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Reaction Mechanism of Borane/Oxygen Radical Initiators during the Polymerization of Fluoromonomers

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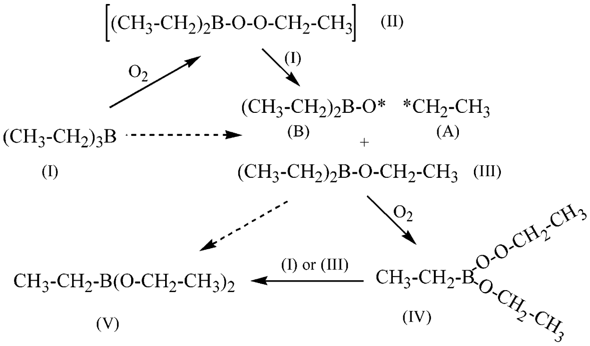
Fluoropolymers[1] are commonly used in high-end applications, such as aerospace and microelectronic.[2] A few years ago, we reported a borane/oxygen radical initiator system[3] for controlled radical polymerization of acrylic monomers at low temperatures. Recently, the same initiator was found to be effective for fluoromonomers, such as vinylidene fluoride (VDF), trifluoroethylene (TrFE), and chlorotrifluoroethylene (CTFE). The resulting VDF/TrFE/CTFE terpolymers exhibit interesting dielectric and ferroelectric properties.[4]

Despite the well-known autoxidation reaction of trialkylborane (BR_3) by oxygen which results in quantitative formation of the three corresponding alcohols (R−OH) after hydrolysis,[5] the detailed oxidation mechanism is complicated. Following the initial formation of a B−O−O−C moiety, one suggested mechanism is asymmetric cleavage of the C−O bond to produce B−O−O* and C* radicals.[6] However, the high bonding energy in the C−O relative to the O−O bond makes this pathway unlikely at ambient temperature. Some reports suggest an intramolecular rearrangement of the R_2B−O−O−R intermediate to form a $RB(O{-}R)_2$ molecule.[7] Others point to homolytic cleavage of the O−O bond to form B−O* and R−O* radicals.[8] Although the above autoxidation mechanisms of organoboranes are generally accepted for explaining various experimental results, they cannot be vigorously verified. The problem relates to the complexity of the oxidation products from three reactive B−C bonds and the formation of two possible moieties (B−O−R and B−O−O−R) from each B−C bond. The reaction intermediates are too unstable to permit isolation.

In this paper, we compare two oxidation adducts of $B(C_2H_5)_3$ and $B(OCH_3)(C_2H_5)_2$ and carry out the oxidation reactions in the presence of VDF monomers to form PVDF polymers under various conditions. The idea is to capture the unstable intermediate radicals that in situ initiate the polymerization and are incorporated in the beginning of polymer chains. The distinctive chemical shifts of PVDF, separated from those of borane oxidation fragments, greatly help the end-group analysis by the NMR technique.

Figure 1 compares two sets of the ^{11}B NMR spectra of the oxidation adducts of $B(Et)_3$ and $B(OMe)(Et)_2$ by varying amounts of oxygen at ambient temperature. In general, the oxidation adducts are quite complicated in $B(Et)_3$ yet are better controlled in $B(OMe)(Et)_2$. Under a stoichiometric amount of oxygen ($[O_2]/[B(Et)_3] < 1$) with an incremental amount of oxygen, in addition to the original $B(Et)_3$ chemical shift at 87 ppm, there are two new chemical shifts at 56 and 32 ppm, corresponding to $B(OEt)(Et)_2$ and $B(OEt)_2Et$, respectively. A minor peak at 36 ppm may be associated with a B−O−B species that is persistent throughout the oxidation process. Increasing the oxygen concentration toward $[O_2]/[B(Et)_3] > 1$, the $B(Et)_3$ completely disappears, and the main oxidation products become dioxidation adducts with a very small amount of trioxidization one at around 19 ppm.

Scheme 1. Oxidation Mechanism of Triethylborane



On the other hand, the incremental oxidation of $B(OMe)(Et)_2$ with oxygen ($[O_2]/[B(OMe)(Et)_2] < 0.5$) is a clean reaction. Only a new chemical shift at 32 ppm for B(OMe)(OEt)Et is shown with the presence of the unreacted $B(OMe)(Et)_2$ at 56 ppm. After increasing oxygen concentration to a stoichiometric amount, the $B(OMe)(Et)_2$ is completely converted to B(OMe)(OEt)Et without any detectable trioxidization adducts.

Almost no peroxyl species of $B(O{-}O{-}Et)Et_2$ (II) and B(OEt)(OOEt)Et (IV) were observed in both cases, although they should form before intermolecular reactions (Scheme 1). As shown in the Supporting Information (Figure S1), one-shot addition of excess oxygen ([oxygen]/[borane] = 4/1) to both $B(Et)_3$ and $B(OMe)(Et)_2$ results in almost identical ^{11}B NMR spectra with a chemical shift at 34 ppm, corresponding to B(OR)(OOEt)(Et) (IV) intermediate species, which were captured before having a chance to engage in an intermolecular reaction with B−C bonds. However, the monooxidized peroxide $B(OOEt)Et_2$ (II) is too unstable to survive during this oxidation process. In the Supporting Information (Figure S2), the peroxyl group in B(OR)(OOEt)(Et) (IV) further reacts with $B(Et)_3$ and $B(OMe)(Et)_2$.

The best way to observe the initial oxidation adduct of $B(OOEt)(Et)_2$ (II) and its subsequent reaction with $B(Et)_3$ (I) is to carry out this control oxidation in the presence of large amounts of VDF monomers ($[VDF]/[B(Et)_3] > 100$). The unstable intermediates containing free radicals during the intermolecular reaction should in situ initiate the radical polymerization to form poly(vinylidene fluoride) (PVDF) and deposit the adduct in the beginning of the PVDF chain. The polymerization procedures are shown in the Supporting Information. Table 1 summarizes the experimental results. Overall, this polymerization is unexpectedly effective at ambient temperature to obtain PVDF polymers with an almost quantitative yield in 5 h (runs B-4 and B-5). Comparing a set of reaction runs (A-1 to A-6) under similar reaction conditions, except the reaction time, the polymer molecular weight increases with the monomer conversion, which exhibits some characteristics of control radical polymerization.[10] Plots of the polymer molecular weight vs the monomer conversion (shown in Figure S3 of the Supporting Information), the line is well above the theoretical line for the ideal control polymerization. Some uncontrolled radical polymerization may take place in the beginning of polymerization. The protecting borinate radical (B), in situ

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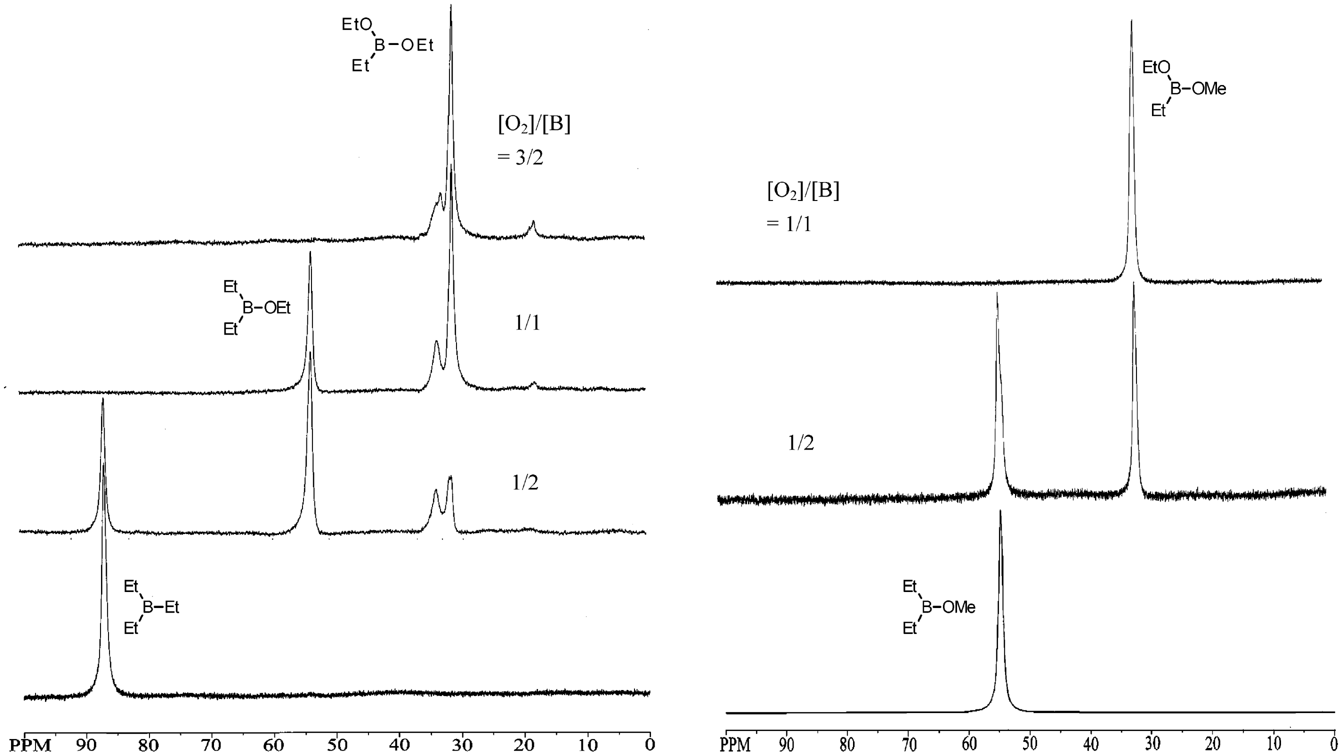

Figure 1. ^{11}B NMR spectra of the oxidation adducts of (left) $B(Et)_3$ and (right) $B(OMe)(Et)_2$ by varying amount of oxygen at ambient temperature.

Table 1. Summary of VDF Polymerization Conditions and Results by $B(Et)_3/O_2$ Radical Initiator at Room Temperature

					end groups				mol wt	
run	TEB/O_2 (mmol)	time (h)	yield (g)	cov (%)	CH_3CH_2* CH_2CF_2 , CF_2CH_2	CH_3CH_2-O-	CF_2CH_2-OH	CF_2COX (X = F or OH)	M_n[b] (NMR)	M_v[c]
A-1	2.4/1.6	0.25	1.6	11.9	1.58 (95.2%)	0.08 (4.8%)	n.d.[a]	n.d.	9 700	14 500
A-2	2.4/1.6	0.5	3.2	23.9	1.49 (96.1%)	0.06 (3.9%)	n.d.	n.d.	13 900	29 000
A-3	2.4/1.6	0.75	5.1	38.1	1.48 (95.5%)	0.07 (4.5%)	n.d.	n.d.	14 100	27 457
A-4	2.4/1.6	1	5.6	41.8	1.51 (96.8%)	0.05 (3.2%)	n.d.	n.d.	14 900	31 000
A-5	2.4/1.6	2.5	7.5	56.0	1.30 (97.0%)	0.04 (3.0%)	n.d.	n.d.	17 100	66 000
A-6	2.4/1.6	5	9.1	67.9	1.49 (98.0%)	0.03 (2.0%)	n.d.	n.d.	17 500	78 000
B-1	2.4/0.8	5	5.4	40.3	1.38 (96.5%)	0.05 (3.5%)	n.d.	n.d.	18 300	47 000
B-2	2.4/1.6	5	9.1	67.9	1.49 (98.0%)	0.03 (2.0%)	n.d.	n.d.	17 500	78 000
B-3	2.4/2.4	5	11.5	85.8	1.39 (92.7%)	0.11 (7.3%)	n.d.	n.d.	14 000	63 000
B-4	2.4/2.8	5	12.8	95.5	1.34 (91.2%)	0.13 (8.8%)	n.d.	n.d.	28 600	100 000
B-5	2.43.2	5	12.0	89.6	1.33 (85.8%)	0.15 (9.7%)	0.04 (2.6%)	0.03 (1.9%)	36 600	101 000
B-6	2.4/3.6	5	10.8	80.6	1.33 (82.6%)	0.17 (10.6%)	0.06 (3.7%)	0.05 (3.1%)	42 200	100 000
B-7	2.4/4.0	5	6.0	44.8	1.40 (64.2%)	0.20 (9.2%)	0.25 (11.5%)	0.33 (15.1%)	49 000	127 000
B-8	2.4/4.4	5	4.9	36.6	1.17 (40.2%)	0.34 (11.7%)	0.60 (20.6%)	0.80 (27.5%)	48 400	97 000
B-9	2.4/4.8	5	4.7	35.1	1.17 (41.5%)	0.37 (13.1%)	0.50 (17.7%)	0.78 (27.7%)	35 600	110 000
B-10	2.4/5.2	5	4.5	34.3	1.23 (62.4%)	0.27 (13.7%)	0.25 (12.7%)	0.22 (11.2%)	55 900	101 000
B-11	2.4/6.0	5	0	0						

[a] Not detectable. [b] M_n is based on the chain end group analysis, obtained from NMR spectrum. [c] M_v is determined by intrinsic viscosity[9] in dimethylacetamide at 25 °C.

formed during the oxidation of $B(Et)_3$ (Scheme 1), may not have a sufficient quantity to mediate all propagating radicals. Usually, excess mediates (vs propagating radicals) are needed to have a successful control radical polymerization.[10]

The polymer molecular weight reaches $M_v > 63\,000$ g/mol in about 5 h. The relatively slow propagating rate, compared to that of the regular free radical polymerization mechanism, removes the safety concern for heat transport and temperature control usually associated with bulk or solution polymerization of fluoromonomers. In addition, this process produces fluoropolymers with high purities, without any contaminants from surfactants or suspension agents in most of commercial fluoropolymers, which are difficult to remove but detrimental in electric applications.

Figure 2 shows the ^1H and ^{19}F NMR spectra of a typical PVDF polymer (run A-6) prepared by an $B(Et)_3/O_2$ initiator (mole ratio = 3/2). In addition to two major chemical shifts at 2.9 and 2.3 ppm, corresponding to a head-to-tail ($CF_2-C\mathbf{H}_2-CF_2-C\mathbf{H}_2$) sequence and a head-to-head ($CF_2-C\mathbf{H}_2-C\mathbf{H}_2-CF_2$) sequence, respectively, three minor chemical shifts at 1, 1.5, and 2.0 ppm are associated with three types of protons at the $C\mathbf{H}_3-C\mathbf{H}_2-C\mathbf{H}_2-CF_2-$ end group, which is originated from the oxidation adduct (CH_3-CH_2*) of $B(Et)_3$. The same chain-end assignments were observed in the ^{19}F NMR spectrum. In addition to several main chain peaks at near 91, 95, 113, and 116 ppm, there were several weak chain-end peaks near 93 ppm ($C\mathbf{F}_2-CH_2-CH_2-CH_3$) and 100 ppm ($C\mathbf{F}_2-CH_2-CH_3$). The detailed chemical shift assignments are shown in the Supporting Information (Figures S4 and S5). In fact, all reaction runs with $[O_2]/[B(Et)_3] < 1$ (Table 1) show the same CH_3-CH_2- polymer chain-end structure. There is no detectable CH_3-

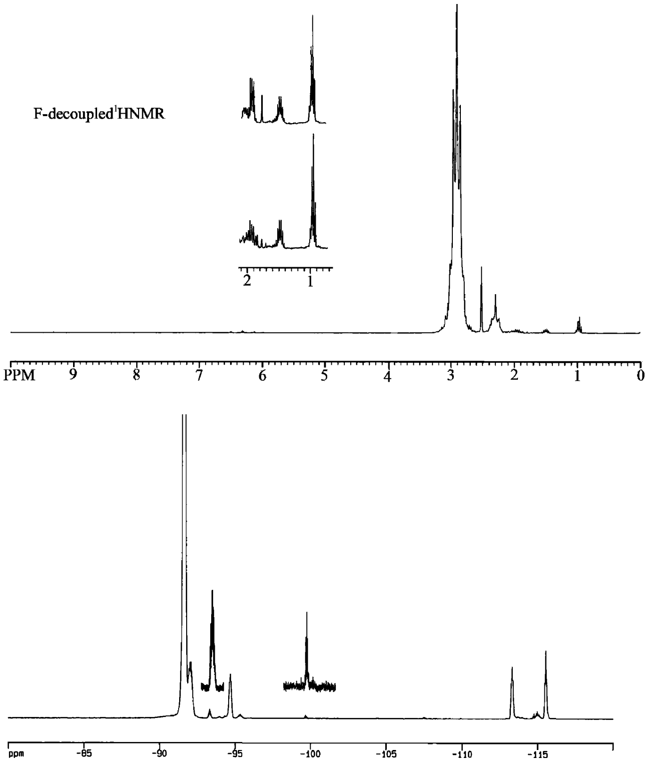

Figure 2. (top) ^{1}H and (bottom) ^{19}F NMR spectra of a PVDF polymer (run A-6) prepared by a $B(Et)_3/O_2$ initiator (mole ratio = 3/2).

$CH_2{-}O{-}$ group and borane fragment existing at the polymer chain end.

Scheme 1 illustrates the possible oxidation mechanism of $B(Et)_3$ (I) that can explain all our observations. In the early stage of the oxygen reaction ($[O_2]/[B(Et)_3] < 1$), the first oxidation adduct shall be $B(OOEt)(Et)_2$ (II), which is very unstable and immediately reacts with the unreacted $B(Et)_3$ (I) to form a $B(OEt)(Et)_2$ (III) and two intermediate radicals, including $CH_3{-}CH_2{*}$ radical (A) and borinate radical (B). Without monomers presence, two radicals just combine to form another $B(OEt)(Et)_2$ (III). With VDF monomers, the $CH_3{-}CH_2{*}$ radical (A) in situ initiates the radical polymerization of VDF at ambient temperature. However, borinate radical (B) may be too stable to react with the monomer due to electron back-donating to the empty p-orbital of boron. But it may serve as the end-capping agent to form a reversible bond with the growing PVDF chain end to prolong the propagating process. Evidently, the monooxidation product $B(OEt)(Et)_2$ (III) is still very reactive, which is subjective to further oxidation, either by oxygen to form B(OOEt)(OEt)Et (VI) or by another $B(OOEt)(Et)_2$ (II) to form $B(OEt)_2Et$ (V). After the dioxidation reaction, the peroxyl group in B(OOEt)(OEt)Et (VI) is still unstable, but is a little bit more stable than that in the monooxidized $B(OOEt)(Et)_2$ (II). The observed amount of B(OOEt)(OEt)Et (VI) is dependent on the availability of B−C bonds in $B(Et)_3$ (I) and $B(OEt)(Et)_2$ (III). With the further increase of oxygen concentration and reaction temperature, all three B−C bonds in $B(OMe)(Et)_2$ and $B(Et)_3$ are eventually oxidized to form trioxidation species.

In summary, the combined information from oxidation adducts of two related boranes (triethylborane and diethylmethoxylborane) and the polymer chain end structure presents a complete picture of oxidation and the initiation mechanism of broane/oxygen-mediated radical polymerization of fluoromonomers at ambient temperature. This borane/oxygen initiator offers a safe and effective route to prepare fluoropolymers with high molecular weights and high purities. It also provides the control of polymer chain end structure by initiator.

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Supporting Information Available: Oxidation of $B(C_2H_5)_3$ and $B(OCH_3)(C_2H_5)_2$ with excess O_2; VDF polymerization by using $B(C_2H_5)_3$ and $B(OCH_3)(C_2H_5)_2$ initiators; ^{1}H and ^{19}F NMR chemical shift assignments for PVDF polymer prepared by $B(C_2H_5)_3/O_2$ initiator. This material is available free of charge via Internet at http://pubs.acs.org.

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