Communication

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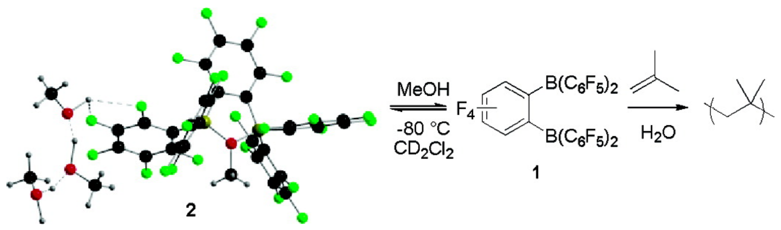

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Aqueous Suspension Polymerization of Isobutene Initiated by $1,2\text{-}C_6F_4[B(C_6F_5)_2]_2$

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Aqueous suspension or emulsion polymerization processes are of practical utility, combining high conversion with control over latex morphology.[1] In recent years, the aqueous suspension or emulsion polymerization of common alkenes such as ethylene, using transition-metal catalysts,[2] and styrene, using cationic initiators,[3] has been reported. However, early attempts at the polymerization of isobutene (IB) in aqueous suspension yielded only dimers and trimers,[4] thus leading to the general belief that cationic polymerization of this monomer in the presence of significant quantities of water is unfeasible.[5] We report here the first polymerization of IB and synthesis of butyl rubber (IIR) in aqueous suspension using diborane $1,2\text{-}C_6F_4[B(C_6F_5)_2]_2$ (**1**).

Recently, we reported on the use of diborane **1** (Scheme 1) as an initiator of IB polymerization, in combination with either cumyl chloride or adventitious moisture, in hydrocarbon media.[6] Further work has revealed that diborane **1** is effective for protic initiation at $[\mathbf{1}] \approx 10^{-5}$ M in hexane.[7] In view of the heightened reactivity of **1** in the presence of water, the reaction of **1** with MeOH was investigated by NMR spectroscopy to identify the products formed.

The addition of 0.5 equiv of MeOH to **1** in CD_2Cl_2 solution at −80 °C leads to formation of an ion pair **2** featuring the [**1**(μ-OMe)] counteranion,[8] partnered with an oxonium ion, which, based on the ^1H NMR spectrum,[7] corresponds to $[(MeOH)_2H]$ (Scheme 1). On warming above −60 °C this ion pair decomposes, and all of the added MeOH is consumed, forming equimolar amounts of borinic ester **3** (independently prepared from $(C_6F_5)_2BCl$ and MeOH)[7] and borane **4**, which was identified from its ^1H and ^{19}F NMR spectra (Figure 1a).[7] Evidently, **2** is susceptible to chemoselective protonolysis of the B−C bonds of the *o*-C_6F_4 moiety.

In contrast, ion pair **2** is *stable* in the presence of *excess* MeOH, even at 25 °C (Figure 1b), a feature that we attribute to the reduced acidity of the oxonium acid, as the solvation of the proton by MeOH is increased.[9] Single crystals of the ion pair $[(MeOH)_3H]$[**1**(μ-OMe)] could be grown from a solution of **1** in toluene and MeOH, and the X-ray structure appears in Scheme 1.[10]

The anion of this ion pair is analogous to that found in $[(Et_2O)_2H]$-[*o*-$C_6F_4\{B(C_6F_5)_2\}_2$(μ-OMe)],[11] but features a μ-OMe group that is planar at O1 with essentially equivalent B−O bond lengths of 1.558(3) and 1.566(3) Å, respectively. The endocyclic C−B−O angles at the two B atoms are reduced from the tetrahedral value to 97.8(2) and 97.6(2)°, reflecting angular strain within the five-membered ring, while the B1−O1−B2 angle is 118.0(2)°.

The $[(MeOH)_3H]$ cation has not been observed in oxonium acids derived from methanol,[12] but is similar to the $H_7O_3^+$ ion found in a number of structurally characterized salts.[13] The central $MeOH_2$ moiety of this oxonium acid is disordered with the one electron (and two protons) occupying sites between O2−O3 and O3−O4,[7] while the O2−O3 and O3−O4 separations of 2.465(5) and 2.495(5) Å differ slightly within experimental error. There are six H-bonds or short contacts between the remaining two, ordered MeOH molecules, and F-atoms of different counterions[7] that stabilize this monomeric, oxonium ion within the lattice.

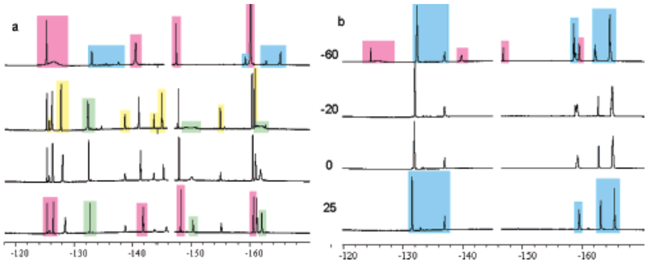

Figure 1. Variable-temperature ^{19}F NMR spectra of a solution of (a) diborane **1** and MeOH (0.5 equiv) and (b) diborane **1** and a 10-fold excess MeOH in CD_2Cl_2 solution. Signals due to **1** are highlighted in pink, **2** in blue, **3** in green, and **4** in yellow.

Because the basicity of water and MeOH are similar,[9] we expected that aqueous suspension polymerization of IB should be possible at sufficiently low *T*. Experiments involving the addition of a hexane solution of **1** to IB suspended in a 68:32 MeOH/H_2O solution at −60 °C were encouraging, but only a low yield (<10%) of PIB (M_w = 102 K, PDI = 3.3) formed under these conditions.

In contrast, the use of aqueous solutions of strong electrolytes such as a eutectic salt mixture consisting of LiCl, NaCl, and H_2O,[14] 38% aqueous H_2SO_4 or 48% aqueous HBF_4 proved more promising, giving moderate to high yields of PIB of moderate to high MW over the *T* range −60 to −80 °C (Table 1). The addition of a polar cosolvent such as CH_2Cl_2 led to a pronounced increase in MW accompanied by a slight decrease in conversion (Table 1, entry 2 vs 1). We interpret these positive results as arising from partial "drying" of the organic phase through physical contact with these electrolyte solutions.[15]

Polymerization in the presence of the surfactants sodium dodecyl sulfate (SDS) or dodecyltrimethylammonium bromide (DTBr), triflate (DTOTf), and tetrafluoroborate (DTFB) led to a decrease in yields, and this was especially true for those polymerization reactions using DTBr (Table 1, entry 3 vs 6). In contrast, when partnered with a weakly nucleophilic counteranion, as in DTOTf or DTFB, the yields of PIB were comparable to those obtained in the presence of SDS (Table 1, entry 9 vs 10, 13 vs 14).

Copolymerizations of IB were carried out with 8 mol % isoprene (IP) in the feed in a manner similar to homopolymerizations (entries 4 and 8). Although IP normally acts as a chain transfer agent in traditional copolymerizations,[5] this comonomer led to the production of higher MW polymer (albeit in lower yield) in suspension. We

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Scheme 1

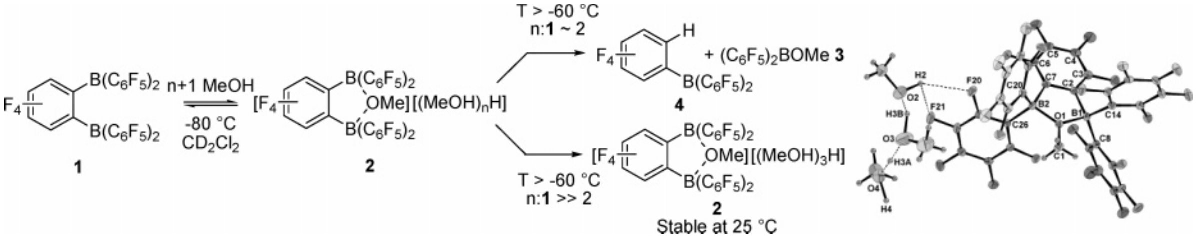

Table 1. Polymerization of IB in Aqueous Suspension[a]

entry	medium[b]	[**1**] (mM)	T (°C)	yield (%)	M_w (K)	PDI
1	A[c]	0.43	−60	48	66.1	2.55
2	A[c,d]	0.43	−60	32	121	1.96
3	A	0.63	−60	44	19.8	2.30
4[e]	A	0.57	−60	24	86.2	2.89
5	A/SDS	0.63	−60	32	25.4	2.37
6	A/DTBr	0.63	−60	5	57.2	2.74
7	B	0.63	−60	29	38.4	2.05
8[e]	B	0.57	−60	19	57.1	2.97
9	B/SDS	0.63	−60	18	61.0	2.69
10	B/DTOTf	0.63	−60	14	55.7	2.82
11	C[c]	0.43	−80	85	138	2.16
12	C	0.63	−80	58	50.8	2.36
13	C/SDS	0.63	−80	42	36.3	2.35
14	C/DTFB	0.63	−80	52	39.9	2.12

[a] Suspension polymerizations were conducted by the addition of a toluene solution of diborane **1** over a period of 10 s (*Caution:* strongly exothermic) to a vigorously stirred suspension of IB in aqueous media (ca. 50:50 v:v) at the indicated T for 1 h. [b] A = 7.2 M LiCl, 0.22 M NaCl in water; B = 38 wt % aqueous H_2SO_4; C = 48 wt % aqueous HBF_4 with 0.1 g of surfactant where applicable. [c] A hexane solution of diborane **1** was added over 5 min. [d] The organic phase was 50:50 v:v IB/CH_2Cl_2. [e] 8.0 mol % IP was added to the initial feed.

tentatively attribute this unusual observation to stabilization of the allylic chain ends toward termination by water.

^{1}H NMR spectroscopic analysis of the copolymers produced with 8 mol % IP feed indicated an average of 5 mol % *trans*-1,4 IP units of which an average of 16% served as branch points.[5,16]

Other water-resistant co-initiators of IB polymerization, including $[Li(Et_2O)_n][B(C_6F_5)_4]$,[16] $[Ph_3C][B(C_6F_5)_4]$,[16] and $B(C_6F_5)_3$ [16] were ineffective, even in the presence of a polar solvent such as CH_2Cl_2. Even the strongly Lewis acidic, but nonchelating, diboraanthracene 9,10-$(C_6F_5B)_2C_{12}F_8$ [17] failed to yield PIB. Finally, a strong Brønsted acid such as $[(Et_2O)_2H][B(C_6F_5)_4]$ (**5**)[18] (pK_a = −5.1[9b]) did not lead to polymerization.

We suspect the features that allow use of **1**, either in very dilute solution in hydrocarbon media or in aqueous suspension, relate to its ability to chelate water or related donors, thus transiently generating the acid $[o\text{-}C_6F_4\{B(C_6F_5)_2\}_2(\mu\text{-}OH_2)]$. Because both **5** and **2** fail to initiate IB polymerization under these conditions,[7] the pK_a of such an acid is no *higher* than −5. Future work will concentrate on the generality and applications of this novel process.

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Supporting Information Available: Experimental procedures and selected NMR spectra, crystallographic, refinement, and metrical data for ion pair **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Molecular structure of oxonium acid **2** with 30% thermal ellipsoids depicted: triclinic, P_1; $a = 9.796(2)$ Å, $b = 12.566(5)$ Å, $c = 15.497(5)$ Å, $\alpha = 71.61(1)°$, $\beta = 86.79(2)°$, $\gamma = 83.47(2)°$; $V = 1798(1)$ Å^3; $Z = 2$; $R = 0.058$, $R_w = 0.147$ for 8200 unique reflections with $I > 2\sigma(I)$.[7]
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