] Reaction at -80 °C generated the desired $[Cumyl]^+[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2\ (\mu\text{-}OMe)]^-$ ion pair; however, as the reaction temperature was allowed to rise the ^{19}F NMR spectra became increasingly complex. At first it was thought that a decomposition process similar to that witnessed for the $[Cumyl]^+[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2\ (\mu\text{-}Cl)]^-$ ion pair was occurring and this gives rise to 1/2 equivalent of 1-phenyl-1,3,3-trimethylindane and 1 equivalent MeOH, the latter which becomes coordinated to the regenerated diborane **1**. ^{19}F NMR data for the unsymmetrical methanol adduct of diborane **1** produced from the reaction between MeOH and diborane **1** as reported by previous investigators[7] appeared to support this mode of decomposition; however, this convenient explanation became complicated by the fact that subsequent ^1H and ^{19}F VT NMR spectroscopic studies on the CumOMe/diborane **1** system showed that the final outcome of reaction varied greatly with [CumOMe]. The variance in the product distribution coupled with the presence of a complex signal in the aromatic region of the ^1H NMR spectra suggested that decomposition might involve protolytic cleavage of a $B\text{-}C_{aryl}$ bond. If this was the case the resultant products of such a cleavage were incorrectly identified as unsymmetrical methanol adducts of diborane **1** by previous investigators. In order to verify this assumption the reaction between MeOH and diborane **1** was reinvestigated and the synthesis of one of the expected products of $B\text{-}C_{aryl}$ bond cleavage , $[MeOB(C_6F_5)_2]$, was undertaken. These studies[3c,6a,8] confirmed that decomposition of the $[Cumyl]^+[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2\ (\mu\text{-}OMe)]^-$ ion pair did involve protolytic cleavage of a $B\text{-}C_{aryl}$ bond to generate 1-bis(pentafluorophenyl)boron-2,3,4,5-tetrafluorobenzene, $MeOB(C_6F_5)_2$, and 1-phenyl-1,3,3-trimethylindane while disproving the existence of any stable unsymmetrical methanol adduct of diborane **1**.

Act IV: Aqueous Carbocationic Polymerization.

According to the chemical literature,[7] reaction of two equivalents of methanol with diborane **1** gives rise to an unsymmetrical bis-methanol adduct in which one equivalent of methanol is hydrogen bonded to the methanol that is coordinated to a single boron of diborane **1**. The ^{19}F NMR spectrum for this compound was stated[7] to be identical to that for the unsymmetrical mono-methanol adduct. Therefore, I rationalized that use of excess methanol with diborane **1** would be an easy way of generating ^{19}F NMR spectra corresponding to methanol adducts of diborane **1** for elucidation of the mechanism for decomposition of the $[Cumyl]^+[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2\ (\mu\text{-}OMe)]^-$ ion pair. As a result, the reaction of diborane **1** with excess methanol was conducted at low temperature and studied using VT ^1H and ^{19}F NMR spectroscopy. From this it was discovered that reaction of excess methanol with diborane **1** leads to the production of the $[(MeOH)_n H]^+[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2\ (\mu\text{-}OMe)]^-$ as a stable ion pair containing an undefined number of coordinating methanol molecules![3c,6a] Armed with the knowledge that diborane **1** is stable in excess methanol and given the fact that methanol and water have similar pKa values I sought to investigate the use of diborane **1** for the aqueous suspension and emulsion polymerization of isobutylene and butyl rubber. Before beginning actual work I devised the following set of criterion that I felt were required for carbocationic polymerization to readily occur in hydroxylic media.[3c]

Dr. Lewis' Rules for Aqueous Carbocationic Polymerization

1. The coinitiator must not only be stable towards hydroxylic species but in their presence must readily give rise to a Brönsted acid of sufficient strength capable of inducing protic initiation.
2. Both the coinitiator stock and monomer droplets must possess high degrees of hydrophobicity, or in a broader sense, very low affinities for any protic material in order for polymerization to be successful. This serves two purposes.
    a. By lowering the number of hydroxylic species that can coordinate to the Brönsted acid formed *in situ* the high level of acidity required for successful protic initiation is maintained.
    b. Since protic species act as chain transfer agents, lowering the concentration of such species present in the monomer droplet during polymerization reduces chain transfer and termination allowing for the production of high molecular weight polymer.

Following my set of rules, it was speculated that polymerization could be initiated by metering a solution of diborane **1** dissolved in a hydrophobic solvent (*e.g.* hexanes) into an aqueous suspension or emulsion of isobutylene. It was envisioned that initiation of polymerization would result from protonation of isobutylene by the Brönsted acid, $[H]^+$ $[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2\ (\mu\text{-}OH)]^-$, formed *in situ* from diborane **1** and background moisture present in the initiator stock and monomer droplets. It was also believed that use of a hydrophobic solvent for the initiator stock would prevent diborane **1** from coordinating with too many water molecules prior to entering the monomer droplet, as this would reduce the acidity of the resultant Brönsted acid and thus disfavor protonation of monomer. Due to the fact that isobutylene has a low boiling point (-6.9 °C at 760 torr) and that carbocationic polymerization requires low temperatures for the production of high molecular weight polymer it was realized that the continuous phase would have to consist of an aqueous mixture of low freezing point to avoid formation of ice during polymerization. Preliminary experiments on suspension polymerization were conducted in two vastly different media; one consisting of an obscure and little known eutectic mixture of $LiCl/NaCl/H_2O$[9] and the other comprised of a simple aqueous methanol solution described in the *CRC Handbook.*[10]

Initial suspension polymerization at -45 °C conducted in the $LiCl/NaCl/H_2O$ eutectic involved the slow addition of a hexane solution of diborane **1** to a stirred suspension of isobutylene in the aforementioned medium.[3c,6] This resulted in the formation of a milky white mixture that temporarily phase separated into a gelatinous mass of polymer half way through addition of initiator stock due to problems encountered with stirring resulting from increases in viscosity. From this experiment, it became evident that polymerization of isobutylene to high molecular weight polymer in aqueous media had finally become a reality! Encouraged by these results, a similar experiment was attempted using the aqueous solution of methanol as the polymerization medium. Although addition of the hexane solution of diborane **1** to a suspension of isobutylene in this medium caused it to become slightly cloudy the overall viscosity did not change much and polymerization in this medium is not favorable.[3c]

The differences in polymerization behavior in these two media are in line with my criterion for aqueous carbocationic polymerization and arise from several key physical characteristics of these different media. First, the background moisture level in the monomer droplets within the eutectic solution is lower compared to that present in monomer droplets suspended in pure water because the activity of the eutectic favors migration of the water from the monomer droplet to the continuous phase. For polymerization conducted in the aqueous methanol solution the monomer droplets will not only contain water but also methanol. Due to the higher solubility of the latter within isobutylene the monomer droplets will contain a high background level of methanol. This methanol coordinates to the Brönsted acid formed from diborane **1** as it enters the monomer droplet lowering its acidity and preventing initiation from occurring.

The aqueous suspension polymerization of isobutylene was conducted in a variety of aqueous media including: 12 N HCl (aq), 38 wt% H_2SO_4, and 50 wt% HBF_4 (aq) in addition to the LiCl/NaCl/H_2O eutectic and coinitiated using both hexane and toluene stock solutions of diborane **1**.[3c,6] Polymerizations were conducted over a wide temperature range (-78 to -25 °C) as permitted by the freezing point of the continuous phase. Regardless of the type of diborane **1** stock solution (hexanes or toluene) used it was found that reductions in polymerization temperature and in the nucleophilicity of the continuous phase led to increases in both polymer molecular weights and yields. Polymerizations involving the use of hexane stock solutions of diborane **1** gave rise to polymers of higher molecular weights in higher yields compared to those produced under similar conditions (*i.e.* identical polymerization temperature and continuous phase) using toluene stock solutions of diborane **1**. Whereas polymerizations coinitiated using hexane stock solutions involved the slow addition of a dilute (1.19×10^{-3} M) solution of diborane **1** and exhibited modest exotherms, those coinitiated using toluene stock solutions involved the rapid addition of the same number of moles of diborane **1** in a more concentrated (1.19×10^{-2} M) solution and were violently[11] exothermic causing immediate vaporization of monomer.

This difference in polymerization behavior is the direct result of the large variance in exothermicity of polymerization witnessed for each type of coinitiator stock where the greater exothermicity of the latter system leads to an overall reduction in polymer molecular weights and yields. The physical appearance of the polymerization charge also depended greatly on the identity of the coinitiator stock solution used. Polymerizations coinitiated by hexane stock solutions of diborane **1** went from initially clear suspensions to milky white suspensions whereas those coinitiated using toluene stock solutions turned bright yellow immediately upon addition of diborane **1** before gradually assuming a milky white appearance.[3c,6] The intermediate yellow coloration of the latter systems is indicative for the presence of ion pairs and the lifetime of this coloration was found to be inversely proportional to the polymerization temperature and nucleophilicity of the polymerization media.

The polymerization of isobutylene in aqueous suspension was also attempted with a variety of additional coinitiators including: $B(C_6F_5)_3$, $[Ph_3C]^+[B(C_6F_5)_4]^-$, $[Li]^+[B(C_6F_5)_4]^-$, $[H(Et_2O)_2]^+[B(C_6F_5)_4]^-$, and octafluoro-9,10-bis(bispentafluorophenylbora)anthracene.[3c,6] None of the aforementioned coinitiators including the perfluoroarylated non-chelating diborane octafluoro-9,10-bis(bispentafluorophenylbora)anthracene were active for the polymerization of isobutylene in aqueous suspension indicating that diborane **1** derives its activity from its chelating ability.

As an extension of the work done on the polymerization of isobutylene in suspension, experiments were conducted involving the use of different surfactants for the emulsion polymerization of isobutylene as coinitiated by diborane **1**.[3c,6] These experiments centered on the use of two different classes of surfactants: anionic surfactants [sodium dodecylsulfate (SDS)] and cationic surfactants [dodecyltrimethylammonium bromide, triflate, and tetrafluoroborate (DTB, DOTf, and DTFB)]. With the exception of the use of surfactants, emulsion polymerization was conducted in a manner identical to that for suspension polymerization as coinitiated by hexane and toluene solutions of diborane **1**.

Regardless of the class of surfactant used, polymerizations under emulsion conditions led to a reduction in polymer yields compared to analogous polymerizations conducted in suspension. Polymer yields were most drastically reduced for emulsions using DTB. This behavior can be attributed to the increase in surface area of the monomer droplets due to the presence of an emulsifier that in turn increases the rate of termination of the growing polymer chain with the continuous phase with respect to the rate of chain transfer within the droplet as compared to similar polymerization in suspension.

The molecular weights for polymers formed under emulsion conditions were similar or slightly lower than those yielded in suspension under identical conditions with the exception of polymerizations conducted in the presence of DTB where molecular weights were higher. The unusual behavior of polymerizations conducted in the presence of DTB results from preferential and premature termination of growing polymer chains with the more nucleophilic bromide counteranion, as this surfactant is more lipophilic compared to SDS and will be expected to migrate in the monomer droplet to a certain extent. This is supported by the fact that emulsions conducted in aqueous H_2SO_4 and aqueous HBF_4, in the presence of DOTf and DTFB respectively, produced polymers with similar molecular weights and yields as those obtained in the same media but in the presence of the anionic surfactant SDS.

The physical characteristics of the polymerizations conducted in emulsion demonstrated a similar dependence on the identity of diborane **1** stock solution used as witnessed for systems conducted in suspension. That is, polymerizations coinitiated by hexane stock solution of diborane **1** went from initially clear to milky white emulsions and exhibited modest exotherms whereas those using toluene stock solutions were highly exothermic and turned bright yellow immediately upon addition of diborane **1** before gradually assuming a milky white appearance. In most cases, polymerization resulted in the formation of very stable emulsions that required the addition of methanol for recovery of the polymer products.

The copolymerization of isobutylene with isoprene in aqueous media was also explored for the preparation of butyl rubber.[3c,6] Preliminary copolymerization studies conducted in hydrocarbon solution indicated that the presence of isoprene led to a large increase in the reactivity of the system that was manifested by the extremely violent and exothermic nature that these polymerizations assumed upon the inclusion of this comonomer.[3b,c] From this behavior I theorized that inclusion of this comonomer might led to increased yields and/or higher molecular weights as the resonance stabilized isopropenyl carbocation would continue to perpetuate polymerization within the monomer droplet for extended periods of time compared to similar homopolymerizations. Regardless of whether copolymerization was conducted in suspension or emulsion the addition of isoprene led to the production of polymers with higher molecular weights, albeit in lower yields, than those produced in its absence. This unusual copolymerization behavior may be due to longer lived polymer chains that grow for greater periods of time resulting from the presence of more stable isopropenyl carbocations or from branching reactions where growing chain-ends add to the residual double bond of isoprene units contained within the polymer backbone. The presence of the WCA, $[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2(\mu\text{-}OH)]^-$, may further enhance these effects.

ACT V: Conclusion.

Diborane **1** is a highly effective coinitiator for the polymerization of isobutylene in conjunction with cationogens or protogens under demanding circumstance (*i.e.* nonpolar organic solvents or aqueous media). Diborane **1** derives its unique efficacy from its perfluoroarylated substituents that provide for high Lewis acidity, enhanced solubility in nonpolar solvents, and tolerance towards hydroxylic species in addition to its chelating ability that further intensifies Lewis acid strength. In addition to inventing several new compositions of matter, improved reaction conditions for the synthesis of diborane **1**, and the first aqueous carbocationic polymerization system this work refutes the long standing misconception that proton trap is benign toward carbocations and exposes the severe limitations present in the complex counteranion theory.

References:

(1) (a) Williams, V. C.; Piers, W. E.; Clegg, W.; Collins, S.; Marder, T.B. *J. Am. Chem. Soc.* **1999**, *121*, 3244-3245. (b) Williams, V. C.; Piers, W. E.; Clegg, W.; Elsegood, M. R. J., Dai, Z. Li; Collins, S.; Marder, T. B. *Angew. Chem. Int. Ed.* **1999**, *38*, 3695-3698. (c) Williams, V. C.; Irvine, G. J.; Piers, W. E.; Li, Z.; Collins, S.; Clegg, W.; Elsegood, M. R. J.; Marder, T. B. *Organometallics* **2000**, *19*, 1619.
(2) This work was conducted under the supervision of Dr. S. Collins. A public disclosure of events and other research leading up to the Summer of 2001 will be posted on this site in the future.
(3) (a) Lewis, Stewart P.; Piers, W. E.; Taylor, N.; Collins, S. *J. Am. Chem. Soc.* **2003**, *125*, 14686-14687. (b) Lewis, Stewart P.; Piers, W. E.; Collins, S. W.O. 2004094481 (2004) (c) Lewis, Stewart P., Ph.D. Dissertation, The University of Akron, 2004.
(4) Kennedy, J. P.; Trivedi, P. *Adv. Poly. Sci.* **1978**, *28*, 115-151.
(5) Kennedy, J. P.; Rengachary, S. *Adv. Poly. Sci.* **1974**, *14*, 1-48.
(6) (a) Lewis, Stewart P.; Henderson, Lee; Parvez, M. R.; Piers, W. E.; Collins, S. *J. Am. Chem. Soc.* **2005**, *127*, 46-47.(b) Lewis, Stewart P.; Kennedy, J. P.; Collins, S. U.S. 2005027086 (2005).
(7) Henderson, L. D.; Piers, W. E.; Irvine, G. J.; McDonald, R. *Organometallics*, **2002**, *21*, 340-345.
(8) The assignments listed on page 145 of 3c are incorrectly assigned due to formatting changes that occurred during last minute revisions to this document. For compound **16** start at the top-most (*p*-F of the $B(C_6F_5)_2$ group), assign this as peak "f" and moving counterclockwise progressively assign each fluorine the next letter that follows in the alphabet. Several other (minor) mistakes are present in this document. Please feel free to send corrections to my attention.
(9) Akopov, E. *Ah. Prikl. Kim.* **1963**, *36*, 1916-1919.
(10) *CRC Handbook of Chemistry and Physics*; Lide, D. R., Ed.; CRC: Boca Raton, FL, 1996; 77th ed.
(11) Caution must be exercised while conducting these polymerizations with concentrated stock solutions of diborane **1**. These polymerizations are extremely exothermic leading to immediate and rapid vaporization of monomer and present a severe explosion risk!