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

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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-$C_6F_4[B(C_6F_5)_2]_2$ (**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 $[(Et_2O)_2H][o\text{-}C_6F_4\{B(C_6F_5)_2\}_2(\mu\text{-OMe})]$,[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.

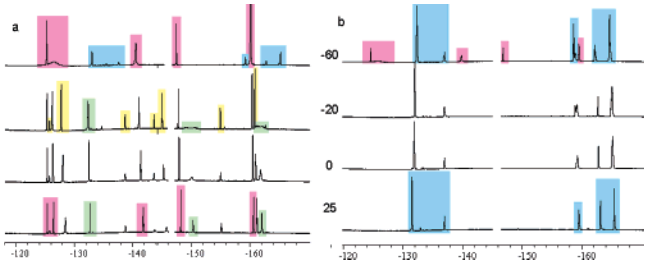

Figure 1. Variable-temperature ^{19}F NMR spectra of a solution of (a) diborane **1** and MeOH (0.5 equiv) and (b) diborane **1** and a 10-fold excess MeOH in CD_2Cl_2 solution. Signals due to **1** are highlighted in pink, **2** in blue, **3** in green, and **4** in yellow.

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

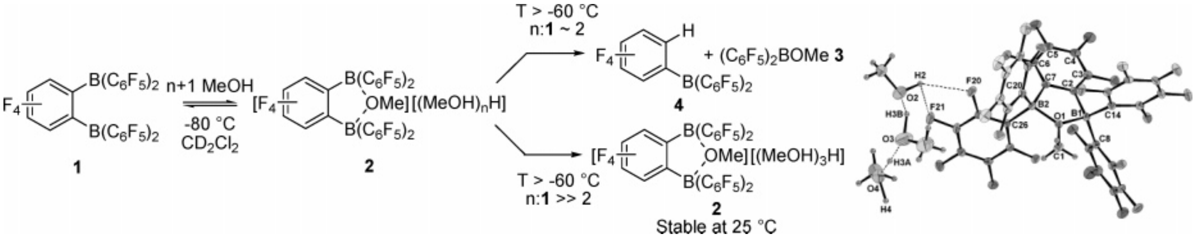

Table 1. Polymerization of IB in Aqueous Suspension[a]

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.

References

(1) (a) Lovell, P. *Emulsion Polymerization and Emulsion Polymers*; Wiley: New York, NY, 1997. (b) Gilbert, R. G. *Emulsion Polymerization*; Academic: San Diego, CA, 1995. (c) Athey, R. D. *Emulsion Polymer Technology*; Dekker: New York, NY, 1991.
(2) (a) Bauers, F. M.; Chowdhry, M. M.; Mecking, S. *Macromolecules* **2003**, *36*, 6711−6715. (b) Bauers, F. M.; Thomann, R.; Mecking, S. *J. Am. Chem. Soc.* **2003**, *125*, 8838−8840. (c) Soula, R.; Saillard, B.; Spitz, R.; Claverie, J.; Llaurro, M. F.; Monnet, C. *Macromolecules* **2002**, *35*, 1513−1523. (d) Soula, R.; Novat, C.; Tomov, A.; Spitz, R.; Claverie, J.; Drujon, X.; Malinge, J.; Saudemont, T. *Macromolecules* **2001**, *34*, 2022−2026, (e) Bauers, F. M.; Mecking, S. *Macromolecules* **2001**, *34*, 1165−1171.
(3) (a) Satoh, K.; Masami, K.; Sawamoto, M. *Macromolecules* **1999**, *32*, 3827−3832. (b) Satoh, K.; Masami, K.; Sawamoto, M. *Macromolecules* **2000**, *33*, 4660−4666. (c) Satoh, K.; Masami, K.; Sawamoto, M. *Macromolecules* **2000**, *33*, 5405−5410. (d) Satoh, K.; Masami, K.; Sawamoto, M. *Macromolecules* **2000**, *33*, 5830−5835. (e) Satoh, K.; Masami, K.; Sawamoto, M. *Macromolecules* **2000**, *33*, 5836−5840. (f) Satoh, K.; Masami, K.; Sawamoto, M. *Macromolecules* **2001**, *34*, 396−401. (g) Cauvin, S.; Sadoun, A.; Santos, R. D.; Belleney, J.; Ganachaud, F.; Hemery, P. *Macromolecules* **2002**, *35*, 7919−7927.
(4) Hedrik, H. W.; van Melsen, J. A. U.S. Patent 2,133,732, 1938.
(5) (a) Cationic Polymerization: Fundamentals and Applications; Faust, R., Shaffer, T. D., Eds.; ACS Symposium Series 665; American Chemical Society: Washington, DC, 1997. (b) Cationic Polymerizations: Mechanisms, Synthesis, and Applications; Matyjaszewski, K., Ed.; Plastics Engineering (N.Y.) 35; Dekker: New York, NY, 1996.
(6) Lewis, S. P.; Taylor, N. J.; Piers, W. E.; Collins, S. *J. Am. Chem. Soc.* **2003**, *125*, 14686−14687.
(7) See Supporting Information for details.
(8) Williams, V. C.; Irvine, G. J.; Piers, W. E.; Li, Z.; Collins, S.; Clegg, W.; Elsegood, M. R. J.; Marder, T. D. *Organometallics* **2000**, *19*, 1619−1621.
(9) (a) Fărcaşiu, D.; Hâncu, D. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2161−2165. (b) Arnett, E. M.; Quirk, R. P.; Burke, J. J. *J. Am. Chem. Soc.* **1970**, *92*, 1260−1266.
(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]
(11) Henderson, L. D.; Piers, W. E.; Irvine, G. J.; McDonald, R. *Organometallics* **2002**, *21*, 340−345.
(12) (a) Mootz, D.; Steffen, M. *Z. Anorg. Allg. Chem.* **1981**, *482*, 193−200. (b) Hursthouse, M. B.; Newton, J.; Page, P. R.; Villax, I. *Polyhedron* **1988**, *7*, 2087. (c) Bonadies, J. A.; Kirk, M. L.; Lah, M. S.; Kessissoglou, D. P.; Hatfield, W. E.; Pecoraro, V. L. *Inorg. Chem.* **1989**, *28*, 2037.
(13) (a) Stasko, D. J.; Perzynski, K. J.; Wasil, M. A. *Chem. Commun.* **2004**, 708−709. (b) Calleja, M.; Mason, S. A.; Prince, P. D.; Steed, J. W.; Wilkinson, C. *New J. Chem.* **2001**, *25*, 1475−1478. (c) Calleja, M.; Johnson, K.; Belcher, W. J.; Steed, J. W. *Inorg. Chem.* **2001**, *40*, 4978−4985. (d) Atwood, J. L.; Junk, P. C. *J. Coord. Chem.* **2000**, *51*, 379−397. (e) Minkwitz, R.; Schneider, S. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1989−1993. (f) Lundgren, J. O. *Acta Crystallogr., Sect. B* **1979**, *B35*, 780−783. (g) Roziere, J.; Williams, J. M. *J. Chem. Phys.* **1978**, *68*, 2896−2901.
(14) Akopov, E. K. *Zh. Prikl. Khim.* **1963**, *36*, 1916−1919.
(15) Control experiments in the absence of diborane **1** using these mineral acids failed to consume monomer.
(16) Shaffer, T. D.; Ashbaugh, J. R. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 329−344.
(17) Metz, M. V.; Schwartz, D. J.; Stern, C. L.; Nickias, P. N.; Marks, T. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 1312.
(18) Jutzi, P.; Müller, C.; Stammler, A.; Stammler, H.-G. *Organometallics* **2000**, *19*, 1442−1444.

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