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

CHAPER V

SUSPENSION/EMULSION POLYMERIZATION OF IB AND COPOLYMERIZATION WITH IP COINITIATED BY 1,2-$C_6F_4[B(C_6F_5)_2]_2$

5.1 Historical Aspects of Ionic Polymerization in Aqueous Suspension/Emulsion

5.1.1 Advantages to Conducting Polymerization in Water

Ionic reactions are typically carried out under anhydrous conditions because even small amounts of water deactivate/decompose catalysts and ionic intermediates; however, water is an abundant and environmentally friendly solvent and thus, reactions that operate in aqueous media are desirable. In the field of polymerization, emulsion and suspension processes, which operate in aqueous media, possess several distinct advantageous over those conducted in bulk or in solution. The required use of solvents for the removal of heat generated during polymerization is negated as the continuous phase consists of water, which has a very high heat capacity and as a result serves as an excellent heat sink. Polymerization of monomer can be conducted in a more efficient manner compared to more traditional methods as these systems essentially consist of suspended or emulsified miniature polymerization reactors, resulting in benefits in terms of polymerization rate and yield. Due to the fact that monomer is dispersed as droplets within water these polymerizations are easier to stir and do not suffer from viscosity related problems encountered in bulk or solution polymerization. The products as yielded by these processes generally can be used directly without further separation/modification, reducing the overall cost of the final product. Due to these advantages, there is continual interest in the development of aqueous suspension or emulsion polymerizations for new and existing polymers.

Although an in-depth discussion of suspension/emulsion polymerization is beyond the scope of this dissertation, a brief overview of these systems is considered here. The reader is referred to other resources for a more advanced treatment of these topics.[189] Suspension polymerization is heterogeneous polymerization where water forms the continuous phase in which monomer is suspended as droplets with an average diameter of 50-500 μm. The initiators used for suspension are soluble within the monomer droplets and each droplet can be considered a mini bulk polymerization system. This two-phase system can only be maintained by continuous agitation and in many cases droplet stabilizers are added to prevent coalescence of monomer droplets from occurring. Monomers such as styrene, vinyl chloride, and tetrafluoroethylene are polymerized by the suspension method.

Emulsion polymerization as its name implies involves the polymerization of monomers that are in the form of colloidal dispersions in water. This involves the use of an emulsifier or surfactant at concentrations above the critical micelle concentration (CMC) in which excess surfactant forms small colloidal clusters (micelles) with average diameters of 2-10 nm. Addition of monomer to the soap mixture results in the formation of monomer droplets that are stabilized by surfactant molecules, and these account for the bulk of the added monomer. Most of the remaining monomer resides in micelles while a small portion becomes dissolved in the continuous phase. Monomer droplets have diameters in the range of 1-10 μm and thus are not only outnumbered by micelles but the total surface area of the micelles is larger than that of the droplets by more than two orders of magnitude. Polymerization is induced by a water-soluble initiator in which active radicals are predominately captured by the micelles due to their overwhelming surface area compared to monomer droplets and polymerization ensues to form polymer particles that grow steadily by absorption of monomer from droplets and from solution. Two types of polymer particles exist throughout radical polymerization; active growing particles that have a single propagating radical and dead particles, resulting from a radical entering an active particle that combines with an already present propagating polymer chain generating a dead chain. Although the stages of emulsion polymerization will not be discussed final polymer particles as yielded by this process have diameters typically on the order of 50-200 nm. Emulsion polymerization is the predominant process for commercial polymerization of vinyl acetate, chloroprene, and copolymerization of styrene with butadiene and acrylonitrile.

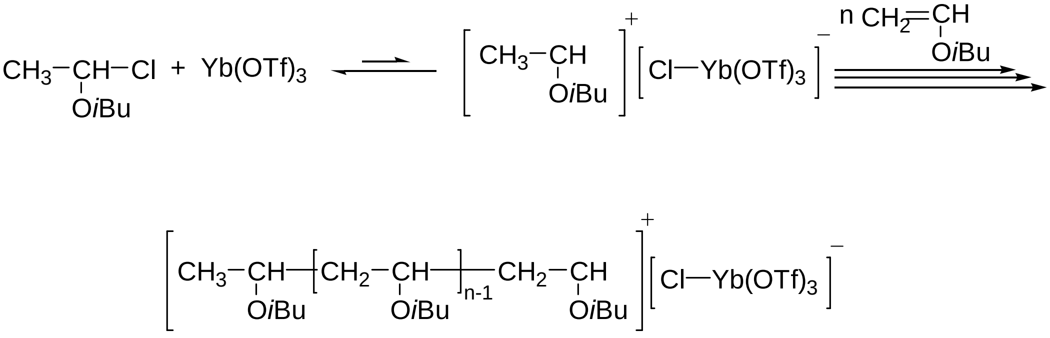
5.1.2 Early History of Ionic Polymerizations in Water

From the foregoing discussion one might conclude that ionic polymerization cannot be conducted in aqueous suspension/emulsion; however, several well-established examples of such processes do exist. For instance, attempts at the aqueous suspension polymerization of isobutylene can be traced back to the late 1930s.[190] This research revolved around the use of 50-75 wt % sulfuric acid as the continuous phase for the suspension polymerization of isobutylene; however, this only resulted in the generation of dimers and trimers of isobutylene and required reaction temperatures of 100 °C to produce such oligomers in good yields. Ionic polymerization in emulsion (IPE) dates back to the late 1950s when it was used for the preparation of poly(dimethylsiloxane) latexes by cationic and anionic polymerizations of cyclosiloxane in emulsion.[191] Cationic suspension/emulsion polymerization of reactive monomers bearing electron donating groups (i.e. vinyl ethers, *p*-substituted styrenes) have recently become the focus of intense research. The details of these more recent studies are given below as a means of setting the stage for the topic of this chapter, discovery of the first suspension and emulsion processes for polyisobutylene and butyl rubber.

5.1.3 Controlled Cationic Polymerization in Water

5.1.3.1 Rare Earth Metal Triflates as Coinitiators for Polymerization in Water

Sawamoto et al.[192] were the first to disclose the use of water-tolerant Lewis acids for controlled cationic polymerization in water. This group of researchers concluded that for polymerization to be living it was necessary that the coinitiators not only be water-tolerant but also possess sufficient Lewis acidity to reversibly activate dormant polymer chain-ends. As a result, they investigated the use of lanthanide triflates as coinitiators for cationic polymerization of reactive monomers in water. This research found its beginnings during the investigation of the suspension polymerization of isobutyl vinyl ether (IBVE) and *p*-methoxystyrene (pMOS) as induced by ytterbium triflate [$Yb(OTf)_3$; OTf = OSO_2CF_3] in conjunction with the corresponding hydrogen chloride-vinyl monomer adduct [$CH_3CH(R)Cl$; R = O*i*Bu, *p*-C_6H_4-OCH_3]. For example, they found that when neat IBVE and the IBVE-HCl adduct were added to an aqueous solution of $Yb(OTf)_3$ suspension polymerization occurred. Polymerization of IBVE was conducted in the presence of large amounts of water (organic/aqueous phase = 1/1 v/v) and resulted in high yields of polymer (60-80%; $\overline{M}_n = 3\text{-}6\text{x}10^3$ g mol^{-1}; $\overline{M}_w/\overline{M}_n = 2.5\text{-}3.0$) within two hours at room temperature. Neither $Yb(OTf)_3$ nor the IBVE-HCl adduct alone were able to induce polymerization of IBVE in suspension. It was found that trifluoromethanesulfonic acid, which is a possible hydrolysis product of $Yb(OTf)_3$, was very ineffective for initiation of IBVE polymerization in suspension resulting in very low yields (0.7 % for 2 hours). They speculated that polymerization may be initiated by $Yb(OTf)_3$ entering the monomer droplet and activating the C–Cl bond of the IBVE-HCl adduct resulting in the formation of an initiating carbocation (Scheme 41).[192]

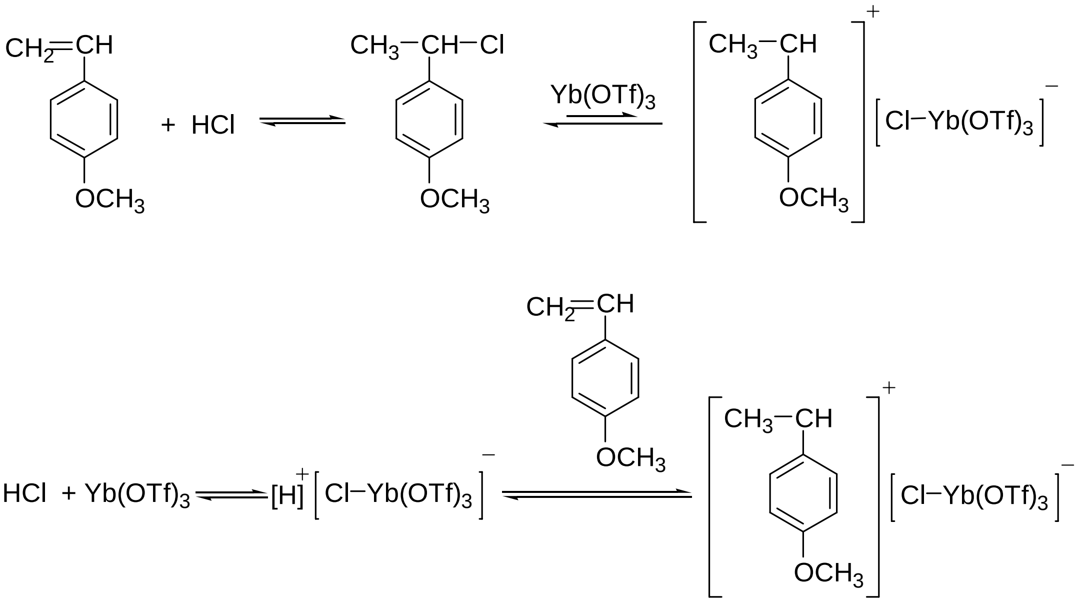


Scheme 41. Polymerization of iBVE as initiated by HCl/Yb(OTf)3.

They continued this work by studying the suspension polymerization of pMOS as induced by the $Yb(OTf)_3$/pMOS-HCl adduct system.[192] As with IBVE, neither $Yb(OTf)_3$ nor the pMOS-HCl adduct alone were able to induce polymerization of pMOS in suspension. pMOS polymerization occurred smoothly without an induction phase resulting in quantitative conversion of monomer to polymer, albeit slowly. Polymerization rate depended on the concentration of the cationogen pMOS-HCl adduct and was found to decrease with decreasing cationogen concentration.

From this work they found evidence for the existence of long-lived polymers of pMOS as yielded by this system supporting the assumption that $Yb(OTf)_3$ reversibly activates the C–Cl end groups of dormant polymer chains.[192] For example, $\overline{M}_n$ was found to increase in direct proportion to monomer conversion and agreed well with the calculated value assuming one molecule of cationogen generates one polymer chain. Only at later stages of polymerization was $\overline{M}_n$ found to deviate from the theoretical value and this behavior was attributed to chain transfer. Molecular weight distributions were unimodal and relatively narrow ($\overline{M}_w/\overline{M}_n$ = 1.4) throughout polymerization. ^1H NMR spectroscopy of poly(pMOS) as yielded by this polymerization exhibited signals associated with a CH_3 group (ca. 1.0 ppm) for the α-end and a CHCl group (ca. 4.1 ppm) associated with the ω-end, supporting initiation arising from a carbocation originally derived from the pMOS-HCl adduct. Polymerization by a carbocationic mechanism was further supported by the fact that addition of NaOH readily quenched polymerization; whereas, 1,4-benzoquinone a known radical inhibitor had no affect on polymerization.

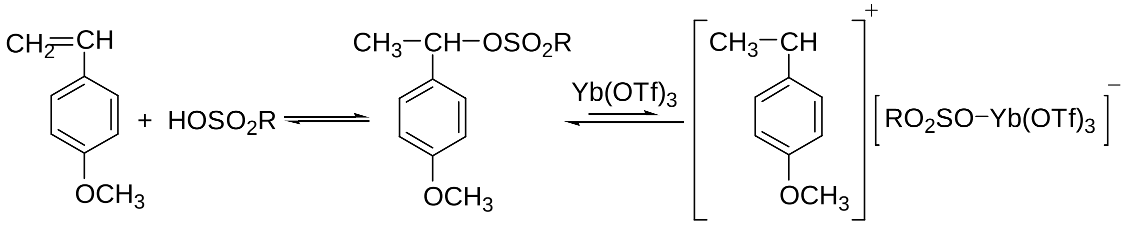
Sawamoto et al. further demonstrated that polymerization of pMOS as induced by $Yb(OTf)_3$ could be conducted by using HCl in place of the pMOS-HCl adduct.[192] This was accomplished by adding pMOS to an aqueous solution of HCl and $Yb(OTf)_3$. Polymerization as conducted in this manner also gave rise to long lived polymers of pMOS in quantitative yields. Although $\overline{M}_n$ increased with monomer conversion, initial values were larger than calculated values assuming one polymer chain per HCl molecule due to slow initiation; at later stages of polymerization, $\overline{M}_n$ values were lower than the theoretical due to chain transfer. The researchers did not comment on how initiation occurred but it may be envisioned that HCl can either react with $Yb(OTf)_3$ to generate a strong Brönsted acid that initiates polymerization by protonation of monomer or that HCl reacts with pMOS to form the pMOS-HCl adduct *in situ* that is then ionized by $Yb(OTf)_3$ (Scheme 42).



Scheme 42. Polymerization of pMOS as initiated by $HCl/Yb(OTf)_3$.

Sawamoto et al.[193] discovered that aqueous sulfonic acids ($HOSO_2R$; $R = CH_3$, Ph-*p*-CH_3, and Ph-*p*-NO_2) coupled with $Yb(OTf)_3$ initiated the cationic suspension polymerization of p-MOS. These systems gave rise to long lived polymers in quantitative yields where $\overline{M}_n$ showed similar behavior with conversion as demonstrated with systems using HCl. The strength of the acid was found to strongly affect the rate of polymerization and the strongest acid, 4-nitrobenzenesulfonic acid, induced the fastest polymerization when coupled with $Yb(OTf)_3$. They postulated that the sulfonic acid reacts directly with monomer to form a pMOS-sulfonic acid adduct that is ionized by

$Yb(OTf)_3$ resulting in initiation of polymerization (Scheme 43). They also speculated



R = CH_3, p-C_6H_4-NO_2, p-C_6H_4-CH_3

Scheme 43. Polymerization of pMOS as initiated by $RSO_3H/Yb(OTf)_3$.

that polymerization involved reversible ionization of the sulfonic ester group of the polymer chain-end by $Yb(OTf)_3$. This assumption was supported by ^{1}H NMR spectroscopy that showed the presence of α-CH_3 groups (ca. 1.0 ppm) in addition to ω-CH–OSO_2CH_3 groups (ca. 5.2 ppm) and ω-CH–OH groups (ca. 3.7 ppm) the latter being derived from hydrolysis of the sulfonyl end group.

Sawamoto et al.[194] further expanded their research on suspension polymerization of pMOS to include the use of other rare earth metal triflates [$Ln(OTf)_3$; Ln = Dy, Sm, Gd, and Nd; OTf = OSO_2CF_3] in conjunction with the pMOS-HCl adduct to supplement previous work conducted with $Yb(OTf)_3$. Polymerization rate showed a strong dependence on the Lewis acidity of the rare earth metal triflate, which increases as the radius of the central metal decreases. Thus, polymerization rates were highest with $Sc(OTf)_3$ whose central metal has the smallest ionic radius. On the other hand, $Nd(OTf)_3$, which has the largest radius, did not induce polymerization.

They then turned their attention to emulsion polymerization of pMOS as induced by the aforementioned rare earth triflates in conjunction with the pMOS-HCl adduct.[194] For example, in the $Yb(OTf)_3$/pMOS-HCl adduct induced polymerization of pMOS it was found that the cationic surfactants dodecyltrimethylammonium chloride and bromide both gave rise to polymerization rates double that for systems with no surfactant while narrowing the molecular weight distribution of the product ($\overline{M}_w / \overline{M}_n \sim 1.3$ vs. 1.4, respectively). Use of tetrabutylammonium chloride, which does not form a stable emulsion, had no major effect on polymerization. These results indicate that although all of the aforementioned ammonium salts can be sources of common ions (halides) that have the potential to shift the equilibrium towards dormant polymer chains, retarding propagation, they do not function in this manner. The ammonium salts that are surfactants led to faster polymerization with narrower MWD's by increasing the surface area of the monomer droplets which in turn facilitates transfer of $Yb(OTf)_3$ into the organic phase. Use of cationic surfactants led to increases in polymerization rate as induced by all rare earth triflates and this enhancement was greatest for $Yb(OTf)_3$. In contrast both the anionic surfactant sodium laurylbenzene sulfonate and the nonionic surfactant poly(vinyl methyl ether) (PMVE) gave rise to reduced polymerization rates without a reduction in MWD compared to polymerization conducted in the absence of surfactant. Although these surfactants do not crucially affect the long lived nature of the growing chain-ends, it is believed that they retard polymerization by acting as bases that coordinate with $Yb(OTf)_3$ reducing its overall Lewis acidity.[194]

5.1.3.2 Other Water Stable Metal Triflates as Coinitiators for Polymerization in Water

Given the success with lanthanide triflates, Sawamoto et al.[195] explored the use of other water-tolerant triflates [$Sn(OTf)_2$, $Zn(OTf)_2$, and $Cu(OTf)_2$] in combination with the pMOS-HCl adduct and dodecyltrimethylammonium chloride for the emulsion polymerization of pMOS. In all cases pMOS emulsion polymerization occurred smoothly without an induction period where rate increased in the order of increasing Lewis acidity of the central metal (Yb > Sn > Zn ~ Cu). The use of another water-tolerant Lewis acid, $Zn(BF_4)_2$, was also explored for emulsion polymerization of pMOS; however, polymerization rates were even slower than those obtained with $Zn(OTf)_2$ requiring 150 h to reach 35 % conversion.

5.1.3.3 Polymerization in Water in the Absence of Rare Earth Triflates

Little follow up work has been conducted on the use of water-tolerant rare earth triflates for cationic suspension/emulsion polymerization following the original research as conducted by Sawamoto et al; however, some recent investigations conducted by Ganachaud et al.[196] at the attempted emulsion polymerization of pMOS as induced by the $Yb(OTf)_3$/pMOS-HCl adduct system in the presence of dodecylbenzenesulfonic acid (DBSA) may explain some of the behavior witnessed in these systems. Ganachaud et al. discovered that DBSA was able to induce the emulsion polymerization of pMOS on its own. In this manner DBSA acts as an initiator/surfactant (INISURF). Although polymerization rates were slower than emulsion polymerization of pMOS as induced by the systems involving $Yb(OTf)_3$; $\overline{M}_n$ showed a similar steady increase with conversion, which eventually tapers off at later stages of polymerization. Polymerization rates were found to increase steadily with increasing [DBSA] with similar behavior in $\overline{M}_n$ regardless of the [DBSA]. ^{1}H NMR spectroscopic analysis of poly(pMOS) as yielded by these polymerizations showed the presence of α-CH_3 groups (c.a. 1.0 ppm) and ω-OH groups (c.a. 3.7 ppm). Given the structure of the resultant polymers and the consistent behavior of $\overline{M}_n$ with respect to conversion, Ganachaud et al.[196] concluded that DBSA initiates polymerization protically and does not led to reversible termination by reactivation of ω-OH groups. They proposed that initiation occurs at the surface of the micelle and these initially produced chains quickly terminate with water forming a layer of lower $\overline{M}_n$ oligomers that protrude from the micelle with their ω-OH functionalities extending outward. This in turn expels water from the interface allowing generationof longer chains to occur. Such behavior may account for some of the results as reported by Sawamoto and co-workers.

5.1.3.5 BF_3OEt_2 Coinitiated Polymerization in Water

Sawamoto et al.[197] also focused their attention on the use of BF_3OEt_2 for the polymerization of reactive styrenes in the presence of fairly large amounts of water. Although not frequently noted, BF_3OEt_2 is a highly water-tolerant Lewis acid.[198] Use of BF_3OEt_2 as a Lewis acid coinitiator began with the attempted polymerization of *p*-hydroxystyrene (pHS) in acetonitrile, which is a good solvent for both the monomer and polymer. It was discovered that although acetonitrile is a strongly coordinating solvent and thus not often used for cationic polymerization, use of BF_3OEt_2 in the presence or absence of various protogens and cationogens led to quantitative yields of poly(pHS) in this solvent. From their work, it was found that $\overline{M}_n$ of the afforded polymers was much higher than the theoretical value (10^4 g mol^{-1}) assuming one chain per initiator molecule for systems employing acetic acid and the pMOS-HCl adduct as initiators; however, the alcohol and water adducts of pMOS functioned efficiently as initiators for polymerization of pHS producing polymers with $\overline{M}_n$ values closely approximating the theoretical value.

This difference in initiator efficiencies was attributed to the C–O bonds of the latter cationogens that are easily activated by boron trifluoride to generate initiating carbocations.

Given successful polymerization in acetonitrile, they rationalized that water could be potentially used as a base to modify the Lewis acidity of BF_3OEt_2 to effect more controlled polymerization of pHS.[197] For example, use of a six-fold excess of water to BF_3OEt_2 resulted in quantitive polymerization, although rates were lowered for all systems. A lowering of $\overline{M}_n$ was witnessed for polymers produced by all initiators with values more closely approximating the theoretical and this reduction was accompanied by simultaneous narrowing of MWDs for the polymers produced by these systems. These systems proved to be significantly long-lived as addition of a fresh charge of pHS prior to full consumption of the initial charge led to further growth with final $\overline{M}_n$ closely approximating the theoretical value based on the total amount of monomer used. Additional experiments showed that polymerization could be conducted in a controlled manner even in the presence of large amounts of water ($[H_2O] = [pHS]$). ^1H NMR spectroscopic analyses of the polymers produced using the pMOS-H_2O adduct showed the presence of CH_3 groups (c.a 1.0 ppm) in addition to *p*-CH_3O groups (c.a. 3.7 ppm) at the α-end of the polymer chain verifying that this cationogen did indeed initiated polymerization. Sawamoto et al.[199,200] found that other styrenic monomers such as pMOS, *p*-chlorostyrene, and *p*-methylstyrene could be controllably polymerized by the BF_3OEt_2/pMOS-H_2O adduct system in the presence of large amounts of water. The polymerization behavior of these monomers was similar to that witnessed for pHS varying mainly in polymerization rate due to differences in monomer reactivity.

5.2 Results and Discussion for Aqueous Suspension/Emulsion Polymerization of IB and Copolymerization with IP Coinitiated by 1,2-$C_6F_4[B(C_6F_5)_2]_2$

5.2.1 Events Leading to the Discovery of the First Suspension/Emulsion Polymerization of Isobutylene

According to the chemical literature,[160] 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 boron. The ^{19}F NMR spectrum for this compound was stated[160] to be identical to that for the mono-methanol adduct. Therefore, this author rationalized that use of excess methanol with diborane **1** would be an easy way of generating ^{19}F NMR spectra corresponding to the bis-methanol adduct of diborane **1** for elucidation of the mechanism for decomposition of the [Cumyl][1,2-$C_6F_4\{B(C_6F_5)_2\}_2$ (μ-OMe)] ion pair. As a result, the reaction of diborane **1** with excess methanol was conducted at low temperature and studied using variable-temperature ^1H and ^{19}F NMR spectroscopy. Stacked plots of ^{19}F and ^1H NMR spectra corresponding to reaction of diborane **1** with excess methanol initially preformed at – 80 °C in CD_2Cl_2 are provided in Figures 40 and 41, respectively.

As can be seen in Figure 40, reaction of excess methanol with diborane **1** leads to the production of the [1,2-$C_6F_4\{B(C_6F_5)_2\}_2$ (μ-OMe)] counteranion as a stable species. ^{19}F NMR spectra for initial reaction of diborane **1** with excess methanol at low temperatures (– 80 to – 40 °C) appears to indicate that two main species are produced that

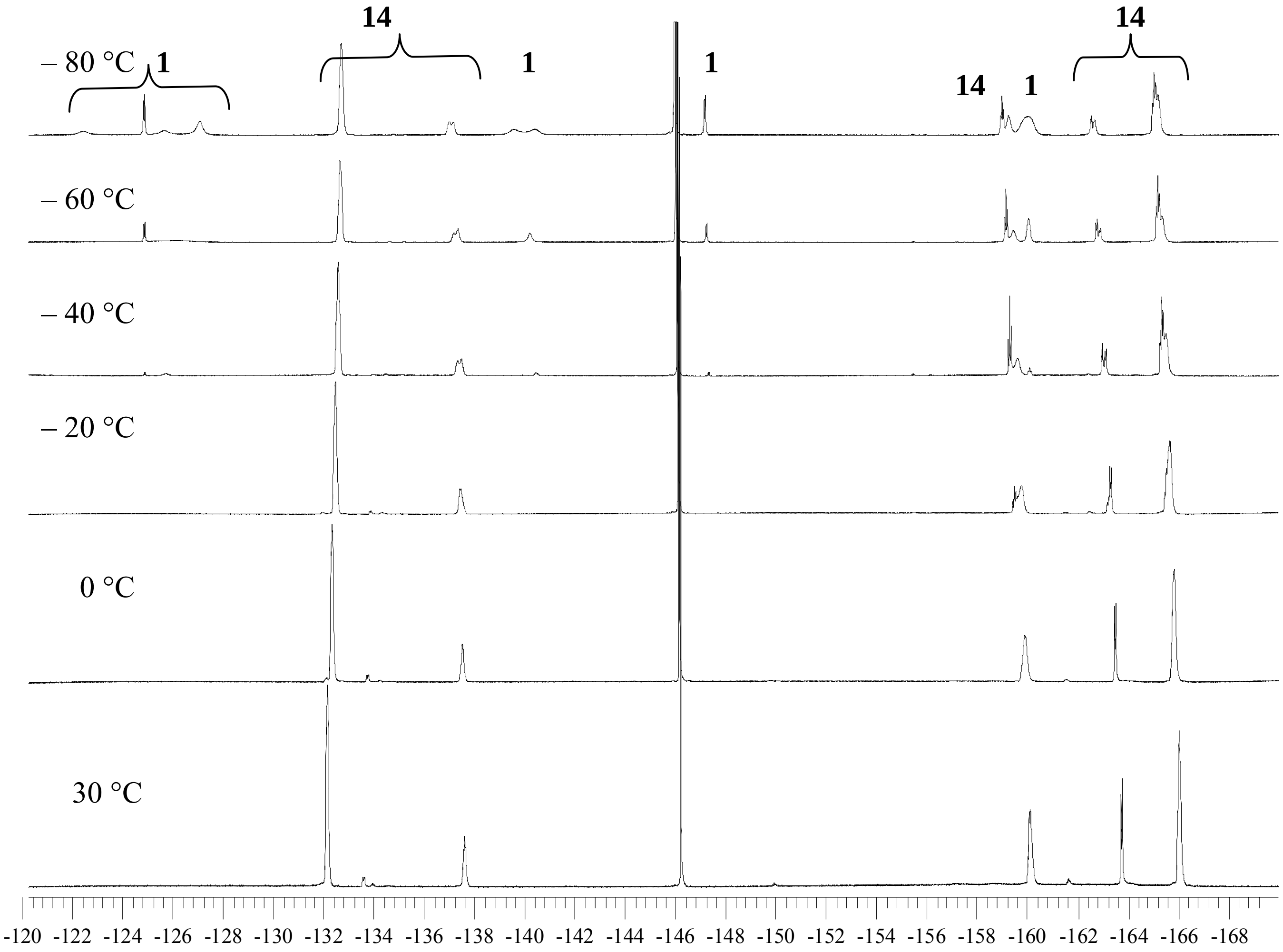


Figure 40. ^{19}F NMR (CD_2Cl_2) spectra overlay for reaction of 1,2-$C_6F_4[B(C_6F_5)_2]_2$ with excess MeOH.

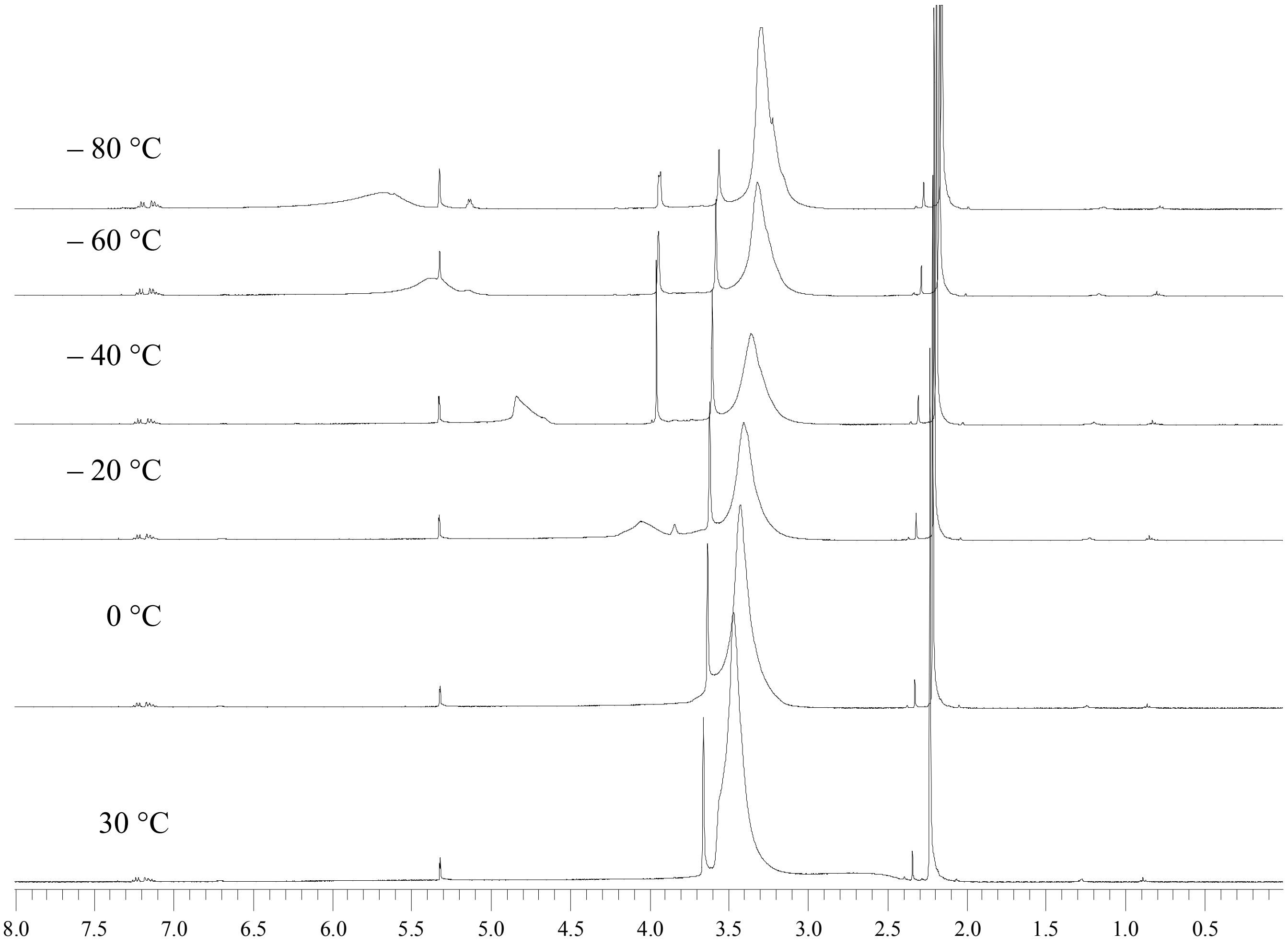
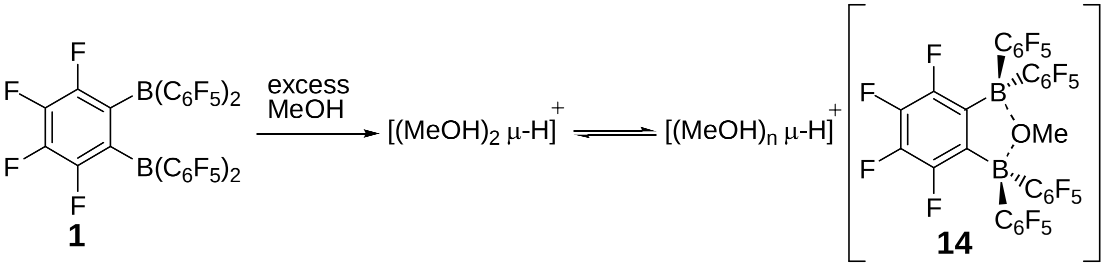


Figure 41. ^{1}H NMR (CD_2Cl_2) spectra overlay for reaction of 1,2-$C_6F_4[B(C_6F_5)_2]_2$ with excess MeOH.

differ mainly by the number of coordinating methanol molecules they contain. Evidence for this behavior is provided by the fact that the mainset of five symmetrical, sharp ^{19}F signals for the [1,2-C_6F_4\{B(C_6F_5)$_2$\}$_2$ (μ-OMe)] counteranion are accompanied by a sister set of broadened ^{19}F signals that are slightly shifted upfield in comparison to the parent set. Information contained in the ^{1}H NMR spectra at low temperatures (– 80 to – 40 °C) also indicates similar behavior for the countercation. For example, evidence for the [(MeOH)$_2$ μ–H] countercation is contained in the – 80 °C ^{1}H NMR spectrum where a line broadened quartet (5.12 ppm) and a line broadened doublet (3.93 ppm) corresponding to the hydroxyl and methyl protons of the coordinating methanol molecules of this species are visible. Increasing the reaction temperature to 30 °C appears to result in the production of a fluxional species containing an undefined number of coordinating methanol molecules, [(MeOH)$_n$ μ–H][1,2-C_6F_4\{B(C_6F_5)$_2$\}$_2$ (μ-OMe)] (Scheme 44).



Scheme 44. Reaction of diborane **1** with excess MeOH.

Armed with the knowledge that diborane **1** is stable in excess methanol this author sought to investigate the use of diborane **1** for the aqueous suspension and emulsion polymerization of isobutylene and butyl rubber. It was speculated that polymerization could be initiated by metering a solution of diborane **1** dissolved in a hydrophobic solvent (i.e. 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.

5.2.2 Aqueous Suspension Polymerization of Isobutylene

Preliminary experiments on suspension polymerization were conducted in two vastly different media; one consisting of an obscure and little known eutectic mixture of $LiCl/NaCl/H_2O$[201] and the other comprised of a simple aqueous methanol solution described in the *CRC Handbook.*[156] 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. 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. The results for this preliminary experiment are provided in entry 1 of Table 32. 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 appear to change much. From the results for this preliminary experiment as provided in entry 7 of Table 32, polymerization in this medium is not favorable.

The differences in polymerization behavior in these two media are believed to arise from several key physical characteristics of these different media. First, the background moisture level in the monomer droplets within the eutectic solution is probably 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. When a droplet of initiator solution is adsorbed within the monomer droplet the background moisture level is such that diborane **1** forms a very strong Brönsted acid that immediately initiates polymerization. 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 most likely 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.

Table 32. Aqueous suspension polymerization using hexane solutions of diborane **1**.

Entry	Initiator (M^a, identity)	IB [M]	AF	Temp. (°C)	$\overline{M}_w$ ($x10^3$)	PD	Yield (%)
1	$4.11x10^{-4}$ diborane **1**	4.72	$LiCl^b$	-45	88.4	2.04	93.6
2	$4.26x10^{-4}$ diborane **1**	4.93	$LiCl^b$	-60	43.0	2.97	43.4
3	$4.26x10^{-4}$ diborane **1**	4.93	$LiCl^b$	-60	66.1	2.55	48.1
4^f	$4.26x10^{-4}$ diborane **1**	4.93	$LiCl^b$	-60	121	1.96	32.3
5	$8.52x10^{-4}$ $[Ph_3C][B(C_6F_5)_4]$	4.93	$LiCl^b$	-60	—	—	—
6	$8.52x10^{-4}$ $B(C_6F_5)_3$	4.93	$LiCl^b$	-60	—	—	—
7^g	$3.98x10^{-4}$ diborane **1**	0.97	$MeOH^c$	-60	102	3.26	7.64
8	—	4.93	$H_2SO_4^d$	-60	—	—	—
9	$4.26x10^{-4}$ diborane **1**	4.93	$H_2SO_4^d$	-60	74.1	2.38	47.0
10	$4.26x10^{-4}$ diborane **1**	4.93	$H_2SO_4^d$	-60	74.5	2.33	50.4
11	—	4.93	HBF_4^e	-78	—	—	—
12	$4.26x10^{-4}$ diborane **1**	4.93	HBF_4^e	-78	138	2.16	85.4

a. Concentration in organic phase, initiator stock dissolved in 10.0 mL hexane except for $[Ph_3C][B(C_6F_5)_4$ dissolved in 10.0 mL, CH_2Cl_2/hexane, 60/40 v/v. add. time = 5 min.

b. LiCl (23 wt %)/NaCl (1.2 wt %)/H_2O (75.8 wt %)

c. MeOH/H_2O, 68/32 wt/wt

d. 38 wt % H_2SO_4 (aq)

e. 50 wt % HBF_4 (aq)

f. solvent = CH_2Cl_2

g. solvent = hexane

Given the initial success of suspension polymerization of isobutylene in the LiCl/NaCl/H_2O eutectic as induced by diborane **1**, a more in-depth study of this subject was undertaken. This involved conducting polymerization under more controlled conditions (i.e. mechanically vs. magnetically stirred) in conjunction with different aqueous media and at different polymerization temperatures. Follow-up studies focusing on polymerization in LiCl/NaCl/H_2O yielded polymers with lower molecular weights and in lower yields than those obtained in preliminary experiment first conducted in this medium (entries 2 and 3 vs. 1, Table 32). This is the result of more efficient stirring used in subsequent polymerizations compared to that for the preliminary experiments. It is possible that following initiation, polymerization is perpetuated within the monomer droplet by direct chain transfer to monomer until the propagating chain-end migrates to the droplet surface undergoing irreversible termination with the continuous phase. Higher stirring efficiency leads to an increase in the rate of termination compared to chain transfer as the droplet surface area increases due to the production of smaller droplets. This in turn leads to an overall reduction in polymer molecular weights and yields.

It was also found that addition of a polar solvent (entry 4, Table 32) could be used to increase polymer molecular weight, although this defeats one of the purposes of conducting polymerization in suspension. Attempts to initiate suspension polymerization of isobutylene in the LiCl/NaCl/H_2O eutectic using $[Ph_3C][B(C_6F_5)_4]$ and $B(C_6F_5)_3$ in place of diborane **1** ended in failure (entries 5-6, Table 32). The success of suspension polymerization of isobutylene coinitiated by diborane **1** can be attributed to the fact that it is a highly Lewis acidic but water tolerant compound.

Additional experiments on the suspension polymerization of isobutylene as coinitiated by diborane **1** were conducted in other aqueous media and at different polymerization temperatures. Polymerization was conducted in aqueous sulfuric acid at –60 °C to investigate the effect that the nucleophilicity of the continuous phase had on the outcome of polymerization (entries 8-10, Table 32). Although this medium was of too low acidity to initiate polymerization in the absence of diborane **1,** its lower nucleophilicity as compared to the LiCl/NaCl/H_2O eutectic led to the production of higher molecular weight polymer in higher yields at identical temperatures. The use of aqueous HBF_4 not only provides a polymerization medium of even lower nucleophilicity but also allows for polymerization at even lower temperatures (entries 11-12, Table 32). Although this medium is strongly acidic it still is not strong enough to initiate polymerization of isobutylene in the absence of diborane **1**. Due to the lower obtainable polymerization temperatures in this medium in addition to its lower nucleophilicity polymerization in this medium led to increased yields of even higher molecular weight polymer.

In an attempt to avoid fluctuation in molecular weights and yields caused by variances in the rate of addition of the hexane solution of diborane **1**, additional experiments on suspension polymerization were conducted using a more concentrated toluene solution of diborane **1** that could be injected at a more reproducible rate. Use of toluene solutions of diborane **1** led to faster rates of addition for a fixed number of moles of diborane **1** with little variation in the rate of injection between different runs as compared to that achieved using hexane solutions of diborane **1**. This shorter injection period (3 sec vs. 5 min) resulted in a large difference in the exotherms witnessed for polymerization using toluene vs. hexane solutions of diborane **1**. Polymerizations using the former were very exothermic and evolved isobutylene gas during addition of diborane **1**. In some instances gas evolution was so violent that the stir bearing broke free of the retaining Keck clamp and shot up the stir shaft. Whereas addition of hexane solutions of diborane **1** resulted in production of a milky white mixture, injection of toluene solutions of diborane **1** caused the charge to turn bright yellow for a brief period of time after which the charge became milky white in appearance. Suspensions conducted in aqueous HBF_4 maintained a yellow coloration throughout the entire course of polymerization although the final color became paler than that initially observed after injection as the charge took on a milky consistency.

The results for suspension polymerization as coinitiated using toluene solutions of diborane **1** are provided in Table 33. Polymerization as conducted in this manner was shown to give rise to lower molecular weight polymers in lower yields as compared to polymerization coinitiated by hexane solutions of diborane **1** (entries 1-14, Table 33 vs. entries 1-12, Table 32). This behavior is believed to be the result of the higher exotherms experienced in polymerizations coinitiated by toluene solutions of diborane. Similar trends were witnessed for polymer molecular weight and yield as a function of the polymerization medium; at a given temperature polymer molecular weight and yields increased with decreasing nucleophilicity of the polymerization medium while

Table 33. Aqueous suspension polymerization using toluene solutions of diborane **1**.

Entry	Initiator (M[a], identity)	IB [M]	AF	Temp. (°C)	$\overline{M}_w$ (x10^3)	PD	Yield (%)
1	6.28x10^{-4} Diborane **1**	6.13	LiCl[b]	-60	23.9	2.38	39.1
2	6.28x10^{-4} Diborane **1**	6.13	LiCl[b]	-60	19.8	2.30	44.5
3	6.28x10^{-4} Diborane **1**	8.10	LiCl[b]	-60	22.1	2.52	40.0
4	1.26x10^{-3} $LiB(C_6F_5)_4$	6.13	LiCl[b]	-60	—	—	—
5[h]	6.45x10^{-4} $LiB(C_6F_5)_4$	4.12	LiCl[b]	-60	—	—	—
6	1.26x10^{-3} $H(Et_2O)_2B(C_6F_5)_4$	6.13	LiCl[b]	-60	—	—	—
7	6.28x10^{-4} Diborane **7**	6.13	LiCl[b]	-60	—	—	—
8	1.08x10^{-3} Diborane **1**	4.06	MeOH[c]	-60	—	—	—
9	—	6.13	H_2SO_4[d]	-60	—	—	—
10	6.28x10^{-4} Diborane **1**	6.13	H_2SO_4[d]	-60	38.4	2.05	29.0
11	6.28x10^{-4} Diborane **1**	6.13	H_2SO_4[d]	-60	33.0	2.21	27.1
12	—	6.13	HBF_4[e]	-78	—	—	—
13	6.28x10^{-4} Diborane **1**	6.13	HBF_4[e]	-78	50.8	2.36	57.5
14	6.28x10^{-4} Diborane **1**	6.13	HBF_4[e]	-78	49.1	2.42	54.0
15	—	6.13	HCl[f]	-25	—	—	—
16	6.28x10^{-4} Diborane **1**	6.13	HCl[f]	-25	17.8	3.35	17.8
17	6.28x10^{-4} Diborane **1**	6.13	HCl[f]	-25	20.3	1.88	15.5
18	6.28x10^{-4} Diborane **1**	6.13	$LiClO_4$[g]	-10	—	—	—
19	6.28x10^{-4} Diborane **1**	6.13	LiCl[b]	-10	—	—	—

a. Concentration in organic phase, initiator stock dissolved in 1.00 mL toluene.
b. LiCl (23 wt %)/NaCl (1.2 wt %)/H_2O (75.8 wt %) c. MeOH (67.25 wt %)/H_2O (31.65 wt%)/NaCl (1 wt%) d. 38 wt % H_2SO_4 (aq) e. 50 wt % HBF_4 (aq) f. 12 N HCl (aq)
g. 30 wt% $LiClO_4$ (aq) h. solvent = CH_2Cl_2

polymerization at lower temperatures led to the production of higher molecular weight polymer in higher yields. As was the case for polymerization coinitiated by hexane solutions of diborane **1**, polymerization as coinitiated by toluene solutions of diborane **1** did not readily occur in media containing methanol (entry 8, Table 33). The unique ability of diborane **1** to coinitiate polymerization of isobutylene in suspension was further demonstrated by the fact that other potential water stable initiators/coinitiators were incapable of initiating polymerization (entries 4-7, Table 33). Even the highly Lewis acidic octafluoro-9,10-bis(bispentafluorophenylbora)anthracene **7** was unable to coinitiate polymerization of isobutylene in suspension. These results indicate that the activity of diborane **1** for the polymerization of isobutylene in suspension is in part due to its chelating ability.

The use of other polymerization media and temperatures was also explored in conjunction with toluene solutions of diborane **1**. For instance, suspension polymerization as initiated by toluene solutions of diborane **1** was conducted in aqueous HCl at higher temperatures (– 25 °C) due to the elevated freezing point of this medium compared to those previously investigated. Even though this medium is strongly acidic, it was incapable of initiating polymerization on its own. Although such polymerizations gave rise to lower yields as compared to those conducted at lower temperatures, polymer molecular weights did not differ greatly from those obtained at – 60 °C (entries 16 and 17, Table 33). The attempted polymerization in the LiCl/NaCl/H_2O eutectic or in 30 wt % $LiClO_4$ (aq) conducted at – 10 °C did not produce polymer (entries 18 and 19, Table 33).

5.2.3 Aqueous Emulsion Polymerization of Isobutylene

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**. These experiments centered around 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** (Table 34).

Introductory experiments on emulsion polymerization were conducted in the LiCl/NaCl/H_2O eutectic with a large amount of DTB and were coinitiated by hexane solutions of diborane **1** (entries 1 and 2, Table 34). As with suspension polymerization under similar conditions, addition of diborane **1** caused the charge to become milky white; although the viscosity of the charge appeared lower than that previously witnessed for suspension. As can be seen from the data corresponding to these experiments, molecular weight of the polymer was higher than that obtained in suspension; however, yields were greatly decreased in the presence of this surfactant. Follow-up studies using reduced amounts of DTB in conjunction with toluene solutions of diborane **1** in the LiCl/NaCl/H_2O eutectic also gave rise to polymers with molecular weights higher than those obtained in suspension under identical conditions (entries 3 and 4, Table 34). Although yields appeared to increase with decreasing amounts of DTB,

Table 34. Aqueous emulsion polymerization of isobutylene coinitiated by diborane **1**.

Entry	Initiator (M, type)	IB [M]	AF	Soap (g, type)	Temp. (°C)	$\overline{M}_w$ ($x10^3$)	PD	Yield (%)
1	$4.26x10^{-4}$ Diborane **1**[a]	4.93	LiCl[c]	1.00 DTB	-60	145	2.10	0.95
2	$4.26x10^{-4}$ Diborane **1**[a]	4.93	LiCl[c]	1.00 DTB	-60	246	1.85	1.52
3	$6.28x10^{-4}$ Diborane **1**[b]	6.13	LiCl[c]	0.100 DTB	-60	57.2	2.74	4.70
4	$6.28x10^{-4}$ Diborane **1**[b]	6.13	LiCl[c]	0.100 DTB	-60	49.3	2.68	3.70
5	$6.28x10^{-4}$ Diborane **1**[b]	6.13	LiCl[c]	0.100 SDS	-60	25.4	2.37	32.3
6	$6.28x10^{-4}$ Diborane **1**[b]	6.13	LiCl[c]	0.100 SDS	-60	23.4	2.47	29.9
7	$6.28x10^{-4}$ Diborane **1**[b]	6.13	H_2SO_4[d]	0.100 DTB	-60	111	3.16	2.29
8	$6.28x10^{-4}$ Diborane **1**[b]	6.13	H_2SO_4[d]	0.100 DTB	-60	108	2.86	2.91
9	$6.28x10^{-4}$ Diborane **1**[b]	6.13	H_2SO_4[d]	0.100 SDS	-60	45.6	2.24	17.0
10	$6.28x10^{-4}$ Diborane **1**[b]	6.13	H_2SO_4[d]	0.100 SDS	-60	61.0	2.69	18.3
11	$6.28x10^{-4}$ Diborane **1**[b]	6.13	H_2SO_4[d]	0.100 DOTf	-60	45.0	2.32	17.8
12	$6.28x10^{-4}$ Diborane **1**[b]	6.13	H_2SO_4[d]	0.100 DOTf	-60	55.7	2.82	14.4
13	$4.26x10^{-4}$ Diborane **1**[a]	4.93	HBF_4[e]	0.100 SDS	-78	67.2	2.31	46.3
14	$6.28x10^{-4}$ Diborane **1**[b]	6.13	HBF_4[e]	0.100 SDS	-78	36.3	2.35	42.5
15	$6.28x10^{-4}$ Diborane **1**[b]	6.13	HBF_4[e]	0.100 DTFB	-78	43.7	2.22	47.0
16	$6.28x10^{-4}$ Diborane **1**[b]	6.13	HBF_4[e]	0.100 DTFB	-78	39.9	2.12	51.9

a. Concentration in organic phase, hexane stock (addition time 5 min).

b. Concentration in organic phase, toluene stock.

c. LiCl (23 wt %)/NaCl (1.2 wt %)/H_2O (75.8 wt %)

d. 38 wt% H_2SO_4 (aq)

e. 50 wt% HBF_4 (aq)

they were still drastically reduced compared to those for suspension. Studies involving SDS in conjunction with toluene solutions of diborane **1** in the LiCl/NaCl/H_2O eutectic gave rise to polymers with molecular weights similar to those obtained in suspension under similar conditions, but in slightly reduced yields compared to latter. For both surfactants, emulsion polymerizations as coinitiated by toluene solutions of diborane **1** were highly exothermic resulting in vaporization of monomer. As with suspension polymerizations using toluene solutions of diborane **1**, the charges of the corresponding emulsion polymerizations turned yellow briefly upon addition of diborane **1** before finally assuming a milky white appearance.

Several explanations exist for the behavior as witnessed for emulsion polymerization using DTB and SDS. Regardless of the identity of the surfactant, emulsion polymerization results in reduced yields compared to suspension polymerization. This may be the direct result of the surfactant increasing the surface area of the monomer droplet leading to an increase in the rate of termination of the growing chain with the continuous phase with respect to the rate of chain transfer within the droplet as compared to suspension polymerization. The increases in polymer molecular weight seen for emulsions using DTB may result 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 into the monomer droplet to a certain extent.

Emulsion polymerization was further investigated in other media using other cationic surfactants in addition to the more traditional DTB in an attempt to verify the above conclusions. Emulsion polymerizations conducted in aqueous sulfuric acid as coinitiated by toluene solutions of diborane **1** in the presence of DTB or SDS behaved similarly to corresponding emulsions conducted in the LiCl/NaCl/H_2O eutectic (entries 7-10 vs. 3-6, Table 34). Both surfactants led to an overall decrease in yields, especially for DTB; whereas, molecular weights increased dramatically for emulsion containing DTB compared to suspension under identical conditions. SDS appeared to give rise to slightly higher molecular weight polymer compared to that produced in suspension in aqueous sulfuric acid. Use of DOTf for emulsion polymerization in aqueous sulfuric acid resulted in almost similar polymerization behavior to corresponding emulsion using SDS (entries 11 and 12 vs. 9 and 10, Table 34). These results further support the assumption that molecular weights are higher for systems using DTB due to preferential/premature termination of the growing polymer as DOTf, which possesses the weakly coordinating triflate anion in place of the nucleophilic bromide anion, does not engage in similar behavior. DOTf behaves almost identically to SDS in regards to the emulsion polymerization of isobutylene as coinitiated by toluene solutions of diborane **1**.

Emulsion polymerization as conducted in aqueous HBF_4 (entries 13-16, Table 34) shows similar behavior to that witnessed for corresponding polymerizations conducted in the LiCl/NaCl/H_2O eutectic and in aqueous sulfuric acid. As with the latter two systems, emulsion polymerization in aqueous HBF_4 results in the production of polymers with lower molecular weights in reduced yields compared to suspension polymerization under identical conditions regardless of the identity of the surfactant [(entry 13, Table 34 vs. entry 12, Table 32) and (entries 14-16, Table 34 vs. entries 13 and 14, Table 33)]. As was the case for emulsion polymerization in aqueous sulfuric acid using DOTf, the behavior of DTFB mirrors that of SDS in emulsion polymerization conducted in aqueous HBF_4. This finding is in line with the assumption that increases in molecular weights for polymers produced from systems using DTB are due to the action of the nucleophilic bromide anion of this lipophilic surfactant.

5.2.4 Aqueous Suspension/Emulsion Copolymerization of Isobutylene with Isoprene

The copolymerization of isobutylene with isoprene as conducted in suspension and emulsion was investigated to supplement previous experiments on the homopolymerization of isobutylene under similar conditions (Table 35). From a preliminary experiment on the copolymerization of isobutylene with isoprene under anhydrous conditions very violent polymerization behavior was observed as compared to homopolymerization. This author reasoned that use of this comonomer might lead to similar increases in reactivity for suspension/emulsion. Indeed suspension and emulsion copolymerizations using toluene solutions of diborane **1** were very exothermic and maintained a yellow color for longer periods of time as compared to corresponding homopolymerizations.

Initial studies on copolymerization in suspension and emulsion were conducted in the LiCl/NaCl/H_2O eutectic and were coinitiated by toluene solutions of diborane **1**. Introductory suspension copolymerizations involved the use of 8 mol % IP in the feed and resulted in the production of butyl rubber with higher molecular weights but in lower yields compared to polyisobutylene produced under essentially identical conditions (entries 1 and 2, Table 35 vs. entries 1-3, Table 33). ^1H NMR ($CDCl_3$) spectroscopic

Table 35. Aqueous emulsion/suspension copolymerization of isobutylene coinitiated by diborane **1**.

Entry	Initiator M, identity	IB [M]	IP [M]	AF	Soap g, type	Temp ºC	$\overline{M}_w$ x10^3	PD	Yield %
1	5.68x10^{-4} Diborane **1**^{a}	5.79	0.51	LiCl^c	—	-60	86.2	2.89	23.9
2	5.68x10^{-4} Diborane **1**^{a}	5.79	0.51	LiCl^c	—	-60	76.4	2.55	20.0
3	6.28x10^{-4} Diborane **1**^{a}	3.05	2.43	LiCl^c	—	-60	286	7.16	9.87
4	6.28x10^{-4} Diborane **1**^{a}	3.05	2.43	LiCl^c	—	-60	212	5.74	9.23
5	5.68x10^{-4} Diborane **1**^{a}	5.79	0.51	LiCl^c	0.100 SDS	-60	59.3	2.25	14.4
6	5.68x10^{-4} Diborane **1**^{a}	5.79	0.51	LiCl^c	0.100 SDS	-60	77.3	2.75	17.8
7	6.28x10^{-4} Diborane **1**^{a}	3.05	2.43	LiCl^c	0.100 SDS	-60	—	—	23.3^g
8	6.28x10^{-4} Diborane **1**^{a}	3.05	2.43	LiCl^c	0.100 SDS	-60	—	—	27.5^g
9	6.28x10^{-4} Diborane **1**^{a}	3.05	2.43	LiCl^c	0.100 DTB	-60	—	—	26.1^g
10	6.28x10^{-4} Diborane **1**^{a}	3.05	2.43	LiCl^c	0.100 DTB	-60	—	—	23.8^g

a. Concentration in organic phase, toluene stock.

b. Concentration in organic phase, hexane stock.

c. LiCl (23 wt %)/NaCl (1.2 wt %)/H_2O (75.8 wt %) d. 38 wt% H_2SO_4 (aq) e. 50 wt% HBF_4 (aq)

f. solvent = hexane g. highly crosslinked

Table 35 continued. Aqueous emulsion/suspension copolymerization of isobutylene coinitiated by diborane **1**.

Entry	Initiator M, identity	IB [M]	IP [M]	AF	Soap g, type	Temp ºC	$\overline{M}_w$ x10^3	PD	Yield %
11	$5.68\text{x}10^{-4}$ Diborane **1**[a]	5.79	0.51	H_2SO_4[d]	__	-60	57.1	2.97	19.4
12	$5.68\text{x}10^{-4}$ Diborane **1**[a]	5.79	0.51	H_2SO_4[d]	__	-60	51.0	2.88	18.8
13	$5.68\text{x}10^{-4}$ Diborane **1**[a]	5.79	0.51	H_2SO_4[d]	0.100 SDS	-60	72.2	1.63	5.25
14[f]	$6.28\text{x}10^{-4}$ Diborane **1**[a]	3.05	0.27	HBF_4[e]	__	-78	80.9	2.90	39.4
15	$4.26\text{x}10^{-4}$ Diborane **1**[b]	2.46	1.96	HBF_4[e]	__	-78	89.0	1.70	7.35
16	$4.26\text{x}10^{-4}$ Diborane **1**[b]	2.46	1.96	HBF_4[e]	__	-78	90.4	1.58	6.93
17[f]	$6.28\text{x}10^{-4}$ Diborane **1**[a]	3.05	0.27	HBF_4[e]	0.100 SDS	-78	71.6	2.40	30.8
18[f]	$6.28\text{x}10^{-4}$ Diborane **1**[a]	3.05	0.27	HBF_4[e]	0.100 DTFB	-78	106	1.91	38.1
19	$6.28\text{x}10^{-4}$ Diborane **1**[a]	3.05	2.43	HBF_4[e]	0.100 SDS	-78	__	__	23.3[g]
20	$6.28\text{x}10^{-4}$ Diborane **1**[a]	3.05	2.43	HBF_4[e]	0.100 SDS	-78	__	__	27.5[g]

a. Concentration in organic phase, toluene stock.

b. Concentration in organic phase, hexane stock.

c. LiCl (23 wt %)/NaCl (1.2 wt %)/H_2O (75.8 wt %) d. 38 wt% H_2SO_4 (aq) e. 50 wt% HBF_4 (aq)

f. solvent = hexane g. highly crosslinked analysis showed that these copolymers to consist of an average of 5 mol % IP present in the *trans*-1,4 configuration of which an average of 16 % of these IP units serve as branchpoints (Figure 42). These values were determined from integration of the methine protons for IP *trans*-1,4 repeat units for the main chain (t, 5.05 ppm) and methine protons corresponding to IP *trans*-1,4 repeat units that serve as branch points (d, 4.90 ppm) to those for the methylene protons of the IB repeat unit (s, 1.45 ppm). Additional copolymerizations were conducted in suspension using higher amounts of IP (44 mol %) in the feed (entries 3 and 4, Table 35). This resulted in the production of butyl rubber of even higher molecular weight but at reduced yields compared to copolymerization conducted in suspension at lower IP feed. ^{1}H NMR ($CDCl_3$) spectroscopic analysis showed that these copolymers consisted of an average of 60 mol % IP present in the *trans*-1,4 configuration of which an average of 10 % of these IP units serve as branch points. Although IP normally acts as a chain transfer agent in traditional copolymerizations this monomer leads to higher molecular butyl rubber in suspension and emulsion compared to polyisobutylene compared under similar conditions. Possibly IP leads to longer lived polymers within the monomer droplet due to the higher stability of the allylic carbocation and thus polymer chains have more time to grow. Additionally, IP may increase molecular weight as hydride abstraction from such a repeat unit leads to the generation of an active carbocation from which secondary branches can grow.

Introductory emulsion copolymerizations were conducted in the LiCl/NaCl/H_2O eutectic using 8 mol % IP in the feed in conjunction with SDS and yielded butyl rubbers with higher molecular weights in lower yields compared to polyisobutylene produced

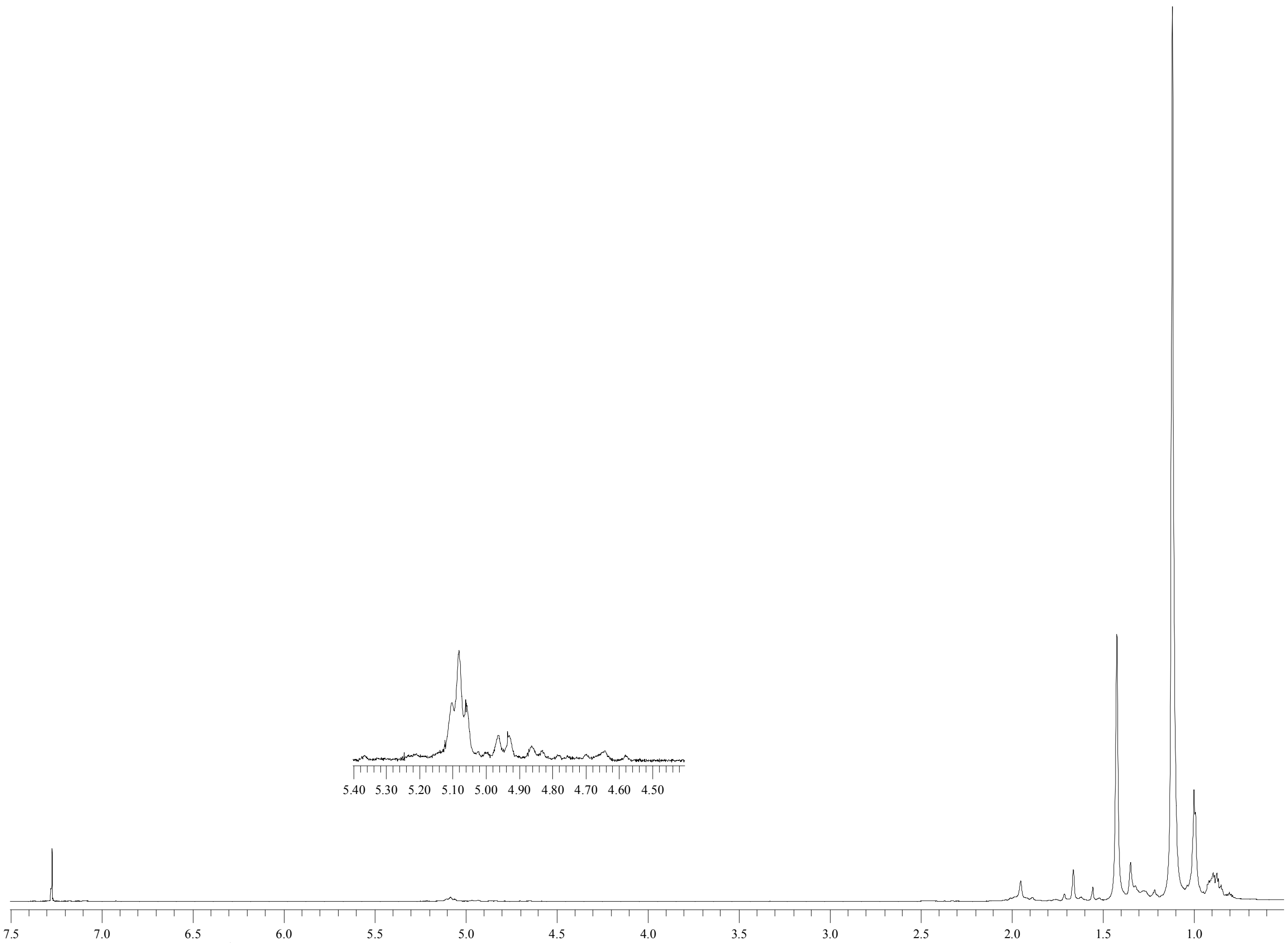


Figure 42. ^{1}H NMR ($CDCl_3$) spectrum for copolymer from suspension polymerization. (LiCl/NaCl/H_2O eutectic using 8 mol% IP)

under similar conditions (entries 5 and 6, Table 35). There was little difference in molecular weight or yield for butyl rubber produced in suspension or in emulsion within the LiCl/NaCl/H_2O eutectic. ^{1}H NMR ($CDCl_3$) spectroscopic analysis showed that these copolymers consisted of an average of 5.2 mol % IP present in the *trans*-1,4 configuration of which an average of 16.7 % of these IP units serve as branch points. Emulsion copolymerizations conducted with higher amounts of IP in the feed (44 mol %) resulted in the production of highly crosslinked, intractable butyl rubber in higher yields as compared to similar copolymerizations as conducted at lower IP feed contents regardless of the identity of the surfactant (entries 7-10, Table 35).

Additional studies on the copolymerization of isobutylene with isoprene in suspension and emulsion were also conducted in other media. Copolymerizations in suspension and emulsion using 8 mol % IP in the feed as coinitiated by toluene solutions of diborane **1** were conducted in aqueous sulfuric acid (entries 11-13, Table 35). The results of these experiments were shown to parallel those obtained in the LiCl/NaCl/H_2O eutectic under similar conditions. Suspension copolymerization as conducted in this medium was shown to produce butyl rubber with higher molecular weights but in lower yields as compared to polyisobutylene produced under similar conditions (entries, 11 and 12, Table 35). Emulsion copolymerization conducted using SDS was also found to produce high molecular weight butyl rubber albeit in lower yields compared to butyl rubber obtained in suspension under identical conditions (entry 13, Table 35). ^{1}H NMR ($CDCl_3$) spectroscopic analysis showed that these copolymers consisted of an average of

5.4 mol % IP present in the *trans*-1,4 configuration of which an average of 16.7 % of these IP units serve as branch points.

Copolymerization in suspension and emulsion was further studied in aqueous HBF_4. Initial suspension copolymerizations in this medium as coinitiated by toluene and hexane solutions of diborane **1** were conducted in the presence of 9 mol % IP in the feed (entries 14-16, Table 35). Copolymerization under these conditions as coinitiated by toluene solutions of diborane **1** gave rise to butyl rubber of higher molecular weight in lower yields compared to polyisobutylene prepared under similar conditions (entries 15 and 16, Table 35). On the other hand, both the molecular weight and yield of butyl rubber produced by hexane solution of diborane **1** was lower than that of polyisobutylene produced in the LiCl/NaCl/H_2O eutectic under similar conditions (entry 14 , Table 35). Currently there is no obvious explanation for this behavior. ^1H NMR ($CDCl_3$) spectroscopic analysis showed that all of these copolymers consisted of an average of 14 mol % IP present in the *trans*-1,4 configuration of which an average of 10 % of these IP units serve as branch points.

Emulsion copolymerizations in HBF_4 using SDS and DTFB as coinitiated by toluene solutions of diborane **1** resulted in similar behavior as witnessed for emulsion copolymerizations conducted in the LiCl/NaCl/H_2O eutectic and aqueous sulfuric acid (entries 17-20, Table 35). Emulsion copolymerizations conducted at lower IP feeds (9 mol %) gave rise to butyl rubbers with higher molecular weights in lower yields compared to polyisobutylene produced under essentially identical conditions. ^1H NMR ($CDCl_3$) spectroscopic analysis of these copolymers showed that they consisted of an average of 15 mol % IP present in the *trans*-1,4 configuration of which an average of 9 % of these IP units serve as branch points. Emulsion copolymerizations conducted at higher IP feeds (44 mol %) produced high molecular weight, intractable butyl rubber in yields similar to that witnessed for essentially identical copolymerizations conducted in the LiCl/NaCl/H_2O eutectic.

5.3 Conclusions for Aqueous Suspension/Emulsion Polymerization of Isobutylene

In an attempt to produce a ^{19}F NMR spectrum corresponding to the unsymmetrical bis-methanol adduct of diborane **1**, it was decided to use an excess amount of methanol with respect to diborane **1** in order to facilitate the synthesis of this compound. This reaction instead resulted in the production of the $[1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2(\mu\text{-OMe})]$ counteranion as a stable species. Armed with this knowledge this author decided to investigate the use of diborane **1** for the aqueous suspension and emulsion polymerization of isobutylene and butyl rubber. It was conceived that the Brönsted acid formed *in situ* from diborane **1** and background moisture present in the initiator stock and the monomer droplets could protically initiate polymerization of isobutylene. It was also speculated that use of hydrophobic solvents for the initiator stock solution would prevent diborane **1** from coordinating with too many water molecules prior to entering the monomer droplet since this would disfavor protonation of the monomer by reducing the strength of the Brönsted acid derived from diborane **1**. Moreover, it was realized that the continuous phase would have to consist of an aqueous mixture of low freezing point in order to avoid ice formation while providing temperatures suitable for the polymerization of isobutylene. Armed with a unique knowledge of obscure eutectic aqueous salt mixtures it was decided that a system based on a mixture of LiCl/NaCl/H_2O would be an ideal medium for aqueous suspension/emulsion polymerization of isobutylene.

A preliminary experiment on the polymerization as isobutylene in this medium as coinitiated by a hexane solution of diborane **1** resulted in the first successful attempt at the aqueous suspension polymerization of this monomer. Initial attempts at polymerization under similar conditions in a medium consisting of an aqueous solution of methanol were not very encouraging. The differences in the results for polymerization as conducted in these two media is assumed to be the result of the higher solubility of methanol in isobutylene which in turn leads to a reduction in initiation by reducing the strength of the Brönsted acid derived from diborane **1**.

Follow up studies on suspension using hexane solutions of diborane **1** were conducted under conditions with more controlled stirring in additional media and at different polymerization temperatures. This resulted in an overall reduction in both polymer molecular weight and yield for polymerizations conducted in the LiCl/NaCl/H_2O eutectic compared to the introductory experiment. These results appear to imply that increased surface area of the monomer droplet leads to higher rates of irreversible termination of propagating chains with the continuous phase. Through use of aqueous sulfuric acid and aqueous HBF_4 it was found that higher molecular weight polymers could be produced in higher yields by lowering the nucleophilicity of the continuous phase and the polymerization temperature. The unique ability of diborane **1** to coinitiate polymerization of isobutylene in suspension was further illustrated by the fact that $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ were inactive under similar conditions.

The use of more concentrated toluene solutions of diborane **1** was investigated as a means of conducting suspension polymerization under more controlled conditions. As opposed to polymerizations using hexane solutions of diborane **1**, those employing toluene solutions were very exothermic. Instead of the charge assuming a milky white appearance upon addition of diborane **1,** as is the case for suspension polymerizations using hexane solutions of this compound, addition of toluene solutions of diborane **1** caused the charge to turn yellow briefly before becoming milky. Suspension polymerizations using toluene solutions of diborane **1** gave rise to lower molecular weight polymers in lower yields as compared to similar polymerizations using hexane solutions of diborane **1**. This is believed to be the direct result of the higher exotherms witnessed for the former. The unique ability of diborane **1** as a coinitiator for aqueous suspension polymerization was demonstrated as other stable coinitiators/initiators [$LiB(C_6F_5)_4$, $H(Et_2O)_2B(C_6F_5)_4$, and octafluoro-9,10-bis(bispentafluorophenylbora)anthracene (**7**)] failed to induce polymerization under similar conditions. Since even the highly Lewis acidic diborane **7** was unable to coinitiate polymerization of isobutylene in suspension, the activity of diborane **1** must be in part due to its chelating ability.

As a continuation of the work done in suspension, the emulsion polymerization of isobutylene as coinitiated by diborane **1** was explored. Emulsion was conducted under conditions similar to those employed for suspension polymerization in the presence of anionic (SDS) and cationic (DTB, DOTf, DTFB) surfactants. Emulsion led to a reduction in polymer yield compared to suspension under similar conditions. With the exception of DTB, use of surfactant led to the production of polymer with lower molecular weights compared to those produced under identical conditions in the absence of surfactant. This behavior is believed to result from an increase in the ratio of the rate of termination to that for transfer as the surface area of the droplet is increased by the surfactant. Emulsions using DTB gave rise to polymers with molecular weights exceeding those produced under similar conditions in suspension albeit at greatly reduced yield. This behavior is believed to be partly due to the termination of the polymer chain with the highly nucleophilic bromide anion of this lipophilic surfactant.

From a preliminary experiment on the copolymerization of isobutylene with isoprene under anhydrous conditions extremely violent polymerization behavior was witnessed in which polymer exploded up into the bellows of the vacuum line. From this observation it was speculated that addition of IP to suspension/emulsion polymerizations might also increase the reactivity of these systems. Not only were such polymerizations exothermic but those initiated by toluene solutions of diborane **1** remained yellow for much longer periods compared to similar homopolymerizations. In all cases except for copolymerization conducted in HBF_4 using hexane solution of diborane **1**, the use of IP led to higher molecular weight polymers overall for both suspension and emulsion. This behavior is believed to partially stem from the higher stability of the allylic carbocation derived from IP which leads to longer lived chains. Incorporation of IP may increase molecular weight as hydride abstraction from such a repeat unit leads to the generation of an active carbocation from which secondary branches can grow.

From these findings it can be concluded that the first successful suspension and emulsion polymerizations of isobutylene and copolymerizations with isoprene have been conducted using diborane **1** as a coinitiator. This compound is unique among Lewis acids in this regard due to its high stability in water and because of its chelating ability. The use of droplet stabilizers in future suspension and polymerizations of isobutylene and copolymerizations with isoprene as coinitiated by diborane **1** may give rise to higher molecular weight polymers in higher yields. Use of nonionic surfactants may also prove beneficial to emulsion homo- and copolymerizations as coinitiated by diborane **1**. Additional types of chelating Lewis acids might prove useful in polymerization under similar conditions.

5.4 Experimental for Aqueous Suspension/Emulsion Polymerization of Isobutylene

5.4.1 Materials

Compounds $B(C_6F_5)_3$, $[Li][B(C_6F_5)_4]$, and $[Ph_3C][B(C_6F_5)_4]$ were obtained commercially and used without further modification. Diborane **7** was supplied by the Piers research group and used without further purification. $[H(Et_2O)_2][B(C_6F_5)_4]$ was synthesized according to a previous literature procedure.[202]

5.4.2 NMR Reaction of Diborane **1** with Excess Methanol

To a screw-top, septum-sealed, 5mm NMR tube was added 13 mg (0.016 mmole) of **1** followed by 0.500 mL of a solution of 2,3,5,6-tetrafluoro-*p*-xylene in CD_2Cl_2 (65 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 0.050 mL (120 mmol) of dry methanol was injected via syringe. The sample tube was then shaken to produce a yellow colored solution 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 to monitor formation and subsequent decomposition of the resulting ion pair.

5.4.3 Synthesis of DOTf

To a 100-mL, round-bottom flask bearing a single 24/40 joint was added 2.04 g dodecyltrimethylammonium bromide (6.6 mmoles) and 1.70 g silver (I) triflate (6.6 mmoles) followed by 25 mL distilled water. The flask was fitted with a reflux condenser and heated to reflux for a period of 2 hours after which the resulting reaction mixture was filtered and the filtrate was collected and dried under reduced pressure. The resultant solid was then recrystallized from dichloromethane to yield 2.3g (92 % yield) of white crystals. Evidence for the triflate group was shown by ^{19}F NMR ($CDCl_3$, 300K, 282 MHz) δ – 98.0 (s, 3F).

5.4.4 Synthesis of DTFB

To a 100-m, round-bottom flask bearing a single 24/40 joint was added 2.44 g dodecyltrimethylammonium bromide (7.9 mmoles) and 1.54 g silver (I) tetrafluoroborate (7.9 mmoles) followed by 25 mL distilled water. The flask was fitted with a reflux condenser and heated to reflux for a period of 2 hours after which the resulting reaction mixture was filtered and the filtrate was collected and dried under reduced pressure. The resultant solid was then recrystallized from dichloromethane to yield 2.2 g (88 % yield) as white crystals. Evidence for the tetrafluoroborate group was shown by ^{19}F NMR ($CDCl_3$, 300K, 282 MHz) δ -27.2 (s, 4F).

5.4.5 General Polymerization Procedures

Two types of initiator solutions were used:

1. Those with a volume of 10.0 mL consisted of diborane **1** (1.19×10^{-5} mol) and $B(C_6F_5)_3$ (2.39×10^{-5} mol) dissolved in hexane while $[Ph_3C][B(C_6F_5)_4]$ (2.39×10^{-5} mol) was dissolved in a 60/40 vol/vol mixture of CH_2Cl_2 and hexane. These solutions were injected over a period of 5 min.

A general polymerization procedure is given for polymerization of IB in aqueous suspension as initiated by hexane solution of diborane **1**. To a 3-neck, round-bottom flask equipped with an overhead mechanical stirrer was added 18 mL of LiCl (23 wt %)/NaCl (1.2 wt %)/H_2O (75.8 wt %). Then 18 mL (0.226 mol) of isobutylene was condensed into this flask at –60 °C under static vacuum. The mixture was then stirred at 500 rpm under N_2 (g) while adding 10.0 mL (1.19 mM) of a hexane solution of diborane **1** over a 5 min period by syringe. During this period the mixture turned milky white in appearance. After 1 h at –60 °C, the mixture was allowed to warm to 25 °C while venting the flask to the air. The mixture was diluted with 100 mL of water and 50 mL of dichloromethane and transferred to a separatory funnel. The aqueous phase was extracted with two 50 mL portions of dichloromethane and the organic extracts were dried over MgSO4, filtered and concentrated to dryness in vacuo. Polyisobutylene (6.10

g, 48 % conversion) was obtained with $\overline{M}_w = 66.1\text{x}10^3$ gmol^{-1} and $\overline{M}_w/\overline{M}_n$ =2.55. Polymerizations involving the use of other media, solvents, surfactants, and isoprene were conducted in an analogous manner and these materials were charged to the reactor prior to vacuum transfer of isobutylene.

2. Those with a volume of 1.0 mL consisted of diborane **1** ($1.19\text{x}10^{-5}$ mol), $B(C_6F_5)_3$ ($2.39\text{x}10^{-5}$ mol), $[H(Et_2O)_2][B(C_6F_5)_4]$ ($2.39\text{x}10^{-5}$ mol), and diborane **7** ($1.19\text{x}10^{-5}$ mol) dissolved in toluene. These solutions were injected over a period of 2.5-3 s.

A general polymerization procedure is given for polymerization of IB in aqueous suspension as initiated by a toluene solution of diborane **1**. To a 3-neck, round-bottom flask equipped with an overhead mechanical stirrer was added 18 mL of LiCl (23 wt %)/NaCl (1.2 wt %)/H_2O (75.8 wt %). Then 18 mL (0.226 mol) of isobutylene was condensed into this flask at –60 °C under static vacuum. The mixture was then stirred at 500 rpm under N_2 (g) while adding 1.0 mL (1.19 mM) of a toluene solution of diborane **1** over a 3 sec period by syringe. During this period the mixture turned yellow and remained so for 10 sec before turning milky white in appearance. The reaction was vigorously exothermic as witnessed by refluxing of the monomer. After 1 h at –60 °C, the mixture was allowed to warm to 25 °C while venting the flask to the air. The mixture was diluted with 100 mL of water and 50 mL of dichloromethane and transferred to a separatory funnel. The aqueous phase was extracted with two, 50 mL portions of dichloromethane and the organic extracts were dried over $MgSO_4$, filtered and concentrated to dryness in vacuo. Polyisobutylene (4.95 g, 39 % conversion) was obtained with $\overline{M}_w = 23.9\text{x}10^3$ gmol^{-1} and $\overline{M}_w/\overline{M}_n$ =2.38. Polymerizations involving the use of other media, solvents, surfactants, and isoprene were conducted in an analogous manner and these materials were charged to the reactor prior to vacuum transfer of isobutylene.